University of Southampton

HEAVY METAL REMOVAL USING POLYMER IMMOBILISED BIOMASS

A thesis submitted to the University of Southampton

for the degree of Doctor of Philosophy



By

Mohamed Salem Alhakawati

January 2003

Faculty of Engineering and Applied Science

Department of Civil and Environmental Engineering

UNIVERSITY OF SOUTHAMPTON

SOUTHAMPTON

SO17 1BJ

Dedication

I would like to dedicate this work to the almighty Allah for the brain, power, health and knowledge that he has given to me to be able to think, learn, search, compare and carry out this research.

Acknowledgements

I would like to thank my supervisor Dr. C. J. Banks for the novel idea of this research and his encouragement, endless support and advice during the course of this investigation.

I would like, also to acknowledge Dr. David Smallman for his technical help and guidance throughout this project.

Finally I am especially grateful to my parents for their encouragement and to my wife who was so patient and supportive during the hard days in this project.

ABSTRACT

A comparative study of the bio-adsorption capacity and kinetics of non viable *Rhizopus oryzae* (fungal biomass) immobilized in six selected types of polymers (polyvinlformal, polysulfone, alginate, polyacrylamide, k-carrageenan and polyethyleneimine) was undertaken. The results were compared with those for non immobilised biomass and biomass that had been cultured in the open pore structure of reticulated polyurethane foam. Only the latter method gave a copper uptake capacity equal to that of the free biomass, but this method had the disadvantage that it was necessary to cultivate the fungus in association with the support matrix.

Research was conducted to assess the potential for immobilisation of *Rhizopus oryzea* and *Ascophyllum nodosum* (seaweed) into an inert polyurethane carrier matrix during the production process. Two types of polyurethane were used: a conventional hydrophobic polyurethane, and hydrophilic polyurethane (Hypol®). The conventional hydrophobic foam was found to be unsuitable and exhibited no potential for biosorption of copper from aqueous solution.

Biomass immobilised in Hypol had an adsorptive capacity equal to that of free biomass when compared on a weight basis. Copper adsorption using both types of biomass immobilised in this way showed good agreement with the Langmuir isotherm model. *Rhizopus oryzae* had an adsorption capacity of between 10 and 13 mg $Cu.g^{-1}$ and *Ascophyllum nodosum* 39 mg Cu g^{-1} dry wt.

The immobilised seaweed was used in five consecutive adsorption experiments and showed an initial lowering of adsorption capacity but stabilised at an uptake capacity of 15 mg $Cu.g^{-1}$ dry wt. by the third re-use. The maximum uptake capacity of the immobilised biomass was shown to be pH dependent whilst temperature had no significant effect.

A technique was developed to cast the biomass/polymer matrix into columns that could then be used as fixed bed reactors in adsorption studies. The adsorption capacity using the seaweed as the biosorbent in this type of column was 19.37, 17.96, 14.16, 16.6 and 15 $mg.g^{-1}$ over 5 consecutive cycles of operation.
Flow rate through the column and the weight ratio of biomass incorporated into the polymer were found to effect adsorption capacity. The presence of Zn(II), Fe(II), Cr (VI) and Ni (II) were found to have a small negative effect on the biomass copper adsorption capacity, which was reduced by between 10-20% depending on the metal. Experiments were also carried out using column reactors in series.

It was concluded that polyurethane immobilisation could provide a robust method of producing a biosorbent for use in a variety of reactor types.

Table of Contents

CHAPTER 1 Background: Heavy metals and the environment **1**

1.1 Introduction 1

1.2 The objective of this study 4

1.3 Heavy metal definitions 4

1.4 Heavy metals removal technologies 5

1.4.1 Precipitation 6

1.4.2 Ion exchange 10

1.4.3 Membrane technology 11

1.4.4 Activated carbon adsorption 12

1.4.5 Other removal technologies 13

1.5 Biosorption technologies 14

CHAPTER 2 Biosorption as an approach to heavy metals removal from aquatic systems **15**

2.1 Definition of bio-sorption and bio-adsorption 15

2.2 Classification of metals according to biosorption process 15

2.3 Mechanism of metals uptake by micro-organisms 23

2.3.1 Binding sites in yeast 23

2.3.2 Binding sites in bacteria 24

2.3.3 Binding sites in algae 25

2.3.4 Binding sites in fungi 25

2.4 Biomass used in this study 28

2.4.1 Brief adsorption history of *Rhizopus oryzae* and factors affecting its metal uptake capacity 28

2.4.1.1 Growth media effects 29

2.4.1.2 The effect of metabolic inactivation 30

2.4.1.3 The effect of pH 31

2.4.1.4 The effect of other ions 31

2.4.1.5 The effect of temperature 32

2.4.2 Brief adsorption history of *Ascophyllum nodosum* and factors affecting its metal uptake capacity 33

2.4.2.1 pH 34
2.4.2.2 The presence of other ions 34
2.4.2.3 Pre-treatment and modification 35
2.5 Regeneration process of the biomass particles 36
2.6 Analysis and representation of adsorption data 37
2.6.1 Adsorption isotherms 37
2.6.1.1 Langmuir isotherms 38
2.6.1.2 Freundlich isotherms 40
2.6.1.3 The Brunauer, Emmett, Teller (BET) isotherms 42
2.6.1.4 Choice of isotherms 42
2.6.2 Adsorption kinetics 43
2.6.2.1 The pseudo-first order equation 43
2.6.2.2 The pseudo-second order equation 44
2.6.2.3 The Elovich equation 45
2.6.2.4 Choice of kinetic equation 45

CHAPTER 3 Polyurethane as a supportive matrix for the immobilisation of bio-sorbents 46
3.1 The use of immobilised biomass in metal uptake 46
3.1.1 Alginate and Carrageenan 47
3.1.2 Polyacrylamide 48
3.1.3 Polysulfone 48
3.1.4 Growth on inert media 48
3.2 Problems with biomass immobilisation 49
3.3 Application of immobilised cell biosorption systems 49
3.4 Polyurethane: a brief history 49
3.4.1 General methods of foam preparation 53
3.4.1.1 Chemical methods 53
3.4.1.2 Physical methods 54
3.4.1.3 Mechanical methods 54
3.5 The use of polyurethane for immobilisation and sorption 55

CHAPTER 4 Materials and methods 62
4.1 Preparation of glassware, plastic ware and experimental tools 62

4.2 Preparation of the biomass 62
4.2.1 Preparation of *Rhizopus oryzae* 62
4.2.1.1 Preservation of *Rhizopus oryzae* 63
4.2.1.2 Growing and harvesting of *R. oryzae* 63
4.2.2 Preparation of *Ascophyllum nodosum* 63
4.2.3 Sizing of the biomass 64
4.3 Immobilisation techniques using seven selected types of polymers 64
4.3.1 Immobilisation in alginate 64
4.3.2 Immobilisation in polyacrylamide 65
4.3.3 Immobilisation in polyvinlformal 66
4.3.4 Immobilisation by growth in polyurethane 67
4.3.5 Immobilisation in k-carrageenan 69
4.3.6 Immobilisation in polysulfone 70
4.3.7 Immobilisation in polyethyleneimine (PEI) 71
4.4 Polyurethane immobilisation techniques 72
4.4.1 Biomass incorporation in conventional hydrophobic polyurethane foam 72
4.4.2 Biomass incorporation in hydrophilic polyurethane foam (Hypol 2002) 73
4.4.3 Direct casting of biomass-polyurethane columns for sorption studies. 73
4.4.4 Conditioning of the columns 76
4.4.5 Column set up and operation 76
4.5 Analytical techniques 77
4.5.1 Measurement of metal ion concentrations 77
4.5.2 Measurement of carbon 78
4.6 Expression of experimental data 79

CHAPTER 5 Results 80
5.1 Comparison of different immobilisation matrices for copper removal using *R. oryzae* 80
5.1.1 Microscopic examinations 80
5.1.2 Copper sorption by free and polymer immobilised fungal biomass 82
5.2 Preliminary investigation on polyurethane foam manufacture and the

copper adsorption characteristics of biomass immobilised during this process 89
5.2.1 Preliminary investigation into the manufacture of conventional hydrophobic polyurethane 89
5.2.2 Preliminary investigation on manufacturing of hydrophilic polyurethane foam (Hypol 2002) 94
5.3 Preliminary experiments on copper adsorption using immobilised and non immobilised *R. oryzae* fungal biomass and *A. nodosum* seaweed biomass 98
5.3.1 Methodology 99
5.3.2 Results from experiments using non immobilised biomass 99
5.3.3 Results from experiments using fungal biomass immobilised in conventional hydrophobic polyurethane 101
5.3.4 Results from experiments using fungal biomass immobilised in hydrophilic polyurethane (Hypol 2002) 103
5.4 Copper recovery from beads of fungi-hydrophilic polyurethane (Hypol 2002) 110
5.5 Copper precipitation experiments 111
5.6 Biosorption experiments on beads of biomass-Hypol foam 114
5.6.1 Isotherms experiments on beads of fungi-Hypol foam 114
5.6.2 Isotherms experiments on beads of seaweed-Hypol foam 118
5.6.2.1 Isotherm experiments and beads reuse 118
5.6.2.2 Effect of temperature on the adsorption of copper by seaweed/Hypol beads 122
5.6.2.3 Effect of pH on the adsorption of copper by seaweed/Hypol beads 125
5.7 Columns experiments 128
5.7.1 Copper adsorption and elution from the seaweed-Hypol foam column 129
5.7.1.1 Methodology 129
5.7.1.2 Biomass loss on conditioning of the column 130
5.7.1.3 Results of the adsorption and desorption cycles 131
5.7.2 The effect of flow rate on copper adsorption using seaweed-Hypol foam columns 140

5.7.3 The effect of biomass weight on copper adsorption in seaweed-Hypol foam columns 143
5.7.4 The effect of initial copper concentration adsorption seaweed-Hypol columns 147
5.7.5 The effect of competing ions on copper adsorption 151
5.7.5.1 Adsorption of Cu (II), Zn (II) and Fe (II) from a simulated metal finishing industry effluent using a column of seaweed-Hypol foam 151
5.7.5.2 Adsorption of Cu (II), Zn (II), Ni (II) and Cr (VI) from a simulated automatic plating of zinc base die casting effluent using column of seaweed-Hypol foam 157
5.7.6 Adsorption of Cu (II), Zn (II), Ni (II) and Cr (VI) from a simulated automatic plating of zinc base die casting effluent using two columns in series of seaweed-Hypol foam 164

CHAPTER 6 Discussion and conclusion **169**
6.1 Immobilisation of *Rhizopus oryzea* in seven selected types of polymers 169
6.2 Manufacturing of hydrophobic and hydrophilic polyurethane 172
6.3 Use of hydrophobic and hydrophilic polyurethane immobilised *Rhizopus oryzea* and *Ascophyllum nodosum* in copper removal 173
6.3.1 Beads (cubes) of biomass/Hydrophilic foam experiments 173
6.3.2 Columns of seaweed/hydrophilic polyurethane experiments 176
6.4 Cost of the hydrophilic polyurethane (Hypol 2002) 178
6.5 Conclusions 179

References **180**
Appendix A: Results tables **195**
Appendix B: Analytical instruments used in the study **291**
Appendix C: Brief explanation of the statistics used in the study to present the experimental data **296**

Table of Figures

Fig. 1.1	Global Production and Consumption of Selected Toxic Metals, 1850-1990, (Nriagu, 1996)	2
Fig. 1.2	Periodic table, showing the elements, including heavy metals, and their density ($g.cm^{-3}$)	5
Fig. 1.3	Residual soluble metal concentration as a function of pH using NaOH as precipitant. Precipitate stood for 30 minutes before filtration (Eilbeck and Mattock, 1987)	7
Fig. 1.4	Residual soluble metal concentration as a function of pH using Na_2CO_3 as precipitant. Solid lines: precipitate stood for 30 minutes before filtration. Broken lines: precipitate stood for 24 hours before filtration. Broken dotted lines: precipitate stood for 30 minutes before filtration, with polyelectrolyte present (Eilbeck and Mattock, 1987)	8
Fig. 1.5	Residual soluble metal concentration as a function of pH using Ca $(OH)_2$ as precipitant. Solid lines: precipitate stood for 30 minutes before filtration. Broken lines: precipitate stood for 24 hours before filtration. Broken dotted lines: co-presence of excess phosphate (Eilbeck and Mattock, 1987)	8
Fig. 2.1	The electronegativity of heavy metals and other elements of interest to the biosorptive process in the periodic table. The shaded area comprises heavy metals (CRC Handbook of Chemistry and Physics, 1997)	18
Fig. 2.2	Charged groups in bacteria cell wall (Hancock, 1986)	24
Fig. 2.3	The exchange mechanism between polypeptide chain (proteins) and metal ions (Hunt, 1986)	26
Fig. 2.4	Chitin (poly-N-acetyl-D-glucosamine) (Mackay et al., 1986)	27
Fig. 2.5	Chitosan (deacelylated [poly-N-acetyl-D-glucosamine]) (Mackay et al., 1986)	28
Fig. 2.6	A general representation of adsorption isotherms	38
Fig. 5.1	Copper uptake by free and polymer immobilised fungal biomass from 95 ml of a 2 mgl^{-1} copper solution at an initial pH 7.0, room temperature and 1 hour contact time; in all cases the quantity of biomass used was 100 mg	84

Fig. 5.2 Copper uptake by biomass free polymers from 95 ml of a 2 mgl^{-1} copper solution at an initial pH 7.0 and room temperature 85

Fig. 5.3 The one hour copper uptake capacity of free fungal biomass, free polymers and biomass-polymers when they were exposed to 95 ml of a 2 mgl^{-1} copper solution at an initial pH 7.0 at room temperature 86

Fig. 5.4 Copper uptake by free and polymer immobilised biomass from 95 ml of a 2 mgl^{-1} copper solution at an initial pH 7.0, room temperature and 4 hours contact time; in all cases the quantity of biomass used was 100 mg 87

Fig. 5.5 The one and four hour copper uptake capacity of free and polymer immobilised fungal biomass when they were exposed to 95 ml of a 2 mgl^{-1} copper solution at an initial pH 7.0 and room temperature (N.B. The 1 hour uptake capacity is taken from the results of the first experiment, figure 5.3) 88

Fig. 5.6 The determination of equilibrium time for the adsorption of copper by non-immobilised fungal biomass using 145 ml of 2 mgl^{-1} Cu solution, at room temperature, neutral pH and a biomass dry wt. concentration of 0.69 gl^{-1} 100

Fig. 5.7 The determination of equilibrium time for the adsorption of copper by non-immobilised seaweed biomass using 145 ml of 2 mgl^{-1} Cu solution, at room temperature, neutral pH and a biomass dry wt. concentration of 0.69 gl^{-1} 100

Fig. 5.8 Copper adsorption by non-immobilised fungal biomass and immobilised fungal biomass in conventional hydrophobic polyurethane, using a 2 mgl^{-1} Cu solution, at room temperature, neutral initial pH and a biomass dry weight concentration of 0.69 gl^{-1} 102

Fig. 5.9 Copper adsorption by pre-conditioned beads of immobilised fungal biomass in conventional hydrophobic polyurethane with 1 $mole.l^{-1}$ of H_2SO_4 and 1 $mole.l^{-1}$ of NaOH. The adsorption experiment was conducted using a 2 mgl^{-1} Cu solution, at room temperature, neutral initial pH and biomass dry weight concentration of 0.69 gl^{-1} 103

Fig. 5.10 Copper uptake capacity and equilibrium time for fungi-Hypol beads manufactured without surfactants when they were suspended in a solution of 2 mgl^{-1} Cu at room temp., neutral initial pH and a biomass dry weight concentration of 0.69 gl^{-1} (Error bars were not put to avoid overlap, see results table, A24, for the values of standard deviation) 104

Fig. 5.11 Copper uptake capacity and equilibrium time for fungi-Hypol

beads manufactured with addition of Pluronic85 surfactant. The beads were suspended in a solution of 2 mgl^{-1} Cu at room temperature, neutral initial pH and biomass dry weight concentration of 0.69 gl^{-1} (Error bars were not put to avoid overlap, see results tables, A25 and A26, for the values of standard deviation) 105

Fig. 5.12 Copper uptake capacity and equilibrium time for fungi-Hypol beads manufactured with the addition of Tween80 surfactant. The beads were suspended in a solution of 2 mgl^{-1} Cu at room temperature, neutral initial pH and biomass dry weight concentration of 0.69 gl^{-1} (Error bars were not put to avoid overlap, see results tables, A27 and A28, for the values of standard deviation) 107

Fig. 5.13 Copper uptake capacity and equilibrium time for fungi-Hypol beads manufactured with addition of TritonX-100 surfactant. The beads were suspended in a solution of 2 mgl^{-1} Cu at room temperature, neutral initial pH and biomass dry weight concentration of 0.69 gl^{-1} 108

Fig. 5.14 Copper uptake capacity and equilibrium time of non-immobilised fungi and immobilised fungi in Hypol foam manufactured with and without the addition of 2% wt. (surfactant : pre-polymer). In all cases he beads were suspended in a solution of 2 mgl^{-1} Cu at room temperature, neutral initial pH and biomass dry weight concentration of 0.69 gl^{-1} (Error bars were not put to avoid overlap) 109

Fig. 5.15 Copper recovery from beads of fungi-Hypol at pH < 2 after exposure to 45 ml of 2 mgl^{-1} Cu solution at an initial pH 7.0 and room temperature 110

Fig. 5.16 Copper solubility at 20° C for different copper concentrations with respect to pH 112

Fig. 5.17 Isotherms of four consecutive cycles of copper uptake by beads of fungi-Hypol foam containing 100 mg dry wt. of biomass at pH 5.0, 20° C and initial copper concentrations of (2-15) mgl^{-1} (Error bars were not put to avoid overlap, see results tables, A35-A38, for the values of standard deviation) 115

Fig. 5.18 Freundlich isotherms for four consecutive cycles of copper uptake by beads of fungi-Hypol foam containing 100 mg dry wt. of biomass at pH 5.0, 20° C and initial copper concentrations of (2-15) mgl^{-1} 116

Fig. 5.19 Langmuir isotherms of four consecutive cycles of copper uptake by beads of fungi-Hypol foam containing 100 mg dry wt. of biomass at pH 5.0, 20° C and initial copper

concentrations of (2-15) mgl^{-1} 116

Fig. 5.20 Freundlich isotherms of five consecutive cycles of copper uptake by beads of seaweed-Hypol foam containing 100 mg dry wt. of biomass at pH 5.0, 20° C and initial copper concentrations of (2-60) mgl^{-1} 119

Fig. 5.21 Langmuir isotherms of five consecutive cycles of copper uptake by beads of seaweed-Hypol foam containing 100 mg dry wt. of biomass at pH 5.0, 20° C and initial copper concentrations of (2-60) mgl^{-1} 119

Fig. 5.22 The Langmuir Isotherm plot compared to the experimental data for five consecutive cycles of copper uptake by beads of seaweed-Hypol foam containing 100 mg dry wt. of biomass at pH 5.0, 20° C and initial copper concentrations of (2-60) mgl^{-1} 122

Fig. 5.23 Freundlich isotherms for copper adsorption by 100 mg dry wt. of immobilised seaweed in Hypol beads with respect to temperature at pH 5.0 and initial copper concentrations (2-60) mgl^{-1} 123

Fig. 5.24 Langmuir isotherms for copper adsorption by 100 mg dry wt. of immobilised seaweed in Hypol beads with respect to temperature at pH 5.0 and initial copper concentrations (2-60) mgl^{-1} 123

Fig. 5.25 Isotherm lines according to Langmuir compared with the obtained data for copper adsorption by 100 mg dry wt. of immobilised seaweed in Hypol beads with respect to temperature at pH 5.0 and initial copper concentrations (2-60) mgl^{-1} 125

Fig. 5.26 Freundlich isotherms for copper adsorption by 100 mg dry wt. of immobilised seaweed in Hypol beads with respect to pH at 20° C and initial copper concentrations (2-60) mgl^{-1} 126

Fig. 5.27 Langmuir isotherms for copper adsorption by 100 mg dry wt. of immobilised seaweed in Hypol beads with respect to pH at 20° C and initial copper concentrations (2-60) mgl^{-1} 126

Fig. 5.28 Isotherm lines according to Langmuir compared with the obtained data for copper adsorption by 100 mg dry wt. of immobilised seaweed in Hypol beads with respect to pH at 20° C and initial copper concentrations (2-60) mgl^{-1} 128

Fig. 5.29 Copper uptake capacity over 5 consecutive adsorption-desorption cycles using a column of Hypol-seaweed. Influent pH 5.0, 20° C, initial copper concentration of 6 mgl^{-1}, flow rate

	4.7 l/hr and biomass net dry wt. of 3.5 g (approximate)	132
Fig. 5.30	Summary of copper equilibrium uptake by immobilised seaweed in Hypol foam and cast in plastic column for five consecutive cycles	133
Fig. 5.31	The percentage difference between the influent and the effluent copper concentration (%) over 5 consecutive adsorption-desorption cycles using a column of Hypol-seaweed. Influent pH 5.0, 20° C, initial copper concentration of 6 mgl^{-1}, flow rate 4.7 l/hr and biomass net dry wt. of 3.5 g (approximate)	134
Fig. 5.32	Copper removal using a column of biomass free Hypol foam. Influent pH 5.0, 20° C, initial copper concentration of 6 mgl^{-1} and flow rate 4.7 l/hr	135
Fig. 5.33	Cu recovery after the first adsorption cycle	136
Fig. 5.34	Cu recovery after the second adsorption cycle	136
Fig. 5.35	Cu recovery after the third adsorption cycle	136
Fig. 5.36	Cu recovery after the fourth adsorption cycle	136
Fig. 5.37	Summary of Cu elution efficiency observed during the 5 cycles of the column operation	137
Fig. 5.38	pH changes during the first adsorption cycle	138
Fig. 5.39	pH changes during the second adsorption cycle	138
Fig. 5.40	pH changes during the third adsorption cycle	138
Fig. 5.41	pH changes during the fourth adsorption cycle	138
Fig. 5.42	pH changes during the fifth adsorption cycle	139
Fig. 5.43	The effect of flow rate on copper adsorption using columns of Hypol-seaweed at an influent pH 5.0, 20° C, initial copper concentration of 6mgl^{-1}, and approximate biomass proportion of 7.5%	141
Fig. 5.44	The effect of flow rate on the percentage difference between the influent and the effluent copper concentrations by columns of cast Hypol-seaweed at influent an pH 5.0, 20° C, initial copper concentration of 6 mgl^{-1}, and approximate biomass proportion of 7.5%	142
Fig. 5.45	The effect of water flow rate through columns of seaweed-foam on copper adsorption capacity of the immobilised seaweed	142

Fig. 5.46	pH changes during copper adsorption at flow rate of 2.25 l/hr	143
Fig. 5.47	pH changes during copper adsorption at flow rate of 7.04 l/hr	143
Fig. 5.48	The effect of seaweed load on copper adsorption by Hypol-seaweed columns at an influent pH 5.0, 20° C, initial copper concentration of 6 mgl^{-1}, and flow rate of 4.7 l/hr	144
Fig. 5.49	The effect of seaweed weight on the percentage difference between the influent and the effluent copper concentrations by columns of cast in Hypol-seaweed at influent pH 5.0, T 20° C, initial copper concentration of 6 mgl^{-1}, and flow rate of 4.7 l/hr	145
Fig. 5.50	Copper uptake capacity as a function of biomass weight in Hypol-seaweed columns	146
Fig. 5.51	pH changes during copper adsorption at biomass weight of 11%	146
Fig. 5.52	pH changes during copper adsorption at biomass weight of 14.2%	146
Fig. 5.53	The uptake capacity and the percentage difference between the influent and the effluent copper concentrations for 4 different initial copper concentrations (6, 10, 20 and 30 mgl^{-1}) in seaweed-Hypol columns at an influent pH 5.0, 20° C, biomass weight 7.5% (approximate), and flow rate of 4.7 l/hr	148
Fig. 5.54	Langmuir isotherm of copper adsorption at different initial copper concentrations using data from seaweed-Hypol columns. In all cases the influent pH was 5.0, 20° C, biomass weight of 7.5% (approximate), and a flow rate of 4.7 l/hr	149
Fig. 5.55	pH changes in relation to the percentage difference between the influent and the effluent copper concentrations at different initial copper concentrations in seaweed-Hypol columns at an influent pH 5.0, 20° C, biomass weight of 7.5% (approximate), and flow rate of 4.7 l/hr	150
Fig. 5.56	pH changes during copper adsorption at different initial copper concentrations. Influent pH 5.0, 20° C, biomass weight of 7.5% (approximate), and a flow rate of 4.7 l/hr	150
Fig. 5.57	Adsorption of Cu (II), Zn (II) and Fe (II) from a simulated metal finishing wastewater using a seaweed-Hypol column at influent pH 5.0, 20° C, approximate biomass weight of 7.5%, initial Cu (II), Zn (II) and Fe (II) of 6 mgl^{-1} and flow rate of 4.7 l/hr	152
Fig. 5.58	Relation between the covalent index of the adsorbed metal	

species calculated at CN=4 and the uptake values 154

Fig. 5.59 Relation between the covalent index of the adsorbed metal species calculated at CN=6 and the uptake values 154

Fig. 5.60 Relation between the polarizing power of the adsorbed metal species calculated at CN=4 and the uptake values 154

Fig. 5.61 Relation between the polarizing power of the adsorbed metal species calculated at CN=6 and the uptake values 154

Fig. 5.62 Relation between the electronegativity of the adsorbed metal species and the uptake values 155

Fig. 5.63 Relation between the ionic radius of the adsorbed metal species and the uptake values 155

Fig. 5.64 pH changes during the removal of Cu (II), Zn (II) and Fe (II) from a simulated metal finishing wastewater using a seaweed-Hypol column at influent pH 5.0, 20° C, approximate biomass weight of 7.5%, initial Cu (II), Zn (II) and Fe (II) of 6mgl^{-1} and flow rate of 4.7 l/hr 156

Fig. 5.65 Removal of Cu (II), Zn (II) and Fe (II) from a simulated metal finishing wastewater using a control column of biomass free Hypol foam at influent pH 5.0, T 20° C, initial Cu (II), Zn (II) and Fe (II) of 6mgl^{-1} and flow rate of 4.7 l/hr 157

Fig. 5.66 Adsorption of Cu (II), Zn (II), Ni (II) and Cr (VI) from a simulated automatic plating of zinc base die casting effluent using a seaweed-Hypol column at an influent pH 5.0, 20° C, approximate biomass weight of 7.5%, initial Cu (II), Zn (II), Ni (II) and Cr (VI) of 6 mgl^{-1} and flow rate of 4.7 l/hr 159

Fig. 5.67 Relation between the covalent index of the adsorbed metal species calculated at CN=4 and the uptake values 161

Fig. 5.68 Relation between the covalent index of the adsorbed metal species calculated at CN=6 and the uptake values 161

Fig. 5.69 Relation between the polarizing power of the adsorbed metal species calculated at CN=4 and the uptake values 161

Fig. 5.70 Relation between the polarizing power of the adsorbed metal species calculated at CN=6 and the uptake values 161

Fig. 5.71 Relation between the electronegativity of the adsorbed metal species and the uptake values 162

Fig. 5.72 Relation between the ionic radius at CN=4 of the adsorbed

metal species and the uptake values 162

Fig. 5.73 Relation between the ionic radius at CN=6 of the adsorbed metal species and the uptake values 162

Fig. 5.74 pH changes during removal of Cu (II), Zn (II), Ni (II) and Cr (VI) from a simulated automatic plating of zinc base die casting effluent using a seaweed-Hypol column at an influent pH 5.0, 20° C, approximate biomass weight of 7.5%, initial Cu (II), Zn (II), Ni (II) and Cr (VI) of 6 mgl^{-1} and flow rate of 4.7 l/hr 163

Fig. 5.75 Removal of Cu (II), Zn (II), Ni (II) and Cr (VI) from a simulated automatic plating of zinc base die casting effluent using a control column of biomass free Hypol foam at an influent pH 5.0, 20° C, initial Cu (II), Zn (II), Ni (II) and Cr (VI) of 6 mgl^{-1} and flow rate of 4.7 l/hr 164

Fig. 5.76 Adsorption of Cu (II), Zn (II), Ni (II) and Cr (VI) from a simulated automatic plating of zinc base die casting effluent using 2 columns in series of seaweed-Hypol foam at an influent pH 5.0, 20° C, approximate biomass weight of 7.5% in each column, initial Cu (II), Zn (II), Ni (II) and Cr (VI) of 6 mgl^{-1} and flow rate of 4.7 l/hr 167

Fig. 5.77 pH changes during the removal of Cu (II), Zn (II), Ni (II) and Cr (VI) from a simulated automatic plating of zinc base die casting effluent using 2 columns in series of seaweed-Hypol foam at an influent pH 5.0, 20° C, approximate biomass weight of 7.5% in each column, initial Cu (II), Zn (II), Ni (II) and Cr (VI) of 6 mgl^{-1} and flow rate of 4.7 l/hr 168

Table of Plates

Plate 4.1	Non-viable powder of *Rhizopus oryzae* (particles D < 150 μm)	64
Plate 4.2	Alginate beads with (left) and without (right) fungal biomass	65
Plate 4.3	Polyacrylamide beads with (right) and without (left) fungal biomass	66
Plate 4.4	Polyvinlformal beads with (right) and without (left) fungal biomass	67
Plate 4.5	Hydrophobic polyurethane beads with (right) and without (left) fungal	68
Plate 4.6	K-Carrageenan beads with (right) and without (left) fungal biomass	69
Plate 4.7	Polysulfone beads with fungal biomass (the beads with and without biomass look exactly the same as the biomass is entirely covered by the polymer)	70
Plate 4.8	PEI beads without fungal biomass (top) and threads of PEI-biomass	72
Plate 4.9	Column with extensions	75
Plate 4.10	Column after casting the foam in	75
Plate 4.11	Foam in the column after removing the extensions and trimming back the foam	75
Plate 4.12	Column with end flanges assembled and ready for an experiment	75
Plate 5.1	Fungal biomass (x 100)	81
Plate 5.2	Fungi-polyurethane bead (x 40)	81
Plate 5.3	Fungi-PEI bead (x 40)	81
Plate 5.4	Fungi-alginate bead (x 40)	81
Plate 5.5	Fungi/k-carrageenan bead (x 40)	82
Plate 5.6	Fungi-polyacrylamide bead (x 40)	82

Plate 5.7	Fungi-polyvinlformal bead (x 40)	82
Plate 5.8	Fungi-polysulfone bead (x 40)	82
Plate 5.9	Mixers used in the experiments	89
Plate 5.10	Mixing device used in the experiments (variable speed controller)	89
Plate 5.11	Cross section in foam made using 2 pins mixer at 1rps and 20-30 sec mixing time	91
Plate 5.12	Cross section in foam made using paint mixer at 1rps and 20-30 sec mixing time	91
Plate 5.13	Cross section in foam made using flat mixer at 1rps and 20-30 sec mixing time	91
Plate 5.14	Cross section in foam made by hand mixing using a spatula 20-30 sec mixing time	91
Plate 5.15	Cross section in hydrophobic foam manufactured at 1rps and 20-30 sec mixing time using 2 pins mixer	93
Plate 5.16	Cross section in hydrophobic foam manufactured at 8 rps and 20-30 sec mixing time using 2 pins mixer	93
Plate 5.17	Cross section in foam manufactured at a mixing time of 90-120 sec and 40 rps	94
Plate 5.18	Cross section in foam manufactured at mixing time of approximately 5 seconds and 40 rps	94
Plate 5.19	Side view of a column of seaweed-Hypol foam after taking it from the moulding and removing the thin shell that covers it	97
Plate 5.20	Cross section in a column of Seaweed-Hypol	97
Plate 5.21	Two columns of seaweed-Hypol foam connected in series	165

Table of Tables

Table 2.1	Groups V, VI and VII which include majority of inorganic ligands	16
Table 2.2	Hard, Soft and Borderline metals and simple ligands (Pearson, 1963)	16
Table 2.3	Preferences of metal ions for ligand donor groups (Hughes and Poole, 1991)	17
Table 2.4	The ionic radii of some metallic ions of interest (Source: CRC Handbook of Chemistry and Physics, 1997). CN: Coordination number, Ri: radius in Angstrom	19
Table 2.5	Covalent index values and classification of some metal ions (Brady and Tobin, 1995)	20
Table 2.6	Metal ions uptake capacity reported by Tobin et al. (1984) using *R. arrhizus*	21
Table 4.1	Detection limits of atomic absorption spectrophotometer based on flame for selected elements (Skoog et al., 1988)	77
Table 5.1	Polymer bead weights used in adsorption experiments so as to give a comparable biomass content of 100 mg	83
Table 5.2	Freundlich and Langmuir isotherm parameters for Cu adsorption by Hypol immobilised fungal biomass for 4 consecutive adsorption cycles	117
Table 5.3	Freundlich and Langmuir isotherm parameters for Cu adsorption by Hypol immobilised seaweed biomass for 4 consecutive adsorption cycles.	120
Table 5.4	Freundlich and Langmuir isotherm parameters for Cu adsorption by 100 mg dry wt. of immobilised seaweed in Hypol beads with respect to temperature at pH 5.0 and initial copper concentrations (2-60) mgl^{-1}	124
Table 5.5	Freundlich and Langmuir isotherm parameters for Cu adsorption by 100 mg dry wt. of immobilised seaweed in Hypol beads with respect to pH at 20° C and initial copper concentrations (2-60) mgl^{-1}	127
Table 5.6	Langmuir isotherm parameters for Cu adsorption using seaweed-Hypol columns at 20° C, influent pH 5.0, biomass weight of 7.5 % (approximate) and initial copper concentrations of 5.9, 10.7, 20.2 and 31.7 mgl^{-1}	149

Table 5.7	Calculated values of covalent index and polarizing power of the adsorbed species (Cu, Zn and Fe)	153
Table 5.8	Calculated values of covalent index and polarizing power of the adsorbed species (Cu, Zn, Ni and Cr)	160
Table 6.1	Copper uptake capacity and the percentage difference between the initial and final copper concentrations of non-immobilised and immobilised *Rhizopus oryzea* in seven selected types of polymers at 2 mgl^{-1} Cu concentration, initial pH 7.0, 200 rpm shaking speed, 20° C and contact time of 1 and 4 hours	170
Table 6.2	Copper adsorption results using beads of biomass/Hypol foam at different experimental conditions	175
Table 6.3	Summary of the effect of flow rate on copper adsorption using columns of seaweed-Hypol hydrophilic foam (All experiments were conducted at 6 mgl^{-1} Cu concentration and 7% biomass weight ratio, 20° C and initial solution's pH 5.0)	177
Table 6.4	Summary of the effect of biomass weight ratio on copper adsorption using columns of seaweed-Hypol hydrophilic foam (All experiments were conducted at 6 mgl^{-1} Cu concentration and 4.7 $l.hr^{-1}$ flow rate, 20° C and initial solution's pH 5.0)	178
Table 6.5	Summary of the effect of initial Cu concentrations on copper adsorption using columns of seaweed-Hypol hydrophilic foam (All experiments were conducted at flow rate of 4.7 $l.hr^{-1}$ and 7% biomass weight ratio, 20° C and initial solution's pH 5.0)	178
Table 6.6	Summary of the effect of the presence of competing ions on copper adsorption using columns of seaweed-Hypol hydrophilic foam (All experiments were conducted at 6 mgl^{-1} Cu initial concentration, 4.7 $l.hr^{-1}$ flow rate and 7% biomass weight ratio, 20° C and initial solution's pH 5.0)	178

CHAPTER 1

Background: Heavy metals and the environment

1.1 Introduction

The pollution of the environment by heavy metals has attracted a lot of attention due to their potential effects on human health and the environment. Contamination of the aquatic environment by heavy metals is considered to be one of the most serious problems because of the potential for heavy metal bioaccumulation. Natural processes such as weathering can introduce these pollutants into the environment, but only in small quantities, so most are man-made. Usually high concentrations of heavy metals are only found when discharged from chemical processes or as a bi-product of mining operations.

Since the Industrial Revolution, the production of heavy metals such as lead, copper, and zinc has increased exponentially. Between 1850 and 1990, production of these three metals increased nearly 10-fold, with emissions rising in tandem (Nriagu, 1996), Figure 1.1.

Heavy metals are used extensively by human society in commerce and industry and they are nearly taking part in most things around us. However the discharge of effluents laden metals into the environment without treatment or control could lead to catastrophic effects on the environment. Once in the seas and oceans, heavy metals do not decompose, but they accumulate and can become concentrated in food chain or buried by the build up of sediments.

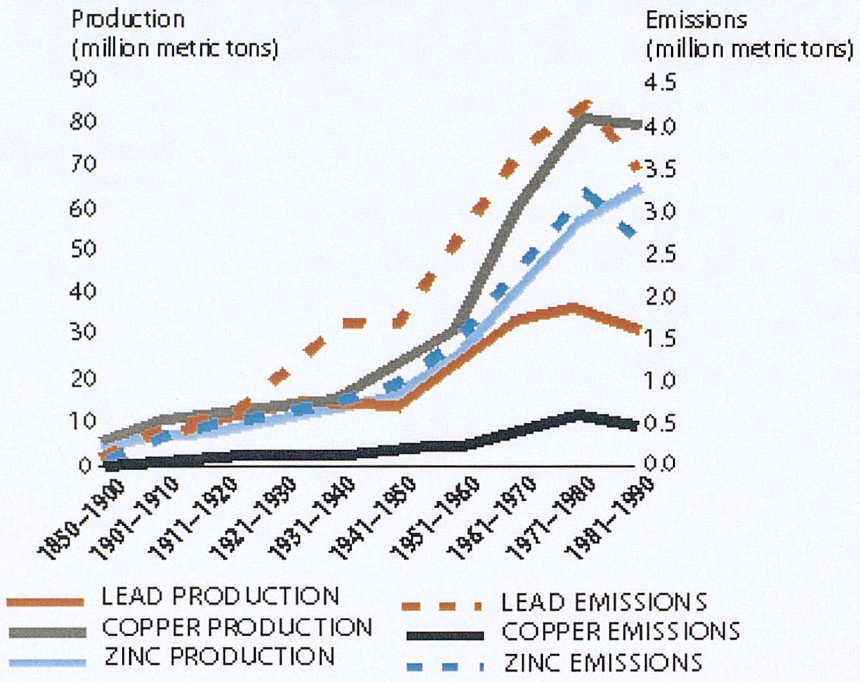


Fig. 1.1: Global Production and Consumption of Selected Toxic Metals, 1850-1990, (Nriagu, 1996).

The toxicity of heavy metals has been documented throughout history. Greek and Roman physicians diagnosed symptoms of acute lead poisoning long before toxicology became a science (Wri.org, 2003). Today, much more is known about the health effects of heavy metals. In Japan between 1940 and 1965 a disease called Itai-Itai was probably associated with a high intake of the toxic metal cadmium from eating rice grown on land irrigated with cadmium-contaminated water caused the death and injury of several people. Symptoms included kidney and gastrointestinal damage, with bone softening (Nomiyama, 1973). In January 2000, a tailings dam failure at a mine complex in northwest Romania resulted in a 100,000 m^3 spillage of toxic waste into a tributary of the river Danube. The spill plume, containing copper, cyanide and other heavy metals, reached the Black Sea via the rivers Sasar, Lapus, Somes, Tisza and the Danube itself. Romania suffered widespread disruption to public water supplies and costly interruptions to industry and to operations on wastewater plants. Further down stream, Hungary reported over 1200 tonnes of dead fish and heavy kills were also observed in Yugoslavia (MacCann, 2003).

Arsenic contamination of groundwater has been found in Bangladesh, India, Taiwan,

Ghana, Mongolia and New Zealand, in addition to several countries in South, Central and North America. New cases have emerged in several other countries like Hungary, Greece, the Baltic States, Nepal, Sri Lanka and Nicaragua (Petrusevski et al., 2002). Arsenic presence in groundwater is consequently recognised as a threat to public health world-wide and specifically in rural areas of several developing countries. Situation is most serious in Bangladesh where millions of people in 50,000 out of 80,000 villages are exposed to arsenic poisoning of drinking water. In total 3.5 million out of 8 million tubewells have arsenic concentration above the Bangladeshi standard of 50 μg/l, which incidently is five times higher than the WHO and EU standards (Petrusevski et al., 2002). Long-term exposure to very low arsenic concentrations causes cancer of the skin, lungs, urinary bladder and kidney, in addition to skin pigmentation changes and skin thickening known as hyperkeratosis (WHO 2001, Smith *et al.* 1999). Arsenic potentially present in drinking water is the main source of human intake of inorganic arsenic, known to be much more toxic than organic arsenic found in the food (Donohue and Abernathy 1999).

In the UK, contaminated water emanating from deserted mines still represents a big threat to the environment. Agricultural land in the Vale of York was contaminated with dangerous levels of heavy metals during the floods of 2001. Soil samples showed that metals originating from disused mines in the Yorkshire Dales were washed 50 miles downstream by the flooded River Swale. 70% of the examined flood sediments had lead deposits 10 times higher than the accepted safe limits (News.com, 2003). Lead is particularly toxic to the brain, kidneys, reproductive system, and cardiovascular system. Exposures can cause impairments in intellectual functioning, kidney damage, infertility, miscarriage, and hypertension (Wri.org, 2003).

For these reasons, the removal of heavy metals from aquatic solutions has been thoroughly investigated. Common heavy metal treatment methods are precipitation, oxidation/reduction, ion-exchange, membrane technology, evaporation, solid/liquid separation and adsorption using activated carbon. These methods have significant disadvantages such as incomplete metal removal, high reagent or energy requirements, the generation of toxic sludges or other waste products. In addition, such methods are generally expensive (Sag and Kutsal, 1995).

The sorption of metals by bio-materials has also received a lot of attention from researchers because of its high efficiency regarding the removal of heavy metals and its relatively inexpensive compared with other methods. However, further research is

needed in order to make it fully applicable and economically viable for practical application.

1.2 The objective of this study

The main objective of this research is to investigate the possibility of converting the removal of heavy metals from aquatic solutions using non viable biomasses especially readily available and/or wasted biomasses from laboratorial scale into a full practical scale. This can be achieved by incorporating the biomass into a suitable immobilisation matrix where the immobilised biomass can be reused in successive cycles either in batch or other types of reactors. The immobilisation matrix should not reduce the adsorption capacity of the immobilised biomass, should allow the incorporation of wasted or readily available biomasses, should be porous and hydrophilic as to allow solutions to pass through without pressure drop or diffusion limitations and to be robust and durable. For this reason experiments will be conducted first to compare the sorption capacities and kinetics of biomass immobilized in a number of selected types of polymers that had previously been reported as successful matrices for this purpose. Further experiments and investigation will be conducted, in the second stage of the study, on the best matrix between the tested matrices in order to develop the use of the matrix in to a full practical scale.

1.3 Heavy metal definitions

The term "heavy metals" is often used very loosely in the literature and many definitions have been applied. Hackh's chemical dictionary (1969) defined heavy metals as those metals having a specific gravity greater than 4. Alloway and Ayres (1993) defined them as a group of metals and metalloids with an atomic density greater than 6 $g.cm^{-3}$, yet reported As and Ba as heavy metals despite their density being less than 6 $g.cm^{-3}$. Finally, the McGraw-Hill dictionary of scientific and technical terms (1974) defined heavy metals as those whose specific gravity is approximately 5 or higher. The latest definition has been used widely in different references (Jones, 1978; Beveridge and Doyle, 1989), but it should contain "metals, poor metals and metalloids" instead of metals, where many metalloids (Ge, As and

Te) and poor metals (Ga, In, Sn, Sb, TI and Pb), were reported as heavy metals (Beveridge and Doyle, 1989; Alloway and Ayres, 1993). The heavy metals exclude alkali metals, alkaline earth's, Lanthanide's and actinides. Fig.1.2 shows the heavy metals according to the last definition.

H																He
Li 0.53	Be 1.85										B 2.46	C 2.26	N	O	F	Ne
Na 0.97	Mg 1.73										Al 2.7	Si 2.33	P 1.82	S 1.96	Cl	Ar
K 0.86	Ca 1.55	Sc 2.98	Ti 4.50	V 5.96	Cr 7.2	Mn 7.2	Fe 7.86	Co 8.9	Ni 8.9	Cu 8.92	Zn 7.14	Ga 5.9	Ge 15.3	As 5.72	Se 4.81	Br	Kr
Rb 1.53	Sr 2.62	Y 4.47	Zr 6.51	Nb 8.57	Mo 10.2	Tc 11.5	Ru 12.3	Rh 12.3	Pd 12.0	Ag 10.4	Cd 8.65	In 7.31	Sn 7.28	Sb 6.69	Te 6.24	I 4.66	Xe
Cs 1.88	Ba 3.51	La 6.14	Hf 13.3	Ta 16.6	W 19.2	Re 21.0	Os 22.6	Ir 22.6	Pt 21.0	Au 19.3	Hg —	TI 11.8	Pb 11.3	Bi 9.78	Po 9.19	At —	Rn
Fr —	Ra 5.00	Ac 10.0														

The shaded rectangle comprises Heavy metals

La: The first element in Lanthanides

Ac: The first element in Actinides

Se: is non-metal although it was reported as heavy metal (Lesaca, 1975).

Fig. 1.2 Periodic table, showing the elements, including heavy metals, and their density ($g.cm^{-3}$)

1.4 Heavy metals removal technologies

Methods that have traditionally been used for the removal of heavy metals are, (Forster and Wase, 1997):

- Precipitation
- Ion exchange
- Membrane technology
- Adsorption using carbon/activated carbon
- Solid/liquid separation and oxidation/reduction

1.4.1 Precipitation

Precipitation is a physico-chemical process which involves the transformation of a substance in a solution into a solid phase. In the process, the chemical equilibrium which affects the solubility of the components is altered and this can be achieved in a variety of ways:

1-The addition of a substance which will react directly with the substance in the solution to form an insoluble compound.

2-The addition of a substance which will result in a shift in the solubility equilibrium to a point which no longer favours the continued solubility of the original substance in the solution.

3- The change in temperature of a saturated or nearly saturated solution in the direction of decreased solubility (Som, 1995).

Three kinds of precipitation method are used in practice, these are:

1.3.1.1 Hydroxide precipitation

Hydroxide precipitation depends on using an alkaline (e.g. lime or caustic soda) to precipitate the metal ions as insoluble hydroxides which can be easily removed from solution. The formation of the metal hydroxides can be summarised by the following equation:

$$M^{n+} + nOH^- \rightarrow M(OH)n\downarrow$$

where M represents a metal

The residual metal concentration is dependent upon the pH of the solution as shown in figures 1.3, 1.4 and 1.5 using different chemical precipitants. This type of solubility graph is obtained by preparing solutions of simple metal salts and then adjusting these to the required pH values with the chosen reagent. At each stage the sample is vigorously mixed then filtered through a Whatman No. 40 filter paper after the precipitate has formed. The concentration of the metal in the filtrate can then be determined by atomic absorption spectrophotometry or another suitable method. The curves show mean rather than individual values, because the reproducibility of this

type of determination is not high (Eilbeck and Mattock, 1987). Hydroxide precipitation is interfered with by organic substance and complexes. Its use is therefore restricted to industries such as inorganic chemicals production, plating and metal finishing, mining, textiles, steel and iron, non ferrous metal processing and electronics (Little, 1986).

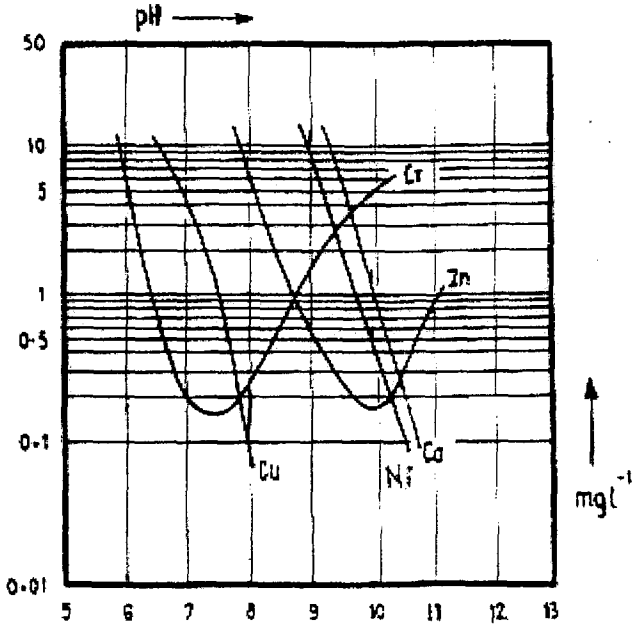


Fig. 1.3 Residual soluble metal concentration as a function of pH using NaOH as precipitant. Precipitate stood for 30 minutes before filtration (Eilbeck and Mattock, 1987)

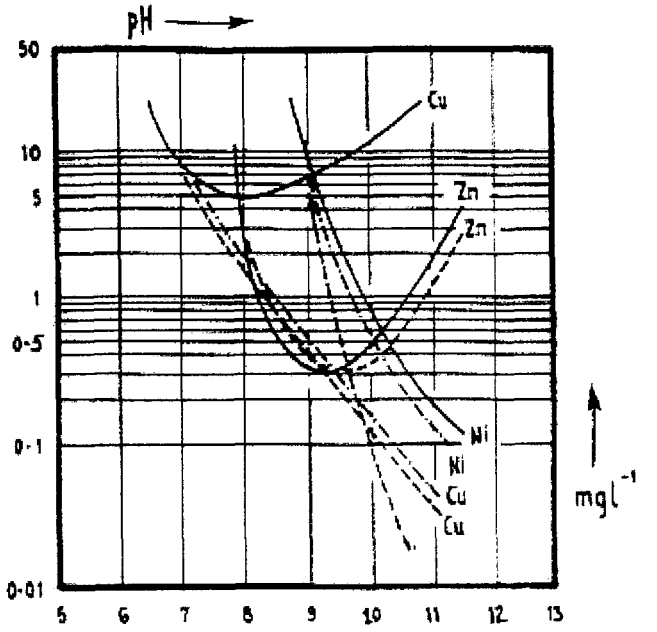


Fig. 1.4 Residual soluble metal concentration as a function of pH using Na_2CO_3 as precipitant. Solid lines: precipitate stood for 30 minutes before filtration. Broken lines: precipitate stood for 24 hours before filtration. Broken dotted lines: precipitate stood for 30 minutes before filtration, with polyelectrolyte present (Eilbeck and Mattock, 1987)

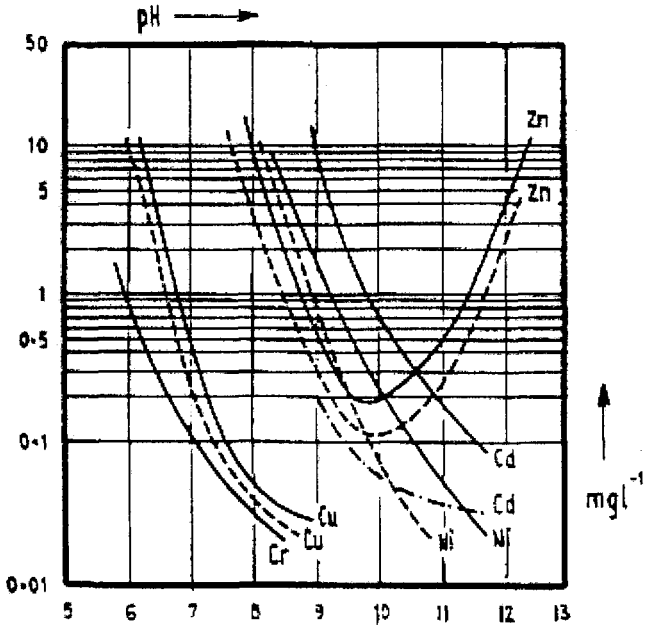


Fig. 1.5 Residual soluble metal concentration as a function of pH using Ca $(OH)_2$ as precipitant. Solid lines: precipitate stood for 30 minutes before filtration. Broken lines: precipitate stood for 24 hours before filtration. Broken dotted lines: co-presence of excess phosphate (Eilbeck and Mattock, 1987)

1.3.1.2 Sulphide precipitation

Either sodium sulphide or sodium bisulphide is added which causes the insoluble metal sulphides to precipitate out of solution. These are then removed by gravity settlement or filtration. The reaction taking place can be represented by the following general equation:

$$M^{n+} + Na_2 S \longrightarrow MS \downarrow + 2Na^{n+}$$

where M represents metal

The major problem in using sulphide precipitation is associated with the extreme toxicity of gaseous sulphides and the pH of the waste stream must be raised to prevent their formation. In addition, care has to be taken in the handling of sulphide prior to its use, and a post-treatment system is required to remove excess sulphide from the effluent stream.

1.3.1.3 Precipitation by xanthate

These can be generated by mixing starch or cellulose with carbon disulphide in a caustic medium. Three types of xanthates have been used in pilot-scale studies, i.e., soluble starch xanthate with a cationic polymer, insoluble starch xanthate, and fibrous cellulose xanthate.

The reactions involved in this process can be summarised by the following generalised equation:

$$2[ROCS\ (=S)\ Na] + M^{n+} \longrightarrow [ROCS\ (=S)\ 2M] + 2Na^{n+}$$

where: R = starch or cellulose

M = metal

This process is reported to be effective in removing metals over a pH range from 3 to 11 with an optimum between 7 and 9. However, care must be taken when handling the carbon disulphide during xanthate production (Little, 1986).

It has been reported that this type of technology (i.e. precipitation) provides an effective removal of the polluting metals and, if coagulation/flocculation stage is also used, removals of up to 99% can be achieved (Forster and Wase, 1997).
However, the precipitation methods pose one very important operating deficiency, that is: they produce a large amount of metal sludge which requires special handling and disposal. In other words, it transforms an aquatic pollution problem to one associated with solid waste disposal. The amount of sludge, as well as its quality, will vary with the chemicals being used and the metals involved. For example, sodium hydroxide often produces a bulky, poor settling sludge whereas lime gives a dense sludge with good settling properties (Forster and Wase, 1997).

1.4.2 Ion exchange

Ion exchangers, by definition, are insoluble solid materials which carry exchangeable cations or anions. These ions can be exchanged for a stoichiometrically equivalent amount of ions of the same charge when the ion exchanger is in contact with an electrolyte solution. Carriers of exchangeable cations are called cation exchangers, and carriers of exchangeable anions, anion exchangers. Certain materials are capable of both cation and anion exchange, these are called amphoteric ion exchangers (Helfferich, 1995).

A typical cation exchange is:

$$2NaX\,(s) + CaCl_2\,(aq) \longleftrightarrow CaX_2\,(s) + 2NaCl\,(aq)$$

and a typical anion exchange is:

$$2XCl\,(s) + Na_2SO_4\,(aq) \longleftrightarrow X_2SO_4\,(s) + 2NaCl\,(aq)$$

where X represents a structural unit of the ion exchanger

Ion exchange is, with a few exceptions, a reversible process. For example, in water softening, a cation exchanger which has lost all its Na^+ ions can be regenerated with a

solution of a sodium salt such as NaCl. Many natural solids in soil, proteins and zeolites have been used for ion exchange, however, synthetic resins are more usually employed (Little, 1986).

The principal industrial use for ion exchange is for removing low levels of ionic impurities from solution and concentrating them in the spent regenerant.

Ion exchangers have found an important role in the decontamination of radioactive waste water. In the UK, an ion exchange plant has been installed by British Nuclear Fuels plc (BNFL) at Sellafield to treat radioactive contaminated water before discharge to the Irish Sea (Little, 1986).

Ion exchange resins are susceptible to fouling by suspended solids, oil and grease, detergents and other organic species. Waste water bearing these items should be pre-treated before passing through the ion exchange (Hill, 1999).

1.4.3 Membrane technology

A membrane is a material through which one type of substance can pass more readily than others, thus presenting the basis of a separation process (Solt, 1999). Membranes can be divided according to their chemical composition and physical structure into dense and porous. Dense membranes, such as those used in reverse osmosis (RO), have chemical selectivity and can separate components through physico-chemical interaction between the permeating components and the membrane materials. Porous membranes, such as nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) membranes, achieve separation mechanically through sieving or straining (Judd, 1999).

Of the above mentioned membranes only reverse osmosis is able to remove and separate metal ions from solutions. Reverse osmosis uses a semi-permeable membrane which has the property of passing water molecules and rejecting elements with a diameter > 0.1-2 nm (Judd, 1999). Reverse osmosis is widely used for desalinating brackish water and seawater, removing bulk ionic material in pure and ultra-pure water production, preparation of pyrogen-free water, colour removal from dye wastewater, heavy metals removal from electroplating rinse water, recovery of lactose and lactic acid from dairy wastes, lignin sulphite/bisulphite removal from pulp/paper industrial wastes and landfill leachate treatment. RO can work at efficiencies of 99.5% for dilute solutions but requires high pressure, 20 bars for

brackish water and up to 80 bars for seawater, to achieve this and this has high associated costs. RO, also, requires expensive pre-treatment to protect the membranes, and membrane materials have limited thermal and chemical stability.

However, recent trends in improved specific fluxes and more robust and inexpensive materials suggest that reverse osmosis is becoming a more viable solution for the treatment of industrial wastewater (Judd, 1999).

The use of NF, UF and MF for the removal of heavy metals is possible if water bearing the dissolved ions is pre-treated to enlarge their size. Golden (2002) reported a method for heavy metals removal from wastewaters by first adjusting the pH to 7 or greater to precipitate oxides and hydroxides of the heavy metals, then introducing a polymeric metal removing agent to substantially precipitate the remaining soluble heavy metals and lastly removing the products of the last two steps by filtering the wastewater through low pressure (maximum of 1 bar), high flow microfilters.

1.4.4 Activated carbon adsorption

Adsorption, by definition, is the process of collecting soluble substances that are in solution onto a suitable interface (Little, 1986). Activated carbons, in either granular or powdered form, have been widely used as adsorbents in water treatment plants to remove taste and odour causing contaminants.

Activated carbon is prepared by first making a char from materials such as almond, coconut, and walnut hulls, other woods, and coal. The char is produced by heating the material to a read heat in a retort to drive off the hydrocarbons, but with an insufficient supply of air to sustain combustion. The char particle is then activated by exposure to an oxidising gas at a high temperature. The gas enables a porous structure in the char to be formed and thus creates a large internal surface area. After activation, the carbon can be separated into, or prepared into, different sizes with different adsorption capacities. The two size classifications are powdered which has a diameter of less than 0.075 mm, and granular with a diameter greater than 0.1 mm (Tchobanoglous and Burton, 1991).

Trace metal adsorption by activated carbon from aqueous solutions has been studied in some details. Kim and Zoltek (1977) and Bowers and Huang (1981) reported the use of Filtrasorb 400 (Granular Activated Carbon) for the removal of hexavalent chromium, while Alaerts et al. (1989) used a carbon produced from coconut shells.

GAC filters are also being evaluated for the 'point of use' removal of lead from drinking water (Kuennen et al., 1992).

An activated carbon was modified to have bactericidal properties to enhance its adsorption capacity and used to purify drinking water from heavy metals and other toxic substances (Pimenov, 1998).

Archer (2001) has patented a filter of different layers, one of them is a granulated activated carbon for treating tap water to remove major water contaminants found in municipal water, including heavy metals.

However, poor adsorption has been demonstrated for some metals and in these cases an organic complexing agent is needed (Bhattacharya and Cheng, 1987). Also carbon adsorption is an expensive treatment process and, with environmental concern growing in developing countries, there has been considerable research interest into the use of alternative low-cost adsorbents which would be considered as single-use materials (Forster and Wase, 1997).

1.4.5 Other removal technologies

Other removal technologies such as electrolysis, electrodialysis, and adsorption using materials other than activated carbon have been reported.

Suyama et al., (1995) used egg shell membrane powder to accumulate Au (III), Pb (II), Pt (III) and Rd (III) from their dilute aqueous solution. Benjamin et al., (1999) patented an adsorbent material which consists of an iron oxide coated mineral having olivine structure to remove metal contaminants and natural organic matters from water.

Kreisler (2001) developed a method that employs a unique complexing agent comprising a carbamate compound and an alkali metal hydroxide to facilitate the formation of metals into ionic metal particles enabling them to be readily separated, removed and recovered. The author reported that this technique removes, separates and recovers metals in a cost effective manner with more than 95% removal from waste streams and with minimal amounts of unprocessed solids and sludge remaining in the environment.

Cody et al. (1997) used organo-clay to sorb heavy metals from aqueous solutions which are then removed by flotation.

Bakhir et al. (1997) used an apparatus for electrochemical purification of water solutions and removal of heavy metals. The apparatus consisted of at least one electrochemical cell which contains vertical coaxial cylindrical and rod electrodes made from material which is not soluble during electrolysis and an ultrafiltration ceramic diaphragm installed in the bushings between the electrodes to create inter-electrode space in the electrode chambers.

Morkovsky et al. (1999) employed an apparatus for electro-coagulative treatment and removal of contaminants including heavy metals from industrial waste water. The process worked by passing waste water containing contaminants susceptible to electro-coagulation between pairs of electrodes within a reactor cell, energizing the electrodes with direct current, thereby breaking down and chemically altering contaminants in the electrolyzed water to form a flocculate which can be separated from cleaned water by sedimentation.

1.5 Biosorption technologies

Heavy metals removal technologies mentioned in section 1.4 have significant disadvantages such as incomplete metal removal, high reagent or energy requirements, the production of large amount of toxic sludges (in the case of precipitation), high cost, and the need for expert operators in some technologies (e.g. membranes, electrolysis and electrodialysis).

Biosorption technology which uses low-cost bio-materials for the removal of heavy metals from aquatic solutions represents a potential effective and low cost alternative compared to the current available technologies. The definition and full background about the use of this technology is given in chapter 2.

CHAPTER 2

Biosorption as an approach to heavy metals removal from aquatic systems

2.1 Definition of bio-sorption and bio-adsorption

Sorption processes include a number of separation processes in which molecules of a particular species (the sorbate) are transferred from a liquid or gas phase to a solid phase (the sorbent). There are two principal types of sorption process; absorption, in which at equilibrium the sorbate is homogeneously distributed through the sorbent, and adsorption, in which the sorbate is uniformly distributed on the surface of the sorbent (Hill, 1998). If the sorbent is a biomaterial, then the adsorption process called bio-adsorption.

Generally the selective sequestering of metal ions and organic molecules from aquatic solution by microbial biomass has been termed "Biosorption" (Beveridge, 1978; Friis and Myers-Keith, 1986).

2.2 Classification of metals according to biosorption process

The extent to which a metal ion will bind to a ligand depends largely on the chemistry of the metal ion and its preference to form ionic or covalent bonds (Nieboer and Richardson, 1980). Metal ions act as Lewis acids by accepting electron pairs from ligands. The majority of all inorganic ligands are from groups V, VI, and VII from the periodic table of elements (table 2.1).

Table 2.1 Groups V, VI and VII which include majority of inorganic ligands

V	VI	VII
N	O	F
P	S	Cl
As	Se	Br
Sb	Te	I
Bi	Po	At

According to Pearson (1963), metal ions of biological interest can be classified into three classes: hard (class A), soft (class B) and intermediate. Class A forms their most stable complexes with the first ligand atom of each group, while class B form their most stable complexes with the second or subsequent member of each group. The third class was called borderline metal ions which form an intermediate group that exhibit a high affinity for the class B metal-binding donor atoms and ligands.

Table 2.2 shows the hard, soft and borderline metals in addition to hard, soft and borderline simple ligands. As a general rule, hard ligands prefer to bind to hard metals and soft ligands prefer to bind to soft metal ions. But if both hard and soft metal ions are present, then the soft metal ions will often win the competition for binding ligands, and will displace essential metal ions from their sites (Hughes and Poole, 1991).

Table 2.2 Hard, Soft and Borderline metals and simple ligands (Pearson, 1963)

Metals (Lewis acids)			Simple Ligands (Lewis bases)		
Hard	Borderline	Soft	Hard	Borderline	Soft
Na^{+}	Fe^{2+}	Cu^{+}	H_2O	Pyridine	CN^{-}
K^{+}	Co^{2+}	Pb^{2+}	ROH		RSH
Rb^{+}	Ni^{2+}	Cd^{2+}	$-COO^{-}$		R_2S
Mg^{2+}	Cu^{2+}	Hg^{2+}	NH_3		$S_2O_3^{2-}$
Ca^{2+}	Zn^{2+}	Tl^{+}	RNH_2		
Mn^{2+}		Ag^{+}	Porphrin		
Fe^{3+}		Au (I)	Cl^{-}		
Al^{3+}		Sn (II)	PO_4^{3-}		
Co^{3+}			SO_4^{2-}		

Hughes and Poole (1991) used table 2.2 to draw the preference of metal ions for a ligand donor group, their combinations of metals and ligands are given in table 2.3.

Table 2.3 Preferences of metal ions for ligand donor groups (Hughes and Poole, 1991)

O		O/N/S		N/S	
Na	Al	V	Pb	Co	Hg
K	Fe	Cr	Ga	Ni	Cu
Mg	Ca	Mn	Tl	Zn	
		Fe	Cd		
		Mo			

Nieboer and Richardson (1980) reported that class A metals have the following preference sequence for metal-binding donor atoms in biological ligands: O > N > S, and in contrast, class B metal ions exhibit the opposite preference sequence: S > N > O.

Class A Lewis acids are described as non-polarizable hard metals that prefer to bind to non-polarizable hard bases by bonds that are principally ionic while class B Lewis acids are described as polarizable soft metals that prefer to bind to polarizable soft bases by bonds that are principally covalent (Brady and Tobin, 1995)

An index to class B behaviour of metal ions was devised by Nieboer and Richardson (1980) and called the "Covalent index". The covalent index is calculated by the following expression:

$$\text{Covalent index} = (Xm)^2 \,.\, R_i$$

where Xm = electronegativity and R_i = ionic radius (A^o)

The electronegativity describes, on a relative basis, the tendency of an atom in a molecule to attract bonding electrons. The electronegativity depends on the oxidation state of the element. Figure 2.1 gives the electronegativity values for the most common oxidation state (CRC Handbook of Chemistry and Physics, 1997). The ionic

radii vary and depend on co-ordination number, electronic spin state, covalency, and the presence of strong anion-anion or cation-cation repulsive forces (Shannon and Prewitt, 1968). Table 2.4 gives the ionic radii of some elements of interest (CRC Handbook of Chemistry and Physics, 1997).

H 2.20														
Li 0.98	Be 1.57										B 2.04	C 2.55	N 3.04	O 3.44
Na 0.93	Mg 1.31										Al 1.61	Si 1.90	P 2.19	S 2.58
K 0.82	Ca 1.0	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55
Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.60	Mo 2.16	Tc 2.10	Ru 2.20	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.10
Cs 0.79	Ba 0.89	La 1.10	Hf 1.30	Ta 1.50	W 1.70	Re 1.90	Os 2.20	Ir 2.20	Pt 2.20	Au 2.40	Hg 1.90	TI 1.80	Pb 1.80	Bi 1.90	Po 2.0

Fig. 2.1 The electronegativity of heavy metals and other elements of interest to the biosorptive process in the periodic table. The shaded area comprises heavy metals (CRC Handbook of Chemistry and Physics, 1997)

Table 2.4 The ionic radii of some metallic ions of interest (Source: CRC Handbook of Chemistry and Physics, 1997). CN: Coordination number, Ri: radius in Angstrom

Ion	CN	Ri	Ion	CN	Ri	Ion	CN	Ri
Ag^{+}	4	1.00	Cr^{4+}	4	0.41	Pb^{2+}	6	1.19
	6	1.15		6	0.55		8	1.29
	8	1.28	Cr^{6+}	4	0.26		10	1.40
Ag^{2+}	4	0.79		6	0.44		12	1.49
	6	0.94	Cu^{+}	2	0.46	Pb^{4+}	4	0.65
Al^{3+}	4	0.39		4	0.60		6	0.78
	5	0.48		6	0.77		8	0.94
	6	0..54	Cu^{2+}	4	0.57	K^{+}	4	1.37
As^{3+}	6	0.58		6	0.73		6	1.38
As^{5+}	4	0.34	Fe^{2+}	4	0.63		8	1.51
	6	0.46		6	0.61		12	1.64
Au^{+}	6	1.37		8	0.92	Ti^{+}	6	1.50
Au^{3+}	4	0.64	Fe^{3+}	4	0.49		8	1.59
	6	0.85		6	0.55		12	1.70
Cd^{2+}	4	0.78		8	0.78	U^{3+}	6	1.03
	6	0.95	Mn^{3+}	6	0.58	U^{4+}	6	0.89
	8	1.10	Mn^{4+}	4	0.39		8	1.00
	12	1.31		6	0.53	U^{5+}	6	0.76
Co^{2+}	4	0.56	Mn^{5+}	4	0.33	U^{6+}	2	0.45
	6	0.65	Mn^{6+}	4	0.26		4	0.52
	8	0.90	Mn^{7+}	4	0.25		6	0.73
Co^{3+}	6	0.55	Ni^{2+}	4	0.49	Zn^{2+}	4	0.60
Cr^{2+}	6	0.73		6	0.69		6	0.74
Cr^{3+}	6	0.62	Ni^{3+}	6	0.56		8	0.90

According to Nieboer and Richardson (1980) the greater the covalent index value of a metal ion, the greater its degree of class B character, and consequently its potential to form covalent bonds with biological ligands. Brady and Tobin (1995) reported that Sr^{2+} is a class A metal, whereas Mn^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, and Pb^{2+} are borderline metals. Covalent index values of these metals increases in the order: $Sr^{2+} < Mn^{2+} < Zn^{2+} < Cd^{2+} < Cu^{2+} < Pb^{2+}$ (table 2.5). The authors however did not report what values of radii were used in their calculation of the covalent index. These values are dependent on the type of the ligand in solution that will take part in the bond.

Table 2.5 Covalent index values and classification of some metal ions (Brady and Tobin, 1995)

Metal	$(Xm)^2 R_i$	Class
Sr^{2+}	1.05	A
Mn^{2+}	1.97	Borderline
Zn^{2+}	2.13	Borderline
Cd^{2+}	2.71	Borderline
Cu^{2+}	2.98	Borderline
Pb^{2+}	3.29	Borderline

Tobin et al. (1984) conducted research to remove 17 different types of metal cations and anions from aquatic solutions using non-viable biomass of *Rhizopus arrhizus*.

The absorption process of metal cations was carried out at an initial pH of 4 without the use of buffers. The authors claimed that the amount of uptake of the cations was directly related to ionic radii of La^{3+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ba^{2+}, Hg^{2+}, Pb^{2+}, UO^{2+}_2 and Ag^{+}, and the biomass did not absorb any of the alkali metal ions of Na^{+}, K^{+}, Rb^{+} and Cs^{+}. The ionic radii were reported to be estimated but values were not stated. Table 2.6 shows the reported uptake capacity of each cation. The authors further explained that Cr (III) forms different complex oxy-anions in solutions and the actual charge of these complexes is less than 3 and the actual radii are significantly larger than that for simple Cr (III). No correlation was observed in the study with ionic charge or effective nuclear charge of the ions.

The results of this study cannot be generalised as there is no clear cut linear relationship between the ions uptake capacity and the ionic radius. Also they found copper to be the least absorbed species whilst it has been reported by other authors to be the most strongly sorbed metal ion (Crist et al., 1981; Brady et al., 1994; Lu and Wilkins, 1996).

Table 2.6 Metal ions uptake capacity reported by Tobin et al. (1984) using *R. arrhizus*

Metal ion	Uptake capacity (m.mole/g)
UO_2^{2+}	0.82
Cr^{3+}	0.59
Pb^{2+}	0.5
Ag^{+}	0.5
Ba^{2+}	0.41
La^{3+}	0.35
Zn^{2+}	0.30
Hg^{2+}	0.29
Cd^{2+}	0.27
Cu^{2+}	0.25
Mn^{2+}	0.22

Hughes and Poole (1991) in their review article about metal speciation in microbial growth media reported that the ability of a metal ion to complex a ligand depends upon its *polarizing power.* This is defined as the ratio of "cation charge / cation radius". A cation of high polarizing power is seen by the ligand as a centre of high density of positive charge, and strong interaction takes place between the metal ion and the ligand. Such a metal ion is described as a strong Lewis acid. Ionic size (i.e. radius) decreases from left to right across the periodic table. This means that the alkali cations Na^+ and K^+ interact very weakly with ligands, and can be disregarded from a speciation point of view. The doubly-charged cations Mg^{2+} and Ca^{2+} interact more strongly with ligands than do the cations Na^+ and K^+, but weakly compared to the transition metal ions.

The authors also claimed that the ionic radii of the transition metal ions decrease in size down to Cu^{2+}, with an increase to Zn^{2+}. Thus in broad terms, the strength of interaction between divalent transition metal ions and ligands increases from left to right across the first transition series, Mn (II) < Fe (II) < Co (II) < Ni (II) < Cu (II) > Zn (II). Cations such as Fe^{3+} bind more strongly still, in view of their greater polarizing power (i.e. Lewis acidity). However the authors reported that the binding of some of the toxic metals to ligands cannot be compared straightforwardly with that of

the essential metal ions in terms of polarizing power. The cations K^+ and Ti^+ have similar ionic radii and the same charge, but Ti^+ often interacts about a thousand times more strongly with ligands than does K^+. This situation arises because Ti^+ has more electrons than does K^+ and is therefore polarised more easily.

In their research on metal adsorption by freeze-dried *Rhizopus arrhizus*, Brady and Tobin (1995) reported that equilibrium metal uptake values increased in the order $Sr^{2+} < Mn^{2+} < Zn^{2+} < Cd^{2+} < Cu^{2+} < Pb^{2+}$, and were positively correlated with the covalent index of the metal ions (see table 2.5). Also the potential of the test ions to displace preloaded borderline metals ions from the biomass increased with increasing covalent index. In the case where the hard metal ion Sr^{2+} was preloaded, the displacement potential of the borderline test ions decreased with increasing covalent index, except for Pb^{2+}, which totally displaced the preloaded Sr^{2+}.The authors concluded that the hard metal Sr^{2+} exhibited ionic binding only, whereas the borderline test ions exhibited a significant degree of covalent binding.

Fourest and Volesky (1997) examined the removal of Ca, Zn, Cd, Cu and Pb using four different types of seaweed. The authors found that the binding capacity of the heavy metals is related to their electronegativity and it has followed the trend Pb > Cu $\geq$Cd > Zn $\geq$Ca.

The electronegativity of Pb is 1.8, and is less than that of the Cu which is 1.9. As the ionic radius of Pb is greater than the ionic radius of Cu, the trend found by the authors could be better explained by the covalent index principle.

Hughes and Poole (1991) reported that the interaction of metal ions and ligands can be also described quantitatively by the use of formation constants. The formation constant is usually determined at fixed temperature and ionic strength. The greater the value of the formation constant of metal ion and a ligand, the higher is the affinity of the metal ion for the ligand. Inspection of formation constant data will show which ligand out of those available in the medium will complex the metal. Alternatively, the data will show which metal ion will bind to a particular ligand. These conclusions will depend upon the concentrations of metal and ligands, as a high concentration of a weakly binding ligand may be able to complex a metal ion in the presence of a low concentration of a strongly binding ligand.

2.3 Mechanism of metals uptake by micro-organisms

2.3.1 Binding sites in yeast

There is ambiguity concerning whether live or inactivated biomass is the better metal sorbent. Different yeast strains were reported to accumulate varying amounts of metal (Remacle, 1990) with uptake by living cells only slightly higher than that of dead cells.

Survival of micro-organisms in the presence of toxic metals depends on microbial intrinsic biochemical and structural properties, physiological and genetic adaptation, and environmental modification of metal speciation, availability and toxicity. The cell wall construction of the yeast is crucial for survival and it is composed of several layers bearing anionic groups to which metal cations bind. Up to 90% of the yeast wall is polysaccharide complexed with proteins, lipids and other substances. The yeast cell wall presents a multilaminate, microfibrillar structure- an outer layer of glucans, mannans or galactans and an inner microfibrillar layer, the crystalline properties of which are conferred by the parallel arrangement of chains of chitin or cellulose or non-cellulosic layers (Remacle, 1990).

The adsorptive capacity of the yeast cell wall for heavy metals is not determined solely by its protein component, but rather by the structural organisation of the entire protein-carbohydrate complex and by the degree of dissociation of the negatively charged functional groups and their accessibility to the metals (Davidova and Kasparova, 1992). Phospho-di-ester and carboxyl groups confer the electrical surface potential to the wall. The structural features of the cell wall provide a mechanism to immobilise metals and prevent their entry into the cell.

In experiments to determine the mechanism of the yeast flocculation process, and based on measurements of the cell's mobility and zeta potential, researchers concluded that phospho-di-ester groups account for the majority of the surface charge, while carboxyl groups account for the remaining balance (Beavan et al., 1979; Bowen and Cooke, 1989). Some live yeast species were found to be tolerant to metals, where the yeast is able to produce increased levels of hydrogen sulphide which results in metal sulphide precipitation in and around the cell wall (Kikuchi, 1965).

2.3.2 Binding sites in bacteria

The cell wall in bacteria can be considered the most important part in metals accumulation. Gram-negative cell walls have a very thin layer of peptidoglycan, between membrane bilayers, which carries no covalently linked polyanions, therefore they have more limited metal-binding capacity than Gram-positive bacteria. In Gram-negative bacteria the cell walls and surfaces have a negative charge density owing to the presence of teichoic acid and teichuronic acid attached to the peptidoglycan network. The phospho-di-esters of the teichoic acid and the carboxylate groups of the teichuronic acid contribute ion-exchange capacity to the cell wall (Hancock, 1986).

Fig.2.2 shows an idealised section of the wall of *Bacillus licheniformis*, indicating the various charged and polar groups that might be involved in metal complexation.

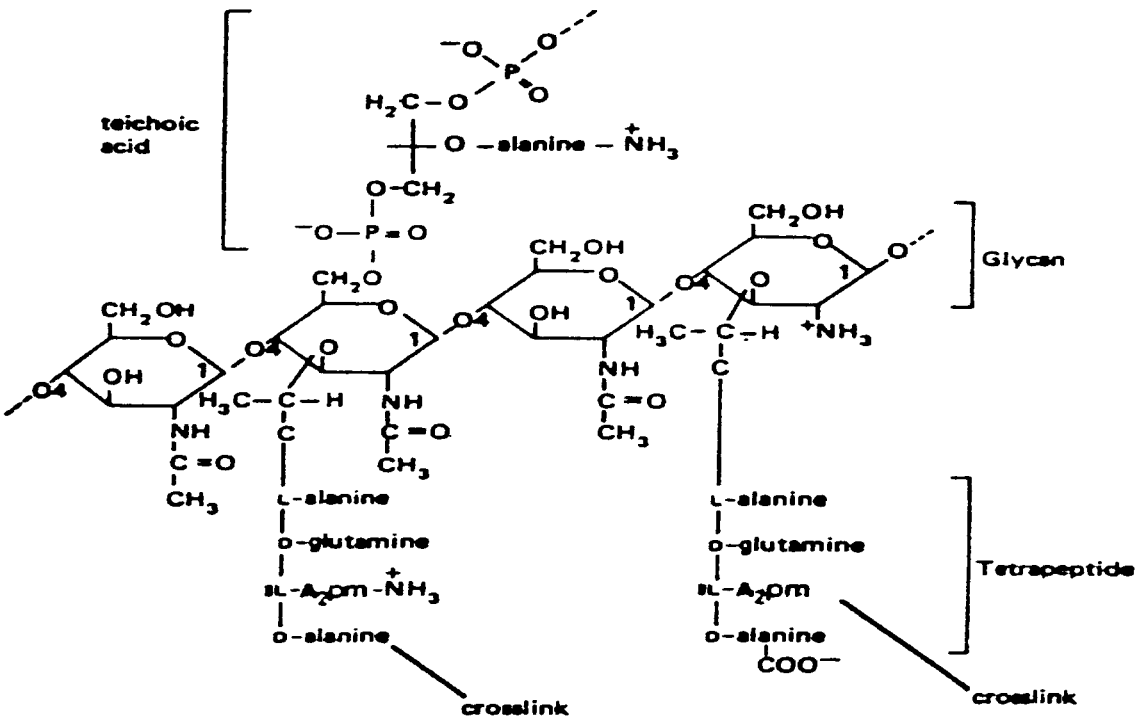


Fig. 2.2 Charged groups in bacteria cell wall (Hancock, 1986)

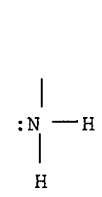
In addition, nitrogen and oxygen ligands in the cell wall might also be expected to contribute to metal ion binding, particularly in the complexation of transitional metal ions, and such complexation would be more sensitive to conformational effects than

purely ionic binding (Hancock, 1986). Beveridge and Doyle (1989) have presented an excellent review of metal ions uptake by bacteria.

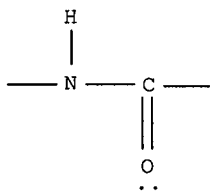
2.3.3 Binding sites in algae

The diverse and unusual metal binding properties exhibited by various algae species are explained by the fact that various genera of algae have different cell wall compositions.

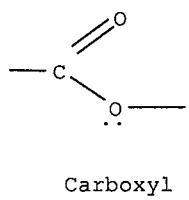
Thus, certain algae species may be much more effective and selective than others for removing particular metal ions from aqueous solution (Darnall, 1991). Crist et al. (1981) reported a protein content of 16-27 % for the *Vaucheria* group. Amino acids in the proteins could provide such functional groups as:



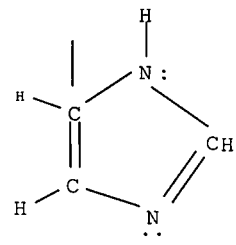
Amine



Amide



Carboxyl



Imidiazol

The polysaccharides of the cell wall could also provide the amino and carboxyl groups as well as the sulphate. The amino and carboxyl groups, the imidazole of histidine, and the nitrogen and oxygen of the peptide bond could be available for characteristic co-ordination bonding with metallic ions like Cu^{2+}; such bond formation could be accompanied by displacement of protons dependent, in part, on the extent of protonation as determined by the pH. Metallic ions could also be electrostatically bonded to unprotonated carboxyl oxygen and sulphate (Crist et al., 1981).

Chitin is also available in green algae (Muzzarelli, 1973), which is considered along with its derivative chitosan as effective metals absorption components.

2.3.4 Binding sites in fungi

The fungi and yeast are used in a variety of industrial fermentation processes. Such industrial fermentation processes can serve as an economical and constant supply of

biomass for biosorption of metal ions. The fungi and yeast can also be easily grown in substantial amounts using unsophisticated fermentation techniques and inexpensive growth media (Kuyucak, 1990).

Both living and dead fungal cells are capable of metal uptake. The use of dead biomass seems to be a preferred alternative for the majority of metal uptake studies reported. The dead fungal cells have been shown to bind metals at levels greater than live cells depending on the methods used to kill (pre-treat) them (Kapoor and Viraraghavan, 1997).

As biosorption of metals by dead biomass is the subject of this work, the mechanism of metals uptake by dead fungi is considered in detail. The binding of metal ions to fungal biomass is likely to be via two major mechanisms:

1-Ion exchange: the polarity of amino acids in the fungal proteins and glycoproteins can play an important role in ions exchange. Fig. 2.3 shows how this can happen (Hunt, 1986), although Muraleedharan and Venkobachar (1990) found that proteins in *Ganoderma lucidum*, a macro-fungus, did not play any substantial role in copper uptake.

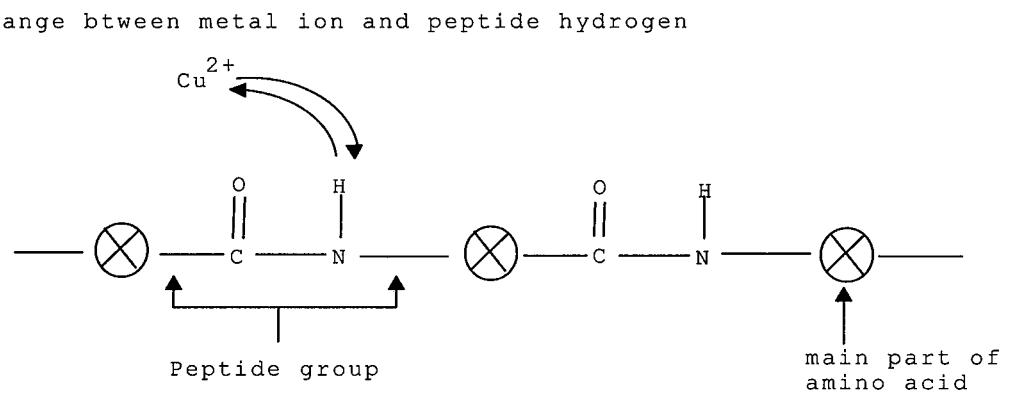


Fig. 2.3 The exchange mechanism between polypeptide chain (proteins) and metal ions (Hunt, 1986)

N-acetyl groupings in chitin in analogy to the peptide bond of proteins are also active sites in ions exchange (Hunt, 1986). Fig. 2.4 shows the chemical composition of chitin (Mckay et al., 1986).

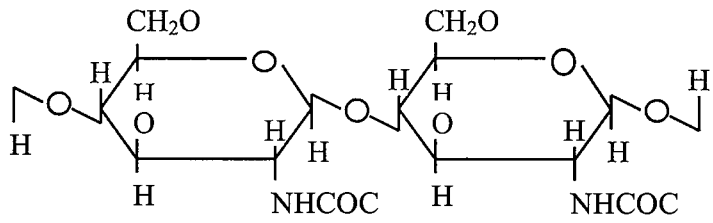


Fig. 2.4 Chitin (poly-N-acetyl-D-glucosamine) (Mackay et al., 1986)

Hunt (1986) reported that the ionizable groups in biopolymers which were most likely to be involved in cation-exchange (centres of negative charge) are carboxyl, organic phosphate, organic sulphate and phenolic hydroxyl groupings, while amino, imidazole, guanidino in proteins, and chitin and chitosan in polysaccharides are the groups which are most likely to be involved in anion-exchange (centres of positive charge).

Kapoor and Viraraghavan (1997) reported that most of the metal uptake was due to ion-exchange. Copper ions were observed to be exchanged with calcium and hydrogen ions, and the results showed that heavy metal ions are exchanged, not only with calcium and hydrogen ions (Muraleedharan et al., 1994), but also with magnesium and potassium ions (Kapoor and Viraraghavan, 1997).

2-Formation of complexes (co-ordination compounds): Complex formation by organic molecules with metal atoms is associated with the presence of an atom having a lone pair of electrons to donate. In the fungal cell wall these are most likely to be neutral trivalent nitrogen atoms, and divalent oxygen or sulphur atoms. The role of chitin in biosorption was ruled out, as the chitin fraction of *G. lucidum* and the fraction devoid of chitin indicated the presence of a free radical (Muraleedharan and Venkobachar, 1990). The presence of this free radical was believed to co-ordinate with metal.

In humic acid removal from raw water using *R. arrhizus*, results showed that the fungal chitin/chitosan had the highest uptake of humic acid, followed by cell wall, whole cell, then protoplast (Banks and Parkinson, 1992).

Chitosan showed greater metal uptake capacity compared to chitin, this may well be due to differences in the nitrogen moiety of the two polymers. The N-acetyl D-

glucosamine groups of the chitin could act as specific chemical binding sites for metal ions capable of forming complex ions, but would not be expected to be as efficient as the free amine sites (in which each nitrogen atom has a pair of electrons) in chitosan (Suder and Wightman, 1983). Fig. 2.5 shows the chemical structure of chitosan (Mckay et al., 1986).

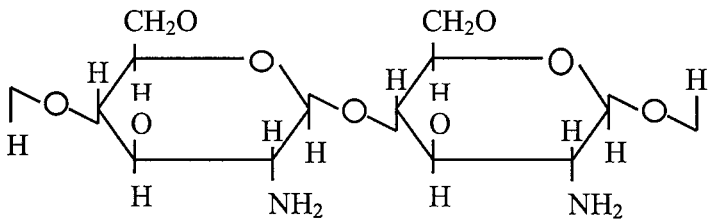


Fig. 2.5 Chitosan (deacelylated [poly-N-acetyl-D-glucosamine]) (Mackay et al., 1986)

2.4 Biomass used in this study

The fungus *Rhizopus oryzae* (formerly known as *Rhizopus arrhizus*) and the seaweed *Ascophyllum nodosum* were used in this research and their application as biosorbants is reviewed below.

2.4.1 Brief adsorption history of *Rhizopus oryzae* and factors affecting its metal uptake capacity

Rhizopus oryzae biomass, which is produced as a by-product of industrial fermentations, has potential for use as a biosorbant of heavy metals. It was reported that the content of chitin in *Rhizopus arrhizus* is small in comparison with other species of fungi (Blumental, 1957). However, the content of chitosan (which is more effective than chitin in metal uptake) in *Rhizopus arrhizus* is ranked next to *Absidia* sp. and suggested the use of *Rhizopus arrhizus* in chitosan production (Shimahara et al., 1989).

Rhizopus arrhizus has a uranium uptake capacity of 15 % of its dry weight. This exceeds by 2.5 times the capacity of a common anionic exchange resin (IRA-400) used by uranium production companies for selective separation of uranium from other

ions in solution (Brierley et al., 1986). *Rhizopus arrhizus* was shown to be a very successful sequester of humic acid molecules from raw water under acid conditions; the adsorption was reversible under alkaline conditions, leading to a successful regeneration system (Banks and Parkinson, 1992). Tobin et al. (1984) showed that *Rhizopus arrhizus* biomass was very effective in the absorption of a variety of different metal ions including (Cr^{3+}, La^{3+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ba^{2+}, Hg^{2+}, Pb^{2+}, UO^{2+} and Ag^{+}), and the amount of uptake of cations was found to be directly related to ionic radius. The same study showed that the alkali metal ions (Na^{+}, K^{+}, Rb^{+} and Cs^{+}) were not absorbed by the biomass, due to the inability of these metals to form complexes with most ligands. The most important factors that could affect metals uptake capacity of *Rhizopus oryzea*, and fungi in general, from aquatic solutions are discussed below.

2.4.1.1 Growth media effects

The ideal medium for growing fungi should contain a carbon source (usually glucose), nitrogen source (usually ammonia or nitrate but often an amino-acid), phosphate, sulphate, magnesium, potassium and trace elements: iron, manganese, zinc, molybdenum, and copper. In addition, complex natural materials are often added to the medium, these include corn-steep liquor, yeast extract, vegetable juices and protein hydrolysates (Turner, 1971). Often, several different media will support the growth of an organism but not all lead to the production of a desired compound. The nitrogen source is the key factor in determining which compound is produced, and the medium pH is known, in some cases, to have a marked effect on secondary metabolism (Turner, 1971).

In humic acid removal from raw water by *Rhizopus arrhizus* it was found that *Rhizopus arrhizus* grown on PAD medium (potato extract agar) had the highest uptake of humic acid, followed by MEA (malt extract agar), YMS (yeast malt sucrose) and YPSS (yeast, phosphate, soluble starch) (Zhou and Banks, 1992). As a result, when biomass is grown specifically for use as a biosorbent, the composition of each growth medium must be optimised with respect to its sorptive binding capacity and the cost of the medium.

2.4.1.2 The effect of metabolic inactivation

The biomass can be inactivated for biosorption by physical or chemical methods. Physical methods include vacuum and freeze drying, boiling, autoclaving and mechanical disruption, while chemical methods include contacting the biomass with various organic and inorganic compounds (Kapoor and Viraraghavan, 1997).

Published information suggests that the way cells are inactivated can affect their metal-binding capacity, and that heat treatment appears to be the best technique (Somers, 1963; Horikoshi et al., 1981; Tsezos, 1990), However Huang and Chiu (1994) found in a comparison between acid-washing of *Rhizopus oryzae* pellets (10^{-2} N $HClO_4$ solution for 15 min) and heat treatment (autoclave at 120° C for 15 min) in Cd (II) uptake, that heat-treated pellets showed less uptake capacity than either the acid-washed pellets or the native pellets. This was because the amino functional groups in the fungal mycelia may lose their adsorption capability through a non-enzymatic brewing reaction resulting from the heat treatment.

Ross and Townsley (1986) pre-treated *P. spinulosum* with detergents (Ariel, Decon 90 and sodium dodecyl sulphate) and reported substantial improvement in copper removal efficiency, especially at higher copper concentrations. They attributed this to the disruption of cell membranes exposing more sites for metal binding.

The alkali treatment of fungal biomass has also been shown to increase significantly the metal sorption capacity as a result of the deacetylation of chitin in the fungal cell wall to form chitosan-glucan complexes with higher affinity for metal ions (Muzzarelli et al., 1981). Kapoor and Viraraghavan (1997) gave a summary of the methods which have been employed to pre-treat biomass and their effect on metal removal.

2.4.1.3 The effect of pH

The pH affects the speciation of the ions in solution as well as the chemistry of the active sites on the biomass. The active sites of the biomass, such as the amino groups in cell wall chitin, cellular phosphate groups and proteins, hydrolyse as pH changes thus affecting the biomass metal-binding capacity (Beveridge, 1978; Friis and Myers-Keith, 1986; Gadd, 1986). Most of the phosphate groups in *R. arrhizus* cell wall present as mono- and diesters will have a negative charge above pH 3.0, and therefore could contribute appreciably to the metal binding (Beveridge and Murray, 1980).

R. arrhizus exhibited a good adsorption for a variety of metal ions (La^{3+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ba^{2+}, Hg^{2+}, Pb^{2+}, UO^{2+} and Ag^{+}) at pH 4.0 (Tobin et al., 1984). This study also showed that buffers could not be used in the metal uptake studies because they all had the ability to complex metal ions to some degree.

In humic acid removal from raw water by *R. arrhizus* over a range of pH values from 3 to 13, the amount of material adsorbed increased with decreasing pH. This was attributed to the presence of H^{+} which makes a bridge between the negatively charged fungal cell wall ligands and the humic acid molecules (Zhou and Banks, 1992).

The uptake of uranium by chitin showed reduction when the pH of the solution decreased from 4 to 2; this was explained by the competition of H_3O^{+} at low pH to the Uranium ions to co-ordinate with the lone electron pair of amine nitrogen (Tsezos, 1983). It was also noticed that there was a decline in the metal uptake capacity of chitin and chitosan for an extended series of metals, when the solution pH was reduced from 7 to 2.5 (Muzzarelli, 1969). Thorium and uranium uptake by *R. arrhizus* was shown to be optimum at pH 4 to 5 (Tsezos and Volesky, 1982).

2.4.1.4 The effect of other ions

The effect of co-ions on the equilibrium of biosorption depends on the ions themselves and their chemistry in solution. Zinc, copper, and iron (II) have been shown to reduce the uranium uptake capacity of *R. arrhizus* by competing with uranium for co-ordination at the cell wall chitin amino nitrogen (Tsezos, 1983). Zhou and Kiff (1991) indicated that Mn, Zn, Cd, Mg and Ca inhibited Cu biosorption by *R. arrhizus*.

In addition to cations, the presence of anions can also affect the metal biosorptive uptake capacity of biomass. In humic acid removal from raw water, the presence of Cu^{2+} ions in solution increased humic acid uptake by *R. arrhizus* as Cu^{2+} worked as a bridge between binding sites on the fungal cell wall and the humic acid molecules both of which have negative charges (Zhou and Banks, 1992).

The presence of EDTA has been found to adversely affect the biosorption of Cu, La, U, Ag, Cd and Pb (Kapoor and Viraraghavan, 1997). The anions present in waste water can form complexes with the metal ions. The stability constants of metal-anion complexes can be high and, if these constants are greater than stability constants for metal biosorption sites on the cell surface, the biosorption can be expected to be considerably reduced; therefore, anion complexation can decrease the biosorption of metal ions (Kapoor and Viraraghavan, 1997).

The biosorption of heavy metals was not affected significantly by the presence of alkali metals like sodium or potassium in solution (Nakajima et al., 1982). This is industrially significant because in many potential applications unwanted alkali ions will be present and in competition for uptake with the desired metal ions.

2.4.1.5 The effect of temperature

The dependence of the metal-binding capacity of the microbial biomass on temperature has been shown to be small. In general, the limited existing information suggests an overall biosorption process that is slightly favoured by increases in temperature (Horikoshi et al., 1981; Nakajima et al., 1982).

Surface binding of copper by *R. arrhizus* increased with increasing temperature (Somers, 1963). Uranium biosorption was found to increase with temperature in the range of 20 to 50° C (Tsezos and Volesky, 1981), indicating that the biosorption process, in this case, was endothermic. Similar findings were obtained by Strandberg et al., (1981).

In humic acid removal from raw water by *R. arrhizus*, the results showed that the adsorption of both (HPO-A) and (HPI-N) increased with decreasing temperature from 36° C to 16° C. It was assumed that the adsorption process was spontaneous and thus accompanied by a decrease in the system's free energy ΔG (Zhou and Banks, 1992).

2.4.2 Brief adsorption history of *Ascophyllum nodosum* and factors affecting its metal uptake capacity

Ascophyllum nodosum is a brown multicellular macroalgae (seaweed). Macroalgae can be found in marine environments in all parts of the world. In some places macroalgae have been cultivated and regularly harvested as a food source, fertiliser or source of bio-chemicals (such as alginate). Large quantities of macroalgal growth occur on beaches and in the sea due to eutrophication caused by pollution. A large amount of money is spent in removing such algae from tourist beaches, e.g. on the east coast of the UK, and the subsequent transport and disposal of the algal biomass is expensive. This could provide a very cheap source for algal biomass. The alginate (or alginic acid) content in the seaweed varies in the proportion of 14 to 40 % of the dry solids of these seaweeds (Muzzarelli, 1973).

Both seaweeds and alginates can accumulate metal ions, however alginate is relatively expensive, particularly in any suitable form (Edyvean et al., 1997). The alginate in seaweeds behaves as a base exchange material, and from the knowledge of the composition of the salts in the seaweed, the conclusion was reached that alginic acid is present as a mixed salt of cations, mostly calcium, able to render it insoluble (Muzzarelli, 1973).

Kuyucak and Volesky, (1988) reported that *A. nodosum* was able to accumulate between 4 % and 15 % of its dry weight of gold and cobalt respectively, and between 10 % and 20.10 % of its dry weight of cadmium and lead respectively (Volesky, 1994). Chong and Volesky (1995) crosslinked *A. nodosum* particles with formaldehyde to eliminate subsequent release of its component materials into solution that could cause some precipitation of the dissolved metal which tends to interfere with sorption studies. The authors claimed a maximum adsorption capacity, using Langmuir isotherms, of the crosslinked biomass of 0.99, 0.75 and 0.68 mmol/g for Cu, Cd and Zn respectively. The experiments were conducted using each metal separately and at pH 4.5 and a temperature between 22 – 25° C.

Many factors have been reported to affect the adsorption capacity of the *A. nodosum*, and seaweed in general, the most important are pH and the presence of other ions.

2.4.2.1 pH

Schiewer et al., (1995) reported that crosslinking non-living particles (0.84 – 1 mm) of *A. nodosum* with formaldehyde showed fast and linear increase up to their maximum Cd uptake capacity (0.2 mmol.g^{-1} per pH unit), using Langmuir isotherms, when the pH was increased from 1 to 4 and became less dependent on pH between pH 4 and pH 7.

Greene and Darnall (1990) classified metal ions into three classes based on their pH dependence of biosorption to algae. The first class of metal ions are tightly bound at pH > 5 and can be desorbed at pH < 2. Metal ions which fall into this class are Al^{3+}, Cu^{2+}, Pb^{2+}, Cr^{3+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Fe^{3+}, Be^{2+} and UO_2^{2+}. This group's pH profile was explained as being consistent with metal cations being bound to cell wall ligands, but as the pH is lowered the overall charge on the cell wall becomes positive, which inhibits the approach of positive ions. However the authors have ignored the speciation of those metals at different pHs and the possibility of metals precipitation at pHs > 5 which could contribute to the overall metal removal from solutions. The second group included anionic metal species such as TcO_4^-, $PtCl_4^{3-}$, CrO_4^{2-}, SeO_4^{2-} and $Au(CN)^{2-}$. Here the algal adsorption capacity increased when pH was decreased. This effect is explained as being due to the increased binding of protons to the active binding sites, which in turn increases anionic binding. The iso-electric point of most algal walls lies between pH 3 and pH 4, thus, the net overall charge on the algal wall under low pH conditions promotes easier access of anions to positively charged binding sites as the pH is decreased below the iso-electric point. The third group included metal species described as "soft" in nature and reported to be independent of pH, These are Ag^+, Hg^{2+} and $AuCl_4^-$ (Garnham, 1997).

2.4.2.2 The presence of other ions

Carvalho et al. (1995) used *A. nodosum* to study the competition between Zn, Cu and Cd for binding sites. The biomass showed a preference for Cu over Zn and Cd. However, the presence of Zn tends to lower the total metal uptake in a two-metal system, but the uptake of Zn could not compensate for the inhibition in biosorption of the other metals. Schiewer et al., (1995), using crosslinked particles of *A. nodosum* (0.84 – 1.00 mm) with formaldehyde, noticed that when those particles were exposed

to low total residual concentration of Zn and Cd, the total metal sorption uptake increased. At higher total metal concentrations, the total metal sorption uptake remained relatively constant. The authors reported competition between these two metals on the available biomass binding sites and concluded that there was a preference of the biosorbent for sorbing Cd in preference to Zn over the equilibrium concentration range examined. Chong and Velosky (1995) also used the same crosslinked *A. nodosum* particles to study the adsorption of Cu, Zn and Cd in a two-metal system. For Cu-Zn system the authors reported that the total uptake capacity of the biomass of this system was predicted to be 0.92 $mmol.g^{-1}$. When the residual concentrations of Cu and Zn were the same (i.e. 0.5 or 2.5 $mmol.l^{-1}$ of each), about 83% of the total metal uptake was due to Cu uptake. On the other hand, when the residual concentration of Zn was equal to 5 times the residual concentration of Cu, the uptake of both metals was similar. This suggested that the equilibrium concentration of Zn would have to be 5 times greater than that of Cu to obtain the same proportion of uptake of each metal. The authors concluded that the biosorbent exhibited a net preference for Cu ions over Zn.

2.4.2.3 Pre-treatment and modification

Modification of the biomass to improve adsorbent properties or physical performance has been extensively documented. Pre-treatment of the biomass with acids or alkali could open more of the structure of seaweed biomass and also remove problematic extracellular polymeric materials. Chong and Volesky (1995) crosslinked particles of *A. nodosum* with formaldehyde and washed it with distilled water for 3 hours to produce standard biosorbent particles which eliminated the subsequent release of its component materials into solutions. Figueira et al. (2000) reported that algal biomass can work as an ion exchanger if the biomass is protonated (i.e. loaded with H^+) or loaded with mono or divalent cations such as K^+, Ca^{2+} and Mg^{2+}. The authors used particles (0.5 – 0.84 mm) of different types of brown algal biomass that was protonated by treatment with 0.2N HNO_3 and then rinsed with distilled water until the solution reached pH 4.5. Part of the protonated particles were, also, loaded with K, Ca or Mg by treatment with 20 mM solutions of $Ca(OH)_2$, $Mg(OH)_2$ or KOH until the pH of the spent hydroxide supernatant solution reached 6.5 . The pre-treated biomass was then used to remove Cd from solutions.

2.5 Regeneration process of the biomass particles

The elution of the sequestered metal ions and other absorbed species from biomass has not been studied as extensively as the respective uptake. The biomass cell surface-bound metal or other contaminants might be easily removed by the use of proper eluant but, in the case of living biomass, the intracellular metal can only be released by destructive treatment. This is one of the major drawbacks of the use of living biomass in the biosorption field.

The use of mineral acids as an eluant has been widely studied (Huang et al., 1990; Luef et al., 1991; Zhou and Kiff, 1991; Akthar et al., 1995). The elution of Ni, Cu, Zn and Cd biosorbed on *Penicillium* biomass can be achieved by using dilute hydrochloric acid or dilute sodium hydroxide solution (Kapoor and Viraraghavan, 1997).

Detailed studies on the elution of uranium from *R. arrhizus* using six eluants (sulphuric acid, nitric acid, hydrochloric acid, ammonium sulphate, sodium carbonate and sodium bicarbonate) showed that sodium bicarbonate solutions appeared the most promising because they can affect near complete uranium recovery and high uranium concentration factors (Tsezos, 1984). Organic chelating agents such as EDTA have also been used to remove heavy metals from loaded biomass (Gadd and Griffiths, 1980). In humic acid removal from raw water, NaOH proved to be an effective desorbent for the humic acid molecules from *R. arrhizus* biomass (Zhou and Banks, 1992).

Other types of eluants have also been reported. Kuyucak and Volesky (1988) used 0.01 M of calcium chloride to recover cobalt from *A. nodosum*. Darnal et al., (1986a) and Greene and Darnall (1990) used mercaptoethanol and thiourea respectively to recover gold from *Chlorella vulgaris*. Organic chelating agents such as EDTA have also been used to remove different types of heavy metals adsorbed to green microalgal species (Horikoshi et al., 1979).

Important considerations should be taken into account to achieve successful elution and reuse of the biomass:

1- The use of a proper eluant, which the biosorbed materials have a higher affinity for than they do for the biomass, or in the case of ion exchange, the

biomass functional sites have a higher affinity for the eluant ions than for the adsorbed ions.

2- As the bio-adsorption process is usually classified as a concentration process the successful eluant should achieve a complete elution with a minimum volume. The volume of an eluant should not exceed, typically, 10% of the treated waste water for complete elution.

3- The eluant should also not reduce the biomass adsorption capacity in further adsorption cycles. Some eluants can disintegrate the biomass resulting in a significant loss in the biomass uptake capacity.

2.6 Analysis and representation of adsorption data

Data generated from bio-adsorption experiments can be analysed and represented in different ways. Equilibrium lines depending on simple mass balance are usually used to indicate whether the biosorption has gone to completion or not. Isotherm equations such as Langmuir, Freundlich, and BET are usually used for the analysis of data produced from biosorption equilibrium experiments. Equilibrium analysis, although it can indicate how far the reaction has gone towards completion, it cannot provide information on the rate or the speed of the reaction. Kinetic equations, such as pseudo-first and second order equations, are usually used to calculate the rate of the adsorption reaction. Each of these is discussed below.

2.6.1 Adsorption isotherms

An adsorption isotherm measures the amount of an adsorbate (Q), at equilibrium, that has been adsorbed on a unit weight of adsorbent at a given temperature over a range of concentrations. Usually (Q) is calculated from the mass balance equation as follow:

$$Q = \frac{(Co - C)V}{B} \qquad (2.1)$$

where:

Co is the initial adsorbate concentration ($mg.l^{-1}$)

C is the adsorbate concentration at equilibrium in solution ($mg.l^{-1}$)

V is the solution volume (l)

B is the adsorbent mass (g)

Adsorption isotherms are generally plotted with the Q (the uptake capacity, $mg.g^{-1}$) on the Y-axis and the adsorbate equilibrium concentrations in the bulk solution (C) along the X-axis as illustrated in figure 2.6.

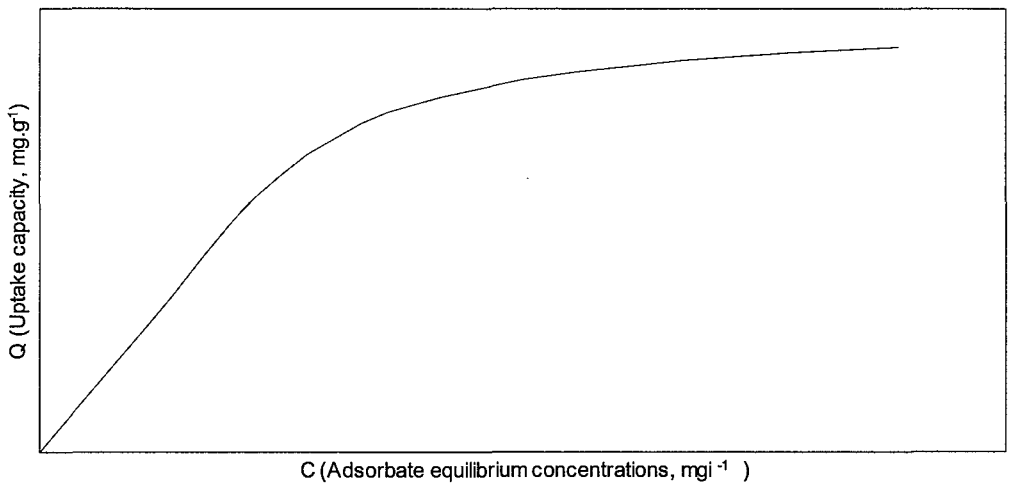


Fig. 2.6 A general representation of adsorption isotherms

Various mathematical models have been used to interpret isotherm data. The most common mathematical models that have been applied to biosorption are given below.

2.6.1.1 Langmuir isotherms

This was derived by Langmuir (1918). The Langmuir model was based on the reasonable assumptions that:

1- The molecules are adsorbed on definite sites on the adsorbent surface.
2- Each site can accommodate only one molecule (i.e. monolayer coverage).
3- The area of each site is a fixed quantity determined solely by the geometry of the surface.
4- The adsorption energy is the same at all sites.
5- Adsorbed molecules can not migrate to interact with neighbouring molecules.

The assumption that only a single layer could exist is a reasonable for gases because the chemical forces bonding the gas to the adsorbent probably do not extend beyond a single layer (Droste, 1997). According to the Langmuir assumptions only molecules striking the bare surface of the adsorbate have an opportunity to be retained because the forces of attraction do not extend over multi-layers of the adsorbed component. Likewise, the rate of removal of adsorbed molecules from the surface is proportional to the surface area covered by them. Therefore, the rate of attachment to the surface should be proportional to a driving force, which is the concentration of solute in the fluid, multiplied by the amount of bare surface. If the fraction of covered surface is Ø, then the adsorption rate per unit of surface is:

Adsorption rate = K_1 C (1 - Ø)

On the other hand, the desorption from the surface is proportional to the amount of surface covered:

Desorption rate = K_2 Ø

where:

K_1, K_2 are rate coefficients of adsorption and desorption, respectively

C is the concentration of solute in the fluid

Ø is the fraction of the surface covered

At equilibrium, the two rates are equal, and therefore:

K_1 C (1 - Ø) = K_2 Ø

$K_1C - K_1C$ Ø = K_2 Ø

K_1 C = K_2 Ø + K_1 C Ø

K_1 C = Ø (K_2 + K_1 C) » $$Ø = \frac{K_1 C}{K_2 + K_1 C}$$

By dividing the numerator and denominator by K_1:

$$Ø = \frac{C}{(\frac{K_2}{K_1} + C)}$$

The adsorption capacity of the surface (Q) is proportional to Ø, therefore:

Q = Constant * Ø

$Q = q_{max}$ * Ø

$$Q = q_{max} \frac{C}{(\frac{K_2}{K_1} + C)}$$

By dividing the numerator and denominator by K_2/K_1, then:

$$Q = q_{max} \frac{\frac{K_1}{K_2} C}{(1 + \frac{K_1}{K_2} C)}$$

$$Q = q_{max} \frac{b.C}{(1 + b.C)} \qquad (2.2)$$

where: b is a constant equal to K_1/K_2, which is the adsorption rate constant over the desorption rate constant.

q_{max} is the maximum adsorption capacity of the surface.

Equation (2.2) can be linearised to one of two forms:

$$\frac{1}{Q} = \frac{1}{q_{max}} + \frac{1}{b.q_{max}} \cdot \frac{1}{C}$$

$$\frac{C}{Q} = \frac{1}{b.q_{max}} + \frac{1}{q_{max}} C$$

A plot of 1/Q against 1/C or C/Q against C will yield a straight line. The values of b and q_{max} can be calculated from the values of the intercept and the slope of the straight line respectively.

2.6.1.2 Freundlich isotherms

Freundlich (1906) proposed the second isotherm equation which is essentially an empirical equation developed for heterogenous surfaces:

$$Q = KC^{\frac{1}{n}} \qquad (2.3)$$

where Q is the amount of adsorbate adsorbed per unit weight of the adsorbent.

C is the equilibrium concentration in solution

K, n are constants

There has been some disagreement about Freundlich constants in the literature in relation to bio-adsorption. Freundlich equation was proposed for the adsorption of

gases on solid matrices. Freundlich defined K as the adsorption value that was the amount of gas adsorbed at unit pressure (i.e. 1 cm of mercury). Further he added that K is characteristic for the adsorbent and the gas adsorbed. 1/n, according to Freundlich, is a constant that lies between 0.2 and 1 depending on the temperature and the nature of the adsorbed gas (Freundlich, 1906). In the literature on bio-adsorption, Banks and Parkinson (1992) reported that K and 1/n are constants that are indicators of adsorption capacity and intensity, respectively. Sag and Kutsal (1995), reported the same definition and added that the forces between the surface layers are attractive if n is less than unity and repulsive if n is greater than unity. Cimino et al. (2000) reported that K represent the moles sorbed from unit mass of substrate, while nothing mentioned was discussed about influences upon n. In a recent report addressing the measurement of partition coefficient (Kd) in soil, the United State Environmental Protection Agency (USEPA) stated that for Freundlich isotherms where n=1, K will be equal to Q/C and it will be equivalent to the value of Kd, which is defined as the ratio of the contaminant concentration associated with the solid to the contaminant concentration in the surrounding aqueous solution when the system is at equilibrium (USEPA, 1999). Other authors have indicated that Freundlich constants have no physical meanings and that they come from the fitting of data to appropriate mathematical curve derivations (personal communication, 2002).

By taking the log to both sides of equation 2.3, then:

$$\log Q = \log K + \frac{1}{n}\log C \qquad (2.4)$$

This equation is the linear form of Freundlich equation. A plot of log Q against log C yields a straight line with a slope of 1/n and an intercept of log K, from which the value of K can be calculated.

Tsezos and Seto (1986), reported that this is an incorrect way of determining the value of model parameters (i.e. n and K), because Q is usually calculated using the mass balance equation (equation 2.1). The mass balance equation indicates that the residual contaminant concentration C is the true dependent parameter and not Q, hence the authors suggested that the Freundlich equation should be applied in the following form:

$$\frac{(Co - C)V}{B} = KC^{\frac{1}{n}} \qquad (2.5)$$

Equation 2.5 is a non-linear equation and a proper non-linear regression should be used to work out the values of n and K.

2.6.1.3 The Brunauer, Emmett, Teller (BET) isotherms

The Brunauer, Emmett, Teller (BET) isotherms equation was developed from theory as an extension to the Langmuir isotherm for the case where multilayer adsorption was occurring (Brunauer et al., 1938). The model was built on the following assumptions:

1- Adsorbed molecules stay in place.
2- Enthalpy of adsorption is the same for any layer.
3- Energy of adsorption is the same for layers other than the first.
4- A new layer can start before another is finished.

The BET isotherm equation is given by:

$$Q = \frac{q_{max}.K.C}{(Cs - C)[1 + (K - 1)(\frac{C}{Cs})]} \qquad (2.6)$$

Where q_{max} is a constant and represents the maximum uptake capacity

K is a constant

C is the residual contaminant concentration

Cs is the concentration at which all layers are filled (saturation concentration)

2.6.1.4 Choice of isotherms

The simplest form of isotherm that gives a good fit to the experimental data should be used. The Freundlich and Langmuir isotherms are often used for adsorption from water while the BET is used less (William, 1999).

Freundlich isotherm has been shown to give a better fit than Langmuir with most cases of adsorption using activated carbon (Gessner and Hassan, 1987), while the Langmuir isotherm provides the best fitting model in most cases of copper adsorption by different types of bio-materials (McKay et al., 1999).

The fact that the data fits the isotherm does not mean that the theory behind the isotherm applies to the data.

2.6.2 Adsorption kinetics

In the adsorption system the solute usually moves from the solution and becomes adsorbed onto the cell surface of the bio-material. At the same time some molecules of the solute move in the opposite direction leaving the biomass surface and go into solution. When the system is stable, it is said to be in equilibrium. Equilibrium usually indicates how far the chemical reaction proceeds to completion (Ann and Fullick, 1994). However, for a reaction to proceed it is not enough for it to be just possible, it must occur rapidly enough for us to observe it and to collect the products. Kinetics or the rate of reaction describes the speed at which the reaction proceeds or at which reactants are converted to products for a particular reaction.

When all the intermediate steps of a reaction are known it is often possible to formulate theoretically the rate model exactly and verify it with experimental data. Otherwise the rate model is simply the empirical model that best correlates with the experimental data (Droste, 1997). Several kinetic models have been used for analysis of bio-adsorption process rates, the following are the most common:

2.6.2.1 The pseudo-first order equation

The pseudo-first order equation of Lagergren (1898) is generally expressed as follows:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \qquad (2.7)$$

Where: q_e: is the sorption capacity at equilibrium ($mg.g^{-1}$)

q_t: is the sorption capacity at time t ($mg.g^{-1}$)

K_1: is the rate constant of pseudo-first order sorption ($l.min^{-1}$)

After integration and applying boundary conditions, t = 0 to t = t and $q_t = 0$ to $q_t = q_t$, the integrated form of equation 2.7 becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}t \qquad (2.8)$$

In order to fit equation 2.8 to experimental data, the equilibrium sorption capacity (q_e) must be known. In many cases q_e is unknown and as chemisorption tends to become immeasurably slow, the amount sorbed is still significantly smaller than the equilibrium amount (Mckay et al., 1999). In most cases in the literature, the pseudo-

first order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable only over the initial 20 to 30 minutes of the sorption process. Furthermore, one has to find some means of extrapolating the experimental data to $t = \infty$, or to treat q_e as an adjustable parameter to be determined by trial and error. For this reason, it is therefore necessary to use trial and error to obtain the equilibrium sorption capacity, q_e, in order to analyse the pseudo-first order model kinetics.

Mckay et al. (1999) reported that in over 50% of literature references, based on analysing sorption kinetics, the authors did not measure an equilibrium isotherm. Aharoni and sparks (1991) reported that the equation applicable to experimental results generally differs from a true first order equation in two ways:

1- The parameter $K_1(q_e - q_t)$ in equation 2.7 does not represent the number of available sites.

2- The parameter $\log(q_e)$ is an adjustable parameter which is often not found equal to the intercept of a plot of $\log(q_e - q_t)$ against t, whereas in a true first order sorption reaction $\log(q_e)$ should be equal to the intercept of a plot of $\log(q_e - q_t)$ against t.

2.6.2.2 The pseudo-second order equation

The pseudo-second order chemisorption kinetic equation is expressed as:

$$\frac{dq_t}{dt} = K(q_e - q_t)^2 \qquad (2.9)$$

where: q_e is the sorption capacity at equilibrium ($mg.g^{-1}$)

q_t is the sorption capacity at time t ($mg.g^{-1}$)

K is the rate constant of pseudo-second order sorption ($g.mg^{-1}.min^{-1}$)

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$; the integrated form of equation 2.9 becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K.t \qquad (2.10)$$

which can be linearised to become:

$$\frac{t}{q_t} = \frac{1}{K.q_e^2} + \frac{1}{q_e}t \qquad (2.11)$$

Equation 2.11 does not have the problem of assigning q_e. If pseudo-second order kinetics is applicable, the plot of t/q_t against t should give a straight line with a slope of $1/q_e$ and an intercept of $1/K.q_e^2$, where q_e and K can be worked out.

2.6.2.3 The Elovich equation

The Elovich equation is generally expressed as follows:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta.q_t) \qquad (2.12)$$

where: qt is the sorption capacity at time t ($mg.g^{-1}$)

α is the initial sorption rate ($mg.g^{-1}.min^{-1}$)

β is the desorption constant ($g.mg^{-1}$)

To simplify the Elovich equation, Chien and Clayton (1980) assumed α. B.t > 1 and by applying the boundary conditions $q_t = 0$ at t = 0 and $q_t = q_t$ at t = t, equation 2.12 becomes:

$$q_t = \beta Ln(\alpha.\beta) + \beta Ln(t) \qquad (2.13)$$

Equation 2.13 is a linear equation and a plot of qt against Ln (t) will yield an intercept of βLn($\alpha.\beta$) and a slope of β.

2.6.2.4 Choice of kinetic equation

As mentioned before in a chemical reaction (i.e. in the case of chemisorption) when all intermediate steps of a reaction are known, it is often possible to formulate theoretically the rate model exactly and verify it with experimental data. Otherwise the rate model is simply the empirical model that best correlates with the experimental data. The above kinetic models were developed for chemical reactions, and if a model fits bio-adsorption data, it does not mean that the bio-adsorption process is a chemical one.

CHAPTER 3

Polyurethane as a supportive matrix for the immobilisation of bio-sorbents

3.1 The use of immobilised biomass in metal uptake

Immobilisation of biomass by its entrapment into polymeric beads, or using polymers to form robust granules, has found the widest application in commercial biosorption processes. The technique is particularly useful as the biosorbent biomass can be prepared independently prior to the immobilisation process and thus optimised to realise its maximum sorptive potential (Banks, 1997). The technique also offers the opportunity to incorporate waste biomass from other processes; most commonly used is the spent biomass from the fermentation industries where fungal species are used extensively for the production of a wide range of products including alcoholic beverages (*Saccharomyces cervisiae*); certain enzymes (*Mucor miehei*, *Aspergillus niger*); penicillin antibiotics (*Penicillium chrysogenum*), and fermented oriental food "tempeh" (*Rhizopus arrhizus*).

Immobilisation, to produce robust granules, overcomes the problems associated with small microbial cells, parts of cells and tangled filaments. Granules of uniform size and consistency are likely to offer more uniform diffusion characteristics and better overall performance. The main advantages of immobilised cells are: increase in mechanical strength, uniform particle size, easier to handle, require less complex separation systems, allow a high biomass density to be maintained, and provide a greater opportunity for reuse and recovery (Banks, 1997).

Although both living and dead biomass can be immobilised, some of the immobilisation processes may render the biomass non-viable, making them unsuitable for metabolic dependent metals removal processes. Dead cells are potentially more useful as biosorbents and for immobilisation purposes than their living counterparts; this view has been expressed by a number of authors whose comments are summarised as follows:

- All heavy metals are toxic to life, although different groups of organisms,

species and even strains show varying degrees of tolerance. Metal ions that are absorbed into the cell (even at concentrations in the μg/L range) will accumulate over a length of time and eventually interfere with the metabolism of the organism by disruption of enzyme systems resulting in death of the organism (Darnall, 1991).

- Dead cells can be stored for prolonged periods.
- Killed organisms pose less of a threat to public health.
- Dead cells do not require a constant supply of growth nutrients and, as new biomass is not produced as a result of growth processes, disposal problems are not aggravated.
- Because the removal is by surface adsorption, metals can usually be eluted from the biomass by acid treatment, non-viable biomass is not usually affected by this type of treatment (Banks, 1997).

Several immobilisation techniques for biomass have been reported, including embedding *Sphagnum moss* in polysulfone (Ferguson et al., 1989), *Bacillus* species in polyethyleneimine (PEI) (Brierley and Brierley, 1993), *Treptomyces albus* in polyacrylamide (Nakajjima and Sakaguchi, 1986), algae in silica gel (Darnall et al., 1986 b), yeast in alginate (de Rome and Gadd, 1991), bacteria in carrageenan (Scott, 1987), *Rhizopus arrhizus* in epoxy resin and polyvinlformal (Tobin et al., 1993).

3.1.1 Alginate and Carrageenan

Alginate is a linear copolymer of D-mannuronic and L-guluronic acid, extracted from seaweed which can be gelled by multivalent ions such as calcium and aluminium. For immobilisation of cells or biomass, the cross-linking of alginate with Ca^{2+} is the preferred method. This method has been used to immobilise very sensitive cells such as plant cells and protoplasts (Klaus, 1987).

K-carrageenan is a readily available non-toxic polysaccharide isolated from seaweed. It is widely used in the food and cosmetic industries as a gelling, thickening and stabilising agent. It is composed of a unit structure of β-D-galactose sulphate and 3, 6-anhydro-α-D-galactose. K -carrageenan becomes a gel by cooling or by contact with a solution containing a gel-inducing agent such as K^+, NH_4^+, Ca^{2+} , Mg^{2+} , Fe^{3+} , amines, or water-miscible organic solvents (Tosa et al., 1979). A disadvantage of K-

carrageenan is that when a gel-inducing reagent is not present in the reaction mixture, biomass or enzymes are released by dissolution of the gel (Klaus, 1987).

3.1.2 Polyacrylamide

Polyacrylamide is a well-known material used in molecular biology laboratories as a gel matrix for resolving DNA fragments in sequence analysis and identifying proteins, both under electric fields. Polyacrylamide is used in water purification to flocculate suspended organic matter. The procedure for the preparation of polyacrylamide gel networks is identical to that employed for the preparation of gels commonly used for electrophoresis. The method is based on the free-radical polymerisation of acrylamide monomer in aqueous solution. The free-radical polymerisation of acrylamide occurs in solution containing the biomass and a cross-linking agent such as N,N`,methylenebisacrylamide. The polymerisation reaction is initiated usually by ammonium persulphate and accelerated by N, N, N`, N`-tetremethylenediamine (TEMED). A major disadvantage of polyacrylamide is the toxicity of the acrylamide monomer, the cross-linking agent, the initiator, and accelerator (Klaus, 1987). Acrylamide is a potent nerve toxin in humans and also affects male reproduction, and causes birth defects and cancer in animals.

3.1.3 Polysulfone

Polysulfone is a plastic material used widely in different applications such as rigid circuit boards, CB radio base, medical instrument trays, dental water tubes, implant trials, hot water tanks, sight gauges, oil well applications, microwave oven components and cookware.

3.1.4 Growth on inert media

The conventional methods of growing biomass as a film on inert media (sand, gravel, furnace slag, fired clay blocks, reticulated urethane foam, P.V.C matrices) for use in waste water treatment have also been investigated for biomass immobilisation techniques, in metals uptake. Cotoras et al. (1993) used a species of *Bacillus* grown as a biofilm on glass rashing rings in a small laboratory column reactor. Huang et al. (1990) used acid-washed *Saccharomyces cerevisiae* which was immobilised onto white sand in a packed column by pumping the yeast through the bed. Lewis and Kiff

(1988) immobilised *Rhizopus arrhizus* in reticulated polyurethane foam, and the immobilisation matrix was used for the removal of Cd, Cu, Fe, Mn, Pb and Zn in upflow packed columns. Whitlock and Mudder (1985) immobilised a mutant bacterium, capable of oxidising the organic components of the waste and accumulating metals at the same time, as a film on the discs of a series of rotating biological contactors (RBCs).

3.2 Problems with biomass immobilisation

A problem with immobilised systems is that, although they are efficient on a small scale, diffusion limitations may be a problem in large processes. Many systems using immobilised biomass suffer from poor cell retention and cell leakage on a commercial scale could cause severe problems. In addition many of the immobilised systems (e.g. alginate or polyacrylamide), tend not to be very robust and fall apart under certain conditions, many of which are found in industrial environments (Garnham 1997).

3.3 Application of immobilised cell biosorption systems

Immobilisation techniques are not yet sufficiently well developed to replace current technologies (e.g. precipitation, ion exchange, etc.), but they could nevertheless be used as an adjunct to existing processes and be utilised as a concentration stage in recovery from very dilute solution as a preliminary step to other conventional treatments. Alternatively immobilised biomass may be used as a polishing stage for removing trace concentrations of metals that ion exchange resins can not deal with (de Rome and Gadd, 1991).

3.4 Polyurethane: a brief history

The term 'polyurethane' refers to a group of polymers which have found widespread application over the last century. In general, they are produced as a result of the reaction between a di-isocyanate and a compound rich in hydroxyl groups, or containing active hydrogen atoms. The foundation for the now well-known polyurethane field was the original isocyanate synthesis carried out by Wurtz in 1849, according to the following formula:

$$R_2SO_4 + 2KNCO \longrightarrow 2RNCO + K_2SO_4$$

The preparation and chemical reactions of isocyanates have therefore been known for over a hundred years but it was not until the 1930's that interest and their industrial importance grew to any proportion (Miles and Briston, 1979).

In 1937 Dr Otto Bayer made an elastomer by reacting toluene di-isocyanate (TDI) with various polyols. Thus it is to Bayer and his co-workers that the credit must go for the discovery of the di-isocyanate poly-addition process. There are two types of di-isocyanates: toluene di-isocyanate (TDI) and diphenylmethane di-isocyanate (MDI). Due to the toxicity problems associated with TDI, ICI (UK) developed the low toxicity urethane system based on diphenylmethane di-isocyanate (MDI) in the early 1950s (Buist, 1978).

Polyurethanes are an essential part of modern life and are used in many applications to provide comfort, safety and environmentally sustainable products. They are used in shoe soles, automobile industry, adhesives, moulding compounds, upholstery, insulation, construction industry, industrial wheels and tires, hose and tubing, films for lamination, industrial belts, tank, pipe liners, and many others.

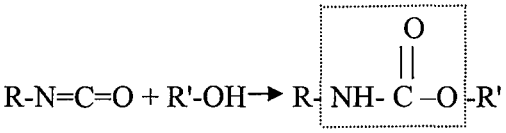
Polyurethane foams are one of the most important polyurethane products. They can be defined as plastic materials in which a proportion of solid phase is replaced by gas in the form of numerous small bubbles (cells). The gas may be in a continuous phase to give an open-cell material or it may be discontinuous to give non-communicating cells (Braun et al., 1985).

There are two techniques used to produce foamed polyurethanes. The first consists of forming a pre-polymer (mixture of poly-hydroxylic compound and poly-isocyanate) and then reacting it at a later stage with water, catalyst and other additives to produce the final foam product. The second is termed "the one-shot technique" and consists of mixing together a polyhydroxylic compound, a di-isocyanate and an aqueous activator mixture.

Water is generally necessary to produce the foaming which is as a result of the liberation of carbon dioxide, although foaming can also be produced by the addition of certain fluorocarbons.

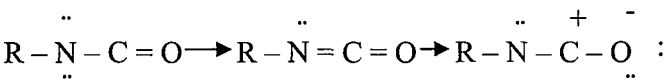
Foams can be produced with different physical properties. Flexible foams are prepared from polyols of moderately high molecular weight and a low degree of branching, whereas rigid foams are prepared from highly branched resins of low molecular weight (Braun et al., 1985).

The two important reactions in the preparation of urethane foams are those between isocyanate and hydroxyl compounds (polyester or polyether polyols) and those between isocyanate and water. The reaction between isocyanate and hydroxyl compounds which produce a urethane group can be considered as a chain-propagating reaction:



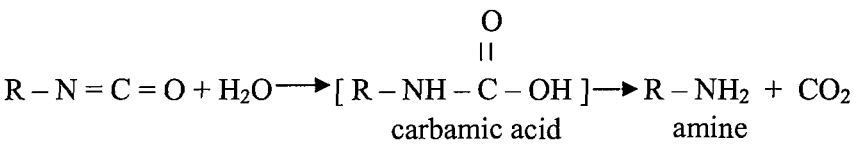
urethane

This isocyanate group is considered to exist in the following resonance forms:

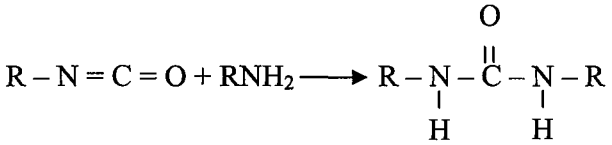


Electron-withdrawing substituents on the isocyanate molecule should move negative charges away from the isocyanate carbon, making it more positive and thus facilitating attack by an electron-donating group such as hydroxyl. The resonance forms may explain the observed relative high reactivity of aromatic isocyanates owing to the electron-withdrawing influence of the aromatic rings.

The second reaction, water-isocyanate is responsible for foam formation by the liberation of carbon dioxide as the in-situ blowing agent. The first step of this reaction is formation of unstable carbamic acid which decomposes to form carbon dioxide and amine. The amine may react with an additional isocyanate to produce substituted urea:

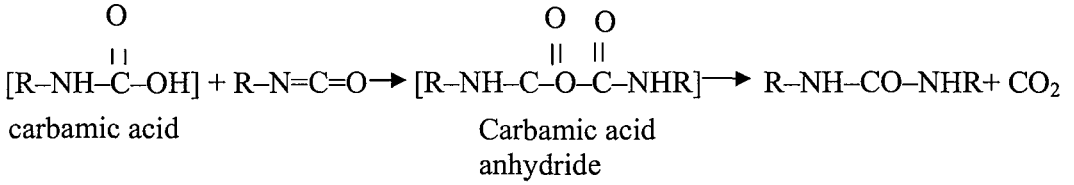


carbamic acid amine

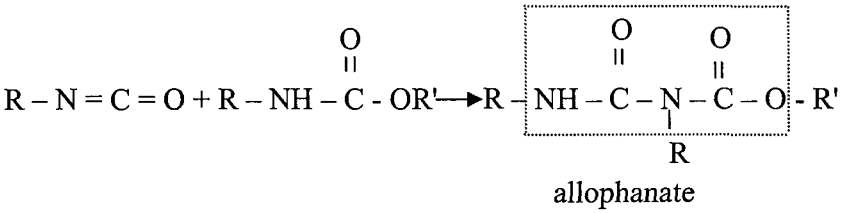


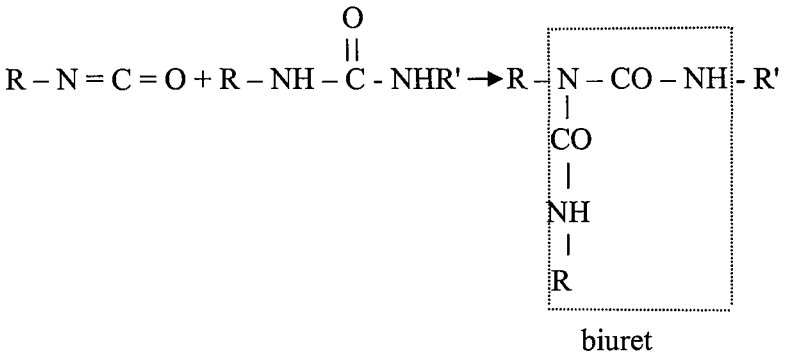
substituted urea

Alternatively, carbamic acid may react with another isocyanate molecule to produce carbamic acid anhydride which decomposes to substituted urea and carbon dioxide:



The main reactions which lead to branching and cross-linking are the isocyanate-urethane reaction producing allophanate linkages and the isocyanate-urea reaction which produces biuret:





During the foam formation the polymer is distributed between the walls of the gas bubbles and the lines where the gas bubbles intersect. The bubbles are called quasi-spherical cells, the lines of intersections are called strands, and the walls are the factual membranes. In open-cell flexible polyurethane foam, at least two windows (from the total) in each cell must be ruptured for fluids to pass freely through the foam. It is necessary for each window to be shared by two cells, and each strand to be shared by three cells. The cell structure (i.e. presence or absence of windows in the cell or the number of windows per cell) is a function of the process by which the foam is made. The structure made up of windowless cells (containing only strands) is called reticulated foam (Braun et al., 1985).

3.4.1 General methods of foam preparation

Methods have been developed by which almost every plastic material can be made in a cellular form. The general principle for preparing cellular plastics is the dispersion of the gas phase in a liquid to obtain liquid foam which will then be solidified to a solid cellular plastic. The main methods for uniform dispersion of the gas bubbles are chemical, physical or mechanical.

3.4.1.1 Chemical methods

a- Thermal decomposition of a chemical blowing agent

This method involves the incorporation of a chemical blowing agent into the plastic polymer in the liquid state. The blowing agent is usually an organic material (such as p-toluene sulfonyl semicarbazide) which decomposes under the action of heat to yield a gas. Heating the mixture of the polymer and the blowing agent to a certain temperature causes a decomposition of the blowing agent. Subsequent expansion of the polymer occur which, under controlled conditions, gives rise to a foamed plastic (Braun et al., 1985).

b- Blowing by in-situ chemical reaction

In this process gas formation is achieved by the reaction between two species, one of which may or may not be a part of the polymer. Reaction between isocyanate and water to produce carbon dioxide in the foam formation as explained before is a good example of this. Cellular phenolic resins can be prepared by mixing the liquid resin with a simple inorganic carbonate or biocarbonate which, when treated with mineral acids, produces carbon dioxide. In this case neither of the reactants is part of the polymer (Braun et al., 1985).

3.4.1.2 Physical methods

a- Low pressure release of dissolved gas

This technique employs the dissolution of gas in the liquid polymer under high pressure. Upon releasing pressure, the expansion of gas from the supersaturated polymer causes the formation of foamed plastic. Expanded ebonite, polystyrene, and polyvinylchloride have been prepared by this method (Thomas, 1965).

b- Blowing by vapour from a volatile liquid

In this method a liquid blowing agent is incorporated into the polymer under atmospheric conditions. On heating the mixture, the liquid blowing agent will be converted into vapour which causes expansion of the polymer and formation of a cellular material. The preparation of polyurethane foams using chlorofluorocarbons (e.g.: $CFCl_3$) is probably the best known example (Ferrigno, 1963).

c- Temporary filler

This system is used to make cellular material from polymers which are difficult to expand. Particles of solid material are fixed with the polymer and processed to give a filled solid plastic. The filler is subsequently removed by leaching with a suitable solvent or by sublimation to leave the plastic material in a cellular form. A good illustration is the preparation of cellular polytetrafluoroethylene, which results from mixing and sintering polymer powder with naphthalene. Naphthalene is then sublimed away leaving a porous form of polytetrafluoroethylene (Braun et al., 1985).

3.4.1.3 Mechanical methods

a- Mechanical entrainment of gas

This is probably the oldest means of forming cellular plastics. Air beaten into the polymer produces stable liquid foam, which is then cured either chemically or by heating. Urea-formaldehyde and polyvinyl chloride have been prepared in this way (Thomas, 1965).

b- The use of micro-spheres

A wide variety of cellular plastics may be made by mixing micro-spheres with the liquid polymer which on solidification gives rise to a cellular product without direct polymer/gas interaction. Micro-spheres are small hollow spheres with extremely thin walls which can be made of phenol-formaldehyde, urea-formaldehyde, glass, etc., (Braun et al., 1985).

3.5 The use of polyurethane for immobilisation and sorption

Natural sponge is considered to be the oldest material to be used as a support matrix in separations chemistry. Brunschwing (1512) used a sponge material loaded with olive oil for the purification of ethanol in a distillation system.

Lal et al. (1964) described a method for the collection of trace elements from sea water employing natural sponge supporting iron (III) hydroxide precipitate. By towing the treated sponge through coastal sea water, these researchers were able to enrich some elements (e.g.: silicon, beryllium, gold and titanium).

Bauman et al. (1965) physically immobilised an enzyme-containing starch gel on reticulated foamed polyurethane. This foam was employed to monitor water and air for enzymic-inhibiting atmospheric pollutants.

The immobilisation of organic reagents in foam material is based mainly on the hydrophobic character of polyurethane foams. Owing to these properties, the foam material swells in contact with hydrophobic solvents. That is, hydrophobic solvents and solutes can be physically immobilised in the foam matrix by swelling. Practically, the foam is immersed in the required solvent for a reasonable time to ensure equilibration, and the excess solvent is then removed by pressing the foam between sheets of filter paper. The foam so obtained contains about 50 to 80% of solvent, depending on the type of both the foam and solvent used. Polyurethane foams supporting solvent extractants and/or liquid ion exchange are prepared by this procedure (Braun et al., 1985).

Sometimes organic reagents are immobilised in foam membranes by dissolving the solid reagent in a volatile organic solvent; after allowing the foam to swell the solvent is gradually evaporated from the swollen foam by gentle heating. This procedure was

employed for the preparation of some reagent foams and foams supporting redox reagents.

Heterogeneous ion exchange foams have been prepared by adding very finely powdered ion exchangers to the polyol solution before mixing it with the isocyanate for foam synthesis. Foams supporting inorganic compounds have also been prepared by converting them to the required cation form and precipitating the inorganic elements within the foam matrix as one of their in-soluble salts, or by reducing them to the metallic form. The foams thus produced are suitable for isotope exchange or redox separations. Furthermore, foams containing certain functional groups chemically bonded to the foam matrix are prepared by anchoring these chelating groups directly or indirectly to the foam matrix (Braun et al., 1985).

Braun et al. (1973) prepared heterogeneous ion exchange foams in which finely ground commercial ion exchange resins are embedded into the thin membrane walls of a polyurethane foam matrix of an open cell polyether type. The authors claimed a fast and successful sorption of copper by these foams with a half-life equilibrium sorption of 0.6 min.

Sonomoto et al. (1980) entrapped acetone-dried cells of *Arthrobacter simplex* in urethane prepolymer for the bio-conversion of hydrocortisone into prednisolone. The urethane prepolymer used was conventional polyurethane used in the rubber industry. The immobilisation process occurred by mixing the biomass cells with the melted prepolymer. The resultant mixture was then poured onto a glass plate to form a gel of polymer-imbedded *A. simplex* cells. The gel film was cut into small pieces (5 x 5 mm) which were used in experiments. The authors reported a transformation rate of the entrapped cells equal to 18% of that exhibited by the free cells.

In the UK, researchers at the University of Manchester Institute of Science and Technology developed what is now commercially marketed as the "Captor Process" (Atkinson et al., 1983). The Captor process is essentially an aerated sludge reactor where reticulated pads (cuboids) of polyurethane (25 x 25 x 12.5 mm) are retained in the aeration tank by screens in the effluent line. Micro-organisms colonise the spaces inside the pads making them loaded with biomass to a concentration which is a function of the strength of the wastewater. Typically 60 to 300 mg of biomass per pad can be obtained which yields an "equivalent" mixed liquor suspended solids (MLSS) concentration of 1860 to 9300 mgl^{-1} at a basin pad concentration of 31 $pads.l^{-1}$(Boyle and Wallace, 1986). The bacterial cells which remain free in the MLSS are intended

to be negligible in the process, thereby eliminating the need for a secondary clarifier and solids recycle. Excess sludge needs to be continually removed by removing a portion of pads via a conveyor and passing the pads through pressure rollers to squeeze out the solids.

A similar process was developed, about the same time, in Germany and named the "Linpor Process" (Reimann and Fush, 1986). The Linpor process used the same polyurethane pads as in the Captor process but with different size (12 x 12 x12 mm) and due to the shearing action in the aeration basin, free MLSS concentration up to 4000 mgl^{-1} can be contained in the free liquor (Givens and Sack, 1987). Thus a secondary clarifier was essential in the process.

The first research to look at the immobilisation of biomass on reticulated polyurethane foam for the removal of heavy metals from aquatic solutions was undertaken by Kiff and Little (1986). They cultivated *Aspergillus oryzae* in reticulated polyurethane pads, similar in size to those used in Captor process, the pads were then used in up flow packed columns for the removal of Cd, Cu, Fe, Mn, Pd and Zn. The system was reported to be unaffected by the presence of low concentrations of organic matter and alkali metals, but was sensitive to low pH, temperature and the presence of competing cations. The polyurethane foam pads used in the study are based on a product called FILTREN T, developed by a Belgium company called Recticel. FILTREN T is reticulated polyurethane foam based on polyether. The cellular network is entirely open and hence does not contain any closed cells. The specific surface area of the pads is 1000 $m^2.m^{-3}$ approx., and the voidage ratio equal to 95% approx. (Banks, 1997).

A pilot scale biosorption column containing *Rhizopus arrhizus* immobilised in the same manner of Kiff and Little was used over an experimental period of 6 months, with repetitive backwashing, to remove humic materials from a raw water supply (Banks and Parkinsons, 1992).

The above mentioned research for immobilisation of biomass in the polyurethane foam has used factory manufactured polyurethane foam and has necessitated the immobilisation to occur by cultivating the biomass in association with the foam pads.

The only exception is the study carried out by Sonomoto et al. (1980) who immobilised live bacteria cells in polyurethane gel (conventional polyurethane used in the rubber industry) during the manufacturing process for the bio-conversion of

hydrocortisone into prednisolone. The authors reported bio-conversion efficiency of the immobilised biomass to be only 18% of that of free biomass.

Conventional hydrophobic polyurethane foam (i.e. un-loaded foam) has been used for the separation of various species from aqueous solutions. The non-selective sorption character of untreated polyurethane foams could be rendered more selective by careful control of the experimental conditions (Braun et al., 1985). Bowen (1970) in his pioneering work used resilient polyether type polyurethane foam in the sorption of a number of substances from aqueous solutions. He reported that there are two classes of substances which are strongly extracted from solution by the foam. These are substances which exist in aqueous solution as free molecules with high polarizability (e.g. iodine, aromatic compounds, metal dithizonates) and univalent anions with high polarizability (e.g. $AuCl^-_4$, $TlCl^-_4$ and $FeCl^-_4$). The sorption capacity of various species, as determined from their isotherms, was found to be far too large, 0.5 to 1.8 $mol.kg^{-1}$ of foam, to be attributed to surface adsorption phenomena, which led to the conclusion that true absorption into the bulk of the polymer must be occurring. This was further confirmed by microscopic examination of cross sections of foam membrane after iodine had been sorbed. The iodine colour was found to be uniform throughout the sections and was not confined to its surface. The author noted that some weak-base anion exchange sites might exist in/on the polymer membrane, because of the presence of amino cross-linkages in the polyether and polyester type foams.

Sukiman (1974) was able to collect Au (III) chloride in acidic aqueous solution using foam columns of 20 mm diameter and 100 mm length. The columns were packed with 0.5 g of unloaded foam cubes by squeezing several times with water. Three different polyether foam samples were examined. Au (III) at trace levels (0.02 to 25 ppm) was recovered from acidic aqueous solution by passing the solution through the foam column at a flow rates (30 to 40 $ml.min^{-1}$). Acetone was then employed for the recovery of Au from the foam column at 3 $ml.min^{-1}$.

In their study on the separation of gallium from acidic aquatic solution, Gesser and Horstall (1977) reported two alternative mechanisms for the sorption of Ga by polyurethane foam. In the first, the foam material behaves as a polymeric sorbent for the gallium chloride complex. The second mechanism results from protonation of the ether sites in the polymer when these come into contact with acids in aqueous

solution, in which case the protonated sites act as anion exchangers in the extraction of $GaCl^-_4$ species.

During the 1970s and 1980s, a family of urethane polymer products was developed at the Research Division of W. R. Grace & Co. which were named HYPOL®, foamable hydrophilic polymers, (Braatz, 1994). The original polymer products were pre-polymers based on toluene di-isocyanate (TDI) terminated linear polyethylene glycols and triol crosslinkers, but were later expanded to consist of a variety of polyethers and aliphatic or aromatic polyisocyanates. Similar type of hydrophilic polyurethane pre-polymers were produced by the German company Bayer AG and named Desmodur T 80 (Klein and Kluge, 1981).

Hypol foam can form upon the reaction between water and Hypol pre-polymers without the aid of catalysts. Inert ingredients can be incorporated during the foaming process up to about 80% by weight of the polymer matrix, and the cellular structure of the resulting foams can be controlled by the addition of different surfactants (Braatz, 1994). The water ratio to pre-polymer is quite broad and the pre-polymer can accommodate a large amount of water and still produce foam. Ferreira-Dias et al. (1999) reported that the ratio of water to pre-polymer varies between 0.5 – 2.5 by weight while other reported that this ratio could reach 7, depending on the type of the pre-polymer used (Klein and Kluge, 1981). Different types of Hypol with different chemical composition were produced by the manufacturer (e.g. Hypol 3000 is a toluene di-isocyanate based pre-polymer, while Hypol 5000 is methylene bis (p-phenylisocyanate) based.

Properties of the foam such as density, cell structure, rate of wetting, and water retention can be modified by controlling the ratio of water to pre-polymer, foaming temperature, pH and the type and amount of surfactant added to the aqueous phase (Havens and Rase, 1993).

The immobilised material in the foam becomes a part of a cross-linked polymer matrix. This cross-linking of the material should impart considerable stability to the immobilised material, allowing a long life time for the material-support formulation (Havens and Rase, 1993). Storey et al. (1990) reported that the immobilised material is covalently attached to the polymers during the process of polymerization. LeJeune and Russell (1996), in their study on immobilising enzyme in Hypol pre-polymer

stated that the degree of covalent bonding between the enzyme and the pre-polymer depends upon the synthesis procedure.

Hypol has been used extensively and successfully in enzyme immobilisation for different purposes (Storey *et al.*, 1990; Dias *et al.*, 1991; Havens and Rase, 1993; LeJeune and Russell, 1996; Ferreira-Dias *et al.*, 1999), for the immobilisation of whole microbial cells for conversion of chemical and bio-chemical compounds in to other forms (Klein *et al.*, 1979; Klein and Kluge, 1981; Fusee *et al.*, 1981), and as a solid support medium in gas-phase bio-filters (Moe and Irvine, 2000). Furthermore, and due to the non-toxic nature of the polymer, Hypol has been used in different bio-medical applications, such as contraceptive foams, as in the TODAY® sponge product which incorporates an active spermicidal compound into the Hypol foam (Braatz, 1994).

Fusee *et al.* (1981) used Hypol containing different levels of isocyanate to immobilise live cells of *Escherichia coli* for the conversion of ammonium fumarate into L-aspartic acid. The authors reported that the pre-polymers with the higher isocyanate content gave decreased immobilised-cell aspartase activity. Chibata et al. (1976) reported that cross-linking *Escherichia coli* cells with 2, 4-toluene diiscocyanate, which is used to manufacture the hydrophilic polyurethane, was detrimental to the aspartase.

Lupton and Zupancic (1991) in their patent used Hypol to immobilise powdered activated carbon and a viable aerobic phenol-degrading microorganism to assist in the degradation of phenolic materials in wastewater. The immobilisation was achieved by mixing powdered activated carbon (PAC) and the microorganisms with the Hypol liquid prior to the foam formation. Both PAC and the microorganisms became a part of the foam matrix. The matrix was then cut into cubes and packed in a glass reactor through which the wastewater was passed. The degradation of phenolic materials was successful with a 500 mgl^{-1} influent concentration being reduced to 20 ppb. There is no report that the manufacturing process had any lethal effects on the immobilised bacteria.

Later, and in his second patent, Lupton et al. (1996) reported that hydrophobic polyurethane can adsorb certain organic pollutant such as phenol, thus enhancing the effectiveness of the microorganisms that metabolise the pollutant. Hence, the authors immobilised aerobic microorganisms capable of biodegrading or metabolising organic

materials (such as phenolic materials) from waste water in flexible open-celled hydrophobic polyurethane foam in the absence, or in the substantial absence, of a carbon adsorbent. The authors defined the hydrophobic polyurethanes as those which can not be wetted by water. They can be either obtained from commercial sources or prepared in accordance with known techniques. The proportion of aromatic isocyanate compound is usually high as this enhances the hydrophobic characteristics of the polymer. Following impregnation of the porous polyurethane support with activated carbon (during the fabrication process) the resultant foam is then cut into an appropriate particle size and loaded as a fixed bed into a reactor. A suspension of pollutant degrading microbes is then added to the reactor, where the biodegradative microbes absorb and attach on and into the spaces of the foam. This process is very similar to the process of microbial colonisation used in the Captor process, and the only difference is the incorporation, if required, of activated carbon into the supporting matrix.

Hermann (1999) in his US Patent, made a composite material by immobilising bioactive organisms (viable and non-viable) in a non-cellular hydrophilic urethane binder for the removal of noxious materials from effluents. To form the composite, a prepolymer was prepared by heating polyethylene glycol, having an average molecular weight of about 1000, to 200° F (= 93.25° C) up to 350° F (= 176.50° C) and reacting a di-isocyanate with it while mixing to form the prepolymer. After cooling, the prepolymer was mixed with aqueous slurry containing the organisms, and optionally a surfactant and bactericide. The resultant mixture is cured to form the composite material containing between 15% and 90% dry solids content of the immobilised bio-materials. The exothermic temperature of the reaction < 110° F (<43.3° C) could be controlled so that the binding capacity of the active ingredients is not significantly altered.

The hydrophilic urethane used in this work was produced by Matrix R & D Corporation of Dover, N.H. under the trade name "BIPOL", and it was claimed that this type of polyurethane exhibited more hydrophilicity than the "HYPOL" type produced by W. R. Grace & Co. At the end of the immobilisation process the resultant hydrophilic binder (urethane) did not contain a cellular structure. This was achieved by controlling the viscosity of the mixture of the aqueous phase and the pre-polymer, where the formed CO_2 gas bubbles produced during the reaction process were broken prior to polymerization and coating of the active ingredients.

CHAPTER 4

Materials and methods

4.1 Preparation of glassware, plastic ware and experimental tools

Glassware, sample polyethylene vials, plastic columns, column tubings and pipettes tips (different sizes) used in the adsorption and precipitation experiments were washed by soap and tap water, immersed in 10% HCl solution for at least 2 hours to elute any metal residual, soaked in 20% Decon 90 to remove the thin film covering the internal walls and then washed thoroughly in deionised water. Cleaned glass conical flasks were then placed upside down on clean tissues to drain the water and the opening covered tightly by a piece of foil. The flasks prepared in this way were used directly and not stored. Sampling vials, tips and other ware and tools were dried in a low temperature oven dryer.

Glassware, plastic ware and tools used for other purposes were washed only using detergent and tap water then thoroughly rinsed in deionised water before hot air drying.

4.2 Preparation of the biomass

The study started with using *Rhizopus oryzae* fungal biomass as it has been reported to be an efficient heavy metals adsorbent (see section 2.4.1). However, with additional progress, the amount of biomass required for the experiments increased considerably, which made the laboratorial cultivation of the fungal biomass cumbersome and time consuming. Therefore *Rhizopus oryzae* was replaced with the abundantly available *Ascophyllum nodosum* seaweed.

4.2.1 Preparation of *Rhizopus oryzae*

Rhizopus oryzae, strain IMI 057412, was obtained from the "International Mycological Institute", Egham, Surrey, UK in a freeze- dried form.

4.2.1.1 Preservation of *Rhizopus oryzae*

The freeze-dried sample of *R. oryzae* was resuscitated following the supplier's instructions. The culture was then maintained by sub-culturing on nutrient agar (Merck) slopes which were incubated for three days at 25° C before being stored at 4° C. The culture viability was maintained by sub-culturing approximately every 6 weeks.

4.2.1.2 Growing and harvesting of *R. oryzae*

R. oryzae biomass was grown in shake flask culture on yeast malt sucrose (YMS) medium containing 10 g malt, 10 g yeast, and 30 g of sucrose per litre at an initial pH 7.0. This culture was then used as an inoculum for 40 litres of the same medium in a 100 litre fermenter (Bioengineering AG CH-8636). The fermenter growth conditions were 25° C, 10 litres of air/min, 200 rpm rotor speed and an initial medium pH of 6.25. The biomass was grown for 48 hours after which it was inactivated by heating the medium to 122° C for 15 min. The final pH of the medium was 3.85. Fungal production was 1.65 g dry wt. of biomass /L of medium.

R. oryzae used in a later set of experiments (sections 4.4.1 and 4.4.2) was grown using shake flasks only. In this case the biomass after harvesting was washed thoroughly with deionised water, and autoclaved for 30 min at 121° C. Fungal production was 2 g dry wt. of biomass /L of medium.

The biomass after inactivation, in both cases, was again washed thoroughly with deionised water, squeezed and dried in the oven at 50° C for 48 hours.

4.2.2 Preparation of *Ascophyllum nodosum*

The seaweed, identified as *Ascophyllum nodosum,* was dried for 24 hours at 101° C to crystallize the salts, crushed by hand to reduce the volume and then washed repeatedly with deionised water until the washings had conductivity < 20 μS (ELE Conductivity Meter, Model No. 4071). It was then acid washed with 0.1M HCl to remove any ionically bound material from the potential metal binding sites. It was further washed with deionised water to remove the acid (conductance < 30 μS). The washed material was again dried for 24 hours at 101° C.

4.2.3 Sizing of the biomass

Both the fungal and the algal biomass were ground finely and size graded using universal sieves to obtain particles of diameter less than 150 μm; these were used in the immobilisation processes and adsorption experiments. Plate 4.1 shows the *R. oryzae* particles used in the study.

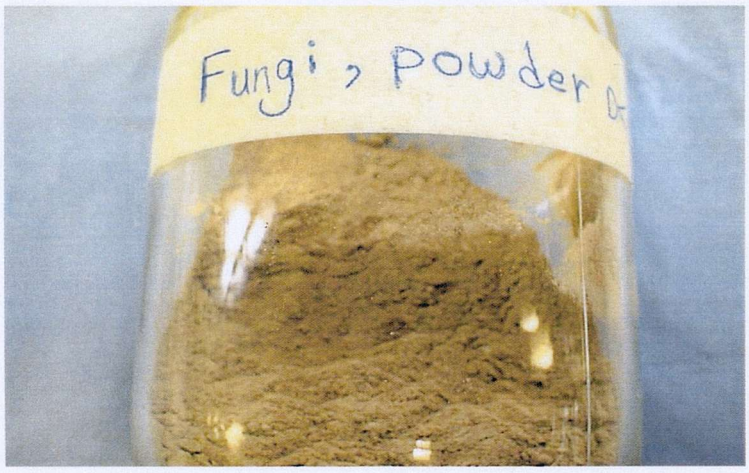


Plate 4.1 Non-viable powder of *Rhizopus oryzae* (particles D < 150 μm)

4.3 Immobilisation techniques using seven selected types of polymers

Rhizopus oryzae was immobilised in the following matrices as part of a comparative first stage study:

1- Alginate
2- Polyacrylamide
3. Polyvinlformal
4- Polyurethane
5- K-Carrageenan
6- Polysulfone
7- Polyethyleneimine (PEI)

4.3.1 Immobilisation in alginate

The Method of Gee and Dudeney (1988) was used which involved the following steps: 200 mg of alginic acid (sodium salt, Aldrich) was dissolved in deionised water at 65° C and the volume made up to 10 ml to give a 2% alginic acid solution. To this was added 2.5 g of biomass and mixed thoroughly. The mixture was delivered, drop wise, through a syringe (1.5 mm internal diameter) into a 0.5 M calcium chloride

solution ($CaCl_2.2H_2O$, 99.5%, BDH) which was continuously stirred on a magnetic stirrer. Beads of biomass embedded in alginate with a diameter of approximately 4mm were formed as soon as the mixture contacted the calcium chloride solution. The beads were allowed to harden for three hours in the solution. Hardened beads were then placed in deionised water, with stirring, for two hours to allow the excess calcium chloride to leach out. The beads were stored in a sealed flask at 4° C prior to use. Beads without biomass were made in the same way as above.

Biomass load in alginate beads

Total weight of the beads = 12.5 g

Biomass load = biomass wt. (g) / total wt. of beads (g) = 2.5/12.5 = 0.2 = 20%

Plate 4.2 shows the alginate beads with and without fungal biomass



Plate 4.2 Alginate beads with (left) and without (right) fungal biomass

4.3.2 Immobilisation in polyacrylamide

The method of Andrews (1986) was used which involved the following steps: 0.95 g of acrylamide (Acrylamide, 97%, Aldrich), and 0.05 g of N,N`-Methylenebisacrylamide (99%, Aldrich) were dissolved in deionised water on a

temperature controlled magnetic stirrer (Stuart Scientific) and the volume made up to 10 ml. The temperature of the solution was increased to 40° C, and 0.005 g of ammonium persulphate (98+%, Aldrich) was added. After completely dissolving the ammonium persulphate, 5 µml of N,N,N`,N`tetramethylethyl endiamin (99%, Aldrich) was added to the mixture. 2 g of biomass was then thoroughly mixed in, and the mixture stirred continuously at a slow speed until a block of solidified gel was formed. The gel was cut into small particles of 4 mm diameter using a knife. Polyacrylamide particles without biomass were made using the same method.

Biomass load in polyacrylamide beads

Total weight of the beads = 12 g

Biomass load = biomass wt. (g) / total wt. of beads (g) = 2/12 = 0.1667 = 16.67 %

Plate 4.3 shows polyacrylamide beads with and without fungal biomass.

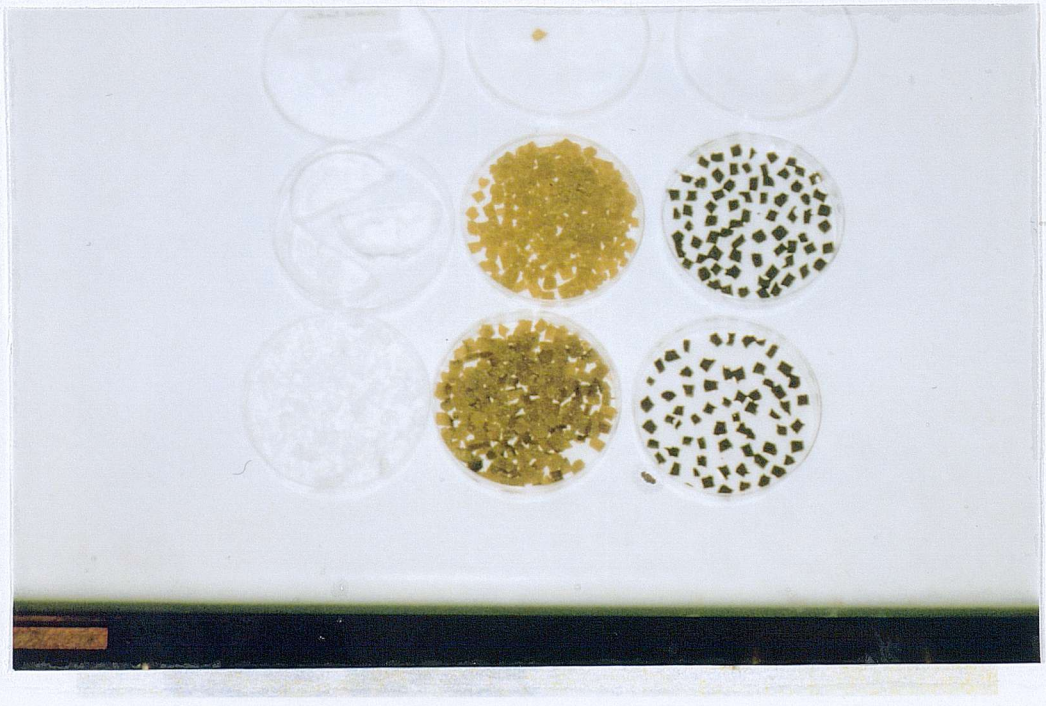


Plate 4.3 Polyacrylamide beads with (right) and without (left) fungal biomass

4.3.3 Immobilisation in polyvinlformal

The method reported by Tobin et al. (1993) was used and involved the following procedure: 2 g of polyvinlformal powder (Aldrich) was dissolved in 35 ml of dichloromethane (99.5%, BDH) at approximately 40° C using a temperature

controlled magnetic stirrer. To this was added 1 g of biomass with continuous stirring until the solvent had evaporated. The resultant sheet of polymer-biomass was cut into squares of 4mm side length and kept at 4° C prior to use.

PVF beads without biomass were made following the same procedures.

Biomass load in polyvinlformal beads

Total wt. of the beads = biomass weight (g) + polyvinlformal weight (g) = 2+1 = 3g

Biomass load = biomass weight (g) / total weight of beads (g) = 1/3 = 0.3333 = 33.333 %

Plate 4.4 shows polyvinlformal beads with and without fungal biomass

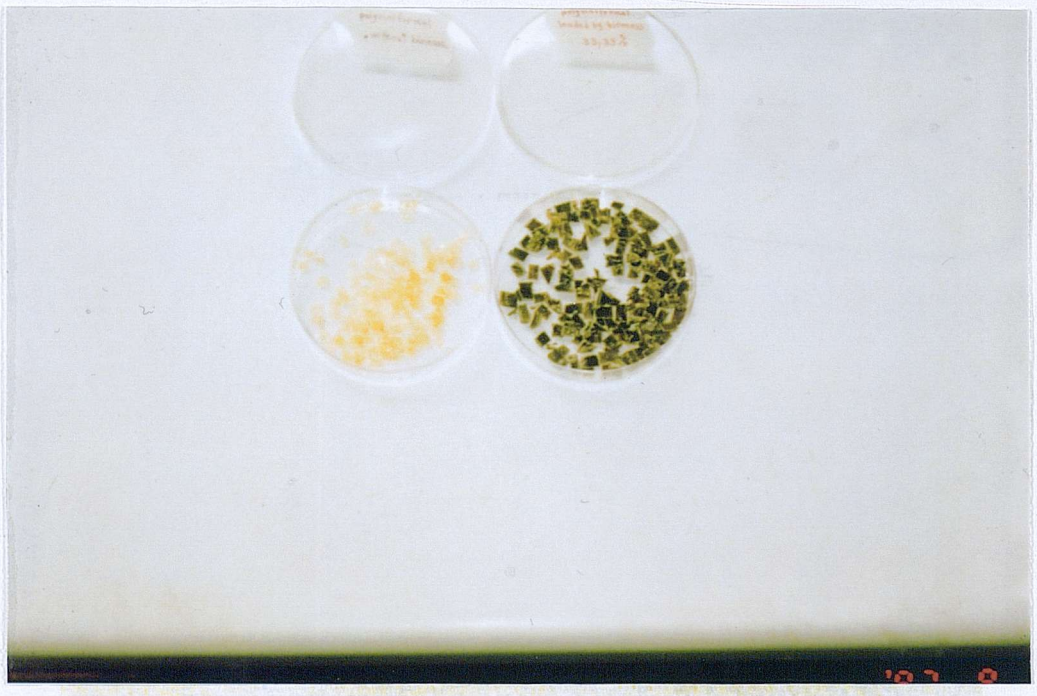


Plate 4.4 Polyvinlformal beads with (right) and without (left) fungal biomass

4.3.4 Immobilisation by growth in polyurethane

The polyurethane cubes used were cut from a product called FILTREN T (Recticel, Belgium) to give a size of 2.1 x 2.1 x 1.2 cm. Biomass was grown into the cubes by placing them in YMS medium, initial pH 6.25, in conical flasks on an orbital shaker and inoculating with a culture of *R. oryzae*. The flask was incubated for three days at a shaker speed of 200 rpm after which the pads were removed, washed with deionised water, autoclaved at 121° C for half an hour, washed again with deionised water and

left to dry completely in a desiccator. The pads were then cut into uniform particles of approximately 4 mm side length.

Biomass load in polyurethane foam

The polyurethane cubes were weighed before and after immobilisation.

Average weight of cubes before immobilisation = 0.25348g

Average weight of cubes after immobilisation = 0.40835g

The average weight of biomass in each cube =

The average weight of loaded cube - The average weight of free cube

= 0.40835 - 0.25348 = 0.15487g

Biomass load = biomass weight in cube (g) / total weight of loaded cube (g) =

0.15487 / 0.40835 = 0.379 = 37.9%

Plate 4.5 shows polyurethane beads with and without fungal biomass

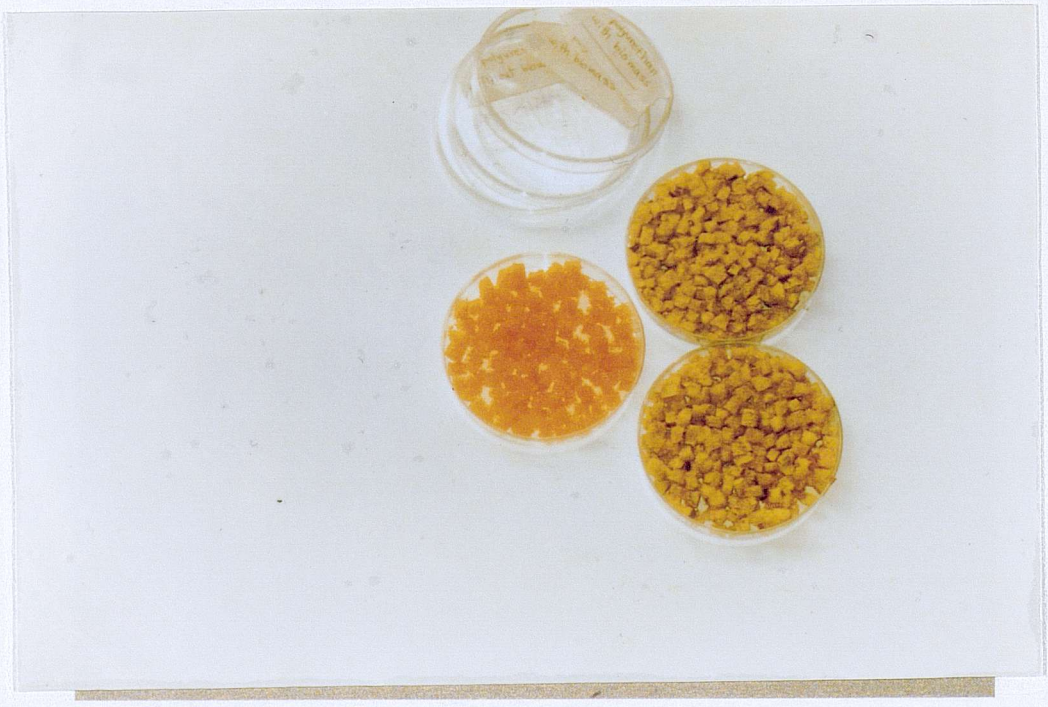


Plate 4.5 Hydrophobic polyurethane beads with (right) and without (left) fungal biomass

4.3.5 Immobilisation in k-carrageenan

The method described by Klaus (1987) was used. 200 mg of k-carrageenan was dissolved in deionised water at 80° C using a temperature controlled stirrer and the volume was then made up to 10 ml. To this 2.5 g of biomass were mixed thoroughly and the mixture was delivered drop wise through a syringe (1.5 mm ID) into 0.5 M of KCl solution. Beads of approximately 4 mm diameter were formed as the mixture contacted the KCl solution. The beads were left in KCl solution for 3 hours to cure, washed with D.W.and stored in a well sealed container at 4° C prior to use.

Biomass load in k-carrageenan beads

Total weight of the beads = biomass weight (g) + weight of k-carrageenan gel (g)

$$= 2.5 + 10 = 12.5 \text{ g}$$

Biomass load = biomass weight (g) / total weight of beads (g) = 2.5 / 12.5 =0.2=20 %

Plate 4.6 shows k-carrageenan beads with and without fungal biomass

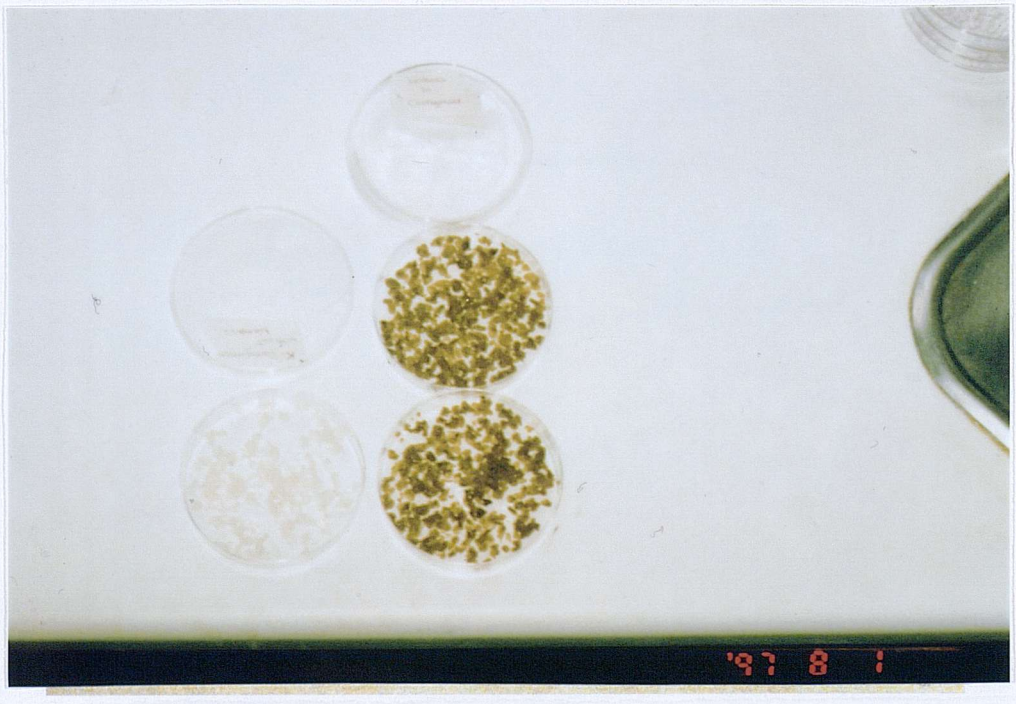


Plate 4.6 K-Carrageenan beads with (right) and without (left) fungal biomass

4.3.6 Immobilisation in polysulfone

The method used by Bennett et al., (1991) was used. 5 g of polysulfone (Aldrich) was dissolved in 50 ml of Dimethylformamide (99%, BDH), on the magnetic stirrer hotplate at 70° C. 2 g of biomass was added to the slurry, whilst stirring continuously. The mixture was delivered through a P.V.C tube (3 mm ID, Merk limited) using a variable speed peristaltic pump (model 7519, Cole-Parmer instrument Co.) at a flow rate of 10 $ml.min^{-1}$, into deionised water. Beads, of approximately 4 mm diameter, were formed as soon as the mixture contacted the deionised water. The beads were kept in the deionised water for 4 hours to allow the solvent to leach out, washed thoroughly by deionised water, put under the fume cupboard for 48 hours for drying, and kept at 4° C prior to use. Polysulfone beads without biomass were made following the same procedures.

Biomass load in polysulfone beads

Total weight of the beads = polysulfone weight (g) + biomass weight (g) = 5 + 2 = 7 g

Biomass load = biomass weight (g) / total weight of beads (g) =2/7= 0.2857= 28.57%

Plate 4.7 shows polysulfone beads with fungal biomass



Plate 4.7 Polysulfone beads with fungal biomass (the beads with and without biomass look exactly the same as the biomass is entirely covered by the polymer)

4.3.7 Immobilisation in polyethyleneimine (PEI)

The method described by Brierley and Brierley (1993) was used. 2000 mg of dried biomass was mixed with 18 ml of deionised water to give a slurry of 10% solids. 6.6 g of PEI (PEI solution 50%, BDH), which contains 3.3 g of PEI, was dissolved in deionised water and made up to 10 ml to give a solution of 33% PEI. 121.2 mg of PEI solution (which contains 40 mg of PEI) was added to the slurry and stirred continuously. 40 mg of glutaraldehyde solution (glutaraldehyde solution 50%, BDH), which contains 20 mg of glutaraldehyde, was added to the mixture and stirring continued until the slurry was smooth and a paste-like dough had formed. The dough was then extruded through a syringe (1.5 mm internal diameter). The extruded dough, which had a noodle-like appearance, was dried for 6 hours in the fume cupboard. 4 mm sections were cut by knife and stored at 4° C before use. The ratio of PEI:glutaraldehyde:biomass used was (2:1:100). Polymer without biomass was prepared using the same technique.

Biomass load in PEI

Total weight of embedded biomass and polymer = weight of biomass + weight of PEI + weight of glutaraldehyde = 2000+40+20 = 2060 mg

Biomass load = biomass weight (mg) / total weight of beads (mg) = 2000 / 2060 = 0.97087 = 97.087%.

Plate 4.8 shows PEI matrix with and without fungal biomass.

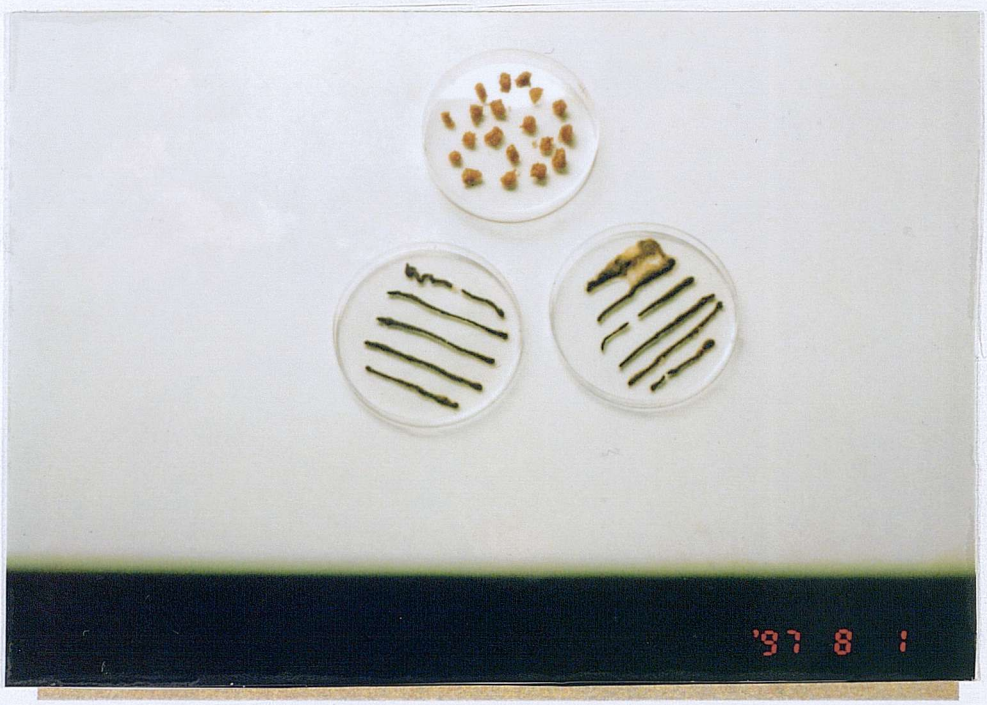


Plate 4.8 PEI beads without fungal biomass (top) and threads of PEI-biomass

4.4 Polyurethane immobilisation techniques

Two types of polyurethane polymers were used for immobilisation of biomass. Conventional polyurethane was purchased as separate components (resin and isocyanate) from Bentley Chemicals Ltd (UK), in 1 kg containers. Hypol 2002 was kindly given by the Dow Chemical Company (UK), in a 25 kg barrel. It was then distributed into 2 kg glass bottles and sealed until used.

4.4.1 Biomass incorporation in conventional hydrophobic polyurethane foam

5 g of the biomass was mixed thoroughly with 12 g of resin using a spatula in a plastic container. 8 g of isocyanate was then added and mixed with a 2-pinned mechanical shear mixer rotating at 2400 rpm until a homogenous cream was obtained (20-30 seconds). The mixture was left for 15 minutes to allow the foam to expand to its final volume and solidify. It was then cut into cubes with a side length of 4 to 5 mm. Foam without biomass was manufactured using the same basic technique.

4.4.2 Biomass incorporation in hydrophilic polyurethane foam (Hypol 2002)

5 g of Hypol was added to a mixing vessel with an internal diameter only slightly larger than the diameter of the mechanical mixer blade. 2.5 g of biomass and 0.163 g $NaHCO_3$ were then added and mixed thoroughly. 7.5 ml of deionised water, 0.117 g of concentrated glacial acetic acid and a surfactant (if used) were mixed in a separate container and then added to the mixing vessel. The complete mixture was then mechanically mixed as in the conventional polyurethane for 20-30 seconds. This homogenous mix 'biofoam' was then allowed to stand and cure for 5 minutes before it was cut up into circular slices, further dried in a fume cupboard and then cut into 4-5 mm cubes. Foam without any biomass inclusion was made in the same way and used as a control. Three surfactants were tested in the foam manufacturing process to assess their effect on pore formation and the immobilised biomass adsorption capacity. These were used at 0.1 g (2% of the prepolymer wt.) and 0.5 g (10% of the prepolymer wt.) per mix. These were: Pluronic 85, Tween 80 and Triton X-100.

4.4.3 Direct casting of biomass-polyurethane columns for sorption studies.

This technique was used to immobilise *Ascophyllum nodosum* in Hypol 2002 foam in column reactors.

By using an appropriate manufacturing technique an open pore hydrophilic polyurethane foam containing biomass particles can be cast into any shape or size of reactor or column. In this work two columns of identical dimensions were manufactured, one with biomass included in the foam matrix and the other without biomass. Each column consisted of a Perspex tube with an internal diameter of 4.4 cm and a length of 15.5 cm giving an internal volume 235.7 cm^3. The tube was made so that a flanged end plates could be attached and held in place by tension exerted by means of threaded stainless steel rods passing between the two flanges and secured by locking nuts. Each end plate was fitted with a tubing connector to allow solutions to pass into and out of the column reactor. Before commencing the foam casting process all column parts were washed thoroughly with detergent and tap water, then with 20% Decon 90, then rinsed thoroughly with deionised water and then hot air dried.

The following procedures were followed to cast foam into the central Perspex tube:

1- A cardboard extension ring was fitted to each end of the Perspex tube as shown in plate 4.9. One of these extensions was padded out so as to have an external diameter

equal to the internal diameter of the mixing vessel. This was necessary so as to force the foam to rise up inside the tube and not escaping around the edges.

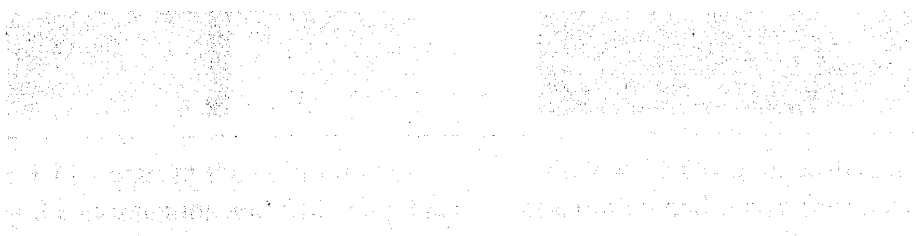
2- 50g of Hypol was placed in a plastic mixing vessel. To this was added 10g of size graded prepared seaweed (section 4.2.2) and mixed thoroughly by hand using a spatula.

3- In a separate plastic container, 75 g of deionised water (150% of the pre-polymer wt.) and 1 g of Pluronic 85 surfactant were mixed vigorously together using a vortex mixer until the surfactant was dissolved completely.

4- The contents of this second container were then added to the main mixing vessel containing the biomass/pre-polymer. The mixture was then vigorously mixed to obtain a homogenous biomass/pre-polymer cream (20-30 seconds) using a mechanical shear mixer (2 pin type) at 2400 rpm.

5- The Perspex tube, with the extension ring having the same diameter as the mixing vessel, was vertically aligned inside the mixing vessel. The foam forming in the mixing vessel was thus forced up inside the tube until it overflowed the top extension tube (plate 4.10). The resultant bio-foam was then allowed to stand and cure for 1 min before the Perspex tube was removed from the mixing vessel and the extensions cut off in line with the ends of the Perspex tube (plate 4.11). The two end plates were then secured onto the tube (plate 4.12).

6- The same procedure was used for preparing the second column except that biomass was not mixed with the pre-polymer.



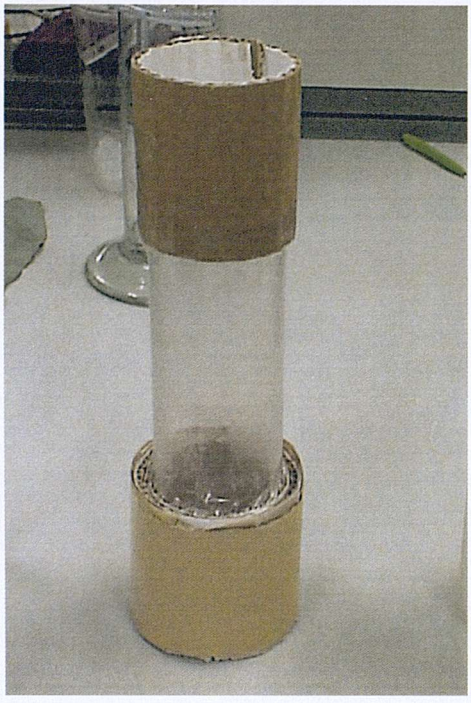


Plate 4.9 Column with extensions



Plate 4.10 Column after casting the foam in

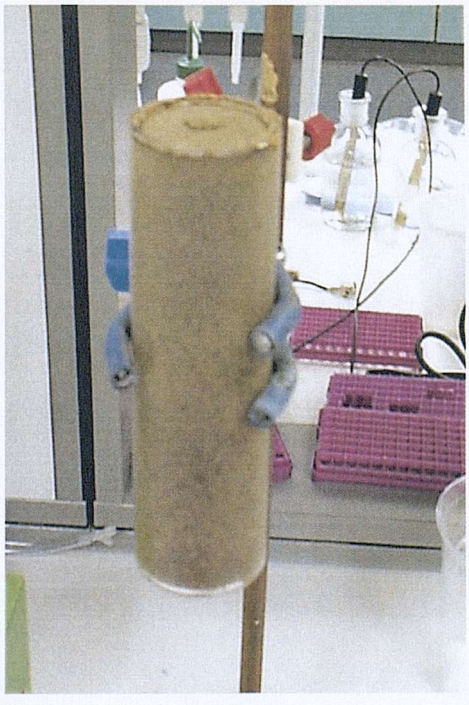


Plate 4.11 Foam in the column after removing the extensions and trimming back the foam



Plate 4.12 Column with end flanges assembled and ready for an experiment

4.4.4 Conditioning of the columns

After casting the foam-biomass in the column's central tube, the column was mounted directly to prevent any evaporation of moisture that would result in foam shrinkage inside the column. Each column was mounted vertically using clamps and operated in up flow mode.

Before using the columns or adsorption experiments 10 litres of deionised water were passed through the column in up flow mode at gradually increasing flow rate starting with flow rate < 1 l/hour, and gradually increasing this to 5 l/hour after passage of 3 litres. The purpose of this conditioning with deionised water was to wash out biomass that had not been immobilised (incorporated) properly in the matrix as well as other water soluble materials that could leach out of the foam matrix. These materials could include alginate, surfactant, and sodium acetate, the latter is a product of the reaction between sodium bio-carbonate and acetic acid. 10 ml samples were taken at specific volumes to analyse the carbon content of the column effluent discharge water.

Washing the column with deionised water also saturated the foam matrix and expelled air bubbles that could otherwise have caused short circuiting and allowed the first portion of a metal laden solution to pass without treatment.

4.4.5 Column set up and operation

Test solutions containing metal ions were prepared using deionised water in a 75 litres polypropylene container. In all cases the solution pH was measured and found to be around 5 so no adjustment was necessary. Solutions were pumped through the columns using a variable speed peristaltic pump with feed tubes made from PVC (Nalgene 180) and pump tubes of silicone rubber. Effluent was collected in a 1 litre graduated glass cylinder. 10 ml samples were taken directly from the effluent tubing and the same volume was compensated in the collecting cylinder to correct the volume. The volume at which the sample was taken was registered precisely. All samples were acidified by 30 μl of 3 M HNO_3 which took the sample's pH to < 2.

pH of the effluent was measured by taking 50 ml sample directly from the effluent discharge. The volume at which the pH was measured was registered and the sample was returned into the collecting cylinder to maintain correct volume.

4.5 Analytical techniques

4.5.1 Measurement of metal ion concentrations

The metal ions Cu, Zn, Fe, Cr, Co were measured using an atomic absorption spectrophotometer (Model: Spectr AA-200, Varian, Australia). This is a singled beam instrument and the expected detection limit for the metal species analysed are given in table 4.1. A brief theoretical explanation on how this machine works is given in appendix B1.

Table 4.1 Detection limits of atomic absorption spectrophotometer based on flame for selected elements (Skoog et al., 1988)

Element	Detection limit (x 10^{-3} mgl $^{-1}$)
Cu	2
Fe	2
Zn	2
Cr	3

The machine was calibrated using at least 3 standards before samples were analysed from each experiment. The instrument's operating conditions (i.e. wavelength and slit width) were set according to the expected range of copper concentrations in the samples as stated in the operator's manual. An optimum calibration graph of up to 10 mgl^{-1} copper concentration was given in the manual as a reference. Samples with copper concentration above 10 mgl^{-1} were read directly against a calibration curve using standards of an appropriate concentration and constructing a calibration curve.
The accuracy (i.e. average value – true value) and precision (i.e. standard deviation) of the machine was determined by making eight replicate (appendix table A116) after calibrating the machine using appropriate standards. The difference between the true and average readings value was in all cases less than 0.05 mgl^{-1} (appendix table A116), indicating that there was no systematic error in operating the machine (see appendix C).

The precision of the machine at the different standard concentrations were 1 ± 0.055, 2 ± 0.065, 4 ± 0.082, 10 ± 0.1046, 20 ± 0.12, 40 ± 0.1458, and 60 ± 0.1513 mgl^{-1}.
All samples for metal analysis were transferred to 15 ml polyethylene vials and the sample's pH was brought down to < 2 by acidifying with concentrated acid (see material and methods). A clean pipette's tip was used for each sample. Analysis was performed as soon after sampling as possible, usually within 24 hours. 1.25 ml of sample is usually enough for analysis. The machine was continuously checked for measurement quality by reading the standards after every 10 samples. If the difference between the read and true value of any standard was ≥0.05 mgl^{-1} the machine was recalibrated. Each sample was read once and concentration was corrected for acidification.

4.5.2 Measurement of carbon

A Dohrmann DC-190 (Dohrman, USA) was used to measure total carbon (TC), inorganic carbon (IC) and as a result total organic carbon (TOC). The instrument has a vertical quartz combustion tube packed with supported platinum catalyst which receives a continuous flow of air at 200 ml/min, appendix B2. The furnace was operated at 680° C and samples for total carbon analysis were automatically injected into the combustion tube via an air-actuated injection port. Inorganic carbon (IC) samples were automatically injected into the IC reactor, which contains acidic water solution at room temperature, via an air-operated injection port.
The instrument is a single point calibration machine and requires only one standard for calibration. Samples could be read manually by direct injection using a syringe or automatically by transferring the samples to automatic sampler vials and injection takes place automatically using a PTF sampler probe. Manual injection proved to give more consistent results than automatic injection, but due to the large number of samples measurements were taken using the auto-injector. To provide the best possible result the instrument was set to read each sample three times and was programmed to give the average of the readings and the standard deviation (i.e. average ± SD) as both a numeric value and as a percentage (see appendix table A117).
The accuracy and precision of the instrument were determined by reading a standard solution of 200 mgl^{-1} organic carbon, appendix table A117. This was sub-divided into nine sample vials (4 ml each). The instrument was set to auto-inject from each of

these sample vials 5 times. The average, standard deviation and the percentage of the standard deviation was calculated by the instrument as part of its normal programming functions, these were: 200.83 mgl^{-1}, 12.14 mgl^{-1} and 6.05% respectively taken across the 45 readings

The results confirm that there was no systematic error in operating the machine (see appendix C). However the precision of the machine was poor as the standard deviation for the 45 readings was 12.14 mgl^{-1} which represent 6% of the average value.

4.6 Expression of experimental data

Appendix C gives an explanation of the statistical methods used to interpret the results.

All flasks experiments were conducted in duplicates and graphs were plotted using the mean value of the results with error bars being drawn as ± standard deviation (s). In addition the 95% confidence limits of the mean were calculated where possible and reported in the corresponding results tables.

Column experiments were conducted once and graphs were plotted using the experimental results.

CHAPTER 5

Results

5.1 Comparison of different immobilisation matrices for copper removal using *R. oryzae*

Dried fungi with a particle size of less than 150 μm was prepared as described in section 4.2.1 and incorporated into the various polymers as described in sections 4.4. The different immobilisation matrices were evaluated with regard to structure and their ability to remove copper ions from solution.

5.1.1 Microscopic examinations

Microscopic examination of the prepared fungal biomass, plate 5.1, showed that it was clear of any kind of contamination (i.e. bacterial contamination is recognised usually by scattered dark black spots). Observations of the polymer/biomass matrices, plates 5.2-5.8, showed the porosity of polyurethane biomass/polymer matrix to be highest, and fungal hyphae were clearly visible within the pore structure. Polysulfone, alginate and k-carrageenan biomass/polymer matrices gave nearly homogenous distribution of biomass, however beads of polysulfone/biomass had to be cut into two sections in order to view the biomass inside the bead which was covered entirely by the polymer. In the polyacrylamide and polyvinlformal biomass/polymer matrices the biomass appeared as localised dense clusters indicating a non-uniform heterogeneous biomass distribution. In PEI biomass/polymer matrix a dark area of concentrated biomass appeared without any pores.

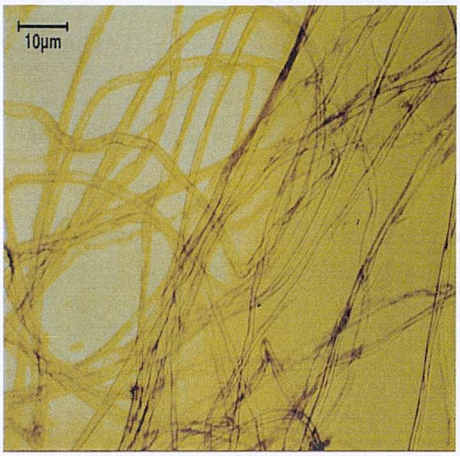


Plate 5.1 Fungal biomass (x 100)

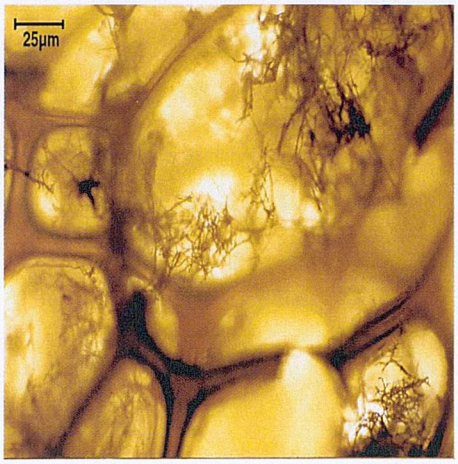


Plate 5.2 Fungi-polyurethane bead (x 40)



Plate 5.3 Fungi-PEI bead (x 40)

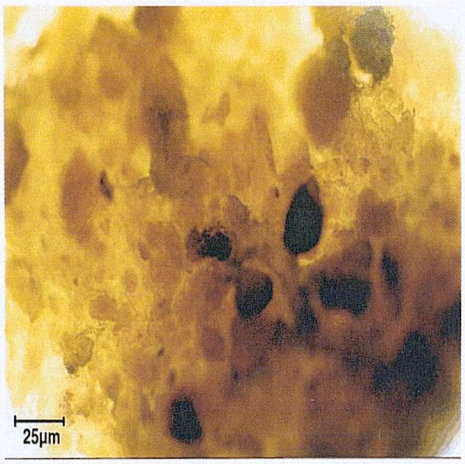


Plate 5.4 Fungi-alginate bead (x 40)

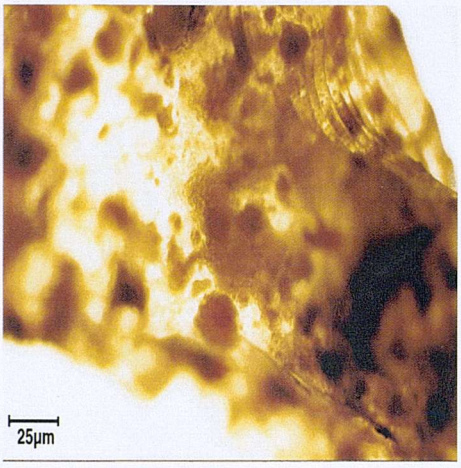


Plate 5.5 Fungi/k-carrageenan bead (x 40)



Plate 5.6 Fungi-polyacrylamide bead (x 40)

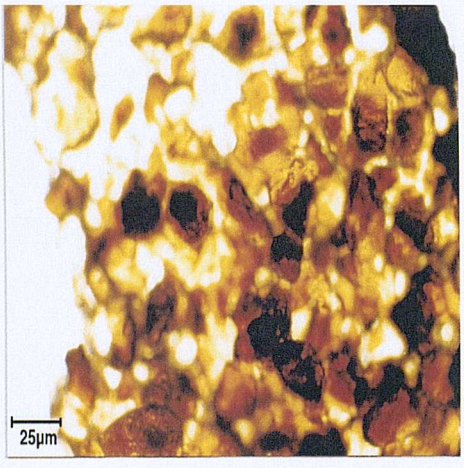


Plate 5.7 Fungi-polyvinlformal bead (x 40)

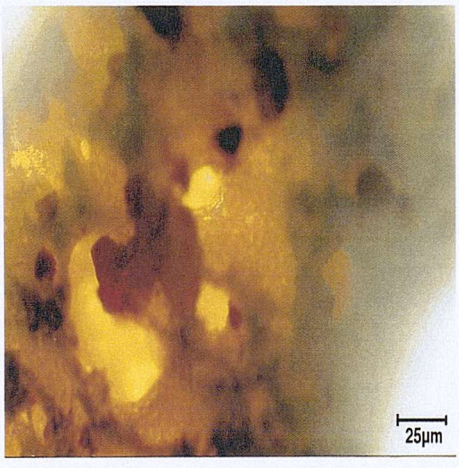


Plate 5.8 Fungi-polysulfone bead (x 40)

5.1.2 Copper sorption by free and polymer immobilised fungal biomass

All experiments were carried out in 250 ml conical flasks placed on an orbital shaker at 200 rpm over a time period of 60 minutes. Duplicate flasks were set up for each polymer/biomass bead type, biomass free polymer beads and native biomass. To each flask was added 100 ml of a 2 mgl^{-1} copper solution and the pH was adjusted to 7 using dilute solution of NaOH or H_2SO_4. For the polymer/biomass bead and native biomass experiments an equivalent weight of 100 mg of biomass was used in each

flask. For polymer bead experiments the equivalent weight of polymer to that used to immobilise 100 mg of biomass was used. 5 ml (single) samples were taken at specific time intervals as reported in appendix tables A1-A15, centrifuged, when necessary, at 12000 rpm (Jouan M14.11, AB 10.12 Angle Rotor) for 5 minutes and the supernatant analysed for copper using an atomic absorption spectrophotometer.

Full results for each experiment are given in appendix tables A1-A15, with a summary of these shown graphically in figures 5.1-5.3.

Table 5.1 gives the biomass polymer ratio for each type of bead formed as well as the bead weight used in the adsorption experiments to achieve equivalent biomass quantity of 100 mg.

Table 5.1 Polymer bead weights used in adsorption experiments so as to give a comparable biomass content of 100 mg

Polymer used for biomass immobilization	% of bead weight as biomass	Weight of beads containing (100) mg of biomass. (mg)	Weight of polymer in the beads. (mg)
Polyvinlformal	33.33	300	200
K-Carrgeenan	20.00	500	400
Polysulfone	28.57	350	250
Polyacrylamide	16.67	600	500
Alginate	20.00	500	400
PEI	97.01	103	3
Polyurethane	37.92	264	164

For both free biomass and that immobilised in polyurethane approximately 80% of the final adsorption capacity was reached within 10 minutes and an equilibrium was reached within 20 minutes of exposure to the copper solution. Removal of copper was still taking place up until the end of the 1 hour experimental time for the biomass immobilised in polysulfone, polyacrylamide, PEI and alginate.

The final adsorption capacity (i.e. 1 hour adsorption capacity) of both free biomass and polyurethane immobilised biomass was 1.5 mg of copper per g of biomass (figure 5.1). With the exception of the k-carrageenen/biomass matrix the final adsorption capacity of all the other polymer/biomass matrices was lower. The 60 minute adsorption capacities, as a percentage of that achieved by free biomass were: 42.63% for polysulfone, 37.67% for polyacrylamide, 26.1% for PEI, 25.96% for alginate and 12.82% for polyvinlformal. The k-carrageenan-biomass/polymer matrix showed a final adsorption capacity equal to that of free biomass, however, the result is

erroneous as the beads were unstable and dissolved after 30 minutes, releasing the biomass into free suspension. This result supports the findings of Chibata et al. (1987) who reported that the main disadvantage of k-carrageenan is that when a gel-inducing reagent is not present in the reaction mixture, the immobilised material (e.g. enzyme or biomass) is released by dissolution of the gel. Of the available copper in solution (95 ml of a 2 mgl^{-1} solution) the free biomass had removed 86% of this at the end of 60 minutes exposure, whilst biomass immobilised in polyurethane, polysulfone, polyacrylamide, alginate, PEI, and polyvinlformal showed removals of 77, 31.8, 30.7, 25.1, 21.5 and 11% respectively.

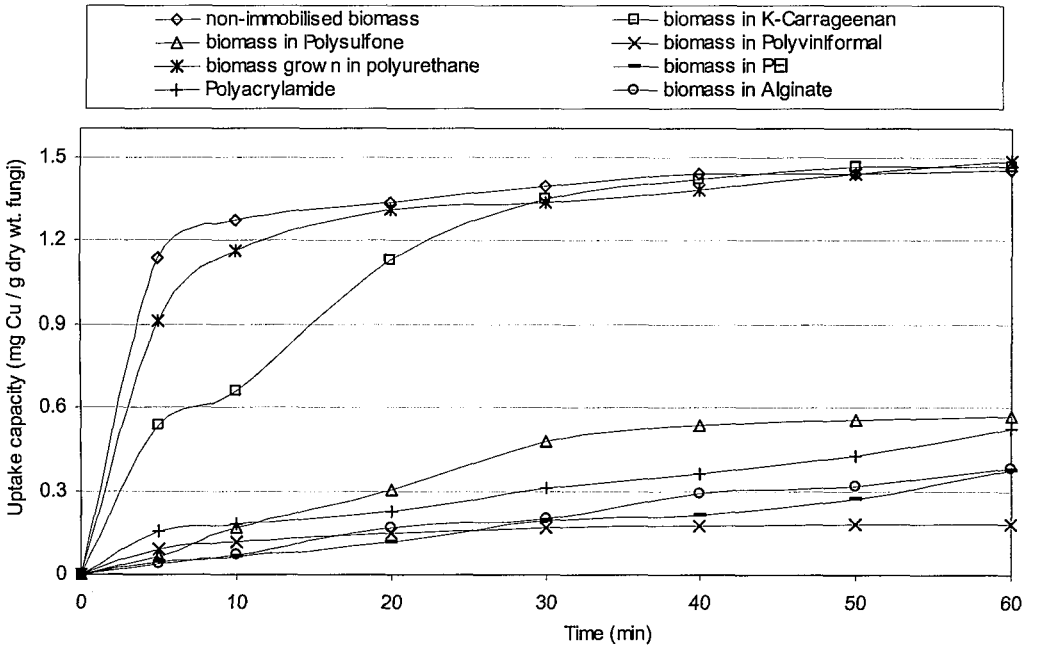


Fig. 5.1 Copper uptake by free and polymer immobilised fungal biomass from 95 ml of a 2 mgl^{-1} copper solution at an initial pH 7.0, room temperature and 1 hour contact time; in all cases the quantity of biomass used was 100 mg

The polymer matrices without biomass did not show a noticeable copper adsorption capacity, except k-carrageenan, alginate and polysulfone beads which removed approximately 21, 20 and 17.5% of copper respectively from the solution at the end of the 1 hour contact period (figure 5.2.).

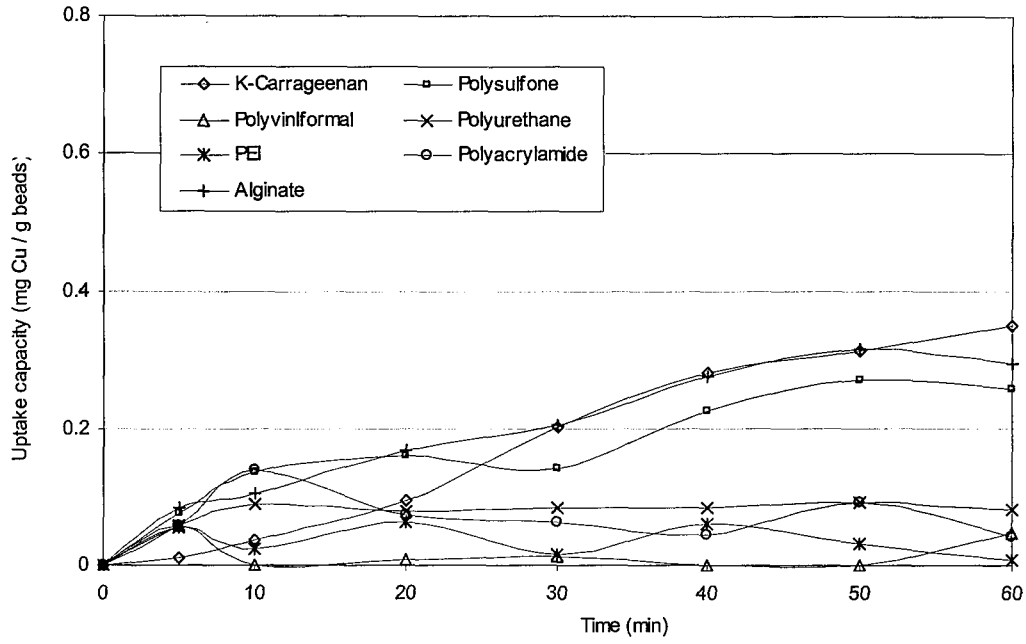


Fig. 5.2 Copper uptake by biomass free polymers from 95 ml of a 2 mgl^{-1} copper solution at an initial pH 7.0 and room temperature

Figure 5.3 gives a summary of the 60 minutes final uptake capacity of the free biomass, free polymers and polymer immobilised biomass.

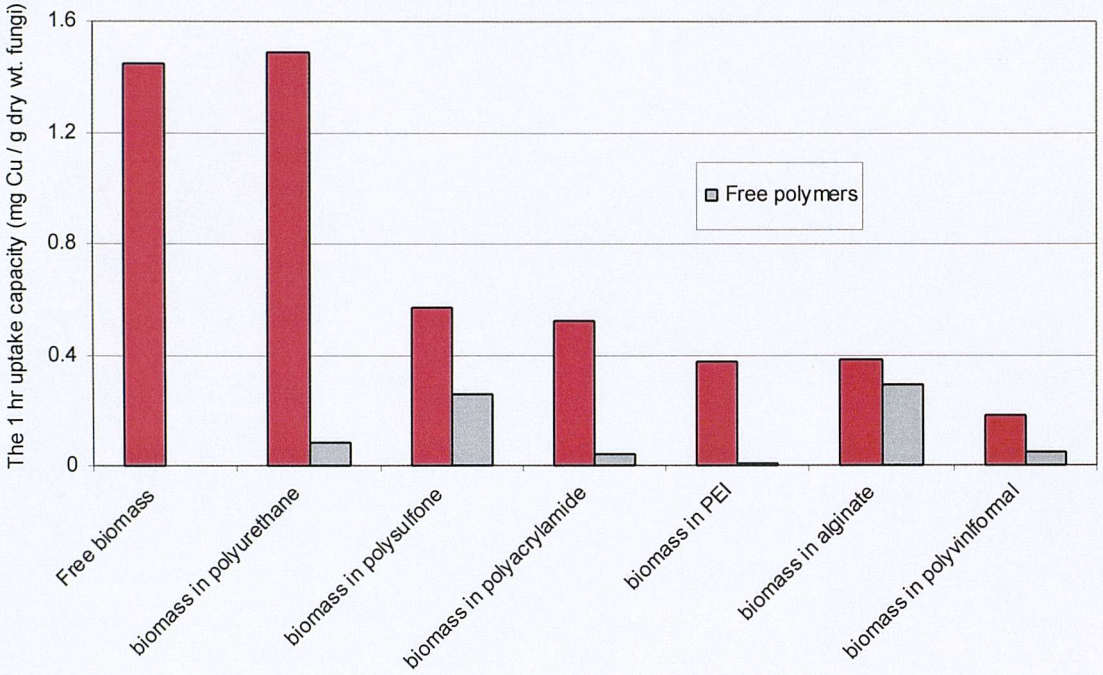


Fig. 5.3 The one hour copper uptake capacity of free fungal biomass, free polymers and biomass-polymers when they were exposed to 95 ml of a 2 mgl^{-1} copper solution at an initial pH 7.0 at room temperature

Biomass leaching from the biomass/polymer matrix was observed in the case of polyurethane and PEI with a 20% and 4% respective loss in weight at the end of the experiment. This was probably as a result of the flask shaking of the biomass/polymer matrix, and would probably not occur in a static packed bed reactor. No biomass leaching was observed from the other polymer matrices, except for the k-carrageenan as previously mentioned.

The copper sorption experiments by free and polymer immobilised fungal biomass mentioned at the top of this section were repeated but at a contact time of 4 hours to investigate the effect of contact time on the biomass adsorption capacity. Results showed that increasing the contact time from 1 to 4 hours did not affect, relatively, the adsorption capacity of the non-immobilised biomass, polyurethane and polyvinlformal immobilised biomasses. However, this increased the uptake capacity of alginate, polysulfone, PEI and polyacrylamide immobilised biomasses from 0.38, 0.57, 0.375, 0.52 $mg.g^{-1}$ at 1 hour to 0.853, 0.785, 0.61, 0.838 $mg.g^{-1}$ respectively (appendix table A16 and figures 5.4-5.5). This indicates that these polymers have a low porosity,

which cause low diffusion rate, and that a longer time is required for the biomass to reach equilibrium compared with the polyurethane immobilised biomass.

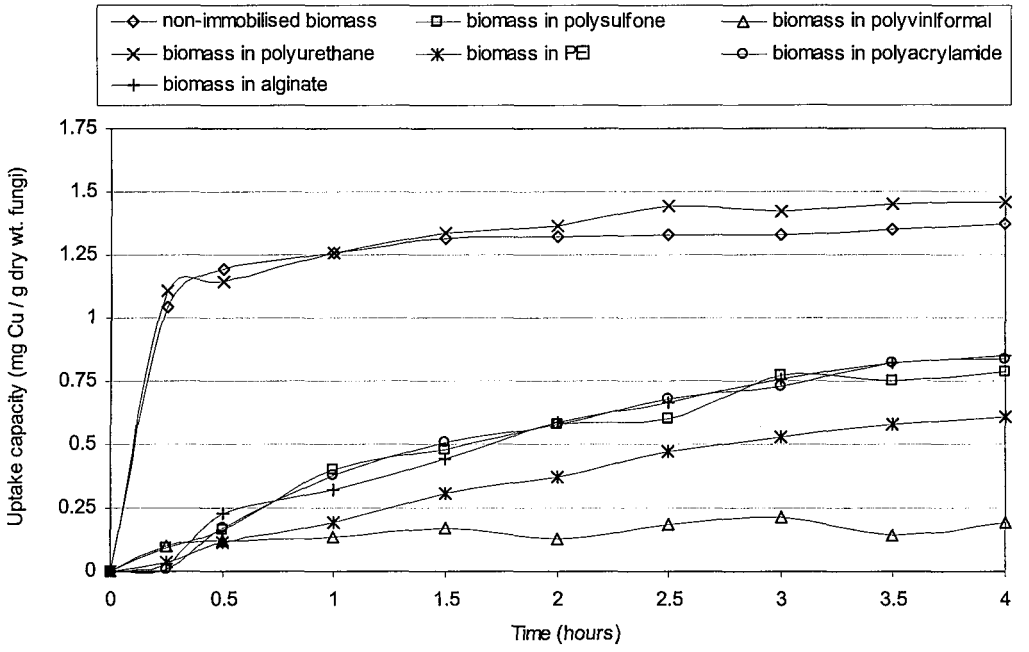


Fig. 5.4 Copper uptake by free and polymer immobilised biomass from 95 ml of a 2 mgl^{-1} copper solution at an initial pH 7.0, room temperature and 4 hours contact time; in all cases the quantity of biomass used was 100 mg

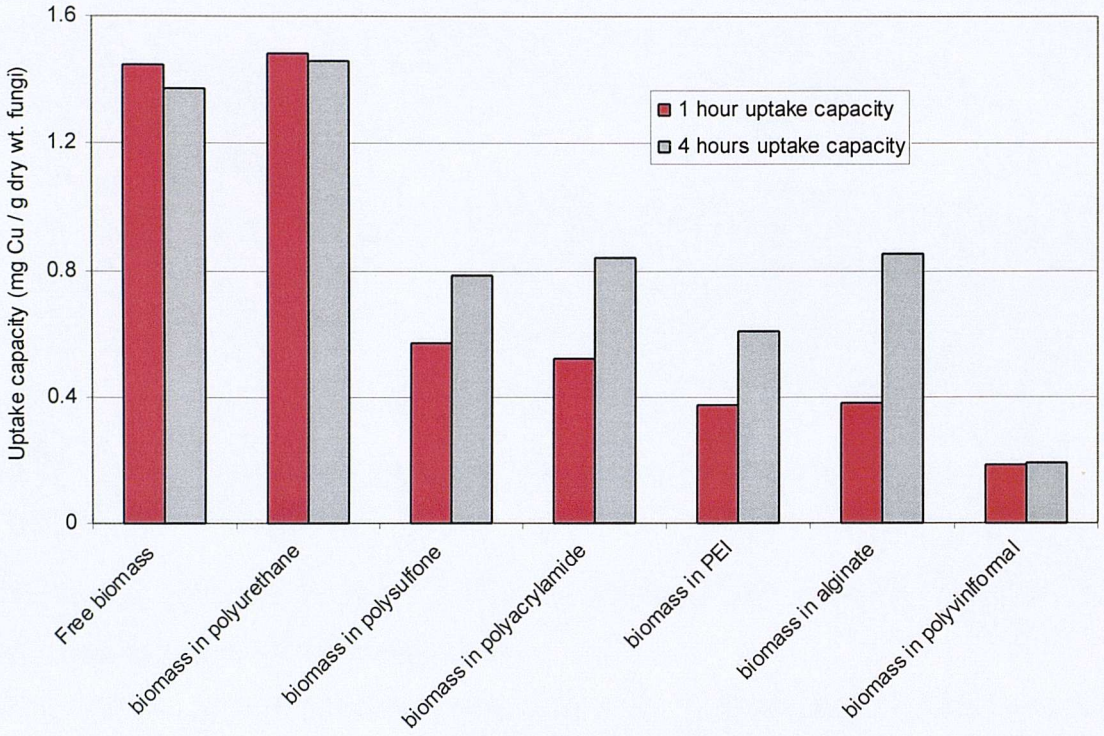


Fig. 5.5 The one and four hour copper uptake capacity of free and polymer immobilised fungal biomass when they were exposed to 95 ml of a 2 mgl^{-1} copper solution at an initial pH 7.0 and room temperature (N.B. The 1 hour uptake capacity is taken from the results of the first experiment, figure 5.3)

The promising performance of biomass grown in reticulated polyurethane foam is diminished by the necessity to cultivate the fungus in association with the support particle, as an adequate technique for achieving this at a large scale has still to be developed. More importantly, the technique excludes the use of spent waste biomass and the cost of reticulated foam is high. Thus, the use of cast reticulated polyurethane for immobilisation, although researched extensively for different types of microorganisms (Lewis and Kiff, 1988; Banks and Parkinson, 1992; Tyagi et al., 1993), has not progressed from laboratory to full scale application. The limiting factor appears to be in colonisation of the open pore structure at a large scale.

5.2 Preliminary investigation on polyurethane foam manufacture and the copper adsorption characteristics of biomass immobilised during this process

The aim of this part of the work was to experiment with different foam production techniques so as to produce an open pore foam into which finely ground biomass particles could be immobilised. Experiments were then designed to assess the effect the immobilisation process had on the uptake of copper by the biomass/foam matrix.

5.2.1 Preliminary investigation into the manufacture of conventional hydrophobic polyurethane.

The method given in section 4.4.1 of the materials and methods section is that optimised as a result of these experiments.

Three types of mixer (Plate 5.9) were manufactured in the department and used in the mixing process. The first was an oar like 4 blades mixer, the second was a paint mixer and the third a 2 pin mixer. Each mixer was designed to have a slightly smaller diameter than the internal mixing vessel to achieve high quality mixing. These were used in conjunction with a variable speed laboratory mixer or an electric drill depending on the speed range required (Plate 5.10).



Plate 5.9 Mixers used in the experiments

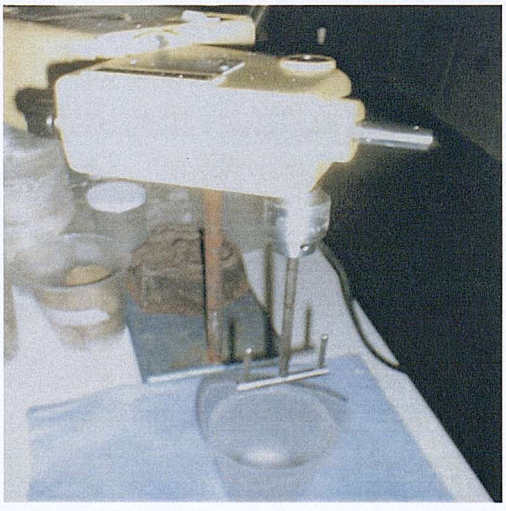


Plate 5.10 Mixing device used in the experiments (variable speed controller)

The supplier instructions required the mixing of 3 parts of resin with 2 parts of the isocyanate 284 on a weight basis, without addition of water. Water can be added, according to the instructions, to reduce the foam free rise density provided that it does not exceed 0.25 % wt of the total mixture weight.

Experiments were conducted to determine the best method of producing a foam with an open pore matrix with pore size > 1 mm, interconnected pores, and a durable/resilient matrix. Factors investigated were the ratio of resin to isocyanates, ratio of water to resin and isocyanates, the mixing speed, mixing time and the shape of the mixer.

The main aim was to produce a porous foam that allows water to flow through it without pressure loss. Each element that plays a significant role in the foam porosity was individually tested by varying the ratio of this element while keeping the ratio of other elements constant. The foam porosity and pore inter-connections were visually monitored using a magnifying glass and a light microscope fitted with a graticule.

Effect of the mixer shape: Mixer shape was found to be an important factor in achieving a satisfactory level of mixing during the limited time over which mixing could take place. Of the three mixers tested the 2 pin mixer was the best followed by the paint mixer and then the oar mixer. Plates 5.11-5.14 show the foam structure quality obtained by the three mixers. The mixers were only tested on small volumes of the foam components and it is appreciated that the results could be quite different if large quantities were being mixed. Hand mixing with a spatula resulted in a very good foam structure due to the small quantity of the mixed components as shown by plate 5.14, however once biomass material was added to the mixture this method was inefficient.

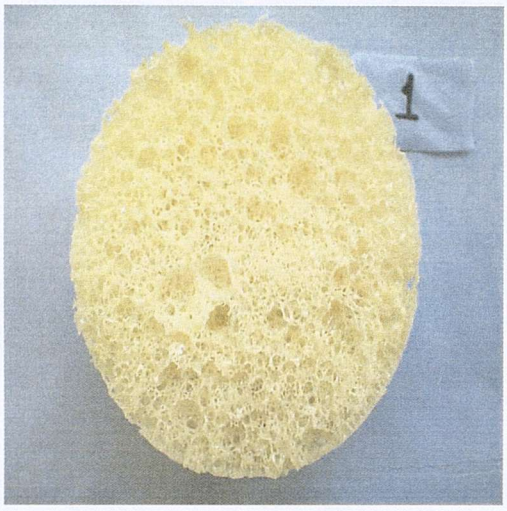


Plate 5.11 Cross section in foam made using 2 pins mixer at 1rps and 20-30 sec mixing time



Plate 5.12 Cross section in foam made using paint mixer at 1rps and 20-30 sec mixing time



Plate 5.13 Cross section in foam made using flat mixer at 1rps and 20-30 sec mixing time



Plate 5.14 Cross section in foam made by hand mixing using a spatula 20-30 sec mixing time

Effect of the water on the foam porosity: The experiments showed that the water ratio can reach 12% of the foam mixture's total weight without noticeable effect on the foam pore size. Water beyond 12% will gradually turn the foam into a fluffy structure eventually ending with "gel like" structure. The pore size measurements of

microscopic slices of foam manufactured at different water ratios (10 rounds per seconds (rps) mixing speed and 20-30 sec mixing time using 2 pins mixer) were obtained using a light microscope fitted with a graticule. From each slice 30 random pore size readings were taken and the average was calculated to give an estimate of the mean pore size of the foam. Results, Appendix table A17, show that the average pore sizes were 1.4, 1.66, 1.58, 1.64, and 1.11 mm for the foams manufactured with no water, 0.25%, 0.55, 1% and 1.5% water ratio respectively. This clearly shows that water does not play a significant role in determination of the pore size in polyurethane foams.

Effect of the ratio of resin and isocyanates: 3 parts of resin: 2 parts of isocyanate, on weight basis yielded a flexible foam with a free rise density of approximately 43 $kg.m^{-3}$. Increasing the ratio of the isocyanates increased the hardness of the foam without affecting the foam pore sizes. On the other hand increasing the ratio of resin resulted in softer foam, also without affecting the foam pore sizes.

Effect of the biomass load: After mixing and formation, the initial foam components (i.e. resin and isocyanate) expanded approximately 12 fold. When 20% of the biomass (on weight basis) was added to the foam mixture (without adding water) the initial increase in volume was reduced to approximately 8 fold. Increasing the biomass load resulted in a further reduction of the final volume. A biomass ratio of 26% and 28.5% resulted in a 5 and 4 fold increase in the initial foam volume respectively. Beyond this ratio the biomass could not be mixed with foam components as a dense lump of sticky biomass resulted.

Effect of the mixing speed and mixing time: These are the most important factors that affect the foam pore sizes. At a fixed mixing time of 20-30 sec, the mixing speed should be $\geq$3 rps (or 180 rpm) in order to get a homogenous structure (i.e. uniform pore size). If the mixing speed is decreased below 3 rps incomplete mixing will result, leaving some un-reacted components at the bottom of the mixing vessel, hence the final volume will be affected. The volume of the initial foam components increased approximately 10, 11 and 12 fold at a mixing speed of 1, 2 and 3 rps respectively. After foam formation the volume remained at a constant level of 13 fold when the mixing speed was $\geq$ 6 rps. Plate 5.15 shows the poor structure of foam and

heterogeneous pore size when manufactured at a mixing time of 20-30 seconds and mixing speed of 1rps. Plate 5.16 shows a good structure to the foam and a homogenous pore size when manufactured with the same mixing time but with a mixing speed of 8rps. A 2 pin mixer was used in both cases.

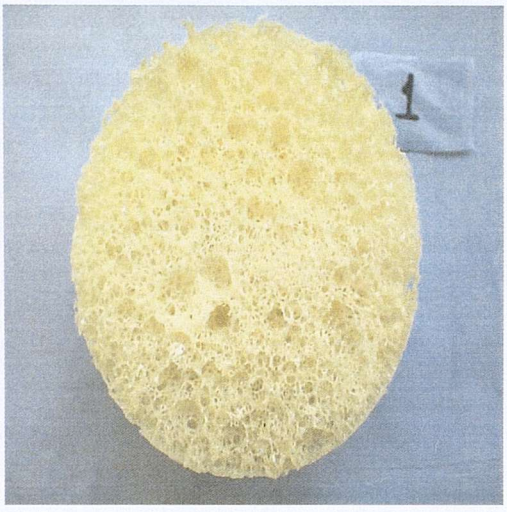


Plate 5.15 Cross section in hydrophobic foam manufactured at 1rps and 20-30 sec mixing time using 2 pins mixer

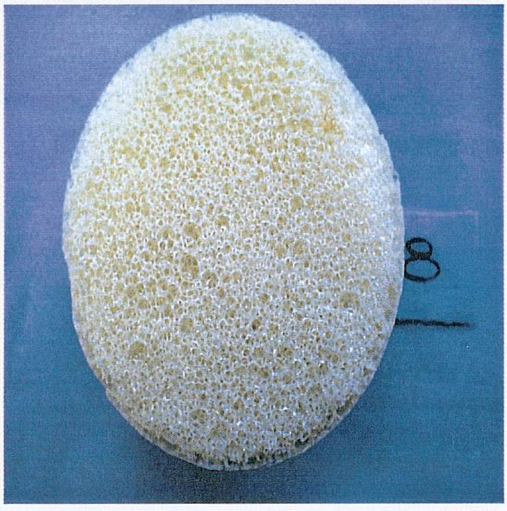


Plate 5.16 Cross section in hydrophobic foam manufactured at 8rps and 20-30 sec mixing time using 2 pins mixer

Increasing the mixing speed further, whilst maintaining the same mixing time, will only help to achieve good mixing when external materials are added to the initial foam components.

Mixing time was found to be the most important factor affecting the foam pore size. Mixing the ingredients for a prolonged time allows gas to escape, resulting in a small pore size and a reduced final foam volume. On the other hand, mixing for a short time resulted in a large pore size with heterogeneous foam structure. Plate 5.17 shows a good foam structure but with a very fine pore size; this was produced at a mixing speed of 40rps and mixing time of 90-120 sec. Plate 5.18 shows a poor foam with a heterogeneous structure; this was manufactured at the same mixing speed but with a 5 seconds mixing time.





Plate 5.17 Cross section in foam manufactured at a mixing time of 90-120 sec and 40 rps	Plate 5.18 Cross section in foam manufactured at mixing time of approximately 5 seconds and 40 rps

Other factors such as temperature, pressure and pH could play an important role in the manufacturing process but were not investigated as this would necessitate special tools and equipment not available.

5.2.2 Preliminary investigation on manufacturing of hydrophilic polyurethane foam (Hypol 2002)

As both the hydrophobic and hydrophilic foams are 'blown' by carbon dioxide gas produced as a result chemical reactions the effect of mixer shape, mixing speed and mixing time are the same for both types of foam. The major difference between the two types of foam is the water ratio. Hydrophobic polyurethane cannot tolerate more than 12% of the total weight of initial foam components, whilst the hydrophilic polyurethane can stand water up to 250% of the pre-polymer weight. High water ratio in the foam manufacturing is crucially important as it facilitates the incorporation of the biomass in the foam matrix.

As the nature of the two polymers varied more factors were tested in the Hypol foam case, these were: ratio of water to pre-polymer, mixing speed, mixing time, shape of the mixer, surfactant addition, and chemical addition (carbonate or bicarbonate with mineral acid) to produce further carbon dioxide gas.

Effect of the water ratio: According to the manufacturer, water used in the foam manufacturing process can be 0.5 – 2.5 times the weight of the pre-polymer (i.e. 50 – 250%). Experiments showed that a water ratio below 50% led to foam shrinkage and structural damage within minutes. On the other hand a water ratio above or equal to 200% left water residues at the bottom of the mixing vessel. Typically a ratio of 1 part water: 1 part pre-polymer was used in the manufacturing process, but if external materials are to be added the water quantity should be increased to 1.5 or 2 so as to ease the mixing process. Using these ratios the volume of the initial foam components increased by around 12 fold after foam formation.

Previous research has suggested that pore size in hydrophilic foam is related to the ratio of water to polymer (Klein and Kluge, 1981; Klein *et al.*, 1979). In this work, however, it was found that the key element affecting the pore size, in both the conventional hydrophobic and the hydrophilic polyurethane, was the mixing time and then the mixing speed (see section 5.2.1.).

Effect of surfactants: The word surfactant is short for "surface active agent". Surfactants are usually used in manufacturing of cleaning agents and work at the boundary layer (i.e. the interface) between the soil (i.e. dirt) and the solvent. Each surfactant molecule has two chemical groups; one that is attracted to water (the hydrophile) and one that is attracted to soil (the hydrophobe).



Hydrophobe Hydrophile

In a cleaning solution, the hydrophobic end of the surfactant molecule orients toward the soil. Many surfactant molecules will attack the soil, breaking it up into small pieces and completely surrounding it. The hydrophilic ends of the surfactant molecules project into the solvent causing the soil to be broken up. Then the broken soil will be removed from the surfaces, lifted and suspended into the cleaning solution (BMJ.com, 2002)

In the production of foam the hydrophobic end will attack the foam body breaking the foam textile and any thin film of gas bubbles that may not have ruptured during the

foam formation. This separates the pores and prevent them from closure and gives the foam into a structure resembles a bee hive. The foam's reticulated structure after using Pluronic85 surfactant was visible by the naked eye and subsequently verified by magnifying glass and light microscope (see Plates 5.19 and 5.20).

The carbon dioxide produced during the foam formation plays an important role in this as well, however Moe and Irvine (2000) reported that the thin film separating individual gas bubbles may or may not be ruptured in the final stage of expansion, depending on the relative rate of molecular growth (gelation) and gas reaction to produce a pore structure that is open (bubbles interconnect) or closed (bubbles do not connect). Also, due to the high quantity of water used in the manufacturing process some of the generated gas may be dissolved (in the water) reducing the overall quantity of evaporated gas and the pores interconnection.

Plate 5.19, which is the external surface of a column of foam-biomass (after taking off part of the thin shell that covers the surface inside the moulding) manufactured using Pluronic85 surfactant, it clearly shows the porous structure of the foam's external surfaces. Plate 5.20 shows a cross section of the same column.



Plate 5.19 Side view of a column of seaweed-Hypol foam after taking it from the moulding and removing the thin shell that covers it

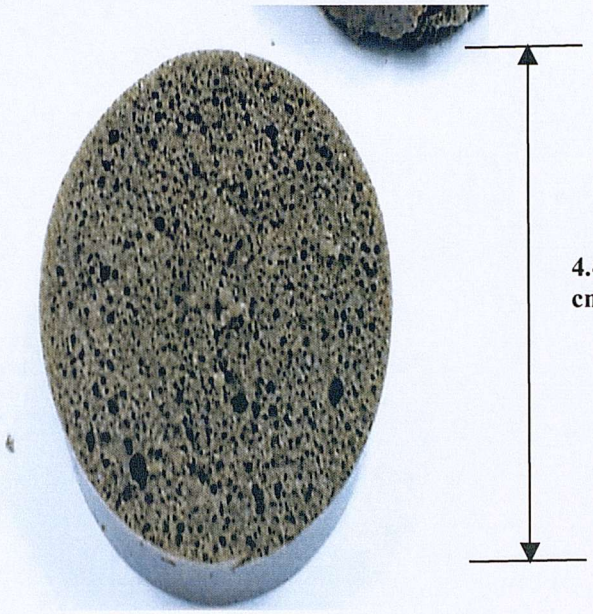


Plate 5.20 Cross section in a column of Seaweed-Hypol

Our finding is supported by Lupton and Zupancic (1991) who reported that surfactants may play a role in giving the foam interconnected pores.

Surfactants were also reported to affect the hydrophilicity of the foam (i.e. water absorption), (Havens and Rase, 1993).

Effect of introducing external carbon dioxide: Braun et al. (1985) reported that one way of turning non-open cell structure polyurethane into a reticulated or open-cell structure was by *in-situ* blowing with gas produced by an ancillary chemical reaction. This could be, for example, by introducing inorganic carbonate or bicarbonate and reacting with mineral acids within the foam mixture. Lupton and Zupancic (1991) used this method by adding sodium bicarbonate and acetic acid to their foam mixture, however structural improvements were not outlined.

Sodium bio-carbonate reacts with acetic acid according to the following equation:

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + CO_2 + H_2O$$

According to the components molecular weights, 1 mole of sodium bio-carbonate (84g) will react with 1 mole of acetic acid (60g) to produce 1 mole of carbon dioxide. Experiments on the effect of adding external carbon dioxide on the foam were conducted by mixing 5 g of Hypol, 2.5 g of biomass, 5 g of water, acetic acid and sodium bio-carbonate according to the procedures outlined in section 4.4.2. Results showed that when the ratio of generated carbon dioxide reached ≥7.8125 mM the foam matrix was destroyed. This is may be due to a very low pH associated with the high ratio of acetic acid.

No differences were observed between the structures of foams manufactured with or without generating carbon dioxide by this method. Therefore it is a theoretical assumption that the gas generated by this method will improve the foam matrix structure. Further studies can be conducted on this issue, taking into consideration the factors, which affect the process. It was found that generating 1.953125 mM of CO_2 by adding 0.163125g of $NaHCO_3$ and 0.1171874 g of CH_3COOH to the initial foam components (5 g of Hypol, 2.5 g of biomass and 5 g of water) neither had a positive or a negative effect on the foam structure.

Other factors: Previous research has reported that factors such as temperature, pH (Havens and Rase, 1993) and pressure (Klein and Kluge, 1981) could play an important role in the properties of a manufactured foam. These factors were not investigated in this study as special tools and equipment are needed to investigate them.

5.3 Preliminary experiments on copper adsorption using immobilised and non immobilised *R. oryzae* fungal biomass and *A. nodosum* seaweed biomass

The preliminary experiments were designed to examine whether the immobilisation matrices of both types of polyurethane has any adverse effect on the biomass copper adsorption capacity. Also to investigate the effect of surfactants (in the case of hydrophilic polyurethane) on the biomass adsorption capacity and the possibility of copper elution from the immobilised biomass using diluted acid.

5.3.1 Methodology

150 ml of a 2 mg/l copper solution was dispensed into 200 ml conical flask. The solution's pH was adjusted to 7 using either dilute NaOH or H_2SO_4. A 5 ml sample was taken to measure the initial copper concentration. 100 mg of non-immobilised fungal biomass was then added to the flask and the flask was shaken for 12 hours on the orbital shaker at 200 rpm. 3 ml samples were taken as detailed in the results tables (appendix tables A18-A30), centrifuged at 12000 rpm (Jouan M14.11, AB 10.12 Angle Rotor) for 10 minutes and the supernatant taken for measurement of the residual copper concentration. The same procedures was repeated using 100 mg dry weight of biomass immobilised in cubes of both types of polyurethane and also for biomass-free foam cubes (in these two cases there was no need for centrifugation).
All experiments were conducted in duplicate and the mean value is presented in the graphs.
At the end of the adsorption experiments the solutions pH was lowered to < 2 using 0.1 M HCl and the flasks were agitated for a further 2 hours on the orbital shaker at 200 rpm. 2 ml samples were taken at specific time intervals to determine copper concentration in the solution.

5.3.2 Results from experiments using non immobilised biomass

Results for copper adsorption by non-immobilised fungal and seaweed biomass and the control flask are given in appendix tables A18, A19 and A20 respectively, while figures 5.6 and 5.7 show the results graphically.
The adsorption process for both biomass types was very fast with the seaweed reaching 94.17% removal of its final uptake capacity within 15 minutes and equilibrium within 90 minutes whilst the fungal biomass reached 81.7% of its final uptake capacity in 15 minutes and equilibrium in 150 minutes.

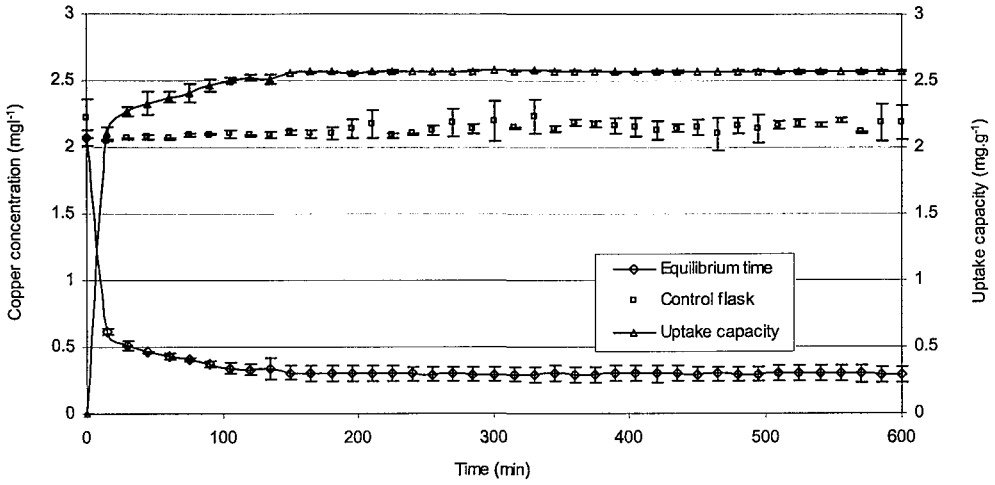


Fig. 5.6 The determination of equilibrium time for the adsorption of copper by non-immobilised fungal biomass using 145 ml of 2 mgl^{-1} Cu solution, at room temperature, neutral pH and a biomass dry wt. concentration of 0.69 gl^{-1}

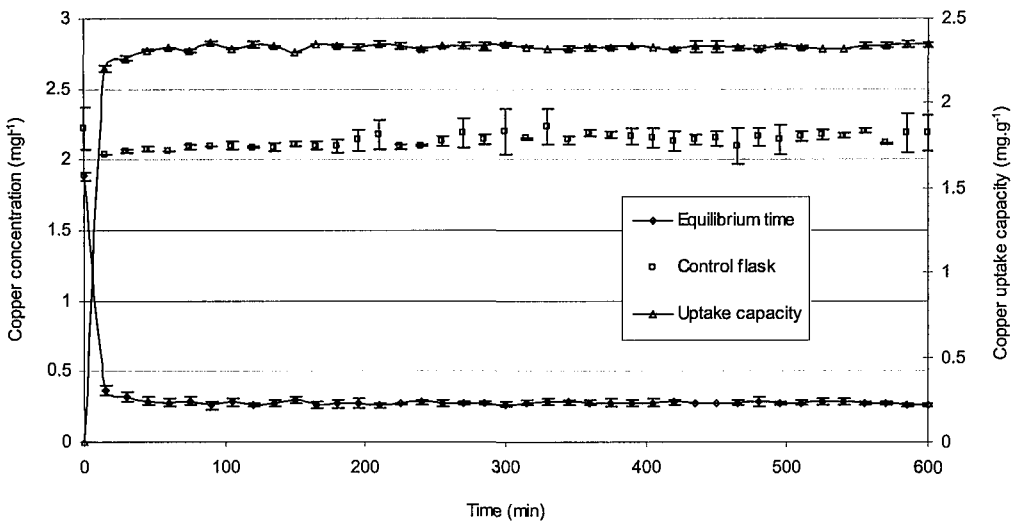


Fig. 5.7 The determination of equilibrium time for the adsorption of copper by non-immobilised seaweed biomass using 145 ml of 2 mgl^{-1} Cu solution, at room temperature, neutral pH and a biomass dry wt. concentration of 0.69 gl^{-1}

The equilibrium uptake capacity of the fungal biomass was 2.57 mg Cu / g of dry biomass weight at an initial copper concentration of 2.032 mgl^{-1}, while the seaweed

biomass uptake capacity was 2.34 mg Cu / g of dry biomass weight at an initial copper concentration of 1.886 mgl^{-1}. Although the results show that the adsorption capacity of the fungal biomass is greater than that of seaweed, it should be noted that it was initially exposed to a higher copper concentration than the seaweed biomass. The copper removal ratio was exactly the same for both at 85.78%, which indicates that the adsorbents uptake capacity should be combined with the sorbate (i.e. solute) concentration.

Comparison between the uptake capacity of the fungal and seaweed biomasses should take into consideration their adsorption capacities at different concentrations. The appropriate isotherm equation should be used to analyse the results, however in this experiment the main objective was to investigate the effect of the immobilisation matrices on the behaviour of the biosorbents.

5.3.3 Results from experiments using fungal biomass immobilised in conventional hydrophobic polyurethane

The results for the adsorption of copper by immobilised fungal biomass in hydrophobic polyurethane are given in appendix table A21, and shown in figure 5.8.

The immobilised fungal biomass in the hydrophobic foam was not able to adsorb any copper. Microscopic investigation of the foam-biomass matrix showed that the biomass particles were coated by the polymer, effectively isolating it from contact with the copper solution. The hydrophobicity of the polymer is assumed to play an important role in preventing the solution entering the foam/biomass matrix and as a result the solute from coming into intimate contact with the functional groups on the biomass surface. Also, one of the polymer components or the whole polymer may have led to the inactivation of the biomass functional groups due to their chemical composition.

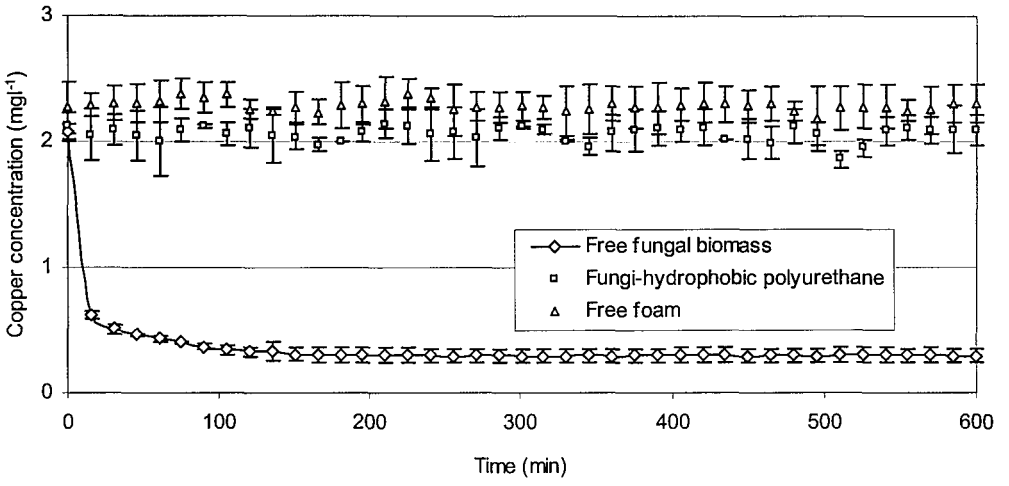


Fig. 5.8 Copper adsorption by non-immobilised fungal biomass and immobilised fungal biomass in conventional hydrophobic polyurethane, using a 2 mgl^{-1} Cu solution, at room temperature, neutral initial pH and a biomass dry weight concentration of 0.69 gl^{-1}

Attempts to expose the biomass were investigated in two separate experiments. Beads were washed for 2 hours with solutions of 1 $mole.l^{-1}$ of H_2SO_4 acid and 1 $mole.l^{-1}$ of NaOH in shake flasks at 200 rpm. The beads were subsequently washed with distilled water and reused for copper adsorption investigations using the same method described in section 5.3.1. The results are given in Appendix tables A22 and A23 and shown in figure 5.9.

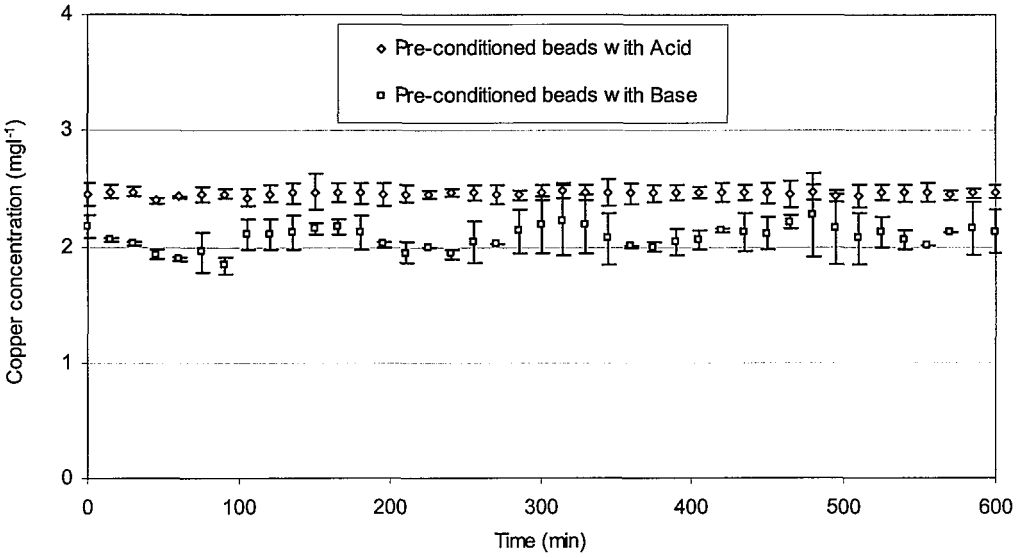


Fig. 5.9 Copper adsorption by pre-conditioned beads of immobilised fungal biomass in conventional hydrophobic polyurethane with 1 mole.l^{-1} of H_2SO_4 and 1 mole.l^{-1} of NaOH. The adsorption experiment was conducted using a 2 mg/l Cu solution, at room temperature, neutral initial pH and biomass dry weight concentration of 0.69 gl^{-1}

Figure 5.9 shows that the acid and alkaline treatment could not expose the biomass or affect the adsorption capacity of the immobilised biomass. The immobilised biomass was not able to remove any copper after being pre-conditioned.

Based on these results the hydrophobic polyurethane was excluded from further experiments and investigations.

5.3.4 Results from experiments using fungal biomass immobilised in hydrophilic polyurethane (Hypol 2002)

Adsorption experiments were conducted on biomass-foam with and without surfactants.

Surfactant free beads: The results from experiments using beads manufactured without surfactants are given in Appendix table 24, and shown in figure 5.10.

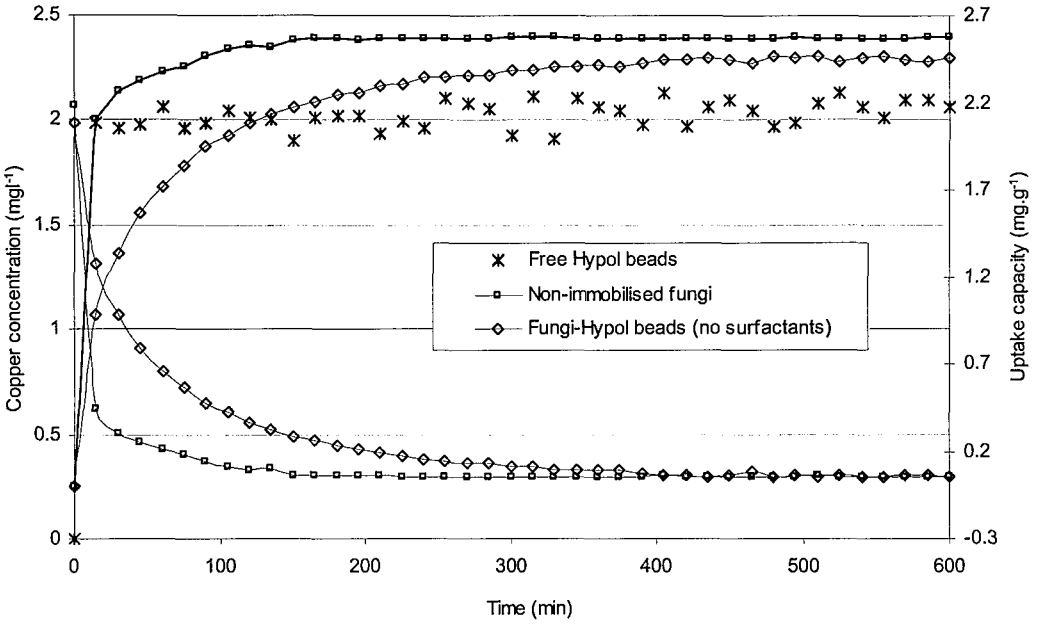


Fig. 5.10 Copper uptake capacity and equilibrium time for fungi-Hypol beads manufactured without surfactants when they were suspended in a solution of 2 mgl^{-1} Cu at room temp., neutral initial pH and a biomass dry weight concentration of 0.69 gl^{-1} (Error bars were not put to avoid overlap, see results table, A24, for the values of standard deviation)

As we can see from figure 5.10, copper adsorption by the immobilised biomass in Hypol foam (manufactured without surfactants) is much slower than that of the non-immobilised fungal biomass. Beads of the immobilised biomass took around 405 minutes to reach equilibrium that is approximately 2.7 times longer than for non-immobilised biomass. This could be related to the further time that is needed for the solute (i.e. carried by the solvent) to diffuse through the foam membrane and reach the functional groups on the biomass surface. The adsorption capacity of the immobilised biomass was 2.46 $mg.g^{-1}$ which was less than 2.57 $mg.g^{-1}$ for the non-immobilised biomass. This is a 4% difference and could be related to several different factors, one of which is the gravitational method used to measure the biomass weight in the beads. Another important factor is the biomass distribution in the beads which may differ due to the manufacturing process. The experiment was conducted in duplicate (Appendix table A24) giving adsorption capacity of the immobilised biomass of 2.35 $mg.g^{-1}$ (around 8.5% less than that of the non-immobilised biomass) and 2.57 $mg.g^{-1}$ which was exactly equal to that of the non-immobilised biomass

Figure 5.10 plots the mean values for the experiments using immobilised fungal biomass and it can be seen that the standard deviation error bars overlap with the non-immobilised biomass lines suggesting that there is no significant difference between free and immobilised biomass copper uptake capacity.

Beads with surfactants 0.1 g and 0.5 g of surfactants per mix (i.e. each mix consists of 5g of Hypol pre-polymer, 7.5 g of water, 2.5 g of biomass, 0.163 g $NaHCO_3$ and 0.117 g CH_3COOH) were used in the manufacturing process. This means that a ratio of 2% and 10% of surfactant to pre-polymer was used in the experiments.

Beads manufactured with Pluronic 85

Results of the adsorption experiments conducted on fungi-foam beads which were manufactured by adding 2% and 10% of Pluronic 85 surfactant are given in Appendix tables A25 and A26 respectively, and shown in figure 5.11.

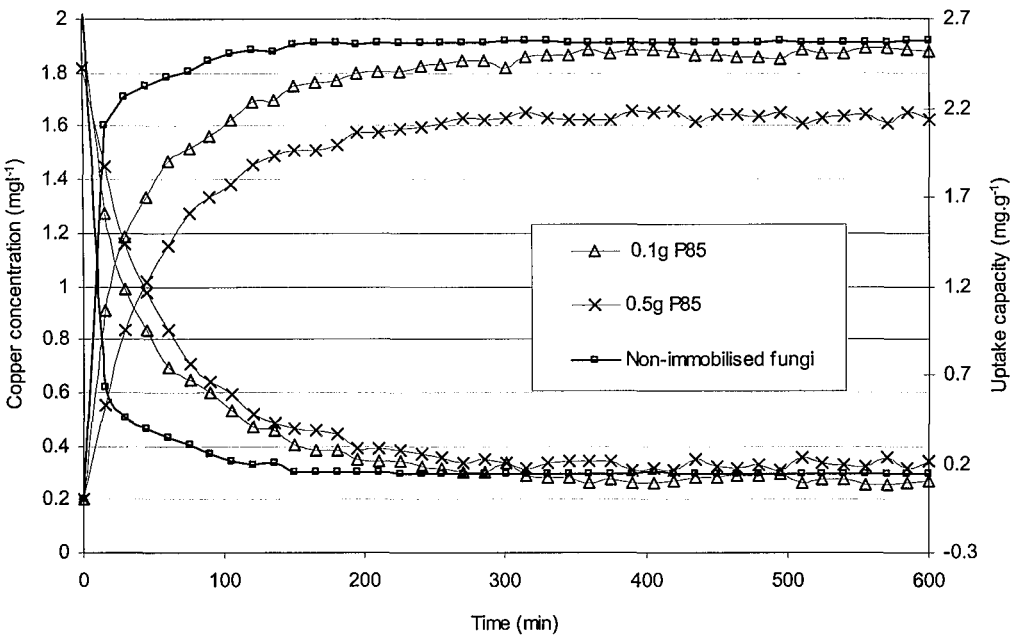


Fig. 5.11 Copper uptake capacity and equilibrium time for fungi-Hypol beads manufactured with addition of Pluronic85 surfactant. The beads were suspended in a solution of 2 mgl^{-1} Cu at room temperature, neutral initial pH and biomass dry weight concentration of 0.69 gl^{-1} (Error bars were not put to avoid overlap, see results tables, A25 and A26, for the values of standard deviation)

Both types of bead reached equilibrium at approximately 315 minutes, however the beads manufactured with 2% surfactant reached an equilibrium uptake capacity of 2.5 $mg.g^{-1}$ compared to 2.17 $mg.g^{-1}$ for those manufactured with 10% surfactant. Although the initial copper concentration in the 2% case, ≈ 2 mgl^{-1}, was higher than that of the 10% case, ≈ 1.8 mgl^{-1}, the removal ratio of copper in the 10% case, 82.5 %, was still lower than that of the 2% case which was 86.2%.

The adsorption capacity decrease when the surfactant ratio was increased may be related to the interaction between the surfactant and the solute (i.e. Cu). Surfactants used in the manufacturing process can re-dissolve into the test solution during the adsorption experiment. The dissolved surfactants may then complex with the copper reducing the available copper in solution for adsorption hence lowering the overall uptake capacity.

The equilibrium adsorption capacity of 2.5 $mg.g^{-1}$ for the biomass immobilised in the foam manufactured with 2% surfactant was approximately equal to that of the non-immobilised biomass. However it took 315 minutes for the former to reach equilibrium compared to 150 minutes for the later. The reasons for this were explained in section of surfactant free beads (5.3.4).

The adsorption capacity of 2.5 $mg.g^{-1}$ for the immobilised biomass in the foam manufactured with 2% surfactant was approximately equal to the 2.46 $mg.g^{-1}$ of the immobilised biomass in the foam manufactured without surfactants. The slight difference may be attributed to the biomass distribution inside the beads as previously explained and not as a consequence of the surfactant. It is believed that the role of the surfactant is to provide interconnected pores which could improve the rate or speed of the adsorption process without affecting the uptake capacity of the immobilised biomass. This could explain why the beads with 2% surfactant reached an equilibrium in 315 minutes compared to 405 minutes for surfactant-free beads.

Beads manufactured with Tween80: Results of the adsorption experiments conducted on fungi-foam beads manufactured by adding 2% and 10% of Tween 80 surfactant are given in appendix tables A27 and A28 respectively and shown in figure 5.12.

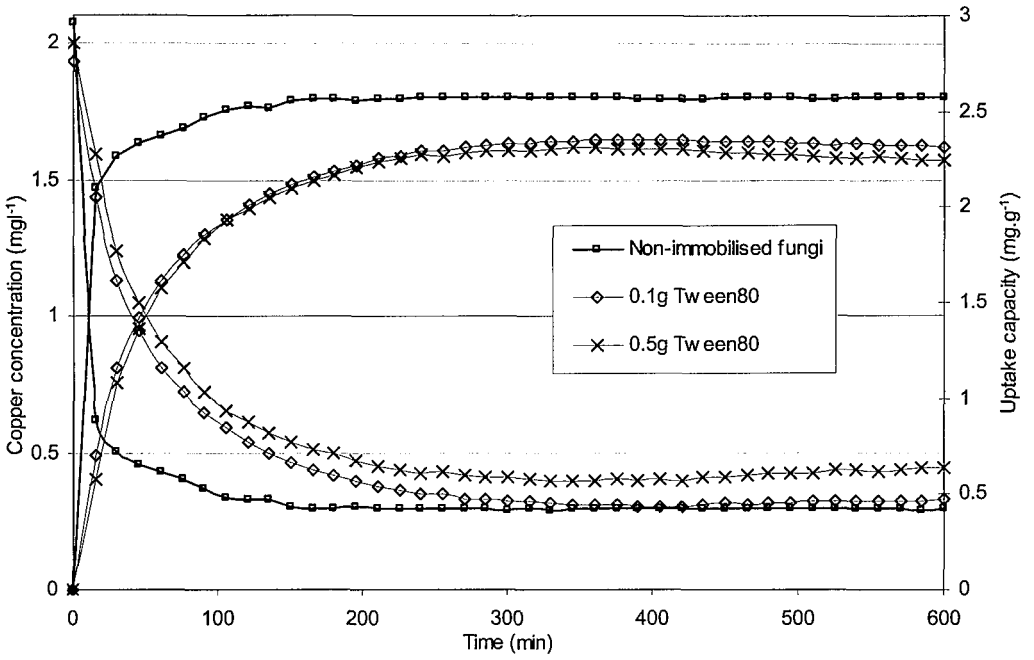


Fig. 5.12 Copper uptake capacity and equilibrium time for fungi-Hypol beads manufactured with the addition of Tween80 surfactant. The beads were suspended in a solution of 2 mgl^{-1} Cu at room temperature, neutral initial pH and biomass dry weight concentration of 0.69 gl^{-1} (Error bars were not put to avoid overlap, see results tables, A27 and A28, for the values of standard deviation)

In both cases, the beads manufactured with a surfactant ratio of 2% and 10% reached equilibrium at approximately 330 minutes, with very similar uptake capacities of 2.35 $mg.g^{-1}$ and 2.3 $mg.g^{-1}$. The uptake capacity of the immobilised biomass incorporating Tween 80 is approximately 8.5% lower than that of non-immobilised biomass. The reasons for this considerable difference are beyond the scope of this research.

Beads manufactured with TritonX-100 Results of the adsorption experiments conducted on fungi-foam beads manufactured by adding 2% and 10% of TritonX-100 surfactant are given in appendix tables A29 and A30 respectively, and shown in figure 5.13.

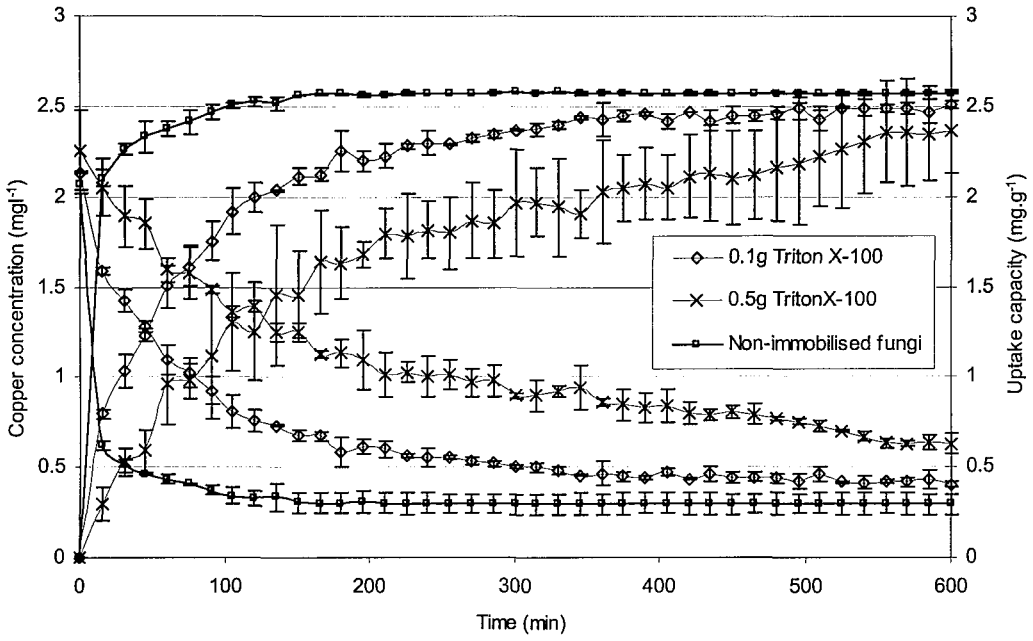


Fig. 5.13 Copper uptake capacity and equilibrium time for fungi-Hypol beads manufactured with addition of TritonX-100 surfactant. The beads were suspended in a solution of 2 mgl^{-1} Cu at room temperature, neutral initial pH and biomass dry weight concentration of 0.69 gl^{-1}

Figure 5.13 shows that the TritonX-100 surfactant is un-suitable for manufacturing beads for the removal of heavy metals from solutions. Beads containing 2% of surfactant reached an adsorption equilibrium at approximately 495 minutes, while beads containing 10% failed to reach a state of equilibrium during the 12 hours duration of the experiment. The equilibrium adsorption capacity for the beads containing 2% surfactant was 2.48 $mg.g^{-1}$, which is 4% less than that of the non-immobilised biomass. On the other hand, beads containing 10% of the surfactant could only remove 2.36 $mg.g^{-1}$ in 12 hours, which is over 8% less than that of the non-immobilised biomass. The adsorption rate of the beads containing 10% of the surfactants was very slow and after 1 hour had only reached 40% of the non-immobilised biomass uptake capacity at the same time. Additionally, the adsorption line is not stable and the standard deviation is high.

The above results show that increasing the ratio of surfactant to pre-polymer has no positive effect on the biomass adsorption capacity, while in some cases it had negative effect (as in the TritonX-100 case).

The combined results for non-immobilised biomass, immobilised biomass containing a 2% surfactant concentration and those without surfactants are shown in figure 5.14. The results indicate that the final uptake capacities of immobilised biomass are similar and almost equal to that of non-immobilised biomass regardless of bead type, however, beads manufactured with Pluronic85 surfactant are favoured due to their faster adsorption rate, in comparison to the other test variables.

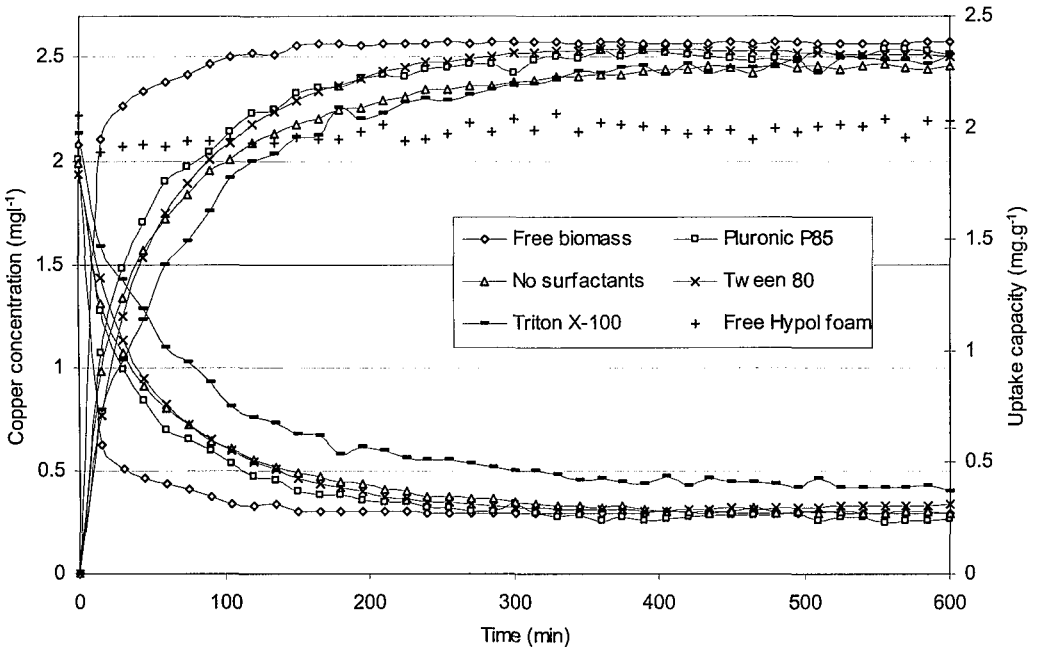


Fig. 5.14 Copper uptake capacity and equilibrium time of non-immobilised fungi and immobilised fungi in Hypol foam manufactured with and without the addition of 2% wt. (surfactant : pre-polymer). In all cases he beads were suspended in a solution of 2 mgl^{-1} Cu at room temperature, neutral initial pH and biomass dry weight concentration of 0.69 gl^{-1} (Error bars were not put to avoid overlap)

5.4 Copper recovery from beads of fungi-hydrophilic polyurethane (Hypol 2002)

At the end of the adsorption experiment, copper was recovered by keeping the beads inside the flask whilst lowering the solution pH to < 2 using 0.1 M HCl and the flasks were agitated for a further 2 hours on the orbital shaker at 200 rpm. This was to avoid possible problems (such as recovering copper more than the adsorbed amount) that could result from foam swelling. 2 ml samples were taken at specific time intervals to determine copper concentration in the solution.

Results are given in appendix table A 31, and shown in figure 5.15.

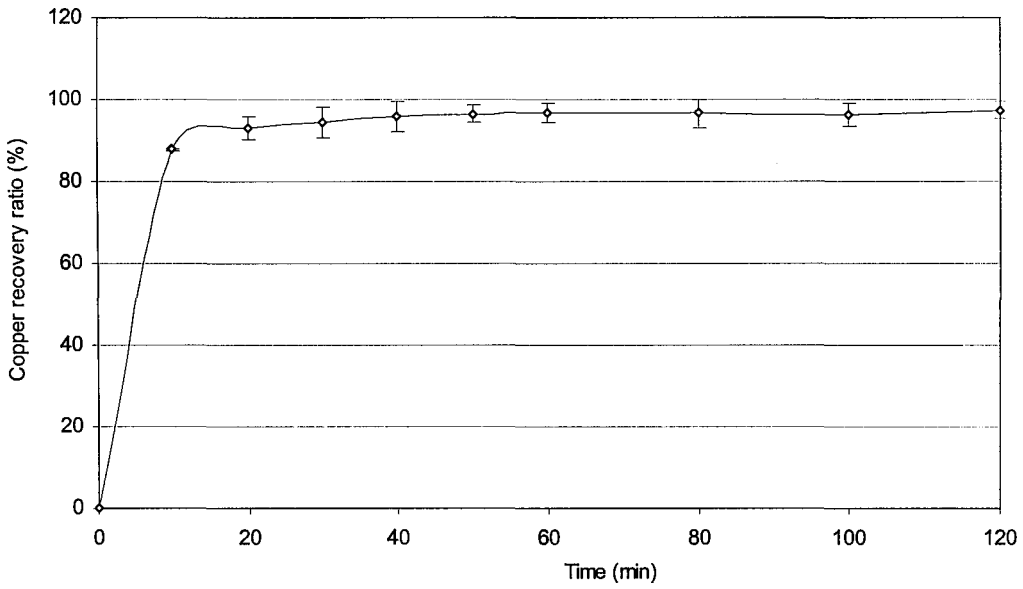


Fig. 5.15 Copper recovery from beads of fungi-Hypol at pH < 2 after exposure to 45 ml of 2 mgl^{-1} Cu solution at an initial pH 7.0 and room temperature

Full copper recovery was obtained when the pH was lowered to < 2 (figure5.15). The graph shows the mean value of two experiments and the standard deviation error bars cover 100% copper recovery.

5.5 Copper precipitation experiments

At high copper concentrations and neutral pH there is potential for metal precipitation to occur during the course of an adsorption experiment. This would contribute to the overall metal removal and makes interpretation of the results difficult. To assess any potential precipitation effect an experiment was carried out under conditions similar to those used in the adsorption experiments in order to assess the precipitation potential at different pH values. Copper sulphate solutions of 1, 2, 4, 6, 8, 10, 15, 20, 30, 40, 50, 60, 100, 150 and 200 mgl^{-1} as Cu (II) were made up in 200 ml conical flasks. A 5 ml sample from each flask was taken for initial Cu concentration measurement. The solutions pH was then adjusted to 5.0 and the flasks were shaken continuously on an orbital shaker at 200 rpm for 2 hours. The pH was checked every 20 min using a pH probe and readjusted to 5 using either dilute acid or base. After 2 hours a 1.5 ml sample was taken from each flask and centrifuged at 14000 rpm to remove precipitates (Eppendorf Centrifuge 5417C), and the supernatant soluble (residual) copper concentration was measured. The experiment was repeated at pH 6.0 and pH 7.0.

All experiments were conducted in duplicate and the results are given in appendix tables A32 to A34, and shown in figure 5.16 where soluble Cu concentration was plotted as a function of total Cu (0-200 mgl^{-1}) and pH.

Figure 5.16 shows that copper precipitated at concentrations as low as 4 mgl^{-1} at pH 7.0 and 10 mgl^{-1} at pH 6.0. Soluble Cu attained maximal equilibrium concentrations of approximately 5 mgl^{-1} and 40 mgl^{-1} at pH 7.0 and 6.0 respectively. However, the results indicate that adsorption experiments carried out at pH 5.0 will not to be affected by Cu precipitation at concentrations < 100 $mg1^{-1}$.

The results obtained infer that, soluble copper will not exceed 5 and 40 mgl^{-1} at a pH of 6 and 7 respectively, regardless of total copper concentration. At pH 5.0 copper will begins to precipitate at a 100 mgl^{-1} concentration and therefore soluble copper concentrations up to this level could be expected.

UNIVERSITY OF SOUTHAMPTON LIBRARY

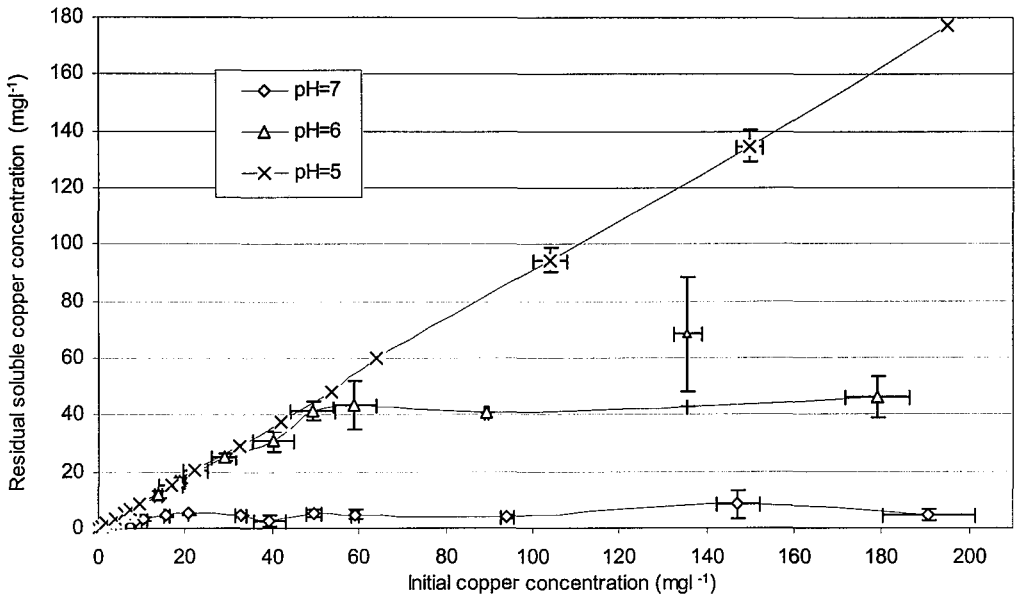


Fig. 5.16 Copper solubility at 20° C for different copper concentrations with respect to pH

The solubility experiments were undertaken in solutions maintained at the appropriate pH value by adjustments made at 20 minute intervals. However, it was impossible to maintain constant values at pH 6 and 7 due to the rapidity of change. At the end of each experiment at these pH values the pH was measured and found to be below the required value despite the several adjustments made during the course of the experiment. This result may be related to the precipitate components having a slow rate of reaction. Because of this problem the experiments undertaken at pH 6.0 and pH 7.0 were difficult to replicate and produced high standard deviation values for the soluble (final) copper concentration with respect to the average soluble concentration (appendix tables A32, A33). For example, at pH 7.0 and initial copper concentrations of 147 and 190 mgl^{-1} the average values for the duplicate experiments with standard deviations were 8.51 ± 4.912 and 4.541 ± 2.17 mgl^{-1} respectively. Whilst, at pH 6.0 with initial copper concentrations of 135 and 180 mgl^{-1} the average values with standard deviations were 42.8 ± 20.327 and 46 ± 7.3 mgl^{-1} respectively. Experiments carried out at pH 5.0 could be replicated much better (appendix table A34), for example, at an initial copper concentrations of 63.78, 150 and 195 mgl^{-1} the average values with standard deviations were 60.05 ± 1.66, 134.76 ± 5.38 and 177.17 ± 2.75 mgl^{-1} respectively.

Theoretically, precipitation in the experimental solutions can be calculated by the use of solubility product of copper hydroxide, as this is likely to be the main precipitate in the experiment. De-ionised water (i.e. free of any salt ions) was used to prepare the experimental solutions. Copper (II) sulphate was used as a copper source, while diluted NaOH and H_2SO_4 were used to adjust the pH. Therefore, the following calculations can be performed:

Ksp (solubility product of Cu $(OH)_2$) at 25° C = 2.2×10^{-20}

At pH = 7

$[OH^-] = [H^+] = 10^{-7}$ mole.l^{-1}

Formation constant of Cu $(OH)_2 = [Cu^{2+}] \times [OH^-]^2$

Therefore, the value upon which copper will start precipitating at pH 7.0 can be calculated, via substituting the values of product solubility and hydroxide ion concentration into the last equation:

$2.2 \times 10^{-20} = [Cu^{2+}] \times (10^{-7})^2$ » $[Cu^{2+}] = 2.2 \times 10^{-6}$ mole.l^{-1} = 0.14 mgl^{-1}

Similarly at pH 6.0

$[OH^-] = 1 \times 10^{-8}$ mole.l^{-1} » $[Cu^{2+}] = 2.2 \times 10^{-4}$ mole.l^{-1} = 14 mgl^{-1}

and at pH 5.0

$[OH^-] = 1 \times 10^{-9}$ mole.l^{-1} » $[Cu^{2+}] = 22 \times 10^{-3}$ mole.l^{-1} = 1398.54 mgl^{-1}

Theoretically at 25° C copper will precipitate at concentrations equal to or greater than 0.14, 14 and 1398.54 mgl^{-1} at pH 7.0, pH 6.0 and pH 5.0 respectively. The theoretical calculations do not support the results of the experiment. However, there are known difficulties in using the solubility product and there are variations in the published values for this. The results of the experiments were comparable to those obtained by other researchers. Eilbeck and Mattock (1987) found that at pH 7.0 the copper soluble residual concentration was around 5 mgl^{-1} (figure 1.3), which is similar to the value obtained in this study. Elibeck and Mattock's experiments were conducted using prepared solutions of simple metal salt and NaOH was used to adjust the pH. Vigorous mixing was used to simulate controlled conditions, followed by filtration

through a Whatman No. 40 filter paper after an elapse of 30 minutes. The filtrates metal concentration was then determined by atomic absorption measurements. He reported that replicability of the experiment was not high and no data was reported regarding the soluble residual copper concentration at pH 6.0 and pH 5.0 using the same reagent and procedures.

The precipitation levels observed were comparable to those obtained by Davis et al. (2000) using predictions obtained via MINEQL$^+$ software. The authors reported that the solid compounds of anterlite ($CuSO_4.2Cu(OH)_2$), tenorite (CuO), and brochantite ($CuSO_4.3Cu(OH)_2$) were calculated to be the most stable phases above pH 5.0 at copper concentration in the range 0.16 – 3.9 mM or 10.2 – 248 mgl^{-1}.

5.6 Biosorption experiments on beads of biomass-Hypol foam

5.6.1 Isotherms experiments on beads of fungi-Hypol foam

These were carried out using 100 mg of dried size graded (D < 150 μm) *R. oryzae* immobilised in Hypol foam beads. The experiments were conducted at pH 5.0 with copper concentrations in the range 2-15 mgl^{-1} and at 200 rpm shaking speed for 12 hour. The pH was kept as constant as possible by checking and adjusting its value back to pH 5 after 20 minutes, 2 hours and 4 hours. At the end of the experiment, the pH was lowered to < 2 using 3M HNO_3 to elute any adsorbed copper over a further 2 hour period. During this time the flasks were continued to be shaken at the same speed. The polyurethane beads were recovered and washed thoroughly in deionised water before being reused again for copper adsorption. Adsorption isotherm experiments were conducted over four consecutive cycles using the same immobilised biomass. Two flasks (duplicate) were performed for each experiment and one 5 ml sample was taken from each flask for copper and carbon measurement. Total organic carbon was measured to monitor any loss of the immobilised biomass during the four consecutive adsorption cycles.

The experimental results are given in Appendix tables A35-A38. Figure 5.17 shows the adsorption isotherms lines for the four cycles. These lines are relatively close to each other, but there is some indication that the biomass lost some of its adsorption capacity during the second cycle and then partially regained this in the third and

fourth cycles. Because there is no clear plateau, indicating saturation adsorption, it is not possible to specify the maximum uptake capacity over this concentration range, or the rate of adsorption to desorption.

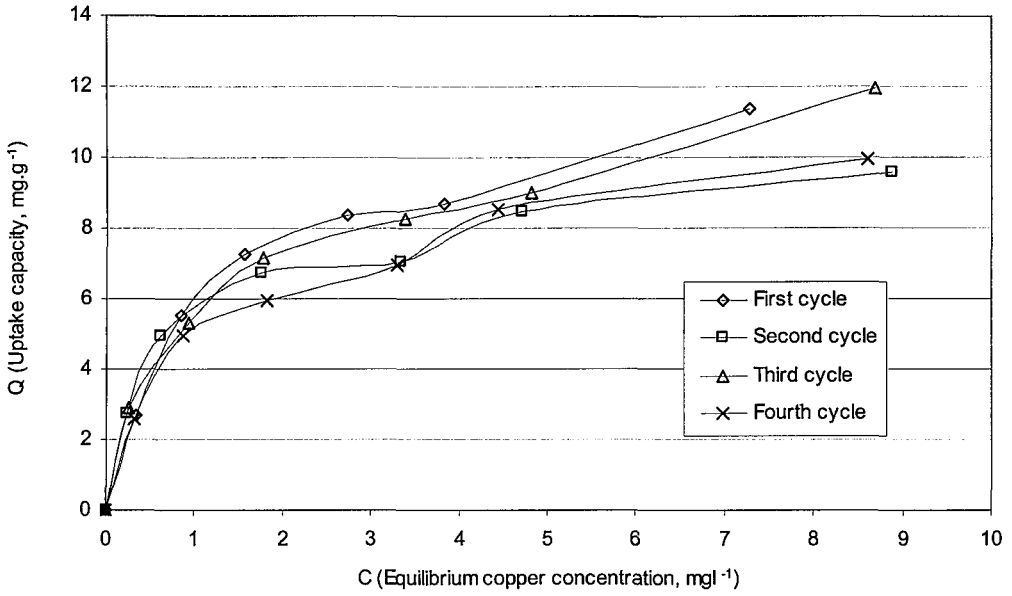


Fig. 5.17 Isotherms of four consecutive cycles of copper uptake by beads of fungi-Hypol foam containing 100 mg dry wt. of biomass at pH 5.0, 20° C and initial copper concentrations of (2-15) mgl^{-1} (Error bars were not put to avoid overlap, see results tables, A35-A38, for the values of standard deviation)

Both Freundlich and Langmuir isotherm plots were used to analyse the data. Figures 5.18 and 5.19 show the plots for Freundlich and Langmuir respectively, while table 5.2 displays the parameters derived using the respective model equations.

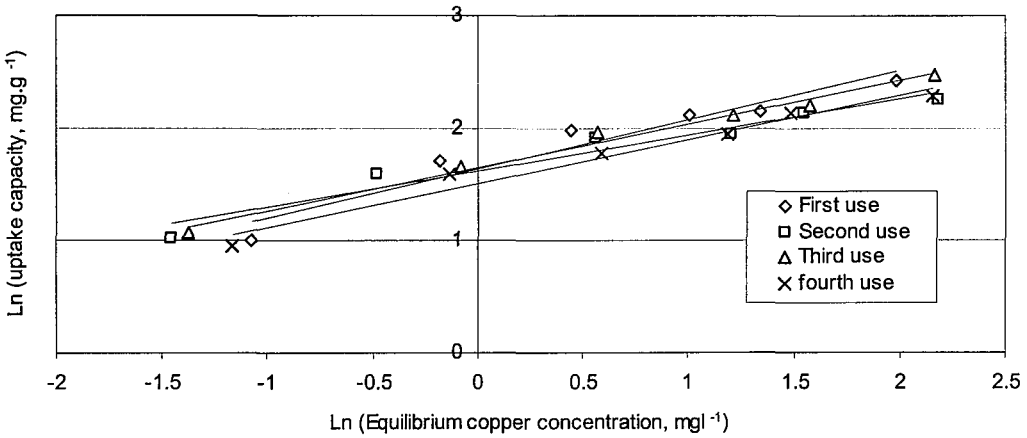


Fig. 5.18 Freundlich isotherms for four consecutive cycles of copper uptake by beads of fungi-Hypol foam containing 100 mg dry wt. of biomass at pH 5.0, 20° C and initial copper concentrations of (2-15) mgl^{-1}

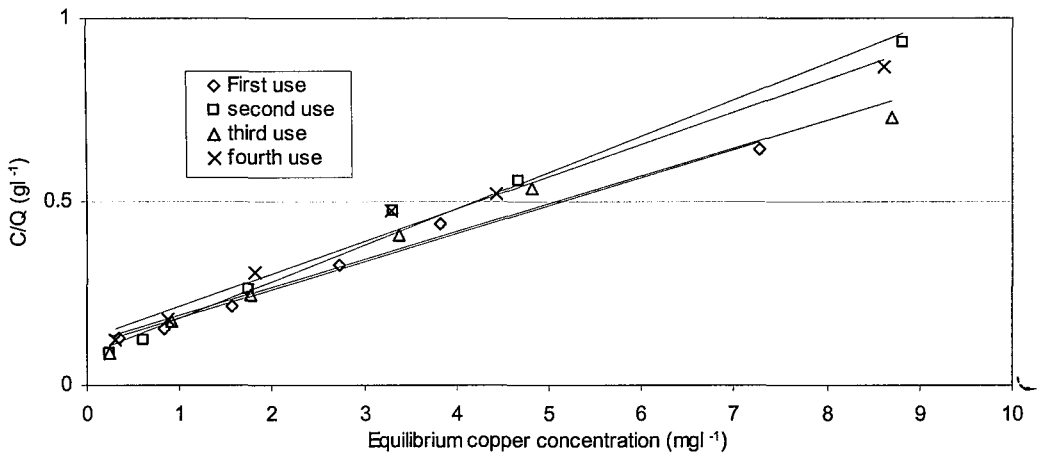


Fig. 5.19 Langmuir isotherms of four consecutive cycles of copper uptake by beads of fungi-Hypol foam containing 100 mg dry wt. of biomass at pH 5.0, 20° C and initial copper concentrations of (2-15) mgl^{-1}

Table 5.2 Freundlich and Langmuir isotherm parameters for Cu adsorption by Hypol immobilised fungal biomass for 4 consecutive adsorption cycles

Cycle	Freundlich			Langmuir		
	K	n	R^2	q_{max}	b	R^2
First cycle	5.16	2.27	0.932	13.04	0.73	0.985
Second cycle	5.05	3.08	0.944	10.07	1.17	0.989
Third cycle	5.22	2.58	0.984	13.12	0.68	0.971
Fourth cycle	4.55	2.54	0.967	11.24	0.72	0.985

Table 5.2 shows that the data fitted both the Freundlich and Langmuir equations, however Langmuir gave higher values for R^2 and subsequently a better representation of the data than Freundlich.

The immobilised biomass reached a maximum uptake capacity (q_{max}) of approximately 13 $mg.g^{-1}$, according to Langmuir. The total organic carbon measurement indicated that immobilised biomass was lost during the first cycle. The TOC concentration of each flask was $\cong$ 35.5 mgl^{-1} at the end of the 1st adsorption cycle (this represents $\cong$ 5.15 mg of the original 100 mg dry wt. of biomass). This loss could be attributed to the small biomass particle size (< 150 μm). The loss of the biomass in the first cycle lowered the uptake capacity during the second uptake cycle, but this capacity was subsequently recovered. This could possibly be attributed to repeated washing with acid during the regeneration process, which may have exposed new adsorption sites.

Carbon leaching was not observed during the second, third and fourth cycles.

After acid regeneration the beads were washed with distilled water to wash out the acid retained within the beads.

The results are in agreement with previous research. In their review of fungi as biosorbents, Kapoor and Viraraghavan (1997) reported that *Rhizopus oryzea* (formerly *Rhizopus arrhizus*) had copper uptake capacities of between 7 and 16 $mg.g^{-1}$.

5.6.2 Isotherms experiments on beads of seaweed-Hypol foam

5.6.2.1 Isotherm experiments and beads reuse

Isotherm experiments were carried out at initial Cu concentrations of 2-60 mgl^{-1} and pH 5.0. Seaweed-Hypol cubes containing the equivalent 100 mg dry wt. of seaweed were suspended in 145 ml of Cu (II) solution in 200 ml conical flasks and shaken for 12hrs at 200 rpm. The solution pH was checked 20 minutes after the start of the experiment and adjusted to pH 5.0. At the end of the experiment, the pH was lowered to < 2.0 and the flasks were shaken for a further 2 hrs to elute the adsorbed copper. The immobilised biomass beads were then recovered and washed thoroughly in deionised water and then in 100ml of 0.1M $NaHCO_3$ to remove any residual acid and finally re-washed in deionised water for subsequent copper adsorption experiments. The beads were reused for up to four further adsorption experiments.

Results of these experiments are given in appendix tables A39a-A43. Figures 5.20 and 5.21 show the isotherm plots according to the Freundlich and Langmuir models respectively, while table 5.3 shows the parameters derived from the model equations.

As can be seen from the R^2 values in table 5.3 the data did not give a good fit to the Freundlich isotherms, with increasing disparity as the number of reuse cycles increased, having only an R^2 value of 0.66 in the last cycle.

The Langmuir isotherm showed a very good fit to the data and the R^2 values did not drop below 0.96 over the five cycles. The Langmuir parameter q_{max}, showed that, when used for the first time, the immobilised seaweed had a maximum adsorption capacity of 39 $mg.g^{-1}$ dry wt., which represents 4% of the immobilised biomass dry wt. The immobilised biomass uptake capacity declined to 32.5 $mg.g^{-1}$ when beads were used for a second time and dropped to 15 $mg.g^{-1}$ during the third, fourth, and fifth procedure.

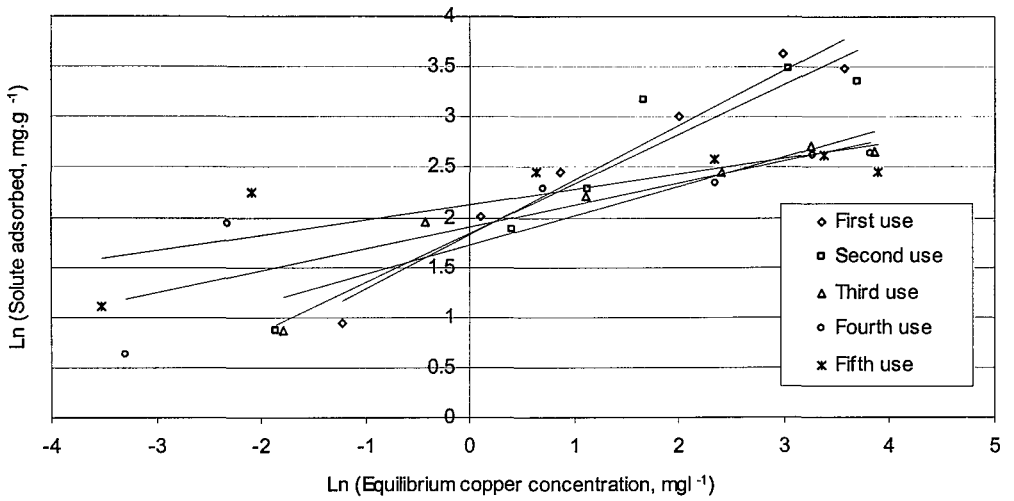


Fig. 5.20 Freundlich isotherms of five consecutive cycles of copper uptake by beads of seaweed-Hypol foam containing 100 mg dry wt. of biomass at pH 5.0, 20° C and initial copper concentrations of (2-60) mgl^{-1}

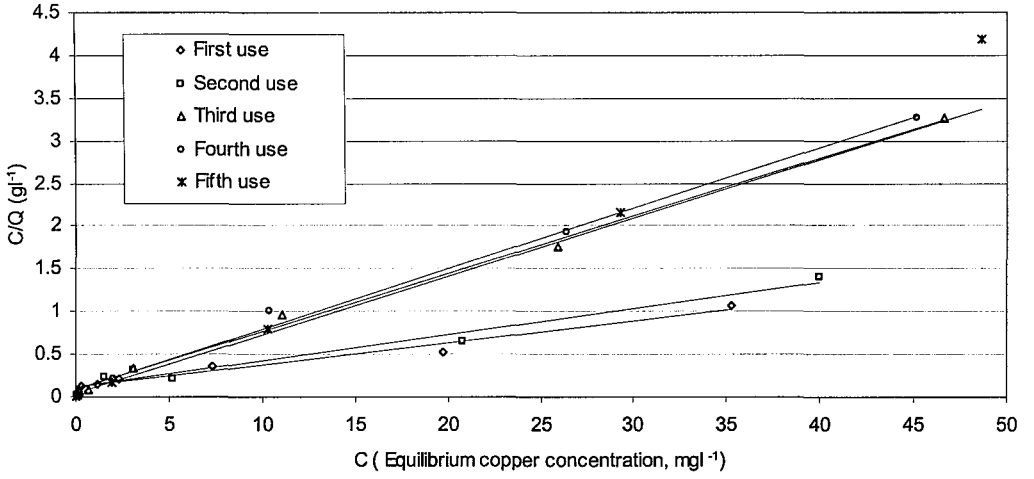


Fig. 5.21 Langmuir isotherms of five consecutive cycles of copper uptake by beads of seaweed-Hypol foam containing 100 mg dry wt. of biomass at pH 5.0, 20° C and initial copper concentrations of (2-60) mgl^{-1}

Table 5.3 Freundlich and Langmuir isotherm parameters for Cu adsorption by Hypol immobilised seaweed biomass for 4 consecutive adsorption cycles.

Cycle	Freundlich			Langmuir		
	K	n	R^2	q_{max}	b	R^2
First cycle	6.25	1.82	0.96	38.91	0.21	0.975
Second cycle	6.32	2.02	0.919	32.467	0.27	0.969
Third cycle	5.65	3.42	0.875	14.77	0.72	0.997
Fourth cycle	6.73	4.49	0.767	14.04	0.98	0.995
Fifth cycle	8.34	6.48	0.661	14.598	1.73	0.993

The progressive reduction in the metal uptake capacity could be related to several factors. The alginate in seaweed acts as a base exchange material, therefore alginic acid that is present as a mixed salt of cations (mostly calcium) is able to render it insoluble (Muzzarelli, 1973). The seaweeds used in our study were initially pre-treated with distilled water and diluted HCl, which removed salts and other adsorbed substances. The seaweed was "full size" (i.e. not pulverised), therefore only small part of calcium ions would have been dissolved in conjunction with alginate and polymer leaching. Muzzarelli (1973) reported that the isolation of seaweed alginate is initially undertaken by hot water and lime water treatment giving a solution of mannitol, laminarin, fucoidan, and salts. Then a diluted acid treatment eliminates acid soluble substances, while converting the alginate to free alginic acid. After filtration, the residue is stirred with a sodium carbonate solution and the alginic acid is dissolved to form soluble sodium alginate. Consequently, several precipitation processes are performed which purify the alginic acid. The author added that *Ascophyllum nodosum* is treated with sulphuric acid (i.e. to eliminate acid soluble substances) and extracted with soda. After filtration (to remove insoluble residues) potassium chloride and sulphuric acid are added to cause precipitation of the alginic acid. Also Fourest and Volesky (1997) used a 2% solution of Na_2CO_3 to extract alginate from different types of dry seaweed.

Alginate is known to contribute towards Cu binding (Edyvean et al., 1997) and this may have been the case during the initial adsorption experiments. An acid/alkali wash took place between each adsorption experiment, subsequently further alginate and/or other polymers could have been removed during these procedures. Therefore, a progressive reduction in copper adsorption may have taken place until these substances were exhausted. This could also be true for other potential metal-binding agents within the biomass. To minimise this problem Chong and Volesky (1995),

crosslinked *A. nodosum* particles with formaldehyde, which inhibited the subsequent release of its components into solution. There are other possible reasons for the reduction in the binding capacity, such as the loss of biomass from the matrix. Analysis of the total carbon (TC) at the end of each experiment showed that there was 37 mgl^{-1} of carbon in each flask at the end of the 1st cycle (appendix table A39b), which is equal to 5.4 mg of biomass. No TC was detected at the end of second, third, fourth, and fifth cycles, however it is expected that the major loss in alginate occurred when the beads were washed with 0.1 M of $NaHCO_3$ to remove the residual acid after copper recovery process.

Values of b increased while the biomass uptake decreased to reach a constant level with further use of the beads. This increase in b values means that the rate of copper adsorption to desorption increased during the experiment as the beads were further employed.

To clarify the similarity between the experimental data points and the Langmuir isotherm plot, the values of b and q_{max} for each cycle can be compensated for in equation 2.2 to give the relation between C (equilibrium Cu concentration) and Q (biomass adsorption uptake capacity). Assuming different values for C and attaining the corresponding values for Q, the isotherm lines can be drawn for each cycle. Figure 5.22 shows the lines obtained from the utilization of this method and the experimental data points.

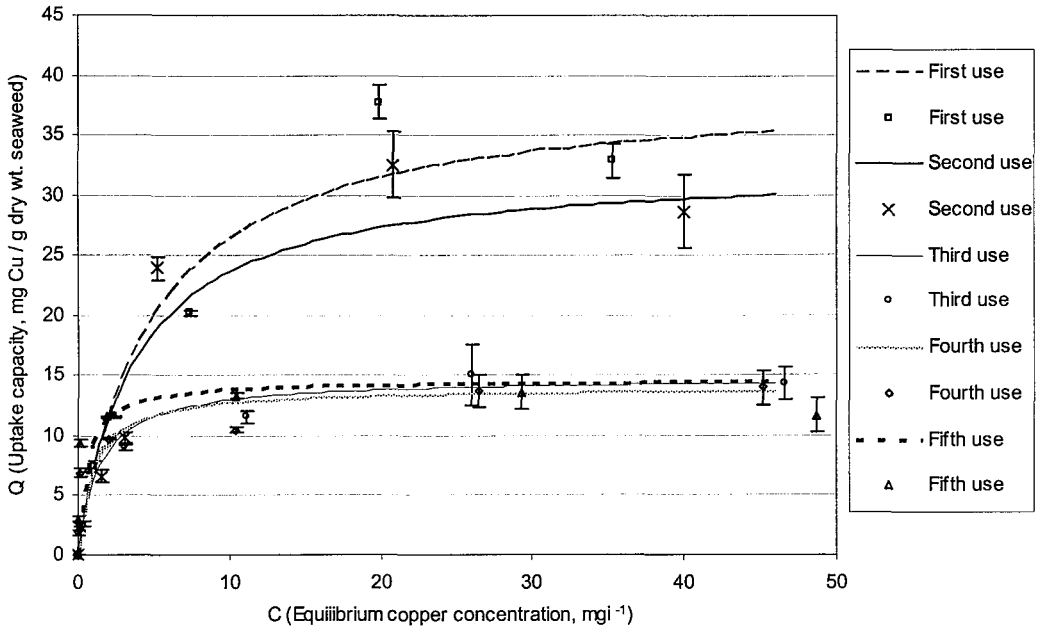


Fig. 5.22 The Langmuir Isotherm plot compared to the experimental data for five consecutive cycles of copper uptake by beads of seaweed-Hypol foam containing 100 mg dry wt. of biomass at pH 5.0, 20° C and initial copper concentrations of (2-60) mgl^{-1}

5.6.2.2 Effect of temperature on the adsorption of copper by seaweed/Hypol beads

The experimental procedure was identical to that followed in section 5.6.2.1 except a temperature controlled orbital shaker was used. Three temperatures were investigated: 30° C, 20° C, and 10° C. The experimental results are given in appendix tables A39, A44 and A45. Figures 5.23 and 5.24 show Freundlich and Langmuir plots respectively, while table 5.4 gives the respective parameters calculated from the model equations. Again, the data corresponded more closely to the Langmuir isotherms than to that of Freundlich as seen by the respective R^2 values.

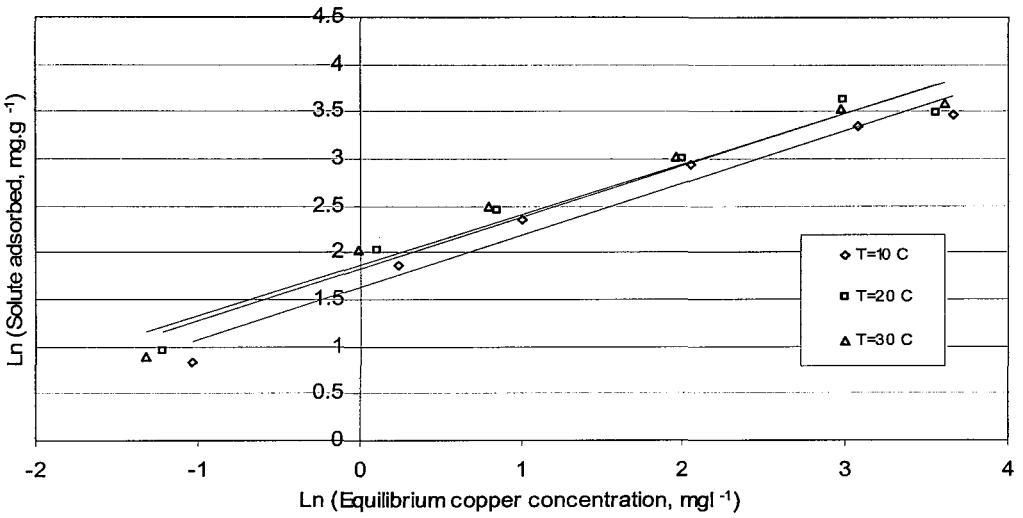


Fig. 5.23 Freundlich isotherms for copper adsorption by 100 mg dry wt. of immobilised seaweed in Hypol beads with respect to temperature at pH 5.0 and initial copper concentrations (2-60) mgl^{-1}

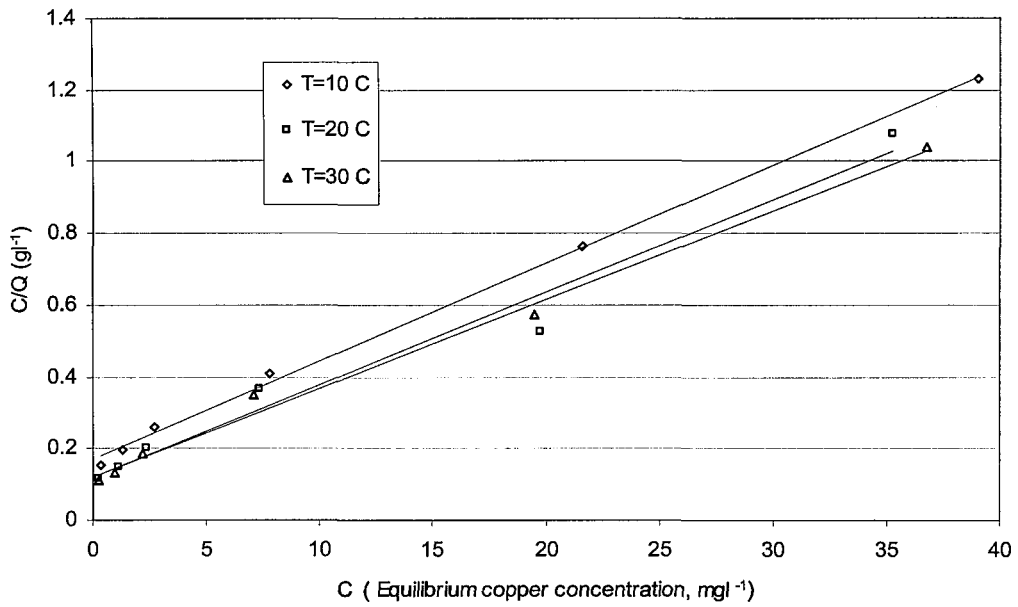


Fig. 5.24 Langmuir isotherms for copper adsorption by 100 mg dry wt. of immobilised seaweed in Hypol beads with respect to temperature at pH 5.0 and initial copper concentrations (2-60) mgl^{-1}

Using the Langmuir equation the maximum adsorption capacity (q_{max}) increased from 36.63 $mg.g^{-1}$ at 10° C to 38.91 $mg.g^{-1}$ at 20° C and 40.486 $mg.g^{-1}$ at 30° C. This was also apparent from the Freundlich model as the partition coefficient (K) increased with increasing temperature. This may indicate that the adsorption process is at least partly chemical in nature; however analysis of the adsorption rate should be undertaken to confirm this.

Table 5.4 Freundlich and Langmuir isotherm parameters for Cu adsorption by 100 mg dry wt. of immobilised seaweed in Hypol beads with respect to temperature at pH 5.0 and initial copper concentrations (2-60) mgl^{-1}

Temperature	Freundlich			Langmuir		
	K	n	R^2	q_{max}	b	R^2
10° C	5.156	1.804	0.968	36.630	0.161	0.998
20° C	6.254	1.825	0.960	38.910	0.211	0.975
30° C	6.473	1.850	0.963	40.486	0.201	0.993

Figure 5.25 shows the Langmuir isotherm plot obtained by substituting b and q_{max} values from table 5.4 into equation 2.2 and compares the model generated lines with those of the original experimental data.

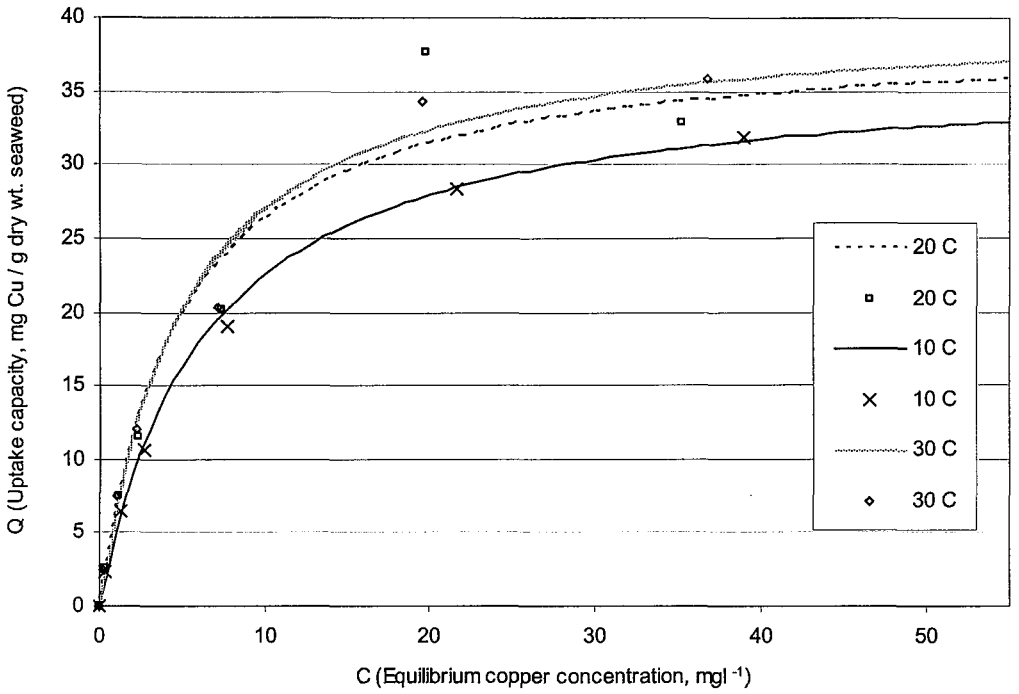


Fig. 5.25 Isotherm lines according to Langmuir compared with the obtained data for copper adsorption by 100 mg dry wt. of immobilised seaweed in Hypol beads with respect to temperature at pH 5.0 and initial copper concentrations (2-60) mgl^{-1}

5.6.2.3 Effect of pH on the adsorption of copper by seaweed/Hypol beads

The experimental procedure was identical to that followed in section 5.6.2.1 but this was repeated at pH values of 3 and 4.

Results of these experiments are given in appendix tables A39, A46 and A47. Figures 5.26 and 5.27 show Freundlich and Langmuir plots respectively, while table 5.5 shows the respective parameters for these equations.

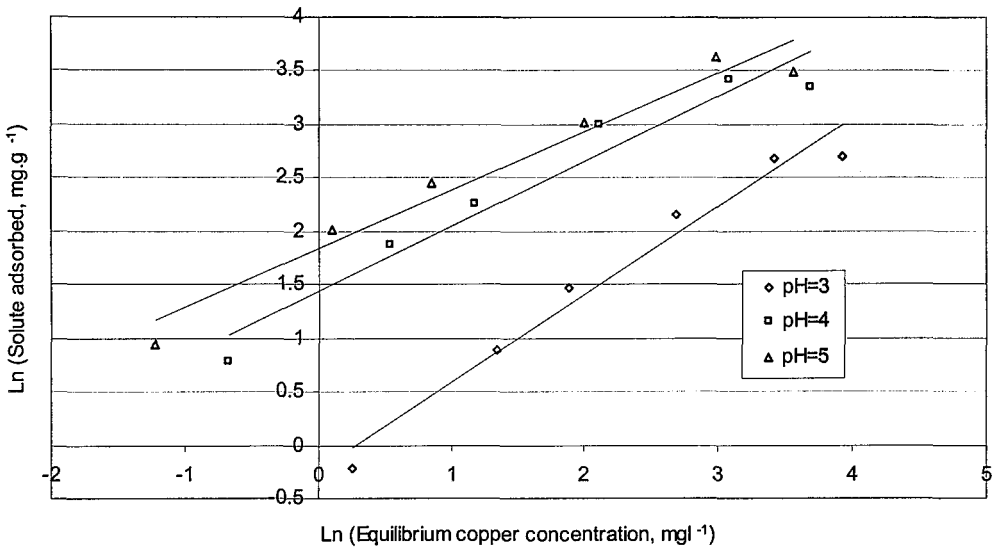


Fig. 5.26 Freundlich isotherms for copper adsorption by 100 mg dry wt. of immobilised seaweed in Hypol beads with respect to pH at 20°C and initial copper concentrations (2-60) mgl^{-1}

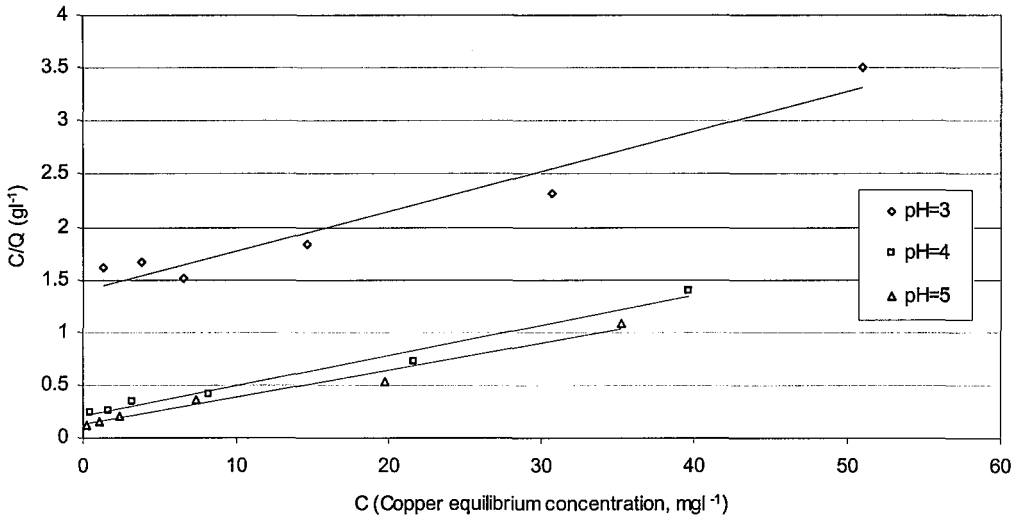


Fig. 5.27 Langmuir isotherms for copper adsorption by 100 mg dry wt. of immobilised seaweed in Hypol beads with respect to pH at 20° C and initial copper concentrations (2-60) mgl^{-1}

Figures 5.26 and 5.27 show that both Freundlich and Langmuir fitted the data very well and the high values of R^2 in table 5.5 confirm this.

The biomass maximum adsorption capacity, q_{max}, increased sharply from 26 to 35 and 39 $mg.g^{-1}$ when the solution's pH was increased from 3 to 4 and 5 respectively.

Table 5.5 Freundlich and Langmuir isotherm parameters for Cu adsorption by 100 mg dry wt. of immobilised seaweed in Hypol beads with respect to pH at 20° C and initial copper concentrations (2-60) mgl^{-1}

pH	Freundlich			Langmuir		
	K	n	R^2	q_{max}	b	R^2
3.0	0.78	1.21	0.970	26.385	0.027	0.941
4.0	4.2	1.64	0.945	34.965	0.14	0.981
5.0	6.25	1.82	0.960	38.911	0.21	0.975

The values of b were also elevated by increasing the solution's pH. This means that the rate of solute (i.e. copper) adsorption on the biomass surface to the solute desorption from the biomass surface increased during the adsorption process when the pH was increased. This was expected as the number of H^+ ions available in solution (that can compete with the solute ions on the available adsorption sites on the biomass surface) are reduced by an increase in pH (Greene and Darnall, 1990). Therefore, the number of copper ions adsorbed at pH 3.0 was low, in comparison to those desorbed from the biomass surface, this results in a low b value.

A negative overall charge may result on the biomass surface if the pH increases and will attract more positive charged ions.

A variation in pH would also alter the speciation and availability of metallic elements in solution, and the chemical state of the functional groups that are responsible for biosorption (Kapoor and Viraraghavan, 1997).

Figure 5.28 shows the isotherm lines obtained from the Langmuir equation after substituting values b and q_{max} from table 5.5 in equation 2.2, and compared to the experimental data.

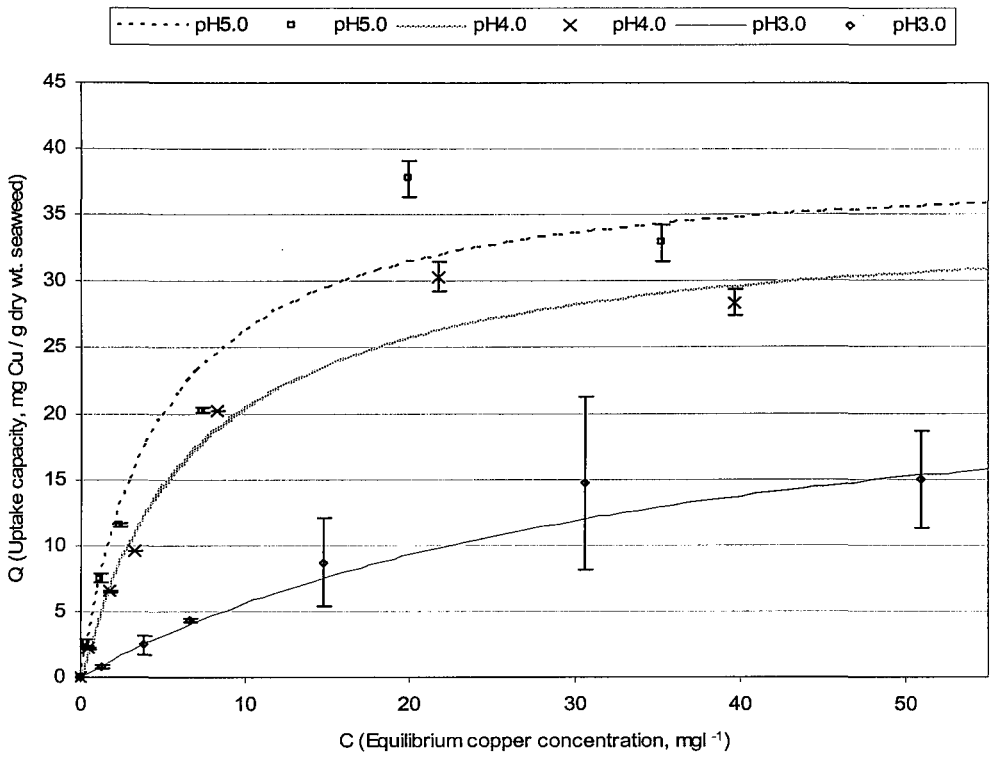


Fig. 5.28 Isotherm lines according to Langmuir compared with the obtained data for copper adsorption by 100 mg dry wt. of immobilised seaweed in Hypol beads with respect to pH at 20° C and initial copper concentrations (2-60) mgl^{-1}

5.7 Columns experiments

The seaweed/Hypol foam was cast into columns as described in section 4.4.3. The resultant matrix is attached strongly to the internal walls of the column to a degree that would prevent any by-pass of test solutions between the foam and the column internal wall. The cast foam/biomass had an open pore structure (0.5-2 mm diameter pores) that allowed solutions to pass through. Plate 5.20 shows a cross section of the foam/biomass cut from the column.

By taking into account the weights of all components used in the manufacturing process before and after the reaction, the quantity of foam-biomass cut from the ends of the column, and any residual materials (for example, foam-biomass stuck on the mixer) the biomass concentration inside the column could be calculated.

5.7.1 Copper adsorption and elution from the seaweed-Hypol foam column

5.7.1.1 Methodology

The experiment involved five cycles of operation with elution of the copper from the seaweed/Hypol foam column between cycles and at the end of the experiment.

A column of cast foam-seaweed was made as described in section 4.4.3, but in this case 1.17 g of acetic acid was added to the container containing the liquid components and 1.63 g of $NaHCO_3$ was added to the container containing solids (i.e. mixing vessel). The acetic acid and bicarbonate on mixing produced additional carbon dioxide (see section 5.2.2).

Initial column conditions were as follow:

Total weight of the foam-biomass in the column	51.57 g
The dry weight of the biomass in the column	3.88 g
Biomass load in the column	7.53 %
Influent flow rate	4.7 l/hour
Influent copper concentration	6 mgl^{-1}
Influent solution pH:	
First cycle	5.43
Second cycle	5.29
Third cycle	5.31
Fourth cycle	5.32
Fifth cycle	5.34
Volume to be treated (in each cycle)	60 litres

The adsorption experiment at each cycle involved passing 60 litres of a 6.0 mgl^{-1} copper solution at a pH close to 5.0 in an upflow mode through the column. Samples for copper analysis were taken as detailed in the results tables (appendix tables A50, A56, A63, A70 and A77). At the end of an adsorption cycle 2 litres of deionised water was passed through the column to flush any copper solution that had not adsorbed either to the foam itself or onto the functional sites of the biomass. To elute the adsorbed copper, 10 litres of 0.1 M of HCl (pH $\approx$1.3) solution was passed through the

column in up flow mode at a flow rate of 2.3 l/hour and samples were taken as detailed in the results tables (appendix tables A53, A60, A67 and A74) for copper analysis.

After acid washing, the column was washed with deionised water until the outgoing water pH reached approached 5; this generally required around 10 litres of deionised water to be passed. The column was then ready for another subsequent adsorption cycle.

5.7.1.2 Biomass loss on conditioning of the column

Carbon measurement (appendix table A48) made on the wash water that was used to condition the columns after manufacture (section 4.4.4) indicate that there was 775 mg of organic carbon (TOC) and 2.3mg of inorganic carbon (IC) leached from the column during the washing process. To verify the source of this carbon two control columns were manufactured, the first contained free Hypol foam manufactured with the addition of sodium bicarbonate and acetic acid (to produce extra carbon dioxide) and the second with water and surfactant only. These were prepared using the procedures given in section 4.4.3. 10 litres of distilled water was passed through each column, samples were collected and carbon was measured. Results (appendix table A49) showed that the foam column which was manufactured with the addition of acetic acid and sodium bicarbonate gave 450.75 and 2.664 mg of TOC and IC respectively in the wash water. The high TOC could be due to surfactant and/or sodium acetate (i.e. product of the reaction between acetic acid and bicarbonate) both of which comprise organic carbon. The low level of IC in the wash water may indicate either that the reaction between the bicarbonate and acetic acid was near completion, or most of inorganic carbon were transformed into CO_2 gas as a result of the low pH caused by acetic acid.

By subtraction, the net loss of organic matter from the immobilised seaweed in the column is estimated to be around 325 mg of TOC. This is equivalent to reducing the amount of immobilised biomass in the column from 3.88 g to 3.55 g; this was the figure used to calculate the biomass adsorption capacity in the first cycle. The loss in biomass was estimated to be 8% of the original weight of immobilised seaweed. It is assumed that this loss was due to seaweed that was not immobilised or retained within the pores of the immobilisation matrix. The leached organics could also have been

alginate (which is a main component of seaweed) or any other biomass components. Any leached organic carbon in subsequent cycles was considered to be a loss of immobilised biomass as it is assumed that the surfactants or acetate produced as part of the manufacturing process would have been completely lost during the first cycle.

For the foam manufactured with water and surfactant only 113.4 and 9.5 mg of TOC and IC were detected respectively in the wash water. The decrease in the TOC compared with the first case came as a result of not using acetic acid, while the increase in IC value could be due to the carbon dioxide that is produced as a result of the reaction between Hypol pre-polymer and water that could dissolve in the matrix or be turned into bicarbonate which contributes to the final inorganic carbon. The results of the control columns were used to correct the results in all following column experiments.

Precise calculation of the organic carbon lost in the wash water is difficult as the concentration of TOC varied considerably with time (i.e. each second there was a different concentration), and would require continuous monitoring throughout the washing process to obtain an accurate figure of the total weight of carbon lost. The calculation was therefore based on the concentration of TOC measured in the spot sample taken of the wash water that had passed and assumed the concentration of TOC had remained constant since the previous sample had been taken. With hindsight it would have been better to have collected the entire volume of wash water, mixed this and then determined the TOC of a well mixed sample.

5.7.1.3 Results of the adsorption and desorption cycles

The results of the adsorpsion and desorption experiment are given in Appendix tables A50 to A79, and shown graphically in figures 5.29 to 5.31. Figure 5.29 shows the amount of copper that has been absorbed per unit weight of seaweed immobilised in the column. This was worked out by measuring the concentration difference in soluble copper between the influent and effluent, knowing the biomass weight in the column and the flow rate (i.e. volume of solution passed through the column). In the 1st cycle, the immobilised biomass reached equilibrium at a adsorption capacity of 19.367 mg.g^{-1} after treating 44 litres of copper containing test solution. This adsorption capacity declined to 17.96 mg.g^{-1} after treating 42 litres in the second cycle and 14.16 mg.g^{-1} after treating 32 litres in the third cycle. This decline could be explained by the loss of

biomass that occurred between the three adsorption-desorption cycles, although the weight of biomass used in the calculations for each cycle took into account these losses. It might be that the lost biomass is greater than that estimated and used in the calculation (i.e. some components of the biomass could have leached out such as carrageenan and alginate which the TOC measurement is not adequate to determine their virtual quantity).

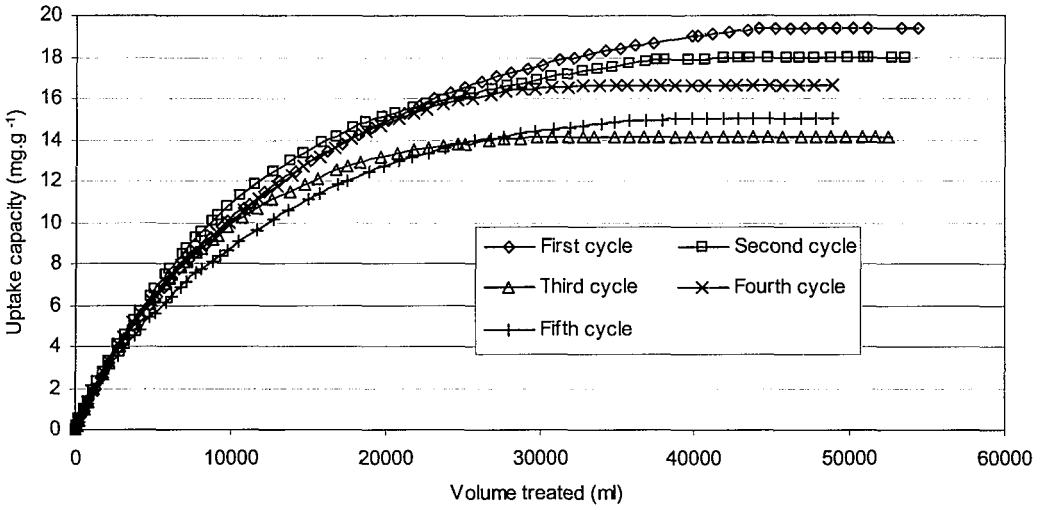


Fig. 5.29 Copper uptake capacity over 5 consecutive adsorption-desorption cycles using a column of Hypol-seaweed. Influent pH 5.0, 20° C, initial copper concentration of 6 mgl^{-1}, flow rate 4.7 l/hr and biomass net dry wt. of 3.5 g (approximate)

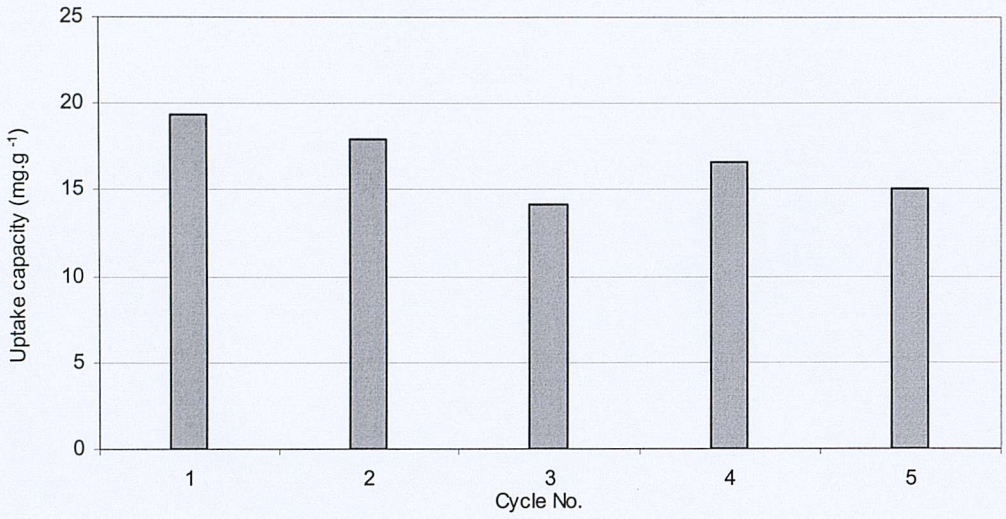


Fig. 5.30 Summary of copper equilibrium uptake by immobilised seaweed in Hypol foam and cast in plastic column for five consecutive cycles

During the fourth and fifth cycles the immobilised seaweed recovered some of its lost capacity reaching equilibrium at 16.6 and 15 $mg.g^{-1}$ after treating 35, and 38 litres respectively (figure 5.30). This improvement in uptake may be attributed to the consecutive regeneration of the column by diluted acid, which could have enhanced the adsorption capacity by exposing extra biomass surface to the solute. Also washing the column with distilled water after each regeneration process (to neutralise the remaining acid in the column) could have been incomplete, therefore leaving some hydrogen cations on the column, which may have exchanged with further copper cations.

This fluctuation in copper uptake (through the consecutive cycles of use) has been seen by other researchers using different biomass types. In a pilot plant operated to adsorb uranium from mine leach solutions using a reactor of immobilised *R. arrhizus* for 10 consecutive cycles, the initial uptake capacity for the immobilised biomass dropped from 77.2 $mg.g^{-1}$ in the first cycle to 35.9 $mg.g^{-1}$ in the fourth, (Tsezos, 1997). The uptake then increased to 36.5 $mg.g^{-1}$ in the fifth cycle, gradually declining to 27.3 $mg.g^{-1}$ by the eighth. It increased again in the ninth to 29.3 $mg.g^{-1}$ and subsequently dropped to 22.1 $mg.g^{-1}$ in the final cycle.

Figure 5.31 shows the percentage difference between the influent and the effluent copper concentrations for the five consecutive adsorption cycles. The lines are relatively close to each others.

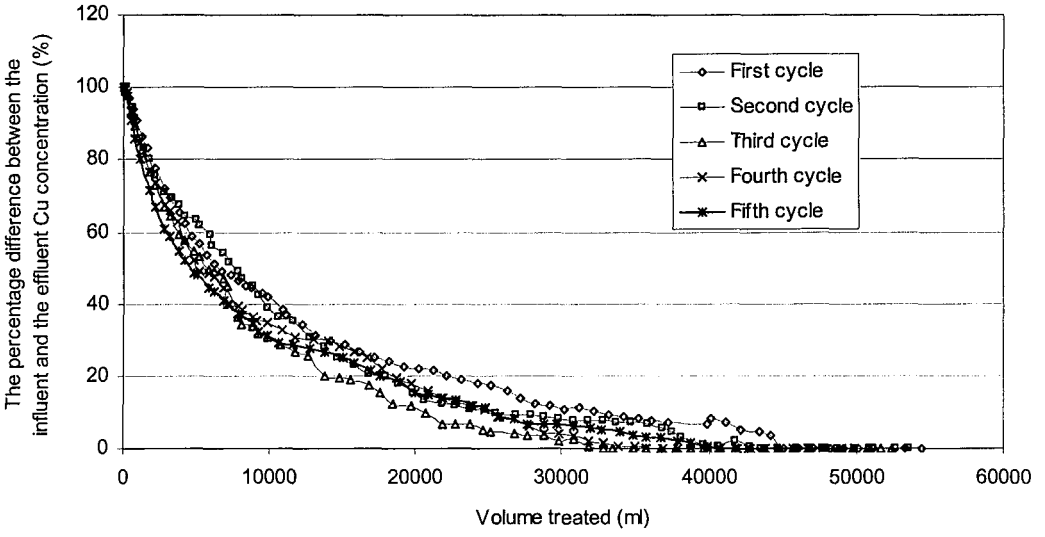


Fig. 5.31 The percentage difference between the influent and the effluent copper concentration (%) over 5 consecutive adsorption-desorption cycles using a column of Hypol-seaweed. Influent pH 5.0, 20° C, initial copper concentration of 6 mgl^{-1}, flow rate 4.7 l/hr and biomass net dry wt. of 3.5 g (approximate)

Appendix table A50 gives the results from passing a copper solution through a control column of biomass free Hypol foam, while figure 32 shows these results. Figure 32 indicates that biomass free foam did not contribute to the copper removal from solution.

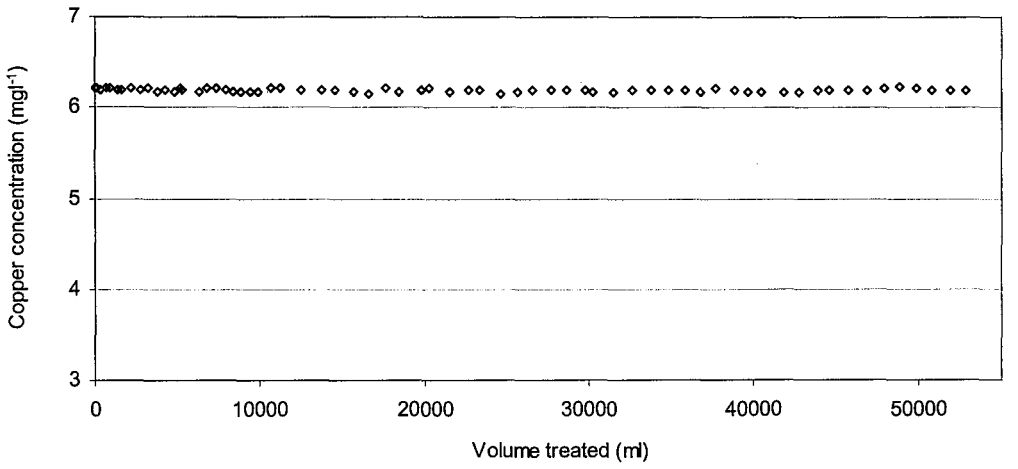


Fig. 5.32 Copper removal using a column of biomass free Hypol foam. Influent pH 5.0, 20° C, initial copper concentration of 6 mgl^{-1} and flow rate 4.7 l/hr

As can be seen from figures 5.33 to 5.37 complete recovery of copper was obtained during each desorption cycle by using dilute HCl. In fact the recovery graphs show that the minimum equilibrium recovered copper ratio was 120% and this is probably due to the swelling effect of the foam and its retention of pore water which may itself contain soluble copper. A similar phenomena has been encountered by other researchers using different types of adsorbing materials, for example, extra uranium has been reported in the regeneration process of some cycles of a pilot plant operated to remove uranium from biological leachates of uranium-bearing pyretic ore from the Elliot Lake district of Canada using *R. arrhizus* (Tsezos, 1997).

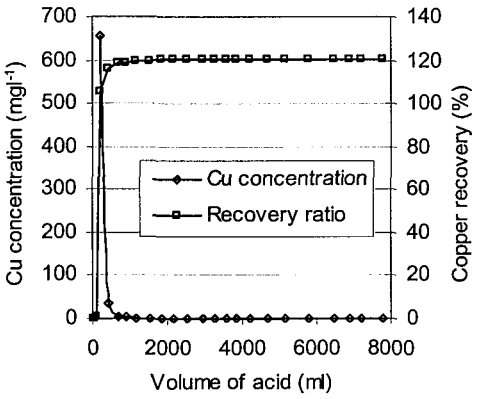


Fig. 5.33 Cu recovery after the first adsorption cycle

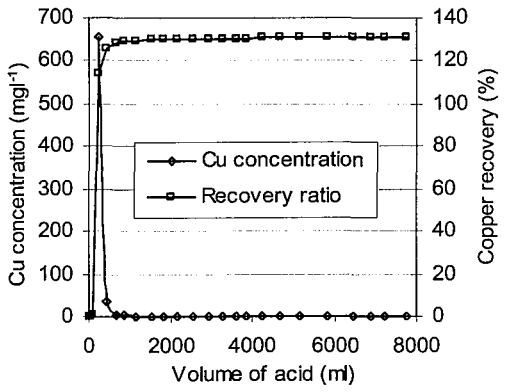


Fig. 5.34 Cu recovery after the second adsorption cycle

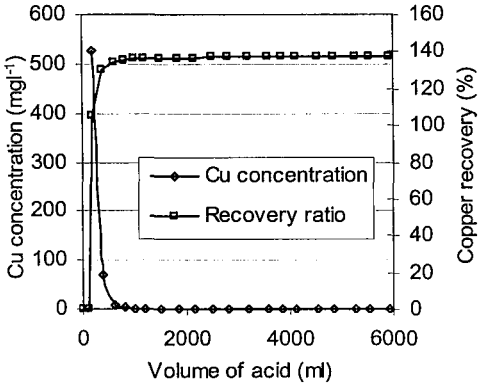


Fig. 5.35 Cu recovery after the third adsorption cycle

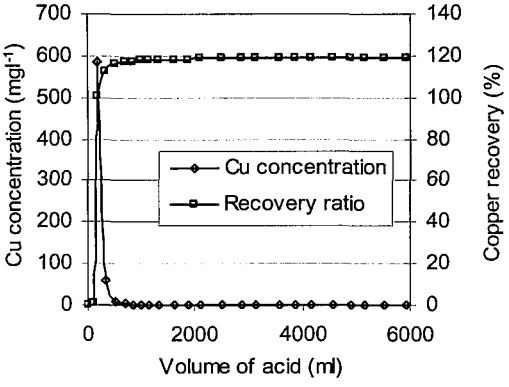


Fig. 5.36 Cu recovery after the fourth adsorption cycle

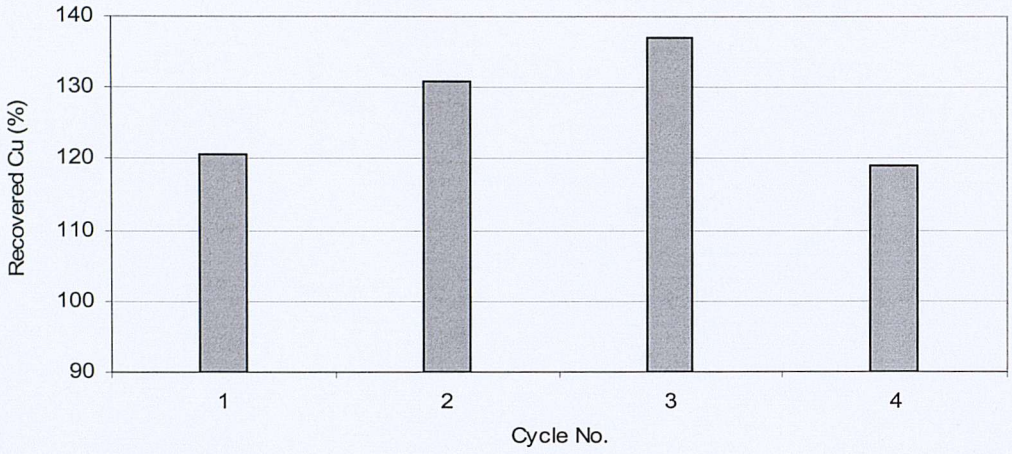


Fig. 5.37 Summary of Cu elution efficiency observed during the 5 cycles of the column operation

The results from the desorption cycles (Figures 5.33 to 5.36) suggest that less than 2 litres of dilute acid was needed for the complete elution of copper from the column. This quantity represents only 5-6 % of the total volume of copper solution treated. This means that copper laden solution was concentrated to 5% of its original volume, which makes final copper recovery much easier and less expensive. The pH readings for the effluent during each adsorption cycle are given in tables A51, A57, A64, A71 and A78, and shown in figures 5.38 to 5.42. There is a noticeable drop from pH 5 to pH 4 corresponding to the passage of the first few litres of influent in each adsorption cycle; this coincides with the period of time where the copper removal ratio was high. There is then a gradual increase in pH as the copper removal ratio declined. This result indicates that ion exchange could be one of the mechanisms that taken part in copper uptake. This mechanism has been reported by a number of researchers (Yakubu and Dudeney, 1986; Muraleedharan et al., 1994; Yetis et al., 2000).

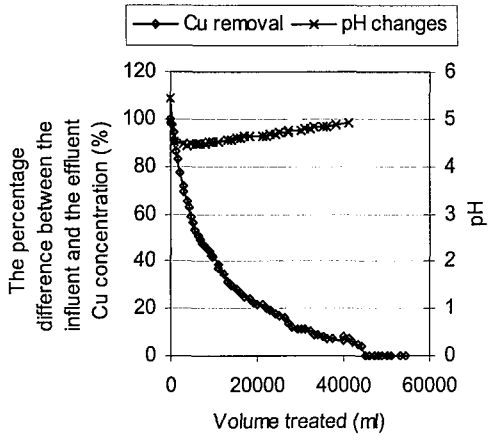


Fig. 5.38 pH changes during the first adsorption cycle

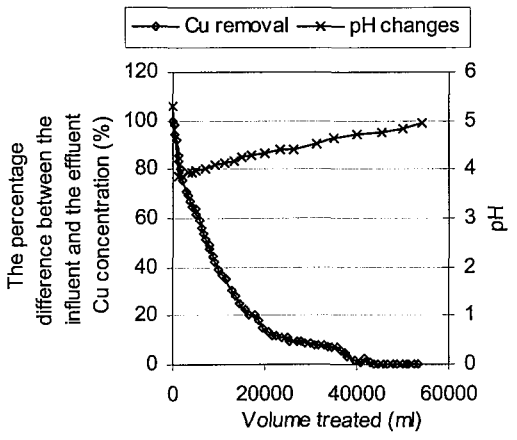


Fig. 5.39 pH changes during the second adsorption cycle

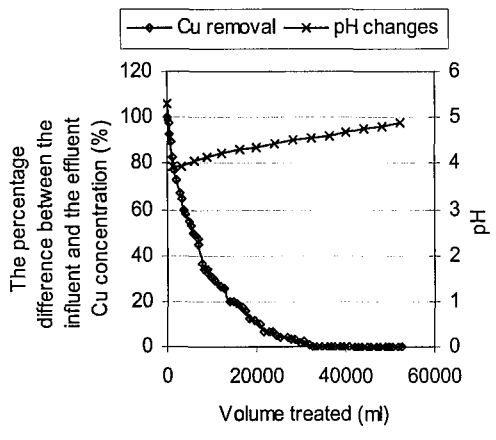


Fig. 5.40 pH changes during the third adsorption cycle

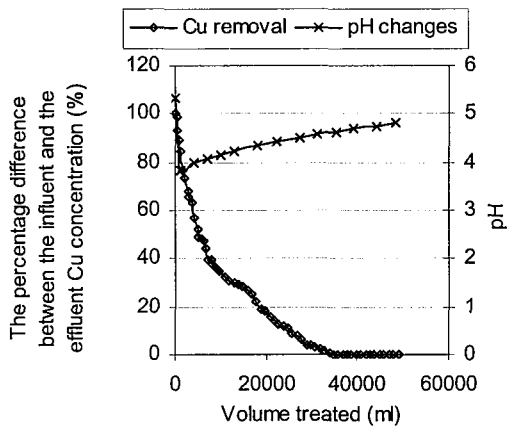


Fig. 5.41 pH changes during the fourth adsorption cycle

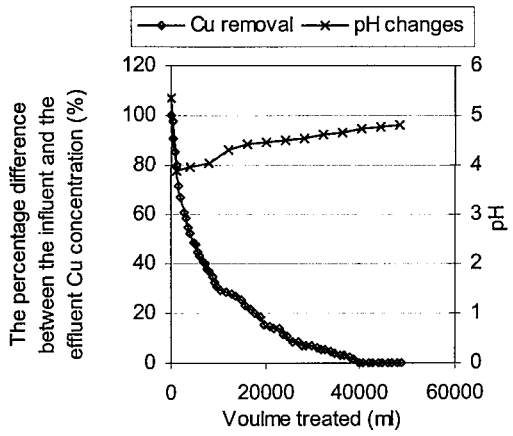


Fig. 5.42 pH changes during the fifth adsorption cycle

The maximum pH reductions recorded were 1.0, 1.44, 1.39, 1.48 and 1.45 units in the first, second, third, fourth and fifth cycles respectively. The pH drop in the first cycle was gradual and occurred after the treatment of approximately 4 litres, while the drop was more abrupt in the subsequent cycles, and reached its lowest value within the passage of 1 litre of effluent. It may therefore also be the case that there are still traces of acid remaining in the column after each regeneration process, and that the washing by distilled water was not completely successful. To verify this possibility, a control column of biomass free Hypol foam was manufactured according to the procedures detailed in section 5.7.1.1. The column was washed with 5 litres of distilled water, then by 3 litres of 0.1M HCl, then with 10 litres of distilled water with continuous monitoring of pH of the effluent. The column was then drained completely and then left for two hours. After washing the connecting tubes with distilled water, distilled water was again passed through the column with continuous pH monitoring to see if this repeat washing with water removed further traces of acid from the column. Results (appendix table A80) showed that after reaching a stable pH value of 5.22 in the first wash cycle, the pH of the wash water dropped to 4.7 on the second washing. This drop in the pH, although not significant (0.5 unit), indicated that a single wash of water was not enough to remove traces of acid completely; to do this several washes might be required. This may be an explanation for the abrupt pH drop in the second, third, fourth and fifth cycles, and could also indicate that part of the biomass

adsorption capacities in these cycles is related to exchange with protons left in the foam during the regeneration process.

After the fifth regeneration cycle, the column was washed with 500ml of 0.1M $NaHCO_3$ to investigate the effect of neutralising the remaining acid traces in the column. The biomass in the column lost approximately 300 mg as total organic carbon (TOC) during this alkaline washing process indicating a loss in biomass or its components. It is thought that the loss in carbon is probably mainly alginate as this represents the main constituent of seaweed 14-40 %. However, there is no specific analytical data to support this supposition.

5.7.2 The effect of flow rate on copper adsorption using seaweed-Hypol foam columns

Two columns were used to examine the effect of flow rate on copper adsorption. The first column was operated at flow rate of 2.25 l/hour and the second at 7 l/hour. The results were also compared to the column operated at 4.7 l/hour (section 5.7.1.3).

The operating conditions of the columns were as follows:

	Column 1	Column 2
Total weight of the foam-biomass in the column	46.18 g	43.28 g
The dry weight of the biomass in the column	3.52 g	3.42 g
Biomass load in the column	7.62 %	7.9 %
Influent flow rate	2.25 l/hour	7 l/hour
Influent copper concentration	6 mgl^{-1}	6 mgl^{-1}
Influent solution pH	5.36	5.39
Volume treated	60 litres	60 litres

Results of the experiment are given in tables A50, A82 and A86, and shown in figures 5.43 and 5.44.

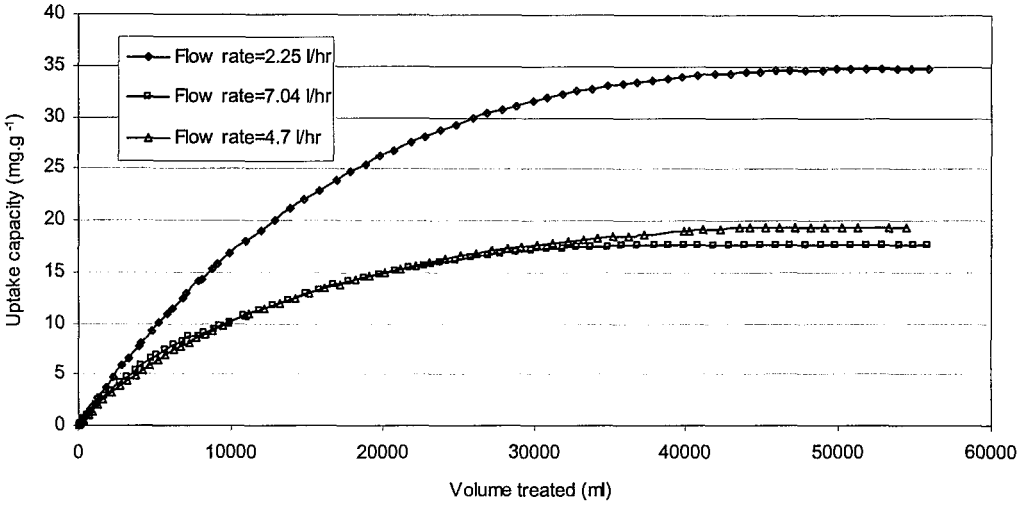


Fig. 5.43 The effect of flow rate on copper adsorption using columns of Hypol-seaweed at an influent pH 5.0, 20° C, initial copper concentration of 6 mgl^{-1}, and approximate biomass proportion of 7.5%

Figure 5.43 shows that reducing the flow rate of solution passing through the column increased the biomass adsorption capacity from 19.36 $mg.g^{-1}$ to approximately 35 $mg.g^{-1}$ when the flow rate decreased from 4.7 l/hr to 2.25 l/hr. This was expected as the contact time of the solution with the seaweed-Hypol adsorption matrix inside the column is increased. This provided a longer time for the solute to diffuse through the foam membrane and make contact with the functional groups on the biomass surface. The retention time in the column increased from around 3 to 6.2 minutes as the flow rate decreased from 4.7 to 2.25 l/hr. As can be seen in figure 5.43 increasing the flow rate from 4.7 l/hr to 7.04 l/hr did not have a noticeable effect on the adsorption capacity of the immobilised seaweed. In both columns the adsorption capacities were identical until 30 litres of test solution had been passed. After this there was divergence with the final copper adsorption capacity equilibrium reaching 19.36 $mg.g^{-1}$ for the first and 17.7 $mg.g^{-1}$ for the second column respectively.

Figure 5.44 shows a similar trend to that shown in figure 5.43, however the percentage difference between the influent and the effluent copper concentrations of the columns operated at 4.7 and 7.04 l/hr were not identical. The percentage difference between the influent and effluent copper concentration was slightly higher

at 4.7 l/hr than at a flow rate 7.04 l/hr and in both cases it was significantly lower than at a flow rate of 2.25 l/hr.

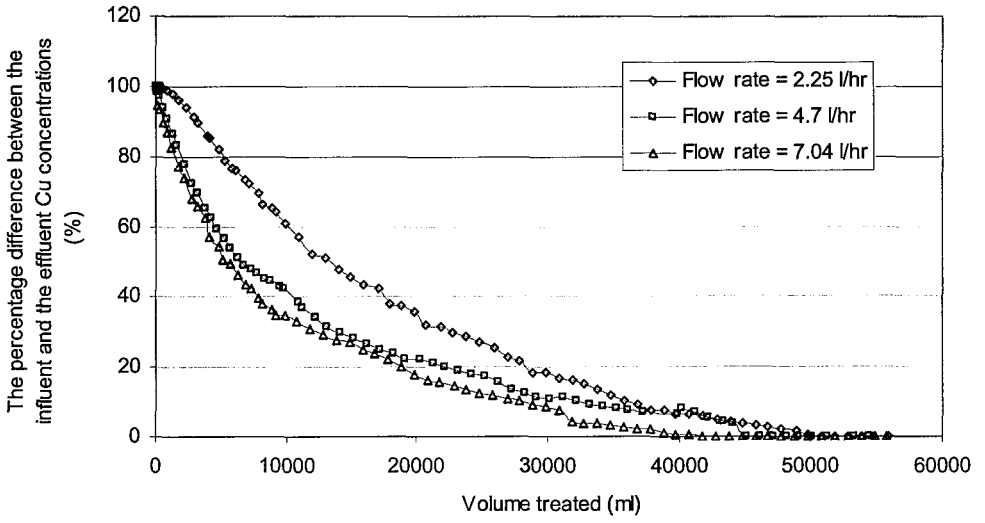


Fig. 5.44 The effect of flow rate on the percentage difference between the influent and the effluent copper concentrations by columns of cast Hypol-seaweed at influent an pH 5.0, 20° C, initial copper concentration of 6 mgl^{-1}, and approximate biomass proportion of 7.5%

Figure 5.45 shows the relationship between the flow rate and biomass uptake capacity and indicates that at a flow rate less than 5 litres per hour the biomass uptake capacity is increased but not altered when the flow rate increased above 5 litres per hour. The number of data points (i.e. 3 points) is very restricted and further work needs to be carried out to substantiate this.

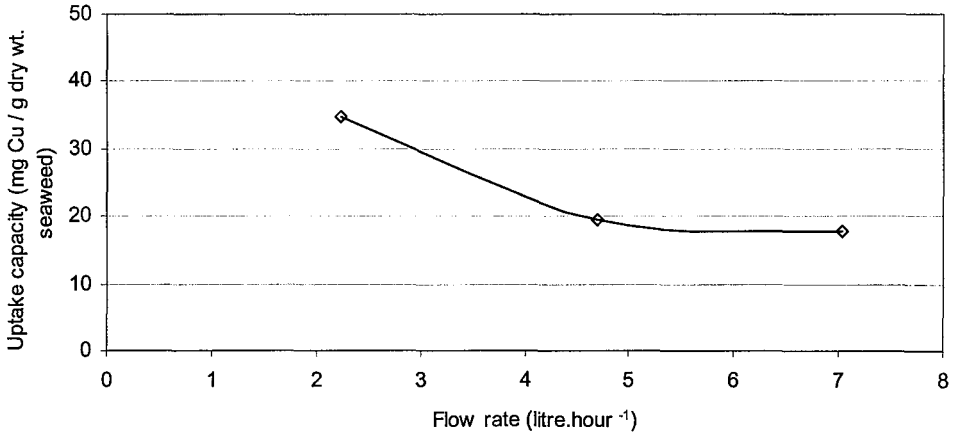


Fig. 5.45 The effect of water flow rate through columns of seaweed-foam on copper adsorption capacity of the immobilised seaweed.

The changes in pH over the course of the experiments are given in the appendix tables A51, A83 and A87, and shown in figures 5.38, 5.46 and 5.47. The pH changes observed were consistent with the biomass uptake capacity in each experiment. The drop between the initial pH value and the lowest value was 1 unit, in columns operated at flow rates of 4.7 and 7.04 l/hr, whilst the pH drop was equal to 1.32 units in the column operated at a flow rate of 2.25 l/hr. This is again is supporting evidence that there is an exchange between hydrogen and copper ions during the adsorption process.

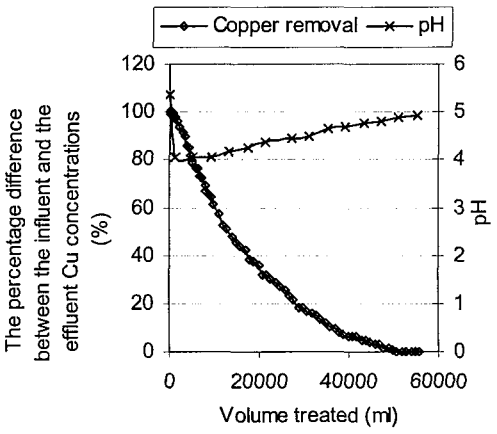


Fig. 5.46 pH changes during copper adsorption at flow rate of 2.25 l/hr

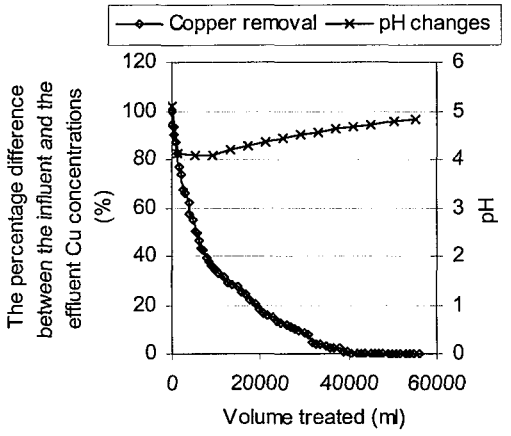


Fig. 5.47 pH changes during copper adsorption at flow rate of 7.04 l/hr

5.7.3 The effect of biomass weight on copper adsorption in seaweed-Hypol foam columns

Two columns of seaweed-Hypol foam were used to examine the effect of biomass weight on copper adsorption. The first column had biomass weight ratio of 11 %, while the second had 14.2 %. The results of these two columns were compared with the results of the column operated at 7.5 % biomass weight described in section 5.7.1.3.

The column parameters and operating conditions were as follows:

	Column 1	Column 2
Total weight of the foam-biomass in the column	47.49 g	53.33 g
The dry weight of the biomass in the column	5.23 g	7.57 g
Biomass load in the column	11.02 %	14.2 %

Influent flow rate	4.7 l/hour	4.7 l/hour
Influent copper concentration	6 mgl^{-1}	6 mgl^{-1}
Influent solution pH	5.46	5.45
Volume treated	70 litres	80 litres

Results are given in appendix tables A50, A90 and A93and shown in figures 5.48 and 5.49. The results show that removal of copper increased with increased biomass weight. The copper uptake equilibrium at a biomass weight of 7% was 19.367 $mg.g^{-1}$ after treating approximately 44 litres of a 6 mgl^{-1} copper solution. At a biomass weight of 11% this increased to 35.41 $mg.g^{-1}$ after treating approximately 69 litres of a 6 mgl^{-1} copper solution. At a biomass weight of 14.2% a copper uptake equilibrium was not reached after passing 76 litres of solution (the maximum volume capacity of the solution storage container).

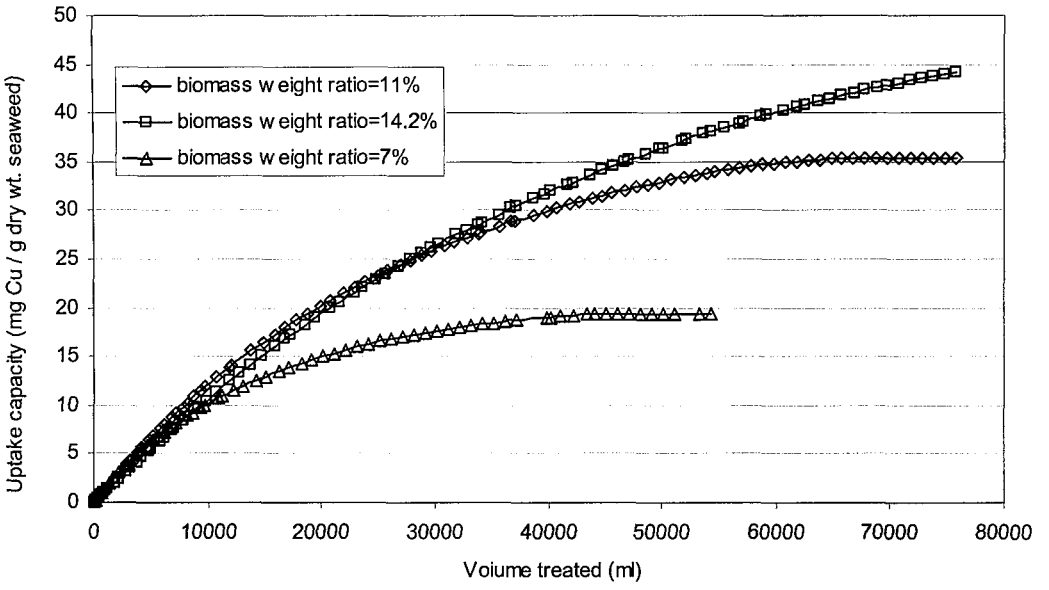


Fig. 5.48 The effect of seaweed load on copper adsorption by Hypol-seaweed columns at an influent pH 5.0, 20° C, initial copper concentration of 6 mgl^{-1}, and flow rate of 4.7 l/hr

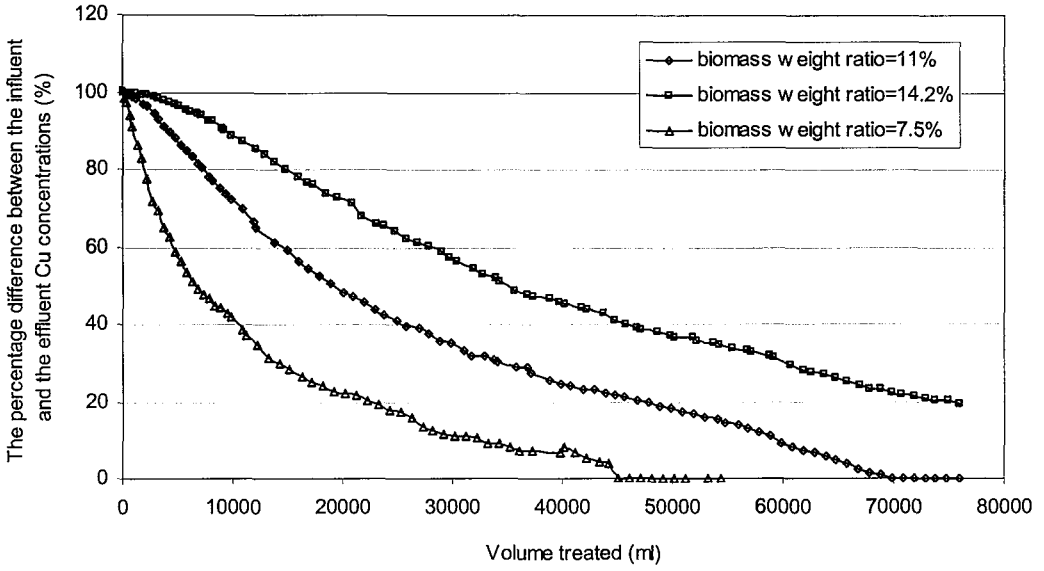


Fig. 5.49 The effect of seaweed weight on the percentage difference between the influent and the effluent copper concentrations by columns of cast in Hypol-seaweed at influent pH 5.0, T 20° C, initial copper concentration of 6 mgl^{-1}, and flow rate of 4.7 l/hr

Figure 5.50 shows the relationship between the biomass weight and copper uptake capacity which appears to increase in a linear manner. As the biomass did not reach a copper uptake equilibrium at biomass weight of 14.2%, it is represented by a dotted line on the graph. The dry weight biomass to the Hypol pre-polymer ratio is 40% when the biomass load is 14.2%, which is less than half of the 85% maximum rate that the Hypol polymer can tolerate. It should therefore be possible to double the uptake capacity doubling the biomass load to its maximum.

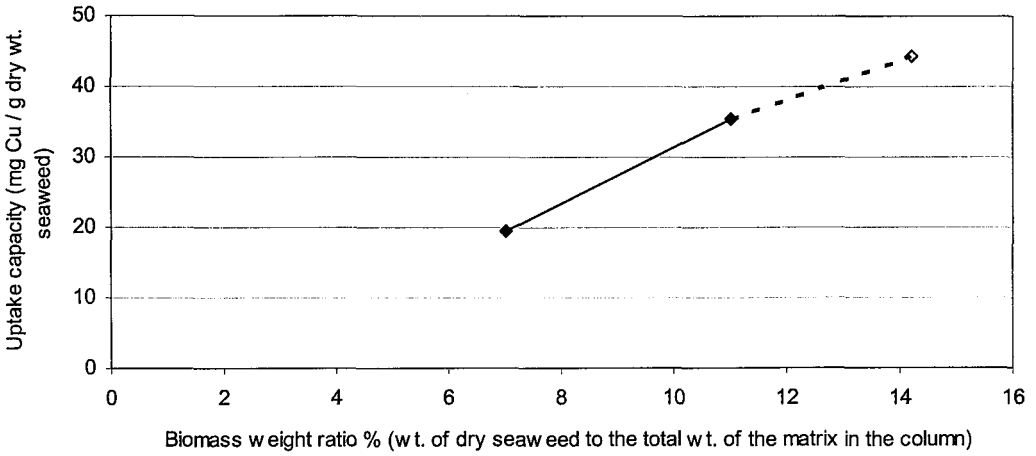


Fig. 5.50 Copper uptake capacity as a function of biomass weight in Hypol-seaweed columns

Changes in values of pH over the duration of the experiment are given in the appendix tables A51, A91 and A94, and shown in figures 5.38, 5.51 and 5.52. The reduction between the initial and the lowest pH values obtained during the adsorption processes were 1, 1.55 and 1.65 units at a column biomass weights of 7, 11 and 14.2% respectively. This increase in the hydrogen ions production when the biomass weight was increased was expected as copper uptake increased.

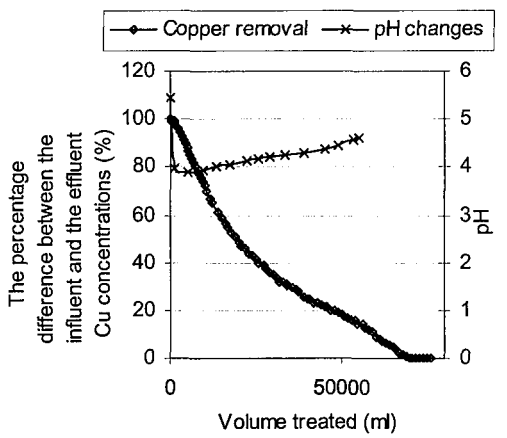


Fig. 5.51 pH changes during copper adsorption at biomass weight of 11%

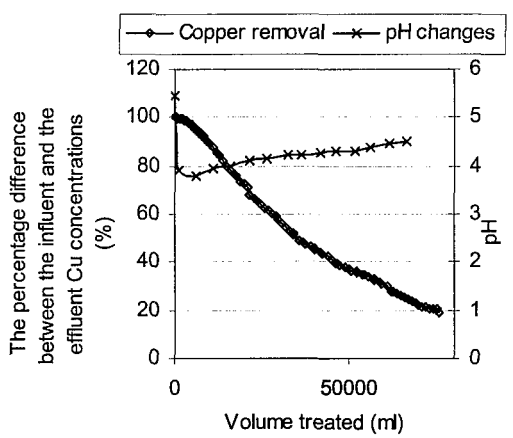


Fig. 5.52 pH changes during copper adsorption at biomass weight of 14.2%

5.7.4 The effect of initial copper concentration adsorption seaweed-Hypol columns

Three columns were used to examine the effect of different initial copper concentrations. The first, second and third columns were operated at initial copper concentration of 10, 20, and 30 mgl^{-1} respectively. The results were compared with the results of the column run at initial copper concentration of 6 mgl^{-1} as described in section 5.7.1.3.

The column parameters and operating conditions were as follows:

	Column 1	Column 2	Column 3
Total weight of the foam-biomass in the column	43.96 g	42.73g	46.60 g
The dry weight of the biomass in the column	3.28 g	3.28 g	3.65 g
Biomass load in the column	7.465 %	7.67 %	7.83 %
Influent flow rate	4.7 l/hour	4.7 l/hour	4.7 l/hour
Influent copper concentration	10 mgl^{-1}	20 mgl^{-1}	30 mgl^{-1}
Influent solution pH	5.28	5.30	5.03
Volume treated	60 litres	50 litres	50 litres

The results are given in tables A50, A96, A99 and A102, and shown in figure 5.53. The results show that both the removal and uptake of copper by the immobilised biomass increased with increasing initial copper concentration. The equilibrium copper adsorption capacity was 19.367, 26.4, 44.074 and 48.03 $mg.g^{-1}$ for initial copper concentrations of 6, 10, 20 and 30 mgl^{-1} respectively. As anticipated the higher the initial copper concentration the smaller the volume that could be treated before an equilibrium was reached. This corresponded to 44, 33, 33, 26 litres of solution at an initial copper concentration of 6, 10, 20 and 30 mgl^{-1} respectively.

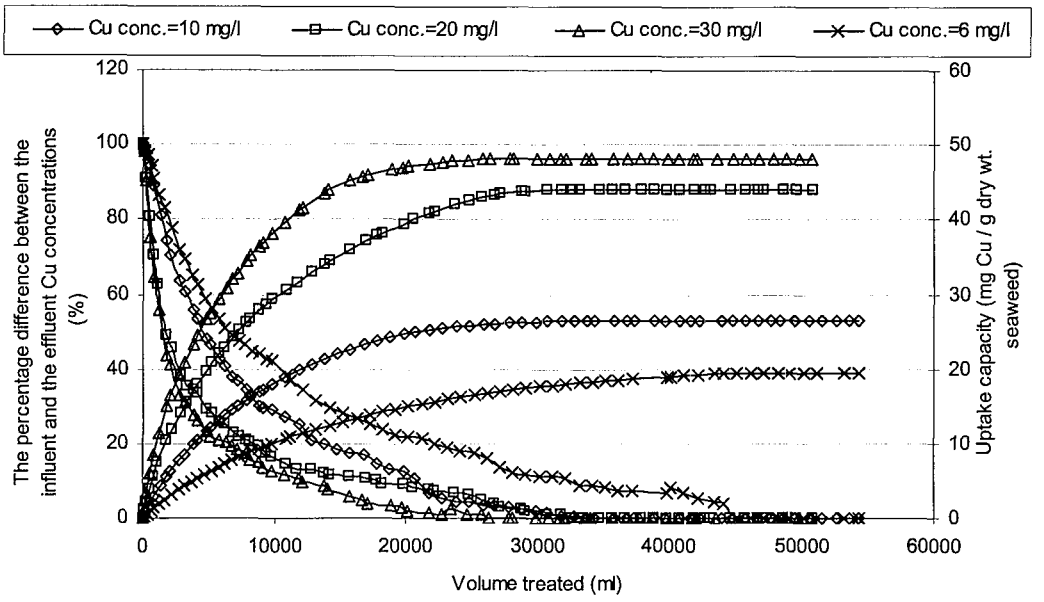


Fig. 5.53 The uptake capacity and the percentage difference between the influent and the effluent copper concentrations for 4 different initial copper concentrations (6, 10, 20 and 30 mgl^{-1}) in seaweed-Hypol columns at an influent pH 5.0, 20° C, biomass weight 7.5% (approximate), and flow rate of 4.7 l/hr

The biomass uptake capacity at equilibrium conditions for the different initial copper concentrations and their corresponding copper concentration equilibrium were used to produce a Langmuir isotherm plot. This allowed the maximum biomass copper uptake capacity to be calculated over this range of concentrations (figure 5.54). Table 5.6 gives the values used for the Langmuir isotherm plot and a calculated maximum uptake capacity (q_{max}) of 78.125 $mg.g^{-1}$. This is double the maximum capacity predicted for the beads of seaweed-Hypol foam at copper concentrations between 2-60 mgl^{-1}. The biomass load in the beads was 33.33% compared to an average of 7.5% in the columns. This could indicate that the beads should have a higher copper adsorption capacity than columns, however each mg of biomass in the columns was exposed to approximately 10.3 ml of solution (i.e. average solution volume passed through the column was 34 litres with a biomass weight of 3.3 g) at 6 – 30 mgl^{-1} Cu concentration compared to 1.45 ml of solution (i.e. 145 ml of solution for 100 mg of biomass) at Cu concentration of 2 – 60 mgl^{-1}. Also the static conditions within the columns could have allowed the solute (i.e. copper) to pass through without disturbance and make contact with the functional sites on the biomass surface

(laminar conditions), while the beads, on the other hand, were exposed to turbulent conditions (i.e. flasks shaking speed of 200 rpm).

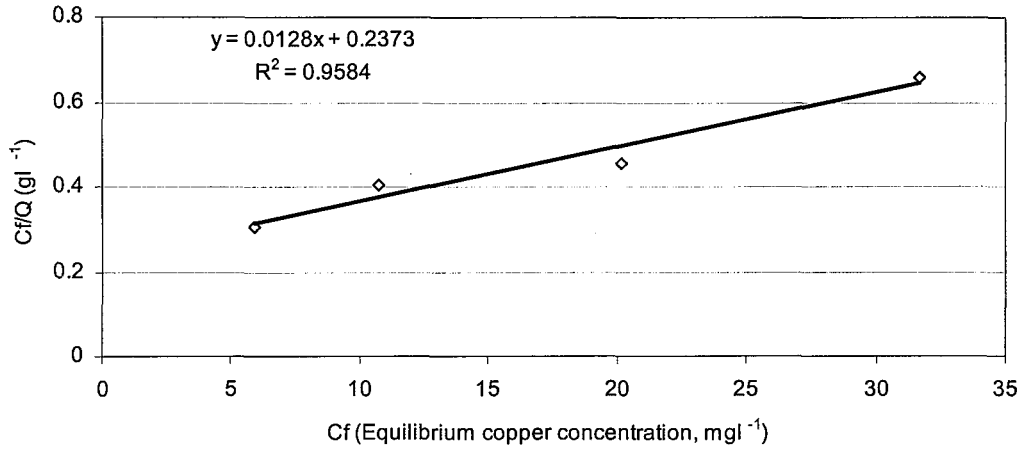


Fig. 5.54 Langmuir isotherm of copper adsorption at different initial copper concentrations using data from seaweed-Hypol columns. In all cases the influent pH was 5.0, 20° C, biomass weight of 7.5% (approximate), and a flow rate of 4.7 l/hr

Table 5.6 Langmuir isotherm parameters for Cu adsorption using seaweed-Hypol columns at 20° C, influent pH 5.0, biomass weight of 7.5 % (approximate) and initial copper concentrations of 5.9, 10.7, 20.2 and 31.7 mgl^{-1}

Cf (mgl^{-1}) *	Q ($mg.g^{-1}$)	Cf/Q (gl^{-1})	b	q_{max} ($mg.g^{-1}$)	R^2
5.9	19.367	0.305	0.054	78.125	0.96
10.73	26.405	0.406			
20.173	44.074	0.458			
31.67	48.03	0.66			

* = the average concentration of copper from the time the biomass reached equilibrium uptake capacity until the end of the experiment

The pH changes recorded during the experiments are given in appendix tables A51, A97, A100 and A103, and shown in figures 5.55 and 5.56. The drop between the initial and the lowest pH values during the adsorption processes were 1, 1.50, 1.53 and 1.55 units at an initial copper concentration of 6, 10, 20 and 30 mgl^{-1} respectively. The greater differentials in pH values as the copper uptake increased with a rise in the solutions initial copper concentration were expected.

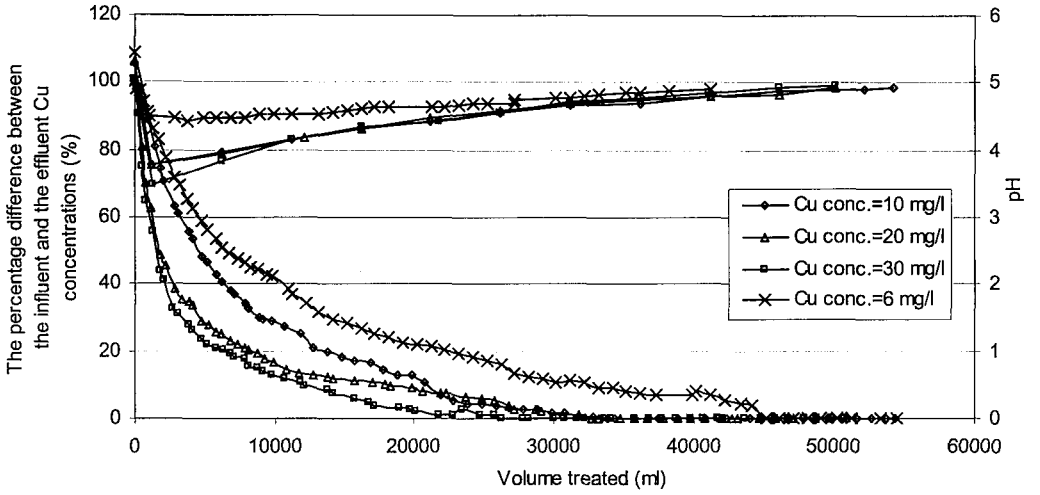


Fig. 5.55 pH changes in relation to the percentage difference between the influent and the effluent copper concentrations at different initial copper concentrations in seaweed-Hypol columns at an influent pH 5.0, 20° C, biomass weight of 7.5% (approximate), and flow rate of 4.7 l/hr

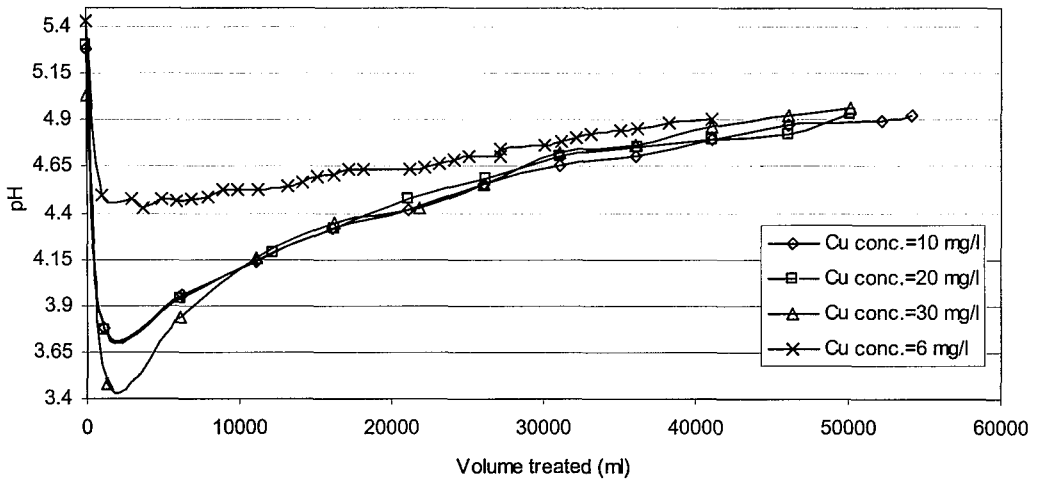


Fig. 5.56 pH changes during copper adsorption at different initial copper concentrations. Influent pH 5.0, 20° C, biomass weight of 7.5% (approximate), and a flow rate of 4.7 l/hr

5.7.5 The effect of competing ions on copper adsorption

5.7.5.1 Adsorption of Cu (II), Zn (II) and Fe (II) from a simulated metal finishing industry effluent using a column of seaweed-Hypol foam.

Effluents from metal finishing industry usually contain metals in solution within the following concentration ranges: copper 20 – 90 mgl^{-1}, iron 2 – 2300 mgl^{-1}, and zinc 10 – 35 mgl^{-1} (Patterson and Minear, 1973).

A single column of seaweed-Hypol foam was used to treat a mixed metal solution under the following conditions:

Total weight of the foam-biomass in the column	42.67 g
The dry weight of the biomass in the column	3.3 g
Biomass load in the column	7.73 %
Influent flow rate	4.7 l/hour
Influent Cu (II) concentration	6 mgl^{-1}
Influent Fe (II) concentration	6 mgl^{-1}
Influent Zn (II) concentration	6 mgl^{-1}
Influent solution pH	5.00
Volume treated	50 litres

The results are given in tables A105a, A105b and A105c, and shown in figures 5.57. They show that the presence of Zn (II) and Fe (II) had a negative effect on the adsorption of copper, and the biomass uptake capacity decreased from 19.367 $mg.g^{-1}$ when copper was the only element present (section 5.7.1.3) to 15.82 $mg.g^{-1}$ when Zn (II) and Fe (II) were also present in the solution. This decrease indicates that metal ions, other than copper, were competing for available functional groups on the biomass surface. Figure 5.57 also shows that the biomass prefers to bind to metal ions in the following order Cu (II) > Zn (II) > Fe (II). The immobilised biomass adsorption capacity for Cu (II), Zn (II) and Fe (II) were 15.82, 2.965 and 2.04 $mg.g^{-1}$ respectively.

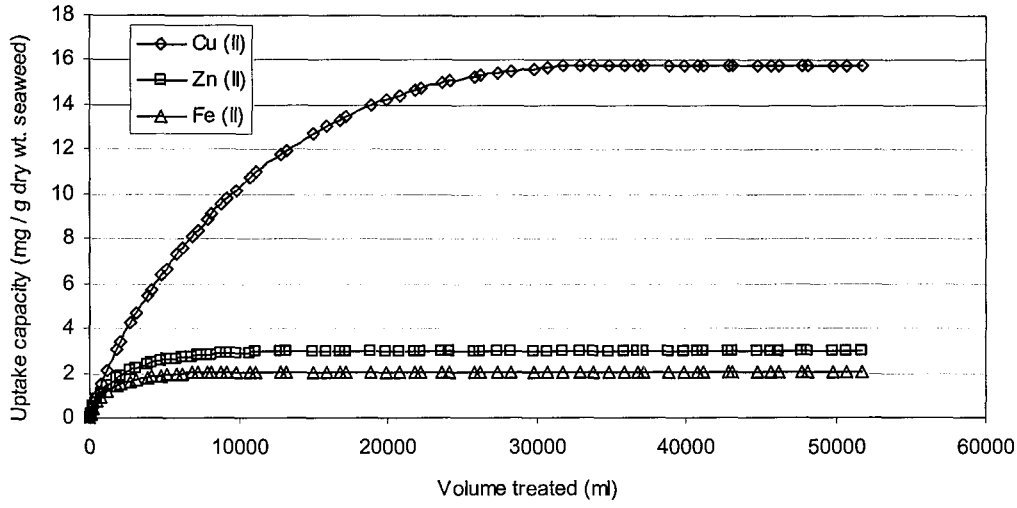


Fig. 5.57 Adsorption of Cu (II), Zn (II) and Fe (II) from a simulated metal finishing wastewater using a seaweed-Hypol column at influent pH 5.0, 20° C, approximate biomass weight of 7.5%, initial Cu (II), Zn (II) and Fe (II) of 6 mgl^{-1} and flow rate of 4.7 l/hr

The interaction between metal species in solution and ligands or functional groups on the biomass surface depends on several factors as discussed in section 2.2. Table 5.7 gives the calculated values for the covalent index and the polarizing power of the adsorbed metal species. In order to determine the ionic radius, and hence the covalent index and polarizing power, the co-ordination number is necessary. In this case it was difficult to predict the co-ordination number as we do not know the type or ligand composition that may be involved in the binding process. Therefore, the covalent index and polarizing power were calculated for all the possible co-ordination number combinations that the metal ion withstands.

Table 5.7 Calculated values of covalent index and polarizing power of the adsorbed species (Cu, Zn and Fe)

Ion	CN	Ionic radius (A°)	Electronegativity	Covalent index	Polarising power
Cu^{+2}	4	0.57	1.9	2.0577	3.51
	6	0.73		2.635	2.74
Zn^{+2}	4	0.60	1.65	1.6335	3.3333
	6	0.74		2.015	2.703
	8	0.90		2.45	2.222
Fe^{+2}	4	0.63	1.83	2.11	3.175
	6	0.61		2.043	3.278
	8	0.92		3.081	2.174

Covalent index = $(\text{electronegativity})^2$ x (ionic radius)
Polarizing power = (ion charge / ionic radius) (see section 2.2)

Figures 5.58 and 5.59 show that there was no relationship between the equilibrium adsorption capacity of Cu (II), Zn (II) and Fe (II), and their covalent index. This may be because covalent binding did not occur between the adsorbed species and ligands, and that other mechanisms could have been responsible for this uptake.

Figure 5.60 shows that the quantity of adsorbed species increased when the polarising power of the metals (at a co-ordination number of 4) increased. This may support the theory of polarizing power, as explained in section 2.2, and could also indicate that 4 ligands are shared in the complexation of these ions. However, the affiliation between the polarizing power at CN = 4 and the adsorbed quantity is not entirely linear (i.e. R^2 = 0.823) and the relationship could be exponential or polynomial. Figure 5.61 shows that no relationship exists between the polarizing power at CN = 6 and the adsorbed ions quantity.

No correlation was found to exist between the quantity of ions adsorbed and their electronegativities as shown in figure 5.62.

Figure 5.63 shows that a relationship may exist between the quantity adsorbed and ionic radii. The uptake of the adsorbed species increased as their radii (at co-ordination number of 4) decreased. This is in agreement with the results shown in

figure 5.60. Again the relation between the adsorbed quantity and ionic radii at CN = 4 is not completely linear (i.e. $R^2 = 0.8$) and may be exponential or polynomial.

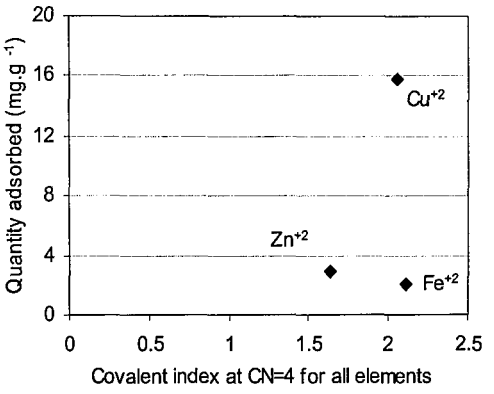


Fig. 5.58 Relation between the covalent index of the adsorbed metal species calculated at CN=4 and the uptake values

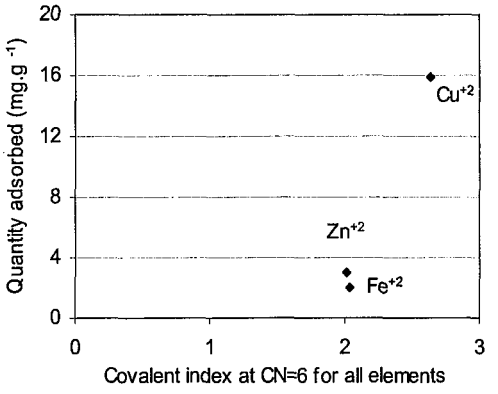


Fig. 5.59 Relation between the covalent index of the adsorbed metal species calculated at CN=6 and the uptake values

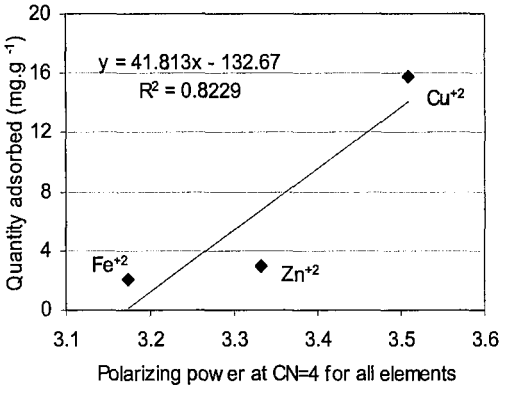


Fig. 5.60 Relation between the polarizing power of the adsorbed metal species calculated at CN=4 and the uptake values

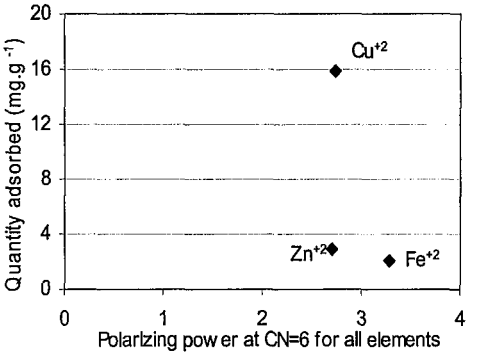


Fig. 5.61 Relation between the polarizing power of the adsorbed metal species calculated at CN=6 and the uptake values

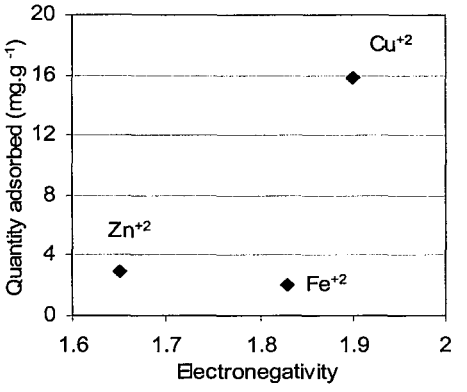


Fig. 5.62 Relation between the electronegativity of the adsorbed metal species and the uptake values

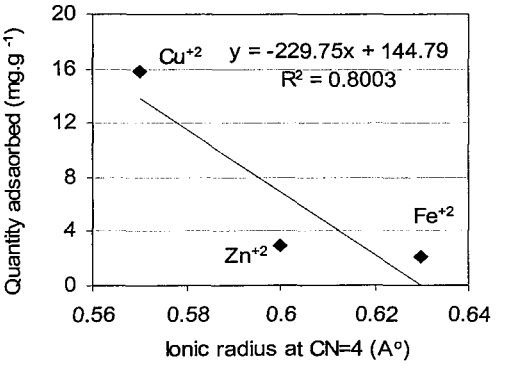


Fig. 5.63 Relation between the ionic radius of the adsorbed metal species and the uptake values

The pH changes recorded during the experiment are given in appendix table A106, and shown in figure 5.64. The change between the initial pH and lowest pH recorded during the adsorption process was 1.17, which is greater than the pH reduction recorded when copper was the only metallic ion in solution. This is logical as the total metal uptake by the biomass was greater than that for copper alone.

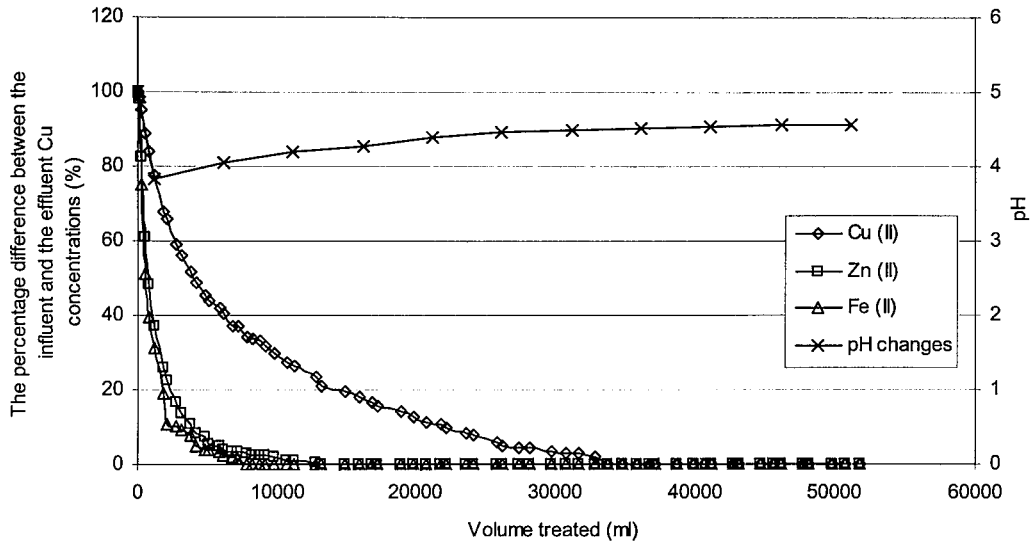


Fig. 5.64 pH changes during the removal of Cu (II), Zn (II) and Fe (II) from a simulated metal finishing wastewater using a seaweed-Hypol column at influent pH 5.0, 20° C, approximate biomass weight of 7.5%, initial Cu (II), Zn (II) and Fe (II) of 6mgl^{-1} and flow rate of 4.7 l/hr

Figure 5.64 shows that the copper uptake by the biomass ceased after treating 35 litres, while the biomass uptake ceased after treating 13 and 8 litres for Zn (II) and Fe (II) respectively.

Appendix table A107 gives the results of the control column while figure 5.65 shows these results. Figure 5.65 indicates clearly that the biomass free Hypol foam was unable to adsorb any Cu (II), Zn (II) or Fe (II) from the solution.

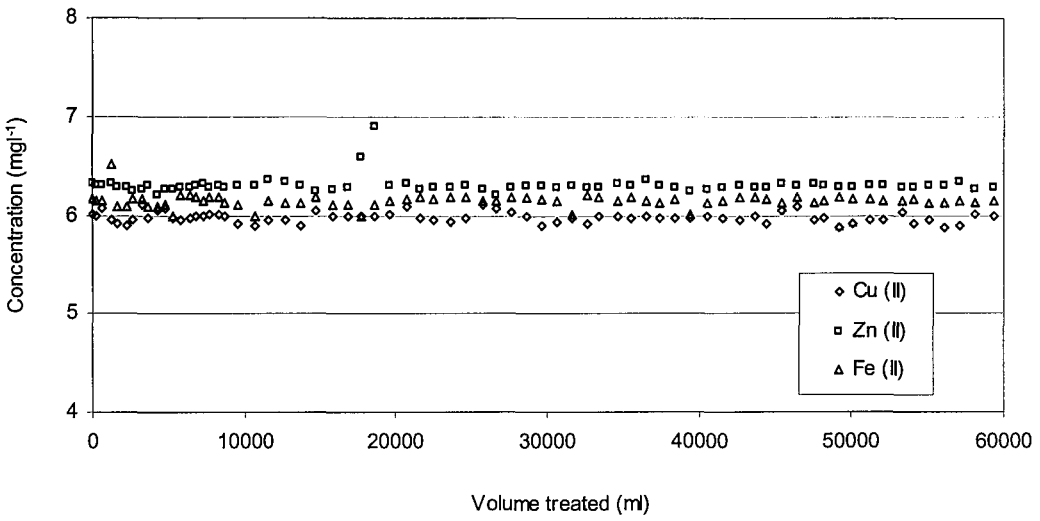


Fig. 5.65 Removal of Cu (II), Zn (II) and Fe (II) from a simulated metal finishing wastewater using a control column of biomass free Hypol foam at influent pH 5.0, T 20°C, initial Cu (II), Zn (II) and Fe (II) of 6mgl^{-1} and flow rate of 4.7 l/hr

5.7.5.2 Adsorption of Cu (II), Zn (II), Ni (II) and Cr (VI) from a simulated automatic plating of zinc base die casting effluent using column of seaweed-Hypol foam

Effluents from automatic plating of zinc base die casting industries usually contain copper, chromium, nickel and zinc in the range of (20 – 30), (5 – 10), (45 – 55) and (3 – 8) mgl^{-1} respectively, Patterson and Minear (1973).

The column used in the experiment had the following characteristics and operating conditions:

Total weight of the foam-biomass in the column	43.87 g
The dry weight of the biomass in the column	3.36 g
Biomass load in the column	7.66 %
Influent flow rate	4.7 l/hour
Influent Cu (II) concentration	6 mgl^{-1}
Influent Cr (VI) concentration	6 mgl^{-1}
Influent Ni (II) concentration	6 mgl^{-1}
Influent Zn (II) concentration	6 mgl^{-1}
Influent solution pH	5.00
Volume treated	50 litres

The results of the experiment are given in tables A109a, A109b, A109c and A109d, and shown in figure 5.66.

Figure 5.66 shows that the copper uptake reached an equilibrium at 15.752 $mg.g^{-1}$, while Zn (II), Cr (VI) and Ni (II) reached an uptake equilibrium at 3.335, 0.562 and 3.138 $mg.g^{-1}$ respectively. The uptake of copper declined from 19.36 $mg.g^{-1}$ in the presence of copper (section 5.7.1.3) to 17.16 $mg.g^{-1}$ when Zn (II), Cr (VI) and Ni (II) were added to the solution. This uptake capacity is similar to that obtained when Cu (II), Zn (II) and Fe (II) were in solution, which was 15.82 $mg.g^{-1}$. Also the adsorption of Zn is similar to that obtained in the co-presence of Cu (II) and Fe (II) that is 2.965 $mg.g^{-1}$. The slight difference in the capacities recorded between the two experiments can be ignored and could be attributed to the approximate way in which the biomass adsorption capacity was calculated. This result shows that the adsorption capacities of Cu (II) and Zn (II) did not alter in the presence of Fe (II) (section 5.7.5.1) or Cr (VI) and Ni (II) at similar initial concentrations, suggesting that the biomass may have specific functional groups, which prefer to bind to particular elements.

The biomass adsorption of Cu (II), Zn (II), Cr (VI) and Ni (II) were favoured in the following order Cu (II) > Zn (II) > Ni (II) > Cr (VI). However, figure 5.74 shows that the percentage difference between the influent and the effluent concentrations for Zn (II) and Ni (II) were virtually identical.

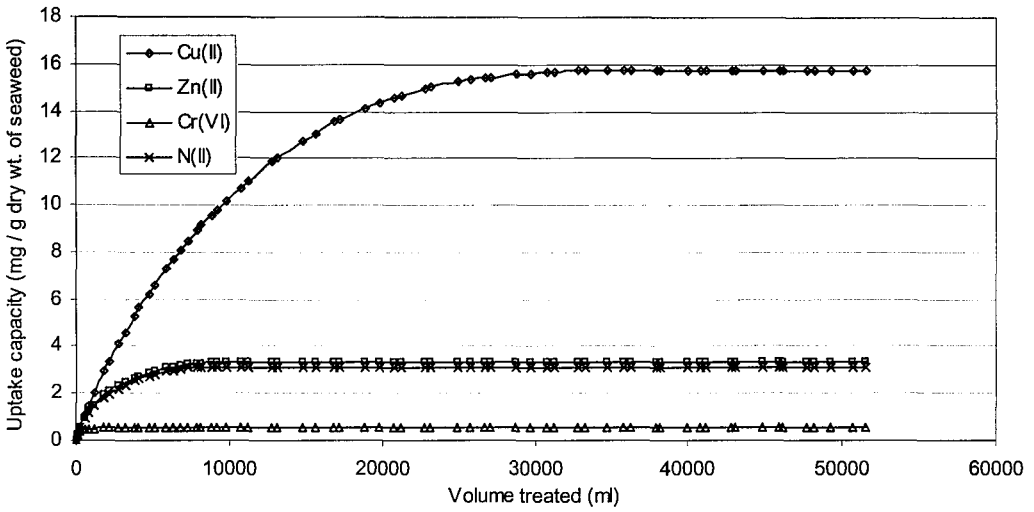


Fig. 5.66 Adsorption of Cu (II), Zn (II), Ni (II) and Cr (VI) from a simulated automatic plating of zinc base die casting effluent using a seaweed-Hypol column at an influent pH 5.0, 20° C, approximate biomass weight of 7.5%, initial Cu (II), Zn (II), Ni (II) and Cr (VI) of 6 mgl^{-1} and flow rate of 4.7 l/hr

Table 5.8 represents the covalent index and polarizing power values for the adsorbed metal species, while figures 5.67 to 5.73 show the relationship between the values obtained in table 5.8 and the adsorption values for the adsorbed metal species.

Table 5.8 Calculated values of covalent index and polarizing power of the adsorbed species (Cu, Zn, Ni and Cr)

Ion	CN	Ionic radius (A^o)	Electronegativity	Covalent index	Polarising power
Cu^{+2}	4	0.57	1.9	2.06	3.51
	6	0.73		2.635	2.74
Zn^{+2}	4	0.60	1.65	1.633	3.333
	6	0.74		2.015	2.703
	8	0.90		2.45	2.222
Ni^{+2}	4	0.49	1.91	1.787	4.082
	6	0.69		2.52	2.898
Cr^{+6}	4	0.26	1.66	0.716	23.077
	6	0.44		1.212	13.64

Covalent index = $(\text{electronegativity})^2$ x (ionic radius)
Polarizing power = (ion charge / ionic radius) (see section 2.2)

In contrast to the findings in section 5.7.5.1, figures 5.67 to 5.73 indicate that no clear correlation existed between quantities of the adsorbed metal species and their covalent indices, polarizing powers, electro negativities or radii.

It is believed that clearer picture for the relation between metals physical characteristics and their biomass adsorption capacity could be obtained using non immobilised biomasses.

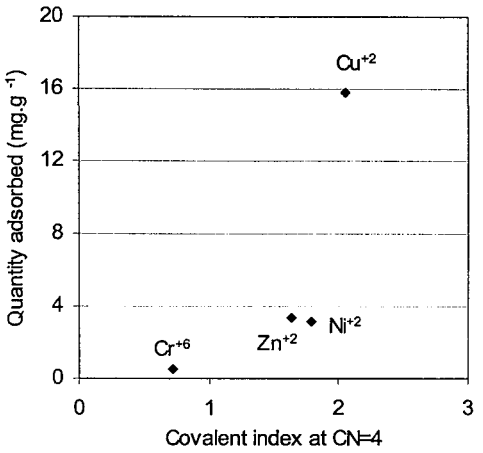


Fig. 5.67 Relation between the covalent index of the adsorbed metal species calculated at CN=4 and the uptake values

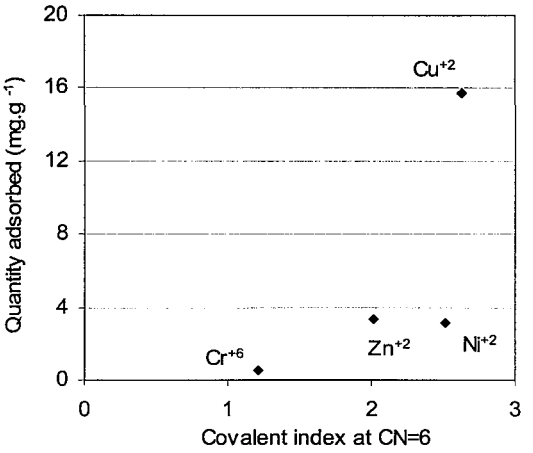


Fig. 5.68 Relation between the covalent index of the adsorbed metal species calculated at CN=6 and the uptake values

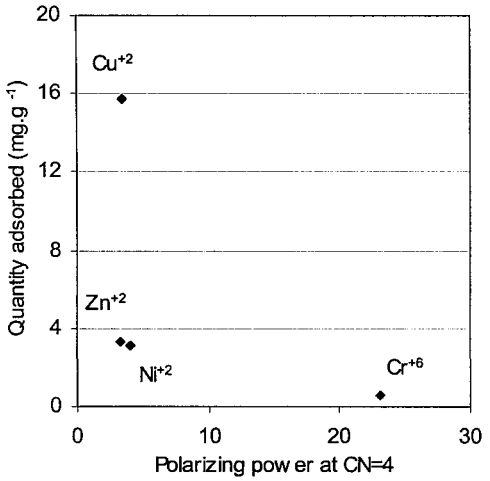


Fig. 5.69 Relation between the polarizing power of the adsorbed metal species calculated at CN=4 and the uptake values

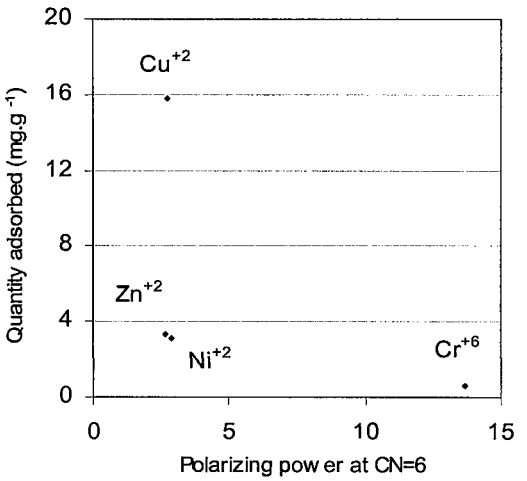


Fig. 5.70 Relation between the polarizing power of the adsorbed metal species calculated at CN=6 and the uptake values

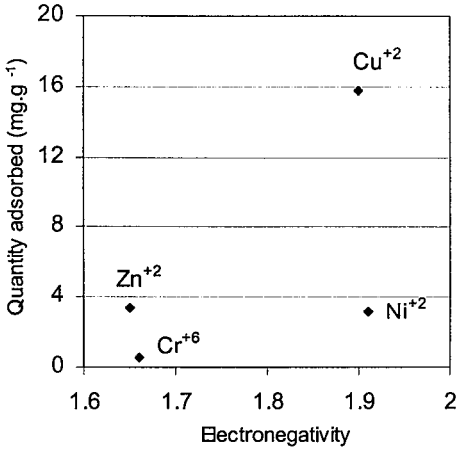


Fig. 5.71 Relation between the electronegativity of the adsorbed metal species and the uptake values

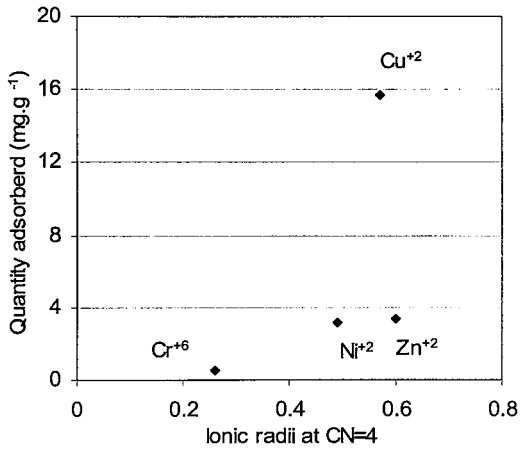


Fig. 5.72 Relation between the ionic radius at CN=4 of the adsorbed metal species and the uptake values

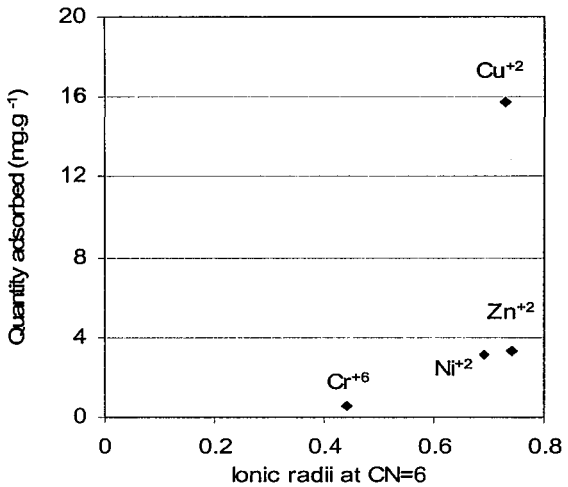


Fig. 5.73 Relation between the ionic radius at CN=6 of the adsorbed metal species and the uptake values

In figure 5.74, the results for Cu (II), Zn (II), Ni (II) and Cr (VI) show that break through occurred after passing 35, 11, 10, and 3 litres of solution.

The pH changes recorded over the experiment are given in the appendix table A110, and shown in figure 5.74. The change in value between the initial pH and lowest value obtained was 1.25, which is greater than the fall of 1.17 units recorded in the presence of Zn (II), Fe (II) and Cu (II) and 1 unit when Cu (II) was the only element in solution. Again, the total biomass uptake capacity for the four elements was greater than that of either copper alone or a combination of copper, zinc and iron.

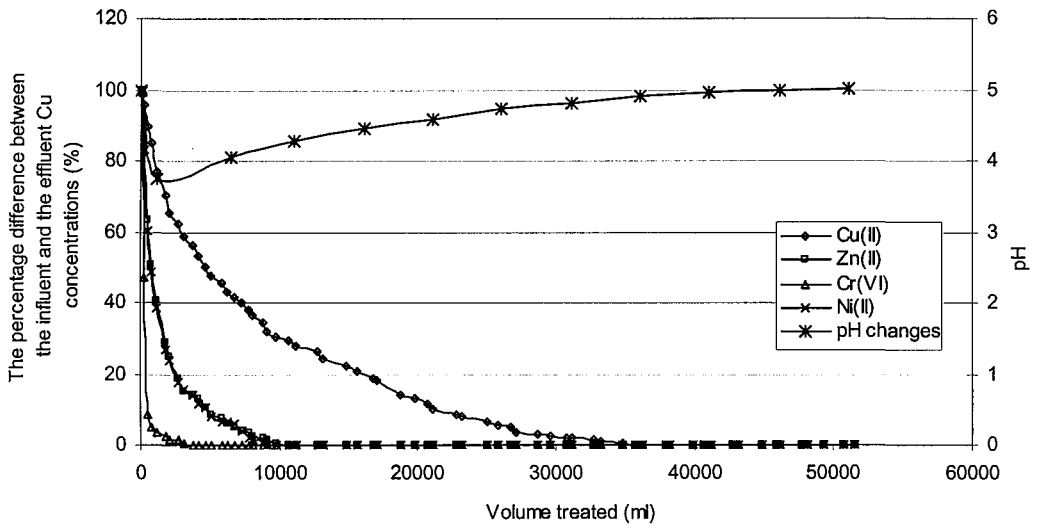


Fig. 5.74 pH changes during removal of Cu (II), Zn (II), Ni (II) and Cr (VI) from a simulated automatic plating of zinc base die casting effluent using a seaweed-Hypol column at an influent pH 5.0, 20° C, approximate biomass weight of 7.5%, initial Cu (II), Zn (II), Ni (II) and Cr (VI) of 6 mgl^{-1} and flow rate of 4.7 l/hr

Appendix table A111 gives the results of the control column while figure 5.75 shows these results. Figure 5.75 shows that the biomass free Hypol foam was unable to adsorb any Cu (II), Zn (II), Ni (II) or Cr (VI) from the solution.

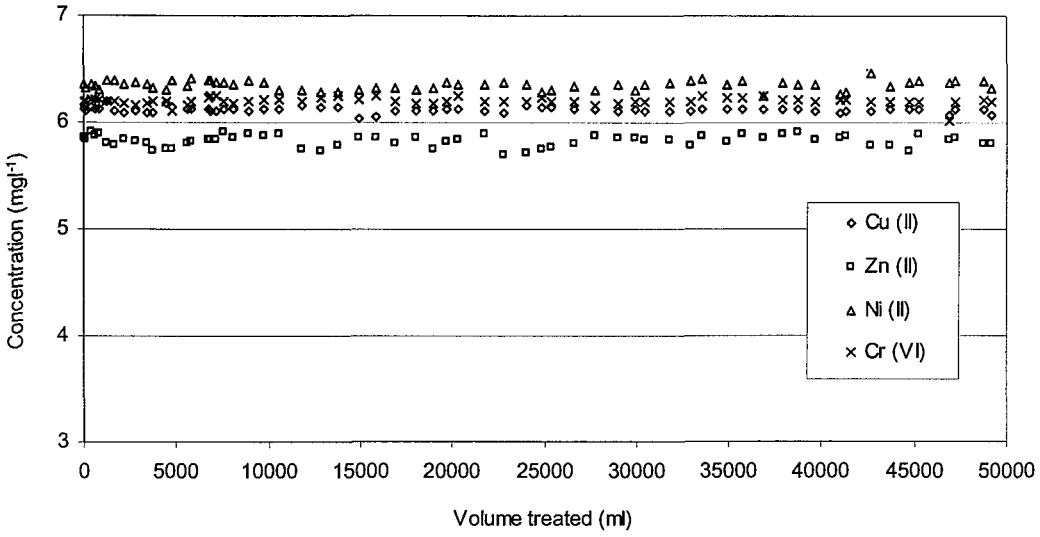


Fig. 5.75 Removal of Cu (II), Zn (II), Ni (II) and Cr (VI) from a simulated automatic plating of zinc base die casting effluent using a control column of biomass free Hypol foam at an influent pH 5.0, 20° C, initial Cu (II), Zn (II), Ni (II) and Cr (VI) of 6 mgl^{-1} and flow rate of 4.7 l/hr

5.7.6 Adsorption of Cu (II), Zn (II), Ni (II) and Cr (VI) from a simulated automatic plating of zinc base die casting effluent using two columns in series of seaweed-Hypol foam

The experiment in section 5.7.5.2 was repeated using 2 columns of seaweed-Hypol foam connected in series as shown in plate 5.21.



Plate 5.21 Two columns of seaweed-Hypol foam connected in series

The operating conditions for the two columns were:

	Column 1	Column 2
Total weight of the foam-biomass in the column	44.11 g	42.68 g
The dry weight of the biomass in the column	3.43 g	3.39 g
Biomass load in the column	7.78 %	7.95 %

The two columns where connected on series and used in up flow mode to treat synthetic solution under the following parameters:

Influent flow rate	4.7 l/hour
Influent Cu (II) concentration	6 mgl^{-1}
Influent Cr (VI) concentration	6 mgl^{-1}
Influent Ni (II) concentration	6 mgl^{-1}
Influent Zn (II) concentration	6 mgl^{-1}
Influent solution pH	5.00
Volume to be treated	50 litres

The results are given in tables A114a, A114b, A114c and A114d, and shown in figure 5.76. The biomass uptake of copper had not reached an equilibrium after treating 65 litres of solution and reached an uptake of 19.8856 $mg.g^{-1}$ at this volume. This indicates that the columns could have removed even more copper (i.e. treating a greater volume of solution). The biomass reached an equilibrium uptake of 3.482, 3.34 and 1.4254 $mg.g^{-1}$ for Zn (II), Ni (II) and Cr (VI) respectively.

Compared to one column, the uptake of Cu increased from an equilibrium uptake capacity of 15.752 $mg.g^{-1}$ after treating 35 litres to a non-equilibrium uptake of 19.88 $mg.g^{-1}$ after treating 65 litres. For Zn (II), Cr (VI) and Ni (II) the biomass equilibrium uptake capacity increased from 3.335, 0.562 and 3.138 $mg.g^{-1}$ in one column after treating 11, 3 and 10 litres respectively to 3.482, 1.4254 and 3.34 $mg.g^{-1}$ after treating 21.5, 12 and 21 litres of solution in two columns.

In both columns the ratio of biomass to Hypol pre-polymer used in the manufacturing process is approximately 20%, which could be increased 4 fold to further increase the removal capacity of the columns as suggested in section 5.7.3.

Two or more columns could be used in series where the first column can be removed from the process line when it is exhausted and replaced with a new one at the end of the sequence. The removed column can be regenerated and returned to the treatment line in the same manner.

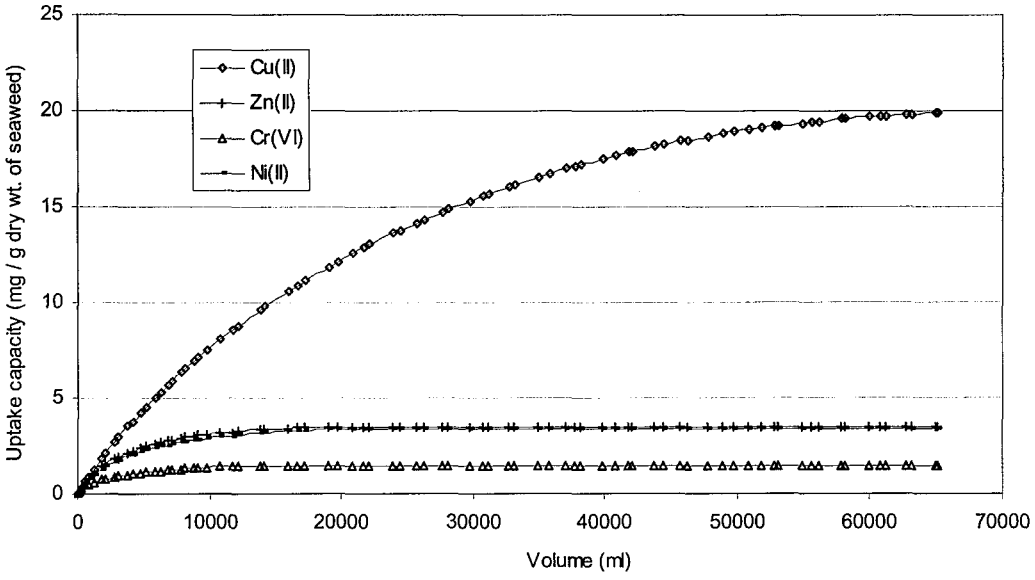


Fig. 5.76 Adsorption of Cu (II), Zn (II), Ni (II) and Cr (VI) from a simulated automatic plating of zinc base die casting effluent using 2 columns in series of seaweed-Hypol foam at an influent pH 5.0, 20° C, approximate biomass weight of 7.5% in each column, initial Cu (II), Zn (II), Ni (II) and Cr (VI) of 6 mgl^{-1} and flow rate of 4.7 l/hr

The pH changes recorded during the experiment are given in the appendix table A115, and shown in figure 5.77. The change between the initial and lowest pH values obtained during the adsorption process was 1.39. This is greater than the reduction of 1.25 recorded when only one column was used. This was expected as the total biomass uptake capacity of the four metallic ions in two columns is greater than that in one column.

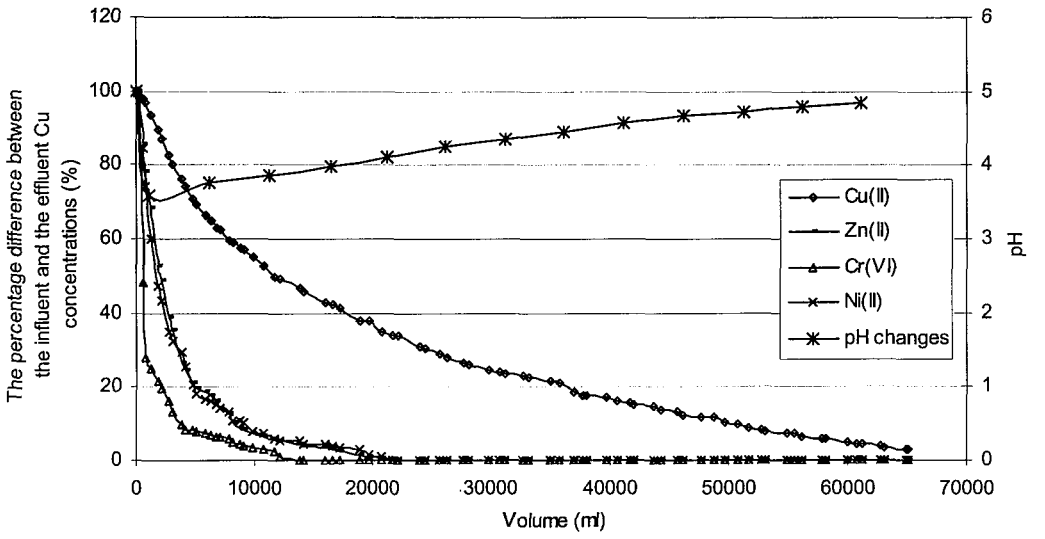


Fig. 5.77 pH changes during the removal of Cu (II), Zn (II), Ni (II) and Cr (VI) from a simulated automatic plating of zinc base die casting effluent using 2 columns in series of seaweed-Hypol foam at an influent pH 5.0, 20° C, approximate biomass weight of 7.5% in each column, initial Cu (II), Zn (II), Ni (II) and Cr (VI) of 6 mgl^{-1} and flow rate of 4.7 l/hr

CHAPTER 6

Discussion and conclusion

6.1 Immobilisation of *Rhizopus oryzea* in seven selected types of polymers

The 60 minutes adsorption capacity of both free and polyurethane immobilised *Rhizopus oryzea* was 1.5 mg of copper per g of biomass. With the exception of the k-carrageenan/biomass matrix the 60 minutes adsorption capacity of all the other polymer/biomass matrices was lower. The 60 minute adsorption capacities of alginate, polysulfone, PEI, polyacrylamide and polyvinlformal immobilised biomasses were 0.38, 0.622, 0.38, 0.55 and 0.187 $mg.g^{-1}$ respectively. As a percentage of that achieved by free biomass these capacities represented: 42.63% for polysulfone, 37.67% for polyacrylamide, 26.1% for PEI, 25.96% for alginate and 12.82% for polyvinlformal. The k-carrageenan-biomass/polymer matrix showed a 60 minutes adsorption capacity equal to that of free biomass, however, the result is erroneous as the beads were unstable and dissolved after 30 minutes, releasing the biomass into free suspension.
Increasing the contact time from 1 to 4 hours did not affect the adsorption capacity of the non-immobilised biomass, polyurethane and polyvinlformal immobilised biomasses. However, this increased the uptake capacity of alginate, polysulfone, PEI and polyacrylamide immobilised biomasses to 0.853, 0.785, 0.61, 0.838 $mg.g^{-1}$ respectively. This indicates that these polymers have a low porosity and that a longer time may be required for the biomass to reach equilibrium compared with the polyurethane immobilised biomass. Of the available copper in solution (95 ml of a 2 mgl^{-1} solution) the free fungal biomass had removed 86% of this at the end of 60 minutes exposure whilst biomass immobilised in polyurethane, polysulfone, polyacrylamide, alginate, PEI, and polyvinlformal showed removals of 77, 31.8, 30.7, 25.1, 21.5 and 11% respectively. Table 6.1 summarizes these results.

Table 6.1: Copper uptake capacity and the percentage difference between the initial and final copper concentrations of non-immobilised and immobilised *Rhizopus oryzea* in seven selected types of polymers at 2 mgl^{-1} Cu concentration, initial pH 7.0, 200 rpm shaking speed, 20° C and contact time of 1 and 4 hours.

Matrix tested	Adsorption capacity (mg Cu / g dry wt. of biomass)		% difference between initial and final copper concentration	
	1 hour	4 hours	1 hour	4 hours
Non-immobilised fungal biomass	1.5	1.5	86	81.3
Biomass/polyurethane	1.5	1.5	77	80
Biomass/k-carrageenan	-	-	-	-
Biomass/alginate	0.38	0.853	25.1	57.27
Biomass/polysulfone	0.622	0.785	31.8	49.4
Biomass/PEI	0.38	0.61	21.5	35.37
Biomass/polyacrylamide	0.55	0.838	30.7	48.38
Biomass/polyvinlformal	0.187	0.191	11	12.27

Biomass leaching from the biomass/polymer matrix was observed in the case of polyurethane and PEI with a 20% and 4% respective loss in weight at the end of the experiment. This was probably as a result of shaking of the biomass/polymer matrix in the flasks, and would probably not occur in a static packed bed reactor. No biomass leaching was observed from the other polymer matrices.

It is difficult to compare these results to those of previous work where the same polymers have been used. This is because a variety of different micro-organisms and metals were used with experimental conditions developed unique to that research. It was not the intention of this work to repeat the work of others, but to simply compare the polymer immobilisation systems previously reported under comparable experimental condition. In doing this biomass adsorption capacities and percentage removals were measured for copper in the various matrices; these can be compared to the findings of the original work using these polymers, but with caution.

Pfister and Kuhn (1990) reported that *Z. Ramigera* immobilised in Ca-alginate was able to adsorb at least 97% of cadmium, at an initial concentration of 2 mgl^{-1}, at pH 6-8 within a contact period of 30 minutes while free alginate polymer was able to remove 54% of Cd under the same conditions. The removal potential for cadmium is therefore greater than that seen for copper in this study both for the polymer and polymer/biomass matrix.

Tobin et al (1993) reported that the biosorptive capacity of *Rhizopus arrhizus* immobilised in alginate, polyacrylamide and polyvinlformal to be approximately

equal to the capacity of the free biomass; these tests were carried out with cadmium at a concentration of 160 mgl^{-1} and a pH of 6.2. The same fungal species was used as in the present study, but with a different metal and concentration which produced a much more favourable metal removal than reported here.

Darnall et al (1986) reported that polyacrylamide polymer without biomass did not adsorb Au^{3+}, Cu^{2+} and Zn^{2+} when a solution containing these metals was passed through a column; this agrees with the findings reported here which showed that biomass free polyacrylamide had no affinity for Cu^{2+}.

Brierly and Brierley (1993) reported that when 0.5 g of PEI immobilised *Bacillus* was suspended in 100 ml of 100 mg of Cu^{2+} at an initial pH 4.0 and 30° C, it adsorbed 114 mg of Cu^{2+} per g of granule dry wt. at exposure time of 24 hour and shaking speed of 150 rpm.

Ferguson et al. (1989) reported that polysulfone beads containing 50 g of yeast per litre of wet-settled beads extracted 64% of the copper from a waste water solution containing 2.1 mgl^{-1} of copper in 24 hours which agrees with our findings taking in consideration the contact time.

The polymer matrices without biomass did not show a noticeable copper adsorption capacity, except k-carrageenan, alginate and polysulfhone beads which removed approximately 21, 20 and 17.5% of copper respectively from the solution at the end of the 1 hour contact period. These results agree well with previous work when considering the low initial concentration of copper as used in these experiments. Pfister and Kuhn (1990) reported that free alginate beads were able to remove 54% of Cd when they were exposed to a 2 mgl^{-1} solution for 30 min at pH 6 to 8.

Tobin et al. (1993) reported that free polyacrylamide and polyvinlformal did not show any removal capacity of Cd^{2+} at an initial Cd^{2+} concentration of 160 mgl^{-1} and pH 6.2 which agree with the findings presented here. They also found that free alginate beads were able to remove an equivalent amount to that of the free biomass, this does not agree with the results presented here.

Brierly and Brierley (1993) reported that free PEI polymer with cross-linking agent glutaraldehyde at ratio equal to (2:1) respectively was able to adsorb 74 mg of Cu per g of granule-dry weight when exposed to a 100 ml of 100 mgl^{-1} of Cu (II) at pH 4.0 and 30° C for 24 hours, this does not agree with the findings presented here.

6.2 Manufacturing of hydrophobic and hydrophilic polyurethane

Mixer shape, mixing speed and mixing time had the same effect on manufacturing of both the hydrophobic and hydrophilic foams as they are both 'blown' by the carbon dioxide gas produced during the manufacturing process. Mixing time was found to be the most important factor affecting the foam pore size. Mixing the ingredients for a prolonged time allows gas to escape, resulting in a small pore size and a reduced final foam volume, while mixing for a short time resulted in a large pore size with heterogeneous foam structure.

Mixer shape was also found to be an important factor in achieving a satisfactory mixing during the limited time over which mixing could take place. Of the three mixers tested the 2 pin mixer was the best, followed by the paint mixer and then the oar mixer. The mixers were only tested on small volumes of the foam components and the results could be quite different if large quantities were being mixed. Hand mixing with a spatula resulted in a very good foam structure due to the small quantity of the mixed components, however once biomass material was added to the mixture this method was inefficient.

Experiments showed that the water ratio could be as much as 12% of the foam mixture's total weight in the hydrophobic polyurethane while it could be as much as 250% of the pre-polymer weight in the hydrophilic polyurethane. Results showed that water does not play a significant role in determination of the pore size in polyurethane foams.

Pore size measurements of microscopic slices of hydrophobic foam manufactured at different water ratios gave an average pore sizes of 1.4, 1.66, 1.58, 1.64, and 1.11 mm for the foams manufactured with no water, 0.25%, 0.55, 1% and 1.5% water ratio respectively. Previous research has suggested that pore size in hydrophilic foam is related to the ratio of water to polymer (Klein and Kluge, 1981; Klein *et al.*, 1979). In this work, however, it was found that the key element affecting the pore size, in both the conventional hydrophobic and hydrophilic polyurethane, was the mixing time and then mixing speed.

The hydrophobic polyurethane experiments showed that increasing the ratio of the isocyanates increased the hardness of the foam, while increasing the ratio of resin resulted in softer foam without affecting the foam pore sizes.

The hydrophilic polyurethane experiments showed that a water ratio below 50% led to foam shrinkage and structural damage within minutes. On the other hand a water ratio above or equal to 200% left water residues at the bottom of the mixing vessel. Typically a ratio of 1 part water: 1 part pre-polymer was used in the manufacturing process, but if external materials are to be added the water quantity should be increased to 1.5 or 2 so as to ease the mixing process.

Surfactants were found to play a major role in giving the hydrophilic foam interconnected pores. They attack the foam body breaking the foam textile and rupturing any thin film of gas bubbles that may had not ruptured during the foam formation giving interconnected pores. This agrees with the findings of Lupton and Zupancic (1991) who reported that surfactants may play a role in giving the foam interconnected pores.

Lupton and Zupancic (1991) also used sodium bicarbonate and acetic acid in their foam manufacturing to produce extra carbon dioxide to improve the foam's structure, however no differences were observed in this study between the structures of foam manufactured with or without generating carbon dioxide by this method. When the ratio of generated carbon dioxide reached ≥ 7.8125 mM the foam matrix was destroyed and may be due to a very low pH associated with the high ratio of acetic acid.

Previous research has reported that factors such as temperature, pH (Havens and Rase, 1993) and pressure (Klein and Kluge, 1981) could play an important role in the properties of manufactured foam. These factors were not investigated in this study as special tools and equipment are needed to investigate them.

6.3 Use of hydrophobic and hydrophilic polyurethane immobilised *Rhizopus oryzea* and *Ascophyllum nodosum* in copper removal

6.3.1 Beads (cubes) of biomass/Hydrophilic foam experiments

The hydrophobic polyurethane did not work as an immobilisation matrix for biomass for copper removal. Immobilised *Rhizopus oryzea* in beads (4 mm side length) did not adsorb any copper from a 2 mgl^{-1} initial concentration solution. Microscopic

investigation of the foam-biomass matrix showed that the biomass particles were coated by the polymer, effectively isolating them from contact with the copper solution. The solution could not diffuse through the polymer to reach the biomass. Attempts at exposing the biomass by acid and alkaline treatments were unsuccessful in improving the uptake.

The hydrophilic polyurethane proved to be a successful matrix for the immobilisation of both *Rhizopus oryzea* and *Ascophyllum nodosum* for copper removal. Beads (4 mm side length) of *Rhizopus oryzea*/Hypol foam were used in 4 consecutive cycles and showed copper adsorption capacity between 10 and 13 mg g^{-1} at copper concentration (2-15) mgl^{-1} and pH 5.0. The results showed good agreement with Langmuir isotherm equation.

Beads (4 mm side length) of *Ascophyllum nodosum*/Hypol foam showed a maximum immobilised biomass uptake capacity (q_{max}) of 39 mg Cu g^{-1} at copper concentrations of (2-60) mgl^{-1}, pH 5.0 and 20°C. Copper was successfully eluted by lowering the solution pH < 2 and the beads were reused in five consecutive adsorption experiments and showed an initial lowering of adsorption capacity but stabilised at an uptake capacity of 15 $mg.g^{-1}$ dry wt. by the third re-use. The maximum uptake capacity of the immobilised biomass was shown to be pH dependent and was reduced to 35 and 26.4 mg of Cu g^{-1} dry wt. at pH's of 4.0 and 3.0 respectively. Changing the solution's temperature increased the immobilised biomass copper capacity slightly from 36.63 to 38.91 and to 40.486 $mg.g^{-1}$ when the temperature was raised from 10 to 20 and then to 30° C respectively. Although these changes could be considered insignificant, however wider range of temperature should be investigated to draw a clearer picture of the temperature effect on the immobilised biomass adsorption capacity. Table 6.2 summarizes the results of copper adsorption using beads of biomass/foam.

Table 6.2: Copper adsorption results using beads of biomass/Hypol foam at different experimental conditions

Type of biomass	Cu conc. used (mgl^{-1})	Investigated factor		Max. uptake capacity calculated using Langmuir ($mg.g^{-1}$)
Rhizopus oryzea	2 - 15	Experiments were conducted at 20° C, pH 5.0, and 0.69 gl^{-1} biomass concentration		13
Ascophyllum nodosum	2 - 60	**Temperature** (Other factors were kept constant at pH 5.0 and 0.69 gl^{-1})	30° C	40.5
			20° C	39
			10° C	36.63
		pH (Other factors were kept constant at 20° C and 0.69 gl^{-1})	5	39
			4	35
			3	26.4

Comparing the results from this study with results with other research is not possible as this is the first study in which biomass has been immobilised in hydrophilic polyurethane foam during the fabrication process and then used for the removal of contaminants from aquatic solutions. Kapoor and Viraraghavan (1997), in their review of fungi as biosorbents, reported copper uptake capacities equal of 7 and 16 $mg.g^{-1}$ for *Rhizopus arrhizus* (the former name for *Rhizopus oryzea*) which is in agreement of our results.

Other workers have reported copper removal using *A. nodosum,* however, for the most part the seaweed has been used without acid pre-treatment. Chong and Volesky (1995) found a q_{max} of 63 $mg.g^{-1}$ (0.99 mmol Cu g^{-1}) dry wt. when *A. nodosum* was crosslinked with formaldehyde and washed with distilled water and used to adsorb Cu at pH 4.5.

Leush *et al.* (1995) reported a q_{max} equal to 77, 83, and 51 mg Cu g^{-1} dry wt. of biomass when fresh dried *A. nodosum* was cross linked with PEI, formaldehyde and glutaraldehyde respectively at pH 5.0.

Results on the effect of pH on the seaweed adsorption capacity are generally in agreement with other research conducted on heavy metal uptake using different biosorbents (Harris and Ramelow, 1990; Kappor and Virarchavan, 1997; Zouboulis *et al.*, 1999; Urrutia, 1997). It is accepted that at low pH the hydrogen ions tend to

compete with metal ions for the available sites on the biomass, thus lowering the metal uptake capacity. Increasing the pH tends to reduce the concentration of protons, inducing net negative charge on the biomass cell wall thereby attracting more copper cations, consequently increasing capacity. Also solution's pH affects ligands speciation on the biomass surface which in turn affects the biomass adsorption capacity.

Results on the effect of temperature are difficult to be compared with other studies as most metal biosorption studies using algae have been carried out at temperatures close to ambient (Garnham, 1997). In studies where temperature has been varied between 0 and 30°C little effect was observed on the adsorptive capacities of manganese or molybdenum by *Chlorella sp.* cells (Garnham, 1997).

6.3.2 Columns of seaweed/hydrophilic polyurethane experiments

Columns of foam/seaweed were successfully manufactured by casting the foam/biomass into plastic columns so as to form an integral part of the column. The cast foam/biomass was found to be firmly attached to the column's internal walls preventing any short circuiting or passage of the solution between the foam and the column internal wall. A cross section of the foam/biomass column showed a porous structure allowing solutions to pass through the column without a pressure drop.

Experiments on copper uptake using a column of seaweed/Hypol foam over 5 consecutive adsorption-desorption cycles at influent pH 5.0, T 20°C, initial copper concentration of 6 mgl^{-1}, flow rate 4.7 $l.hr^{-1}$ and biomass weight ratio of 7% showed an equilibrium adsorption capacity of 19.367, 17.96, 14.16, 16.6 and 15 $mg.g^{-1}$ in the first, second, third, fourth and fifth cycle respectively. This fluctuation in copper uptake (through the consecutive cycles of use) has been observed by other researchers using different biomass types. In a pilot plant operated to adsorb uranium from mine leach solutions using a reactor of immobilised *R. arrhizus* for 10 consecutive cycles, the initial uptake capacity for the immobilised biomass dropped from 77.2 $mg.g^{-1}$ in the first cycle to 35.9 $mg.g^{-1}$ in the fourth, Tsezos (1997). The uptake then increased to 36.5 $mg.g^{-1}$ in the fifth cycle, gradually declining to 27.3 $mg.g^{-1}$ by the eighth. It increased again in the ninth to 29.3 $mg.g^{-1}$ and subsequently dropped to 22.1 $mg.g^{-1}$ in the final cycle.

Reducing the flow rate of solution passing through the column (while maintaining other conditions) increased the biomass adsorption capacity from 19.36 $mg.g^{-1}$ to 35 $mg.g^{-1}$ when the flow rate decreased from 4.7 $l.hr^{-1}$ to 2.25 $l.hr^{-1}$, while increasing the flow rate from 4.7 $l.hr^{-1}$ to 7.04 $l.hr^{-1}$ decreased the biomass adsorption capacity slightly from 19.36 $mg.g^{-1}$ to 17.7 $mg.g^{-1}$. The little reduction in the biomass uptake capacity when the flow rate increased from 4.7 $l.hr^{-1}$ to 7.04 $l.hr^{-1}$ is very important flnding as it show that columns of biomass/foam can be operated at high flow rates relatively when dealing with large volumes of industrial waste water without reducing the biomass adsorption capacity significantly.

The biomass weight ratio had a major impact on the biomass adsorption capacity. Increasing the biomass weight ratio in the column (while maintaining other conditions) from 7 to 11% increased the biomass adsorption capacities from 19.367 to 35.41 $mg.g^{-1}$ while no equilibrium was reached when the biomass weight was increased to 14.2% after treating 76 litres of solution reaching an uptake of 45 $mg.g^{-1}$.

Increasing solute concentration in solution showed to increase in the biomass uptake capacity. The seaweed adsorption capacity increased from 19.367 to 26.4, 44.074 and 48.03 $mg.g^{-1}$ when the initial copper concentration increased from 6 to 10, 20 and 30 mgl^{-1} respectively.

The presence of other heavy metal ions in solution was found to have a small negative effect on the biomass copper adsorption capacity. The presence of Zn (II) and Fe (II) (at the same initial concentration) lowered the biomass uptake capacity of copper from 19.367 $mg.g^{-1}$ (when copper was the only element present) to 15.82 $mg.g^{-1}$. Also the uptake of copper declined from 19.36 $mg.g^{-1}$ in the presence of copper alone to 17.16 $mg.g^{-1}$ when Zn (II), Cr (VI) and Ni (II) were added to the solution. Tables 6.3 to 6.6 summarizes the columns results.

Table 6.3: Summary of the effect of flow rate on copper adsorption using columns of seaweed-Hypol hydrophilic foam (All experiments were conducted at 6 mgl^{-1} Cu concentration and 7% biomass weight ratio, 20° C and initial solution's pH 5.0)

Flow rate ($l.hr^{-1}$)	Equilibrium biomass copper uptake capacity on weight basis ($mg.g^{-1}$)
2.25	35
4.7	19.36
7.04	17.7

Table 6.4: Summary of the effect of biomass weight ratio on copper adsorption using columns of seaweed-Hypol hydrophilic foam (All experiments were conducted at 6 mgl^{-1} Cu concentration and 4.7 $l.hr^{-1}$ flow rate, 20° C and initial solution's pH 5.0)

Biomass weight ratio (%)	Equilibrium biomass copper uptake capacity on weight basis ($mg.g^{-1}$)
7	19.36
11	35.41
14.2	45

Table 6.5: Summary of the effect of initial Cu concentrations on copper adsorption using columns of seaweed-Hypol hydrophilic foam (All experiments were conducted at flow rate of 4.7 $l.hr^{-1}$ and 7% biomass weight ratio, 20° C and initial solution's pH 5.0)

Cu initial concentration (mgl^{-1})	Equilibrium biomass copper uptake capacity on weight basis ($mg.g^{-1}$)
6	19.36
10	26.40
20	44.07
30	48.03

Table 6.6: Summary of the effect of the presence of competing ions on copper adsorption using columns of seaweed-Hypol hydrophilic foam (All experiments were conducted at 6 mgl^{-1} Cu initial concentration, 4.7 $l.hr^{-1}$ flow rate and 7% biomass weight ratio, 20° C and initial solution's pH 5.0)

Presence of other heavy metals in solution	Equilibrium biomass copper uptake capacity on weight basis ($mg.g^{-1}$)
Zn(II) and Fe(II) at 6 mgl^{-1} initial concentrations	15.82
Zn(II), Cr(VI) and Ni(II) at 6 mgl^{-1} initial concentrations	17.16

6.4 Cost of the hydrophilic polyurethane (Hypol 2002)

Prices for Hypol 2002, according to the supplier, are quantity dependent. Assuming an annual usage of 5 mtpa, the price will be £8.50 per kg for 4 drum lots (1000kg total, UK delivered). Assuming that the cost associated with obtaining the biomass is negligible, simple calculations show that a reactor of 1.57 m^3 volume (i.e. diameter = 1m and height = 2m) will cost £92.67. This reactor, which needs approximately 11 kg of Hypol pre-polymer to fill it, can accommodate 8.8 kg of biomass (i.e. 80% of the pre-polymer weight). Assuming that the used biomass is *Ascophyllum nodosum* then this column would be able to uptake 0.4 kg of copper from an effluent containing 6

mgl^{-1} copper concentration at 20° C, pH 5.0 and 4.7 $l.hr^{-1}$ flow rate (N.B. calculation of the uptake was made using the biomass copper uptake capacity at 14.2% biomass weight, however the virtual biomass weight ratio in the column at 80% wt. biomass to pre-polymer could be twice this value which would be expected to increase the biomass uptake capacity, see section 5.7.3).

6.5 Conclusions

This work is the first reported investigation into the potential for immobilisation of non viable biomasses into open pore hydrophilic polyurethane at the point of manufacture and then using the resultant biomass/foam matrix for the removal of heavy metals from aquatic solutions. The study is particularly important as it allows the use of readily available by products and waste biomass which should make the process cost competitive with other processes for heavy metals adsorption from solution.

- The immobilisation technique proved to overcome most of the deficiencies that have been reported in other immobilisation matrices such as diffusion limitations, poor matrix mechanical strength, the suitability for use in reactors, isolation of the biomass from the surrounding solution.
- Any type of biomass or adsorbent could be immobilised in the foam and the foam/biomass can be manufactured to be suitable for use in any reactor design.
- Beads of foam/adsorbent can be packed in columns or reactors, used in an expanded bed reactor, used in continuous flow stirred reactor, etc.
- The biomass/foam matrix can also be cast so as to occupy the volume, and take the shape of, any designed reactor. This type of process would be most useful in the manufacture of a static bed reactor for the treatment of effluents. This sort of column reactor can contain as much as 80% biomass weight of the foam pre-polymer and a number of columns could be used in series.

References

Aharoni C. and Sparks D. L. (1991) Kinetic of soil chemical reactions- A theoretical treatment. In: *Rates of soil chemical processes*, Sparks D. L. and Suarez D. L. (eds.), Soil Society of America, Madison, WI.

Akthar M. N., Sastry K. S. and Mohan P. M. (1995) Biosorption of silver ions by processed *Aspergillus niger* biomass. *Biotechnology Letters*, **17**, 551-556.

Alaerts G. J., Jitjaturant V. and Kelderman P. (1989) Use of coconut shell based activated carbon for chromium (VI) removal. *Water Science and Technology*, **21**, 1701-1704.

Alloway B. J and Ayres D. C. (1993). Chemical Principles of Environmental Pollution. Chapman and Hall, 140-167.

Andrews A. T. (1986) Electrophoresis: theory, techniques and biochemical and clinical applications. (2nd edition), Oxford science publications, 5-27.

Ann and Patrick Fullick (1994). Chemistry. Heinemann Educational Publishers, Oxford, UK.

Archer V. L. (2001) Drinking water filter. US Patent 6,197,193.

Atkinson B., Black G. M., Pinches A. and Lewis P. J. S. (1983) Growth of biomass. US Patent 4,419,243.

Bakhir V. M., Zadorozhny J. G. and Barabash T. (1997) Apparatus for electrochemical treatment of water and/or water solutions. US Patent 5,628,888.

Banks C. J. (1997) Scavenging trace concentrations of metals. In: *Biosorbents for metal ions*, Wase J. and Forster C. (eds.) , Taylor and Francis Ltd.

Banks C. J. and Parkinson M. E. (1992) The mechanism and application of fungal biosorption to colour removal from raw waters. *Journal of Chemical Technology and Biotechnology*, **54**, 192-196.

Bauman E. K., Goodson L. H., Guilbault G. G. and Kramer D. N. (1965) Preparation of immobilised cholinesterase for use in analytical chemistry. *Analytical Chemistry*, **37**, page 1378.

Beavan M. J., Belk D. M., Stewart G. G. and Rose A. H. (1979) Changes in

electrophoretic mobility and lytic enzyme-activity associated with development of flocculating ability in *Saccharomyces-cerevisiae*. *Canadian Journal of Microbiology*, **25** (8), 888-895.

Benjamin M. M., Change Y. and McMeen C. R. (1999) Removing contaminants from water using iron oxide coated mineral having olivine structure. US Patent 5,911,882.

Bennett P. G., Ferguson C. R. and Jeffers T. H. (1991) Biosorption of metal contaminants from acidic mine waters. In: Process mineralogy XI -characterization of metallurgical and recyclable products, Hausen D. M., Petruk W., Hagni R. D. and Vassiliou A. (Eds.), The Minerals, Metals and Materials Society, Warrendale, Pennsylvania, 213-222.

Beveridge T. J. (1978) The response of cell walls of *B. Sultitis* to metals and microscopic stains. *Canadian Journal of Microbiology*, **24**, 89-104.

Beveridge T. J and Doyle R. J. (1989) Metal ions and bacteria. John Wiley and Sons Inc.

Beveridge T. J. and Murray R. G. E. (1980) Sites of metal deposition in the cell wall of *Bacillus subtilis*. *Journal of Bacteriology*, **141**, 876-887.

Bhattacharya D. and Cheng C. Y. R. (1987) Activated carbon adsorption of heavy metal chelates from single and multicomponent systems, *Environmental Progress*, **6**, 110-117.

Blumental H. J. and Roseman S. (1957) Quantitative estimation of fungi in chitin. *Journal of Bacteriology*, **74**, p 222.

BMJ.com (2002) http://www.bmj.com/collections/statsbk/2.shtml. Site visited August 2002.

Bowen H. J. M. (1970) Absorption by polyurethane foams; new method of separation. *Journal of the Chemical Society A-Inorganic Physical Theoretical*, **7**, p. 1082.

Bowen W. R. and Cooke R. J. (1989) Studies of Saccharomyces cerevisiae during fermentation- An invivo electrokinetic investigation. *Biotechnology and Bioengineering*, **33** (6), 706-715.

Bowers A. R. and Huang C. P. (1981) Activated carbon process for the treatment of chromium (VI)-containing wastewaters. *Water Science and Technology*, **13**, 629-650.

Boyle W. C. and Wallace A. L. (1986) Status of porous biomass support systems for

wastewater treatment: An innovative and alternative technology assessment. EPA / 600 / 52-86 / 019.

Braatz J. A. (1994) Biocompatible polyurethane-based hydrogel. *Journal of Biomaterials Applications*, **9**, 71-96.

Brady J. M. and Tobin J. M. (1995) Binding of hard and soft metal ions to *Rhizopus arrhizus* biomass. *Enzyme and Microbial Technology*, **17**, 791-796.

Brady D., Stoll A. and Ducan J. R. (1994) Biosorption of heavy metal cations by non-viable yeast biomass. *Environmental Technology*, 15, 429-438.

Braun T., Bekeffy O., Haklits I., Kadar K. and Majoros G. (1973) Ion-exchange foam chromatography; part I. preparation of rigid and flexible ion-exchange foams. *Analytica Chimica Acta*, **64** (1), 45-54.

Braun T., Navratil J. D. and Farag A. B. (1985) Polyurethane foam sorbents in separation science. CRC Press Inc., Boca Raton, USA

Brierley C. L. and Brierley J. A. (1993) Immobilisation of biomass for industrial application of Biosorption. In: *Biohydrometallurgical Technologies*. Vol.**2**, Torma A. E., Apel M. L. and Brierley C. L., (eds.), The Minerals, Metals and Materials Society, Warrendale, USA, 35-44.

Brierley J. A., Goyak G. M. and Brierley C. L. (1986) Consideration for commercial use of natural products for metals recovery. In: Immobilisation of ions by biosorption, Eccles H. and Hunt S., (eds.), Ellis Horwood, Chichester, UK, 105-117.

Brunauer S., Emmett P. H. and Teller E. (1938) Adsorption of gases in multimolecular layers. *Journal of American Chemistry Society*, **60**, 309-319.

Brunschwig H. (1512) Liber de Arte Distillandi.

Buist J. M. (1978) Introduction. In: Developments in polyurethane-1, Buist J. M. (ed.), Applied Science Publishers ltd.

Carvalho De. R. P., Chong K. H. and Volesky B. (1995) Evaluation of Cd, Cu and Zn Biosorption in two-metal system using algal biosorbent. Biotechnology Progress, **11**, 39-44.

Chibata I., Tosa T. and Sato T. (1976) Production of L-aspartic acid by immobilized cells. *Methods in Enzymology*, **44**, 739-746.

Chibata I., Tosa T., Sato T. and Takata I. (1987) Immobilization of cell in carrageenan. *Methods in Enzymology*, **135**, part B, 189-198.

Chien S. H. and Clayton W. R. (1980) Application of Elovich equation to the kinetics of phosphate release and sorption in soils. *Soil Science Society of America Journal*, 44 (2), 265-268.

Chong K. H. and Volesky B. (1995) Description of two-metal biosorption equilibria by Langmuir-type models, *Biotechnology and Bioengineering*, **47**, 451-460.

Cimino G., Passerini A. and Toscano G. (2000) Removal of toxic cations and Cr(VI) from aqueous solution by hazelnut shell. *Water Research*, **34**(11), 2955-2962.

Cody C. A. and Kemnetz S. J. (1997) Process for the removal of heavy metals from aqueous systems using organoclays. US Patent No. 5,667,694

Cotoras D., Viedma P. and Pimentel J. (1993) Biosorption of metal ions by attached bacterial cells in a packed-bed bioreactor. In: *Biohydrometallurical Technologies*, Vol 2, Torma A. E., Apel M. L. and Brierley C. L., (Eds.), The Minerals, Metals and Materials Society, Warrendale, USA, 103-110.

CRC Handbook of Chemistry and Physics (1997-1998). Editor-in-Chief: David R. Lide, 78th edition, CRC Press, Boca Raton, USA.

Crist R. H., Oberholser K. and Nguyen M. (1981) Nature of bonding between metallic ions and algal cell walls. *Environmental Science and Technology* , **15**, 1212-1217.

Darnall D. W. (1991) Removal and recovery of heavy metal ions from waste water using a new biosorbent; AlgaSORB. *Innovative Hazardous Waste Treatment, Technology Series*. Vol. **3**, *Biological Processes*, 65-72.

Darnall D. W., Greene B., Henzl M. T., Hosea J. M., McPherson R. A., Sneddon J. and Alexander M. D. (1986 a) Selective recovery of gold and other metal ions from an algal biomass. *Environmental Science and Technology*, **20**, 206-208.

Darnall D. W., Greene B., Hosea M., McPherson R. A., Henzl M. and Alexander M. D. (1986 b) Recovery of metals by immobilised algae. In: *Trace metal removal from aqueous solutions*. Thompson R., (ed.), Litho ltd, Whitstable, UK, 1-24.

Davidova E. and Kasparova S. (1992) Adsorption of metals by yeast cell walls. *Microbiology*, **61**, 1018-1022.

Davis T.A., Volesky B. and Vieira R.H.S.F. (2000). *Sargassum* seaweed as biosorbent for heavy metals. *Water Research,* **34** (17), 4270-4278.

de Rome L. and Gadd G. M. (1991) Use of pelleted and immobilised yeast and fungal biomass for heavy metal and radionuclide recovery. *Journal of Industrial*

Microbiology, **7**, 97-104.

Dias S. A., Vilas-Boas L., Cabral J. M. S., and Fonseca M. M. R. (1991) Production of ethyl butyrate by *Candia rudosa* lipase immobilised in polyurethane. *Biocatalysis*, **5**, 21-34.

Donohue J.M. and Abernathy C.O. (1999) Exposure to inorganic arsenic from fish and shellfish. In: *Arsenic Exposure and Health Effects.* Elsevier.

Droste R. L. (1997) Theory and practice of water and wastewater treatment. John Wiley & Sons, Inc, 485-507.

Edyvean R. G. J., Williams C. J., Wilson M. W. and Aderhold D. (1997) Biosorption using unusual biomass. In: *Biosorbents for metal ions*, Wase J. and Forster C. (eds.), Taylor and Francis ltd., UK.

Elibeck W. J. and Mattock G. (1987) Chemical processes in waste water treatment. Ellis Horwood Ltd., Chichester, UK.

Ferguson C. R., Peterson M. R. and Teffers T. H. (1989) Removal of metal contaminants from waste water using biomass immobilised in polysulfone beads. *Biotechnology in Minerals and Metal Processing*, Scheiner.B.J., Doyle F. M. and Kawatra S. K., (eds.), Society of Mining Engineers, Littleon, Colorado, 193-199.

Ferreira-Dias S., Correia A.C. and Baptista F. O. (1999) Activity and batch operational stability of *Candida rugosa* lipase immobilised in different hydrophilic polyurethane foams during hydrolysis in a biphasic medium. *Bioprocess Engineering*, **21**, 517-524.

Ferrigno T. H. (1963) Rigid plastic foams. Reinhold, New York.

Figueira M. M., Volesky B., Ciminelli V. S. T and Roddick F. A. (2000) Biosorption of metals in brown seaweed biomass. *Water Research*, **34**(1), 196-204.

Forster C. F. and Wase A. J. (1997) Biosorption of heavy metals: An introduction. In: *Biosorbents for metal ions*, Wase J. and Forster C. (eds.), Taylor and Francis Ltd.

Fourest E. and Volesky B. (1997) Alginate properties and heavy metal Biosorption by marine algae. *Applied Biochemistry and Biotechnology*, **76**, 215-226.

Freundlich H. (1906) Adsorption solution. *Zeitschrift Fur Physikalische Chemie-International Journal of Research in Physical Chemistry & Chemical Physics*, **57**, 384-470.

Friis N. and Myers-Keith P. (1986) Biosorption of uranium and lead by *Streptomyces*

Longwoodensis. Biotechnology and Bioengineering, **28**, 21-28.

Fusee M. C., Swann W. E. and Calton G. J. (1981) Immobilization of *Escherichia coli* cells containing Aspartase activity with polyurethane and its application for L-Aspartic acid production. *Applied and Environmental Microbiology*, **42** (4), 672-676.

Gadd G. M. (1986) The uptake of heavy metals by fungi and yeast: The chemistry and physiology of the process and application for biotechnology. In: Immobilisation of ions by biosorption, Eccles H. and Hunt F. (eds.), Ellis Horwood, Chichester,UK, 149-157.

Gadd G. M. and Griffiths A. J. (1980) Influence of pH on toxicity and uptake of copper in Aureobasidium pullulans. *Transactions of the British Mycological Society*, **75**, 91-96.

Garnham G. W. (1997) The use of algae as metal biosorbents. In: Biosorbents for metal ions, Wase J. and Forster C. (eds.), Taylor and Francis Ltd.

Garnham G. W., Codd G. A. and Gadd G. M. (1992) Uptake of technetium by freshwater green microalgae. *Journal of Applied Microbiology and Biotechnology*, **37**, 679-684.

Gee A. R. and Dudeney A. W. L. (1988) Adsorption and crystallisation of gold at biological surfaces. In: *Biohydrometallurgy*, Norris P. R. and Kelly D. P., (eds.), Science and Technology Letters, Kew, 437-451.

German Chemists Association (1981). Preservation of water samples. *Water Research*, **15**, 233-241.

Gesser H. D. and Horsfall G. A. (1977) Separation and concentration of gallium by polyurethane. J. Chim. Phys, **74**, page 1072.

Gessner P. K. and Hasan M. M. (1987) Freundlich and Langmuir isotherms as models for the adsorption of toxicants on activated charcoal. *Journal of Pharmaceutical Sciences*, **76**(4), 319-327.

Golden J. H. (2002) Process and apparatus for removal of heavy metals from wastewater. US Patent No. 20020003112.

Givens S. W. and Sack W. A. (1987) Evaluation of carbon impregnated polyurethane foam media for biological removal of carbon and nitrogen from chemical industry wastewater. *42 ND Industrial Waste Conference Proceedings*, Purdue University, 93-102.

Greene B. and Darnall D. W. (1988) Temperature dependence of metal ion sorption

by *Spirulina. Biorecovery*, **1**, 27-41.

Greene B. and Darnall D. W. (1990) Microbial oxygenic photoautotrophes (cyanobacteria and algae) for metal-ion binding. In: *Microbial mineral recovery*, Ehrlich H. L. and Brierly C. L. (eds.), McGraw-Hill, New York, 227-302.

Guthrie J. L. (1984) Microorganisms immobilized with hydrolysis resistant polyurethane foam. US Patent No. 4,456,685.

HACKH'S Chemical Dictionary (1969). MC Graw-Hill Inc., page 315.

Hancock I. C. (1986) The use of gram-positive bacteria for the removal of metals from aqueous solution. In: Trace metal removal aqueous solution, R.Thompson (ed.), The Royal Society of Chemistry, London, 25-43.

Havens P. L. and Rase H. F. (1993) Reusable immobilised enzyme/polyurethane sponge for removal and detoxification of localised organophosphate pesticide spills. *Industrial and Engineering Chemistry Research*, **32** (10), 2254-2258.

Helfferich F. G. (1995) Ion exchange. Dover Science Books, USA.

Hermann P. (1999) Hydrophilic urethane binder immobilizing organisms having active sites for binding noxious materials. US Patent No. 5,976,847.

Hill R. (1999) Sorption processes. In: *Water and wastewater treatment principles*, Module 2, MSc in Water Pollution Control Technology, School of Water Scinces, Cranfield University, UK.

Horikoshi T., Nakajima A. and Sakaguchi T. (1979) Studies on the accumulation of heavy metal elements in biological systems IV: Uptake of uranium by Chlorella regularis. *Agriculture, Biology and Chemistry*, **43**, 617-623.

Horikoshi T., Nakajima A. and Sakaguchi T. (1981) Studies on the accumulation of heavy metals in biological systeme XIX: accumulation of uranium by microorganisms, *European Journal of Applied Microbiology Biotechnology*, **12**, 90-96.

Huang C. and Chiu H-H. (1994) Removal of trace Cd (II) from aqueous solution by fungal adsorbents: An evaluation of self-immobilisation of *Rhizopus-Oryzae. Water Science and Technology,* **30** (3), 245-253.

Huang C., Huang C. P. and Morehart A. L. (1990) The removal of Cu (II) from dilute aqueous by *Saccharomyces cerevisiae. Water Research*, **24**, 433-439.

Hughes M. N and Poole R. K. (1991) Metal speciation and microbial growth-the hard (and soft) facts. *Journal of General Microbiology*, **37**, 725-734.

Hunt S. (1986) Diversity of biopolymer structure and its potential for ion-binding applications. In: Immobilisation of ions by Biosorption, Hunt S. and Eccles H. (eds.). Society of Chemical Industry, Ellis Horwood Ltd.

International Mycological Institute, Bakeham Lane, Egham, Surrey TW20 9TY.

Jones R. E. (1978) Heavy metals in the estuarine environment. Technical Report TR73. Water Research Centre, Stevenage, UK.

Judd S. (1999) Introduction to membrane technology. In: *Membrane processes*, Module 5, MSc in Water Pollution Control Technology, School of Water Scinces, Cranfield University, UK.

Kapoor A. and Viraraghavan T. (1997) Fungi as Biosorbents. In: Biosorbents for metal ions, Wase J. and Froster C. (eds.), Taylor and Francis, Ltd.

Kiff R. J. and Little D. R. (1986) Biosorption of heavy metals by immobilised fungal biomass. In: Immobilisation of ions by Biosorption, Eccles H. and Hunt S., (eds.), Ellis Horwood, Chichester, 71-80.

Kikuchi T. (1965) Studies on the pathway of production in a copper adapted yeast. *Plant and Cell Physiology*, **6**, 195-210.

Kim J. I. and Zoltek J. (1977) Chromium removal with activated carbon. *Progress in Water Technology*, **9**, 143-155.

Klaus M. (1987) Methods in Enzymology. *Immobilized Enzymes and Cells*, V **135**, Part B.

Klein J., Eng H., Kluge M. and Vorlop K.-D. (1979). New polymeric networks for entrapment of whole microbial cells. *IUPAC Makro Polymer Symposium*. Mainz, Germany, 1547-1549.

Klein J. and Kluge M. (1981) Immobilisation of microbial cells in polyurethane matrices. *Biotechnology Letters*, **3**(2), 65-70.

Kreisler L. (2001) Method for recovering and separating metals from waste streams. US Patent 6,254,782

Kuennen R. W., Taylor R. M., Vandyke K. and Groenevelt K. (1992) Removing lead from drinking-water with a point-of-use GAC fixed-bed adsorber. *Journal of the American Water Works Association*, **84**, 91-101.

Kuhn S. P. and Pfister R. M. (1990) Accumulation of cadmium by immobilised *Zoogloea ramigera* 115. *Journal of Industrial Microbiology*, **6**, 123-128.

Kuyucak N. (1990) Feasibility of biosorbents application. In: *Biosorption of heavy metals*, Volesky B. (ed.), CRC Press, Boca Raton, Florida, pp.371-380.

Kuyucak N. and Volesky B. (1988) Biosorbents for the recovery of metals from industrial solutions, *Biotechnology Letters*, **10**, 137-142.

Lagergren S. (1898) Zur theorie der sogenannten adsorption gelöster stoffe. *K. Sven. Vetenskapsakad. Handl.*, **24**, 1-39.

Lal D., Arnold J. R. and Somayajulu B. L. K. (1964) Methods for the extraction of trace elements from sea water. *Geochimica et Cosmochimica Acta*, **28**, page 111.

Langmuir I. (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of American Chemical Society*, **40**, 1361-1403.

LeJeune K. E. and Russell A. J. (1996) Covalent binding of a nerve agent hydrolysing enzyme within polyurethane foam. *Biotechnology and Bioengineering*, **51**, 450-457.

Lesaca M. R. (1975) Monitoring of heavy metals in Philippine rivers, bay waters and Lakes. In: Proceedings of the International conference on heavy metals in the environment, Toronto, Canada, October, page 285-306.

Lewis D. and Kiff R. J. (1988) The removal of heavy metals from aqueous effluents by immobilised fungal biomass. *Environmental Technology Letters*, **9**, 991-998.

Little D. R. (1986) A study of bioaccumulation for toxic metal recovery. Ph.D. thesis, Institute of Science and Technology, University of Manchester.

Lu Y. and Wilkins E. (1996) Heavy metal removal by caustic-treated yeast immobilised in alginate. *Journal of Hazardous Materials*, **49**, 165-179.

Luef E., Prey T. and Kubiceck C. P. (1991) Biosorption of zinc by fungal mycelial waste. *Applied Microbiology and Biotechnology*, **34**, 688-692.

Lupton F. S. and Zupancic D. M. (1991) Removal of phenols from waste water by a fixed bed reactor. US Patent No. 4,983,299.

Lupton F. S., William G. and Marion R. (1996) Process for removal of organic pollutants from waste water. US Patent No. 5,543,052

Math-help.co.uk(2002): http://www.maths-help.co.uk/Knowldge/Stat/Twostdev/Question.htm Site visited August 2002.

McCann B. (2003) Filling the liability gap. *Water 21*, Magazine of the International

Water Association, February, UK, 18-19.

MC Graw-Hill Dictionary of Scientific and Technical Terms, (1974), page 733.

Mckay G., Blair H. S. and Findon A. (1986) Sorption of metal ions by chitosan. In: Immobilisation of ions by biosorption, Eccles H. and Hunt S., (eds.), Ellis Horwood Ltd., Chichester, UK, 59-69.

Mckay G. and Allen S. J. (1997) Low-cost adsorbents in continuous processes. In: *Biosorbents for metal ions*, Wase J. and Forster C. (eds.), Taylor and Francis ltd.

Mckay C., Ho Y. S. and Ng J. C. Y. (1999) Biosorption of copper from waste waters: A review. *Separation and Purification Methods*, **28**(1), 87-125.

Meier P. C. and Zund R. E. (2000) Statistical methods in analytical chemistry. Second edition, John Wiley & Sons, Inc, New York.

Miles D. C. and Briston J. H. (1979) Polymer Technology. Second edition, Chemical Publishing, New York.

Miller J. C. and Miller J. N. (1988) Statistics for analytical chemistry. Second edition, Ellis Horwood Limited, UK.

Moe W. M. and Irvine R. L. (2000) Polyurethane foam medium for biofiltration. I: Characterization. *Journal of Environmental Engineering*, **126** (9), 815-825.

Morkovsky P. E., Kaspar D. D. and Petru J. M. (1999) Process and apparatus for electrocoagulative treatment of industrial waste water. US Patent 5,928,493.

Muraleedharan T. R. and Venkobachar C. (1990) Mechanism of biosorption of copper (II) by *Ganoderma lucidum. Biotechnology and Bioengineering*, **35**, 320-325.

Muraleedharan T. R., Iyengar L. and Venkobachar C. (1994) Further insight into the mechanism of biosorption of heavy metals by *Ganoderma lucidum. Environmental Technology*, **15**, 1015-1027.

Muzzarelli R. A. A. (1973) Natural chelating polymers. Pergamon press, Oxford, UK.

Muzzarelli R. A. A., Tanfani F. and Emanuelli M. (1981) The chelating ability of chitinous materials from *Streptomyces*, *Mucor rouxii*, *Phycomcyes blakesleeanus*, and *Choanephora cucurbitaruM. Journal of Applied Biochemistry*, **3**, 322-327.

Nakajima A., Horikoshi T. and Sakaguchi T. (1982) Recovery of uranium by

immobilised microorganisms. *European Journal of Applied Microbiology and Biotechnology*, **6**, 88-91.

Nakajima A., Horikoshi T. and Sakaguchi T. (1979) Uptake of manganese ion by Chlorella regularis. *Agriculture, Biology and Chemistry*, **43**, 1461-1466.

Nakajjima A. and Sakaguchi T. (1986) Selective accumulation of heavy metals by micro-organisms. *Applied Microbiology and Biotechnology*, **24**, 59-64.

News.com (2003): http://news.bbc.co.uk/1/low/uk/1535698.stm

Nieboer E. and Richardson D. H. S. (1980) The replacement of the non-descript term 'Heavy Metals' by a biologically and chemically significant classification of metal ions. *Environmental Pollution Series B*, **1**, 3-26.

Nriagu J. O. (1996) History of Global Metal Pollution. *Science*, **272**, 223-224.

Patterson J. W. and Minear R. A. (1973) Physical-Chemical methods of heavy metals removal. In: Heavy metals in the aquatic environment, Proceedings of the International Conference held in Nashville, Tennessee, December, 261-276.

Pearson R. G. (1963) Hard and soft acids and bases. *Journal of the American Chemical Society*, **85**, 3533-3539.

Personal communication: http://www.lib.rip.edu/dept/chemeng/Biotech

Peters W. C. (1978) Exploration and mining geology. John wiley and son, NewYork.

Petrusevski B., Sharma S. K., Kruis F., Omeruglu P. and Schippers J. C. (2002) Family filter with iron coated sand: solution for arsenic removal in rural areas. Proceedings of the IWA World Water Congress, Melbourne, Australia, 7-12 April, 351.

Pimenov A. V., Lieberman A. I. and Shmidt J. L. (1998) Modified activated carbon. US Patent No. 5,705,269.

Reimann H. and Fuchs U. (1986) Process and apparatus for the biological purification of wastewater. United States Patent No. 4,566,971.

Remacle J. (1990) The cell wall and heavy metals. In: *Biosorption of heavy metals*, Volesky B. (ed.), CRC Press, Boca Raton, Florida, 83-92.

Riponcomputer.com (2002): http://www.riponcomputer.com/riponcomputer/dawnchemical/ Site visited August 2002.

Ross I. S. and Townsley C. C. (1986) The uptake of heavy metals by filamentous

Fungi. In: *Immobilisation of ions by biosorption*, Hunt S. and Eccles H., (eds.), Society of Chemical Industry, Ellis Horwood Ltd.

Sag Y. and Kutsal T. (1995) Copper (II) and nickel (II) adsorption by *Rhizopus arrhizus* in batch stirred reactors in series. *The Chemical Engineering Journal*, **58**, 265-273.

Sakaguchi T., Nakajima A. and Horikoshi T. (1981) Studies on the accumulation of heavy metal elements in biological systems XVII: accumulation of molybdenum by green microalgae. *European Journal of Applied Microbiology and Biotechnology*, **12**, 84-89.

Schiewer S., Fourest E., Chong K. H. and Volesky B. (1995) Ion exchange in metal Biosorption by dried seaweed: experiments and model predictions. In: Biohydrometallurgical processing: Proceedings of the International Biohydrometallurgy Symposium, Jerez C. A., Vargas T., Toledo H. and Wiertz J. V., (eds.), University of Chile, Santiago, 219-228.

Scott C. D. (1987) Dispersed-Phase Adsorbents for Biotechnology applications. Paper presented at the second international conference on separation technology, Schloss Elmau, Klais, Germany, 26-28 April, 11.

Shannon R. D. and Prewitt C. T. (1968) Effective ionic radii in oxides and fluorides. Acta Crystallographica Section B, **25** (5), 925-946.

Shimahara K., Takiguch Y., Kobayashi T., Uda K. and Sannan T. (1989) Screening of mucoraceae strains suitable for chitosan production. In: *Chitin and Chitosan: Sources, chemistry, biochemistry, physical properties and applications*, Skjak-Braek G., Anthonsen T. and Sandford P., (eds.), Elsevier Science Publishers Ltd., London, 171-178.

Skoog D. A., West D. M. and Holler F. J. (1988) Fundamentals of analytical chemistry. Fifth edition, Saunders College Publishing.

Smith A. H., Biggs M. L., Moore L., Haque R., Steinmaus C., Chung J., Hernandez A. and Lopipero P. (1999) Cancer risks from arsenic in drinking water: implications for drinking water standards. In: *Arsenic Exposure and Health Effects III*, Proceedings of the Third International Conference on Arsenic Exposure and Health Effects, San Diego, California, 12-15 July.

Soeder C. J. and Stengel E. (1974) Physico-chemical factors affecting metabolism and growth rate. In: *Algal physiology and biochemistry*, Stewart W. D. P., (ed.), Blackwell, Oxford, 714-740.

Solt G. (1999) Introduction. *In: Membrane processes*, Module 5, MSc in Water Pollution Control Technology, School of Water Scinces, Cranfield University, UK.

Som A. M. (1995) Development of a process selection model for industrial waste water treatment using expert systems. MSc thesis, Institute of Science and Technology, University of Manchester, UK.

Somers E. (1963) The uptake of copper in fungal spores. *Annals of Applied Biology*, **5**, 425-437.

Sonomoto K., Jin I-N, Tanaka A. and Fukui S. (1980) Application of urethane prepolymers to immobilisation of biocatalysts: Δ^1-Dehydrogenation of hydrocortisone by *Arthrobacter simplex* cells entrapped with urethane prepolymers. *Agricultural Biological Chemistry*, **44**(5), 1119-1126.

Standard Methods (1985) 16th edition, prepared and published jointly by: American Public Health Association, American Water Works Association and Water Pollution Control Federation.

Storey K. B., Duncan J. A. and Chakrabarti A. C. (1990) Immobilisation of amylogucosidase using two forms of polyurethane polymer. *Applied Biochemistry and Biotechnology*, **23**, 221-236.

Strandberg G. W., Shumate S. E. and Parrott J. R. (1981) Microbial cells as biosorbents for heavy metals: accumulation of uranium by *Saccharomyces Cerevisiae* and *Pseudomonas aevuginosa. Applied and Environmental Microbiology*, **41**, 237-245.

Suder J. B. and Wightman J. P. (1983) Interaction of heavy metals with chitin and Chitosan. II. Cadmium and zinc. In: Adsorption from solution, Ottewill R. H., Rochester C. H. and Smith A. L., Academic Press, London, pages 235-244.

Sukiman S. (1974) The extraction of gold from aqueous solution with treated and untreated polyurethane foam. *Radiochemical and Radioanalytical Letters*, **18**, page 129.

Suyama K., Fukazawa Y. and Umetsu Y. (1994) A new biomaterial, hen egg shell membrane, to eliminate heavy metal ion from their dilute waste solution. *Applied Biochemistry and Biotechnology*, **45-46**, 871-879.

Tchobanoglous G. and Burton F. L. (1991) Waste water engineering: treatment, disposal and reuse. (Third edition), McGraw-Hill, Inc., USA, page 315-324.

Thomas C. R. (1965) The formation of cellular plastics. *British Plastics*, **38** (9), 552-

5528.

Tobin J. M., L'homme B. and Roux J. C. (1993) Immobilisation protocols and effects on cadmium uptake by *Rhizopus arrhizus* biosorbents. *Biotechnology Techniques*, **7**, 739-744.

Tobin J. M., Cooper D. G. and Neufeld R. J. (1984) Uptake of metal ions by *Rhizopus arrhizus* biomass. *Applied and Environmental Microbiology*, **47**, 821-824.

Tosa T., Sato T., Mori T., Yamamoto K., Takata I, Nishida Y. and Chibata I. (1979) Immobilisation of enzymes and microbial cells using carrageenan as matrix. *Biotechnology and Bioengineering*, **21**, 1697-1709.

Tsezos M. (1983) The role of chitin in uranium adsorption by *Rhizopus arrhizus*. *Biotechnology and Bioengineering*, **25**, 2025-2040.

Tsezos M. (1984) Recover of uranium from biological adsorbents-desorption equilibrium. *Biotechnology and Bioengineering,* **26**, 973-981.

Tsezos M. (1990) Engineering aspects of metal binding by biomass. In: *Microbial mineral recovery*, Enhrlich H. L. and Brierley C. L. (eds.), McGraw-Hill, New York, 325-329.

Tsezos M. (1997) Biosorption of lanthanides, actinides and related materials. In: *Biosorbents for metal ions*, Wase J. and Forster C. (eds.), Taylor and Francis Ltd.

Tsezos M. and Seto W. (1986) The adsorption of chloroethanes by microbial biomass. *Water Reaserch*, **20**, page 7.

Tsezos M. and Volesky B. (1981). Biosorption of uranium and thorium. *Biotechnology and Bioengineering*, **23**, 583-604.

Tsezos M. and Volesky B. (1982) The mechanism of thorium Biosorption by *Rhizopus arrhizus*. *Biotechnology and Bioengineering*, **24**, 955-969.

Turner W. B. (1971) Fungal Metabolites. Academic press, London and New York, *Chapter 2.

Tyagi R. D, Tran F. T., and Chowdhury A. K. M. M. (1993). A pilot study of biodegradation of petroleum refinery wastewater in a polyurethane-attached RBC. *Process Biochemistry*, **28**, 75-82.

Ulman J. A (1984) Control of heavy metal discharge in the printed circuit industry with sodium borohydride. Presented at the 1984 AES SUR/FIN annual technical conference and ehibit, New York, USA, July.

USEPA (1999) Understanding variation in partition coefficient, Kd, values, Volume I:

The Kd model, methods and measurement, and application of chemical reaction codes. A cooperative effort by: Office of Radiation and Indoor Air, Office of Solid Waste and Emergency Response, and U.S. Environmental Protection Agency, Washington, DC 20460, August.

Volesky B. (1994) Advances in biosorption of metals: selection of biomass type. *FEMS Microbiology Reviews*, **14**, 291-302.

Whitlock J. L. and Mudder T. I. (1985) The homestake waste water treatment process: biological removal of toxic parameters from cyanidation waste waters and bio-assay effluent evaluation. In: Proceedings of the 6th International Symposium on Bio-hydrometallurgy, Vancouver, British Columbia, 327-339.

WHO (2001) Arsenic in drinking water (Fact Sheet No 210). Web site: www.who.int

Williams M. (1999) Adsorption theory. *In: Advanced chemical processes*, Module 4, MSc in Water Pollution Control Technology, School of Water Scinces, Cranfield University, UK.

Wri.com (2003): http://www.wri.org/wr-98-99/metals.htm

Yakubu N. A. and Dudeney A. W. L. (1986) Biosorption of uranium with *Aspergillus niger*. In: Immobilization of ions by Biosorption, Eddles H. H. and Hunt S. (eds.), Ellis Horwood, Chichester, 183-200.

Yetis U., Dolek A., Dilek F. B. and Ozcengiz G. (2000) The removal of Pb (II) by *Phanerochaete chrysosporium*. *Water Research*, **34** (16), 4090-4100.

Zhou J. L. and Banks C. J. (1992) Humic acid removal from water by biosorption. *Environmental Technology*, **13**, 727-737.

Zhou J. L. and Kiff R. J. (1991) The uptake of copper from aqueous solution by immobilised fungal biomass. *Journal of Chemical Technology and Biotechnolgy*, **52**, 317-330.

Appendix A: Results tables

Table A1: Copper uptake by 100mg of non-immobilised fungal biomass from 95ml of $2mgl^{-1}$ copper solution at an initial pH 7.0 and room temperature

Time (min)	Exp (1)		Exp (2)		**Cu conc. Average C (mg/l)**	C Stdev	**Uptake capacity average Q (mg/g)**	Q Stdev	95% confidence limits on the mean of Cu conc. (C)	95% confidence limits on the mean of uptake (Q)
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	1.787	0	1.77	0	**1.7785**	0.01202	**0**	0	0.108035	0
5	0.556	1.16945	0.609	1.10295	**0.5825**	0.03748	**1.1362**	0.04702	0.336815	0.4226075
10	0.432	1.28725	0.445	1.25875	**0.4385**	0.00919	**1.273**	0.02015	0.082615	0.1811175
20	0.37	1.34615	0.37	1.33	**0.37**	0	**1.338075**	0.01142	0	0.10263325
30	0.307	1.406	0.319	1.37845	**0.313**	0.00849	**1.392225**	0.01948	0.07626	0.17508025
40	0.272	1.43925	0.262	1.4326	**0.267**	0.00707	**1.435925**	0.0047	0.06355	0.04226075
50	0.251	1.4592	0.272	1.4231	**0.2615**	0.01485	**1.44115**	0.02553	0.133455	0.2294155
60	0.25	1.46015	0.257	1.43735	**0.2535**	0.00495	**1.44875**	0.01612	0.044485	0.144894

Table A2: Copper uptake by 100mg of immobilised biomass in k-carrageenan from 95ml of $2mgl^{-1}$ copper solution at an initial pH 7.0 and room temperature

Time (min)	Exp (1)		Exp (2)		**Cu conc. Average C (mg/l)**	C Stdev	**Uptake capacity average Q (mg/g)**	Q Stdev	95% confidence limits on the mean of Cu conc. (C)	95% confidence limits on the mean of uptake (Q)
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	2.132	0	2.122	0	**2.127**	0.00707	**0**	0	0.06355	0
5	1.553	0.55005	1.57	0.5244	**1.5615**	0.01202	**0.537225**	0.01814	0.108035	0.16300575
10	1.431	0.66595	1.432	0.6555	**1.4315**	0.00071	**0.660725**	0.00739	0.006355	0.06640975
20	0.95	1.1229	0.93	1.1324	**0.94**	0.01414	**1.12765**	0.00672	0.1271	0.0603725
30	0.705	1.35565	0.711	1.34045	**0.708**	0.00424	**1.34805**	0.01075	0.03813	0.096596
40	0.631	1.42595	0.634	1.4136	**0.6325**	0.00212	**1.419775**	0.00873	0.019065	0.07848425
50	0.591	1.46395	0.58	1.4649	**0.5855**	0.00778	**1.464425**	0.00067	0.069905	0.00603725
60	0.589	1.46585	0.578	1.4668	**0.5835**	0.00778	**1.466325**	0.00067	0.069905	0.00603725

Table A3: Copper uptake by 100mg of immobilised biomass in polysulfone from 95ml of 2mgl^{-1} copper solution at an initial pH7.0 and room temperature

Time (min)	Exp (1)		Exp (2)		Cu conc. Average C (mg/l)	C Stdev	Uptake capacity average Q (mg/g)	Q Stdev	95% confidence limits on the mean of Cu conc. (C)	95% confidence limits on the mean of uptake (Q)
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	2.01	0	1.992	0	**2.001**	0.01273	**0**	0	0.11439	0
5	1.969	0.03895	1.891	0.09595	**1.93**	0.05515	**0.06745**	0.04031	0.49569	0.362235
10	1.836	0.1653	1.807	0.17575	**1.8215**	0.02051	**0.170525**	0.00739	0.184295	0.06640975
20	1.685	0.30875	1.677	0.29925	**1.681**	0.00566	**0.304**	0.00672	0.05084	0.0603725
30	1.501	0.48355	1.491	0.47595	**1.496**	0.00707	**0.47975**	0.00537	0.06355	0.048298
40	1.436	0.5453	1.441	0.52345	**1.4385**	0.00354	**0.534375**	0.01545	0.031775	0.13885675
50	1.421	0.55955	1.413	0.55005	**1.417**	0.00566	**0.5548**	0.00672	0.05084	0.0603725
60	1.406	0.5738	1.397	0.56525	**1.4015**	0.00636	**0.589525**	0.00605	0.057195	0.05433525

Table A4: Copper uptake by 100mg of immobilised biomass in polyvinlformal from 95ml of 2mgl^{-1} copper solution at an initial pH 7.0 and room temperature

Time (min)	Exp (1)		Exp (2)		Cu conc. Average C (mg/l)	C Stdev	Uptake capacity average Q (mg/g)	Q Stdev	95% confidence limits on the mean of Cu conc. (C)	95% confidence limits on the mean of uptake (Q)
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	1.808	0	1.788	0	**1.798**	0.01414	**0**	0	0.1271	0
5	1.698	0.1045	1.706	0.0779	**1.702**	0.00566	**0.0912**	0.01881	0.05084	0.169043
10	1.692	0.1102	1.664	0.1178	**1.678**	0.0198	**0.114**	0.00537	0.17794	0.048298
20	1.633	0.16625	1.651	0.13015	**1.642**	0.01273	**0.1482**	0.02553	0.11439	0.2294155
30	1.614	0.1843	1.626	0.1539	**1.62**	0.00849	**0.1691**	0.0215	0.07626	0.193192
40	1.612	0.1862	1.623	0.15675	**1.6175**	0.00778	**0.171475**	0.02082	0.069905	0.18715475
50	1.609	0.18905	1.606	0.1729	**1.6075**	0.00212	**0.180975**	0.01142	0.019065	0.10263325
60	1.611	0.18715	1.598	0.1805	**1.6045**	0.00919	**0.183825**	0.0047	0.082615	0.04226075

Table A5: Copper uptake by 100mg of immobilised biomass in polyurethane from 95ml of 2mgl^{-1} copper solution at an initial pH 7.0 and room temperature

Time (min)	Exp (1)		Exp (2)		Cu conc. Average C (mg/l)	C Stdev	Uptake capacity average Q (mg/g)	Q Stdev	95% confidence limits on the mean of Cu conc. (C)	95% confidence limits on the mean of uptake (Q)
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	2.02	0	2.109	0	**2.0645**	0.06293	**0**	0	0.565595	0
5	1.085	0.88825	1.129	0.931	**1.107**	0.03111	**0.909625**	0.03023	0.27962	0.27167625
10	0.754	1.2027	0.933	1.1172	**0.8435**	0.12657	**1.15995**	0.06046	1.137545	0.5433525
20	0.626	1.3243	0.749	1.292	**0.6875**	0.08697	**1.30815**	0.02284	0.781665	0.2052665
30	0.645	1.30625	0.669	1.368	**0.657**	0.01697	**1.337125**	0.04366	0.15252	0.39242125
40	0.595	1.35375	0.633	1.4022	**0.614**	0.02687	**1.377975**	0.03426	0.24149	0.30789975
50	0.515	1.42975	0.587	1.4459	**0.551**	0.05091	**1.437825**	0.01142	0.45756	0.10263325
60	0.465	1.47725	0.535	1.4953	**0.5**	0.0495	**1.486275**	0.01276	0.44485	0.11470775

Table A6: Copper uptake by 100mg of immobilised biomass in PEI from 95ml of $2mgl^{-1}$ copper solution at an initial pH 7.0 and room temperature

Time (min)	Exp (1)		Exp (2)		Cu conc. Average C (mg/l)	C Stdev	Uptake capacity average Q (mg/g)	Q Stdev	95% confidence limits on the mean of Cu conc. (C)	95% confidence limits on the mean of uptake (Q)
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	1.869	0	1.913	0	**1.891**	0.03111	**0**	0	0.27962	0
5	1.827	0.0399	1.864	0.04655	**1.8455**	0.02616	**0.043225**	0.0047	0.235135	0.04226075
10	1.817	0.0494	1.831	0.0779	**1.824**	0.0099	**0.06365**	0.02015	0.08897	0.1811175
20	1.758	0.10545	1.784	0.12255	**1.771**	0.01838	**0.114**	0.01209	0.16523	0.1086705
30	1.655	0.2033	1.721	0.1824	**1.688**	0.04667	**0.19285**	0.01478	0.41943	0.1328195
40	1.65	0.20805	1.689	0.2128	**1.6695**	0.02758	**0.210425**	0.00336	0.247845	0.03018625
50	1.577	0.2774	1.632	0.26695	**1.6045**	0.03889	**0.272175**	0.00739	0.349525	0.06640975
60	1.468	0.38095	1.5225	0.37098	**1.49525**	0.03854	**0.3759625**	0.00705	0.3463475	0.063391125

Table A7: Copper uptake by 100mg of immobilised biomass in polyacrylamide from 95ml of $2mgl^{-1}$ copper solution at an initial pH 7.0 and room temperature

Time (min)	Exp (1)		Exp (2)		Cu conc. Average C (mg/l)	C Stdev	Uptake capacity average Q (mg/g)	Q Stdev	95% confidence limits on the mean of Cu conc. (C)	95% confidence limits on the mean of uptake (Q)
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	1.887	0	1.633	0	**1.76**	0.17961	**0**	0	1.61417	0
5	1.702	0.17575	1.489	0.1368	**1.5955**	0.15061	**0.156275**	0.02754	1.353615	0.24752725
10	1.67	0.20615	1.464	0.16055	**1.567**	0.14566	**0.18335**	0.03224	1.30913	0.289788
20	1.621	0.2527	1.42	0.20235	**1.5205**	0.14213	**0.227525**	0.0356	1.277355	0.31997425
30	1.543	0.3268	1.324	0.29355	**1.4335**	0.15486	**0.310175**	0.02351	1.391745	0.21130375
40	1.478	0.38855	1.285	0.3306	**1.3815**	0.13647	**0.359575**	0.04098	1.226515	0.36827225
50	1.382	0.47975	1.24	0.37335	**1.311**	0.10041	**0.42655**	0.07524	0.90241	0.676172
60	1.308	0.55005	1.114	0.49305	**1.211**	0.13718	**0.52155**	0.04031	1.23287	0.362235

Table A8: Copper uptake by 100mg of immobilised biomass in alginate from 95ml of $2mgl^{-1}$ copper solution at an initial pH 7.0 and room temperature

Time (min)	Exp (1)		Exp (2)		Cu conc. Average C (mg/l)	C Stdev	Uptake capacity average Q (mg/g)	Q Stdev	95% confidence limits on the mean of Cu conc. (C)	95% confidence limits on the mean of uptake (Q)
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	1.59	0	1.61	0	**1.6**	0.01414	**0**	0	0.1271	0
5	1.548	0.0399	1.567	0.04085	**1.5575**	0.01344	**0.040375**	0.00067	0.120745	0.00603725
10	1.489	0.09595	1.561	0.04655	**1.525**	0.05091	**0.07125**	0.03493	0.45756	0.313937
20	1.378	0.2014	1.471	0.13205	**1.4245**	0.06576	**0.166725**	0.04904	0.591015	0.44071925
30	1.374	0.2052	1.404	0.1957	**1.389**	0.02121	**0.20045**	0.00672	0.19065	0.0603725
40	1.269	0.30495	1.32	0.2755	**1.2945**	0.03606	**0.290225**	0.02082	0.324105	0.18715475
50	1.287	0.28785	1.253	0.33915	**1.27**	0.02404	**0.3135**	0.03627	0.21607	0.3260115
60	1.191	0.37905	1.207	0.38285	**1.199**	0.01131	**0.38095**	0.00269	0.10168	0.024149

Table A9: Copper uptake by unloaded beads of k-carrageenan from 95ml of 2mgl^{-1} copper solution at an initial pH 7.0 and room temperature

Time (min)	Exp (1)		Exp (2)		**Cu conc. Average C (mg/l)**	C Stdev	**Uptake capacity average Q (mg/g)**	Q Stdev	95% confidence limits on the mean of Cu conc. (C)	95% confidence limits on the mean of uptake (Q)
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	1.58	0	1.84	0	**1.71**	0.183848	**0**	0	1.6523	0
5	1.573	0.00665	1.827	0.01235	**1.7**	0.179605	**0.0095**	0.004031	1.61417	0.0362235
10	1.542	0.0361	1.801	0.03705	**1.6715**	0.183141	**0.036575**	0.000672	1.645945	0.0060373
20	1.438	0.1349	1.783	0.05415	**1.6105**	0.243952	**0.094525**	0.057099	2.192475	0.5131663
30	1.357	0.21185	1.636	0.1938	**1.4965**	0.197283	**0.202825**	0.012763	1.773045	0.1147077
40	1.338	0.2299	1.492	0.3306	**1.415**	0.108894	**0.28025**	0.071206	0.97867	0.6399485
50	1.272	0.2926	1.493	0.32965	**1.3825**	0.156271	**0.311125**	0.026198	1.404455	0.2354528
60	1.246	0.3173	1.442	0.3781	**1.344**	0.138593	**0.3477**	0.042992	1.24558	0.386384

Table A10: Copper uptake by unloaded beads of polysulfone from 95ml of 2mgl^{-1} copper solution at an initial pH 7.0 and room temperature

Time (min)	Exp (1)		Exp (2)		**Cu conc. Average C (mg/l)**	C Stdev	**Uptake capacity average Q (mg/g)**	Q Stdev	95% confidence limits on the mean of Cu conc. (C)	95% confidence limits on the mean of uptake (Q)
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	1.532	0	1.568	0	**1.55**	0.025456	**0**	0	0.22878	0
5	1.433	0.09405	1.509	0.05605	**1.471**	0.05374	**0.07505**	0.02687	0.48298	0.24149
10	1.372	0.152	1.442	0.1197	**1.407**	0.049497	**0.13585**	0.02284	0.44485	0.2052665
20	1.305	0.21565	1.456	0.1064	**1.3805**	0.106773	**0.161025**	0.077251	0.959605	0.6942837
30	1.297	0.22325	1.505	0.05985	**1.401**	0.147078	**0.14155**	0.115541	1.32184	1.038407
40	1.361	0.16245	1.266	0.2869	**1.3135**	0.067175	**0.224675**	0.087999	0.603725	0.7908798
50	1.259	0.25935	1.271	0.28215	**1.265**	0.008485	**0.27075**	0.016122	0.07626	0.144894
60	1.251	0.26695	1.306	0.2489	**1.2785**	0.038891	**0.257925**	0.012763	0.349525	0.1147078

Table A11: Copper uptake by unloaded beads of polyvinlformal from 95ml of 2mgl^{-1} copper solution at an initial pH 7.0 and room temperature

Time (min)	Exp (1)		Exp (2)		**Cu conc. Average C (mg/l)**	C Stdev	**Uptake capacity average Q (mg/g)**	Q Stdev	95% confidence limits on the mean of Cu conc. (C)	95% confidence limits on the mean of uptake (Q)
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	1.589	0	1.577	0	**1.583**	0.008485	**0**	0	0.07626	0
5	1.506	0.07885	1.536	0.03895	**1.521**	0.021213	**0.0589**	0.028214	0.19065	0.2535645
10	1.597	-0.0076	1.577	0	**1.587**	0.014142	**0**	0.005374	0.1271	0.048298
20	1.586	0.00285	1.562	0.01425	**1.574**	0.016971	**0.00855**	0.008061	0.15252	0.072447
30	1.564	0.02375	1.577	0	**1.5705**	0.009192	**0.011875**	0.016794	0.082615	0.1509312
40	1.6	-0.0104	1.571	0.0057	**1.5855**	0.020506	**0**	0.01142	0.184295	0.1026333
50	1.599	-0.0095	1.566	0.01045	**1.5825**	0.023335	**0.000475**	0.014107	0.209715	0.1267822
60	1.533	0.0532	1.535	0.0399	**1.534**	0.001414	**0.04655**	0.009405	0.01271	0.0845215

Table A12: Copper uptake by unloaded beads of polyurethane from 95ml of 2mgl^{-1} copper solution at an initial pH 7.0 and room temperature

Time (min)	Exp (1)		Exp (2)		**Cu conc. Average C (mg/l)**	C Stdev	**Uptake capacity average Q (mg/g)**	Q Stdev	95% confidence limits on the mean of Cu conc. (C)	95% confidence limits on the mean of uptake (Q)
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	1.386	0	1.606	0	**1.496**	0.155563	**0**	0	1.3981	0
5	1.266	0.114	1.605	0.00095	**1.4355**	0.239709	**0.057475**	0.079938	2.154345	0.7184327
10	1.299	0.08265	1.507	0.09405	**1.403**	0.147078	**0.08835**	0.008061	1.32184	0.072447
20	1.251	0.12825	1.578	0.0266	**1.4145**	0.231224	**0.077425**	0.071877	2.078085	0.6459858
30	1.261	0.11875	1.557	0.04655	**1.409**	0.209304	**0.08265**	0.051053	1.88108	0.458831
40	1.315	0.06745	1.499	0.10165	**1.407**	0.130108	**0.08455**	0.024183	1.16932	0.217341
50	1.219	0.15865	1.581	0.02375	**1.4**	0.255973	**0.0912**	0.095389	2.30051	0.8572895
60	1.294	0.0874	1.527	0.07505	**1.4105**	0.164756	**0.081225**	0.008733	1.480715	0.0784842

Table A13: Copper uptake by unloaded beads of PEI from 95ml of 2mgl^{-1} copper solution at an initial pH 7.0 and room temperature

Time (min)	Exp (1)		Exp (2)		**Cu conc. Average C (mg/l)**	C Stdev	**Uptake capacity average Q (mg/g)**	Q Stdev	95% confidence limits on the mean of Cu conc. (C)	95% confidence limits on the mean of uptake (Q)
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	1.432	0	1.651	0	**1.5415**	0.154856	**0**	0	1.391745	0
5	1.373	0.05605	1.594	0.05415	**1.4835**	0.156271	**0.0551**	0.001344	1.404455	0.0120745
10	1.4193	0.012065	1.616	0.03325	**1.51765**	0.139088	**0.0226575**	0.01498	1.2500285	0.1346307
20	1.369	0.05985	1.579	0.0684	**1.474**	0.148492	**0.064125**	0.006046	1.33455	0.0543353
30	1.399	0.03135	1.649	0.0019	**1.524**	0.176777	**0.016625**	0.020824	1.58875	0.1871548
40	1.416	0.0152	1.539	0.1064	**1.4775**	0.086974	**0.0608**	0.064488	0.781665	0.579576
50	1.422	0.0095	1.596	0.05225	**1.509**	0.123037	**0.030875**	0.030229	1.10577	0.2716763
60	1.424	0.0076	1.641	0.0095	**1.5325**	0.153442	**0.00855**	0.001344	1.379035	0.0120745

Table A14: Copper uptake by unloaded beads of polyacrylamide from 95ml of 2 mgl^{-1} copper solution at an initial pH 7.0 and room temperature

Time (min)	Exp (1)		Exp (2)		**Cu conc. Average C (mg/l)**	C Stdev	**Uptake capacity average Q (mg/g)**	Q Stdev	95% confidence limits on the mean of Cu conc. (C)	95% confidence limits on the mean of uptake (Q)
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	1.44	0	1.616	0	**1.528**	0.124451	**0**	0	1.11848	0
5	1.423	0.01615	1.513	0.09785	**1.468**	0.06364	**0.057**	0.057771	0.57195	0.5192035
10	1.354	0.0817	1.408	0.1976	**1.381**	0.038184	**0.13965**	0.081954	0.34317	0.7365445
20	1.426	0.0133	1.475	0.13395	**1.4505**	0.034648	**0.073625**	0.085312	0.311395	0.7667308
30	1.397	0.04085	1.527	0.08455	**1.462**	0.091924	**0.0627**	0.030901	0.82615	0.2777135
40	1.441	-0.0009	1.52	0.0912	**1.4805**	0.055861	**0.045125**	0.06516	0.502045	0.5856133
50	1.401	0.03705	1.463	0.14535	**1.432**	0.043841	**0.0912**	0.07658	0.39401	0.6882465
60	1.432	0.0076	1.533	0.07885	**1.4825**	0.071418	**0.043225**	0.050381	0.641855	0.4527938

Table A15: Copper uptake by unloaded beads of alginate from 95ml of 2mgl^{-1} copper solution at an initial pH 7.0 and room temperature

Time (min)	Exp (1)		Exp (2)		Cu conc. Average C (mg/l)	C Stdev	Uptake capacity average Q (mg/g)	Q Stdev	95% confidence limits on the mean of Cu conc. (C)	95% confidence limits on the mean of uptake (Q)
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	1.424	0	1.636	0	**1.53**	0.149907	**0**	0	1.34726	0
5	1.379	0.04275	1.505	0.12445	**1.442**	0.089095	**0.0836**	0.057771	0.80073	0.5192035
10	1.393	0.02945	1.444	0.1824	**1.4185**	0.036062	**0.105925**	0.108152	0.324105	0.9719973
20	1.358	0.0627	1.351	0.27075	**1.3545**	0.00495	**0.166725**	0.147114	0.044485	1.3221578
30	1.376	0.0456	1.254	0.3629	**1.315**	0.086267	**0.20425**	0.224365	0.77531	2.0164415
40	1.249	0.16625	1.23	0.3857	**1.2395**	0.013435	**0.275975**	0.155175	0.120745	1.3946048
50	1.224	0.19	1.176	0.437	**1.2**	0.033941	**0.3135**	0.174655	0.30504	1.569685
60	1.251	0.16435	1.193	0.42085	**1.222**	0.041012	**0.2926**	0.181373	0.36859	1.6300575

Table A16: Copper uptake by free and polymer immobilised biomass from 95ml of 2mgl^{-1} copper solution at an initial pH7.0, room temperature and 4 hours contact time; in all cases the quantity of biomass used was 100mg

Time (hrs)	1- Non-immobilised biomass		2- biomass in polysulfone		3- biomass in polyvinlformal	
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)
0	1.78	0	1.673	0	1.638	0
0.25	0.682	1.0431	1.578	0.09025	1.529	0.10355
0.5	0.523	1.19415	1.503	0.1615	1.507	0.12445
1	0.46	1.254	1.251	0.4009	1.493	0.13775
1.5	0.393	1.31765	1.166	0.48165	1.46	0.1691
2	0.388	1.3224	1.064	0.57855	1.506	0.1254
2.5	0.383	1.32715	1.042	0.59945	1.44	0.1881
3	0.38	1.33	0.862	0.77045	1.416	0.2109
3.5	0.356	1.3528	0.885	0.7486	1.488	0.1425
4	0.333	1.37465	0.846	0.78565	1.437	0.19095

Table 16: continued

Time (hrs)	4- biomass in polyurethane		5- biomass in PEI		6- biomass in polyacrylamide		7- biomass in alginate	
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)
0	1.92	0	1.812	0	1.823	0	1.568	0
0.25	0.751	1.11055	1.771	0.03895	1.814	0.00855	1.535	0.03135
0.5	0.715	1.14475	1.69	0.1159	1.639	0.1748	1.33	0.2261
1	0.594	1.2597	1.61	0.1919	1.427	0.3762	1.226	0.3249
1.5	0.513	1.33665	1.491	0.30495	1.286	0.51015	1.101	0.44365
2	0.484	1.3642	1.418	0.3743	1.214	0.57855	0.954	0.5833
2.5	0.403	1.44115	1.318	0.4693	1.112	0.67545	0.868	0.665
3	0.425	1.42025	1.256	0.5282	1.058	0.72675	0.772	0.7562
3.5	0.392	1.4516	1.206	0.5757	0.962	0.81795	0.7	0.8246
4	0.384	1.4592	1.171	0.60895	0.941	0.8379	0.67	0.8531

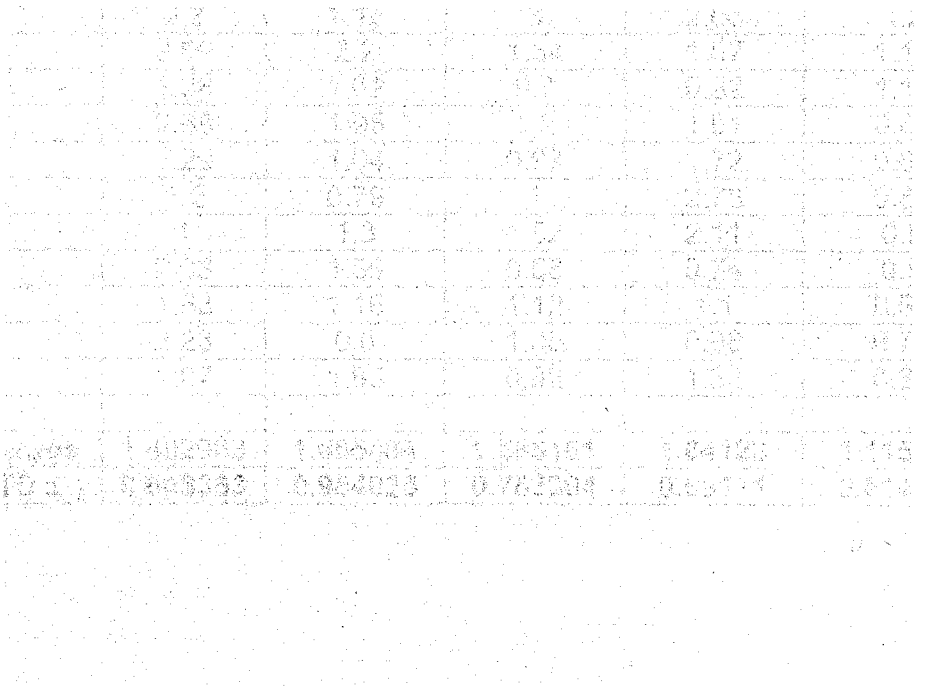


Table A17: Pore sizes of different hydrophobic foams manufactured at 10 rps mixing speed, 20-30 sec mixing time using 2 pins mixer

	Pores diameter (mm)				
Water ratio	no water	0.25%	0.50%	1%	1.50%
	1	1	2.58	1.99	0.85
	1.5	2.82	1.45	2.9	1.68
	0.5	5.2	2.02	2.11	2.23
	1	1.25	1.07	1.55	1.88
	1	1.77	1.39	2.15	1.56
	1.13	0.97	0.96	1.23	0.98
	1.5	1.74	2.38	2.53	1.38
	1.06	1.72	1.34	1.75	0.64
	0.84	4.69	1.31	1.04	0.89
	3	1.58	4.28	1.11	0.86
	2	1.03	1.83	1.47	1.21
	1.58	1.63	0.88	2.25	0.64
	1	1.48	1.69	1.42	3.56
	1.5	1.23	1.68	1.04	0.95
	1	1.2	1.63	1.41	0.94
	1.25	1.27	2.35	1.24	0.54
	1	1.3	1.46	2.54	0.71
	1.35	1.4	1.68	1.13	1.31
	1	1.99	1.58	2.06	1.26
	1	1.13	2.3	1.65	1.45
	2.3	1.16	3	2.06	1.2
	2.69	2.2	1.34	1.67	1.15
	1.36	1.62	0.7	0.92	1.16
	0.88	1.95	1.2	1.01	0.64
	1.29	1.04	0.97	1.72	0.61
	1.2	0.79	1	2.78	0.84
	1	1.3	1.52	2.11	0.8
	2.63	1.56	0.56	0.74	0.5
	1.63	1.16	1.12	1.1	0.57
	2.23	0.6	1.05	0.88	0.71
	1.07	1.85	0.82	1.32	0.89
Average	**1.402903**	**1.665484**	**1.585161**	**1.64129**	**1.115806**
STD ±	**0.603353**	**0.984025**	**0.763304**	**0.59111**	**0.614762**

Table A18: Copper adsorption using non-immobilised fungi particles (D<150μm), at initial copper concentration of 2 mgl^{-1}, initial pH 7.0, room temp., and 0.69 gl^{-1} biomass concentration

Time (min)	Exp (1)		Exp (2)		Cu conc. Average C (mg/l)	C Stdev	Uptake capacity average Q (mg/g)	Q Stdev	95% confidence limits on the mean of Cu conc.	95% confidence limits on the mean of uptake
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	2.11232	0	2.032078	0	**2.072198**	0.05674	**0**	0	0.5099252	0
15	0.6378	2.1344	0.602594	2.07275	**0.620199**	0.0249	**2.1035759**	0.04359	0.2237596	0.3917743
30	0.53117	2.2881	0.484892	2.24342	**0.50803**	0.03272	**2.2657599**	0.03159	0.294084	0.2839433
45	0.45773	2.39395	0.46779	2.26822	**0.46276**	0.00711	**2.3310838**	0.08891	0.0639313	0.7990294
60	0.45069	2.4041	0.414472	2.34553	**0.43258**	0.02561	**2.3748144**	0.04142	0.2301527	0.3722206
75	0.41145	2.46065	0.4024	2.36303	**0.406927**	0.0064	**2.4118416**	0.06903	0.0575382	0.6203554
90	0.38832	2.494	0.353106	2.43451	**0.370711**	0.0249	**2.4642547**	0.04207	0.2237595	0.3780628
105	0.37222	2.5172	0.31186	2.49432	**0.34204**	0.04268	**2.5057581**	0.01618	0.3835878	0.1454272
120	0.35713	2.53895	0.3018	2.5089	**0.329465**	0.03912	**2.5239266**	0.02125	0.3516222	0.190948
135	0.39033	2.4911	0.279668	2.54099	**0.334998**	0.07825	**2.5160473**	0.03528	0.7032443	0.3170795
150	0.34305	2.55925	0.26659	2.55996	**0.304818**	0.05406	**2.5596038**	0.0005	0.4858779	0.0044968
165	0.34103	2.56215	0.260554	2.56871	**0.300794**	0.05691	**2.5654299**	0.00464	0.5114504	0.0416875
180	0.34204	2.5607	0.259548	2.57017	**0.300794**	0.05833	**2.5654343**	0.0067	0.5242367	0.0601723
195	0.34808	2.552	0.26156	2.56725	**0.304818**	0.06118	**2.5596256**	0.01078	0.5498092	0.0969207
210	0.34003	2.5636	0.262566	2.56579	**0.301297**	0.05477	**2.5646962**	0.00155	0.492271	0.0139327
225	0.34103	2.56215	0.25653	2.57454	**0.298782**	0.05975	**2.5683473**	0.00876	0.5370229	0.0787677
240	0.33701	2.56795	0.257536	2.57309	**0.297273**	0.0562	**2.570518**	0.00363	0.5050573	0.0326386
255	0.33299	2.57375	0.257536	2.57309	**0.295261**	0.05335	**2.573418**	0.00047	0.4794848	0.0042204
270	0.336	2.5694	0.259548	2.57017	**0.297776**	0.05406	**2.5697843**	0.00054	0.4858779	0.0048838
285	0.33198	2.5752	0.260554	2.56871	**0.296267**	0.05051	**2.5719549**	0.00459	0.4539122	0.0412452
300	0.33097	2.57665	0.255524	2.576	**0.293249**	0.05335	**2.5763267**	0.00046	0.4794848	0.0041098
315	0.33399	2.5723	0.255524	2.576	**0.294758**	0.05549	**2.5741517**	0.00262	0.4986641	0.0235345
330	0.33399	2.5723	0.252506	2.58038	**0.293249**	0.05762	**2.5763397**	0.00571	0.5178435	0.0513446
345	0.33802	2.5665	0.25653	2.57454	**0.297273**	0.05762	**2.5705223**	0.00569	0.5178435	0.0511234
360	0.336	2.5694	0.254518	2.57746	**0.295261**	0.05762	**2.573431**	0.0057	0.5178435	0.051234
375	0.33701	2.56795	0.254518	2.57746	**0.295764**	0.05833	**2.572706**	0.00673	0.5242367	0.0604488
390	0.33902	2.56505	0.257536	2.57309	**0.298279**	0.05762	**2.569068**	0.00568	0.5178435	0.0510681
405	0.34204	2.5607	0.259548	2.57017	**0.300794**	0.05833	**2.5654343**	0.0067	0.5242367	0.0601723
420	0.34103	2.56215	0.255524	2.576	**0.298279**	0.06046	**2.5690767**	0.0098	0.5434161	0.0880377
435	0.34103	2.56215	0.25653	2.57454	**0.298782**	0.05975	**2.5683473**	0.00876	0.5370229	0.0787677
450	0.33399	2.5723	0.25653	2.57454	**0.295261**	0.05477	**2.5734223**	0.00159	0.492271	0.0142644
465	0.336	2.5694	0.258542	2.57163	**0.297273**	0.05477	**2.5705136**	0.00157	0.492271	0.0141539
480	0.33701	2.56795	0.255524	2.576	**0.296267**	0.05762	**2.5719767**	0.00569	0.5178435	0.0511787
495	0.33198	2.5752	0.257536	2.57309	**0.294758**	0.05264	**2.574143**	0.00149	0.4730916	0.0134351
510	0.34003	2.5636	0.258542	2.57163	**0.299285**	0.05762	**2.5676136**	0.00568	0.5178435	0.0510129
525	0.34003	2.5636	0.25653	2.57454	**0.298279**	0.05904	**2.5690723**	0.00774	0.5306298	0.0695529
540	0.33902	2.56505	0.25653	2.57454	**0.297776**	0.05833	**2.5697973**	0.00671	0.5242367	0.0603382
555	0.33802	2.5665	0.257536	2.57309	**0.297776**	0.05691	**2.569793**	0.00466	0.5114504	0.0418534
570	0.34003	2.5636	0.255524	2.576	**0.297776**	0.05975	**2.5698017**	0.00877	0.5370229	0.078823
585	0.33399	2.5723	0.254518	2.57746	**0.294255**	0.0562	**2.574881**	0.00365	0.5050573	0.0328045
600	0.336	2.5694	0.253512	2.57892	**0.294758**	0.05833	**2.5741604**	0.00673	0.5242367	0.060504

Table A19: Copper adsorption using non-immobilised seaweed particles (D<150μm), at initial copper concentration of 2 mgl^{-1}, initial pH 7.0, room temperature and biomass concentration of 0.69 gl^{-1}

Time (min)	Exp (1)		Exp (2)		Cu conc. Average C (mg/l)	C Stdev	Uptake average Q (mg/g)	Q Stdev	95% confidence limits on the mean of Cu conc.	95% confidence limits on the mean of uptake
	Cu conc. (mg/l)	Seaweed uptake capacity (mg/g)	Cu conc. (mg/l)	Seaweed uptake capacity (mg/g)						
0	1.9047	0	1.867586	0	**1.88614**	0.0262414	**0**	0	0.2358404	0
15	0.3883	2.19385	0.33701	2.219335	**0.36266**	0.0362788	**2.206593**	0.01802	0.3260496	0.1619584
30	0.3471	2.2533	0.298782	2.274766	**0.32293**	0.0341448	**2.264033**	0.01518	0.3068702	0.1364152
45	0.3078	2.30985	0.269608	2.317068	**0.28872**	0.0270313	**2.313459**	0.0051	0.2429389	0.045871
60	0.2998	2.32145	0.260554	2.330196	**0.28017**	0.0277426	**2.325823**	0.00618	0.2493321	0.0555834
75	0.3149	2.2997	0.268602	2.318527	**0.29174**	0.0327221	**2.309113**	0.01331	0.294084	0.1196443
90	0.2817	2.34755	0.240434	2.35937	**0.26106**	0.0291653	**2.35346**	0.00836	0.2621183	0.0751186
105	0.2998	2.32145	0.264578	2.324362	**0.28218**	0.0248972	**2.322906**	0.00206	0.2237596	0.0185032
120	0.2726	2.3606	0.25995	2.331072	**0.26629**	0.008963	**2.345836**	0.02088	0.0805534	0.1876529
135	0.2887	2.3374	0.26156	2.328738	**0.27514**	0.0192064	**2.333069**	0.00613	0.1726145	0.0550489
150	0.3168	2.29695	0.280674	2.301022	**0.29873**	0.0255374	**2.298984**	0.00288	0.2295134	0.0259119
165	0.2827	2.3461	0.24647	2.350618	**0.26458**	0.0256086	**2.348359**	0.00319	0.2301527	0.0287132
180	0.2927	2.3316	0.252506	2.341866	**0.27263**	0.028454	**2.336733**	0.00726	0.2557252	0.0652404
195	0.3028	2.3171	0.254518	2.338949	**0.27866**	0.0341448	**2.328024**	0.01545	0.3068702	0.1388479
210	0.2736	2.35915	0.250494	2.344783	**0.26206**	0.016361	**2.351967**	0.01016	0.147042	0.0912997
225	0.2767	2.3548	0.263572	2.32582	**0.27011**	0.0092475	**2.34031**	0.02049	0.0831107	0.184166
240	0.2968	2.3258	0.273632	2.311233	**0.2852**	0.016361	**2.318517**	0.0103	0.147042	0.0925714
255	0.2887	2.3374	0.260554	2.330196	**0.27464**	0.0199178	**2.333798**	0.00509	0.1790076	0.0457789
270	0.2797	2.35045	0.264578	2.324362	**0.27212**	0.0106702	**2.337406**	0.01845	0.095897	0.1657918
285	0.2787	2.3519	0.269608	2.317068	**0.27414**	0.0064021	**2.334484**	0.02463	0.0575382	0.2213567
300	0.2787	2.3519	0.255524	2.33749	**0.26709**	0.016361	**2.344695**	0.01019	0.147042	0.0915762
315	0.2907	2.3345	0.263572	2.32582	**0.27715**	0.0192064	**2.33016**	0.00614	0.1726145	0.0551595
330	0.3038	2.31565	0.269608	2.317068	**0.28671**	0.0241859	**2.316359**	0.001	0.2173664	0.009012
345	0.2927	2.3316	0.272626	2.312692	**0.28269**	0.014227	**2.322146**	0.01337	0.1278626	0.1201603
360	0.2897	2.33595	0.269608	2.317068	**0.27967**	0.014227	**2.326509**	0.01335	0.1278626	0.1199945
375	0.3008	2.32	0.25653	2.336031	**0.27866**	0.0312994	**2.328016**	0.01134	0.2812977	0.1018783
390	0.2877	2.33885	0.262566	2.327279	**0.27514**	0.0177837	**2.333065**	0.00818	0.1598283	0.0735337
405	0.2968	2.3258	0.26156	2.328738	**0.27917**	0.0248972	**2.327269**	0.00208	0.2237596	0.0186691
420	0.2968	2.3258	0.27162	2.314151	**0.2842**	0.0177837	**2.319975**	0.00824	0.1598283	0.0740313
435	0.2746	2.3577	0.274638	2.309775	**0.27464**	0	**2.333737**	0.03389	0	0.3045659
450	0.2767	2.3548	0.272626	2.312692	**0.27464**	0.0028454	**2.333746**	0.02977	0.0255725	0.2675963
465	0.2907	2.3345	0.269608	2.317068	**0.28017**	0.0149383	**2.325784**	0.01233	0.1342557	0.1107797
480	0.3068	2.3113	0.260554	2.330196	**0.28369**	0.0327221	**2.320748**	0.01336	0.294084	0.1200866
495	0.2847	2.3432	0.265584	2.322903	**0.27514**	0.0135156	**2.333051**	0.01435	0.1214695	0.1289881
510	0.2907	2.3345	0.268602	2.318527	**0.27967**	0.0156497	**2.326513**	0.01129	0.1406489	0.1015097
525	0.2998	2.32145	0.26659	2.321444	**0.28319**	0.0234745	**2.321447**	4.1E-06	0.2109733	3.686E-05
540	0.3008	2.32	0.269608	2.317068	**0.2852**	0.0220518	**2.318534**	0.00207	0.198187	0.0186322
555	0.2807	2.349	0.262566	2.327279	**0.27162**	0.0128043	**2.33814**	0.01536	0.1150763	0.138037
570	0.2797	2.35045	0.26156	2.328738	**0.27061**	0.0128043	**2.339594**	0.01535	0.1150763	0.1379817
585	0.2726	2.3606	0.258542	2.333114	**0.26558**	0.0099589	**2.346857**	0.01944	0.0895038	0.1746748
600	0.2767	2.3548	0.259548	2.331655	**0.2681**	0.0120929	**2.343228**	0.01637	0.1086832	0.1470858

Table A20: Control flask contains only 145 ml of 2 mgl^{-1} copper concentration, at pH 7.0, room temperature

Time (min)	Cu concentration (mg/l)			Stdev	95% confidence limits on the average
	Exp(1)	Exp(2)	**Average**		
0	2.323	2.117	**2.22**	0.14566	1.30913
15	2.043	2.042	**2.0425**	0.00071	0.006355
30	2.056	2.072	**2.064**	0.01131	0.10168
45	2.091	2.064	**2.0775**	0.01909	0.171585
60	2.065	2.064	**2.0645**	0.00071	0.006355
75	2.102	2.082	**2.092**	0.01414	0.1271
90	2.092	2.098	**2.095**	0.00424	0.03813
105	2.12	2.08	**2.1**	0.02828	0.2542
120	2.092	2.085	**2.0885**	0.00495	0.044485
135	2.073	2.106	**2.0895**	0.02333	0.209715
150	2.102	2.121	**2.1115**	0.01344	0.120745
165	2.12	2.081	**2.1005**	0.02758	0.247845
180	2.132	2.066	**2.099**	0.04667	0.41943
195	2.19	2.087	**2.1385**	0.07283	0.654565
210	2.249	2.099	**2.174**	0.10607	0.95325
225	2.078	2.104	**2.091**	0.01838	0.16523
240	2.099	2.103	**2.101**	0.00283	0.02542
255	2.157	2.102	**2.1295**	0.03889	0.349525
270	2.259	2.115	**2.187**	0.10182	0.91512
285	2.161	2.113	**2.137**	0.03394	0.30504
300	2.309	2.089	**2.199**	0.15556	1.3981
315	2.153	2.142	**2.1475**	0.00778	0.069905
330	2.319	2.142	**2.2305**	0.12516	1.124835
345	2.159	2.12	**2.1395**	0.02758	0.247845
360	2.168	2.202	**2.185**	0.02404	0.21607
375	2.188	2.154	**2.171**	0.02404	0.21607
390	2.203	2.12	**2.1615**	0.05869	0.527465
405	2.199	2.099	**2.149**	0.07071	0.6355
420	2.178	2.078	**2.128**	0.07071	0.6355
435	2.169	2.121	**2.145**	0.03394	0.30504
450	2.188	2.11	**2.149**	0.05515	0.49569
465	2.188	2.01	**2.099**	0.12587	1.13119
480	2.2	2.117	**2.1585**	0.05869	0.527465
495	2.215	2.066	**2.1405**	0.10536	0.946895
510	2.189	2.144	**2.1665**	0.03182	0.285975
525	2.197	2.155	**2.176**	0.0297	0.26691
540	2.179	2.155	**2.167**	0.01697	0.15252
555	2.211	2.187	**2.199**	0.01697	0.15252
570	2.11	2.12	**2.115**	0.00707	0.06355
585	2.288	2.089	**2.1885**	0.14071	1.264645
600	2.279	2.1	**2.1895**	0.12657	1.137545

Table A21: Copper adsorption by fungi-hydrophobic polyurethane beads using $2mgl^{-1}$ Cu solution at an initial pH 7.0, room temperature and immobilised biomass concentration of $0.69\ gl^{-1}$

Time (min)	Exp (1)		Exp (2)		C average (mg/l)	C Stdev	Q average (mg/g)	Q Stdev	95% confidence limits on the mean of Cu conc.	95% confidence limits on the mean of uptake
	Cu conc. (mg/l)	Beads uptake capacity (mg/g)	Cu conc. (mg/l)	Beads uptake capacity (mg/g)						
0	2.19858	0	2.032078	0	**2.115327**	0.11773	**0**	0	1.0580948	0
15	2.19308	0.0174	1.903352	0.186653	**2.048216**	0.20487	**0.1020264**	0.1197	1.8412214	1.0756009
30	2.17497	0.0435	2.010994	0.030572	**2.092983**	0.11595	**0.0370359**	0.0091	1.0420802	0.0821587
45	2.18403	0.03045	1.910394	0.176442	**2.04721**	0.19349	**0.1034459**	0.1032	1.7389314	0.9277779
60	2.18704	0.0261	1.809794	0.322312	**1.998419**	0.26676	**0.1742059**	0.2095	2.3974238	1.882426
75	2.15083	0.0783	2.023066	0.013067	**2.086947**	0.09034	**0.0456837**	0.0461	0.8119275	0.4145532
90	2.13574	0.10005	2.114612	-0.11967	**2.125175**	0.01494	**-0.009812**	0.1554	0.1342557	1.3963479
105	2.12769	0.11165	1.998922	0.048076	**2.063306**	0.09105	**0.0798631**	0.045	0.8183206	0.4040115
120	2.2132	-0.0116	2.000934	0.045159	**2.107067**	0.15009	**0.0167794**	0.0401	1.3489504	0.3607022
135	2.20012	0.00725	1.89128	0.204157	**2.045701**	0.21838	**0.1057036**	0.1392	1.9626909	1.2513446
150	2.10355	0.14645	1.965724	0.096213	**2.034635**	0.09745	**0.1213317**	0.0355	0.8758588	0.3192542
165	2.01099	0.27985	1.93655	0.138516	**1.973772**	0.05264	**0.2091828**	0.0999	0.4730916	0.8981801
180	2.00093	0.29435	1.998922	0.048076	**1.999928**	0.00142	**0.1712131**	0.1741	0.0127863	1.56507
195	2.11461	0.1305	2.023066	0.013067	**2.068839**	0.06473	**0.0717837**	0.083	0.5817748	0.7462842
210	2.22427	0.02755	2.063306	-0.04528	**2.143786**	0.11382	**-0.036415**	0.0125	1.0229008	0.112678
225	2.22427	0.02755	2.024072	0.011609	**2.124169**	0.14156	**-0.007971**	0.0277	1.2722329	0.2488535
240	2.20113	0.0058	1.908382	0.179359	**2.054755**	0.207	**0.0925796**	0.1227	1.8604008	1.1029687
255	2.21119	-0.0087	1.92649	0.153103	**2.068839**	0.20131	**0.0722013**	0.1144	1.8092558	1.0282555
270	2.19006	0.02175	1.870154	0.23479	**2.030108**	0.22621	**0.1282699**	0.1506	2.0330153	1.3538679
285	2.17296	0.0464	2.045198	-0.01902	**2.109079**	0.09034	**0.013688**	0.0463	0.8119275	0.4157695
300	2.11059	0.1363	2.11763	-0.12405	**2.114109**	0.00498	**0.0061248**	0.1841	0.0447519	1.6545268
315	2.12367	0.11745	2.06733	-0.05112	**2.095498**	0.03984	**0.0331673**	0.1192	0.3580153	1.0712331
330	1.99691	0.30015	2.009988	0.03203	**2.003449**	0.00925	**0.1660903**	0.1896	0.0831107	1.7038994
345	1.91039	0.42485	2.007976	0.034948	**1.959185**	0.069	**0.2298989**	0.2757	0.6201336	2.4778278
360	2.17095	0.0493	1.967736	0.093296	**2.069342**	0.14369	**0.0712979**	0.0311	1.2914123	0.2795939
375	2.2132	-0.0116	1.967736	0.093296	**2.090468**	0.17357	**0.0408479**	0.0742	1.5599237	0.6666134
390	2.20012	0.00725	2.012	0.029113	**2.106061**	0.13302	**0.0181815**	0.0155	1.1955153	0.13894
405	2.14781	0.08265	2.023066	0.013067	**2.085438**	0.08821	**0.0478587**	0.0492	0.7927481	0.4421974
420	2.2132	-0.0116	2.010994	0.030572	**2.112097**	0.14298	**0.0094859**	0.0298	1.2850191	0.2680018
435	2.01099	0.27985	2.009988	0.03203	**2.010491**	0.00071	**0.1559403**	0.1752	0.0063931	1.5748929
450	2.13272	0.1044	1.910394	0.176442	**2.021557**	0.15721	**0.1404209**	0.0509	1.4128817	0.4578256
465	1.90134	0.4379	2.07739	-0.0657	**1.989365**	0.12449	**0.1860988**	0.3561	1.1187978	3.2003933
480	2.22326	-0.0261	2.026084	0.008691	**2.124672**	0.13942	**-0.008704**	0.0246	1.2530535	0.2210987
495	1.99892	0.29725	2.123666	-0.1328	**2.061294**	0.08821	**0.0822237**	0.3041	0.7927481	2.7329843
510	1.91039	0.42485	1.809794	0.322312	**1.860094**	0.07113	**0.3735809**	0.0725	0.639313	0.6516303
525	2.00093	0.29435	1.899328	0.192487	**1.950131**	0.07185	**0.2434188**	0.072	0.6457061	0.6473362
540	2.16793	0.05365	2.008982	0.033489	**2.088456**	0.11239	**0.0435696**	0.0143	1.0101145	0.1281219
555	2.18101	0.0348	2.043186	-0.01611	**2.112097**	0.09745	**0.0093467**	0.036	0.8758588	0.3235114
570	2.16189	0.06235	2.012	0.029113	**2.086947**	0.10599	**0.0457315**	0.0235	0.9525764	0.2112205
585	2.22628	-0.03045	1.963712	0.099131	**2.094995**	0.18566	**0.0343403**	0.0916	1.6686069	0.8234853
600	2.18201	0.03335	2.009988	0.03203	**2.096001**	0.12164	**0.0326902**	0.0009	1.0932252	0.0083854

Table A22: Copper removal by pre-conditioned fungi-Hydrophobic polyurethane beads with 1 mole.l^{-1} H_2SO_4 using 2mgl^{-1} Cu solution at an initial pH 7.0, room temperature and immobilised biomass concentration of 0.69 gl^{-1}

Time (min)	Exp (1)		Exp (2)		Cu conc. average C (mg/l)	C Stdev	Uptake capacity average Q (mg/g)	Q Stdev	95% confidence limits on the mean of Cu conc.	95% confidence limits on the mean of uptake
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	2.38413	0	2.51753	0	**2.450831**	0.09433	**0**	0	0.8477506	0
15	2.4315	-0.058	2.512988	0.006586	**2.472245**	0.05762	**-0.025707**	0.0457	0.5178435	0.4104434
30	2.43854	0.06815	2.502928	0.021173	**2.470736**	0.04553	**-0.023489**	0.0632	0.4091603	0.567647
45	2.4144	0.03335	2.373154	0.209345	**2.393777**	0.02917	**0.0879976**	0.1716	0.2621183	1.542328
60	2.42144	-0.0435	2.433514	0.121823	**2.427478**	0.00854	**0.0391616**	0.1169	0.0767176	1.0506289
75	2.40836	0.02465	2.495886	0.031384	**2.452125**	0.06189	**0.0033669**	0.0396	0.5562023	0.3560948
90	2.42848	0.05365	2.481802	0.051806	**2.455143**	0.0377	**-0.000922**	0.0746	0.3388359	0.6701703
105	2.36712	0.0348	2.472748	0.064934	**2.419933**	0.07469	**0.0498669**	0.0213	0.6712786	0.1915009
120	2.40434	0.01885	2.502928	0.021173	**2.453634**	0.06971	**0.0011614**	0.0283	0.6265267	0.2543455
135	2.39629	0.00725	2.52506	-0.01092	**2.460676**	0.09105	**-0.009084**	0.0026	0.8183206	0.0233133
150	2.36209	0.04205	2.583408	-0.09552	**2.472748**	0.1565	**-0.026737**	0.0973	1.4064886	0.8742771
165	2.41339	-0.0319	2.52506	-0.01092	**2.469227**	0.07896	**-0.021409**	0.0148	0.7096374	0.1333374
180	2.39931	-0.0116	2.515	0.003668	**2.457155**	0.08181	**-0.003966**	0.0108	0.7352099	0.0970313
195	2.3802	0.01595	2.515	0.003668	**2.447598**	0.09532	**0.0098092**	0.0087	0.8566794	0.0780489
210	2.40233	0.01595	2.503934	0.019714	**2.453131**	0.07185	**0.0018821**	0.0252	0.6457061	0.226646
225	2.42446	0.04785	2.46973	0.06931	**2.447095**	0.03201	**0.01073**	0.0828	0.2876909	0.7445518
240	2.43553	-0.0638	2.482808	0.050347	**2.459167**	0.03343	**-0.006727**	0.0807	0.3004771	0.7254035
255	2.4144	0.03335	2.503934	0.019714	**2.459167**	0.06331	**-0.006818**	0.0375	0.5689886	0.337223
270	2.39126	0	2.501922	0.022632	**2.446592**	0.07825	**0.0113158**	0.016	0.7032443	0.1438238
285	2.41239	0.03045	2.470736	0.067851	**2.441562**	0.04126	**0.0187006**	0.0695	0.3708015	0.6247048
300	2.42446	0.04785	2.516006	0.00221	**2.470233**	0.06473	**-0.02282**	0.0354	0.5817748	0.31813
315	2.42949	-0.0551	2.52506	-0.01092	**2.477275**	0.06758	**-0.033009**	0.0312	0.6073474	0.2807734
330	2.41541	-0.0348	2.515	0.003668	**2.465203**	0.07042	**-0.015566**	0.0272	0.6329199	0.2444673
345	2.3802	0.01595	2.54518	-0.04009	**2.462688**	0.11666	**-0.012071**	0.0396	1.0484733	0.3561501
360	2.39931	-0.0116	2.521036	-0.00508	**2.460173**	0.08607	**-0.008342**	0.0046	0.7735687	0.0414111
375	2.40333	-0.0174	2.515	0.003668	**2.459167**	0.07896	**-0.006866**	0.0149	0.7096374	0.1338903
390	2.41339	-0.0319	2.510976	0.009503	**2.462185**	0.069	**-0.011198**	0.0293	0.6201336	0.263118
405	2.42446	0.04785	2.49991	0.025549	**2.462185**	0.05335	**-0.011151**	0.0519	0.4794848	0.4664506
420	2.4144	0.03335	2.52506	-0.01092	**2.46973**	0.07825	**-0.022134**	0.0159	0.7032443	0.1425522
435	2.4144	0.03335	2.515	0.003668	**2.4647**	0.07113	**-0.014841**	0.0262	0.639313	0.2352526
450	2.39931	-0.0116	2.515	0.003668	**2.457155**	0.08181	**-0.003966**	0.0108	0.7352099	0.0970313
465	2.37315	0.0261	2.53512	-0.02551	**2.454137**	0.11453	**0.0002972**	0.0365	1.0292939	0.327953
480	2.41339	-0.0319	2.513994	0.005127	**2.463694**	0.07113	**-0.013386**	0.0262	0.639313	0.2353079
495	2.39227	0.00145	2.465706	0.075145	**2.428987**	0.05193	**0.0368474**	0.0542	0.4666985	0.48676
510	2.36913	0.0319	2.49991	0.025549	**2.43452**	0.09248	**0.0287245**	0.0045	0.8311069	0.0403606
525	2.4144	0.03335	2.516006	0.00221	**2.465203**	0.07185	**-0.01557**	0.0251	0.6457061	0.2259825
540	2.40535	-0.0203	2.511982	0.008045	**2.458664**	0.0754	**-0.006128**	0.02	0.6776718	0.1801299
555	2.40032	0.01305	2.517012	0.000751	**2.458664**	0.08252	**-0.006149**	0.0098	0.7416031	0.087706
570	2.4144	0.03335	2.472748	0.064934	**2.443574**	0.04126	**0.0157919**	0.0695	0.3708015	0.6245942
585	2.42446	0.04785	2.490856	0.038677	**2.457658**	0.04695	**-0.004586**	0.0612	0.4219466	0.549881
600	2.42949	-0.0551	2.515	0.003668	**2.472245**	0.06046	**-0.025716**	0.0416	0.543416	0.3734738

Table A23: Copper removal using pre-conditioned fungi-hydrophobic polyurethane beads with 1 mole.l^{-1} NaOH using 2mgl^{-1} Cu solution at neutral initial pH, room temperature and immobilised biomass concentration of 0.69 gl^{-1}

Time (min)	Exp (1)		Exp (2)		Cu conc. average C (mg/l)	C Stdev	Uptake average Q (mg/g)	Q Stdev	95% confidence limits on the mean of Cu conc.	95% confidence limits on the mean of uptake
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	2.24672	0	2.099279	0	**2.173**	0.10426	**0**	0	0.9369876	0
15	2.06431	0.2726	2.046204	0.076959	**2.055258**	0.0128	**0.1747794**	0.1383	0.1150763	1.2433001
30	2.03715	0.31175	2.010994	0.128013	**2.024072**	0.0185	**0.2198816**	0.1299	0.1662214	1.167647
45	1.95969	0.4234	1.908382	0.276801	**1.934035**	0.03628	**0.3501003**	0.1037	0.3260496	0.9316389
60	1.88524	0.5307	1.910394	0.273883	**1.897819**	0.01778	**0.4022916**	0.1816	0.1598283	1.6320704
75	1.83293	0.6061	2.069342	0.043409	**1.951137**	0.16717	**0.3247543**	0.3979	1.5023856	3.5759035
90	1.78766	0.67135	1.890274	0.303057	**1.838968**	0.07256	**0.4872036**	0.2604	0.6520993	2.3405004
105	2.20314	0.0725	2.010994	0.128013	**2.107067**	0.13587	**0.1002566**	0.0393	1.2210878	0.3527867
120	2.20012	0.07685	2.012	0.126555	**2.106061**	0.13302	**0.1017023**	0.0351	1.1955153	0.3158724
135	2.22829	0.03625	2.02206	0.111968	**2.125175**	0.14583	**0.0741088**	0.0535	1.3105917	0.481185
150	2.19308	0.087	2.12266	-0.0339	**2.15787**	0.04979	**0.0265488**	0.0855	0.4475191	0.7683351
165	2.2132	0.058	2.123666	-0.03536	**2.168433**	0.06331	**0.0113194**	0.066	0.5689886	0.5933101
180	2.22728	0.0377	2.012	0.126555	**2.119642**	0.15223	**0.0821273**	0.0628	1.3681298	0.5646707
195	2.03715	0.31175	1.998922	0.145518	**2.018036**	0.02703	**0.2286338**	0.1175	0.2429389	1.0564066
210	2.01099	0.34945	1.880214	0.317644	**1.945604**	0.09248	**0.3335471**	0.0225	0.8311069	0.2021255
225	1.99892	0.36685	1.99691	0.148435	**1.997916**	0.00142	**0.2576425**	0.1544	0.0127863	1.388027
240	1.90939	0.4959	1.96673	0.192196	**1.938059**	0.04055	**0.344048**	0.2148	0.3644084	1.9300386
255	2.1629	0.1305	1.9114	0.272425	**2.03715**	0.17784	**0.2014623**	0.1004	1.5982825	0.9019305
270	2.02608	0.3277	2.023066	0.110509	**2.024575**	0.00213	**0.2191044**	0.1536	0.0191794	1.3802498
285	2.2635	-0.0145	2.000934	0.1426	**2.132217**	0.18566	**0.0640501**	0.1111	1.6686069	0.9983721
300	2.3641	-0.1595	2.010994	0.128013	**2.187547**	0.24968	**-0.015743**	0.2033	2.2439886	1.8271467
315	2.43955	0.26825	2.012	0.126555	**2.225775**	0.30232	**-0.070848**	0.2792	2.7170803	2.5089829
330	2.36913	0.16675	2.012	0.126555	**2.190565**	0.25253	**-0.020098**	0.2074	2.2695611	1.8639504
345	2.22728	0.0377	1.909388	0.275342	**2.068336**	0.22479	**0.156521**	0.168	2.0202291	1.5102146
360	2.01099	0.34945	1.990874	0.157187	**2.000934**	0.01423	**0.2533186**	0.136	0.1278626	1.2218298
375	2.02407	0.3306	1.965724	0.193655	**1.994898**	0.04126	**0.2621274**	0.0968	0.3708015	0.8702871
390	2.12367	0.18705	1.96673	0.192196	**2.045198**	0.11097	**0.189623**	0.0036	0.9973283	0.0327031
405	1.99993	0.3654	2.11763	-0.02661	**2.058779**	0.08323	**0.1693955**	0.2772	0.7479962	2.4912169
420	2.15284	0.145	2.123666	-0.03536	**2.138253**	0.02063	**0.0548194**	0.1275	0.1854008	1.1461951
435	2.23332	0.029	2.012	0.126555	**2.12266**	0.1565	**0.0777773**	0.069	1.4064886	0.6199592
450	2.21119	0.0609	2.012	0.126555	**2.111594**	0.14085	**0.0937273**	0.0464	1.2658397	0.4172347
465	2.25746	-0.0058	2.166924	-0.09809	**2.212194**	0.06402	**-0.051943**	0.0653	0.5753817	0.5864728
480	2.52506	-0.3915	2.012	0.126555	**2.26853**	0.36279	**-0.132473**	0.3663	3.2604963	3.2922367
495	2.36611	-0.1624	1.934538	0.238874	**2.150325**	0.30517	**0.0382372**	0.2837	2.7426528	2.5500991
510	2.22326	0.0435	1.910394	0.273883	**2.066827**	0.22123	**0.1586916**	0.1629	1.9882634	1.4640856
525	2.2132	0.058	2.026084	0.106133	**2.119642**	0.13231	**0.0820664**	0.034	1.1891222	0.3058836
540	1.99892	0.36685	2.1126	-0.01932	**2.055761**	0.08038	**0.1737673**	0.2731	0.7224237	2.4540814
555	2.012	0.348	2.012	0.126555	**2.012**	0	**0.2372773**	0.1566	0	1.4072858
570	2.11763	0.19575	2.120648	-0.03099	**2.119139**	0.00213	**0.0823825**	0.1603	0.0191794	1.4409012
585	2.3138	-0.087	1.99691	0.148435	**2.155355**	0.22408	**0.0307175**	0.1665	2.0138359	1.4961897
600	2.25847	0.00725	2.000934	0.1426	**2.129702**	0.18211	**0.0676751**	0.106	1.6366413	0.9522983

Table A24: Copper removal by fungi-Hypol foam beads without surfactants using 2 mgl^{-1} Cu solution at an initial pH 7.0, room temperature and immobilised biomass concentration of 0.69 gl^{-1}

Time (min)	Exp (1)		Exp (2)		Cu conc. Average C (mg/l)	C Stdev	Uptake capacity average Q (mg/g)	Q Stdev	95% confidence limits on the mean of Cu conc.	95% confidence limits on the mean of uptake
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	1.94682	0	2.03408	0	**1.990454**	0.0617	**0**	0	0.5545437	0
15	1.35374	0.85998	1.27133	1.106	**1.31253**	0.05827	**0.9829891**	0.17396	0.5237155	1.5634758
30	1.03817	1.31755	1.10249	1.35082	**1.070325**	0.04548	**1.3341863**	0.02352	0.4087536	0.2113956
45	0.95877	1.43268	0.85928	1.70347	**0.909023**	0.07035	**1.568075**	0.19148	0.6322907	1.7209099
60	0.8432	1.60026	0.76079	1.84628	**0.80199**	0.05827	**1.7232721**	0.17396	0.5237156	1.5634758
75	0.76481	1.71393	0.67938	1.96432	**0.722093**	0.0604	**1.8391235**	0.17706	0.5428759	1.5912583
90	0.69044	1.82176	0.59898	2.0809	**0.644708**	0.06467	**1.9513317**	0.18324	0.5811965	1.6468233
105	0.63717	1.899	0.57386	2.11733	**0.605513**	0.04477	**2.0081645**	0.15439	0.4023668	1.3875202
120	0.5829	1.97769	0.52461	2.18874	**0.553755**	0.04122	**2.0832128**	0.14923	0.370433	1.3412161
135	0.54672	2.03015	0.49346	2.23391	**0.520088**	0.03766	**2.1320307**	0.14408	0.3384991	1.294912
150	0.51959	2.0695	0.46029	2.282	**0.489938**	0.04193	**2.1757482**	0.15026	0.3768197	1.3504769
165	0.49848	2.1001	0.4422	2.30823	**0.47034**	0.0398	**2.2041646**	0.14717	0.3576594	1.3226944
180	0.47135	2.13944	0.41808	2.34321	**0.444713**	0.03766	**2.2413245**	0.14408	0.3384991	1.294912
195	0.4623	2.15256	0.40401	2.36361	**0.433155**	0.04122	**2.2580828**	0.14923	0.370433	1.3412161
210	0.42612	2.20502	0.39095	2.38255	**0.408533**	0.02487	**2.2937855**	0.12553	0.2235371	1.1282171
225	0.4221	2.21085	0.37487	2.40587	**0.398483**	0.0334	**2.308358**	0.1379	0.3001784	1.239347
240	0.40803	2.23125	0.34271	2.4525	**0.375368**	0.04619	**2.3418747**	0.15645	0.4151404	1.4060418
255	0.39396	2.25165	0.35477	2.43501	**0.374363**	0.02772	**2.343332**	0.12966	0.2490842	1.1652604
270	0.3819	2.26914	0.34673	2.44667	**0.364313**	0.02487	**2.3579045**	0.12553	0.2235371	1.1282171
285	0.37989	2.27205	0.34673	2.44667	**0.363308**	0.02345	**2.3593617**	0.12347	0.2107636	1.1096955
300	0.36984	2.28663	0.32562	2.47727	**0.34773**	0.03127	**2.3819491**	0.13481	0.2810181	1.2115645
315	0.35678	2.30557	0.32763	2.47436	**0.342203**	0.02061	**2.389964**	0.11935	0.1852165	1.0726522
330	0.34472	2.32306	0.31859	2.48747	**0.33165**	0.01848	**2.4052651**	0.11626	0.1660562	1.0448697
345	0.34371	2.32451	0.31457	2.4933	**0.329138**	0.02061	**2.4089082**	0.11935	0.1852165	1.0726522
360	0.33668	2.33471	0.31155	2.49767	**0.324113**	0.01777	**2.4161945**	0.11523	0.1596694	1.0356089
375	0.33266	2.34054	0.3216	2.4831	**0.327128**	0.00782	**2.4118227**	0.1008	0.0702545	0.9059574
390	0.33065	2.34346	0.29648	2.51953	**0.31356**	0.02416	**2.4314956**	0.1245	0.2171503	1.1189563
405	0.31356	2.36823	0.29547	2.52099	**0.304515**	0.01279	**2.4446108**	0.10802	0.114962	0.9707831
420	0.31859	2.36095	0.28944	2.52973	**0.304013**	0.02061	**2.4453395**	0.11935	0.1852165	1.0726522
435	0.30653	2.37843	0.28341	2.53848	**0.294968**	0.01634	**2.4584547**	0.11317	0.1468958	1.0170872
450	0.31457	2.36677	0.28944	2.52973	**0.302003**	0.01777	**2.448254**	0.11523	0.1596694	1.0356089
465	0.34673	2.32014	0.28844	2.53119	**0.31758**	0.04122	**2.4256666**	0.14923	0.370433	1.3412161
480	0.30854	2.37552	0.27336	2.55305	**0.290948**	0.02487	**2.4642837**	0.12553	0.2235371	1.1282171
495	0.3216	2.35657	0.27638	2.54868	**0.298988**	0.03198	**2.4526257**	0.13584	0.2874049	1.2208254
510	0.31256	2.36969	0.27135	2.55596	**0.291953**	0.02914	**2.4628265**	0.13172	0.2618578	1.1837821
525	0.34874	2.31723	0.26532	2.56471	**0.307028**	0.05898	**2.4409677**	0.17499	0.5301023	1.5727367
540	0.32261	2.35512	0.26532	2.56471	**0.293963**	0.04051	**2.459912**	0.1482	0.3640462	1.3319553
555	0.30552	2.37989	0.27537	2.55014	**0.290445**	0.02132	**2.4650123**	0.12038	0.1916032	1.081913
570	0.32864	2.34637	0.27336	2.55305	**0.300998**	0.03909	**2.4497112**	0.14614	0.3512726	1.3134336
585	0.34974	2.31577	0.26331	2.56762	**0.306525**	0.06112	**2.4416963**	0.17809	0.5492626	1.6005191
600	0.32562	2.35074	0.2613	2.57054	**0.29346**	0.04548	**2.4606406**	0.15542	0.4087536	1.396781

Table A25: Copper removal by fungi-Hypol foam beads with addition of 0.1g of Pluronic85 surfactant, using 2 mgl^{-1} Cu solution at an initial pH 7.0, room temperature and immobilised biomass concentration of 0.69 gl^{-1}

Time (min)	Exp (1)		Exp (2)		Cu conc. Average C (mg/l)	C Stdev	Uptake capacity average Q (mg/g)	Q Stdev	95% confidence limits on the mean of Cu conc.	95% confidence limits on the mean of uptake
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	1.96087	0	2.05214	0	**2.006502**	0.06454	**0**	0	0.5800399	0
15	1.25927	1.01732	1.28238	1.11615	**1.270823**	0.01634	**1.0667346**	0.06988	0.1468958	0.6280589
30	0.9648	1.44429	1.00902	1.51252	**0.98691**	0.03127	**1.4784077**	0.04824	0.2810181	0.4335816
45	0.81506	1.66142	0.85526	1.73548	**0.835155**	0.02843	**1.6984524**	0.05237	0.255471	0.4706249
60	0.67034	1.87127	0.71958	1.93221	**0.694958**	0.03482	**1.9017388**	0.04309	0.312952	0.3872775
75	0.66431	1.88001	0.62913	2.06336	**0.646718**	0.02487	**1.9716868**	0.12965	0.2235371	1.1651867
90	0.62813	1.93247	0.57185	2.14642	**0.599985**	0.0398	**2.0394489**	0.15129	0.3576594	1.359664
105	0.54773	2.04905	0.5216	2.21929	**0.53466**	0.01848	**2.1341702**	0.12037	0.1660561	1.0818393
120	0.45527	2.18312	0.4814	2.27758	**0.46833**	0.01848	**2.2303487**	0.06679	0.1660562	0.6002765
135	0.47235	2.15835	0.44321	2.33295	**0.457778**	0.02061	**2.2456498**	0.12347	0.1852165	1.1096218
150	0.39597	2.2691	0.41306	2.37667	**0.404513**	0.01208	**2.3228841**	0.07607	0.1085752	0.6836239
165	0.3819	2.2895	0.38793	2.4131	**0.384915**	0.00426	**2.3513004**	0.0874	0.0383206	0.7854929
180	0.39597	2.2691	0.37286	2.43496	**0.384413**	0.01634	**2.3520291**	0.11728	0.1468958	1.0540568
195	0.34773	2.33905	0.35879	2.45536	**0.353258**	0.00782	**2.3972038**	0.08225	0.0702545	0.7391888
210	0.34874	2.33759	0.33768	2.48596	**0.343208**	0.00782	**2.4117763**	0.10492	0.0702545	0.9429269
225	0.36381	2.31573	0.32562	2.50345	**0.344715**	0.027	**2.4095904**	0.13274	0.2426975	1.1929692
240	0.33668	2.35508	0.31356	2.52094	**0.325118**	0.01634	**2.4380068**	0.11728	0.1468958	1.0540568
255	0.31658	2.38422	0.3206	2.51074	**0.318585**	0.00284	**2.4474789**	0.08946	0.0255471	0.8040146
270	0.30854	2.39588	0.29748	2.54425	**0.303008**	0.00782	**2.4700663**	0.10492	0.0702545	0.9429269
285	0.31859	2.38131	0.28643	2.56028	**0.302505**	0.02274	**2.4707949**	0.12656	0.2043768	1.1374042
300	0.38894	2.2793	0.28241	2.56611	**0.33567**	0.07533	**2.4227057**	0.20281	0.6769982	1.8227052
315	0.30854	2.39588	0.27437	2.57777	**0.29145**	0.02416	**2.4868247**	0.12862	0.2171504	1.1559259
330	0.29748	2.41191	0.26331	2.5938	**0.280395**	0.02416	**2.5028544**	0.12862	0.2171503	1.1559259
345	0.29748	2.41191	0.26934	2.58506	**0.28341**	0.0199	**2.4984827**	0.12243	0.1788297	1.1003609
360	0.25829	2.46874	0.26633	2.58943	**0.262305**	0.00569	**2.5290849**	0.08534	0.0510942	0.7669713
375	0.28944	2.42357	0.26432	2.59234	**0.276878**	0.01777	**2.5079548**	0.11934	0.1596694	1.0725785
390	0.25728	2.4702	0.26532	2.59089	**0.2613**	0.00569	**2.5305422**	0.08534	0.0510942	0.7669713
405	0.26733	2.45563	0.26331	2.5938	**0.26532**	0.00284	**2.5247132**	0.0977	0.0255471	0.8781012
420	0.29246	2.41919	0.25125	2.61129	**0.271853**	0.02914	**2.5152411**	0.13583	0.2618578	1.2207517
435	0.29145	2.42065	0.27236	2.58069	**0.281903**	0.0135	**2.5006686**	0.11316	0.1213487	1.0170135
450	0.29949	2.40899	0.27035	2.5836	**0.284918**	0.02061	**2.4962968**	0.12347	0.1852165	1.1096218
465	0.29949	2.40899	0.27939	2.57048	**0.28944**	0.01421	**2.4897392**	0.11419	0.1277355	1.0262744
480	0.30251	2.40462	0.27236	2.58069	**0.28743**	0.02132	**2.4926537**	0.1245	0.1916032	1.1188826
495	0.29849	2.41045	0.29045	2.55445	**0.294465**	0.00569	**2.4824529**	0.10183	0.0510942	0.9151445
510	0.27437	2.44543	0.24924	2.6142	**0.261803**	0.01777	**2.5298136**	0.11934	0.1596694	1.0725785
525	0.2814	2.43522	0.27738	2.5734	**0.27939**	0.00284	**2.5043117**	0.0977	0.0255471	0.8781012
540	0.27035	2.45125	0.28341	2.56466	**0.276878**	0.00924	**2.5079548**	0.08019	0.0830281	0.7206672
555	0.2402	2.49497	0.26633	2.58943	**0.25326**	0.01848	**2.5422002**	0.06679	0.1660561	0.6002765
570	0.27135	2.4498	0.24321	2.62295	**0.25728**	0.0199	**2.5363712**	0.12243	0.1788297	1.1003609
585	0.27135	2.4498	0.25427	2.60692	**0.262808**	0.01208	**2.5283563**	0.1111	0.1085752	0.9984919
600	0.2814	2.43522	0.2603	2.59817	**0.270848**	0.01492	**2.5166983**	0.11522	0.1341223	1.0355352

Table A26: Copper removal by fungi-Hypol foam beads with addition of 0.5g of Pluronic85 surfactant, using 2 mgl^{-1} Cu solution at an initial pH 7.0, room temperature and immobilised biomass concentration of 0.69 gl^{-1}

Time (min)	Exp (1)		Exp (2)		**Cu conc. Average C (mg/l)**	C Stdev	**Uptake capacity average Q (mg/g)**	Q Stdev	95% confidence limits on the mean of Cu conc.	95% confidence limits on the mean of uptake
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	1.91473	0	1.71714	0	**1.815932**	0.13972	**0**	0	1.2556908	0
15	1.53464	0.55113	1.36479	0.5109	**1.449713**	0.1201	**0.5310175**	0.02845	1.079365	0.2556725
30	1.20198	1.03348	1.11354	0.87521	**1.15776**	0.06254	**0.9543487**	0.11191	0.5620362	1.0057992
45	1.00098	1.32493	0.94571	1.11857	**0.973343**	0.03909	**1.2217541**	0.14592	0.3512726	1.3114064
60	0.85727	1.53332	0.81204	1.31239	**0.834653**	0.03198	**1.4228546**	0.15622	0.2874049	1.4040146
75	0.72863	1.71985	0.68843	1.49163	**0.708525**	0.02843	**1.6057394**	0.16137	0.255471	1.4503187
90	0.67536	1.79708	0.60803	1.60821	**0.641693**	0.04761	**1.7026466**	0.13355	0.4279139	1.2002765
105	0.63215	1.85974	0.55074	1.69127	**0.591443**	0.05756	**1.7755091**	0.11913	0.5173288	1.0706249
120	0.53567	1.99964	0.50351	1.75976	**0.519585**	0.02274	**1.8797024**	0.16962	0.2043768	1.5244053
135	0.50552	2.04336	0.45828	1.82534	**0.481898**	0.0334	**1.9343493**	0.15416	0.3001784	1.385493
150	0.5025	2.04773	0.42311	1.87634	**0.462803**	0.05614	**1.9620371**	0.12119	0.5045552	1.0891466
165	0.52059	2.0215	0.39798	1.91278	**0.459285**	0.0867	**1.9671374**	0.07688	0.7791866	0.6909312
180	0.51456	2.03024	0.36783	1.95649	**0.441195**	0.10375	**1.9933679**	0.05215	0.9324692	0.4686714
195	0.43115	2.15119	0.35477	1.97544	**0.392955**	0.05401	**2.0633159**	0.12428	0.4853949	1.1169291
210	0.44924	2.12496	0.33668	2.00167	**0.392955**	0.07959	**2.0633159**	0.08718	0.7153188	0.7835394
225	0.43818	2.14099	0.32562	2.0177	**0.3819**	0.07959	**2.0793457**	0.08718	0.7153188	0.7835394
240	0.43215	2.14974	0.31055	2.03956	**0.371348**	0.08599	**2.0946468**	0.07791	0.7727998	0.700192
255	0.41607	2.17305	0.29949	2.05559	**0.35778**	0.08243	**2.1143197**	0.08306	0.7408659	0.7464961
270	0.37185	2.23717	0.30753	2.04393	**0.33969**	0.04548	**2.1405502**	0.13664	0.4087536	1.2280589
285	0.39095	2.20948	0.30351	2.04976	**0.347228**	0.06183	**2.1296208**	0.11294	0.5556494	1.01506
300	0.3809	2.22406	0.29849	2.05704	**0.33969**	0.05827	**2.1405502**	0.1181	0.5237155	1.0613641
315	0.3608	2.2532	0.27336	2.09348	**0.317078**	0.06183	**2.1733383**	0.11294	0.5556494	1.01506
330	0.38994	2.21094	0.28341	2.0789	**0.336675**	0.07533	**2.1449219**	0.09337	0.6769981	0.8391043
345	0.402	2.19345	0.28643	2.07453	**0.344213**	0.08172	**2.1339926**	0.08409	0.7344791	0.7557569
360	0.401	2.19491	0.28241	2.08036	**0.3417**	0.08386	**2.1376357**	0.081	0.7536394	0.7279745
375	0.39497	2.20365	0.29145	2.06724	**0.343208**	0.0732	**2.1354498**	0.09646	0.6578378	0.8668868
390	0.32562	2.30421	0.29849	2.05704	**0.312053**	0.01919	**2.1806246**	0.17477	0.1724429	1.5707094
405	0.34874	2.27069	0.28844	2.07162	**0.318585**	0.04264	**2.1711524**	0.14077	0.3832065	1.2651022
420	0.34673	2.2736	0.27537	2.09056	**0.311048**	0.05046	**2.1820818**	0.12943	0.453461	1.1632332
435	0.402	2.19345	0.29648	2.05996	**0.349238**	0.07462	**2.1267063**	0.0944	0.6706114	0.8483652
450	0.37386	2.23426	0.27638	2.0891	**0.325118**	0.06893	**2.1616803**	0.10264	0.6195172	0.9224518
465	0.3608	2.2532	0.27839	2.08619	**0.31959**	0.05827	**2.1696952**	0.1181	0.5237156	1.0613641
480	0.36582	2.24592	0.29145	2.06724	**0.328635**	0.05259	**2.1565799**	0.12634	0.4726214	1.1354507
495	0.34673	2.2736	0.27939	2.08473	**0.313058**	0.04761	**2.1791673**	0.13355	0.4279139	1.2002765
510	0.40803	2.18471	0.30251	2.05121	**0.355268**	0.07462	**2.1179628**	0.0944	0.6706114	0.8483652
525	0.35778	2.25757	0.31859	2.0279	**0.338183**	0.02772	**2.1427361**	0.1624	0.2490842	1.4595795
540	0.36281	2.25029	0.30251	2.05121	**0.332655**	0.04264	**2.1507509**	0.14077	0.3832065	1.2651022
555	0.34673	2.2736	0.29547	2.06142	**0.321098**	0.03624	**2.1675093**	0.15004	0.3257255	1.3484497
570	0.39698	2.20074	0.31256	2.03664	**0.354765**	0.05969	**2.1186914**	0.11603	0.5364891	1.0428425
585	0.33366	2.29255	0.30251	2.05121	**0.318083**	0.02203	**2.1718811**	0.17065	0.19799	1.5336661
600	0.36482	2.24737	0.31758	2.02936	**0.341198**	0.0334	**2.1383643**	0.15416	0.3001784	1.385493

Table A27: Copper removal by fungi-Hypol foam beads with addition of 0.1g of Tween80 surfactant, using 2 mgl^{-1} Cu solution at an initial pH 7.0, room temperature and immobilised biomass concentration of 0.69 gl^{-1}

Time (min)	Exp (1)		Exp (2)		**Cu conc. Average C (mg/l)**	C Stdev	**Uptake capacity average Q (mg/g)**	Q Stdev	95% confidence limits on the mean of Cu conc.	95% confidence limits on the mean of uptake
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	1.83549	0	2.03007	0	**1.932781**	0.13759	**0**	0	1.2365686	0
15	1.3658	0.68106	1.52258	0.73587	**1.437**	0.11086	**0.7084642**	0.03876	0.9963369	0.348336
30	1.08339	1.09055	1.1849	1.22551	**1.1285**	0.07177	**1.1580258**	0.09543	0.6450643	0.8576813
45	0.91355	1.33682	0.98993	1.50821	**0.947**	0.05401	**1.4225167**	0.12119	0.4853949	1.0892019
60	0.79395	1.51023	0.84521	1.71806	**0.8155**	0.03624	**1.6141451**	0.14695	0.3257255	1.3207225
75	0.69647	1.65159	0.75777	1.84484	**0.7235**	0.04335	**1.7482121**	0.13665	0.3895933	1.2281142
90	0.62913	1.74922	0.67637	1.96288	**0.6495**	0.0334	**1.8560486**	0.15108	0.3001784	1.3577658
105	0.58089	1.81917	0.61607	2.05031	**0.5955**	0.02487	**1.9347401**	0.16344	0.2235371	1.4688957
120	0.51858	1.90952	0.56582	2.12317	**0.5395**	0.0334	**2.0163461**	0.15108	0.3001784	1.3577658
135	0.48642	1.95615	0.52662	2.18001	**0.504**	0.02843	**2.0680785**	0.15829	0.255471	1.4225915
150	0.44924	2.01007	0.49044	2.23247	**0.4675**	0.02914	**2.1212681**	0.15726	0.2618578	1.4133307
165	0.42813	2.04067	0.45627	2.28201	**0.44**	0.0199	**2.1613425**	0.17065	0.1788297	1.5337214
180	0.401	2.08002	0.44421	2.2995	**0.4205**	0.03056	**2.1897588**	0.1552	0.2746313	1.3948091
195	0.38693	2.10042	0.41607	2.3403	**0.3995**	0.02061	**2.2203611**	0.16962	0.1852165	1.5244606
210	0.3618	2.13685	0.39497	2.37091	**0.3765**	0.02345	**2.2538778**	0.1655	0.2107636	1.4874173
225	0.35778	2.14268	0.37889	2.39422	**0.3665**	0.01492	**2.2684503**	0.17787	0.1341223	1.5985472
240	0.33969	2.16891	0.36482	2.41462	**0.3505**	0.01777	**2.2917663**	0.17375	0.1596694	1.5615039
255	0.33065	2.18203	0.37085	2.40588	**0.349**	0.02843	**2.2939522**	0.15829	0.255471	1.4225915
270	0.32261	2.19368	0.35075	2.43502	**0.335**	0.0199	**2.3143537**	0.17065	0.1788297	1.5337214
285	0.32261	2.19368	0.34371	2.44522	**0.3315**	0.01492	**2.3194541**	0.17787	0.1341223	1.5985472
300	0.30452	2.21991	0.34371	2.44522	**0.3225**	0.02772	**2.3325693**	0.15932	0.2490842	1.4318524
315	0.31356	2.2068	0.33567	2.45688	**0.323**	0.01563	**2.3318407**	0.17684	0.140509	1.5892864
330	0.30552	2.21846	0.32964	2.46563	**0.316**	0.01706	**2.3420415**	0.17478	0.1532826	1.5707647
345	0.3015	2.22429	0.32864	2.46708	**0.3135**	0.01919	**2.3456846**	0.17168	0.1724429	1.5429822
360	0.3005	2.22574	0.32361	2.47437	**0.3105**	0.01634	**2.3500563**	0.17581	0.1468958	1.5800255
375	0.29849	2.22866	0.32562	2.47146	**0.3105**	0.01919	**2.3500563**	0.17168	0.1724429	1.5429822
390	0.29447	2.23449	0.32261	2.47583	**0.307**	0.0199	**2.3551567**	0.17065	0.1788297	1.5337214
405	0.29648	2.23157	0.3206	2.47874	**0.307**	0.01706	**2.3551567**	0.17478	0.1532826	1.5707647
420	0.29748	2.23011	0.3216	2.47728	**0.308**	0.01706	**2.3536995**	0.17478	0.1532826	1.5707647
435	0.30753	2.21554	0.32462	2.47291	**0.3145**	0.01208	**2.3442273**	0.18199	0.1085752	1.6355905
450	0.31055	2.21117	0.32763	2.46854	**0.3175**	0.01208	**2.3398556**	0.18199	0.1085752	1.6355905
465	0.3005	2.22574	0.33165	2.46271	**0.3145**	0.02203	**2.3442273**	0.16756	0.19799	1.5059389
480	0.30954	2.21263	0.32964	2.46563	**0.318**	0.01421	**2.339127**	0.1789	0.1277355	1.607808
495	0.30854	2.21408	0.33467	2.45834	**0.32**	0.01848	**2.3362125**	0.17271	0.1660562	1.5522431
510	0.31758	2.20097	0.33266	2.46125	**0.3235**	0.01066	**2.3311121**	0.18405	0.0958016	1.6541121
525	0.31859	2.19951	0.33869	2.45251	**0.327**	0.01421	**2.3260117**	0.1789	0.1277355	1.607808
540	0.31557	2.20388	0.33969	2.45105	**0.326**	0.01706	**2.327469**	0.17478	0.1532826	1.5707647
555	0.3216	2.19514	0.33467	2.45834	**0.3265**	0.00924	**2.3267403**	0.18611	0.0830281	1.6726338
570	0.3206	2.1966	0.33969	2.45105	**0.3285**	0.0135	**2.3238258**	0.17993	0.1213487	1.6170688
585	0.32361	2.19223	0.33668	2.45543	**0.3285**	0.00924	**2.3238258**	0.18611	0.0830281	1.6726338
600	0.32663	2.18785	0.34572	2.44231	**0.3345**	0.0135	**2.3150823**	0.17993	0.1213487	1.6170688

Table A28: Copper removal by fungi-Hypol foam beads with addition of 0.5g of Tween80 surfactant, using 2 mgl^{-1} Cu solution at an initial pH 7.0, room temperature and immobilised biomass concentration of 0.69 gl^{-1}

Time (min)	Exp (1)		Exp (2)		Cu conc. Average C (mg/l)	C Stdev	Uptake capacity average Q (mg/g)	Q Stdev	95% confidence limits on the mean of Cu conc.	95% confidence limits on the mean of uptake
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	1.96187	0	2.03007	0	**1.99597**	0.04823	**0**	0	0.4334364	0
15	1.67333	0.41839	1.52258	0.73587	**1.59**	0.1066	**0.577129**	0.22449	0.9580163	2.0176064
30	1.31354	0.94008	1.1849	1.22551	**1.243**	0.09096	**1.0827948**	0.20183	0.8175072	1.8138682
45	1.12158	1.21842	0.98993	1.50821	**1.0505**	0.09309	**1.3633154**	0.20492	0.8366675	1.8416507
60	0.97586	1.42972	0.84521	1.71806	**0.906**	0.09238	**1.573888**	0.20389	0.8302808	1.8323899
75	0.87636	1.57399	0.75777	1.84484	**0.813**	0.08386	**1.7094123**	0.19152	0.7536394	1.72126
90	0.78089	1.71243	0.67637	1.96288	**0.725**	0.07391	**1.8376503**	0.17709	0.6642246	1.5916085
105	0.70853	1.81735	0.61607	2.05031	**0.659**	0.06538	**1.9338288**	0.16473	0.5875833	1.4804786
120	0.67335	1.86835	0.56582	2.12317	**0.6165**	0.07604	**1.9957619**	0.18019	0.6833849	1.619391
135	0.63315	1.92664	0.52662	2.18001	**0.577**	0.07533	**2.0533233**	0.17916	0.6769981	1.6101301
150	0.60099	1.97327	0.49044	2.23247	**0.543**	0.07817	**2.1028698**	0.18328	0.7025452	1.6471734
165	0.5819	2.00096	0.45627	2.28201	**0.5165**	0.08883	**2.1414869**	0.19873	0.7983469	1.7860858
180	0.55778	2.03593	0.44421	2.2995	**0.4985**	0.0803	**2.1677174**	0.18637	0.7217056	1.6749559
195	0.53768	2.06508	0.41607	2.3403	**0.4745**	0.08599	**2.2026914**	0.19461	0.7727998	1.7490425
210	0.51054	2.10443	0.39497	2.37091	**0.4505**	0.08172	**2.2376654**	0.18843	0.7344791	1.6934775
225	0.50351	2.11463	0.37889	2.39422	**0.439**	0.08812	**2.2544238**	0.1977	0.7919601	1.776825
240	0.49346	2.1292	0.36482	2.41462	**0.427**	0.09096	**2.2719108**	0.20183	0.8175072	1.8138682
255	0.49748	2.12337	0.37085	2.40588	**0.432**	0.08954	**2.2646245**	0.19976	0.8047337	1.7953466
270	0.49245	2.13066	0.35075	2.43502	**0.4195**	0.1002	**2.2828401**	0.21522	0.9005353	1.934259
285	0.4814	2.14669	0.34371	2.44522	**0.4105**	0.09736	**2.2959554**	0.2111	0.8749882	1.8972157
300	0.48843	2.13649	0.34371	2.44522	**0.414**	0.10233	**2.290855**	0.21831	0.9196956	1.9620414
315	0.48642	2.1394	0.33567	2.45688	**0.409**	0.1066	**2.2981413**	0.22449	0.9580163	2.0176064
330	0.47939	2.1496	0.32964	2.46563	**0.4025**	0.10589	**2.3076134**	0.22346	0.9516295	2.0083455
345	0.47336	2.15834	0.32864	2.46708	**0.399**	0.10233	**2.3127138**	0.21831	0.9196956	1.9620414
360	0.48441	2.14231	0.32361	2.47437	**0.402**	0.1137	**2.308342**	0.2348	1.021884	2.1102146
375	0.48843	2.13649	0.32562	2.47146	**0.405**	0.11512	**2.3039703**	0.23686	1.0346576	2.1287363
390	0.48743	2.13794	0.32261	2.47583	**0.403**	0.11655	**2.3068848**	0.23892	1.0474311	2.1472579
405	0.49245	2.13066	0.3206	2.47874	**0.4045**	0.12152	**2.3046989**	0.24613	1.0921385	2.2120837
420	0.48743	2.13794	0.3216	2.47728	**0.4025**	0.11726	**2.3076134**	0.23995	1.0538179	2.1565187
435	0.49949	2.12046	0.32462	2.47291	**0.41**	0.12365	**2.296684**	0.24922	1.1112989	2.2398661
450	0.50954	2.10588	0.32763	2.46854	**0.4165**	0.12863	**2.2872119**	0.25644	1.1560063	2.3046919
465	0.51155	2.10297	0.33165	2.46271	**0.4195**	0.1272	**2.2828401**	0.25438	1.1432327	2.2861703
480	0.5216	2.0884	0.32964	2.46563	**0.4235**	0.13573	**2.2770111**	0.26674	1.219874	2.3973001
495	0.52361	2.08548	0.33467	2.45834	**0.427**	0.1336	**2.2719108**	0.26365	1.2007137	2.3695177
510	0.53165	2.07382	0.33266	2.46125	**0.43**	0.14071	**2.267539**	0.27396	1.2645815	2.4621259
525	0.54371	2.05634	0.33869	2.45251	**0.439**	0.14497	**2.2544238**	0.28014	1.3029021	2.5176909
540	0.54371	2.05634	0.33969	2.45105	**0.4395**	0.14426	**2.2536951**	0.27911	1.2965153	2.50843
555	0.53969	2.06217	0.33467	2.45834	**0.435**	0.14497	**2.2602528**	0.28014	1.3029021	2.5176909
570	0.54471	2.05488	0.33969	2.45105	**0.44**	0.14497	**2.2529665**	0.28014	1.3029021	2.5176909
585	0.55577	2.03885	0.33668	2.45543	**0.444**	0.15492	**2.2471375**	0.29456	1.392317	2.6473424
600	0.55577	2.03885	0.34572	2.44231	**0.4485**	0.14852	**2.2405799**	0.28529	1.334836	2.563995

Table A29: Copper removal by fungi-Hypol foam beads with addition of 0.1g of TritonX-100 surfactant, using 2 mgl^{-1} Cu solution at an initial pH 7.0, room temperature and immobilised biomass concentration of 0.69 gl^{-1}

Time (min)	Exp (1)		Exp (2)		Cu conc. Average C (mg/l)	C Stdev	Uptake capacity average Q (mg/g)	Q Stdev	95% confidence limits on the mean of Cu conc.	95% confidence limits on the mean of uptake
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	2.13138	0	2.13639	0	**2.133883**	0.00355	**0**	0	0.0318703	0
15	1.57283	0.8099	1.59996	0.77782	**1.586393**	0.01919	**0.7938605**	0.02268	0.1724429	0.2038303
30	1.4663	0.96437	1.37987	1.09696	**1.42308**	0.06112	**1.0306636**	0.09376	0.5492627	0.8426428
45	1.26228	1.26019	1.30449	1.20626	**1.283385**	0.02985	**1.2332214**	0.03814	0.2682446	0.3427426
60	1.04018	1.58224	1.15676	1.42047	**1.098465**	0.08243	**1.5013554**	0.11439	0.7408659	1.0280436
75	0.96581	1.69008	1.07837	1.53414	**1.022085**	0.07959	**1.6121064**	0.11027	0.7153188	0.9910003
90	0.87033	1.82852	0.98088	1.67549	**0.925605**	0.07817	**1.7520024**	0.10821	0.7025453	0.9724786
105	0.74571	2.00921	0.87636	1.82704	**0.811035**	0.09238	**1.9181289**	0.12881	0.8302807	1.1576951
120	0.71154	2.05876	0.79697	1.94217	**0.754253**	0.0604	**2.0004635**	0.08244	0.5428759	0.740958
135	0.72561	2.03836	0.73466	2.03252	**0.730133**	0.0064	**2.0354375**	0.00413	0.057481	0.0371354
150	0.65325	2.14328	0.70049	2.08206	**0.676868**	0.0334	**2.1126718**	0.04329	0.3001784	0.3890467
165	0.65124	2.1462	0.69144	2.09518	**0.67134**	0.02843	**2.1206866**	0.03608	0.255471	0.324221
180	0.52361	2.33127	0.64019	2.1695	**0.581895**	0.08243	**2.2503819**	0.11439	0.7408659	1.0280436
195	0.58793	2.238	0.64622	2.16075	**0.61707**	0.04122	**2.1993781**	0.05462	0.370433	0.4909158
210	0.56481	2.27152	0.63315	2.1797	**0.59898**	0.04832	**2.2256086**	0.06493	0.4343007	0.583524
225	0.55175	2.29046	0.56984	2.2715	**0.56079**	0.01279	**2.2809841**	0.01341	0.1149619	0.1204829
240	0.51657	2.34147	0.58491	2.24965	**0.55074**	0.04832	**2.2955566**	0.06493	0.4343007	0.583524
255	0.54773	2.29629	0.55979	2.28608	**0.553755**	0.00853	**2.2911849**	0.00722	0.0766413	0.0649179
270	0.5216	2.33418	0.54471	2.30794	**0.533153**	0.01634	**2.3210585**	0.01856	0.1468958	0.166787
285	0.50451	2.35895	0.53064	2.32834	**0.517575**	0.01848	**2.3436459**	0.02165	0.1660561	0.1945694
300	0.49547	2.37207	0.50652	2.36331	**0.500993**	0.00782	**2.3676905**	0.00619	0.0702545	0.0556571
315	0.47738	2.3983	0.51858	2.34582	**0.497978**	0.02914	**2.3720623**	0.03711	0.2618578	0.3334818
330	0.46934	2.40996	0.49346	2.38226	**0.481395**	0.01706	**2.3961069**	0.01959	0.1532826	0.1760478
345	0.44823	2.44056	0.46029	2.43035	**0.45426**	0.00853	**2.4354526**	0.00722	0.0766413	0.0649179
360	0.41507	2.48865	0.51054	2.35748	**0.462803**	0.06751	**2.423066**	0.09275	0.6067436	0.8335663
375	0.42914	2.46825	0.4623	2.42743	**0.445718**	0.02345	**2.4478393**	0.02886	0.2107636	0.2593952
390	0.43014	2.46679	0.44622	2.45075	**0.43818**	0.01137	**2.4587686**	0.01134	0.1021884	0.1019612
405	0.48341	2.38956	0.45225	2.442	**0.467828**	0.02203	**2.4157798**	0.03709	0.19799	0.3332975
420	0.42914	2.46825	0.43517	2.46678	**0.43215**	0.00426	**2.4675121**	0.00104	0.0383207	0.009353
435	0.43517	2.4595	0.49346	2.38226	**0.46431**	0.04122	**2.4208801**	0.05462	0.370433	0.4909158
450	0.46532	2.41579	0.42311	2.48426	**0.44421**	0.02985	**2.4500251**	0.04842	0.2682446	0.4351666
465	0.42713	2.47116	0.4613	2.42889	**0.44421**	0.02416	**2.4500251**	0.02989	0.2171504	0.268656
480	0.41708	2.48574	0.45426	2.43909	**0.435668**	0.02629	**2.4624118**	0.03298	0.2363107	0.2964385
495	0.38793	2.528	0.45225	2.442	**0.42009**	0.04548	**2.4849991**	0.06081	0.4087536	0.5464807
510	0.43416	2.46096	0.49346	2.38226	**0.463808**	0.04193	**2.4216088**	0.05565	0.3768197	0.5001766
525	0.41105	2.49448	0.42009	2.48864	**0.415568**	0.0064	**2.4915568**	0.00413	0.057481	0.0371354
540	0.39195	2.52217	0.43718	2.46386	**0.414563**	0.03198	**2.493014**	0.04123	0.2874049	0.3705251
555	0.42813	2.46971	0.41205	2.50029	**0.42009**	0.01137	**2.4849991**	0.02163	0.1021884	0.1943852
570	0.401	2.50905	0.43718	2.46386	**0.419085**	0.02558	**2.4864564**	0.03195	0.2299239	0.2871777
585	0.39396	2.51925	0.46431	2.42452	**0.429135**	0.04974	**2.4718839**	0.06699	0.4470743	0.6020457
600	0.39195	2.52217	0.41406	2.49738	**0.403005**	0.01563	**2.5097724**	0.01753	0.1405091	0.1575262

Table A30: Copper removal by fungi-Hypol foam beads with addition of 0.5g of TritobX-100 surfactant, using 2 mgl^{-1} Cu solution at an initial pH 7.0, room temperature and immobilised biomass concentration of 0.69 gl^{-1}

Time (min)	Exp (1)		Exp (2)		Cu conc. Average C (mg/l)	C Stdev	Uptake capacity average Q (mg/g)	Q Stdev	95% confidence limits on the mean of Cu conc.	95% confidence limits on the mean of uptake
	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)	Cu conc. (mg/l)	Fungi uptake capacity (mg/g)						
0	2.41021	0	2.10129	0	**2.255747**	0.21844	**0**	0	1.963212	0
15	2.16075	0.36172	1.93965	0.23437	**2.0502**	0.15634	**0.2980431**	0.09005	1.4050905	0.8092762
30	2.009	0.58176	1.77282	0.47627	**1.890908**	0.167	**0.5290173**	0.07459	1.5008921	0.6703638
45	1.94769	0.67065	1.75172	0.50688	**1.849703**	0.13858	**0.5887645**	0.11581	1.2454211	1.0407968
60	1.64016	1.11657	1.54871	0.80124	**1.594433**	0.06467	**0.958906**	0.22297	0.5811965	2.0039225
75	1.68639	1.04954	1.47635	0.90616	**1.581368**	0.14852	**0.9778503**	0.10138	1.334836	0.9111453
90	1.47233	1.35993	1.50348	0.86682	**1.487903**	0.02203	**1.1133745**	0.34868	0.19799	3.133743
105	1.38087	1.49254	1.33665	1.10872	**1.35876**	0.03127	**1.3006312**	0.2714	0.2810181	2.4391812
120	1.41504	1.443	1.36881	1.06209	**1.391925**	0.03269	**1.2525419**	0.26934	0.2937917	2.4206595
135	1.21605	1.73153	1.28741	1.18013	**1.251728**	0.05046	**1.4558283**	0.3899	0.453461	3.5041759
150	1.28942	1.62515	1.21304	1.28796	**1.251225**	0.05401	**1.4565569**	0.23843	0.4853949	2.1428348
165	1.13867	1.84374	1.11354	1.43223	**1.126103**	0.01777	**1.6379845**	0.29098	0.1596694	2.6151368
180	1.18791	1.77233	1.07535	1.48761	**1.13163**	0.07959	**1.6299697**	0.20133	0.7153188	1.8094452
195	1.21505	1.73299	0.97787	1.62896	**1.096455**	0.16771	**1.6809734**	0.07356	1.5072789	0.661103
210	1.10349	1.89474	0.92963	1.69891	**1.016558**	0.12294	**1.7968248**	0.13848	1.1049121	1.2445349
225	1.06631	1.94866	0.98892	1.61293	**1.027613**	0.05472	**1.780795**	0.2374	0.4917817	2.133574
240	1.08138	1.9268	0.9236	1.70765	**1.002488**	0.11157	**1.8172263**	0.15496	1.0027237	1.3927081
255	1.07334	1.93846	0.95877	1.65665	**1.016055**	0.08101	**1.7975534**	0.19927	0.7280924	1.7909235
270	1.02008	2.01569	0.91656	1.71785	**0.968318**	0.0732	**1.8667728**	0.21061	0.6578378	1.8927926
285	1.04319	1.98218	0.91656	1.71785	**0.979875**	0.08954	**1.8500144**	0.18691	0.8047337	1.6797936
300	0.90852	2.17745	0.88943	1.7572	**0.898973**	0.0135	**1.967323**	0.29716	0.1213487	2.6707018
315	0.96078	2.10167	0.83717	1.83297	**0.898973**	0.08741	**1.967323**	0.19	0.7855733	1.7075761
330	0.93867	2.13373	0.89646	1.747	**0.917565**	0.02985	**1.9403639**	0.27346	0.2682446	2.4577028
345	1.03113	1.99966	0.85526	1.80674	**0.943193**	0.12436	**1.903204**	0.13642	1.1176856	1.2260133
360	0.87536	2.22554	0.8442	1.82277	**0.859778**	0.02203	**2.0241558**	0.2848	0.19799	2.5595719
375	0.90953	2.17599	0.78189	1.91312	**0.845708**	0.09025	**2.0445573**	0.18588	0.8111204	1.6705328
390	0.8844	2.21242	0.76782	1.93352	**0.82611**	0.08243	**2.0729737**	0.19721	0.7408659	1.7724019
405	0.90551	2.18182	0.77486	1.92332	**0.84018**	0.09238	**2.0525722**	0.18279	0.8302807	1.6427503
420	0.84219	2.27363	0.75476	1.95247	**0.798473**	0.06183	**2.113048**	0.22709	0.5556494	2.0409658
435	0.81104	2.3188	0.7628	1.94081	**0.786915**	0.03411	**2.1298064**	0.26728	0.3065652	2.4021379
450	0.83013	2.29111	0.77988	1.91604	**0.805005**	0.03553	**2.1035759**	0.26522	0.3193387	2.3836162
465	0.83013	2.29111	0.75677	1.94955	**0.793448**	0.05188	**2.1203343**	0.24152	0.4662346	2.1706173
480	0.77084	2.37709	0.75677	1.94955	**0.7638**	0.00995	**2.1633232**	0.30232	0.0894149	2.7170059
495	0.73968	2.42227	0.75978	1.94518	**0.74973**	0.01421	**2.1837247**	0.33735	0.1277355	3.0318739
510	0.74471	2.41498	0.7025	2.02825	**0.7236**	0.02985	**2.2216132**	0.27346	0.2682446	2.4577028
525	0.69446	2.48784	0.70149	2.0297	**0.697973**	0.00497	**2.258773**	0.32395	0.0447074	2.9114832
540	0.68742	2.49804	0.65124	2.10257	**0.66933**	0.02558	**2.3003047**	0.27965	0.2299239	2.5132678
555	0.64823	2.55488	0.61305	2.15794	**0.630638**	0.02487	**2.3564088**	0.28068	0.2235371	2.5225286
570	0.64019	2.56653	0.61908	2.1492	**0.629633**	0.01492	**2.357866**	0.2951	0.1341223	2.6521801
585	0.6633	2.53302	0.60803	2.16523	**0.635663**	0.03909	**2.3491225**	0.26007	0.3512726	2.3373121
600	0.66833	2.52573	0.58592	2.19729	**0.62712**	0.05827	**2.3615092**	0.23225	0.5237155	2.0872699

Table A31: Copper recovery from fungi-Hypol beads at pH<2 after they were exposed to 145ml of 2mgl^{-1} Cu solution at an initial pH 7.0, room temperature and immobilised biomass concentration of 0.69 gl^{-1} (Experiment 1)

Adsorption experiment				Recovery experiment								
Time (min)	Cu conc. (mg/l)	uptake capacity (mg/g)	quantity of ad-sorbed Cu (mg)	Time (min)	Cu conc. (mg/l)	Volume of solution (L)	quantity of Cu re-covered in each stage (mg)	accumlative Cu re-covered in each stage (mg)	quantity of Cu removed by sampling (mg)	Total Cu re-covered (mg)	quantity of ad-sorbed Cu (mg)	Cu recovery ratio (%)
0	2.069	0	0	0	0.218	0.143	0	0	0	0	0.26848	0
720	0.218	2.68478	0.26848	10	1.86	0.143	0.234863	0.2348632	0.00372	0.23486		87.47966
				20	1.9	0.141	0.00564	0.2405032	0.0038	0.24422		90.96598
				30	1.911	0.139	0.001529	0.2420322	0.003822	0.24583		91.56529
				40	1.943	0.137	0.004384	0.2464162	0.003886	0.25024		93.20639
				50	1.979	0.135	0.00486	0.2512762	0.003958	0.25516		95.04044
				60	1.983	0.133	0.000532	0.2518082	0.003966	0.25577		95.26541
				80	1.959	0.131	-0.00314	0.2486642	0.003918	0.25263		94.09734
				100	1.965	0.129	0.000774	0.2494382	0.00393	0.25336		94.36776
				120	1.999	0.127	0.004318	0.2537562	0.003998	0.25769		95.98056

Table A31: Continued (Experiment 2)

Adsorption experiment				Recovery experiment								
Time (min)	Cu conc. (mg/l)	uptake capacity (mg/g)	quantity of ad-sorbed Cu (mg)	Time (min)	Cu conc. (mg/l)	Volume of solution (L)	quantity of Cu re-covered in each stop (mg)	accumlative copper re-covered in each stop (mg)	quantity of copper removed by sampling (mg)	Total copper re-covered (mg)	quantity of ad-sorbed Cu (mg)	Copper recovery ratio (%)
0	2.222	0	0	0	0.315	0.143	0	0	0	0	0.27612	0
720	0.317	2.76121	0.27612	10	2.013	0.143	0.242814	0.242814	0.004026	0.24281		87.93755
				20	2.119	0.141	0.014946	0.25776	0.004238	0.26179		94.80845
				30	2.158	0.139	0.005421	0.263181	0.004316	0.26742		96.8485
				40	2.188	0.137	0.00411	0.267291	0.004376	0.27161		98.36522
				50	2.179	0.135	-0.00122	0.266076	0.004358	0.27045		97.94693
				60	2.19	0.133	0.001463	0.267539	0.00438	0.2719		98.47025
				80	2.201	0.131	0.001441	0.26898	0.004402	0.27336		99.00009
				100	2.189	0.129	-0.00155	0.267432	0.004378	0.27183		98.44743
				120	2.199	0.127	0.00127	0.268702	0.004398	0.27308		98.89868

Table A31: Continued (Average of the two experiments)

Average of the two experiments				
Time (min)	recovery ratio 1	recovery ratio 2	Average recovery ratio (%)	Stdev
0	0	0	0	0
10	87.47966	87.93755	87.708602	0.323776954
20	90.96598	94.80845	92.887215	2.717033686
30	91.56529	96.8485	94.206892	3.735792553
40	93.20639	98.36522	95.785808	3.64784313
50	95.04044	97.94693	96.493684	2.05519783
60	95.26541	98.47025	96.86783	2.266162484
80	94.09734	99.00009	96.548716	3.466764969
100	94.36776	98.44743	96.407595	2.884766551
120	95.98056	98.89868	97.43962	2.063429104

Table A32: Copper solubility at pH 7.0 and 20° C

Exp (1)		Exp (2)		Co average (mg/l)	Co Stdev	Cf average (mg/l)	Cf Stdev	95% confidence limit on the mean of Co	95% confidence limit on the mean of Cf
Initial Cu Conc. Co (mg/l)	Final Cu Conc. Cf (mg/l)	Initial Cu Conc. Co (mg/l)	Final Cu Conc. Cf (mg/l)						
0	0	0	0	**0**	0	**0**	0	0	0
0.90571	0.791384	1.170501	0.80859	**1.038105**	0.187236	**0.79999**	0.0121651	1.6827532	0.1093314
1.67902	1.375308	2.31693	1.33989	**1.997976**	0.451069	**1.3576**	0.0250457	4.0539053	0.2250941
3.89264	2.66662	3.936775	1.94102	**3.914709**	0.031206	**2.30382**	0.5130795	0.2804589	4.6112134
5.53054	3.016772	6.33896	2.40552	**5.934751**	0.571638	**2.71115**	0.4322176	5.1374964	3.884481
8.53854	3.136188	8.400125	2.45612	**8.469332**	0.097873	**2.79616**	0.4808779	0.879621	4.3218067
10.9608	3.995376	10.08316	2.77693	**10.521972**	0.620575	**3.38615**	0.8615728	5.5773069	7.743237
15.1262	4.53376	16.22353	4.04092	**15.674884**	0.775896	**4.28734**	0.3484933	6.9732271	3.1320236
20.6046	4.9082	20.66882	5.42432	**20.636725**	0.045391	**5.16626**	0.364952	0.4079402	3.2799426
33.8051	4.643056	31.99169	4.61877	**32.8984**	1.282284	**4.63091**	0.0171742	11.52431	0.1543502
36.7228	4.350588	42.01066	1.55038	**39.366747**	3.739051	**2.95049**	1.9800432	33.604071	17.795296
48.2192	6.139804	50.76985	4.31517	**49.49454**	1.803567	**5.22749**	1.2902125	16.209247	11.595562
58.3355	6.187368	59.7106	3.6513	**59.02304**	0.972352	**4.91933**	1.7932737	8.7388431	16.116738
95.0994	4.575252	93.08542	3.4327	**94.092433**	1.42413	**4.00398**	0.8079034	12.799123	7.2608925
150.713	11.98309	143.5975	5.03571	**147.15515**	5.031264	**8.5094**	4.9125395	45.217617	44.1506
183.267	6.078072	198.1266	3.00564	**190.69688**	10.50721	**4.54186**	2.1725375	94.431773	19.525305

Table A33: Copper solubility at pH 6.0 and 20° C

Exp (1)		Exp (2)		Co average (mg/l)	Co Stdev	Cf average (mg/l)	Cf Stdev	95% confidence limit on the mean of Co	95% confidence limit on the mean of Cf
Initial Cu Conc. Co (mg/l)	Final Cu Conc. Cf (mg/l)	Initial Cu Conc. Co (mg/l)	Final Cu Conc. Cf (mg/l)						
0	0	0	0	**0**	0	**0**	0	0	0
0.92376	0.907764	1.003	0.9027	**0.9633815**	0.056029	**0.90523**	0.003578	0.5035511	0.0321563
1.69106	1.626284	1.897676	1.71939	**1.794367**	0.146101	**1.67284**	0.0658345	1.3130574	0.5916759
3.67098	3.556168	4.030054	3.36692	**3.850517**	0.253904	**3.46155**	0.1338157	2.2819153	1.2026456
5.45732	5.18144	5.836457	4.93957	**5.64689**	0.268088	**5.06051**	0.1710265	2.4093966	1.5370711
6.64989	6.323988	7.889598	6.89476	**7.269744**	0.876606	**6.60937**	0.4035939	7.8783443	3.6272306
8.38107	7.700308	9.39811	6.57901	**8.889589**	0.719157	**7.13966**	0.792876	6.4633019	7.1258361
13.1052	12.72388	14.24461	10.9792	**13.674902**	0.805683	**11.8515**	1.2336807	7.2409378	11.087492
17.8544	16.03514	19.40705	17.3265	**18.630725**	1.097885	**16.6808**	0.9130955	9.8670526	8.2062878
26.8794	23.98845	30.758	26.1622	**28.818698**	2.742585	**25.0753**	1.5370918	24.648509	13.814346
36.6406	28.27326	43.47303	33.0631	**40.056811**	4.831262	**30.6682**	3.3868972	43.420131	30.439154
45.6435	39.30406	52.76482	43.9967	**49.204171**	5.03552	**41.6504**	3.3182004	45.255862	29.821753
55.3134	49.86124	62.35651	37.7608	**58.834977**	4.9802	**43.811**	8.5563343	44.758684	76.898576
89.6853	41.0872	88.8658	40.8514	**89.275526**	0.579439	**40.9693**	0.166733	5.2076111	1.4984836
133.441	53.96591	137.7771	82.7128	**135.60911**	3.065993	**42.858**	20.327108	27.555083	182.68637
173.855	51.12422	184.203	40.8089	**179.02898**	7.317106	**45.9666**	7.2940299	65.761229	65.553833

Table A34: Copper solubility at pH 5.0 and 20° C

Exp (1)		Exp (2)		Co average (mg/l)	Co Stdev	Cf average (mg/l)	Cf Stdev	95% confidence limit on the mean of Co	95% confidence limit on the mean of Cf
Initial Cu Conc. Co (mg/l)	Final Cu Conc. Cf (mg/l)	Initial Cu Conc. Co (mg/l)	Final Cu Conc. Cf (mg/l)						
0	0	0	0	**0**	0	**0**	0	0	0
0.84653	0.821744	0.898688	0.94217	**0.87261**	0.03688	**0.88196**	0.0851555	0.3314514	0.7653199
1.64091	1.59896	1.834487	1.85803	**1.7376975**	0.136881	**1.7285**	0.1831916	1.2301945	1.6464026
3.54661	3.256616	4.035069	3.62701	**3.7908385**	0.345394	**3.44181**	0.2619067	3.1041697	2.3538412
5.2818	5.06506	6.633842	5.88377	**5.95782**	0.956039	**5.47441**	0.578914	8.5922396	5.2028893
6.79332	6.389768	7.952787	7.35825	**7.373053**	0.819868	**6.87401**	0.6848216	7.3684191	6.1547158
8.62881	8.152672	10.12027	9.54721	**9.3745395**	1.054622	**8.84994**	0.9860859	9.4782347	8.8622763
18.5946	16.39238	14.79525	14.1741	**16.694935**	2.686556	**15.2832**	1.5685778	24.144958	14.097322
24.0941	21.18318	20.2255	19.2209	**22.159781**	2.735493	**20.2021**	1.387533	24.584769	12.470213
33.0559	30.08372	31.2585	28.4888	**32.157183**	1.270937	**29.2863**	1.1277731	11.422324	10.135666
42.9103	37.55026	40.97857	37.4106	**41.944457**	1.365973	**37.4804**	0.0987517	12.276449	0.8875139
54.2011	48.36955	52.54717	48.5264	**53.374144**	1.169517	**48.448**	0.1109168	10.510833	0.9968453
62.8259	58.87917	64.74766	61.2331	**63.786788**	1.358881	**60.0561**	1.6644671	12.212709	14.959111
106.77	97.77843	101.3451	91.4382	**104.05774**	3.836215	**94.6083**	4.4831843	34.477318	40.291844
151.909	138.5732	147.6877	130.957	**149.79855**	2.985141	**134.765**	5.3855459	26.82844	48.401663
195.35	179.12	194.7686	175.222	**195.05943**	0.411352	**177.171**	2.7564606	3.6969577	24.773214

Table A35: First cycle of using beads of fungi-Hypol foam contain 100mg dry wt. of biomass for copper adsorption at pH 5.0, 20° C and initial copper concentration of (2-15) mgl^{-1}

Exp (1)			Exp (2)			Cf average mg/l	Q average mg/g	Cf Stdev	Q Stdev
Initial Cu Con. (Co) mg/l	Equilibrium Cu conc. (Cf) mg/l	Fungi uptake capacity (Q) mg/g	Initial Cu Con. (Co) mg/l	Equilibrium Cu conc. (Cf) mg/l	Fungi uptake capacity (Q) mg/g				
2.225657	0.34255	2.73050515	2.183531	0.33852	2.67526595	**0.340535**	**2.70289**	0.00285	0.03906
4.808382	0.79794	5.8151409	4.457332	0.8714875	5.19947453	**0.8347138**	**5.50731**	0.05201	0.435342
6.684995	1.513265	7.4990085	6.48941	1.6150225	7.06786188	**1.5641438**	**7.28344**	0.07195	0.304867
8.550575	2.8164663	8.31445769	8.427206	2.64519125	8.38392139	**2.7308288**	**8.34919**	0.12111	0.049118
9.923682	3.9221975	8.70215253	9.689983	3.72422375	8.65035091	**3.8232106**	**8.67625**	0.13999	0.036629
14.711	7.1537538	10.9580085	15.50036	7.39152375	11.7578155	**7.2726388**	**11.3579**	0.16813	0.565549

Table A35, continued

Ln (Cf average)	Ln (Q average)	C1/Q1	C2/Q2	average C/Q
-1.07724	0.9943199	0.12545298	0.126537	0.12599496
-0.18067	1.7060759	0.13721766	0.167611	0.15241417
0.447339	1.9856026	0.20179534	0.228502	0.21514881
1.004605	2.1221645	0.33874323	0.315508	0.32712543
1.341091	2.1605896	0.45071578	0.430529	0.44062221
1.984119	2.4299146	0.65283338	0.628648	0.64074055

Table A36: Second cycle of using beads of fungi-Hypol foam contain 100mg dry wt. of biomass for copper adsorption at pH 5.0, 20° C and initial copper concentration of (2-15) mgl^{-1}

Exp (1)			Exp (2)			Cf average mg/l	Q average mg/g	Cf Stdev	Q Stdev
Initial Cu Con. (Co) mg/l	Equilibrium Cu conc. (Cf) mg/l	Fungi uptake capacity (Q) mg/g	Initial Cu Con. (Co) mg/l	Equilibrium Cu conc. (Cf) mg/l	Fungi uptake capacity (Q) mg/g				
2.16648	0.2614463	2.76229894	2.094264	0.20603375	2.73793386	**0.23374**	**2.75012**	0.03918	0.017229
3.908691	0.5168475	4.91817308	4.171477	0.72187375	5.00192471	**0.6193606**	**4.96005**	0.14498	0.059221
6.33896	1.6523	6.795657	6.497434	1.855815	6.73034755	**1.7540575**	**6.763**	0.14391	0.046181
8.088192	3.1700988	7.13123521	8.339945	3.51667875	6.99373606	**3.3433888**	**7.06249**	0.24507	0.097227
10.07714	4.1473738	8.59816251	11.06108	5.273255	8.39235205	**4.7103144**	**8.49526**	0.79612	0.14553
15.77819	8.6448538	10.3433419	15.19645	9.12039375	8.81028591	**8.8826238**	**9.57681**	0.33626	1.084034

Table A36, continued

Ln (Cf average)	Ln (Q average)	C1/Q1	C2/Q2	average C/Q
-1.45355	1.0116432	0.09464807	0.075252	0.0849498
-0.47907	1.6014156	0.10508933	0.144319	0.12470426
0.561932	1.9114669	0.24314058	0.275738	0.25943947
1.206985	1.9547971	0.44453712	0.502833	0.47368488
1.549755	2.139508	0.48235582	0.628341	0.55534818
2.184097	2.259345	0.83578923	1.035198	0.93549381

Table A37: Third cycle of using beads of fungi-Hypol foam contain 100mg dry wt. of biomass for copper adsorption at pH5.0, 20° C and initial copper concentration of (2-15) mgl^{-1}

Exp (1)			Exp (2)			**Cf average mg/l**	**Q average mg/g**	Cf Stdev	Q Stdev
Initial Cu Con. (Co) mg/l	Equilibrium Cu conc. (Cf) mg/l	Fungi uptake capacity (Q) mg/g	Initial Cu Con. (Co) mg/l	Equilibrium Cu conc. (Cf) mg/l	Fungi uptake capacity (Q) mg/g				
2.18654	0.2629575	2.78919463	2.301885	0.2418	2.98712325	**0.2523788**	**2.88816**	0.01496	0.139957
4.441284	0.95108	5.0607958	4.715103	0.88911875	5.54767716	**0.9200994**	**5.30424**	0.04381	0.344277
6.834442	1.8351613	7.24895709	6.592719	1.6956225	7.10078993	**1.7653919**	**7.17487**	0.09867	0.10477
8.902628	3.2779013	8.15585379	9.293798	3.487965	8.41845785	**3.3829331**	**8.28716**	0.14854	0.185689
10.4994	4.5468475	8.63120693	11.54955	5.08837875	9.36869106	**4.8176131**	**8.99995**	0.38292	0.52148
16.56856	8.7002663	11.4090216	17.28169	8.69724375	12.4474471	**8.698755**	**11.9282**	0.00214	0.734278

Table A37, continued

Ln (Cf average)	Ln (Q average)	C1/Q1	C2/Q2	average C/Q
-1.37682	1.0606193	0.09427721	0.080947	0.08761233
-0.08327	1.6685058	0.18793092	0.160269	0.17409979
0.568373	1.9705851	0.25316211	0.238794	0.2459778
1.218743	2.1147068	0.4019078	0.414324	0.40811565
1.572279	2.1972189	0.52679162	0.543126	0.53495876
2.16318	2.4789082	0.76257777	0.698717	0.73064742

Table A38: Fourth cycle of using beads of fungi-Hypol foam contain 100mg dry wt. of biomass for copper adsorption at pH 5.0, 20° C and initial copper concentration of (2-15) mgl^{-1}

Exp (1)			Exp (2)			Cf average mg/l	Q average mg/g	Cf Stdev	Q Stdev
Initial Cu Con. (Co) mg/l	Equilibrium Cu conc. (Cf) mg/l	Fungi uptake capacity (Q) mg/g	Initial Cu Con. (Co) mg/l	Equilibrium Cu conc. (Cf) mg/l	Fungi uptake capacity (Q) mg/g				
2.109309	0.3052725	2.61585293	2.089249	0.3193775	2.56631368	**0.312325**	**2.59108**	0.00997	0.03503
4.345999	0.8815625	5.02343293	4.189531	0.85990125	4.82796314	**0.8707319**	**4.9257**	0.01532	0.138218
5.92773	1.7303813	6.08615569	5.896637	1.89158125	5.80733084	**1.8109813**	**5.94674**	0.11399	0.197159
8.166426	3.2527138	7.12488276	8.025003	3.3277725	6.81098423	**3.2902431**	**6.96793**	0.05307	0.22196
10.29479	4.4163763	8.52370284	10.30883	4.43854125	8.51192449	**4.4274588**	**8.51781**	0.01567	0.008329
15.10418	8.26956	9.91019465	15.81631	8.9466	9.96107515	**8.60808**	**9.93563**	0.47874	0.035978

Table A38, continued

Ln (Cf average)	Ln (Q average)	C1/Q1	C2/Q2	average C/Q
-1.16371	0.9520761	0.11670094	0.12445	0.12057542
-0.13842	1.594466	0.17549005	0.178108	0.17679927
0.593869	1.7828437	0.28431433	0.325723	0.30501867
1.190961	1.9413187	0.45652874	0.488589	0.47255891
1.487826	2.1421597	0.51812884	0.52145	0.51978931
2.152701	2.2961278	0.83444981	0.898156	0.86630293

Table A39a: First cycle of using beads of seaweed-Hypol foam contain 100mg dry wt. of biomass for copper adsorption at pH 5.0, 20° C and initial copper concentration of (2-60) mgl^{-1}

Exp (1)			Exp (2)			Cf average mg/l	Q average mg/g	Cf Stdev	Q Stdev
Initial Cu Con. (Co) mg/l	Equilibrium Cu con. (Cf) mg/l	Seaweed uptake capacity (Q) mg/g	Initial Cu Con. (Co) mg/l	Equilibrium Cu con. (Cf) mg/l	Seaweed uptake capacity (Q) mg/g				
1.952841	0.29771625	2.399930888	2.194564	0.2931825	2.75700318	**0.29545**	**2.57847**	0.003	0.2525
6.39914	1.041755	7.76820825	6.205561	1.18532375	7.27934401	**1.11354**	**7.52378**	0.102	0.3457
10.27574	2.35704625	11.48209869	10.364	2.35352	11.6151946	**2.35528**	**11.5486**	0.002	0.0941
21.33682	7.2791875	20.38356568	21.2967	7.4484475	20.0799647	**7.36382**	**20.2318**	0.12	0.2147
46.19818	19.49965875	38.71285581	45.42587	20.079475	36.7522728	**19.7896**	**37.7326**	0.41	1.3863
58.51201	35.16023875	33.86006976	57.37361	35.389445	31.8770335	**35.2748**	**32.8686**	0.162	1.4022

Table A39a, continue

Ln (Cf average)	Ln (Q average)	C/Q (Exp1)	C/Q (Exp2)	C/Q average
-1.21926	0.947195048	0.12405201	0.106341	0.11519651
0.107544	2.018068157	0.134104927	0.162834	0.1484694
0.856661	2.446568254	0.20528009	0.202624	0.20395217
1.996578	3.007253903	0.357110606	0.370939	0.36402494
2.985155	3.630523496	0.503699826	0.546346	0.52502316
3.56317	3.492516322	1.038398296	1.110186	1.07429229

Table A39b: Measurement of total carbon (TC) at the end of the first cycle of using beads of seaweed-Hypol foam contain 100mg dry wt. of biomass for copper adsorption at pH 5.0, 20° C and initial copper concentration of (2-60) mgl^{-1} (N.B. All numbers were given by the carbon machine and only the average of TC in all flasks was calculated by us)

	Measurement of total carbon (TC) in the experimental flasks											
Cu in the flask	2 mg/l		6mg/l		10 mg/l		20 mg/l		40 mg/l		60 mg/l	
No. of TC readings	flask 1	flask 2	flask 1	flask 2	flask 1	flask 2	flask 1	flask 2	flask 1	flask 2	flask 1	flask 2
TC (1)	51.59	49.24	45.98	43.93	48.46	48.59	42.18	44.92	45.36	40.67	39.94	39.68
TC (2)	38.84	35.92	35.02	35.43	34.23	31.91	31.59	31.59	32.54	32.86	26.36	34.03
TC (3)	36.55	36.03	33.05	34.53	33.67	32.54	30.24	33.13	32.1	32.16	27.69	31.27
Average	42.33 ± 8.1	40.4 ± 7.66	38.02 ± 6.96	37.97 ± 5.18	38.79 ± 8.38	37.68 ± 9.45	34.67 ± 6.54	36.55 ± 7.29	36.67 ± 7.53	35.23 ± 4.72	31.33 ± 7.48	34.99 ± 4.28
%std dev	19.15	18.96	18.33	13.66	21.62	25.09	18.86	19.94	20.54	13.4	23.89	12.25
Average of TC in all the flasks (mg/l)					**37.05**							

Table A40: Second cycle of using beads of seaweed-Hypol foam contain 100mg dry wt. of biomass for copper adsorption at pH5.0, 20° C and initial copper concentration of (2-60) mgl^{-1}

Exp (1)			**Exp (2)**			**Cf average mg/l**	**Q average mg/g**	Cf Stdev	Q Stdev
Initial Cu Con. (Co) mg/l	Equilibrium Cu con. (Cf) mg/l	Seaweed uptake capacity (Q) mg/g	Initial Cu Con. (Co) mg/l	Equilibrium Cu con. (Cf) mg/l	Seaweed uptake capacity (Q) mg/g				
1.757256	0.14054625	2.344229138	1.834487	0.17177875	2.41092696	**0.15616**	**2.37758**	0.022	0.0472
5.705064	1.40193625	6.239535238	6.412179	1.5948725	6.98509443	**1.4984**	**6.61231**	0.136	0.5272
9.509443	3.00386125	9.433093538	10.11124	3.1303025	10.1223637	**3.06708**	**9.77773**	0.089	0.4874
22.81123	5.80168875	24.66383336	20.72198	4.67429625	23.2691414	**5.23799**	**23.9665**	0.797	0.9862
41.55931	20.48046	30.56432525	44.91233	21.1217338	34.4963704	**20.8011**	**32.5303**	0.453	2.7804
61.09173	39.85921875	30.78713696	58.35655	40.0969888	26.476358	**39.9781**	**28.6317**	0.168	3.0482

Table A40, continued

Ln (Cf average)	Ln (Q average)	C/Q (Exp1)	C/Q (Exp2)	C/Q average
-1.85686	0.866082344	0.059954143	0.07125	0.06560211
0.404401	1.888933794	0.224686006	0.228325	0.22650556
1.120727	2.280107211	0.318438616	0.309246	0.31384241
1.655938	3.176656496	0.235230617	0.20088	0.21805512
3.035006	3.482173432	0.670077282	0.612289	0.64118293
3.688332	3.354516154	1.294671174	1.514445	1.4045581

Table A41: Third cycle of using beads of seaweed-Hypol foam contain 100mg dry wt. of biomass for copper adsorption at pH 5.0, 20° C and initial copper concentration of (2-60) mgl^{-1}

Exp (1)			Exp (2)			Cf average mg/l	Q average mg/g	Cf Stdev	Q Stdev
Initial Cu Con. (Co) mg/l	Equilibrium Cu con. (Cf) mg/l	Seaweed uptake capacity (Q) mg/g	Initial Cu Con. (Co) mg/l	Equilibrium Cu con. (Cf) mg/l	Seaweed uptake capacity (Q) mg/g				
1.827466	0.155155	2.42485095	1.789	0.17782375	2.34398771	**0.16649**	**2.38442**	0.016	0.0572
5.550602	0.691145	7.04621265	5.436	0.61306375	7.01690416	**0.6521**	**7.03156**	0.055	0.0207
9.490386	3.10158875	9.263756013	9.1	3.01595125	8.86145569	**3.05877**	**9.06261**	0.061	0.2845
19.07305	11.32480375	11.23495416	19.004	10.850775	11.9048437	**11.0878**	**11.5699**	0.335	0.4737
36.33067	27.19897375	13.24095376	36.155	24.6610813	16.8234564	**25.93**	**15.0322**	1.795	2.5332
54.90121	45.69868875	13.34365726	57.886	47.5595413	15.2251693	**46.6291**	**14.2844**	1.316	1.3304

Table A41, continued

Ln (Cf average)	Ln (Q average)	C/Q (Exp1)	C/Q (Exp2)	C/Q average
-1.79282	0.868955628	0.063985376	0.075864	0.06992457
-0.42755	1.950408361	0.098087446	0.08737	0.0927285
1.118013	2.2041567	0.334808985	0.340345	0.33757694
2.405844	2.448406804	1.007997326	0.911459	0.95972808
3.255402	2.710194906	2.054155179	1.465875	1.760015
3.842225	2.659168962	3.424749891	3.123745	3.27424727

Table A42: Fourth cycle of using beads of seaweed-Hypol foam contain 100mg dry wt. of biomass for copper adsorption at pH5.0, 20° C and initial copper concentration of (2-60) mgl^{-1}

Exp (1)			Exp (2)			Cf average mg/l	Q average mg/g	Cf Stdev	Q Stdev
Initial Cu Con. (Co) mg/l	Equilibrium Cu con. (Cf) mg/l	Seaweed uptake capacity (Q) mg/g	Initial Cu Con. (Co) mg/l	Equilibrium Cu con. (Cf) mg/l	Seaweed uptake capacity (Q) mg/g				
1.369095	0.03878875	1.928944063	1.294873	0.03576625	1.82570479	**0.03728**	**1.87732**	0.002	0.073
4.900658	0.1078025	6.949640475	4.839475	0.08916375	6.88795131	**0.09848**	**6.9188**	0.013	0.0436
8.928706	2.16411	9.8086642	8.55559	1.86337125	9.70371719	**2.01374**	**9.75619**	0.213	0.0742
17.44016	10.39689625	10.21273824	17.73906	10.3762425	10.6760825	**10.3866**	**10.4444**	0.015	0.3276
36.05484	26.785395	13.4406967	35.6747	26.0005525	14.0275197	**26.393**	**13.7341**	0.555	0.4149
55.10181	44.6675125	15.12973283	54.57022	45.7460413	12.7950606	**45.2068**	**13.9624**	0.763	1.6509

Table A42, continue

Ln (Cf average)	Ln (Q average)	C/Q (Exp1)	C/Q (Exp2)	C/Q average
-3.28937	0.629847585	0.0201088	0.01959	0.01984959
-2.31787	1.934241751	0.015511954	0.012945	0.01422842
0.699994	2.277902026	0.220632489	0.192027	0.20632952
2.340514	2.346066941	1.018032188	0.971915	0.99497349
3.273098	2.619882388	1.992857632	1.853539	1.92319823
3.811247	2.636367768	2.952300151	3.575289	3.26379464

Table A43: Fifth cycle of using beads of seaweed-Hypol foam contain 100mg dry wt. of biomass for copper adsorption at pH 5.0, 20° C and initial copper concentration of (2-60) mgl^{-1}

Exp (1)			Exp (2)			Cf average mg/l	Q average mg/g	Cf Stdev	Q Stdev
Initial Cu Con. (Co) mg/l	Equilibrium Cu con. (Cf) mg/l	Seaweed uptake capacity (Q) mg/g	Initial Cu Con. (Co) mg/l	Equilibrium Cu con. (Cf) mg/l	Seaweed uptake capacity (Q) mg/g				
2.084234	0.0292175	2.979773925	2.132378	0.030225	3.04812185	**0.02972**	**3.01395**	7E-04	0.0483
6.779277	0.151125	9.6108204	6.427224	0.09823125	9.17703949	**0.12468**	**9.39393**	0.037	0.3067
10.29479	1.93792625	12.11745534	9.460296	1.84171	11.0469497	**1.88982**	**11.5822**	0.068	0.757
20.28467	10.30068	14.4767884	18.70595	10.3802725	12.0722324	**10.3405**	**13.2745**	0.056	1.7003
38.48411	29.1298475	13.56367628	38.8482	29.4225263	13.6672211	**29.2762**	**13.6154**	0.207	0.0732
56.82797	48.57207875	11.97104811	56.54413	48.7383163	11.3184227	**48.6552**	**11.6447**	0.118	0.4615

Table A43, continued

Ln (Cf average)	Ln (Q average)	C/Q (Exp1)	C/Q (Exp2)	C/Q average
-3.51589	1.10325081	0.009805274	0.009916	0.00986061
-2.08202	2.24006373	0.015724464	0.010704	0.01321424
0.636481	2.449469654	0.159928483	0.166717	0.16332255
2.336066	2.585845684	0.711530743	0.859847	0.78568886
3.376774	2.611205082	2.147636593	2.15278	2.15020851
3.884759	2.454854181	4.057462496	4.306105	4.18178374

Table A44: Copper adsorption by 100mg dry wt. of immobilised seaweed in Hypol foam cubes at pH 5.0, 10° C and initial copper concentration of (2-60) mgl^{-1}

Exp (1)			Exp (2)			Cf average mg/l	Q average mg/g	Cf Stdev	Q Stdev
Initial Cu con. (Co) mg/l	Equilibrium Cu con. (Cf) mg/l	Seaweed uptake capacity (Q) mg/l	Initial Cu con. (Co) mg/l	Equilibrium Cu con. (Cf) mg/l	Seaweed uptake capacity (Q) mg/l				
1.98093	0.344061	2.37345244	1.91673	0.3616925	2.25480873	**0.352877**	**2.31413**	0.01247	0.08389
5.36404	1.21706	6.0131268	6.16845	1.32587	7.021741	**1.271465**	**6.51743**	0.07694	0.7132
9.60974	2.750979	9.94520816	10.4543	2.7172275	11.2187102	**2.734103**	**10.582**	0.02387	0.9005
21.391	7.929025	19.5198362	20.39	7.58446	18.5680142	**7.756743**	**19.0439**	0.24364	0.67304
41.125	21.46076	28.5131603	41.2654	21.783158	28.2492893	**21.62196**	**28.3812**	0.22797	0.18658
58.9684	38.285	29.9908952	62.9764	39.762499	33.6601046	**39.02375**	**31.8255**	1.04475	2.59452

Table A44, continue

Ln (Cf average)	Ln (Q average)	C/Q (exp 1)	C/Q (exp 2)	C/Q average
-1.04164	0.839034	0.14496235	0.16041	0.1526859
0.24017	1.874481	0.20240052	0.18882	0.195612
1.0058	2.359151	0.27661349	0.2422	0.2594092
2.04856	2.946748	0.40620346	0.40847	0.4073363
3.07371	3.345728	0.75266148	0.7711	0.7618831
3.66417	3.460268	1.27655409	1.18129	1.2289243

Table A45: Copper adsorption by 100mg dry wt. of immobilised seaweed in Hypol foam cubes at pH 5.0, 30° C and initial copper concentration of (2-60) mgl^{-1}

Exp (1)			Exp (2)			Cf average mg/l	Q average mg/g	Cf Stdev	Q Stdev
Initial Cu con. (Co) mg/l	Equilibrium Cu con. (Cf) mg/l	Seaweed uptake capacity (Q) mg/l	Initial Cu con. (Co) mg/l	Equilibrium Cu con. (Cf) mg/l	Seaweed uptake capacity (Q) mg/l				
2.01503	0.27404	2.52443115	1.87661	0.2564088	2.34929616	**0.265224**	**2.43686**	0.01247	0.12384
6.018	0.987854	7.29371206	6.40516	1.0029663	7.83317804	**0.99541**	**7.56345**	0.01069	0.38146
10.1403	2.249748	11.4413446	10.8876	2.1857713	12.6176009	**2.217759**	**12.0295**	0.04524	0.83174
20.2175	7.03638	19.112582	22.0399	7.1829713	21.5425786	**7.109676**	**20.3276**	0.10366	1.71827
44.9795	19.64726	36.7318024	41.4801	19.425104	31.9796982	**19.53618**	**34.3558**	0.15709	3.36025
63.8399	36.33146	39.8873098	59.161	37.17272	31.8829364	**36.75209**	**35.8851**	0.59486	5.65995

Table A45, continued

Ln (Cf average)	Ln (Q average)	C/Q (exp 1)	C/Q (exp 2)	C/Q average
-1.32718	0.890712	0.10855515	0.10914	0.108849
-0.0046	2.023327	0.13543909	0.12804	0.1317399
0.7965	2.48736	0.19663314	0.17323	0.1849325
1.96146	3.011979	0.36815434	0.33343	0.3507928
2.97227	3.536769	0.53488411	0.60742	0.571152
3.6042	3.580323	0.91085254	1.16591	1.0383826

Table A46: Copper adsorption by 100mg dry wt. of immobilised seaweed in Hypol foam cubes at pH 3.0, 30° C and initial copper concentration of (2-60) mgl^{-1}

Exp (1)			Exp (2)			Cf average mg/l	Q average mg/g	Cf Stdev	Q Stdev
Initial Cu con. (Co) mg/l	Equilibrium Cu con. (Cf) mg/l	Seaweed uptake capacity (Q) mg/g	Initial Cu con. (Co) mg/l	Equilibrium Cu con. (Cf) mg/l	Seaweed uptake capacity (Q) mg/g				
1.81443	1.30169	0.743469	1.88063	1.283555	0.8657515	**1.29262**	**0.80461**	0.012823	0.086467
5.36304	4.03403	1.927066	5.65993	3.6280075	2.9462862	**3.83102**	**2.43668**	0.287101	0.720698
9.44826	6.489308	4.290481	9.75518	6.6792213	4.4601373	**6.58426**	**4.37531**	0.134289	0.119965
19.1362	14.78305	6.312125	22.2265	14.602705	11.054474	**14.6929**	**8.6833**	0.127521	3.353347
43.9816	30.6144	19.38237	37.6566	30.709608	10.073186	**30.662**	**14.7278**	0.067323	6.582587
58.4599	49.92314	12.37824	64.0716	51.96282	17.557789	**50.943**	**14.968**	1.442274	3.662493

Table A46, Continued

Ln (Cf average)	Ln (Q average)	C/Q (exp 1)	C/Q (exp 2)	C/Q average
0.25667	-0.2174	1.750834	1.48259	1.6167122
1.34313	0.890635	2.093353	1.23138	1.6623683
1.88468	1.475977	1.512489	1.49754	1.5050133
2.68736	2.161402	2.342008	1.32098	1.8314925
3.42302	2.689735	1.579497	3.04865	2.3140731
3.93071	2.705916	4.033136	2.95953	3.4963336

Table A47: Copper adsorption by 100mg dry wt. of immobilised seaweed in Hypol foam cubes at pH 4.0, 30° C and initial copper concentration of (2-60) mgl^{-1}

Exp (1)			Exp (2)			**Cf average mg/l**	**Q average mg/g**	Cf Stdev	Q Stdev
Initial Cu con. (Co) mg/l	Equilibrium Cu con. (Cf) mg/l	Seaweed uptake capacity (Q) mg/g	Initial Cu con. (Co) mg/l	Equilibrium Cu con. (Cf) mg/l	Seaweed uptake capacity (Q) mg/g				
2.024054	0.549088	2.138701	2.01102	0.4765475	2.2249779	**0.512818**	**2.18184**	0.051294	0.061007
6.203555	1.725848	6.492676	6.22261	1.7233288	6.5239607	**1.724588**	**6.508318**	0.001781	0.022122
9.723082	3.152971	9.526661	9.95879	3.3645463	9.5616491	**3.258759**	**9.544155**	0.149606	0.024741
22.1332	8.220696	20.17313	22.055	8.1421113	20.173641	**8.181404**	**20.17339**	0.055568	0.00036
43.30352	21.81338	31.1607	42.0277	21.638078	29.564961	**21.72573**	**30.36283**	0.123959	1.128359
59.06366	39.0235	29.05824	59.4588	40.329218	27.737957	**39.67636**	**28.3981**	0.923283	0.933579

Table A47, continue

Ln (Cf average)	Ln (Q average)	C/Q (exp 1)	C/Q (exp 2)	C/Q average
-0.66784	0.780168	0.256739	0.21418	0.2354598
0.544988	1.873081	0.265815	0.26415	0.2649841
1.181346	2.255929	0.330963	0.35188	0.3414211
2.101864	3.004364	0.407507	0.4036	0.4055543
3.078497	3.413219	0.700029	0.73188	0.7159555
3.680755	3.346322	1.342941	1.45394	1.3984386

Tables of columns experiments

1- Tables of cycles of copper adsorption and elution using column of seaweed-Hypol foam

Table A48: Carbon measured in the washing water that was used to condition the column before the adsorption experiment

Volume of D.W (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)	Amount of IC (mg)
0	0	0	0	0
10	5396	40.5	53.96	0.405
55	2450	20.424	110.25	0.91908
160	1585	8.308	166.425	0.87234
280	1250	0.952	150	0.11424
405	540	0	67.5	0
745	320	0	108.8	0
1120	90.15	0	33.80625	0
1680	50.35	0	28.196	0
2150	40.15	0	18.8705	0
2780	30.25	0	19.0575	0
3250	20.11	0	9.4517	0
3790	10.55	0	5.697	0
4180	7.58	0	2.9562	0
4760	0	0	0	0
5660	0	0	0	0
6360	0	0	0	0
7600	0	0	0	0
8130	0	0	0	0
9950	0	0	0	0
Sum (mg)			**774.97015**	**2.31066**

Table A49: Carbon measured in the washing water that was used to condition control columns of un-loaded Hypol foam

Free Hypol foam (manufactured with water + surfactant + $NaHCO_3$ + CH_3COOH)						**Free Hypol foam (manufactured with water and surfactant only)**					
Volume of D.W (ml)	TC (mg/l)	IC (mg/l)	TOC (TC-IC) (mg/l)	Quantity of TOC (mg)	Quantity of IC (mg)	Volume of D.W (ml)	TC (mg/l)	IC (mg/l)	TOC (TC-IC) (mg/l)	Quantity of TOC (mg)	Quantity of IC (mg)
0	0	0	0	0	0	0	0	0	0	0	0
20	1745.5	24.35	1721.2	34.423	0.487	20	777.6	57.67	719.93	14.3986	1.1534
105	1300	10.7	1289.3	109.591	0.9095	100	277.6	39.38	238.22	19.0576	3.1504
160	1095.5	8.42	1087.1	59.7894	0.4631	200	180.2	26.34	153.86	15.386	2.634
240	875.12	4.915	870.21	69.6164	0.3932	320	106.8	11.11	95.69	11.4828	1.3332
370	510.15	2.152	508	66.0397	0.27976	430	80.68	5.105	75.575	8.31325	0.56155
610	125.15	0.419	124.73	29.9354	0.10056	610	54.27	2.917	51.353	9.24354	0.52506
740	100.25	0.238	100.01	13.0016	0.03094	780	40.21	0.719	39.491	6.71347	0.12223
900	83.5	0	83.5	13.36	0	1000	26.76	0	26.76	5.8872	0
1140	50.45	0	50.45	12.108	0	1160	23.15	0	23.15	3.704	0
1330	40.56	0	40.56	7.7064	0	1430	19	0	19	5.13	0
1640	30.55	0	30.55	9.4705	0	1800	12.57	0	12.57	4.6509	0
1850	20.15	0	20.15	4.2315	0	2000	10	0	10	2	0
2130	15.15	0	15.15	4.242	0	2300	8.5	0	8.5	2.55	0
2360	12.14	0	12.14	2.7922	0	2600	7.15	0	7.15	2.145	0
3630	9.628	0	9.628	12.2276	0	2900	5.5	0	5.5	1.65	0
3950	6.921	0	6.921	2.21472	0	3200	2.35	0	2.35	0.705	0
4250	0	0	0	0	0	3600	1	0	1	0.4	0
4700	0	0	0	0	0	3950	0	0	0	0	0
5200	0	0	0	0	0	4200	0	0	0	0	0
5800	0	0	0	0	0	4800	0	0	0	0	0
6100	0	0	0	0	0	5350	0	0	0	0	0
6750	0	0	0	0	0	5750	0	0	0	0	0
7150	0	0	0	0	0	6300	0	0	0	0	0
7750	0	0	0	0	0	7500	0	0	0	0	0
Sum				**450.749**	**2.66406**	**Sum**				**113.41736**	**9.47984**

Table A50: First use of column of cast in seaweed-Hypol foam to adsorb Cu from 60L of copper solution at T 20° C, pH 5.43, 4.7 l/h flow rate and approximate biomass net dry wt. of 3.56 g

Foam-Seaweed column								Un-loaded column (free foam)	
Volume treated (ml)	**Copper conc. (mg/l)**	**Removal ratio (%)**	Amount of copper in the influent (mg)	approx. amount of copper in the effluent (mg)	approx. copper uptaken at each stage (mg)	approx. amount of adsorbed copper (mg)	**approx. copper uptake by the biomass (mg/g)**	Volume treated (ml)	Copper conc. (mg/l)
0	**5.948793**	**100**	0	0	0	0	**0**	0	6.215
110	**0.11033**	**98.145338**	0.6543672	0.0121363	0.642231	0.6422309	**0.180261181**	100	6.205
360	**0.163489**	**97.251728**	1.4871983	0.04087225	1.446326	2.0885569	**0.58621552**	365	6.199
640	**0.35105**	**94.098803**	1.665662	0.098294	1.567368	3.655925	**1.026143902**	645	6.21
890	**0.540617**	**90.912156**	1.4871983	0.13515425	1.352044	5.007969	**1.405635198**	885	6.22
1300	**0.808418**	**86.410386**	2.4390051	0.33145138	2.107554	7.1155227	**1.997182739**	1350	6.185
1640	**1.009018**	**83.038273**	2.0225896	0.34306612	1.679524	8.7950462	**2.468590881**	1630	6.195
2175	**1.339005**	**77.491148**	3.1826043	0.716367675	2.466237	11.261283	**3.16081341**	2170	6.205
2770	**1.667989**	**71.960883**	3.5395318	0.992453455	2.547078	13.808361	**3.87572659**	2780	6.197
3190	**1.821448**	**69.381217**	2.4984931	0.76500816	1.733485	15.541846	**4.362280601**	3200	6.214
3730	**2.073201**	**65.149216**	3.2123482	1.11952854	2.09282	17.634666	**4.949692588**	3800	6.175
4180	**2.234684**	**62.434665**	2.6769569	1.0056078	1.671349	19.306015	**5.418806328**	4200	6.2
4720	**2.443308**	**58.927668**	3.2123482	1.31938632	1.892962	21.198977	**5.950122295**	4800	6.169
5200	**2.590749**	**56.449165**	2.8554206	1.24355952	1.611861	22.810838	**6.402538981**	5150	6.211
5730	**2.763265**	**53.549149**	3.1528603	1.46453045	1.68833	24.499168	**6.876418884**	5250	6.188
6240	**2.911709**	**51.053785**	3.0338844	1.48497159	1.548913	26.048081	**7.311167265**	6300	6.179
6720	**3.02906**	**49.081099**	2.8554206	1.4539488	1.401472	27.449552	**7.704531953**	6780	6.208
7275	**3.104285**	**47.816557**	3.3015801	1.722878175	1.578702	29.028254	**8.14764153**	7300	6.217
7790	**3.178507**	**46.568875**	3.0636284	1.636931105	1.426697	30.454952	**8.548086489**	7850	6.2
8300	**3.278807**	**44.882819**	3.0338844	1.67219157	1.361693	31.816644	**8.930286024**	8350	6.168
8760	**3.3099**	**44.360142**	2.7364448	1.522554	1.213891	33.030535	**9.271000516**	8770	6.175
9420	**3.399167**	**42.859552**	3.9262034	2.24345022	1.682753	34.713288	**9.743315158**	9400	6.174
9790	**3.445305**	**42.083966**	2.2010534	1.27476285	0.926291	35.639579	**10.00330611**	9850	6.174
10880	**3.655935**	**38.543247**	6.4841844	3.98496915	2.499215	38.138794	**10.70478507**	10700	6.221
11170	**3.750217**	**36.958354**	1.72515	1.08756293	0.637587	38.776381	**10.88374281**	11200	6.22
12190	**3.898661**	**34.462991**	6.0677689	3.97663422	2.091135	40.867516	**11.47068184**	12500	6.199
13150	**4.083213**	**31.360647**	5.7108413	3.91988448	1.790957	42.658473	**11.97336704**	13700	6.189
14180	**4.18251**	**29.691452**	6.1272568	4.3079853	1.819271	44.477744	**12.48399961**	14580	6.185
15150	**4.261747**	**28.359467**	5.7703292	4.13389459	1.636435	46.114179	**12.94331358**	15700	6.178
16210	**4.368065**	**26.572248**	6.3057206	4.6301489	1.675572	47.78975	**13.41361252**	16600	6.155
17180	**4.458335**	**25.054797**	5.7703292	4.32458495	1.445744	49.235495	**13.81940358**	17700	6.21
18200	**4.526539**	**23.908279**	6.0677689	4.61706978	1.450699	50.686194	**14.22658535**	18500	6.175
19140	**4.612797**	**22.45827**	5.5918654	4.33602918	1.255836	51.94203	**14.57907309**	19780	6.185
20180	**4.637872**	**22.036756**	6.1867447	4.82338688	1.363358	53.305388	**14.96173995**	20290	6.215
21210	**4.672977**	**21.446636**	6.1272568	4.81316631	1.31409	54.619478	**15.33057846**	21550	6.177
22160	**4.752214**	**20.114652**	5.6513534	4.5146033	1.13675	55.756228	**15.64964112**	22680	6.2
23150	**4.813397**	**19.086157**	5.8893051	4.76526303	1.124042	56.88027	**15.96513689**	23400	6.2
24190	**4.877589**	**18.007081**	6.1867447	5.07269256	1.114052	57.994323	**16.27782871**	24650	6.158
25180	**4.922724**	**17.248356**	5.8893051	4.87349676	1.015808	59.010131	**16.56294548**	25700	6.168
26215	**5.002964**	**15.899511**	6.1570008	5.17806774	0.978933	59.989064	**16.8377121**	26600	6.188
27210	**5.138369**	**13.623335**	5.919049	5.112677155	0.806372	60.795436	**17.06404431**	27700	6.198
28180	**5.214597**	**12.341932**	5.7703292	5.05815909	0.71217	61.507606	**17.263936**	28700	6.199

29170	**5.260735**	**11.566346**	5.8893051	5.20812765	0.681177	62.188783	**17.45512867**	29800	6.2
30180	**5.296843**	**10.959366**	6.0082809	5.34981143	0.65847	62.847253	**17.63994769**	30300	6.166
31210	**5.284807**	**11.161693**	6.1272568	5.44335121	0.683906	63.531158	**17.8319061**	31500	6.167
32170	**5.326933**	**10.453549**	5.7108413	5.11385568	0.596986	64.128144	**17.99946783**	32600	6.2
33190	**5.414194**	**8.9866802**	6.0677689	5.52247788	0.545291	64.673435	**18.15251994**	33800	6.195
34190	**5.417203**	**8.9360985**	5.948793	5.417203	0.53159	65.205025	**18.30172646**	34800	6.198
35180	**5.468356**	**8.0762097**	5.8893051	5.41367244	0.475633	65.680658	**18.43522688**	35900	6.187
36160	**5.504464**	**7.4692295**	5.8298171	5.39437472	0.435442	66.1161	**18.55744672**	36780	6.179
37280	**5.527533**	**7.0814365**	6.6626482	6.19083696	0.471811	66.587911	**18.68987455**	37700	6.203
39900	**5.548596**	**6.7273647**	15.585838	14.53732152	1.048516	67.636427	**18.98417174**	38800	6.188
40180	**5.457323**	**8.2616759**	1.665662	1.52805044	0.137612	67.774039	**19.02279652**	39670	6.168
41150	**5.537563**	**6.9128309**	5.7703292	5.37143611	0.398893	68.172932	**19.13475771**	40400	6.17
42210	**5.629839**	**5.3616591**	6.3057206	5.96762934	0.338091	68.511023	**19.22965306**	41800	6.18
43450	**5.679989**	**4.5186309**	7.3765033	7.04318636	0.333317	68.84434	**19.32320836**	42750	6.178
44160	**5.729136**	**3.6924633**	4.223643	4.06768656	0.155956	69.000297	**19.36698217**	43900	6.188
45150	**5.841472**	**0**	5.8893051	5.78305728	0	69.000297	**19.36698217**	44580	6.199
46150	**5.914691**	**0**	5.948793	5.914691	0	69.000297	**19.36698217**	45750	6.2
47160	**5.938763**	**0**	6.0082809	5.99815063	0	69.000297	**19.36698217**	46850	6.189
48210	**5.949796**	**0**	6.2462327	6.2472858	0	69.000297	**19.36698217**	47900	6.21
49120	**5.919706**	**0**	5.4134016	5.38693246	0	69.000297	**19.36698217**	48800	6.224
50160	**5.916697**	**0**	6.1867447	6.15336488	0	69.000297	**19.36698217**	49850	6.215
51200	**5.948793**	**0**	6.1867447	6.18674472	0	69.000297	**19.36698217**	50800	6.187
53300	**5.941772**	**0**	12.492465	12.4777212	0	69.000297	**19.36698217**	51900	6.188
54400	**5.951802**	**0**	6.5436723	6.5469822	0	69.000297	**19.36698217**	52780	6.2

Table A51: pH changes during the column's first adsorption cycle

Volume treated (ml)	pH	Volume treated (ml)	pH	Volume treated (ml)	pH
0	5.43	13150	4.54	27210	4.7
1000	4.49	14180	4.56	27170	4.74
2890	4.47	15150	4.59	30180	4.76
3700	4.43	16210	4.6	31210	4.78
4840	4.47	17180	4.63	32170	4.8
5855	4.46	18200	4.63	33190	4.82
6870	4.47	21200	4.63	35180	4.84
7900	4.48	22160	4.64	36160	4.85
8880	4.52	23150	4.66	38270	4.88
9920	4.52	24190	4.68	41150	4.9
11170	4.52	25180	4.7		

Table A52: Carbon measured in the effluent during the first adsorption cycle

Volume (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)
0	0	0	0
110	30	0	3.3
360	3	0	0.75
640	2.5	0	0.7
890	0	0	0
1300	0	0	0
1640	0	0	0
2175	0	0	0
Total amount of lost biomass (mg)			**4.75**

Table A53: Copper elution from the column after the first adsorption cycle by 0.1M HCl

Volume of acid passed in the column (ml)	Copper Conc. (mg/l)	Copper recovered at each stage (mg)	Amount of recovered copper (mg)	Amount of adsorbed copper in the column (mg)	Removal ratio (%)
0	0	0	0	69.000297	0
55	4.409	0.242495	0.242495		0.3514405
110	5.307	0.291885	0.53438		0.7744604
220	654	71.94	72.47438		105.03488
430	36.81	7.7301	80.20448		116.23788
695	5.721	1.516065	81.720545		118.43506
870	2.497	0.436975	82.15752		119.06836
1170	1.351	0.4053	82.56282		119.65575
1520	0.57	0.1995	82.76232		119.94488
1835	0.432	0.13608	82.8984		120.14209
2145	0.269	0.08339	82.98179		120.26295
2540	0.183	0.072285	83.054075		120.36771
2960	0.143	0.06006	83.114135		120.45475
3260	0.122	0.0366	83.150735		120.50779
3600	0.098	0.03332	83.184055		120.55608
3860	0.084	0.02184	83.205895		120.58773
4235	0.075	0.028125	83.23402		120.6285
4680	0.064	0.02848	83.2625		120.66977
5160	0.048	0.02304	83.28554		120.70316
5810	0.024	0.0156	83.30114		120.72577
6480	0.017	0.01139	83.31253		120.74228
6890	0.014	0.00574	83.31827		120.7506
7230	0.013	0.00442	83.32269		120.757
7770	0.015	0.0081	83.33079		120.76874

Table A54: Carbon measured in the effluent during the column regeneration by acid washing after the first adsorption cycle

Volume of acid (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)
0	0	0	0
55	20	0	1.1
110	22.5	0	1.2375
220	40.5	0	4.455
430	12.9	0	2.709
695	3.5	0	0.9275
870	1.5	0	0.2625
1170	0	0	0
1520	0	0	0
Total amount of lost biomass (mg)			**10.6915**

Table A55: Carbon measured in the effluent during the column wash with D.W after column regeneration by acid

Volume of D.W (ml)	TOC (mg/l)	IC (mg/l)	amount of lost biomass (mg)
0	0	0	0
130	5.5	0	0.715
410	0	0	0
710	0	0	0
1000	0	0	0
1250	0	0	0
1650	0	0	0
Total amount of lost biomass (mg)			0.715

Table A56: Second use of column of cast in seaweed-Hypol foam to adsorb Cu from 60L of copper solution at T 20° C, pH 5.29, 4.7 l/h flow rate and approximate biomass net dry wt. of 3.54 g

Volume treated (ml)	**Copper conc. (mg/l)**	**Removal ratio (%)**	Amount of copper in the influent (mg)	approx. amount of copper in the effluent (mg)	approx. copper uptaken at each stage (mg)	approx. amount of adsorbed copper (mg)	**approx. copper uptake by the biomass (mg/g)**
0	**6.187507**	**100**	0	0	0	0	**0**
115	**0.034102**	**99.448857**	0.7115633	0.0039217	0.7076416	0.7076416	**0.1995254**
290	**0.115345**	**98.13584**	1.0828137	0.0201854	1.0626284	1.7702699	**0.4991423**
600	**0.343026**	**94.456152**	1.9181272	0.1063381	1.8117891	3.582059	**1.0099913**
800	**0.520557**	**91.586967**	1.2375014	0.1041114	1.13339	4.715449	**1.3295601**
1140	**0.874616**	**85.864808**	2.1037524	0.2973694	1.8063829	6.521832	**1.8388848**
1435	**1.04312**	**83.141514**	1.8253146	0.3077204	1.5175942	8.0394261	**2.2667831**
1765	**1.231684**	**80.094018**	2.0418773	0.4064557	1.6354216	9.6748477	**2.7279038**
2185	**1.506506**	**75.652456**	2.5987529	0.6327325	1.9660204	11.640868	**3.2822396**
2800	**1.780325**	**71.227103**	3.8053168	1.0948999	2.7104169	14.351285	**4.0464642**
3230	**1.887646**	**69.492624**	2.660628	0.8116878	1.8489402	16.200225	**4.5677883**
3800	**2.018036**	**67.385314**	3.526879	1.1502805	2.3765985	18.576824	**5.23789**
4180	**2.205597**	**64.354028**	2.3512527	0.8381269	1.5131258	20.08995	**5.6645284**
4870	**2.255747**	**63.543524**	4.2693798	1.5564654	2.7129144	22.802864	**6.4294572**
5140	**2.373098**	**61.646944**	1.6706269	0.6407365	1.0298904	23.832754	**6.7198434**
5875	**2.528563**	**59.134382**	4.5478176	1.8584938	2.6893238	26.522078	**7.4781206**
6100	**2.705091**	**56.281407**	1.3921891	0.6086455	0.7835436	27.305622	**7.6990472**
6865	**2.840496**	**54.093046**	4.7334429	2.1729794	2.5604634	29.866085	**8.4209912**
7150	**3.000976**	**51.499433**	1.7634395	0.8552782	0.9081613	30.774247	**8.6770548**
7805	**3.156441**	**48.98687**	4.0528171	2.0674689	1.9853482	32.759595	**9.2368403**
8110	**3.265768**	**47.219971**	1.8871896	0.9960592	0.8911304	33.650725	**9.4881019**
8835	**3.42023**	**44.723618**	4.4859426	2.4796668	2.0062758	35.657001	**10.053788**
9170	**3.577701**	**42.178635**	2.0728148	1.1985298	0.874285	36.531286	**10.3003**
9840	**3.78131**	**38.887988**	4.1456297	2.5334777	1.612152	38.143438	**10.75486**
10670	**3.940787**	**36.310585**	5.1356308	3.2708532	1.8647776	40.008216	**11.280649**
11600	**4.014006**	**35.127249**	5.7543815	3.7330256	2.0213559	42.029572	**11.850587**
12710	**4.306882**	**30.393905**	6.8681328	4.780639	2.0874938	44.117065	**12.439174**

13810	**4.448305**	**28.108283**	6.8062577	4.8931355	1.9131222	46.030188	**12.978594**
14680	**4.628845**	**25.190468**	5.3831311	4.0270952	1.3560359	47.386223	**13.36094**
15840	**4.770268**	**22.904847**	7.1775081	5.5335109	1.6439972	49.030221	**13.824479**
16790	**4.913697**	**20.586805**	5.8781317	4.6680122	1.2101195	50.24034	**14.165682**
17950	**4.948802**	**20.019452**	7.1775081	5.7406103	1.4368978	51.677238	**14.570827**
18780	**5.07518**	**17.976982**	5.1356308	4.2123994	0.9232314	52.600469	**14.83114**
19780	**5.251708**	**15.124007**	6.187507	5.251708	0.935799	53.536268	**15.094996**
20630	**5.371065**	**13.195007**	5.259381	4.5654053	0.6939757	54.230244	**15.290668**
21800	**5.444284**	**12.011671**	7.2393832	6.3698123	0.8695709	55.099815	**15.535851**
22680	**5.475377**	**11.509159**	5.4450062	4.8183318	0.6266744	55.726489	**15.712547**
23700	**5.508476**	**10.974226**	6.3112571	5.6186455	0.6926116	56.419101	**15.907835**
24815	**5.528536**	**10.650024**	6.8990703	6.1643176	0.7347527	57.153854	**16.115005**
25490	**5.602758**	**9.4504782**	4.1765672	3.7818617	0.3947056	57.548559	**16.226295**
26940	**5.615797**	**9.2397471**	8.9718852	8.1429057	0.8289795	58.377539	**16.460033**
27870	**5.617803**	**9.207327**	5.7543815	5.2245568	0.5298247	58.907364	**16.609421**
28825	**5.648896**	**8.7048144**	5.9090692	5.3946957	0.5143735	59.421737	**16.754453**
29835	**5.670962**	**8.3481926**	6.2493821	5.7276716	0.5217105	59.943447	**16.901554**
30800	**5.706067**	**7.7808397**	5.9709443	5.5063547	0.4645896	60.408037	**17.032549**
31870	**5.722115**	**7.5214784**	6.6206325	6.1226631	0.4979694	60.906007	**17.172955**
32790	**5.728133**	**7.4242179**	5.6925064	5.2698824	0.4226241	61.328631	**17.292118**
33730	**5.732145**	**7.3593775**	5.8162566	5.3882163	0.4280403	61.756671	**17.412807**
34740	**5.73716**	**7.2783271**	6.2493821	5.7945316	0.4548505	62.211521	**17.541056**
35820	**5.76725**	**6.7920246**	6.6825076	6.22863	0.4538776	62.665399	**17.669031**
36855	**5.831442**	**5.7545793**	6.4040697	6.0355425	0.3685273	63.033926	**17.77294**
37550	**5.892625**	**4.7657643**	4.3003174	4.0953744	0.204943	63.238869	**17.830725**
38105	**5.994931**	**3.1123359**	3.4340664	3.3271867	0.1068797	63.345749	**17.860861**
39655	**6.112282**	**1.2157562**	9.5906359	9.4740371	0.1165987	63.462348	**17.893737**
40720	**6.149393**	**0.6159831**	6.589695	6.5491035	0.0405914	63.502939	**17.905182**
41835	**6.047087**	**2.2694116**	6.8990703	6.742502	0.1565683	63.659507	**17.949328**
42840	**6.140366**	**0.7618739**	6.2184445	6.1710678	0.0473767	63.706884	**17.962686**
43560	**6.229633**	**0**	4.455005	4.4853358	0	63.706884	**17.962686**
44730	**6.284798**	**0**	7.2393832	7.3532137	0	63.706884	**17.962686**
45970	**6.353002**	**0**	7.6725087	7.8777225	0	63.706884	**17.962686**
46800	**6.146384**	**0**	5.1356308	5.1014987	0	63.706884	**17.962686**
47750	**6.24869**	**0**	5.8781317	5.9362555	0	63.706884	**17.962686**
48820	**6.241669**	**0**	6.6206325	6.6785858	0	63.706884	**17.962686**
49860	**6.253705**	**0**	6.4350073	6.5038532	0	63.706884	**17.962686**
50890	**6.217597**	**0**	6.3731322	6.4041249	0	63.706884	**17.962686**
51150	**6.22863**	**0**	1.6087518	1.6194438	0	63.706884	**17.962686**
52700	**6.204558**	**0**	9.5906359	9.6170649	0	63.706884	**17.962686**
53540	**6.195531**	**0**	5.1975059	5.204246	0	63.706884	**17.962686**

Table A57: pH changes during the column's second adsorption cycle

Volume treated (ml)	pH	Volume treated (ml)	pH	Volume treated (ml)	pH
0	5.29	9170	4.08	26160	4.42
1140	3.84	11150	4.12	31170	4.53
2185	3.85	13130	4.18	35200	4.63
3230	3.93	15150	4.24	40150	4.72
4180	3.95	17150	4.28	45280	4.76
5140	3.98	20150	4.33	50160	4.85
7150	4.02	23140	4.4	54120	4.93

Table A58: Carbon measured in the effluent in the column second adsorption cycle

Volume (ml)	TOC (mg/l)	Amount of TOC (mg)
0	0	0
115	4.5	0.5175
290	3.5	0.6125
600	2	0.62
800	0	0
1140	0	0
1435	0	0
1765	0	0
2185	0	0
Total biomass loss (mg)		1.75

Table A59: Carbon measured in the effluent during the column wash with D.W after the second adsorption experiment

Volume of D.W (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)
0	0	0	0
100	14	0	1.4
220	3	0	0.36
520	0	0	0
760	0	0	0
900	0	0	0
1130	0	0	0
1570	0	0	0
Total amount of lost biomass (mg)			**1.76**

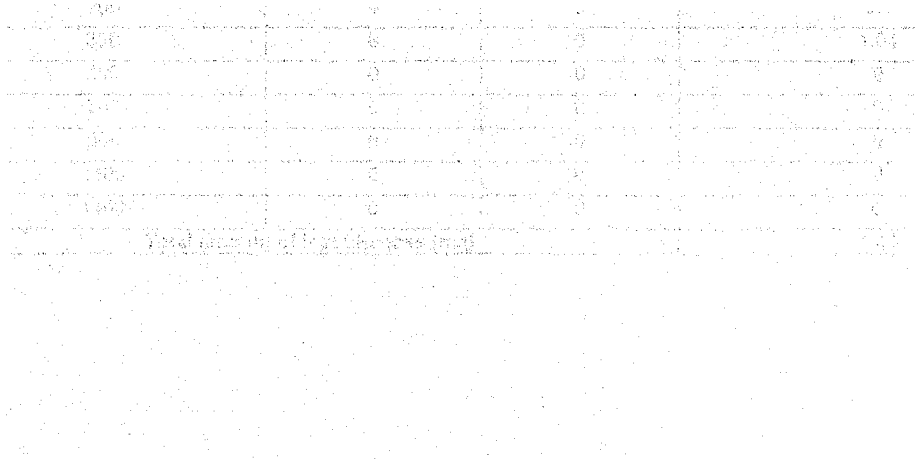


Table A60: Copper elution from the column after the second cycle by 0.1M HCl

Volume of acid passed in the column (ml)	Copper Conc. (mg/l)	Copper recovered at each stage (mg)	Amount of recovered copper (mg)	Amount of adsorbed copper in the column (mg)	Removal ratio (%)
0	0	0	0	63.706884	0
55	4.409	0.242495	0.242495		0.3806418
110	5.307	0.291885	0.53438		0.8388104
220	654	71.94	72.47438		113.76224
430	36.81	7.7301	80.20448		125.8961
695	5.721	1.516065	81.720545		128.27585
870	2.497	0.436975	82.15752		128.96176
1170	1.351	0.4053	82.56282		129.59796
1520	0.57	0.1995	82.76232		129.91111
1835	0.432	0.13608	82.8984		130.12471
2145	0.269	0.08339	82.98179		130.25561
2540	0.183	0.072285	83.054075		130.36907
2960	0.143	0.06006	83.114135		130.46335
3260	0.122	0.0366	83.150735		130.5208
3600	0.098	0.03332	83.184055		130.5731
3860	0.084	0.02184	83.205895		130.60738
4235	0.075	0.028125	83.23402		130.65153
4680	0.064	0.02848	83.2625		130.69624
5160	0.048	0.02304	83.28554		130.7324
5810	0.024	0.0156	83.30114		130.75689
6480	0.017	0.01139	83.31253		130.77477
6890	0.014	0.00574	83.31827		130.78378
7230	0.013	0.00442	83.32269		130.79072
7770	0.015	0.0081	83.33079		130.80343

Table A61: Carbon measured in the effluent during the column regeneration process by acid wash after the second adsorption cycle

Volume of acid (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)
0	0	0	0
100	0	0	0
200	4	0	0.4
330	8	0	1.04
500	0	0	0
700	0	0	0
905	0	0	0
1105	0	0	0
1440	0	0	0
Total amount of lost biomass (mg)			**1.44**

Table A62: Carbon measured in the effluent during the column wash with D.W after acid wash (second cycle)

Volume of D.W (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)
0	0	0	0
110	4	0	0.44
300	0	0	0
530	0	0	0
880	0	0	0
1425	0	0	0
2590	0	0	0
Total amount of lost biomass (mg)			0.44

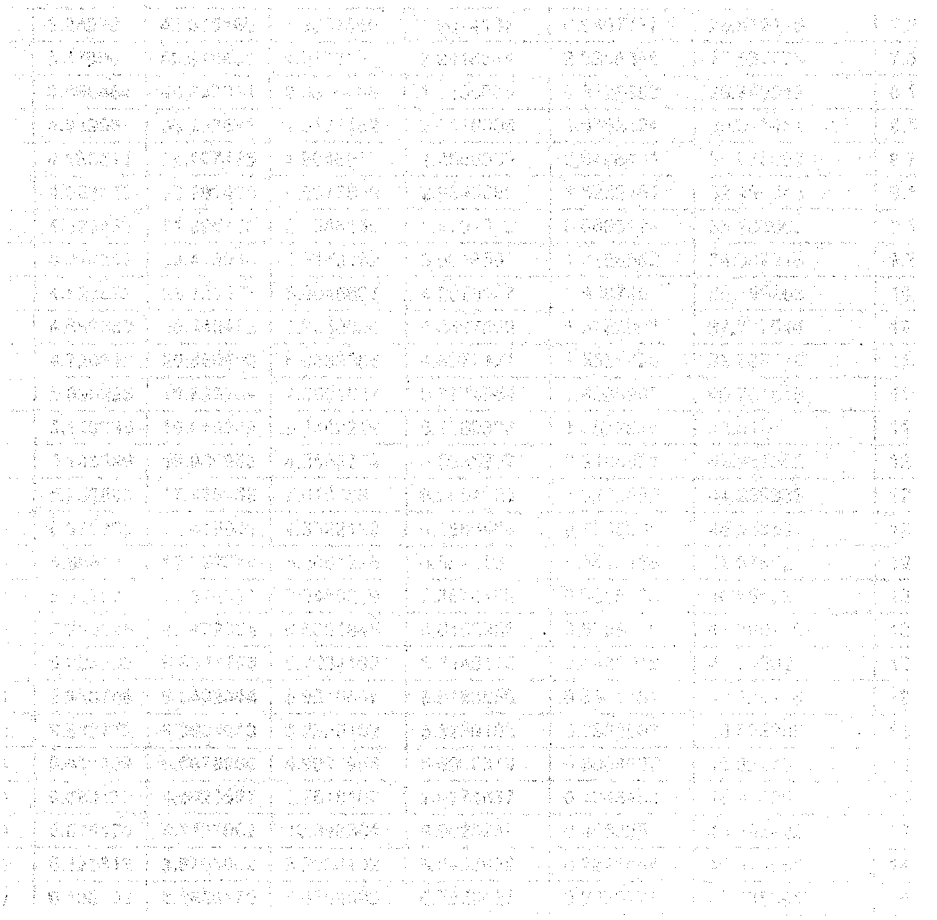


Table A63: Third use of column of cast in seaweed-Hypol foam to adsorb Cu from 60L of copper solution at T 20° C, Ph 5.31, 4.7 l/h flow rate and biomass net dry wt. of 3.54 g

Volume treated (ml)	**Copper conc. (mg/l)**	**Removal ratio (%)**	Amount of copper in the influent (mg)	approx. amount of copper in the effluent (mg)	approx. copper uptaken at each stage (mg)	approx. amount of adsorbed copper (mg)	**approx. copper uptake by the biomass (mg/g)**
0	**6.34899**	**0**	0	0	0	0	**0**
120	**0.047141**	**99.257504**	0.7618788	0.0056569	0.7562219	0.7562219	**0.2135476**
240	**0.129387**	**97.962085**	0.7618788	0.0155264	0.7463524	1.5025742	**0.4243082**
580	**0.455362**	**92.827804**	2.1586566	0.1548231	2.0038335	3.5064078	**0.9901656**
800	**0.673013**	**89.399684**	1.3967778	0.1480629	1.2487149	4.7551227	**1.3427871**
1240	**1.084243**	**82.922591**	2.7935556	0.4770669	2.3164887	7.0716114	**1.9969345**
1750	**1.48444**	**76.619273**	3.2379849	0.7570644	2.4809205	9.5525319	**2.6975154**
2115	**1.728169**	**72.780411**	2.3173814	0.6307817	1.6865997	11.239132	**3.17379**
2805	**2.111315**	**66.745656**	4.3808031	1.4568074	2.9239958	14.163127	**3.9994898**
3130	**2.252738**	**64.518167**	2.0634218	0.7321399	1.3312819	15.494409	**4.3754271**
3820	**2.583728**	**59.304897**	4.3808031	1.7827723	2.5980308	18.09244	**5.1090785**
4200	**2.677007**	**57.835703**	2.4126162	1.0172627	1.3953535	19.487794	**5.5031089**
4765	**2.865571**	**54.865719**	3.5871794	1.6190476	1.9681317	21.455925	**6.0588846**
5140	**2.990946**	**52.890995**	2.3808713	1.1216048	1.2592665	22.715192	**6.4144857**
5820	**3.207594**	**49.478673**	4.3173132	2.1811639	2.1361493	24.851341	**7.0177075**
6130	**3.24972**	**48.815166**	1.9681869	1.0074132	0.9607737	25.812115	**7.289018**
6810	**3.37008**	**46.919431**	4.3173132	2.2916544	2.0256588	27.837774	**7.8610387**
7130	**3.498464**	**44.897314**	2.0316768	1.1195085	0.9121683	28.749942	**8.1186236**
7810	**4.03206**	**36.492891**	4.3173132	2.7418008	1.5755124	30.325454	**8.5635286**
8110	**4.183513**	**34.107425**	1.904697	1.2550539	0.6496431	30.975097	**8.7469796**
8820	**4.203573**	**33.791469**	4.5077829	2.9845368	1.5232461	32.498343	**9.1771253**
9160	**4.323933**	**31.895735**	2.1586566	1.4701372	0.6885194	33.186863	**9.3715545**
9840	**4.414203**	**30.473934**	4.3173132	3.001658	1.3156552	34.502518	**9.7430791**
10770	**4.524533**	**28.736177**	5.9045607	4.2078157	1.696745	36.199263	**10.222219**
11710	**4.669968**	**26.445498**	5.9680506	4.3897699	1.5782807	37.777544	**10.667905**
12665	**4.720118**	**25.655608**	6.0632855	4.5077127	1.5555728	39.333116	**11.10718**
13800	**5.090225**	**19.826224**	7.2061037	5.7774054	1.4286983	40.761815	**11.510626**
14815	**5.110285**	**19.510269**	6.4442249	5.1869393	1.2572856	42.0191	**11.865668**
15580	**5.148399**	**18.909953**	4.8569774	3.9385252	0.9184521	42.937552	**12.125027**
16780	**5.238669**	**17.488152**	7.618788	6.2864028	1.3323852	44.269938	**12.501276**
17560	**5.370062**	**15.418641**	4.9522122	4.1886484	0.7635638	45.033501	**12.716897**
18380	**5.56665**	**12.322275**	5.2061718	4.564653	0.6415188	45.67502	**12.898054**
19695	**5.617803**	**11.516588**	8.3489219	7.3874109	0.9615109	46.636531	**13.169572**
20750	**5.730139**	**9.7472354**	6.6981845	6.0452966	0.6528878	47.289419	**13.35394**
21820	**5.929736**	**6.6034755**	6.7934193	6.3448175	0.4486018	47.738021	**13.480619**
22750	**5.933748**	**6.5402844**	5.9045607	5.5183856	0.3861751	48.124196	**13.58967**
23730	**5.942775**	**6.3981043**	6.2220102	5.8239195	0.3980907	48.522286	**13.702086**
24675	**6.031039**	**5.0078989**	5.9997956	5.6993319	0.3004637	48.82275	**13.786933**
25110	**6.063135**	**4.5023697**	2.7618107	2.6374637	0.1243469	48.947097	**13.822047**
26740	**6.075171**	**4.3127962**	10.348854	9.9025287	0.446325	49.393422	**13.948084**
27720	**6.122312**	**3.5703002**	6.2220102	5.9998658	0.2221444	49.615566	**14.010815**
28740	**6.130336**	**3.4439179**	6.4759698	6.2529427	0.2230271	49.838594	**14.073795**
29845	**6.22863**	**1.8957346**	7.015634	6.8826362	0.1329978	49.971591	**14.111352**
30790	**6.199543**	**2.3538705**	5.9997956	5.8585681	0.1412274	50.112819	**14.151233**

31820	**6.317897**	**0.4897314**	6.5394597	6.5074339	0.0320258	50.144845	**14.160276**
32790	**6.339963**	**0.1421801**	6.1585203	6.1497641	0.0087562	50.153601	**14.162749**
33530	**6.457314**	**0**	4.6982526	4.7784124	0	50.153601	**14.162749**
34805	**6.331939**	**0**	8.0949623	8.0732222	0	50.153601	**14.162749**
35745	**6.263735**	**0**	5.9680506	5.8879109	0	50.153601	**14.162749**
36750	**6.316894**	**0**	6.380735	6.3484785	0	50.153601	**14.162749**
37720	**6.330936**	**0**	6.1585203	6.1410079	0	50.153601	**14.162749**
38780	**6.339963**	**0**	6.7299294	6.7203608	0	50.153601	**14.162749**
39710	**6.34899**	**0**	5.9045607	5.9045607	0	50.153601	**14.162749**
40795	**6.382089**	**0**	6.8886542	6.9245666	0	50.153601	**14.162749**
41855	**6.434245**	**0**	6.7299294	6.8202997	0	50.153601	**14.162749**
42805	**6.321909**	**0**	6.0315405	6.0058136	0	50.153601	**14.162749**
43730	**6.349993**	**0**	5.8728158	5.8737435	0	50.153601	**14.162749**
44725	**6.143375**	**0**	6.3172451	6.1126581	0	50.153601	**14.162749**
45740	**6.271759**	**0**	6.4442249	6.3658354	0	50.153601	**14.162749**
46895	**6.232642**	**0**	7.3330835	7.1987015	0	50.153601	**14.162749**
47835	**6.341969**	**0**	5.9680506	5.9614509	0	50.153601	**14.162749**
48790	**6.317897**	**0**	6.0632855	6.0335916	0	50.153601	**14.162749**
49725	**6.319903**	**0**	5.9363057	5.9091093	0	50.153601	**14.162749**
50760	**6.354005**	**0**	6.5712047	6.5763952	0	50.153601	**14.162749**
51690	**6.361026**	**0**	5.9045607	5.9157542	0	50.153601	**14.162749**
52480	**6.3189**	**0**	5.0157021	4.991931	0	50.153601	**14.162749**

Table A64: pH changes during the column's third adsorption cycle

Volume treated (ml)	pH	Volume treated (ml)	pH	Volume treated (ml)	pH
0	5.31	16140	4.29	36150	4.61
1130	3.92	20130	4.36	40130	4.67
3130	3.95	24120	4.44	44130	4.74
6130	4.04	28130	4.5	48150	4.79
9160	4.13	32130	4.57	52140	4.89
12150	4.2				

Table A65: Carbon measured in the effluent during the column's third adsorption cycle

Volume (ml)	TOC (mg/l)	Amount of TOC (mg)
0	0	0
120	0	0
240	0	0
580	0	0
800	0	0
1240	0	0
1750	0	0
Total biomass loss (mg)		0

Table A66: Carbon measured in the effluent during the column wash with D.W after the third adsorption experiment

Volume of D.W (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)
0	0	0	0
100	6.422	0	0.6422
220	0.664	0	0.07968
400	0	0	0
700	0	0	0
Total amount of lost biomass (mg)			0.72188

Table A67: Copper elution from the column after the third cycle by 0.1M HCl

Volume of acid passed in the column (ml)	Copper Conc. (mg/l)	Copper recovered at each stage (mg)	Amount of recovered copper (mg)	Amount of adsorbed copper In the column (mg)	Removal ratio (%)
0	0	0	0	50.153601	0
100	0.02	0.002	0.002		0.0039877
200	528	52.8	52.802		105.28058
380	70.15	12.627	65.429		130.45723
605	8.558	1.92555	67.35455		134.29654
800	2.747	0.535665	67.890215		135.36459
1000	1.258	0.2516	68.141815		135.86625
1200	0.981	0.1962	68.338015		136.25744
1500	0.397	0.1191	68.457115		136.49491
1860	0.221	0.07956	68.536675		136.65355
2140	0.171	0.04788	68.584555		136.74901
2515	0.124	0.0465	68.631055		136.84173
2820	0.088	0.02684	68.657895		136.89525
3180	0.067	0.02412	68.682015		136.94334
3590	0.047	0.01927	68.701285		136.98176
3860	0.04	0.0108	68.712085		137.00329
4100	0.036	0.00864	68.720725		137.02052
4520	0.028	0.01176	68.732485		137.04397
4860	0.024	0.00816	68.740645		137.06024
5250	0.018	0.00702	68.747665		137.07424
5530	0.017	0.00476	68.752425		137.08373
5915	0.012	0.00462	68.757045		137.09294

Table A68: Carbon measured in the effluent during the column regeneration by acid after the third adsorption cycle

Volume of acid (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)
0	0	0	0
100	0	0	0
200	1.797	0	0.1797
380	1.518	0	0.27324
605	0	0	0
Total amount of lost biomass (mg)			**0.45294**

Table A69: Carbon measured in the effluent during the column wash with D.W after regeneration with acid

Volume of D.W (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)
0	0	0	0
100	0	0	0
300	2.522	0	0.5044
650	4.972	0	1.7402
850	0	0	0
1180	0	0	0
Total amount of lost biomass (mg)			**2.2446**

Table A70: Fourth use of column of cast in seaweed-Hypol foam to adsorb Cu from 60L of copper solution at T 20° C, pH 5.32, 4.7 l/h flow rate and biomass net dry wt. of 3.54 g

Volume treated (ml)	**Copper conc. (mg/l)**	**Removal ratio (%)**	Amount of copper in the influent (mg)	approx. amount of copper in the effluent (mg)	approx. copper uptaken at each stage (mg)	approx. amount of adsorbed copper (mg)	**approx. copper uptake by the biomass (mg/g)**
0	**6.44929**	**100**	0	0	0	0	**0**
100	**0.007021**	**99.8911353**	0.644929	0.0007021	0.6442269	0.6442269	**0.18192161**
225	**0.095285**	**98.5225505**	0.80616125	0.01191063	0.79425063	1.43847753	**0.40620804**
560	**0.433296**	**93.281493**	2.16051215	0.14515416	2.01535799	3.45383552	**0.9753199**
800	**0.690064**	**89.3001555**	1.5478296	0.16561536	1.38221424	4.83604976	**1.3656399**
1130	**0.990964**	**84.6345257**	2.1282657	0.32701812	1.80124758	6.63729734	**1.87428966**
1790	**1.496476**	**76.7962675**	4.2565314	0.98767416	3.26885724	9.90615458	**2.79737402**
2150	**1.717136**	**73.3748056**	2.3217444	0.61816896	1.70357544	11.60973	**3.27844239**
2780	**2.091255**	**67.5738725**	4.0630527	1.31749065	2.74556205	14.3552921	**4.05375473**
3130	**2.199579**	**65.8942457**	2.2572515	0.76985265	1.48739885	15.8426909	**4.47377755**
3710	**2.401182**	**62.7682737**	3.7405882	1.39268556	2.34790264	18.1905936	**5.13679585**
4150	**2.770286**	**57.0451011**	2.8376876	1.21892584	1.61876176	19.8093553	**5.5939139**
4840	**3.091246**	**52.0684292**	4.4500101	2.13295974	2.31705036	22.1264057	**6.24821991**
5130	**3.273792**	**49.2379471**	1.8702941	0.94939968	0.92089442	23.0473001	**6.50826897**
5790	**3.322939**	**48.4758942**	4.2565314	2.19313974	2.06339166	25.1106918	**7.09094494**
6220	**3.377101**	**47.6360809**	2.7731947	1.45215343	1.32104127	26.431733	**7.46399045**
6785	**3.594752**	**44.2612753**	3.64384885	2.03103488	1.61281397	28.044547	**7.91942892**
7140	**3.878601**	**39.8600311**	2.28949795	1.37690336	0.9125946	28.9571416	**8.17713421**
7810	**3.913706**	**39.3157076**	4.3210243	2.62218302	1.69884128	30.6559829	**8.65686571**
8130	**3.986925**	**38.1804044**	2.0637728	1.275816	0.7879568	31.4439397	**8.87937485**
8830	**4.109291**	**36.2830482**	4.514503	2.8765037	1.6379993	33.081939	**9.34192534**
9105	**4.170474**	**35.3343701**	1.77355475	1.14688035	0.6266744	33.7086134	**9.51889034**
9860	**4.22263**	**34.525661**	4.86921395	3.18808565	1.6811283	35.3897417	**9.99361993**
10860	**4.339981**	**32.7060653**	6.44929	4.339981	2.109309	37.4990507	**10.5892624**
11790	**4.481404**	**30.5132193**	5.9978397	4.16770572	1.83013398	39.3291847	**11.1060693**
12980	**4.512497**	**30.0311042**	7.6746551	5.36987143	2.30478367	41.6339683	**11.7569113**
13975	**4.548605**	**29.4712286**	6.41704355	4.52586198	1.89118158	43.5251499	**12.2909573**
14720	**4.626839**	**28.2581649**	4.80472105	3.44699506	1.357726	44.8828759	**12.6743622**
15770	**4.742184**	**26.4696734**	6.7717545	4.9792932	1.7924613	46.6753372	**13.1805308**
16725	**4.827439**	**25.1477449**	6.15907195	4.61020425	1.54886771	48.2242049	**13.6179116**
17730	**5.030045**	**22.0062208**	6.48153645	5.05519523	1.42634123	49.6505461	**14.0206925**
18730	**5.213594**	**19.1601866**	6.44929	5.213594	1.235696	50.8862421	**14.3696376**
19720	**5.294837**	**17.9004666**	6.3847971	5.24188863	1.14290847	52.0291506	**14.6923807**

20820	**5.415197**	**16.0342146**	7.094219	5.9567167	1.1375023	53.1666529	**15.0135971**
21800	**5.544584**	**14.0279938**	6.3203042	5.43369232	0.88661188	54.0532648	**15.2639652**
22720	**5.615797**	**12.9237947**	5.9333468	5.16653324	0.76681356	54.8200783	**15.4805037**
23790	**5.688013**	**11.8040435**	6.9007403	6.08617391	0.81456639	55.6346447	**15.7105271**
24730	**5.756217**	**10.7465008**	6.0623326	5.41084398	0.65148862	56.2861333	**15.8944993**
25600	**5.89764**	**8.55365474**	5.6108823	5.1309468	0.4799355	56.7660688	**16.0300271**
26790	**5.932745**	**8.00933126**	7.6746551	7.05996655	0.61468855	57.3807574	**16.2036074**
27840	**6.041069**	**6.32970451**	6.7717545	6.34312245	0.42863205	57.8093894	**16.3246477**
28835	**6.169453**	**4.33903577**	6.41704355	6.13860574	0.27843782	58.0878273	**16.4032751**
29760	**6.200546**	**3.85692068**	5.96559325	5.73550505	0.2300882	58.3179155	**16.4682491**
30790	**6.231639**	**3.3748056**	6.6427687	6.41858817	0.22418053	58.542096	**16.5315549**
31810	**6.316894**	**2.05287714**	6.5782758	6.44323188	0.13504392	58.6771399	**16.5696896**
32830	**6.342972**	**1.64852255**	6.5782758	6.46983144	0.10844436	58.7855843	**16.6003129**
33865	**6.408167**	**0.63763608**	6.67501515	6.63245285	0.0425623	58.8281466	**16.612332**
34990	**6.428227**	**0.32659409**	7.25545125	7.23175538	0.02369587	58.8518424	**16.6190234**
35700	**6.451296**	**0**	4.5789959	4.58042016	0	58.8518424	**16.6190234**
36890	**6.457314**	**0**	7.6746551	7.68420366	0	58.8518424	**16.6190234**
37850	**6.4192**	**0**	6.1913184	6.162432	0	58.8518424	**16.6190234**
38780	**6.460323**	**0**	5.9978397	6.00810039	0	58.8518424	**16.6190234**
39860	**6.44929**	**0**	6.9652332	6.9652332	0	58.8518424	**16.6190234**
40730	**6.418197**	**0**	5.6108823	5.58383139	0	58.8518424	**16.6190234**
41995	**6.431236**	**0**	8.15835185	8.13551354	0	58.8518424	**16.6190234**
42730	**6.407164**	**0**	4.74022815	4.70926554	0	58.8518424	**16.6190234**
43735	**6.450293**	**0**	6.48153645	6.48254447	0	58.8518424	**16.6190234**
44860	**6.45932**	**0**	7.25545125	7.266735	0	58.8518424	**16.6190234**
45740	**6.398137**	**0**	5.6753752	5.63036056	0	58.8518424	**16.6190234**
46790	**6.4192**	**0**	6.7717545	6.74016	0	58.8518424	**16.6190234**
47720	**6.450293**	**0**	5.9978397	5.99877249	0	58.8518424	**16.6190234**
48950	**6.430233**	**0**	7.9326267	7.90918659	0	58.8518424	**16.6190234**

Table A71: pH changes during the column's fourth cycle

Volume treated (ml)	pH	Volume treated (ml)	pH	Volume treated (ml)	pH
0	5.32	13085	4.22	35170	4.62
1130	3.84	18110	4.33	39170	4.68
4150	3.98	22130	4.41	44160	4.74
7140	4.06	27180	4.49	48130	4.8
10120	4.15	31140	4.56		

Table A72: Carbon measured in the effluent during the column fourth adsorption cycle

Volume (ml)	TOC (mg/l)	Amount of TOC (mg)
0	0	0
100	0	0
225	0	0
560	0	0
800	0	0
1130	0	0
1790	0	0
2150	0	0
Total biomass loss (mg)		**0**

Table A73: Carbon measured in the effluent during column wash with D.W after the end of the fourth adsorption cycle

Volume of D.W (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)
0	0	0	0
100	3.891	0	0.3891
250	0	0	0
480	0	0	0
680	0	0	0
Total amount of lost biomass (mg)			**0.3891**

Table A74: Copper elution from the column after the fourth cycle by 0.1M HCl

Volume of acid passed in the column (ml)	Copper Conc. (mg/l)	Copper recovered at each stage (mg)	Amount of recovered copper (mg)	Amount of adsorbed copper in the column (mg)	Removal ratio (%)
0	0	0	0	58.851842	0
100	7.719	0.7719	0.7719		1.3115987
200	585.45	58.545	59.3169		100.79022
320	58.4	7.008	66.3249		112.69809
500	10.035	1.8063	68.1312		115.76732
700	3.357	0.6714	68.8026		116.90815
830	1.996	0.25948	69.06208		117.34905
1000	1.225	0.20825	69.27033		117.70291
1140	0.885	0.1239	69.39423		117.91344
1335	0.643	0.125385	69.519615		118.12649
1610	0.483	0.132825	69.65244		118.35218
1870	0.282	0.07332	69.72576		118.47677
2110	0.283	0.06792	69.79368		118.59218
2500	0.165	0.06435	69.85803		118.70152
2870	0.116	0.04292	69.90095		118.77445
3140	0.154	0.04158	69.94253		118.8451
3575	0.074	0.03219	69.97472		118.8998
3860	0.062	0.01767	69.99239		118.92982
4150	0.051	0.01479	70.00718		118.95495
4575	0.04	0.017	70.02418		118.98384
4880	0.034	0.01037	70.03455		119.00146
5155	0.031	0.008525	70.043075		119.01594
5510	0.031	0.011005	70.05408		119.03464
5910	0.025	0.01	70.06408		119.05163

Table A75: Carbon measured in the effluent during the column regeneration by acid

Volume of acid (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)
0	0	0	0
100	0	0	0
200	0	0	0
380	0	0	0
605	0	0	0
Total amount of lost biomass (mg)			**0**

Table A76: Carbon measured in the effluent during the column wash with D.W after acid wash

Volume of D.W (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)
0	0	0	0
100	0	0	0
300	0	0	0
650	0	0	0
850	0	0	0
1180	0	0	0
Total amount of lost biomass (mg)			**0**

Table A77: Fifth use of column of cast in seaweed-Hypol foam to adsorb Cu from 60L of copper solution at T 20° C, pH 5.34, 4.7 l/h flow rate and biomass net dry wt. of 3.54 g

Volume treated (ml)	**Copper conc. (mg/l)**	**Removal ratio (%)**	Amount of copper in the influent (mg)	approx. amount of copper in the effluent (mg)	approx. copper uptaken at each stage (mg)	approx. amount of adsorbed copper (mg)	**approx. copper uptake by the biomass (mg/g)**
0	**6.030036**	**100**	0	0	0	0	**0**
100	**0.014042**	**99.7671324**	0.6030036	0.0014042	0.6015994	0.6015994	**0.16988414**
235	**0.144432**	**97.6047904**	0.81405486	0.01949832	0.79455654	1.39615594	**0.39425696**
560	**0.547638**	**90.9181637**	1.9597617	0.17798235	1.78177935	3.17793529	**0.89740913**
810	**0.858568**	**85.7618097**	1.507509	0.214642	1.292867	4.47080229	**1.26249859**
1135	**1.208615**	**79.9567532**	1.9597617	0.39279988	1.56696183	6.03776412	**1.70498899**
1760	**1.709112**	**71.6566866**	3.7687725	1.068195	2.7005775	8.73834162	**2.46759826**
2150	**1.998979**	**66.8496341**	2.35171404	0.77960181	1.57211223	10.3104538	**2.91154307**
2800	**2.365074**	**60.7784431**	3.9195234	1.5372981	2.3822253	12.6926791	**3.58425366**
3105	**2.503488**	**58.4830339**	1.83916098	0.76356384	1.07559714	13.7682763	**3.88798883**
3800	**2.742202**	**54.5242848**	4.19087502	1.90583039	2.28504463	16.0533209	**4.53325682**
4130	**2.895661**	**51.9793746**	1.98991188	0.95556813	1.03434375	17.0876647	**4.82534254**
4820	**3.103282**	**48.5362608**	4.16072484	2.14126458	2.01946026	19.1071249	**5.39561284**
5110	**3.135378**	**48.003992**	1.74871044	0.90925962	0.83945082	19.9465757	**5.63266324**
5830	**3.355035**	**44.3612774**	4.34162592	2.4156252	1.92600072	21.8725765	**6.17654172**
6180	**3.412206**	**43.4131737**	2.1105126	1.1942721	0.9162405	22.788817	**6.43527657**
6810	**3.57068**	**40.7850965**	3.79892268	2.2495284	1.54939428	24.3382112	**6.87280611**
7110	**3.618824**	**39.9866933**	1.8090108	1.0856472	0.7233636	25.0615748	**7.07707494**
7800	**3.778301**	**37.3419827**	4.16072484	2.60702769	1.55369715	26.615272	**7.51581956**
8140	**3.817418**	**36.6932801**	2.05021224	1.29792212	0.75229012	27.3675621	**7.72825687**
8810	**3.948811**	**34.5143047**	4.04012412	2.64570337	1.39442075	28.7619829	**8.12202383**
9270	**4.093243**	**32.1190951**	2.77381656	1.88289178	0.89092478	29.6529076	**8.37360983**
9815	**4.160444**	**31.0046574**	3.28636962	2.26744198	1.01892764	30.6718353	**8.66134224**
10550	**4.263753**	**29.2914172**	4.43207646	3.13385846	1.29821801	31.9700533	**9.02794275**
11650	**4.304876**	**28.6094478**	6.6330396	4.7353636	1.897676	33.8677293	**9.56382269**
12770	**4.358035**	**27.7278776**	6.75364032	4.8809992	1.87264112	35.7403704	**10.0926331**
13770	**4.425236**	**26.6134398**	6.030036	4.425236	1.6048	37.3451704	**10.5458085**
14990	**4.516509**	**25.0998004**	7.35664392	5.51014098	1.84650294	39.1916734	**11.0672378**
15770	**4.626839**	**23.2701264**	4.70342808	3.60893442	1.09449366	40.286167	**11.3763091**
16880	**4.737169**	**21.4404524**	6.69333996	5.25825759	1.43508237	41.7212494	**11.7815584**

17530	**4.826436**	**19.9600798**	3.9195234	3.1371834	0.78234	42.5035894	**12.0024814**
18925	**4.917709**	**18.4464405**	8.41190022	6.86020406	1.55169617	44.0552855	**12.440661**
19905	**5.106273**	**15.3193613**	5.90943528	5.00414754	0.90528774	44.9605733	**12.6963029**
20895	**5.139372**	**14.7704591**	5.96973564	5.08797828	0.88175736	45.8423306	**12.9453002**
21690	**5.201558**	**13.7391883**	4.79387862	4.13523861	0.65864001	46.5009707	**13.1312919**
22760	**5.216603**	**13.4896873**	6.45213852	5.58176521	0.87037331	47.371344	**13.3770744**
23845	**5.311888**	**11.9095143**	6.54258906	5.76339848	0.77919058	48.1505345	**13.5971081**
24725	**5.362038**	**11.0778443**	5.30643168	4.71859344	0.58783824	48.7383728	**13.7631062**
25800	**5.515497**	**8.53293413**	6.4822887	5.92915928	0.55312943	49.2915022	**13.919303**
26790	**5.541575**	**8.10046574**	5.96973564	5.48615925	0.48357639	49.7750786	**14.055859**
27680	**5.615797**	**6.86959415**	5.36673204	4.99805933	0.36867271	50.1437513	**14.1599675**
28750	**5.617803**	**6.83632735**	6.45213852	6.01104921	0.44108931	50.5848406	**14.2845256**
29745	**5.628836**	**6.65335995**	5.99988582	5.60069182	0.399194	50.9840346	**14.397253**
30850	**5.659929**	**6.13772455**	6.66318978	6.25422155	0.40896824	51.3930029	**14.5127405**
31995	**5.706067**	**5.37258816**	6.90439122	6.53344672	0.37094451	51.7639474	**14.6174906**
32770	**5.716097**	**5.20625416**	4.6732779	4.42997518	0.24330272	52.0072501	**14.6861962**
33960	**5.740169**	**4.80705256**	7.17574284	6.83080111	0.34494173	52.3521918	**14.7836035**
34830	**5.811382**	**3.62608117**	5.24613132	5.05590234	0.19022898	52.5424208	**14.8373217**
35800	**5.838463**	**3.17697937**	5.84913492	5.66330911	0.18582581	52.7282466	**14.8897966**
36800	**5.859526**	**2.82767798**	6.030036	5.859526	0.17051	52.8987566	**14.9379465**
37885	**5.909676**	**1.99600798**	6.54258906	6.41199846	0.1305906	53.0293472	**14.9748237**
38815	**5.930739**	**1.64670659**	5.60793348	5.51558727	0.09234621	53.1216934	**15.0009011**
39860	**6.008973**	**0.3493014**	6.30138762	6.27937679	0.02201084	53.1437043	**15.0071167**
40850	**6.031039**	**0**	5.96973564	5.97072861	0	53.1437043	**15.0071167**
41850	**6.030036**	**0**	6.030036	6.030036	0	53.1437043	**15.0071167**
42845	**6.130336**	**0**	5.99988582	6.09968432	0	53.1437043	**15.0071167**
43800	**6.018**	**0**	5.75868438	5.74719	0	53.1437043	**15.0071167**
44800	**6.015994**	**0**	6.030036	6.015994	0	53.1437043	**15.0071167**
45780	**6.231639**	**0**	5.90943528	6.10700622	0	53.1437043	**15.0071167**
46820	**6.031039**	**0**	6.27123744	6.27228056	0	53.1437043	**15.0071167**
47820	**6.033045**	**0**	6.030036	6.033045	0	53.1437043	**15.0071167**
48870	**6.139363**	**0**	6.3315378	6.44633115	0	53.1437043	**15.0071167**

Table A78: pH changes during the column's fifth cycle

Volume treated (ml)	pH	Volume treated (ml)	pH	Volume treated (ml)	pH
0	5.34	16220	4.41	36145	4.66
1125	3.89	20180	4.47	40130	4.72
4130	3.97	24100	4.51	44135	4.77
8140	4.05	28170	4.55	48135	4.79
12130	4.32	32100	4.62		

Table A79: Carbon measured in the effluent during the column fifth adsorption cycle t

Volume (ml)	TOC (mg/l)	Amount of TOC (mg)
0	0	0
100	0	0
235	0	0
560	0	0
810	0	0
1135	0	0
1760	0	0
2150	0	0
Total biomass loss (mg)		**0**

Table A80: Washing acid from free Hypol foam column after it was washed with 3 litres of 0.1M of HCl

Washing of acid traces from a free Hypol foam column washed with 3 litres of 0.1M HCl using distilled water				
pH monitoring of the first batch of washing water (effluent)		►	pH monitoring of the second batch of washing water (effluent)	
Volume (ml)	pH	Draining the column, leaving it for 2 hours then passing the second batch of distilled water	Volume (ml)	pH
100	2.03		20	4.7
650	3.45		140	4.85
1170	3.89		350	5.02
2200	4.48		525	5.15
3200	4.88		725	5.22
4200	5		925	5.21
5200	5.19		1200	5.22
6200	5.21		1500	5.23
7300	5.22		1700	5.22
8250	5.21		1980	5.21

2- Tables of the effect of flow rate on the adsorption process using columns of seaweed-Hypol foam

2.1 Flow rate = 2.25 l/hr

Table A81: Carbon measured in the washing water that was used to condition the column before the adsorption experiment

Volume of D.W (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)	Amount of IC (mg)
0	0	0	0	0
50	950	60	47.5	3
100	837	35	41.85	1.75
210	720.5	20	79.255	2.2
400	545.5	10	103.645	1.9
600	325.5	7	65.1	1.4
800	215.15	0	43.03	0
1000	110.2	0	22.04	0
1145	85.56	0	12.4062	0
1550	55.5	0	22.4775	0
1900	40.15	0	14.0525	0
2120	20.14	0	4.4308	0
2530	17.2	0	7.052	0
2880	10.12	0	3.542	0
3210	8.42	0	2.7786	0
3530	3.12	0	0.9984	0
3870	0	0	0	0
4220	0	0	0	0
4810	0	0	0	0
5310	0	0	0	0
Sum (mg)			**470.158**	**10.25**

Table A82: Copper adsorption using column of cast in seaweed-Hypol foam at Cu initial concentration of 6 mgl^{-1}, T 20° C, pH 5.36, biomass net dry wt. of 3.16 g and a flow rate of 2.25 l/h

Volume treated (ml)	Copper conc. (mg/l)	**Removal ratio (%)**	Amount of copper in the influent (mg)	approx. amount of copper in the effluent (mg)	approx. copper uptaken at each stage (mg)	approx. amount of adsorbed copper (mg)	**approx. copper uptake by the biomass (mg/g)**
0	6.638857	**100**	0	0	0	0	**0**
100	0.037111	**99.4410032**	0.6638857	0.0037111	0.6601746	0.6601746	**0.20868356**
220	0.012036	**99.8187037**	0.79666284	0.00144432	0.79521852	1.45539312	**0.46005498**
440	0.018054	**99.7280556**	1.46054854	0.00397188	1.45657666	2.91196978	**0.92048407**
650	0.036108	**99.4561112**	1.39415997	0.00758268	1.38657729	4.29854707	**1.35878612**
890	0.069207	**98.9575465**	1.59332568	0.01660968	1.576716	5.87526307	**1.85719169**
1290	0.14042	**97.8848769**	2.6555428	0.056168	2.5993748	8.47463787	**2.67886338**
1800	0.254762	**96.1625623**	3.38581707	0.12992862	3.25588845	11.7305263	**3.70806137**
2305	0.393176	**94.0776552**	3.35262279	0.19855388	3.15406891	14.8845952	**4.70507385**
2890	0.567698	**91.4488593**	3.88373135	0.33210333	3.55162802	18.4362232	**5.82775618**

3250	0.696082	**89.5150325**	2.38998852	0.25058952	2.139399	20.5756222	**6.50402787**
3960	0.933793	**85.9344312**	4.71358847	0.66299303	4.05059544	24.6262177	**7.78443559**
4140	0.980934	**85.2243541**	1.19499426	0.17656812	1.01842614	25.6446438	**8.10636374**
4825	1.199588	**81.9308053**	4.54761705	0.82171778	3.72589927	29.3705431	**9.28413384**
5290	1.407209	**78.8034446**	3.08706851	0.65435219	2.43271632	31.8032594	**10.0531242**
5805	1.553647	**76.5976734**	3.41901136	0.80012821	2.61888315	34.4221426	**10.8809625**
6175	1.597779	**75.9329204**	2.45637709	0.59117823	1.86519886	36.2873414	**11.4705586**
6800	1.783334	**73.1379362**	4.14928563	1.11458375	3.03470188	39.3220433	**12.4298387**
7100	1.861568	**71.9595105**	1.9916571	0.5584704	1.4331867	40.75523	**12.8828741**
7900	2.038096	**69.3004986**	5.3110856	1.6304768	3.6806088	44.4358388	**14.0463278**
8100	2.229669	**66.4148663**	1.3277714	0.4459338	0.8818376	45.3176764	**14.3250798**
8820	2.297873	**65.3875208**	4.77997704	1.65446856	3.12550848	48.4431849	**15.3130642**
9150	2.37711	**64.193987**	2.19082281	0.7844463	1.40637651	49.8495614	**15.7576249**
9915	2.596767	**60.8853301**	5.07872561	1.98652676	3.09219885	52.9417602	**16.73508**
10960	2.861559	**56.8968122**	6.93760557	2.99032916	3.94727641	56.8890366	**17.9828282**
11910	3.180513	**52.0924611**	6.30691415	3.02148735	3.2854268	60.1744634	**19.0213634**
12890	3.251726	**51.0197915**	6.50607986	3.18669148	3.31938838	63.4938518	**20.0706339**
13920	3.451323	**48.0132951**	6.83802271	3.55486269	3.28316002	66.7770118	**21.1084526**
14810	3.605785	**45.6866596**	5.90858273	3.20914865	2.69943408	69.4764459	**21.9617533**
15880	3.75122	**43.4959964**	7.10357699	4.0138054	3.08977159	72.5662175	**22.9384412**
16980	3.818421	**42.4837589**	7.3027427	4.2002631	3.1024796	75.6686971	**23.9191461**
17900	4.110294	**38.0873244**	6.10774844	3.78147048	2.32627796	77.9949751	**24.6544909**
18850	4.155429	**37.4074634**	6.30691415	3.94765755	2.3592566	80.3542317	**25.4002604**
19865	4.247705	**36.0175253**	6.73843986	4.31142058	2.42701928	82.781251	**26.1674499**
20735	4.510491	**32.0592234**	5.77580559	3.92412717	1.85167842	84.6329294	**26.752772**
21910	4.536569	**31.6664149**	7.80065698	5.33046858	2.4701884	87.1031178	**27.5336074**
22720	4.648905	**29.9743164**	5.37747417	3.76561305	1.61186112	88.7149789	**28.0431225**
23800	4.739175	**28.6145943**	7.16996556	5.118309	2.05165656	90.7666355	**28.6916585**
24820	4.827439	**27.2850884**	6.77163414	4.92398778	1.84764636	92.6142818	**29.2757061**
25960	4.951811	**25.4116936**	7.56829698	5.64506454	1.92323244	94.5375143	**29.8836468**
26915	5.130345	**22.7224656**	6.34010844	4.89947948	1.44062896	95.9781432	**30.3390347**
27850	5.210585	**21.5138238**	6.2073313	4.87189698	1.33543432	97.3135775	**30.7611703**
28805	5.401155	**18.6432996**	6.34010844	5.15810303	1.18200541	98.4955829	**31.1348065**
29905	5.422218	**18.3260311**	7.3027427	5.9644398	1.3383029	99.8338858	**31.5578488**
30820	5.514494	**16.9360931**	6.07455416	5.04576201	1.02879215	100.862678	**31.8830537**
31830	5.568656	**16.1202599**	6.70524557	5.62434256	1.08090301	101.943581	**32.224731**
32780	5.629839	**15.1986705**	6.30691415	5.34834705	0.9585671	102.902148	**32.5277375**
33780	5.741172	**13.52168**	6.638857	5.741172	0.897685	103.799833	**32.8114989**
34840	5.856517	**11.7842574**	7.03718842	6.20790802	0.8292804	104.629113	**33.0736374**
35855	5.936757	**10.5756157**	6.73843986	6.02580836	0.7126315	105.341745	**33.2989028**
36825	6.030036	**9.17056957**	6.43969129	5.84913492	0.59055637	105.932301	**33.4855798**
37850	6.116294	**7.87127965**	6.80482843	6.26920135	0.53562708	106.467928	**33.6548934**
38870	6.141369	**7.49357909**	6.77163414	6.26419638	0.50743776	106.975366	**33.8152963**
39790	6.201549	**6.58709775**	6.10774844	5.70542508	0.40232336	107.37769	**33.9424722**
40800	6.219603	**6.31515335**	6.70524557	6.28179903	0.42344654	107.801136	**34.0763251**
41845	6.242672	**5.96766883**	6.93760557	6.52359224	0.41401332	108.215149	**34.2071962**
42895	6.313885	**4.89499924**	6.97079985	6.62957925	0.3412206	108.55637	**34.3150573**
43910	6.332942	**4.60794682**	6.73843986	6.42793613	0.31050373	108.866874	**34.4132086**
44840	6.378077	**3.92808581**	6.17413701	5.93161161	0.2425254	109.109399	**34.4898718**
45870	6.418197	**3.32376492**	6.83802271	6.61074291	0.2272798	109.336679	**34.5617157**
46800	6.448287	**2.87052425**	6.17413701	5.99690691	0.1772301	109.513909	**34.6177388**
47810	6.507464	**1.97915093**	6.70524557	6.57253864	0.13270693	109.646616	**34.6596879**

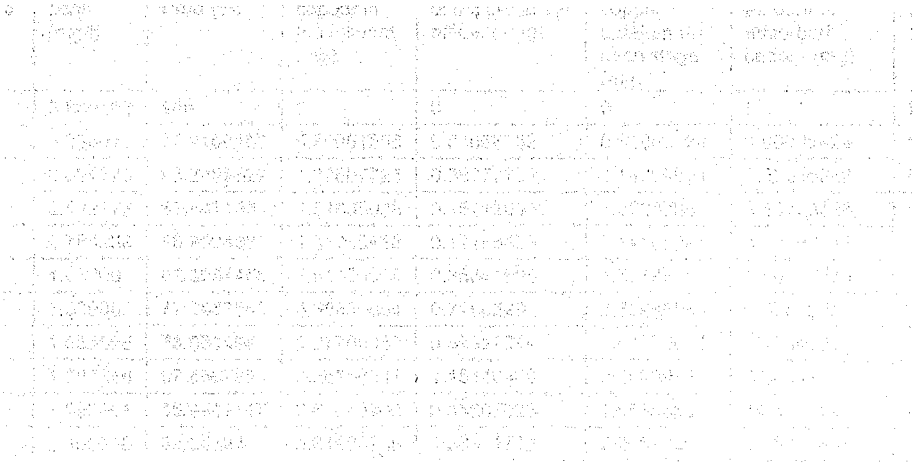
48990	6.520503	**1.78274664**	7.83385126	7.69419354	0.13965772	109.786274	**34.7038342**
49850	6.590713	**0.72518507**	5.70941702	5.66801318	0.04140384	109.827678	**34.7169221**
50800	6.642869	**0**	6.30691415	6.31072555	0	109.827678	**34.7169221**
51830	6.643872	**0**	6.83802271	6.84318816	0	109.827678	**34.7169221**
52810	6.628827	**0**	6.50607986	6.49625046	0	109.827678	**34.7169221**
53905	6.633842	**0**	7.26954842	7.26405699	0	109.827678	**34.7169221**
54765	6.63986	**0**	5.70941702	5.7102796	0	109.827678	**34.7169221**
55910	6.637854	**0**	7.60149127	7.60034283	0	109.827678	**34.7169221**

Table A83: pH changes during the adsorption experiment (2.25 l/hr)

Volume treated (ml)	pH	Volume treated (ml)	pH	Volume treated (ml)	pH
0	5.36	17260	4.25	39200	4.69
1170	4.06	21150	4.37	43200	4.76
5130	4.04	27100	4.47	47100	4.82
9150	4.04	31200	4.5	51100	4.89
13160	4.19	35150	4.64	55250	4.92

Table A84: Carbon measured in the effluent during the adsorption experiment

Volume (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)
0	0	0	0
100	60	0	6
220	15	0	1.8
440	8.2	0	1.804
650	3.1	0	0.651
890	0	0	0
1290	0	0	0
1800	0	0	0
Total amount of TOC (mg)			**10.255**



2.2 Flow rate = 7.04 l/hr

Table A85: Carbon measured in the effluent during the column conditioning process before the adsorption experiment

Volume of D.W (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)	Amount of IC (mg)
0	0	0	0	0
50	954	40.15	47.7	2.0075
100	840	25.14	42	1.257
200	800	15.25	80	1.525
400	540	10.25	108	2.05
600	430.15	5.14	86.03	1.028
800	265.25	3.35	53.05	0.67
1000	118.5	0	23.7	0
1200	62.35	0	12.47	0
1505	31.15	0	9.50075	0
1810	18.45	0	5.62725	0
2200	15.55	0	6.0645	0
2500	14.45	0	4.335	0
2800	10.54	0	3.162	0
3200	8.59	0	3.436	0
3500	5.35	0	1.605	0
3800	0	0	0	0
4200	0	0	0	0
4520	0	0	0	0
4800	0	0	0	0
Sum (mg)			**486.6805**	**8.5375**

Table A86: Copper adsorption using column of cast in seaweed-Hypol foam at Cu initial concentration of 6 mgl^{-1}, T 20° C, pH 5.39, biomass net dry wt. of 3.04 g and a flow rate of 7.05 l/h

Volume treated (ml)	Copper conc. (mg/l)	**Removal ratio (%)**	Amount of copper in the influent (mg)	approx. amount of copper in the effluent (mg)	approx. copper uptaken at each stage (mg)	approx. amount of adsorbed copper (mg)	**approx. copper uptake by the biomass (mg/g)**
0	5.838463	**100**	0	0	0	0	**0**
120	0.338011	**94.2106167**	0.70061556	0.04056132	0.66005424	0.66005424	**0.21664563**
330	0.394179	**93.2485827**	1.22607723	0.08277759	1.14329964	1.80335388	**0.59190399**
590	0.592773	**89.8471053**	1.51800038	0.15412098	1.3638794	3.16723328	**1.03956191**
815	0.764286	**86.9094657**	1.31365418	0.17196435	1.14168983	4.30892311	**1.41429189**
1160	1.03309	**82.3054458**	2.01426974	0.35641605	1.65785369	5.96677679	**1.95843923**
1740	1.339005	**77.0657963**	3.38630854	0.7766229	2.60968564	8.57646243	**2.81500063**
2130	1.536596	**73.681498**	2.27700057	0.59927244	1.67772813	10.2541906	**3.36567124**
2740	1.887646	**67.6687854**	3.56146243	1.15146406	2.40999837	12.6641889	**4.15669049**
3170	1.992961	**65.8649717**	2.51053909	0.85697323	1.65356586	14.3177548	**4.69943046**
3790	2.198576	**62.34324**	3.61984706	1.36311712	2.25672994	16.5744847	**5.44014335**
4140	2.49747	**57.2238447**	2.04346205	0.8741145	1.16934755	17.7438323	**5.82395125**
4830	2.654941	**54.5267136**	4.02853947	1.83190929	2.19663018	19.9404625	**6.54493795**

5150	2.903685	**50.2662773**	1.86830816	0.9291792	0.93912896	20.8795914	**6.8531826**
5740	2.966874	**49.183989**	3.44469317	1.75045566	1.69423751	22.5738289	**7.40927198**
6205	3.158447	**45.9027658**	2.7148853	1.46867786	1.24620744	23.8200364	**7.81830714**
6800	3.300873	**43.4633225**	3.47388549	1.96401944	1.50986605	25.3299024	**8.31388139**
7220	3.359047	**42.4669301**	2.45215446	1.41079974	1.04135472	26.3712571	**8.65567898**
7800	3.526548	**39.5980072**	3.38630854	2.04539784	1.3409107	27.7121678	**8.75991549**
8190	3.627851	**37.8629102**	2.27700057	1.41486189	0.86213868	28.5743065	**9.03244061**
8830	3.723136	**36.2308882**	3.73661632	2.38280704	1.35380928	29.9281158	**9.46038457**
9190	3.800367	**34.9080914**	2.10184668	1.36813212	0.73371456	30.6618304	**9.69231437**
9850	3.812403	**34.7019412**	3.85338558	2.51618598	1.3371996	31.99903	**10.115008**
10800	3.912703	**32.9840234**	5.54653985	3.71706785	1.829472	33.828502	**10.6933106**
11805	4.024036	**31.0771345**	5.86765532	4.04415618	1.82349914	35.6520011	**11.2697252**
12800	4.126342	**29.3248583**	5.80927069	4.10571029	1.7035604	37.3555615	**11.8082268**
13800	4.209591	**27.8989864**	5.838463	4.209591	1.628872	38.9844335	**12.323119**
14875	4.237675	**27.4179694**	6.27634773	4.55550063	1.7208471	40.7052806	**12.867085**
15810	4.388125	**24.8410926**	5.45896291	4.10289688	1.35606603	42.0613466	**13.2957423**
16790	4.438275	**23.9821337**	5.72169374	4.3495095	1.37218424	43.4335309	**13.7294946**
17780	4.540581	**22.2298574**	5.78007837	4.49517519	1.28490318	44.718434	**14.1356571**
18820	4.652917	**20.3057894**	6.07200152	4.83903368	1.23296784	45.9514019	**14.5254027**
19800	4.806376	**17.677375**	5.72169374	4.71024848	1.01144526	46.9628471	**14.8451241**
20800	4.893637	**16.1827865**	5.838463	4.893637	0.944826	47.9076731	**15.143787**
21760	4.930748	**15.5471568**	5.60492448	4.73351808	0.8714064	48.7790795	**15.4192417**
22800	4.987919	**14.5679437**	6.07200152	5.18743576	0.88456576	49.6636453	**15.6988561**
23800	5.059132	**13.348222**	5.838463	5.059132	0.779331	50.4429763	**15.9452054**
24800	5.114297	**12.4033671**	5.838463	5.114297	0.724166	51.1671423	**16.1741169**
25825	5.139372	**11.9738876**	5.98442458	5.2678563	0.71656828	51.8837106	**16.4006267**
26975	5.213594	**10.7026284**	6.71423245	5.9956331	0.71859935	52.6023099	**16.6277785**
27810	5.251708	**10.0498196**	4.87511661	4.38517618	0.48994042	53.0922504	**16.7826504**
28840	5.289822	**9.39701082**	6.01361689	5.44851666	0.56510023	53.6573506	**16.9612807**
29800	5.328939	**8.72702285**	5.60492448	5.11578144	0.48914304	54.1464936	**17.1159005**
30860	5.385107	**7.76498883**	6.18877078	5.70821342	0.48055736	54.627051	**17.2678064**
31900	5.578686	**4.44940732**	6.07200152	5.80183344	0.27016808	54.8972191	**17.3532075**
32810	5.615797	**3.8137777**	5.31300133	5.11037527	0.20262606	55.0998451	**17.4172583**
33740	5.625827	**3.64198591**	5.42977059	5.23201911	0.19775148	55.2975966	**17.4797683**
34800	5.643881	**3.33276069**	6.18877078	5.98251386	0.20625692	55.5038535	**17.5449668**
35800	5.692025	**2.50816011**	5.838463	5.692025	0.146438	55.6502915	**17.5912564**
36800	5.716097	**2.09585982**	5.838463	5.716097	0.122366	55.7726575	**17.6299368**
37880	5.719106	**2.04432228**	6.30554004	6.17663448	0.12890556	55.9015631	**17.6706843**
38870	5.775274	**1.08228827**	5.78007837	5.71752126	0.06255711	55.9641202	**17.6904588**
39800	5.805364	**0.5669129**	5.42977059	5.39898852	0.03078207	55.9949023	**17.7001891**
40800	5.816397	**0.37794193**	5.838463	5.816397	0.022066	56.0169683	**17.7071643**
41820	5.826427	**0.20615015**	5.95523226	5.94295554	0.01227672	56.029245	**17.711045**
42800	5.832445	**0.10307507**	5.72169374	5.7157961	0.00589764	56.0351426	**17.7129092**
43800	6.066144	**0**	5.838463	6.066144	0	56.0351426	**17.7129092**
44810	6.001952	**0**	5.89684763	6.06197152	0	56.0351426	**17.7129092**
45835	5.851502	**0**	5.98442458	5.99778955	0	56.0351426	**17.7129092**
46810	5.839466	**0**	5.69250143	5.69347935	0	56.0351426	**17.7129092**
47800	5.92773	**0**	5.78007837	5.8684527	0	56.0351426	**17.7129092**
48810	6.121309	**0**	5.89684763	6.18252209	0	56.0351426	**17.7129092**
49800	5.816397	**0**	5.78007837	5.75823303	0	56.0351426	**17.7129092**
50770	5.905664	**0**	5.66330911	5.72849408	0	56.0351426	**17.7129092**
51810	5.918703	**0**	6.07200152	6.15545112	0	56.0351426	**17.7129092**

52820	5.868553	0	5.89684763	5.92723853	0	56.0351426	**17.7129092**
53910	5.860529	0	6.36392467	6.38797661	0	56.0351426	**17.7129092**
54870	5.849496	0	5.60492448	5.61551616	0	56.0351426	**17.7129092**
55820	5.9177	0	5.54653985	5.621815	0	56.0351426	**17.7129092**

Table A87: pH changes during the adsorption process (7.04 l/hr)

Volume treated (ml)	pH	Volume treated (ml)	pH	Volume treated (ml)	pH
0	5.09	17190	4.27	37140	4.61
1160	4.11	21180	4.36	41150	4.67
5150	4.09	25140	4.43	45130	4.71
9190	4.09	29140	4.5	50160	4.77
13110	4.19	33130	4.56	55140	4.82

Table A88: Carbon measured in the effluent during the adsorption experiment

Volume (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)
0	0	0	0
100	60	0	6
220	15	0	1.8
440	8.2	0	1.804
650	3.1	0	0.651
890	0	0	0
1290	0	0	0
1800	0	0	0
Sum (mg)			**10.255**

3- Tables of the effect of biomass load on the adsorption process using columns of seaweed-Hypol foam

3.1 Biomass load = 11%

Table A89: Carbon measured in the effluent during the column conditioning process before the adsorption experiment

Volume of D.W (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)	Amount of IC (mg)
0	0	0	0	0
50	1355.1	45.15	67.755	2.2575
100	1200.15	25.15	60.0075	1.2575
200	975.14	15.5	97.514	1.55
400	495.12	10.45	99.024	2.09
600	254.15	5.55	50.83	1.11
800	145.65	2.64	29.13	0.528
1000	100.05	0	20.01	0
1215	80.25	0	17.25375	0
1560	60.14	0	20.7483	0
1840	42.89	0	12.0092	0
2230	31.45	0	12.2655	0
2560	25.15	0	8.2995	0
2880	14.32	0	4.5824	0
3200	11	0	3.52	0
3540	9.5	0	3.23	0
3850	5	0	1.55	0
4160	3	0	0.93	0
4535	3	0	1.125	0
4870	2	0	0.67	0
5180	1	0	0.31	0
5580	0	0	0	0
5860	0	0	0	0
6450	0	0	0	0
6860	0	0	0	0
Sum (mg)			**510.76415**	**8.793**

Table A90: Copper adsorption using column of cast in seaweed-Hypol foam at Cu initial concentration of 6 mgl^{-1}, T 20° C, pH 5.39, 4.7 l/hr flow rate and biomass ratio of 11 % (net dry wt. of biomass = 4.83 g)

Volume treated (ml)	**Copper conc. (mg/l)**	**Removal ratio (%)**	Amount of copper in the influent (mg)	approx. amount of copper in the effluent (mg)	approx. copper uptaken at each stage (mg)	approx. amount of adsorbed copper (mg)	**approx. copper uptake by the biomass (mg/g)**
0	6.785295	**100**	0	0	0	0	**0**
100	0.021063	**99.6895787**	0.6785295	0.0021063	0.6764232	0.6764232	**0.13982605**
250	0.031093	**99.5417591**	1.01779425	0.00466395	1.0131303	1.6895535	**0.34925412**
450	0.035105	**99.4826312**	1.357059	0.007021	1.350038	3.0395915	**0.62832569**
650	0.049147	**99.2756837**	1.357059	0.0098294	1.3472296	4.3868211	**0.90681672**

850	0.07021	**98.9652624**	1.357059	0.014042	1.343017	5.7298381	**1.18443695**
1160	0.115345	**98.3000739**	2.10344145	0.03575695	2.0676845	7.7975226	**1.61185599**
1800	0.2006	**97.0436068**	4.3425888	0.128384	4.2142048	12.0117274	**2.48299053**
2180	0.258774	**96.1862528**	2.5784121	0.09833412	2.48007798	14.4918054	**2.99565702**
2800	0.386155	**94.3089431**	4.2068829	0.2394161	3.9674668	18.4592722	**3.81578739**
3200	0.460377	**93.2150776**	2.714118	0.1841508	2.5299672	20.9892394	**4.33876668**
3800	0.6018	**91.1308204**	4.071177	0.36108	3.710097	24.6993364	**5.10569515**
4240	0.7021	**89.6526238**	2.9855298	0.308924	2.6766058	27.3759422	**5.65898666**
4810	0.79237	**88.3222469**	3.86761815	0.4516509	3.41596725	30.7919094	**6.36511444**
5190	0.921757	**86.4153732**	2.5784121	0.35026766	2.22814444	33.0200539	**6.82570277**
5800	1.030081	**84.8189209**	4.13902995	0.62834941	3.51068054	36.5307344	**7.5514091**
6210	1.115336	**83.5624538**	2.78197095	0.45728776	2.32468319	38.8554176	**8.03195333**
6800	1.256759	**81.4781966**	4.00332405	0.74148781	3.26183624	42.1172538	**8.70622009**
7200	1.340008	**80.2512934**	2.714118	0.5360032	2.1781148	44.2953686	**9.15646661**
7800	1.479425	**78.1966001**	4.071177	0.887655	3.183522	47.4788906	**9.81454473**
8200	1.546626	**77.2062084**	2.714118	0.6186504	2.0954676	49.5743582	**10.2477069**
8800	1.682031	**75.210643**	4.071177	1.0092186	3.0619584	52.6363166	**10.8806562**
9360	1.787346	**73.6585366**	3.7997652	1.00091376	2.79885144	55.4351681	**11.4592175**
9800	1.864577	**72.5203252**	2.9855298	0.82041388	2.16511592	57.600284	**11.906777**
10800	2.059159	**69.6526238**	6.785295	2.059159	4.726136	62.32642	**12.8837348**
11835	2.259759	**66.6962306**	7.02278033	2.33885057	4.68392976	67.0103498	**13.851968**
12100	2.371092	**65.0554324**	1.79810318	0.62833938	1.1697638	68.1801136	**14.0937744**
13810	2.61783	**61.4190687**	11.6028545	4.4764893	7.12636515	75.3064787	**15.5668929**
14860	2.776304	**59.0835181**	7.12455975	2.9151192	4.20944055	79.5159193	**16.4370426**
15880	2.950826	**56.511456**	6.9210009	3.00984252	3.91115838	83.4270776	**17.2455332**
16730	3.087234	**54.5011086**	5.76750075	2.6241489	3.14335185	86.5704295	**17.8953076**
17800	3.210603	**52.6829268**	7.26026565	3.43534521	3.82492044	90.3953499	**18.6859717**
18810	3.345005	**50.7021434**	6.85314795	3.37845505	3.4746929	93.8700428	**19.4042388**
19940	3.513509	**48.2187731**	7.66738335	3.97026517	3.69711818	97.567161	**20.1684844**
20810	3.581713	**47.2135994**	5.90320665	3.11609031	2.78711634	100.354277	**20.74462**
21940	3.683016	**45.7206208**	7.66738335	4.16180808	3.50557527	103.859853	**21.469271**
22955	3.816415	**43.7546194**	6.88707443	3.87366123	3.0134132	106.873266	**22.0921852**
23800	3.898661	**42.5424982**	5.73357428	3.29436855	2.43920573	109.312472	**22.5964029**
24970	3.989934	**41.1973392**	7.93879515	4.66822278	3.27057237	112.583044	**23.2724755**
25830	4.094246	**39.6600148**	5.8353537	3.52105156	2.31430214	114.897346	**23.7508738**
26955	4.124336	**39.2165558**	7.63345688	4.639878	2.99357888	117.890925	**24.3696881**
27880	4.244696	**37.4427199**	6.27639788	3.9263438	2.35005408	120.240979	**24.8554768**
28785	4.352017	**35.8610495**	6.14069198	3.93857539	2.20211659	122.443096	**25.3106849**
29750	4.402167	**35.1219512**	6.54780968	4.24809116	2.29971852	124.742814	**25.7860685**
30940	4.540581	**33.0820399**	8.07450105	5.40329139	2.67120966	127.414024	**26.3382446**
31760	4.612797	**32.0177384**	5.5639419	3.78249354	1.78144836	129.195472	**26.7064947**
32840	4.625836	**31.8255728**	7.3281186	4.99590288	2.33221572	131.527688	**27.188596**
33800	4.703067	**30.6873614**	6.5138832	4.51494432	1.99893888	133.526627	**27.6018044**
34110	4.728142	**30.3178123**	2.10344145	1.46572402	0.63771743	134.164344	**27.7336294**
35690	4.808382	**29.135255**	10.7207661	7.59724356	3.12352254	137.287867	**28.3793048**
36800	4.835463	**28.7361419**	7.53167745	5.36736393	2.16431352	139.45218	**28.8266984**
37130	4.905673	**27.7014043**	2.23914735	1.61887209	0.62027526	140.072455	**28.9549179**
38730	5.054117	**25.5136733**	10.856472	8.0865872	2.7698848	142.84234	**29.5274915**
39900	5.114297	**24.6267554**	7.93879515	5.98372749	1.95506766	144.797408	**29.931631**
40755	5.138369	**24.2719882**	5.80142723	4.3933055	1.40812173	146.20553	**30.2227093**
41880	5.213594	**23.1633407**	7.63345688	5.86529325	1.76816363	147.973693	**30.5882132**
42850	5.218609	**23.0894309**	6.58173615	5.06205073	1.51968542	149.493379	**30.9023533**

43860	5.290825	**22.0251293**	6.85314795	5.34373325	1.5094147	151.002793	**31.2143702**
44800	5.314897	**21.6703622**	6.3781773	4.99600318	1.38217412	152.384968	**31.5000848**
45675	5.340975	**21.286031**	5.93713313	4.67335313	1.26378	153.648748	**31.7613256**
46755	5.415197	**20.1921656**	7.3281186	5.84841276	1.47970584	155.128453	**32.0672013**
47760	5.450302	**19.6747967**	6.81922148	5.47755351	1.34166797	156.470121	**32.3445427**
48800	5.515497	**18.713969**	7.0567068	5.73611688	1.32058992	157.790711	**32.6175269**
49760	5.548596	**18.2261641**	6.5138832	5.32665216	1.18723104	158.977942	**32.862944**
50800	5.613791	**17.2653363**	7.0567068	5.83834264	1.21836416	160.196306	**33.1147968**
51930	5.648896	**16.7479675**	7.66738335	6.38325248	1.28413087	161.480437	**33.3802444**
52920	5.706067	**15.9053954**	6.71744205	5.64900633	1.06843572	162.548873	**33.6011049**
53995	5.730139	**15.5506282**	7.29419213	6.15989943	1.1342927	163.683166	**33.8355789**
54715	5.808373	**14.3976349**	4.8854124	4.18202856	0.70338384	164.38655	**33.9809781**
55850	5.832445	**14.0428677**	7.70130983	6.61982508	1.08148475	165.468034	**34.204536**
56790	5.913688	**12.8455285**	6.3781773	5.55886672	0.81931058	166.287345	**34.3738988**
57820	5.971862	**11.9881744**	6.98885385	6.15101786	0.83783599	167.125181	**34.5470912**
58840	6.016997	**11.322986**	6.9210009	6.13733694	0.78366396	167.908845	**34.7090854**
59835	6.173465	**9.01699926**	6.75136853	6.14259768	0.60877085	168.517616	**34.8349267**
60910	6.219603	**8.33702882**	7.29419213	6.68607323	0.6081189	169.125735	**34.9606333**
61850	6.307867	**7.03621582**	6.3781773	5.92939498	0.44878232	169.574517	**35.0534029**
62820	6.342972	**6.51884701**	6.58173615	6.15268284	0.42905331	170.00357	**35.1420941**
63840	6.408167	**5.55801922**	6.9210009	6.53633034	0.38467056	170.388241	**35.2216109**
64830	6.444275	**5.02586844**	6.71744205	6.37983225	0.3376098	170.725851	**35.2913995**
65800	6.533542	**3.71027347**	6.58173615	6.33753574	0.24420041	170.970051	**35.3418791**
66800	6.617794	**2.46858832**	6.785295	6.617794	0.167501	171.137552	**35.3765039**
67800	6.676971	**1.59645233**	6.785295	6.676971	0.108324	171.245876	**35.3988959**
68800	6.735145	**0.7390983**	6.785295	6.735145	0.05015	171.296026	**35.4092626**
69800	6.789307	**0**	6.785295	6.789307	0	171.296026	**35.4092626**
70800	6.792316	**0**	6.785295	6.792316	0	171.296026	**35.4092626**
71800	6.786298	**0**	6.785295	6.786298	0	171.296026	**35.4092626**
72800	6.801343	**0**	6.785295	6.801343	0	171.296026	**35.4092626**
73800	6.812376	**0**	6.785295	6.812376	0	171.296026	**35.4092626**
74800	6.808364	**0**	6.785295	6.808364	0	171.296026	**35.4092626**
75850	6.79031	**0**	7.12455975	7.1298255	0	171.296026	**35.4092626**

Table A91: pH changes during the adsorption process (11% biomass load)

Volume treated (ml)	pH	Volume treated (ml)	pH	Volume treated (ml)	pH
0	5.46	17170	4.07	39140	4.3
1150	3.98	22150	4.15	45120	4.37
5200	3.91	25350	4.19	49130	4.45
9200	3.94	29140	4.22	53250	4.55
13600	4.01	33170	4.27	55140	4.6

3.2 Biomass load = 14.2%

Table A92: Carbon measured in the effluent during the column conditioning process before the adsorption experiment

Volume of D.W (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)	Amount of IC (mg)
0	0	0	0	0
50	2150.25	35.5	107.5125	1.775
100	1805.25	25.75	90.2625	1.2875
200	1545.1	19.58	154.51	1.958
400	1202.15	15.25	240.43	3.05
600	1000.35	8.5	200.07	1.7
800	833.2	0	166.64	0
1000	610.05	0	122.01	0
1110	400	0	44	0
1530	301.9	0	126.798	0
1880	215.1	0	75.285	0
2200	175.05	0	56.016	0
2580	135.35	0	51.433	0
2850	100.1	0	27.027	0
3150	85.5	0	25.65	0
3550	70.15	0	28.06	0
3865	51	0	16.065	0
4130	30.25	0	8.01625	0
4630	20.1	0	10.05	0
4860	10	0	2.3	0
5230	5.11	0	1.8907	0
5840	0	0	0	0
6230	0	0	0	0
6830	0	0	0	0
7230	0	0	0	0
7630	0	0	0	0
Sum (mg)			**1554.026**	**9.7705**

Table A93: Copper adsorption using column of cast in seaweed-Hypol foam at Cu initial concentration of 6 mgl^{-1}, T 20° C, pH 5.45, 4.7 l/hr flow rate and biomass ratio of 14.2 % (net dry wt. of biomass = 6.13 g)

Volume treated (ml)	**Copper conc. (mg/l)**	**Removal ratio (%)**	Amount of copper in the influent (mg)	approx. amount of copper in the effluent (mg)	approx. copper uptaken at each stage (mg)	approx. amount of adsorbed copper (mg)	**approx. copper uptake by the biomass (mg/g)**
0	**6.272762**	**100**	0	0	0	0	**0**
130	**0.001003**	**99.985218**	0.88208835	0.00013039	0.88195796	0.88195796	**0.14381133**
280	**0.002006**	**99.9704361**	1.01779425	0.0003009	1.01749335	1.89945131	**0.30972295**
475	**0.009027**	**99.8669623**	1.32313253	0.00176027	1.32137226	3.22082357	**0.52518481**
670	**0.012036**	**99.8226164**	1.32313253	0.00234702	1.32078551	4.54160908	**0.74055099**
870	**0.013039**	**99.8078344**	1.357059	0.0026078	1.3544512	5.89606028	**0.96140668**
1200	**0.02006**	**99.7043607**	2.23914735	0.0066198	2.23252755	8.12858783	**1.32544076**
1800	**0.035105**	**99.4826312**	4.071177	0.021063	4.050114	12.1787018	**1.98584898**
2200	**0.052156**	**99.2313378**	2.714118	0.0208624	2.6932556	14.8719574	**2.425009**

2810	**0.087261**	**98.713969**	4.13902995	0.05322921	4.08580074	18.9577582	**3.09123626**
3240	**0.103309**	**98.4774575**	2.91767685	0.04442287	2.87325398	21.8310121	**3.55974666**
3800	**0.131393**	**98.0635625**	3.7997652	0.07358008	3.72618512	25.5571973	**4.16733531**
4260	**0.177531**	**97.383592**	3.1212357	0.08166426	3.03957144	28.5967687	**4.6629653**
4800	**0.207621**	**96.940133**	3.6640593	0.11211534	3.55194396	32.1487127	**5.24214232**
5100	**0.236708**	**96.511456**	2.0355885	0.0710124	1.9645761	34.1132888	**5.56248446**
5810	**0.294882**	**95.654102**	4.81755945	0.20936622	4.60819323	38.721482	**6.31389261**
6170	**0.333999**	**95.0776053**	2.4427062	0.12023964	2.32246656	41.0439486	**6.69259208**
6810	**0.390167**	**94.2498152**	4.3425888	0.24970688	4.09288192	45.1368305	**7.359974**
7110	**0.422263**	**93.7767923**	2.0355885	0.1266789	1.9089096	47.0457401	**7.67123921**
7840	**0.493476**	**92.7272727**	4.95326535	0.36023748	4.59302787	51.6387679	**8.42017451**
8115	**0.503506**	**92.5794531**	1.86595613	0.13846415	1.72749198	53.3662599	**8.70185791**
8900	**0.627878**	**90.7464893**	5.32645658	0.49288423	4.83357235	58.1998323	**9.49001619**
9150	**0.669001**	**90.1404287**	1.69632375	0.16725025	1.5290735	59.7289058	**9.73934564**
9815	**0.754256**	**88.8839616**	4.51222118	0.50158024	4.01064094	63.7395467	**10.3933174**
10800	**0.855559**	**87.390983**	6.68351558	0.84272562	5.84078996	69.5803367	**11.3457118**
11950	**1.001997**	**85.232816**	7.80308925	1.15229655	6.6507927	76.2311294	**12.4301845**
12810	**1.080231**	**84.0798226**	5.8353537	0.92899866	4.90635504	81.1374844	**13.2302107**
13810	**1.225666**	**81.9364375**	6.785295	1.225666	5.559629	86.6971134	**14.1367591**
14800	**1.361071**	**79.9408721**	6.71744205	1.34746029	5.36998176	92.0670952	**15.0123839**
15950	**1.493467**	**77.9896526**	7.80308925	1.71748705	6.0856022	98.1526974	**16.0046971**
16850	**1.579725**	**76.7184035**	6.1067655	1.4217525	4.685013	102.83771	**16.7686314**
17290	**1.627869**	**76.0088692**	2.9855298	0.71626236	2.26926744	105.106978	**17.1386563**
18540	**1.78534**	**73.6881005**	8.48161875	2.231675	6.24994375	111.356922	**18.1577669**
19480	**1.863574**	**72.5351072**	6.3781773	1.75175956	4.62641774	115.983339	**18.9121467**
20850	**1.946823**	**71.308204**	9.29585415	2.66714751	6.62870664	122.612046	**19.9930181**
21635	**2.158456**	**68.1892092**	5.32645658	1.69438796	3.63206862	126.244115	**20.5852602**
22990	**2.29687**	**66.1492979**	9.19407473	3.11225885	6.08181588	132.32593	**21.576956**
23700	**2.335987**	**65.5728012**	4.81755945	1.65855077	3.15900868	135.484939	**22.0920614**
24755	**2.438293**	**64.0650407**	7.15848623	2.57239912	4.58608711	140.071026	**22.8398649**
25740	**2.572695**	**62.0842572**	6.68351558	2.53410458	4.149411	144.220437	**23.5164644**
26760	**2.620839**	**61.3747228**	6.9210009	2.67325578	4.24774512	148.468182	**24.2090982**
27840	**2.710106**	**60.0591279**	7.3281186	2.92691448	4.40120412	152.869386	**24.9267549**
28900	**2.792352**	**58.8470067**	7.1924127	2.95989312	4.23251958	157.101906	**25.616906**
29735	**2.887637**	**57.4427199**	5.66572133	2.4111769	3.25454443	160.35645	**26.1475893**
30415	**2.963865**	**56.3192905**	4.6140006	2.0154282	2.5985724	162.955023	**26.5713103**
31870	**3.093252**	**54.4124169**	9.87260423	4.50068166	5.37192257	168.326945	**27.4472516**
32790	**3.182519**	**53.0968219**	6.2424714	2.92791748	3.31455392	171.641499	**27.98772**
33850	**3.254735**	**52.0325203**	7.1924127	3.4500191	3.7423936	175.383893	**28.5979516**
34220	**3.3099**	**51.2195122**	2.51055915	1.224663	1.28589615	176.669789	**28.8076287**
35655	**3.475395**	**48.7804878**	9.73689833	4.98719183	4.7497065	181.419496	**29.5821119**
36790	**3.537581**	**47.8640059**	7.70130983	4.01515444	3.68615539	185.105651	**30.1831733**
37220	**3.594752**	**47.0214339**	2.91767685	1.54574336	1.37193349	186.477584	**30.4068797**
38800	**3.6108**	**46.7849224**	10.7207661	5.705064	5.0157021	191.493287	**31.2247359**
39735	**3.682013**	**45.7354028**	6.34425083	3.44268216	2.90156867	194.394855	**31.6978632**
40220	**3.713106**	**45.2771619**	3.29086808	1.80085641	1.49001167	195.884867	**31.9408233**
41760	**3.786325**	**44.1980783**	10.4493543	5.8309405	4.6184138	200.503281	**32.693898**
42200	**3.812403**	**43.8137472**	2.9855298	1.67745732	1.30807248	201.811353	**32.9071912**
43760	**3.878601**	**42.8381375**	10.5850602	6.05061756	4.53444264	206.345796	**33.6465737**
44810	**4.008991**	**40.9164819**	7.12455975	4.20944055	2.9151192	209.260915	**34.1219106**
45770	**4.080204**	**39.8669623**	6.5138832	3.91699584	2.59688736	211.857802	**34.5453569**
46730	**4.120324**	**39.2756837**	6.5138832	3.95551104	2.55837216	214.416175	**34.9625229**

47200	**4.181507**	**38.3739837**	3.18908865	1.96530829	1.22378036	215.639955	**35.1620715**
48700	**4.211597**	**37.9305248**	10.1779425	6.3173955	3.860547	219.500502	**35.7915691**
49785	**4.257735**	**37.2505543**	7.36204508	4.61964248	2.7424026	222.242905	**36.238743**
50165	**4.301867**	**36.6001478**	2.5784121	1.63470946	0.94370264	223.186607	**36.3926223**
51810	**4.314906**	**36.4079823**	11.1618103	7.09802037	4.06378991	227.250397	**37.0552605**
52200	**4.380101**	**35.4471545**	2.64626505	1.70823939	0.93802566	228.188423	**37.2082142**
53720	**4.411194**	**34.9889135**	10.3136484	6.70501488	3.60863352	231.797056	**37.796635**
54270	**4.418215**	**34.8854398**	3.73191225	2.43001825	1.301894	233.09895	**38.0089207**
55470	**4.500461**	**33.6733186**	8.142354	5.4005532	2.7418008	235.840751	**38.4559965**
56830	**4.518515**	**33.4072432**	9.2280012	6.1451804	3.0828208	238.923572	**38.9586787**
57200	**4.568665**	**32.6681449**	2.51055915	1.69040605	0.8201531	239.743725	**39.0924122**
58765	**4.624833**	**31.8403548**	10.6189867	7.23786365	3.38112303	243.124848	**39.6437353**
59215	**4.670971**	**31.1603843**	3.05338275	2.10193695	0.9514458	244.076294	**39.7988772**
60720	**4.775283**	**29.6230599**	10.211869	7.18680092	3.02506806	247.101362	**40.2921423**
61885	**4.902664**	**27.7457502**	7.90486868	5.71160356	2.19326512	249.294627	**40.6497743**
62620	**4.915703**	**27.5535846**	4.98719183	3.61304171	1.37415012	250.668777	**40.8738421**
63740	**4.968862**	**26.7701404**	7.5995304	5.56512544	2.03440496	252.703182	**41.2055705**
64690	**5.011991**	**26.1345159**	6.44603025	4.76139145	1.6846388	254.387821	**41.4802663**
65700	**5.094237**	**24.9223947**	6.85314795	5.14517937	1.70796858	256.095789	**41.7587662**
66930	**5.146393**	**24.1537324**	8.34591285	6.33006339	2.01584946	258.111639	**42.0874689**
67840	**5.199552**	**23.3702882**	6.17461845	4.73159232	1.44302613	259.554665	**42.3227676**
68850	**5.231648**	**22.8972653**	6.85314795	5.28396448	1.56918347	261.123848	**42.5786373**
69800	**5.274777**	**22.2616408**	6.44603025	5.01103815	1.4349921	262.558841	**42.8126259**
70750	**5.313894**	**21.6851441**	6.44603025	5.0481993	1.39783095	263.956672	**43.0405551**
71800	**5.332951**	**21.4042868**	7.12455975	5.59959855	1.5249612	265.481633	**43.289214**
72850	**5.375077**	**20.7834442**	7.12455975	5.64383085	1.4807289	266.962362	**43.5306604**
73800	**5.404164**	**20.3547672**	6.44603025	5.1339558	1.31207445	268.274436	**43.7446062**
74850	**5.418206**	**20.1478197**	7.12455975	5.6891163	1.43544345	269.70988	**43.9786684**
75850	**5.488416**	**19.113082**	6.785295	5.488416	1.296879	271.006759	**44.1901364**

Table A94: pH changes during the adsorption experiment (14.2%)

Volume treated (ml)	pH	Volume treated (ml)	pH	Volume treated (ml)	pH
0	5.45	21130	4.10	46150	4.29
1150	3.9	26160	4.16	51580	4.32
6170	3.80	32150	4.21	56140	4.38
11150	3.95	36150	4.23	61150	4.45
16120	4.00	41760	4.25	66160	4.49

4- Tables of the effect of copper initial concentration on the adsorption process using columns of seaweed-Hypol foam

4.1 Initial Cu concentration = 10 mgl^{-1}

Table A95: Carbon measured in the effluent during the column conditioning process before the adsorption experiment

Volume of D.W (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)	Amount of IC (mg)
0	0	0	0	0
50	850.15	60.36	42.5075	3.018
100	721	38.72	36.05	1.936
200	595	18.33	59.5	1.833
400	425.2	8.764	85.04	1.7528
600	299.45	0	59.89	0
800	155.3	0	31.06	0
1000	95.1	0	19.02	0
1165	70.4	0	11.616	0
1520	46.6	0	16.543	0
1850	23.1	0	7.623	0
2215	15.5	0	5.6575	0
2550	9.301	0	3.115835	0
2840	7.524	0	2.18196	0
3140	6.98	0	2.094	0
3540	5.78	0	2.312	0
3850	4.95	0	1.5345	0
4240	3.85	0	1.5015	0
4560	2.59	0	0.8288	0
4850	2	0	0.58	0
5180	0	0	0	0
5800	0	0	0	0
6280	0	0	0	0
6800	0	0	0	0
7300	0	0	0	0
Sum (mg)			**388.6556**	**8.5398**

Table A96: Copper adsorption using column of cast in seaweed-Hypol foam at Cu initial concentration of 10 mgl^{-1}, T 20° C, solution pH 5.28, 4.7 l/hr flow rate and biomass ratio of 7 % (net dry wt. of biomass = 3 g)

Volume treated (ml)	**Copper conc. (mg/l)**	**Removal ratio (%)**	Amount of copper in the influent (mg)	approx. amount of copper in the effluent (mg)	approx. copper uptaken at each stage (mg)	approx. amount of adsorbed copper (mg)	**approx. copper uptake by the biomass (mg/g)**
0	**10.707025**	**100**	0	0	0	0	**0**
100	**0.081243**	**99.2412178**	1.0707025	0.0081243	1.0625782	1.0625782	**0.35419273**
270	**0.262786**	**97.5456674**	1.82019425	0.04467362	1.77552063	2.83809883	**0.94603294**
500	**0.606815**	**94.3325527**	2.46261575	0.13956745	2.3230483	5.16114713	**1.72038238**

840	**1.204603**	**88.7494145**	3.6403885	0.40956502	3.23082348	8.39197061	**2.79732354**
1380	**2.044114**	**80.9086651**	5.7817935	1.10382156	4.67797194	13.0699426	**4.35664752**
1820	**2.760256**	**74.2201405**	4.711091	1.21451264	3.49657836	16.5665209	**5.52217364**
2105	**3.162459**	**70.4637002**	3.05150213	0.90130082	2.15020131	18.7167222	**6.23890741**
2815	**3.910697**	**63.4754098**	7.60198775	2.77659487	4.82539288	23.5421151	**7.8473717**
3115	**4.179501**	**60.9648712**	3.2121075	1.2538503	1.9582572	25.5003723	**8.5001241**
3810	**4.721121**	**55.9063232**	7.44138238	3.2811791	4.16020328	29.6605756	**9.88685853**
4120	**4.99494**	**53.3489461**	3.31917775	1.5484314	1.77074635	31.4313219	**10.4771073**
4810	**5.545587**	**48.206089**	7.38784725	3.82645503	3.56139222	34.9927142	**11.6642381**
5115	**5.723118**	**46.5480094**	3.26564263	1.74555099	1.52009164	36.5128058	**12.1709353**
5800	**6.141369**	**42.6416862**	7.33431213	4.20683777	3.12747436	39.6402801	**13.2134267**
6190	**6.362029**	**40.5807963**	4.17573975	2.48119131	1.69454844	41.3348286	**13.7782762**
6820	**6.638857**	**37.9953162**	6.74542575	4.18247991	2.56294584	43.8977744	**14.6325915**
7130	**6.765235**	**36.8149883**	3.31917775	2.09722285	1.2219549	45.1197293	**15.0399098**
7820	**7.009967**	**34.529274**	7.38784725	4.83687723	2.55097002	47.6706993	**15.8902331**
8170	**7.194519**	**32.8056206**	3.74745875	2.51808165	1.2293771	48.9000764	**16.3000255**
8830	**7.471347**	**30.2201405**	7.0666365	4.93108902	2.13554748	51.0356239	**17.0118746**
9140	**7.555599**	**29.4332553**	3.31917775	2.34223569	0.97694206	52.012566	**17.337522**
9810	**7.606752**	**28.9555035**	7.17370675	5.09652384	2.07718291	54.0897489	**18.0299163**
10750	**7.804343**	**27.1100703**	10.0646035	7.33608242	2.72852108	56.81827	**18.9394233**
11810	**8.000931**	**25.2740047**	11.3494465	8.48098686	2.86845964	59.6867296	**19.8955765**
12810	**8.488389**	**20.7213115**	10.707025	8.488389	2.218636	61.9053656	**20.6351219**
13800	**8.56562**	**20**	10.5999548	8.4799638	2.11999095	64.0253566	**21.3417855**
14800	**8.733121**	**18.4355972**	10.707025	8.733121	1.973904	65.9992606	**21.9997535**
15750	**8.851475**	**17.3302108**	10.1716738	8.40890125	1.7627725	67.7620331	**22.5873444**
16850	**8.909649**	**16.7868852**	11.7777275	9.8006139	1.9771136	69.7391467	**23.2463822**
17810	**9.136327**	**14.6697892**	10.278744	8.77087392	1.50787008	71.2470167	**23.7490056**
18820	**9.303828**	**13.1053864**	10.8140953	9.39686628	1.41722897	72.6642457	**24.2214152**
19810	**9.33793**	**12.7868852**	10.5999548	9.2445507	1.35540405	74.0196498	**24.6732166**
20755	**9.553575**	**10.7728337**	10.1181386	9.02812838	1.09001025	75.10966	**25.0365533**
21830	**9.962799**	**6.95081967**	11.5100519	10.7100089	0.80004295	75.909703	**25.3032343**
22810	**10.132306**	**5.3676815**	10.4928845	9.92965988	0.56322462	76.4729276	**25.4909759**
23820	**10.228594**	**4.46838407**	10.8140953	10.3308799	0.48321531	76.9561429	**25.6520476**
24840	**10.242636**	**4.33723653**	10.9211655	10.4474887	0.47367678	77.4298197	**25.8099399**
25910	**10.317861**	**3.63466042**	11.4565168	11.0401113	0.41640548	77.8462252	**25.9487417**
26820	**10.345945**	**3.37236534**	9.74339275	9.41480995	0.3285828	78.174808	**26.0582693**
27840	**10.419164**	**2.68852459**	10.9211655	10.6275473	0.29361822	78.4684262	**26.1561421**
28870	**10.436215**	**2.529274**	11.0282358	10.7493015	0.2789343	78.7473605	**26.2491202**
29925	**10.520467**	**1.74238876**	11.2959114	11.0990927	0.19681869	78.9441792	**26.3147264**
30730	**10.535512**	**1.60187354**	8.61915513	8.48108716	0.13806797	79.0822471	**26.360749**
31810	**10.629794**	**0.72131148**	11.563587	11.4801775	0.08340948	79.1656566	**26.3885522**
32800	**10.656875**	**0.46838407**	10.5999548	10.5503063	0.0496485	79.2153051	**26.4051017**
33850	**10.721067**	**0**	11.2423763	11.2571204	0	79.2153051	**26.4051017**
34355	**10.707025**	**0**	5.40704763	5.40704763	0	79.2153051	**26.4051017**
35800	**10.713043**	**0**	15.4716511	15.4803471	0	79.2153051	**26.4051017**
36780	**10.674929**	**0**	10.4928845	10.4614304	0	79.2153051	**26.4051017**
37410	**10.690977**	**0**	6.74542575	6.73531551	0	79.2153051	**26.4051017**
38900	**10.74213**	**0**	15.9534673	16.0057737	0	79.2153051	**26.4051017**
39730	**10.753163**	**0**	8.88683075	8.92512529	0	79.2153051	**26.4051017**
40800	**10.724076**	**0**	11.4565168	11.4747613	0	79.2153051	**26.4051017**
41710	**10.808328**	**0**	9.74339275	9.83557848	0	79.2153051	**26.4051017**
42330	**10.711037**	**0**	6.6383555	6.64084294	0	79.2153051	**26.4051017**

43970	**10.734106**	**0**	17.559521	17.6039338	0	79.2153051	**26.4051017**
44810	**10.701007**	**0**	8.993901	8.98884588	0	79.2153051	**26.4051017**
45750	**10.819361**	**0**	10.0646035	10.1701993	0	79.2153051	**26.4051017**
46750	**10.8324**	**0**	10.707025	10.8324	0	79.2153051	**26.4051017**
47750	**10.713043**	**0**	10.707025	10.713043	0	79.2153051	**26.4051017**
48370	**10.714046**	**0**	6.6383555	6.64270852	0	79.2153051	**26.4051017**
49550	**10.706022**	**0**	12.6342895	12.633106	0	79.2153051	**26.4051017**
50650	**10.707025**	**0**	11.7777275	11.7777275	0	79.2153051	**26.4051017**
51630	**10.711037**	**0**	10.4928845	10.4968163	0	79.2153051	**26.4051017**
52710	**10.733103**	**0**	11.563587	11.5917512	0	79.2153051	**26.4051017**
53710	**10.734106**	**0**	10.707025	10.734106	0	79.2153051	**26.4051017**
54385	**10.731097**	**0**	7.22724188	7.24349048	0	79.2153051	**26.4051017**

Table A97: pH Changes during the adsorption experiment (10 mgl^{-1})

Volume treated (ml)	pH	Volume treated (ml)	pH	Volume treated (ml)	pH
0	5.28	21120	4.42	46150	4.87
1150	3.78	26150	4.55	52150	4.89
6180	3.96	31150	4.65	54170	4.92
11150	4.14	36120	4.7		
16140	4.32	41155	4.79		

4.2 Initial Cu concentration = 20 mgl^{-1}

Table A98: Carbon measured in the effluent during the conditioning process before the adsorption experiment

Volume of D.W (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)	Amount of IC (mg)
0	0	0	0	0
50	832.4	37.9	41.62	1.895
100	697.3	25.14	69.73	1.257
200	627.8	19.55	125.56	1.955
400	455.25	10.12	182.1	2.024
600	200	5.3	120	1.06
800	101.1	0	80.88	0
1000	63.5	0	63.5	0
1130	38.5	0	43.505	0
1500	21.3	0	31.95	0
1880	18.5	0	34.78	0
2130	16.58	0	35.3154	0
2500	14.11	0	35.275	0
2820	12.5	0	35.25	0
3180	10.1	0	32.118	0
3570	9.79	0	34.9503	0
3830	7.55	0	28.9165	0
4200	6.55	0	27.51	0
4580	5	0	22.9	0

4820	4.25	0	20.485	0
5340	4	0	21.36	0
5800	3.52	0	20.416	0
6180	0	0	0	0
6840	0	0	0	0
7230	0	0	0	0
7630	0	0	0	0
Sum (mg)			**1108.1212**	**8.191**

Table A99: Copper adsorption using column of cast in seaweed-Hypol foam at Cu initial concentration of 20 mgl^{-1}, T 20° C, solution pH 5.30, 4.7 l/hr flow rate and biomass ratio of 7 % (net dry wt. of biomass = 2.28 g)

Volume treated (ml)	**Copper conc. (mg/l)**	**Removal ratio (%)**	Amount of copper in the influent (mg)	approx. amount of copper in the effluent (mg)	approx. copper uptaken at each stage (mg)	approx. amount of adsorbed copper (mg)	**approx. copper uptake by the biomass (mg/g)**
0	**20.075045**	**100**	0	0	0	0	**0**
130	**0.398191**	**98.0164876**	2.60975585	0.05176483	2.55799102	2.55799102	**1.12015722**
260	**1.841508**	**90.8268798**	2.60975585	0.23939604	2.37035981	4.92835083	**2.15814978**
500	**3.838481**	**80.8793405**	4.8180108	0.92123544	3.89677536	8.82512619	**3.86456743**
780	**5.946787**	**70.3772171**	5.6210126	1.66510036	3.95591224	12.7810384	**5.59688143**
1115	**7.516482**	**62.5580814**	6.72514008	2.51802147	4.20711861	16.988157	**7.43919996**
1830	**10.243639**	**48.97327**	14.3536572	7.32420189	7.02945529	24.0176123	**10.517434**
2170	**10.89258**	**45.7406945**	6.8255153	3.7034772	3.1220381	27.1396504	**11.8845903**
2845	**12.341915**	**38.5211092**	13.5506554	8.33079263	5.21986275	32.3595132	**14.1703946**
3320	**12.951739**	**35.4833875**	9.53564638	6.15207603	3.38357035	35.7430835	**15.6520772**
3835	**13.128267**	**34.604047**	10.3386482	6.76105751	3.57759067	39.3206742	**17.2187223**
4120	**13.346921**	**33.5148639**	5.72138783	3.80387249	1.91751534	41.2381895	**18.058412**
4800	**14.244606**	**29.0432176**	13.6510306	9.68633208	3.96469852	45.2028881	**19.7945735**
5270	**14.464263**	**27.9490382**	9.43527115	6.79820361	2.63706754	47.8399556	**20.9493587**
5830	**14.873487**	**25.9105671**	11.2420252	8.32915272	2.91287248	50.7528281	**22.2249203**
6140	**14.979805**	**25.3809643**	6.22326395	4.64373955	1.5795244	52.3323525	**22.9166021**
6830	**15.449209**	**23.042718**	13.8517811	10.6599542	3.19182684	55.5241793	**24.3143192**
7345	**15.691935**	**21.8336248**	10.3386482	8.08134653	2.25730165	57.781481	**25.302803**
7820	**15.895544**	**20.8193855**	9.53564638	7.5503834	1.98526298	59.7667439	**26.1721597**
8130	**15.994841**	**20.3247564**	6.22326395	4.95840071	1.26486324	61.0316072	**26.7260497**
8810	**16.199453**	**19.3055209**	13.6510306	11.015628	2.63540256	63.6670097	**27.8801059**
9315	**16.543482**	**17.5918061**	10.1378977	8.35445841	1.78343932	65.4504491	**28.661083**
9850	**16.74007**	**16.6125406**	10.7401491	8.95593745	1.78421163	67.2346607	**29.4423983**
10830	**17.158321**	**14.5291032**	19.6735441	16.8151546	2.85838952	70.0930502	**30.6941015**
11690	**17.437155**	**13.1401449**	17.2645387	14.9959533	2.2685854	72.3616356	**31.6875265**
12800	**17.489311**	**12.8803397**	22.2833	19.4131352	2.87016474	75.2318003	**32.9443862**
13740	**17.597635**	**12.3407444**	18.8705423	16.5417769	2.3287654	77.5605657	**33.9641644**
14200	**17.711977**	**11.7711716**	9.2345207	8.14750942	1.08701128	78.647577	**34.4401721**
15730	**17.842367**	**11.1216588**	30.7148189	27.2988215	3.41599734	82.0635744	**35.9360546**
16980	**17.952697**	**10.5720709**	25.0938063	22.4408713	2.652935	84.7165094	**37.0977883**
17860	**18.040961**	**10.1324007**	17.6660396	15.8760457	1.78999392	86.5065033	**37.8816357**
18220	**18.175363**	**9.46290282**	7.2270162	6.54313068	0.68388552	87.1903888	**38.1811126**
19825	**18.268642**	**8.99825131**	32.2204472	29.3211704	2.89927682	90.0896656	**39.4507206**
20620	**18.409062**	**8.29877592**	15.9596608	14.6352043	1.32445649	91.4141221	**40.0307068**

21845	**18.553494**	**7.57931551**	24.5919301	22.7280302	1.86389998	93.2780221	**40.8469181**
22235	**18.579572**	**7.44941294**	7.82926755	7.24603308	0.58323447	93.8612565	**41.1023194**
23750	**18.735037**	**6.67499375**	30.4136932	28.3835811	2.03011212	95.8913687	**41.9913158**
24850	**18.855397**	**6.07544342**	22.0825495	20.7409367	1.3416128	97.2329815	**42.5788148**
25790	**19.051985**	**5.09617787**	18.8705423	17.9088659	0.9616764	98.1946579	**42.9999378**
26750	**19.324801**	**3.7371971**	19.2720432	18.551809	0.72023424	98.9148921	**43.315332**
27180	**19.536434**	**2.68298776**	8.63226935	8.40066662	0.23160273	99.1464948	**43.416752**
28765	**19.573545**	**2.49812641**	31.8189463	31.0240688	0.7948775	99.9413723	**43.7648329**
29140	**19.692902**	**1.90357232**	7.52814188	7.38483825	0.14330363	100.084676	**43.8275862**
30690	**19.844355**	**1.14913815**	31.1163198	30.7587503	0.3575695	100.442245	**43.9841677**
31810	**19.913562**	**0.8043967**	22.4840504	22.3031894	0.18086096	100.623106	**44.0633677**
32730	**20.048967**	**0.12990257**	18.4690414	18.4450496	0.02399176	100.647098	**44.0738738**
33185	**20.185375**	**0**	9.13414548	9.18434563	0	100.647098	**44.0738738**
34815	**20.079057**	**0**	32.7223234	32.7288629	0	100.647098	**44.0738738**
35735	**20.162306**	**0**	18.4690414	18.5493215	0	100.647098	**44.0738738**
36750	**20.048967**	**0**	20.3761707	20.3497015	0	100.647098	**44.0738738**
37915	**20.06**	**0**	23.3874274	23.3699	0	100.647098	**44.0738738**
38870	**21.168315**	**0**	19.171668	20.2157408	0	100.647098	**44.0738738**
39830	**20.014865**	**0**	19.2720432	19.2142704	0	100.647098	**44.0738738**
40830	**20.21045**	**0**	20.075045	20.21045	0	100.647098	**44.0738738**
41975	**20.075045**	**0**	22.9859265	22.9859265	0	100.647098	**44.0738738**
42715	**20.171333**	**0**	14.8555333	14.9267864	0	100.647098	**44.0738738**
43160	**20.215465**	**0**	8.93339503	8.99588193	0	100.647098	**44.0738738**
44700	**20.048967**	**0**	30.9155693	30.8754092	0	100.647098	**44.0738738**
45835	**20.075045**	**0**	22.7851761	22.7851761	0	100.647098	**44.0738738**
46770	**20.079057**	**0**	18.7701671	18.7739183	0	100.647098	**44.0738738**
47180	**20.078054**	**0**	8.23076845	8.23200214	0	100.647098	**44.0738738**
48670	**20.215465**	**0**	29.9118171	30.1210429	0	100.647098	**44.0738738**
49720	**20.275645**	**0**	21.0787973	21.2894273	0	100.647098	**44.0738738**
50920	**20.071033**	**0**	24.090054	24.0852396	0	100.647098	**44.0738738**

Table A100: pH changes during the adsorption experiment

Volume treated (ml)	pH	Volume treated (ml)	pH	Volume treated (ml)	pH
0	5.3	21110	4.47	46150	4.82
1105	3.77	26160	4.58	50140	4.93
6130	3.94	31140	4.7		
12160	4.19	36175	4.75		
16160	4.32	41150	4.79		

4.3 Initial Cu concentration = 30 mgl^{-1}

Table A101: Carbon measured in the effluent during the conditioning process before the adsorption experiment

Volume of D.W (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)	Amount of IC (mg)
0	0	0	0	0
50	815.5	46.37	40.775	2.3185
100	705.9	30.97	70.59	1.5485
200	625.15	18.63	125.03	1.863
400	555.15	14.16	222.06	2.832
600	345.6	3.099	207.36	0.6198
800	102.9	0	82.32	0
1000	51.05	0	51.05	0
1110	40.6	0	45.066	0
1490	32.91	0	49.0359	0
1830	20.17	0	36.9111	0
2115	17.94	0	37.9431	0
2495	17	0	42.415	0
2820	15.44	0	43.5408	0
3130	12.44	0	38.9372	0
3510	11.5	0	40.365	0
3800	10.59	0	40.242	0
4120	9.5	0	39.14	0
4510	8.4	0	37.884	0
4825	7.55	0	36.42875	0
5110	6.45	0	32.9595	0
5520	4.5	0	24.84	0
5820	3.52	0	20.4864	0
6190	0	0	0	0
6840	0	0	0	0
7630	0	0	0	0
Sum (mg)			**1365.3798**	**9.1818**

Table A102: Copper adsorption using column of cast in seaweed-Hypol foam at Cu initial concentration of 30 mgl^{-1}, T 20° C, solution pH 5.03, 4.7 l/hr flow rate and biomass ratio of 7 % (net dry wt. of biomass = 2.4 g)

Volume treated (ml)	**Copper conc. (mg/l)**	**Removal ratio (%)**	Amount of copper in the influent (mg)	approx. amount of copper in the effluent (mg)	approx. copper uptaken at each stage (mg)	approx. amount of adsorbed copper (mg)	**approx. copper uptake by the biomass (mg/g)**
0	**31.864307**	**100**	0	0	0	0	**0**
100	**0.545632**	**98.2876389**	3.1864307	0.0545632	3.1318675	3.1318675	**1.30718225**
270	**3.067174**	**90.3742642**	5.41693219	0.52141958	4.89551261	8.02738011	**3.35047661**
530	**7.891604**	**75.2337184**	8.28471982	2.05181704	6.23290278	14.2602829	**5.95197233**
825	**11.207522**	**64.8273474**	9.39997057	3.30621899	6.09375158	20.3540345	**8.49538897**
1230	**14.065069**	**55.8594857**	12.9050443	5.69635295	7.20869139	27.5627259	**11.5041604**
1850	**17.89352**	**43.8446284**	19.7558703	11.0939824	8.66188794	36.2246138	**15.1194686**
2100	**18.646773**	**41.4806887**	7.96607675	4.66169325	3.3043835	39.5289973	**16.4986557**

2730	**21.374933**	**32.9188832**	20.0745134	13.4662078	6.60830562	46.1373029	**19.2568375**
3140	**22.007826**	**30.9326702**	13.0643659	9.02320866	4.04115721	50.1784601	**20.9435401**
3800	**23.00882**	**27.791243**	21.0304426	15.1858212	5.84462142	56.0230815	**23.3829745**
4120	**23.5705**	**26.0285184**	10.1965782	7.54256	2.65401824	58.6770998	**24.4907115**
4820	**24.375909**	**23.5008971**	22.3050149	17.0631363	5.2418786	63.9189784	**26.6785725**
5110	**24.875403**	**21.9333312**	9.24064903	7.21386687	2.02678216	65.9457605	**27.524513**
5800	**25.220435**	**20.8505147**	21.9863718	17.4021002	4.58427168	70.5300322	**29.4379013**
6320	**25.427053**	**20.2020838**	16.5694396	13.2220676	3.34737208	73.8774043	**30.8350311**
6800	**25.643701**	**19.5221757**	15.2948674	12.3089765	2.98589088	76.8632952	**32.0812855**
7130	**26.048913**	**18.2504958**	10.5152213	8.59614129	1.91908002	78.7823752	**32.8822732**
7800	**26.301669**	**17.4572697**	21.3490857	17.6221182	3.72696746	82.5093427	**34.4378389**
8130	**26.834262**	**15.785829**	10.5152213	8.85530646	1.65991485	84.1692575	**35.1306559**
8810	**27.096045**	**14.9642733**	21.6677288	18.4253106	3.24241816	87.4116757	**36.4839799**
9105	**27.495239**	**13.7114797**	9.39997057	8.11109551	1.28887506	88.7005507	**37.021932**
9820	**27.835256**	**12.6444018**	22.7829795	19.902208	2.88077147	91.5813222	**38.2243115**
10725	**28.118102**	**11.756744**	28.8371978	25.4468823	3.39031553	94.9716377	**39.6393651**
11800	**28.439062**	**10.7494728**	34.25413	30.5719917	3.68213838	98.6537761	**41.17622**
12140	**28.72592**	**9.84922409**	10.8338644	9.7668128	1.06705158	99.7208277	**41.6215872**
13765	**29.101042**	**8.67197583**	51.7794989	47.2891933	4.49030563	104.211133	**43.4957558**
14130	**29.439053**	**7.6111933**	11.6304721	10.7452543	0.88521771	105.096351	**43.8652289**
15740	**30.040853**	**5.72255973**	51.3015343	48.3657733	2.93576094	108.032112	**45.09056**
16715	**30.338744**	**4.78768611**	31.0676993	29.5802754	1.48742393	109.519536	**45.7113826**
17120	**30.605542**	**3.95039189**	12.9050443	12.3952445	0.50979983	110.029336	**45.9241634**
18930	**30.844256**	**3.20123391**	57.6743957	55.8281034	1.84629231	111.875628	**46.6947709**
19705	**31.004736**	**2.69759829**	24.6948379	24.0286704	0.66616753	112.541796	**46.9728166**
20125	**31.218375**	**2.02713337**	13.3830089	13.1117175	0.27129144	112.813087	**47.0860485**
21820	**31.448062**	**1.30630489**	54.0100004	53.3044651	0.70553528	113.518622	**47.3805256**
22785	**31.519275**	**1.08281658**	30.7490563	30.4161004	0.33295588	113.851578	**47.5194951**
23460	**31.090994**	**2.42689414**	21.5084072	20.986421	0.52198628	114.373564	**47.7373623**
24680	**31.605533**	**0.81211244**	38.8744545	38.5587503	0.31570428	114.689269	**47.8691313**
25760	**31.506236**	**1.12373698**	34.4134516	34.0267349	0.38671668	115.075985	**48.0305395**
26320	**31.892391**	**0**	17.8440119	17.859739	0	115.075985	**48.0305395**
27870	**31.745953**	**0**	49.3896759	49.2062272	0	115.075985	**48.0305395**
28180	**32.218366**	**0**	9.87793517	9.98769346	0	115.075985	**48.0305395**
29970	**31.539335**	**0**	57.0371095	56.4554097	0	115.075985	**48.0305395**
30835	**32.063904**	**0**	27.5626256	27.735277	0	115.075985	**48.0305395**
31720	**32.10603**	**0**	28.1999117	28.4138366	0	115.075985	**48.0305395**
32130	**32.135117**	**0**	13.0643659	13.175398	0	115.075985	**48.0305395**
33650	**31.810145**	**0**	48.4337466	48.3514204	0	115.075985	**48.0305395**
34115	**31.385876**	**0**	14.8169028	14.5944323	0	115.075985	**48.0305395**
35790	**31.481161**	**0**	53.3727142	52.7309447	0	115.075985	**48.0305395**
36830	**31.503227**	**0**	33.1388793	32.7633561	0	115.075985	**48.0305395**
37780	**31.615563**	**0**	30.2710917	30.0347849	0	115.075985	**48.0305395**
38800	**31.571431**	**0**	32.5015931	32.2028596	0	115.075985	**48.0305395**
39800	**31.575443**	**0**	31.864307	31.575443	0	115.075985	**48.0305395**
40725	**31.576446**	**0**	29.474484	29.2082126	0	115.075985	**48.0305395**
41750	**31.585473**	**0**	32.6609147	32.3751098	0	115.075985	**48.0305395**
42110	**31.566416**	**0**	11.4711505	11.3639098	0	115.075985	**48.0305395**
43600	**31.553377**	**0**	47.4778174	47.0145317	0	115.075985	**48.0305395**
44800	**31.575443**	**0**	38.2371684	37.8905316	0	115.075985	**48.0305395**
45820	**31.58447**	**0**	32.5015931	32.2161594	0	115.075985	**48.0305395**
46800	**31.585473**	**0**	31.2270209	30.9537635	0	115.075985	**48.0305395**

47850	**31.576446**	**0**	33.4575224	33.1552683	0	115.075985	**48.0305395**
48800	**31.572434**	**0**	30.2710917	29.9938123	0	115.075985	**48.0305395**
49790	**31.553377**	**0**	31.5456639	31.2378432	0	115.075985	**48.0305395**
50750	**31.562404**	**0**	30.5897347	30.2999078	0	115.075985	**48.0305395**

Table A103: pH changes during the adsorption experiment

Volume treated (ml)	pH	Volume treated (ml)	pH	Volume treated (ml)	pH
0	5.03	21800	4.43	46150	4.92
1340	3.48	26150	4.55	50100	4.96
6140	3.84	31100	4.72		
11145	4.16	36100	4.76		
16170	4.35	41100	4.86		

5- Tables of the adsorption of Cu (II), Zn (II) and Fe (II) from a simulated solution of pickling-dipping industry wastewater using a column of seaweed-Hypol foam

Table A104: Carbon measured in the effluent during the column conditioning process before the adsorption experiment

Volume of D.W (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)	Amount of IC (mg)
0	0	0	0	0
50	1120.1	69.77	56.005	3.4885
100	900	50	45	2.5
200	837.7	29.7	83.77	2.97
400	512.2	7.577	102.44	1.5154
600	250.6	0	50.12	0
800	100.3	0	20.06	0
1000	62.6	0	12.52	0
1150	38.9	0	5.835	0
1560	25.4	0	10.414	0
1845	18.1	0	5.1585	0
2200	16.3	0	5.7865	0
2590	14.5	0	5.655	0
2830	13	0	3.12	0
3120	12.15	0	3.5235	0
3570	11.62	0	5.229	0
3830	10.04	0	2.6104	0
4115	9.2	0	2.622	0
4640	8	0	4.2	0
4835	5.55	0	1.08225	0
5180	4.5	0	1.5525	0
5820	3.2	0	2.048	0
6220	0	0	0	0
6900	0	0	0	0
6860	0	0	0	0
Sum (mg)			**428.75165**	**10.4739**

Tables A105: Adsorption of Cu (II), Zn (II) and Fe (II) using column of cast in seaweed-Hypol foam at Cu (II), Zn (II) and Fe (II) initial concentration of 6 mgl^{-1}, T 20° C, solution pH 5.0, 4.7 l/hr flow rate and biomass ratio of 7 % (net dry wt. of biomass = 2.98 g)

Table A105a: Cu (II)

Volume treated (ml)	**Copper conc. (mg/l)**	**Removal ratio (%)**	Amount of copper in the influent (mg)	approx. amount of copper in the effluent (mg)	approx. copper uptaken at each stage (mg)	approx. amount of adsorbed copper (mg)	**approx. copper uptake by the biomass (mg/g)**
0	**6.285801**	**100**	0	0	0	0	**0**
100	**0.099297**	**98.4202968**	0.6285801	0.0099297	0.6186504	0.6186504	**0.20736422**
260	**0.302906**	**95.1811074**	1.00572816	0.04846496	0.9572632	1.5759136	**0.52822739**
540	**0.697085**	**88.9101644**	1.76002428	0.1951838	1.56484048	3.14075408	**1.05274321**
800	**1.026069**	**83.6764002**	1.63430826	0.26677794	1.36753032	4.5082844	**1.51112301**
1160	**1.425263**	**77.3256742**	2.26288836	0.51309468	1.74979368	6.25807808	**2.09763293**
1820	**2.027063**	**67.7517153**	4.14862866	1.33786158	2.81076708	9.06884516	**3.03976844**
2100	**2.15645**	**65.6933142**	1.76002428	0.603806	1.15621828	10.2250634	**3.42731898**
2755	**2.571692**	**59.0872826**	4.11719966	1.68445826	2.4327414	12.6578048	**4.2427448**
3120	**2.767277**	**55.975746**	2.29431737	1.01005611	1.28426126	13.9420661	**4.67321381**
3825	**3.050123**	**51.4759853**	4.43148971	2.15033672	2.28115299	16.2232191	**5.43782902**
4130	**3.227654**	**48.6516675**	1.91716931	0.98443447	0.93273484	17.1559539	**5.75047058**
4820	**3.439287**	**45.2848253**	4.33720269	2.37310803	1.96409466	19.1200486	**6.40881162**
5130	**3.532566**	**43.8008617**	1.94859831	1.09509546	0.85350285	19.9735514	**6.69489557**
5870	**3.652926**	**41.8860699**	4.65149274	2.70316524	1.9483275	21.9218789	**7.34795164**
6160	**3.733166**	**40.609542**	1.82288229	1.08261814	0.74026415	22.6621431	**7.59607933**
6830	**3.942793**	**37.2746131**	4.21148667	2.64167131	1.56981536	24.2319584	**8.12226267**
7175	**3.963856**	**36.9395245**	2.16860135	1.36753032	0.80107103	25.0330295	**8.39077209**
7835	**4.128348**	**34.3226424**	4.14862866	2.72470968	1.42391898	26.4569484	**8.86805271**
8165	**4.159441**	**33.8279879**	2.07431433	1.37261553	0.7016988	27.1586472	**9.10325375**
8800	**4.20257**	**33.1418542**	3.99148364	2.66863195	1.32285169	28.4814989	**9.54665782**
9170	**4.300864**	**31.5781075**	2.32574637	1.59131968	0.73442669	29.2159256	**9.79282886**
9800	**4.409188**	**29.854795**	3.96005463	2.77778844	1.18226619	30.3981918	**10.1891103**
10730	**4.56365**	**27.3974789**	5.84579493	4.2441945	1.60160043	31.9997922	**10.7259477**
11160	**4.616809**	**26.5517792**	2.70289443	1.98522787	0.71766656	32.7174588	**10.9665009**
12740	**4.812394**	**23.4402425**	9.93156558	7.60358252	2.32798306	35.0454419	**11.746813**
13140	**4.960838**	**21.078666**	2.5143204	1.9843352	0.5299852	35.5754271	**11.9244577**
14930	**5.046093**	**19.7223552**	11.2515838	9.03250647	2.21907732	37.7945044	**12.6682659**
15850	**5.160435**	**17.903303**	5.78293692	4.7476002	1.03533672	38.8298411	**13.0152984**
16780	**5.229642**	**16.8022978**	5.84579493	4.86356706	0.98222787	39.812069	**13.3445294**
17165	**5.304867**	**15.6055529**	2.42003339	2.0423738	0.37765959	40.1897286	**13.4711164**
18850	**5.401155**	**14.0737195**	10.5915747	9.10094618	1.49062851	41.6803571	**13.9707572**
19820	**5.480392**	**12.8131482**	6.09722697	5.31598024	0.78124673	42.4616038	**14.2326218**
20760	**5.591725**	**11.0419659**	5.90865294	5.2562215	0.65243144	43.1140352	**14.451309**
21810	**5.600752**	**10.8983565**	6.60009105	5.8807896	0.71930145	43.8333367	**14.6924102**
22165	**5.658926**	**9.97287378**	2.23145936	2.00891873	0.22254063	44.0558773	**14.7670032**
23620	**5.77728**	**8.08999521**	9.14584046	8.4059424	0.73989806	44.7957754	**15.0150082**
24145	**5.78731**	**7.93042923**	3.30004553	3.03833775	0.26170778	45.0574831	**15.1027295**
25810	**5.932745**	**5.61672251**	10.4658587	9.87802043	0.58783824	45.6453214	**15.2997658**
26240	**5.972865**	**4.97845859**	2.70289443	2.56833195	0.13456248	45.7798839	**15.3448696**

27340	**6.002955**	**4.49976065**	6.9143811	6.6032505	0.3111306	46.0910145	**15.4491568**
28210	**6.016997**	**4.27636828**	5.46864687	5.23478739	0.23385948	46.3248739	**15.5275437**
29750	**6.067147**	**3.47853838**	9.68013354	9.34340638	0.33672716	46.6616011	**15.6404106**
30740	**6.089213**	**3.12749322**	6.22294299	6.02832087	0.19462212	46.8562232	**15.7056456**
31710	**6.100246**	**2.95197064**	6.09722697	5.91723862	0.17998835	47.0362116	**15.7659756**
32870	**6.149393**	**2.17009734**	7.29152916	7.13329588	0.15823328	47.1944449	**15.8190135**
33840	**6.27878**	**0.11169619**	6.09722697	6.0904166	0.00681037	47.2012552	**15.8212962**
34830	**6.283795**	**0.0319132**	6.22294299	6.22095705	0.00198594	47.2032412	**15.8219619**
35860	**6.286804**	**0**	6.47437503	6.47540812	0	47.2032412	**15.8219619**
36805	**6.77025**	**0**	5.94008195	6.39788625	0	47.2032412	**15.8219619**
37130	**6.330936**	**0**	2.04288533	2.0575542	0	47.2032412	**15.8219619**
38780	**6.287807**	**0**	10.3715717	10.3748816	0	47.2032412	**15.8219619**
39890	**6.285801**	**0**	6.97723911	6.97723911	0	47.2032412	**15.8219619**
40735	**6.277777**	**0**	5.31150185	5.30472157	0	47.2032412	**15.8219619**
41225	**6.314888**	**0**	3.08004249	3.09429512	0	47.2032412	**15.8219619**
42820	**6.3189**	**0**	10.0258526	10.0786455	0	47.2032412	**15.8219619**
43120	**6.316894**	**0**	1.8857403	1.8950682	0	47.2032412	**15.8219619**
44745	**6.289813**	**0**	10.2144266	10.2209461	0	47.2032412	**15.8219619**
45700	**6.293825**	**0**	6.00293996	6.01060288	0	47.2032412	**15.8219619**
46210	**6.292822**	**0**	3.20575851	3.20933922	0	47.2032412	**15.8219619**
47720	**6.299843**	**0**	9.49155951	9.51276293	0	47.2032412	**15.8219619**
48120	**6.309873**	**0**	2.5143204	2.5239492	0	47.2032412	**15.8219619**
49840	**6.303855**	**0**	10.8115777	10.8426306	0	47.2032412	**15.8219619**
50705	**6.287807**	**0**	5.43721787	5.43895306	0	47.2032412	**15.8219619**
51720	**6.289813**	**0**	6.38008802	6.3841602	0	47.2032412	**15.8219619**

Table A105 b: Zn (II)

Volume treated (ml)	**Zn conc. (mg/l)**	**Removal ratio (%)**	Amount of Zn in the influent (mg)	approx. amount of Zn in the effluent (mg)	approx. Zn uptaken at each stage (mg)	approx. amount of adsorbed Zn (mg)	**approx. Zn uptake by the biomass (mg/g)**
0	**6.385098**	**100**	0	0	0	0	**0**
100	**0.1328975**	**97.9186302**	0.6385098	0.01328975	0.62522005	0.62522005	**0.20956628**
260	**1.1366999**	**82.1976123**	1.02161568	0.18187198	0.8397437	1.46496375	**0.49103833**
540	**2.5028862**	**60.801131**	1.78782744	0.70080814	1.0870193	2.55198305	**0.8553942**
800	**3.296861**	**48.3663211**	1.66012548	0.85718386	0.80294162	3.35492467	**1.12453063**
1160	**4.006985**	**37.2447377**	2.29863528	1.4425146	0.85612068	4.21104535	**1.41149204**
1820	**4.731151**	**25.9032359**	4.21416468	3.12255966	1.09160502	5.30265037	**1.77738499**
2100	**4.946796**	**22.5259189**	1.78782744	1.38510288	0.40272456	5.70537493	**1.91237344**
2755	**5.3390693**	**16.3823437**	4.18223919	3.49709039	0.6851488	6.39052373	**2.14202713**
3120	**5.5179042**	**13.5815269**	2.33056077	2.01403503	0.31652574	6.70704947	**2.24812277**
3825	**5.706067**	**10.6346214**	4.50149409	4.02277724	0.47871686	7.18576632	**2.40858293**
4130	**5.856517**	**8.27835375**	1.94745489	1.78623769	0.16121721	7.34698353	**2.46262101**
4820	**5.929736**	**7.13163682**	4.40571762	4.09151784	0.31419978	7.66118331	**2.56793702**
5130	**6.055111**	**5.16808043**	1.97938038	1.87708441	0.10229597	7.76347928	**2.60222541**
5870	**6.083195**	**4.7282438**	4.72497252	4.5015643	0.22340822	7.9868875	**2.67710917**
6160	**6.121309**	**4.13132265**	1.85167842	1.77517961	0.07649881	8.06338631	**2.70275066**
6830	**6.163435**	**3.4715677**	4.27801566	4.12950145	0.14851421	8.21190052	**2.75253084**
7175	**6.176474**	**3.26735784**	2.20285881	2.13088353	0.07197528	8.2838758	**2.7766561**
7835	**6.197537**	**2.93748036**	4.21416468	4.09037442	0.12379026	8.40766606	**2.81814911**
8165	**6.217597**	**2.62331134**	2.10708234	2.05180701	0.05527533	8.46294139	**2.83667674**

8800	**6.233645**	**2.37197612**	4.05453723	3.95836458	0.09617265	8.55911404	**2.86891266**
9170	**6.243675**	**2.21489161**	2.36248626	2.31015975	0.05232651	8.61144055	**2.88645188**
9800	**6.273765**	**1.74363808**	4.02261174	3.95247195	0.07013979	8.68158034	**2.9099619**
10730	**6.307867**	**1.20955074**	5.93814114	5.86631631	0.07182483	8.75340517	**2.93403673**
11160	**6.3189**	**1.03675778**	2.74559214	2.717127	0.02846514	8.78187031	**2.9435779**
12740	**6.343975**	**0.6440465**	10.0884548	10.0234805	0.06497434	8.84684465	**2.96535652**
13140	**6.385098**	**0**	2.5540392	2.5540392	0	8.84684465	**2.96535652**
14930	**6.387104**	**0**	11.4293254	11.4329162	0	8.84684465	**2.96535652**
15850	**6.38911**	**0**	5.87429016	5.8779812	0	8.84684465	**2.96535652**
16780	**6.387104**	**0**	5.93814114	5.94000672	0	8.84684465	**2.96535652**
17165	**6.420203**	**0**	2.45826273	2.47177816	0	8.84684465	**2.96535652**
18850	**6.400143**	**0**	10.7588901	10.784241	0	8.84684465	**2.96535652**
19820	**6.38911**	**0**	6.19354506	6.1974367	0	8.84684465	**2.96535652**
20760	**6.394125**	**0**	6.00199212	6.0104775	0	8.84684465	**2.96535652**
21810	**6.390113**	**0**	6.7043529	6.70961865	0	8.84684465	**2.96535652**
22165	**6.388107**	**0**	2.26670979	2.26777799	0	8.84684465	**2.96535652**
23620	**6.39914**	**0**	9.29031759	9.3107487	0	8.84684465	**2.96535652**
24145	**6.391116**	**0**	3.35217645	3.3553359	0	8.84684465	**2.96535652**
25810	**6.38911**	**0**	10.6311882	10.6378682	0	8.84684465	**2.96535652**
26240	**6.394125**	**0**	2.74559214	2.74947375	0	8.84684465	**2.96535652**
27340	**6.384095**	**0**	7.0236078	7.0225045	0	8.84684465	**2.96535652**
28210	**6.388107**	**0**	5.55503526	5.55765309	0	8.84684465	**2.96535652**
29750	**6.390113**	**0**	9.83305092	9.84077402	0	8.84684465	**2.96535652**
30740	**6.387104**	**0**	6.32124702	6.32323296	0	8.84684465	**2.96535652**
31710	**6.386101**	**0**	6.19354506	6.19451797	0	8.84684465	**2.96535652**
32870	**6.388107**	**0**	7.40671368	7.41020412	0	8.84684465	**2.96535652**
33840	**6.390113**	**0**	6.19354506	6.19840961	0	8.84684465	**2.96535652**
34830	**6.38911**	**0**	6.32124702	6.3252189	0	8.84684465	**2.96535652**
35860	**6.391116**	**0**	6.57665094	6.58284948	0	8.84684465	**2.96535652**
36805	**6.387104**	**0**	6.03391761	6.03581328	0	8.84684465	**2.96535652**
37130	**6.384095**	**0**	2.07515685	2.07483088	0	8.84684465	**2.96535652**
38780	**6.388107**	**0**	10.5354117	10.5403766	0	8.84684465	**2.96535652**
39890	**6.387104**	**0**	7.08745878	7.08968544	0	8.84684465	**2.96535652**
40735	**6.388107**	**0**	5.39540781	5.39795042	0	8.84684465	**2.96535652**
41225	**6.430233**	**0**	3.12869802	3.15081417	0	8.84684465	**2.96535652**
42820	**6.400143**	**0**	10.1842313	10.2082281	0	8.84684465	**2.96535652**
43120	**6.391116**	**0**	1.9155294	1.9173348	0	8.84684465	**2.96535652**
44745	**6.388107**	**0**	10.3757843	10.3806739	0	8.84684465	**2.96535652**
45700	**6.387104**	**0**	6.09776859	6.09968432	0	8.84684465	**2.96535652**
46210	**6.385098**	**0**	3.25639998	3.25639998	0	8.84684465	**2.96535652**
47720	**6.386101**	**0**	9.64149798	9.64301251	0	8.84684465	**2.96535652**
48120	**6.388107**	**0**	2.5540392	2.5552428	0	8.84684465	**2.96535652**
49840	**6.390113**	**0**	10.9823686	10.9909944	0	8.84684465	**2.96535652**
50705	**6.38911**	**0**	5.52310977	5.52658015	0	8.84684465	**2.96535652**
51720	**6.400143**	**0**	6.48087447	6.49614515	0	8.84684465	**2.96535652**

Table A105 c: Fe (II)

Volume treated (ml)	**Fe(II) conc. (mg/l)**	**Removal ratio (%)**	Amount of Fe(II) in the influent (mg)	approx. amount of Fe(II) in the effluent (mg)	approx. uptaken Fe(II) at each stage (mg)	approx. amount of adsorbed Fe(II) (mg)	**approx. Fe(II) uptake by the biomass (mg/g)**
0	**6.142372**	**100**	0	0	0	0	**0**
100	**0.088264**	**98.5630307**	0.6142372	0.0088264	0.6054108	0.6054108	**0.20292646**
260	**1.525563**	**75.163292**	0.98277952	0.24409008	0.73868944	1.34410024	**0.45052633**
540	**3.011006**	**50.9797518**	1.71986416	0.84308168	0.87678248	2.22088272	**0.74441333**
800	**3.709094**	**39.614631**	1.59701672	0.96436444	0.63265228	2.853535	**0.95647081**
1160	**4.237675**	**31.0091444**	2.21125392	1.525563	0.68569092	3.53922592	**1.1863062**
1820	**4.983907**	**18.8602221**	4.05396552	3.28937862	0.7645869	4.30381282	**1.44258659**
2100	**5.478386**	**10.8099282**	1.71986416	1.53394808	0.18591608	4.4897289	**1.50490343**
2755	**5.509479**	**10.3037231**	4.02325366	3.60870875	0.41454492	4.90427382	**1.64385393**
3120	**5.571665**	**9.29131287**	2.24196578	2.03365773	0.20830806	5.11258187	**1.7136763**
3825	**5.674974**	**7.60940562**	4.33037226	4.00085667	0.32951559	5.44209746	**1.82412598**
4130	**5.841472**	**4.89875898**	1.87342346	1.78164896	0.0917745	5.53387196	**1.8548877**
4820	**5.892625**	**4.06596995**	4.23823668	4.06591125	0.17232543	5.70619739	**1.91264912**
5130	**5.916697**	**3.67406924**	1.90413532	1.83417607	0.06995925	5.77615664	**1.93609863**
5870	**5.942775**	**3.24951012**	4.54535528	4.3976535	0.14770178	5.92385842	**1.9856065**
6160	**5.995934**	**2.3840627**	1.78128788	1.73882086	0.04246702	5.96632544	**1.99984093**
6830	**6.030036**	**1.82887002**	4.11538924	4.04012412	0.07526512	6.04159056	**2.0250689**
7175	**6.064138**	**1.27367734**	2.11911834	2.09212761	0.02699073	6.06858129	**2.03411587**
7835	**6.12833**	**0.22860875**	4.05396552	4.0446978	0.00926772	6.07784901	**2.0372223**
8165	**6.143375**	**0**	2.02698276	2.02731375	0	6.07784901	**2.0372223**
8800	**6.147387**	**0**	3.90040622	3.90359075	0	6.07784901	**2.0372223**
9170	**6.145381**	**0**	2.27267764	2.27379097	0	6.07784901	**2.0372223**
9800	**6.143375**	**0**	3.86969436	3.87032625	0	6.07784901	**2.0372223**
10730	**6.2186**	**0**	5.71240596	5.783298	0	6.07784901	**2.0372223**
11160	**6.230636**	**0**	2.64121996	2.67917348	0	6.07784901	**2.0372223**
12740	**6.19854**	**0**	9.70494776	9.7936932	0	6.07784901	**2.0372223**
13140	**6.16845**	**0**	2.4569488	2.46738	0	6.07784901	**2.0372223**
14930	**6.147387**	**0**	10.9948459	11.0038227	0	6.07784901	**2.0372223**
15850	**6.153405**	**0**	5.65098224	5.6611326	0	6.07784901	**2.0372223**
16780	**6.154408**	**0**	5.71240596	5.72359944	0	6.07784901	**2.0372223**
17165	**6.169453**	**0**	2.36481322	2.37523941	0	6.07784901	**2.0372223**
18850	**6.143375**	**0**	10.3498968	10.3515869	0	6.07784901	**2.0372223**
19820	**6.142372**	**0**	5.95810084	5.95810084	0	6.07784901	**2.0372223**
20760	**6.143375**	**0**	5.77382968	5.7747725	0	6.07784901	**2.0372223**
21810	**6.145381**	**0**	6.4494906	6.45265005	0	6.07784901	**2.0372223**
22165	**6.13836**	**0**	2.18054206	2.1791178	0	6.07784901	**2.0372223**
23620	**6.142372**	**0**	8.93715126	8.93715126	0	6.07784901	**2.0372223**
24145	**6.146384**	**0**	3.2247453	3.2268516	0	6.07784901	**2.0372223**
25810	**6.147387**	**0**	10.2270494	10.2353994	0	6.07784901	**2.0372223**
26240	**6.2186**	**0**	2.64121996	2.673998	0	6.07784901	**2.0372223**
27340	**6.22863**	**0**	6.7566092	6.851493	0	6.07784901	**2.0372223**
28210	**6.207567**	**0**	5.34386364	5.40058329	0	6.07784901	**2.0372223**
29750	**6.173465**	**0**	9.45925288	9.5071361	0	6.07784901	**2.0372223**
30740	**6.147387**	**0**	6.08094828	6.08591313	0	6.07784901	**2.0372223**
31710	**6.147387**	**0**	5.95810084	5.96296539	0	6.07784901	**2.0372223**
32870	**6.150396**	**0**	7.12515152	7.13445936	0	6.07784901	**2.0372223**
33840	**6.149393**	**0**	5.95810084	5.96491121	0	6.07784901	**2.0372223**

34830	**6.15842**	**0**	6.08094828	6.0968358	0	6.07784901	**2.0372223**
35860	**6.150396**	**0**	6.32664316	6.33490788	0	6.07784901	**2.0372223**
36805	**6.152402**	**0**	5.80454154	5.81401989	0	6.07784901	**2.0372223**
37130	**6.145381**	**0**	1.9962709	1.99724883	0	6.07784901	**2.0372223**
38780	**6.219603**	**0**	10.1349138	10.262345	0	6.07784901	**2.0372223**
39890	**6.329933**	**0**	6.81803292	7.02622563	0	6.07784901	**2.0372223**
40735	**6.22863**	**0**	5.19030434	5.26319235	0	6.07784901	**2.0372223**
41225	**6.2186**	**0**	3.00976228	3.047114	0	6.07784901	**2.0372223**
42820	**6.146384**	**0**	9.79708334	9.80348248	0	6.07784901	**2.0372223**
43120	**6.152402**	**0**	1.8427116	1.8457206	0	6.07784901	**2.0372223**
44745	**6.153405**	**0**	9.9813545	9.99928313	0	6.07784901	**2.0372223**
45700	**6.143375**	**0**	5.86596526	5.86692313	0	6.07784901	**2.0372223**
46210	**6.145381**	**0**	3.13260972	3.13414431	0	6.07784901	**2.0372223**
47720	**6.146384**	**0**	9.27498172	9.28103984	0	6.07784901	**2.0372223**
48120	**6.143375**	**0**	2.4569488	2.45735	0	6.07784901	**2.0372223**
49840	**6.14839**	**0**	10.5648798	10.5752308	0	6.07784901	**2.0372223**
50705	**6.149393**	**0**	5.31315178	5.31922495	0	6.07784901	**2.0372223**
51720	**6.143375**	**0**	6.23450758	6.23552563	0	6.07784901	**2.0372223**

Table A106: pH changes during the adsorption of Cu (II), Zn (II) and Fe (II)

Volume treated (ml)	pH	Volume treated (ml)	pH	Volume treated (ml)	pH
0	5	21150	4.4	46150	4.56
1160	3.83	26150	4.47	51100	4.56
6150	4.04	31150	4.49		
11150	4.19	36150	4.51		
16150	4.28	41150	4.53		

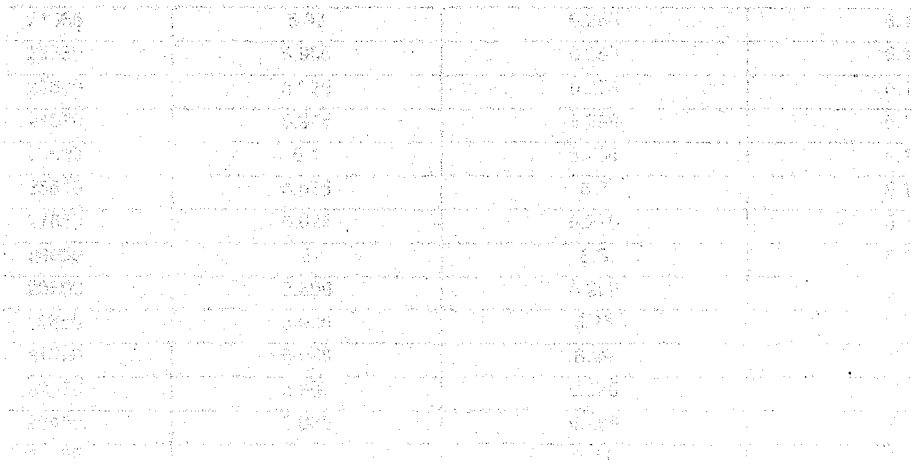


Table A107: Adsorption of Cu (II), Zn (II) and Fe (II) using a control column of un-loaded Hypol foam at Cu (II), Zn (II) and Fe (II) initial concentration of 6 mgl^{-1}, T 20° C, solution pH 5.0 and 4.7 l/hr flow rate.

Volume treated (ml)	Cu (II) concentration (mg/l)	Zn (II) concentration (mg/l)	Fe (II) concentration (mg/l)
0	6.012	6.311	6.155
280	6	6.291	6.145
690	6.058	6.301	6.151
1210	5.95	6.311	6.52
1680	5.919	6.285	6.09
2205	5.9	6.279	6.08
2690	5.955	6.235	6.165
3210	6.105	6.255	6.158
3670	5.965	6.301	6.085
4225	6.055	6.199	6.078
4730	6.075	6.258	6.105
5260	5.978	6.266	6
5720	5.955	6.288	6.21
6380	5.975	6.285	6.2
6750	5.988	6.295	6.185
7310	5.985	6.31	6.145
7710	6.012	6.285	6.178
8265	6.018	6.298	6.189
8695	5.999	6.278	6.125
9580	5.915	6.295	6.115
10610	5.895	6.3	6
11600	5.95	6.35	6.154
12680	5.945	6.345	6.135
13700	5.899	6.299	6.125
14690	6.05	6.248	6.18
15770	6	6.259	6.108
16760	5.985	6.287	6.11
17750	5.995	6.59	6
18620	6	6.899	6.115
19630	6.015	6.3	6.145
20700	6.095	6.314	6.155
21565	5.98	6.268	6.175
22530	5.955	6.289	6.166
23600	5.925	6.278	6.185
24570	5.975	6.298	6.175
25680	6.1	6.254	6.148
26610	6.075	6.2	6.147
27650	6.025	6.275	6.175
28650	6	6.3	6.185
29600	5.899	6.299	6.155
30650	5.925	6.28	6.145
31620	5.978	6.29	6.01
32670	5.905	6.278	6.2
33450	5.985	6.289	6.19
34660	6	6.31	6.145
35510	5.978	6.3	6.175

36550	5.985	6.355	6.145
37400	5.975	6.299	6.135
38460	5.968	6.288	6.155
39460	5.975	6.245	6.019
40510	5.985	6.267	6.125
41530	5.975	6.286	6.145
42620	5.955	6.299	6.185
43645	5.988	6.289	6.178
44450	5.917	6.275	6.155
45400	6.05	6.31	6.135
46410	6.085	6.305	6.19
47540	5.955	6.311	6.12
48140	5.975	6.299	6.145
49180	5.875	6.288	6.175
50130	5.915	6.278	6.165
51170	5.948	6.298	6.155
52115	5.945	6.3	6.148
53330	6.02	6.289	6.147
54160	5.915	6.278	6.155
55115	5.945	6.298	6.125
56140	5.875	6.299	6.135
57150	5.885	6.33	6.143
58135	6.01	6.254	6.122
59310	6	6.285	6.147

6- Tables of the adsorption of Cu (II), Zn (II), Cr (VI) and Ni (II) from a simulated solution of automatic plating of zinc base die casting industry wastewater using a column of seaweed-Hypol foam

Table A108: Carbon measured in the effluent during the column conditioning process before the adsorption experiment

Volume of D.W (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)	Amount of IC (mg)
0	0	0	0	0
50	930.1	75.1	46.505	3.755
100	846.3	41.25	42.315	2.0625
200	785.6	36.55	78.56	3.655
400	515.9	17.5	103.18	3.5
600	320.5	1.5	64.1	0.3
800	215.3	0	43.06	0
1000	85.4	0	17.08	0
1145	55.3	0	8.0185	0
1520	32.1	0	12.0375	0
1825	23.15	0	7.06075	0
2110	16.5	0	4.7025	0
2630	12	0	6.24	0
2840	10.39	0	2.1819	0
3110	9.8	0	2.646	0
3530	8.9	0	3.738	0
3850	7.9	0	2.528	0
4140	6.85	0	1.9865	0
4620	5.95	0	2.856	0
4870	5	0	1.25	0
5160	4	0	1.16	0
5870	3	0	2.13	0
6120	0	0	0	0
6880	0	0	0	0
7500	0	0	0	0
Sum (mg)			**453.33565**	**13.2725**

Tables A109: Adsorption of Cu (II), Zn (II), Cr (VI) and Ni (II) using column of cast in seaweed-Hypol foam at Cu (II), Zn (II), Cr (VI) and Ni (II) initial concentrations of 6 mgl^{-1}, T 20° C, solution pH 5.0, 4.7 l/hr flow rate and biomass ratio of 7 % (net dry wt. of biomass = 3.02 g)

Table A109 a: Cu (II)

Volume treated (ml)	**Copper conc. (mg/l)**	**Removal ratio (%)**	Amount of copper in the influent (mg)	approx. amount of copper in the effluent (mg)	approx. copper uptaken at each stage (mg)	approx. amount of adsorbed copper (mg)	**approx. copper uptake by the biomass (mg/g)**
0	**6.033045**	**100**	0	0	0	0	**0**
100	**0.068204**	**98.8694929**	0.6033045	0.0068204	0.5964841	0.5964841	**0.19748513**
270	**0.251753**	**95.8270989**	1.02561765	0.04279801	0.98281964	1.57930374	**0.522879**
570	**0.619854**	**89.7256858**	1.8099135	0.1859562	1.6239573	3.20326104	**1.06054199**
820	**0.915739**	**84.8212801**	1.50826125	0.22893475	1.2793265	4.48258754	**1.48410394**
1160	**1.376116**	**77.1903574**	2.0512353	0.46787944	1.58335586	6.0659434	**2.00832453**
1810	**1.780325**	**70.4904406**	3.92147925	1.15721125	2.764268	8.8302114	**2.92352384**
2100	**2.107303**	**65.0706567**	1.74958305	0.61111787	1.13846518	9.96867658	**3.30044914**
2750	**2.285837**	**62.1113882**	3.92147925	1.48579405	2.4356852	12.4043618	**4.10686061**
3170	**2.481422**	**58.8694929**	2.5338789	1.04219724	1.49168166	13.8960434	**4.60072952**
3790	**2.642905**	**56.1928512**	3.7404879	1.6386011	2.1018868	15.9979302	**5.29662635**
4110	**2.820436**	**53.2502078**	1.9305744	0.90253952	1.02803488	17.0259651	**5.63699017**
4715	**2.999973**	**50.2743142**	3.64999223	1.81498367	1.83500856	18.8609737	**6.24452843**
5120	**3.146411**	**47.847049**	2.44338323	1.27429646	1.16908677	20.0300605	**6.63159199**
5820	**3.295858**	**45.3699086**	4.2231315	2.3071006	1.9160309	21.9460914	**7.26595529**
6280	**3.436278**	**43.042394**	2.7752007	1.58068788	1.19451282	23.1406042	**7.66143695**
6815	**3.532566**	**41.446384**	3.22767908	1.88992281	1.33775627	24.4783604	**8.10434394**
7240	**3.612806**	**40.1163757**	2.56404413	1.53544255	1.02860158	25.506962	**8.44489538**
7840	**3.732163**	**38.1379884**	3.619827	2.2392978	1.3805292	26.8874912	**8.90196372**
8145	**3.830457**	**36.5087282**	1.84007873	1.16828939	0.67178934	27.5592806	**9.12438106**
8810	**3.965862**	**34.2643392**	4.01197493	2.63729823	1.3746767	28.9339572	**9.57951174**
9145	**4.117315**	**31.7539485**	2.02107008	1.37930053	0.64176955	29.5757268	**9.79199007**
9740	**4.200564**	**30.3740648**	3.58966178	2.49933558	1.0903262	30.666053	**10.1529774**
10720	**4.263753**	**29.3266833**	5.9123841	4.17847794	1.73390616	32.3999592	**10.7270425**
11190	**4.340984**	**28.0465503**	2.83553115	2.04026248	0.79526867	33.1952278	**10.9903416**
12800	**4.441284**	**26.3840399**	9.71320245	7.15046724	2.56273521	35.757963	**11.8388171**
13110	**4.571674**	**24.2227764**	1.87024395	1.41721894	0.45302501	36.210988	**11.9888055**
14820	**4.688022**	**22.2942643**	10.316507	8.01651762	2.29998933	38.5109774	**12.7502905**
15600	**4.792334**	**20.5652535**	4.7057751	3.73802052	0.96775458	39.478732	**13.0706966**
16875	**4.901661**	**18.7531172**	7.69213238	6.24961778	1.4425146	40.9212466	**13.5482872**
17130	**4.942784**	**18.0714879**	1.53842648	1.26040992	0.27801656	41.1992631	**13.6403334**
18820	**5.174477**	**14.2310889**	10.1958461	8.74486613	1.45097992	42.650243	**14.1207267**
19810	**5.233654**	**13.2502078**	5.97271455	5.18131746	0.79139709	43.4416401	**14.382744**
20740	**5.344987**	**11.4048213**	5.61073185	4.97083791	0.63989394	44.0815341	**14.5946014**
21195	**5.433251**	**9.94181214**	2.74503548	2.47212921	0.27290627	44.3544403	**14.6849557**
22810	**5.515497**	**8.57855362**	9.74336768	8.90752766	0.83584002	45.1902803	**14.9616873**
23155	**5.547593**	**8.04655029**	2.08140053	1.91391959	0.16748094	45.3577613	**15.0171372**
24980	**5.620812**	**6.83291771**	11.0103071	10.2579819	0.75232522	46.1100865	**15.2662186**
25820	**5.704061**	**5.45303408**	5.0677578	4.79141124	0.27634656	46.3864331	**15.3577119**
26730	**5.738163**	**4.88778055**	5.49007095	5.22172833	0.26834262	46.6547757	**15.4465553**
27130	**5.804361**	**3.79052369**	2.413218	2.3217444	0.0914736	46.7462493	**15.4768406**

28700	**5.842475**	**3.15876974**	9.47188065	9.17268575	0.2991949	47.0454442	**15.5758986**
29670	**5.892625**	**2.32751455**	5.85205365	5.71584625	0.1362074	47.1816516	**15.6209944**
30730	**5.916697**	**1.92851205**	6.3950277	6.27169882	0.12332888	47.3049805	**15.6618264**
31205	**5.919706**	**1.87863674**	2.86569638	2.81186035	0.05383602	47.3588165	**15.6796505**
32800	**5.942775**	**1.49625935**	9.62270678	9.47872613	0.14398065	47.5027971	**15.7273199**
33270	**5.965844**	**1.11388196**	2.83553115	2.80394668	0.03158447	47.5343816	**15.737777**
34770	**6.004961**	**0.46550291**	9.0495675	9.0074415	0.042126	47.5765076	**15.7517241**
35745	**6.034048**	**0**	5.88221888	5.8831968	0	47.5765076	**15.7517241**
36235	**6.036054**	**0**	2.95619205	2.95766646	0	47.5765076	**15.7517241**
37980	**6.039063**	**0**	10.5276635	10.5381649	0	47.5765076	**15.7517241**
38180	**6.018**	**0**	1.206609	1.2036	0	47.5765076	**15.7517241**
39920	**6.123315**	**0**	10.4974983	10.6545681	0	47.5765076	**15.7517241**
40740	**6.034048**	**0**	4.9470969	4.94791936	0	47.5765076	**15.7517241**
41185	**6.033045**	**0**	2.68470503	2.68470503	0	47.5765076	**15.7517241**
42820	**6.035051**	**0**	9.86402858	9.86730839	0	47.5765076	**15.7517241**
43110	**6.018**	**0**	1.74958305	1.74522	0	47.5765076	**15.7517241**
44805	**6.093225**	**0**	10.2260113	10.3280164	0	47.5765076	**15.7517241**
45870	**6.062132**	**0**	6.42519293	6.45617058	0	47.5765076	**15.7517241**
46220	**6.113285**	**0**	2.11156575	2.13964975	0	47.5765076	**15.7517241**
47720	**6.135351**	**0**	9.0495675	9.2030265	0	47.5765076	**15.7517241**
48180	**6.126324**	**0**	2.7752007	2.81810904	0	47.5765076	**15.7517241**
49310	**6.016997**	**0**	6.81734085	6.79920661	0	47.5765076	**15.7517241**
50725	**6.047087**	**0**	8.53675868	8.55662811	0	47.5765076	**15.7517241**
51515	**6.053105**	**0**	4.76610555	4.78195295	0	47.5765076	**15.7517241**

Table A109 b: Zn (II)

Volume treated (ml)	**Zn conc. (mg/l)**	**Removal ratio (%)**	Amount of Zn in the influent (mg)	approx. amount of Zn in the effluent (mg)	approx. Zn uptaken at each stage (mg)	approx. amount of adsorbed Zn (mg)	**approx. Zn uptake by the biomass (mg/g)**
0	**6.537554**	**100**	0	0	0	0	**0**
100	**0.0905709**	**98.6146057**	0.6537554	0.00905709	0.64469831	0.64469831	**0.21344799**
270	**1.078225**	**83.5072108**	1.11138418	0.18329825	0.92808593	1.57278424	**0.52072051**
570	**2.403188**	**63.2402577**	1.9612662	0.7209564	1.2403098	2.81309404	**0.93136473**
820	**3.234675**	**50.5216324**	1.6343885	0.80866875	0.82571975	3.63881379	**1.20474566**
1160	**3.895652**	**40.4111691**	2.22276836	1.32452168	0.89824668	4.53706047	**1.50213895**
1810	**4.639878**	**29.027309**	4.2494101	3.0159207	1.2334894	5.77054987	**1.91052505**
2100	**4.917709**	**24.7775391**	1.89589066	1.42613561	0.46975505	6.24030492	**2.06605248**
2750	**5.3159**	**18.6867137**	4.2494101	3.455335	0.7940751	7.03438002	**2.32895644**
3170	**5.531545**	**15.3881559**	2.74577268	2.3232489	0.42252378	7.4569038	**2.46884644**
3790	**5.615797**	**14.099417**	4.05328348	3.48179414	0.57148934	8.02839314	**2.65805626**
4110	**5.691022**	**12.9487573**	2.09201728	1.82112704	0.27089024	8.29928338	**2.74774314**
4715	**5.849496**	**10.5247008**	3.95522017	3.53894508	0.41627509	8.71555847	**2.88556432**
5120	**5.973868**	**8.62227677**	2.64770937	2.41941654	0.22829283	8.9438513	**2.96114796**
5820	**6.036054**	**7.67106474**	4.5762878	4.2252378	0.35105	9.2949013	**3.07737429**
6280	**6.150396**	**5.92206198**	3.00727484	2.82918216	0.17809268	9.47299398	**3.13633756**
6815	**6.216594**	**4.90948144**	3.49759139	3.32587779	0.1717136	9.64470758	**3.19318884**
7240	**6.263735**	**4.18840135**	2.77846045	2.66208738	0.11637308	9.76108066	**3.23171787**
7840	**6.316894**	**3.37526849**	3.9225324	3.7901364	0.132396	9.89347666	**3.2755518**
8145	**6.374065**	**2.50076711**	1.99395397	1.94408983	0.04986414	9.9433408	**3.29206092**
8810	**6.417194**	**1.84105554**	4.34747341	4.26743401	0.0800394	10.0233802	**3.31856052**
9145	**6.446281**	**1.39613378**	2.19008059	2.15950414	0.03057646	10.0539567	**3.32868383**
9740	**6.506461**	**0.47560601**	3.88984463	3.8713443	0.01850033	10.072457	**3.33480896**

10720	**6.535548**	**0.03068426**	6.40680292	6.40483704	0.00196588	10.0744229	**3.33545983**
11190	**6.631836**	**0**	3.07265038	3.11696292	0	10.0744229	**3.33545983**
12800	**6.528527**	**0**	10.5254619	10.5109285	0	10.0744229	**3.33545983**
13110	**6.616791**	**0**	2.02664174	2.05120521	0	10.0744229	**3.33545983**
14820	**6.54959**	**0**	11.1792173	11.1997989	0	10.0744229	**3.33545983**
15600	**6.540563**	**0**	5.09929212	5.10163914	0	10.0744229	**3.33545983**
16875	**6.538557**	**0**	8.33538135	8.33666018	0	10.0744229	**3.33545983**
17130	**6.537554**	**0**	1.66707627	1.66707627	0	10.0744229	**3.33545983**
18820	**6.53956**	**0**	11.0484663	11.0518564	0	10.0744229	**3.33545983**
19810	**6.540563**	**0**	6.47217846	6.47515737	0	10.0744229	**3.33545983**
20740	**6.53956**	**0**	6.07992522	6.0817908	0	10.0744229	**3.33545983**
21195	**6.554605**	**0**	2.97458707	2.98234528	0	10.0744229	**3.33545983**
22810	**6.564635**	**0**	10.5581497	10.6018855	0	10.0744229	**3.33545983**
23155	**6.550593**	**0**	2.25545613	2.25995459	0	10.0744229	**3.33545983**
24980	**6.560623**	**0**	11.9310361	11.973137	0	10.0744229	**3.33545983**
25820	**6.6198**	**0**	5.49154536	5.560632	0	10.0744229	**3.33545983**
26730	**6.542569**	**0**	5.94917414	5.95373779	0	10.0744229	**3.33545983**
27130	**6.540563**	**0**	2.6150216	2.6162252	0	10.0744229	**3.33545983**
28700	**6.543572**	**0**	10.2639598	10.273408	0	10.0744229	**3.33545983**
29670	**6.538557**	**0**	6.34142738	6.34240029	0	10.0744229	**3.33545983**
30730	**6.536551**	**0**	6.92980724	6.92874406	0	10.0744229	**3.33545983**
31205	**6.53956**	**0**	3.10533815	3.106291	0	10.0744229	**3.33545983**
32800	**6.538557**	**0**	10.4273986	10.4289984	0	10.0744229	**3.33545983**
33270	**6.537554**	**0**	3.07265038	3.07265038	0	10.0744229	**3.33545983**
34770	**6.53956**	**0**	9.806331	9.80934	0	10.0744229	**3.33545983**
35745	**6.540563**	**0**	6.37411515	6.37704893	0	10.0744229	**3.33545983**
36235	**6.541566**	**0**	3.20340146	3.20536734	0	10.0744229	**3.33545983**
37980	**6.538557**	**0**	11.4080317	11.409782	0	10.0744229	**3.33545983**
38180	**6.543572**	**0**	1.3075108	1.3087144	0	10.0744229	**3.33545983**
39920	**6.544575**	**0**	11.375344	11.3875605	0	10.0744229	**3.33545983**
40740	**6.548587**	**0**	5.36079428	5.36984134	0	10.0744229	**3.33545983**
41185	**6.54959**	**0**	2.90921153	2.91456755	0	10.0744229	**3.33545983**
42820	**6.548587**	**0**	10.6889008	10.7069397	0	10.0744229	**3.33545983**
43110	**6.537554**	**0**	1.89589066	1.89589066	0	10.0744229	**3.33545983**
44805	**6.537554**	**0**	11.081154	11.081154	0	10.0744229	**3.33545983**
45870	**6.538557**	**0**	6.96249501	6.96356321	0	10.0744229	**3.33545983**
46220	**6.53956**	**0**	2.2881439	2.288846	0	10.0744229	**3.33545983**
47720	**6.536551**	**0**	9.806331	9.8048265	0	10.0744229	**3.33545983**
48180	**6.537554**	**0**	3.00727484	3.00727484	0	10.0744229	**3.33545983**
49310	**6.542569**	**0**	7.38743602	7.39310297	0	10.0744229	**3.33545983**
50725	**6.538557**	**0**	9.25063891	9.25205816	0	10.0744229	**3.33545983**
51515	**6.543572**	**0**	5.16466766	5.16942188	0	10.0744229	**3.33545983**

Table A109 c: Cr (VI)

Volume treated (ml)	**Cr conc. (mg/l)**	**Removal ratio (%)**	Amount of Cr in the influent (mg)	approx. amount of Cr in the effluent (mg)	approx. uptaken Cr at each stage (mg)	approx. amount of adsorbed Cr (mg)	**approx. Cr uptake by the biomass (mg/g)**
0	**6.505458**	**100**	0	0	0	0	**0**
100	**0.024072**	**99.6299722**	0.6505458	0.0024072	0.6481386	0.6481386	**0.21458701**
270	**3.443299**	**47.0706136**	1.10592786	0.58536083	0.52056703	1.16870563	**0.38693737**
570	**5.939766**	**8.69565217**	1.9516374	1.7819298	0.1697076	1.33841323	**0.4431245**
820	**6.18851**	**4.87203207**	1.6263645	1.5471275	0.079237	1.41765023	**0.46935844**
1160	**6.282792**	**3.42275671**	2.21185572	2.13614928	0.07570644	1.49335667	**0.49442348**
1810	**6.342972**	**2.49768733**	4.2285477	4.1229318	0.1056159	1.59897257	**0.529391**
2100	**6.405158**	**1.5417823**	1.88658282	1.85749582	0.029087	1.62805957	**0.53902118**
2750	**6.420203**	**1.31051496**	4.2285477	4.17313195	0.05541575	1.68347532	**0.55736834**
3170	**6.471356**	**0.52420598**	2.73229236	2.71796952	0.01432284	1.69779816	**0.56211037**
3790	**6.506461**	**0**	4.03338396	4.03400582	0	1.69779816	**0.56211037**
4110	**6.510473**	**0**	2.08174656	2.08335136	0	1.69779816	**0.56211037**
4715	**6.508467**	**0**	3.93580209	3.93762254	0	1.69779816	**0.56211037**
5120	**6.507464**	**0**	2.63471049	2.63552292	0	1.69779816	**0.56211037**
5820	**6.520503**	**0**	4.5538206	4.5643521	0	1.69779816	**0.56211037**
6280	**6.5195**	**0**	2.99251068	2.99897	0	1.69779816	**0.56211037**
6815	**6.530533**	**0**	3.48042003	3.49383516	0	1.69779816	**0.56211037**
7240	**6.510473**	**0**	2.76481965	2.76695103	0	1.69779816	**0.56211037**
7840	**6.50947**	**0**	3.9032748	3.905682	0	1.69779816	**0.56211037**
8145	**6.514485**	**0**	1.98416469	1.98691793	0	1.69779816	**0.56211037**
8810	**6.511476**	**0**	4.32612957	4.33013154	0	1.69779816	**0.56211037**
9145	**6.506461**	**0**	2.17932843	2.17966444	0	1.69779816	**0.56211037**
9740	**6.505458**	**0**	3.87074751	3.87074751	0	1.69779816	**0.56211037**
10720	**6.504455**	**0**	6.37534884	6.3743659	0	1.69779816	**0.56211037**
11190	**6.510473**	**0**	3.05756526	3.05992231	0	1.69779816	**0.56211037**
12800	**6.508467**	**0**	10.4737874	10.4786319	0	1.69779816	**0.56211037**
13110	**6.510473**	**0**	2.01669198	2.01824663	0	1.69779816	**0.56211037**
14820	**6.511476**	**0**	11.1243332	11.134624	0	1.69779816	**0.56211037**
15600	**6.50947**	**0**	5.07425724	5.0773866	0	1.69779816	**0.56211037**
16875	**6.5195**	**0**	8.29445895	8.3123625	0	1.69779816	**0.56211037**
17130	**6.517494**	**0**	1.65889179	1.66196097	0	1.69779816	**0.56211037**
18820	**6.516491**	**0**	10.994224	11.0128698	0	1.69779816	**0.56211037**
19810	**6.507464**	**0**	6.44040342	6.44238936	0	1.69779816	**0.56211037**
20740	**6.508467**	**0**	6.05007594	6.05287431	0	1.69779816	**0.56211037**
21195	**6.510473**	**0**	2.95998339	2.96226522	0	1.69779816	**0.56211037**
22810	**6.511476**	**0**	10.5063147	10.5160337	0	1.69779816	**0.56211037**
23155	**6.506461**	**0**	2.24438301	2.24472905	0	1.69779816	**0.56211037**
24980	**6.504455**	**0**	11.8724609	11.8706304	0	1.69779816	**0.56211037**
25820	**6.510473**	**0**	5.46458472	5.46879732	0	1.69779816	**0.56211037**
26730	**6.510473**	**0**	5.91996678	5.92453043	0	1.69779816	**0.56211037**
27130	**6.50947**	**0**	2.6021832	2.603788	0	1.69779816	**0.56211037**
28700	**6.511476**	**0**	10.2135691	10.2230173	0	1.69779816	**0.56211037**
29670	**6.514485**	**0**	6.31029426	6.31905045	0	1.69779816	**0.56211037**
30730	**6.506461**	**0**	6.89578548	6.89684866	0	1.69779816	**0.56211037**
31205	**6.505458**	**0**	3.09009255	3.09009255	0	1.69779816	**0.56211037**
32800	**6.506461**	**0**	10.3762055	10.3778053	0	1.69779816	**0.56211037**
33270	**6.508467**	**0**	3.05756526	3.05897949	0	1.69779816	**0.56211037**
34770	**6.506461**	**0**	9.758187	9.7596915	0	1.69779816	**0.56211037**
35745	**6.50947**	**0**	6.34282155	6.34673325	0	1.69779816	**0.56211037**
36235	**6.506461**	**0**	3.18767442	3.18816589	0	1.69779816	**0.56211037**

37980	**6.508467**	**0**	11.3520242	11.3572749	0	1.69779816	**0.56211037**
38180	**6.506461**	**0**	1.3010916	1.3012922	0	1.69779816	**0.56211037**
39920	**6.506461**	**0**	11.3194969	11.3212421	0	1.69779816	**0.56211037**
40740	**6.50947**	**0**	5.33447556	5.3377654	0	1.69779816	**0.56211037**
41185	**6.512479**	**0**	2.89492881	2.89805316	0	1.69779816	**0.56211037**
42820	**6.513482**	**0**	10.6364238	10.6495431	0	1.69779816	**0.56211037**
43110	**6.510473**	**0**	1.88658282	1.88803717	0	1.69779816	**0.56211037**
44805	**6.511476**	**0**	11.0267513	11.0369518	0	1.69779816	**0.56211037**
45870	**6.508467**	**0**	6.92831277	6.93151736	0	1.69779816	**0.56211037**
46220	**6.506461**	**0**	2.2769103	2.27726135	0	1.69779816	**0.56211037**
47720	**6.507464**	**0**	9.758187	9.761196	0	1.69779816	**0.56211037**
48180	**6.510473**	**0**	2.99251068	2.99481758	0	1.69779816	**0.56211037**
49310	**6.50947**	**0**	7.35116754	7.3557011	0	1.69779816	**0.56211037**
50725	**6.5195**	**0**	9.20522307	9.2250925	0	1.69779816	**0.56211037**
51515	**6.508467**	**0**	5.13931182	5.14168893	0	1.69779816	**0.56211037**

Table A109 d: Ni (II)

Volume treated (ml)	**Ni conc. (mg/l)**	**Removal ratio (%)**	Amount of Ni in the influent (mg)	approx. amount of Ni in the effluent (mg)	approx. uptaken Ni at each stage (mg)	approx. amount of adsorbed Ni (mg)	**approx. Ni uptake by the biomass (mg/g)**
0	**6.434245**	**100**	0	0	0	0	**0**
100	**0.029087**	**99.5479345**	0.6434245	0.0029087	0.6405158	0.6405158	**0.21206324**
270	**1.095276**	**82.9773967**	1.09382165	0.18619692	0.90762473	1.54814053	**0.51256143**
570	**2.563668**	**60.1558846**	1.9302735	0.7691004	1.1611731	2.70931363	**0.89700491**
820	**3.292849**	**48.8230709**	1.60856125	0.82321225	0.785349	3.49466263	**1.15701981**
1160	**3.945802**	**38.6749805**	2.1876433	1.34157268	0.84607062	4.34073325	**1.43713854**
1810	**4.693037**	**27.0615744**	4.18225925	3.05047405	1.1317852	5.47251845	**1.81185222**
2100	**4.906676**	**23.7412315**	1.86593105	1.42293604	0.44299501	5.91551346	**1.95851988**
2750	**5.301858**	**17.5993765**	4.18225925	3.4462077	0.73605155	6.65156501	**2.20221329**
3170	**5.421215**	**15.7443492**	2.7023829	2.2769103	0.4254726	7.07703761	**2.3430796**
3790	**5.530542**	**14.0452065**	3.9892319	3.42893604	0.56029586	7.63733347	**2.52858346**
4110	**5.671965**	**11.847233**	2.0589584	1.8150288	0.2439296	7.88126307	**2.60934415**
4715	**5.760229**	**10.4754482**	3.89271823	3.48493855	0.40777968	8.28904275	**2.74435265**
5120	**5.914691**	**8.07482463**	2.60586923	2.39544986	0.21041937	8.49946212	**2.81401871**
5820	**5.995934**	**6.812159**	4.5039715	4.1971538	0.3068177	8.80627982	**2.91560052**
6280	**6.016997**	**6.48480125**	2.9597527	2.76781862	0.19193408	8.9982139	**2.97914644**
6815	**6.030036**	**6.28215121**	3.44232108	3.22606926	0.21625182	9.21446572	**3.05074352**
7240	**6.163435**	**4.20888542**	2.73455413	2.61945988	0.11509425	9.32955997	**3.08884915**
7840	**6.317897**	**1.80826189**	3.860547	3.7907382	0.0698088	9.39936877	**3.11196158**
8145	**6.339963**	**1.46531567**	1.96244473	1.93368872	0.02875601	9.42812478	**3.12148218**
8810	**6.373062**	**0.95089634**	4.27877293	4.23808623	0.0406867	9.46881147	**3.13495281**
9145	**6.418197**	**0.24941543**	2.15547208	2.150096	0.00537608	9.47418755	**3.13673273**
9740	**6.427224**	**0.10911925**	3.82837578	3.82419828	0.00417749	9.47836505	**3.13811583**
10720	**6.435248**	**0**	6.3055601	6.30654304	0	9.47836505	**3.13811583**
11190	**6.434245**	**0**	3.02409515	3.02409515	0	9.47836505	**3.13811583**
12800	**6.43926**	**0**	10.3591345	10.3672086	0	9.47836505	**3.13811583**
13110	**6.43926**	**0**	1.99461595	1.9961706	0	9.47836505	**3.13811583**
14820	**6.440263**	**0**	11.002559	11.0128497	0	9.47836505	**3.13811583**
15600	**6.436251**	**0**	5.0187111	5.02027578	0	9.47836505	**3.13811583**
16875	**6.437254**	**0**	8.20366238	8.20749885	0	9.47836505	**3.13811583**
17130	**6.438257**	**0**	1.64073248	1.64175554	0	9.47836505	**3.13811583**
18820	**6.438257**	**0**	10.8738741	10.8806543	0	9.47836505	**3.13811583**
19810	**6.433242**	**0**	6.36990255	6.36890958	0	9.47836505	**3.13811583**

20740	**6.437254**	**0**	5.98384785	5.98664622	0	9.47836505	**3.13811583**
21195	**6.43926**	**0**	2.92758148	2.9298633	0	9.47836505	**3.13811583**
22810	**6.436251**	**0**	10.3913057	10.3945454	0	9.47836505	**3.13811583**
23155	**6.43926**	**0**	2.21981453	2.2215447	0	9.47836505	**3.13811583**
24980	**6.433242**	**0**	11.7424971	11.7406667	0	9.47836505	**3.13811583**
25820	**6.437254**	**0**	5.4047658	5.40729336	0	9.47836505	**3.13811583**
26730	**6.438257**	**0**	5.85516295	5.85881387	0	9.47836505	**3.13811583**
27130	**6.43926**	**0**	2.573698	2.575704	0	9.47836505	**3.13811583**
28700	**6.435248**	**0**	10.1017647	10.1033394	0	9.47836505	**3.13811583**
29670	**6.436251**	**0**	6.24121765	6.24316347	0	9.47836505	**3.13811583**
30730	**6.437254**	**0**	6.8202997	6.82348924	0	9.47836505	**3.13811583**
31205	**6.438257**	**0**	3.05626638	3.05817208	0	9.47836505	**3.13811583**
32800	**6.437254**	**0**	10.2626208	10.2674201	0	9.47836505	**3.13811583**
33270	**6.438257**	**0**	3.02409515	3.02598079	0	9.47836505	**3.13811583**
34770	**6.440263**	**0**	9.6513675	9.6603945	0	9.47836505	**3.13811583**
35745	**6.437254**	**0**	6.27338888	6.27632265	0	9.47836505	**3.13811583**
36235	**6.43926**	**0**	3.15278005	3.1552374	0	9.47836505	**3.13811583**
37980	**6.434245**	**0**	11.2277575	11.2277575	0	9.47836505	**3.13811583**
38180	**6.436251**	**0**	1.286849	1.2872502	0	9.47836505	**3.13811583**
39920	**6.432239**	**0**	11.1955863	11.1920959	0	9.47836505	**3.13811583**
40740	**6.43926**	**0**	5.2760809	5.2801932	0	9.47836505	**3.13811583**
41185	**6.438257**	**0**	2.86323903	2.86502437	0	9.47836505	**3.13811583**
42820	**6.437254**	**0**	10.5199906	10.5249103	0	9.47836505	**3.13811583**
43110	**6.436251**	**0**	1.86593105	1.86651279	0	9.47836505	**3.13811583**
44805	**6.432239**	**0**	10.9060453	10.9026451	0	9.47836505	**3.13811583**
45870	**6.432239**	**0**	6.85247093	6.85033454	0	9.47836505	**3.13811583**
46220	**6.437254**	**0**	2.25198575	2.2530389	0	9.47836505	**3.13811583**
47720	**6.436251**	**0**	9.6513675	9.6543765	0	9.47836505	**3.13811583**
48180	**6.43926**	**0**	2.9597527	2.9620596	0	9.47836505	**3.13811583**
49310	**6.438257**	**0**	7.27069685	7.27523041	0	9.47836505	**3.13811583**
50725	**6.437254**	**0**	9.10445668	9.10871441	0	9.47836505	**3.13811583**
51515	**6.438257**	**0**	5.08305355	5.08622303	0	9.47836505	**3.13811583**

Table A110: pH changes during the adsorption experiment of Cu (II), Zn (II), Cr (VI) and Ni (II)

Volume treated (ml)	pH	Volume treated (ml)	pH	Volume treated (ml)	pH
0	5	21150	4.59	46150	5
1150	3.75	26150	4.73	51170	5.01
6550	4.05	31150	4.82		
11150	4.29	36150	4.92		
16150	4.46	41150	4.96		

Table A111: Removal of Cu (II), Zn (II), Cr (VI) and Ni (II) using control column of un-loaded Hypol foam at Cu (II), Zn (II), Cr (VI) and Ni (II) initial concentrations of 6 mgl^{-1}, T 20° C, solution pH 5.0 and 4.7 l/hr flow rate

Volume treated (ml)	Cu (II) concentration (mg/l)	Zn (II) concentration (mg/l)	Ni (II) concentration (mg/l)	Cr (VI) concentration (mg/l)
0	6.125	5.85	6.35	6.201
105	6.115	5.845	6.315	6.199
390	6.135	5.91	6.351	6.211
630	6.12	5.88	6.34	6.212
850	6.118	5.901	6.299	6.215
1235	6.19	5.795	6.401	6.201
1700	6.1	5.785	6.4	6.199
2210	6.095	5.845	6.358	6.178
2770	6.115	5.815	6.375	6.158
3400	6.085	5.8	6.358	6.179
3750	6.09	5.725	6.322	6.189
4420	6.185	5.748	6.3	6.201
4800	6.143	5.758	6.39	6.115
5540	6.12	5.799	6.345	6.158
5830	6.125	5.815	6.41	6.2
6700	6.13	5.841	6.388	6.24
6860	6.109	5.835	6.401	6.25
7110	6.112	5.847	6.38	6.25
7540	6.118	5.91	6.38	6.198
8110	6.117	5.86	6.35	6.178
8920	6.115	5.9	6.39	6.205
9780	6.127	5.87	6.378	6.213
10550	6.126	5.89	6.309	6.215
11800	6.155	5.745	6.299	6.201
12830	6.151	5.74	6.289	6.235
13770	6.145	5.781	6.278	6.258
14910	6.035	5.86	6.295	6.211
15860	6.055	5.86	6.315	6.245
16900	6.102	5.799	6.325	6.195
17975	6.105	5.85	6.311	6.185
18995	6.115	5.746	6.325	6.175
19665	6.125	5.813	6.37	6.2
20300	6.124	5.845	6.356	6.25
21710	6.1	5.89	6.358	6.201
22800	6.085	5.699	6.378	6.205
23970	6.155	5.711	6.35	6.205
24800	6.141	5.745	6.29	6.24
25400	6.135	5.768	6.301	6.189
26650	6.125	5.81	6.345	6.189
27695	6.122	5.87	6.298	6.154
28980	6.1	5.86	6.35	6.175
29890	6.123	5.85	6.299	6.189
30440	6.113	5.841	6.358	6.188
31735	6.109	5.835	6.37	6.201
32920	6.115	5.791	6.4	6.198

33590	6.119	5.87	6.41	6.258
34930	6.127	5.815	6.358	6.23
35750	6.128	5.9	6.39	6.24
36810	6.122	5.859	6.258	6.25
37910	6.125	5.901	6.37	6.215
38720	6.129	5.91	6.35	6.215
39635	6.111	5.845	6.36	6.198
40995	6.089	5.862	6.259	6.215
41260	6.105	5.87	6.289	6.215
42670	6.115	5.789	6.459	6.2
43700	6.125	5.784	6.345	6.189
44745	6.131	5.726	6.38	6.199
45260	6.124	5.9	6.39	6.201
46850	6.078	5.84	6.375	6.025
47230	6.128	5.855	6.4	6.2
48725	6.119	5.8	6.389	6.213
49200	6.078	5.8	6.321	6.2

7- Tables of the adsorption of Cu (II), Zn (II), Cr (VI) and Ni (II) from a simulated solution of automatic plating of zinc base die casting industry wastewater using two columns of seaweed-Hypol foam connected on series

Table A112: Carbon measured in the effluent during the first column conditioning process before the adsorption experiment

Volume of D.W (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)	Amount of IC (mg)
0	0	0	0	0
50	1193	43.99	59.65	2.1995
100	828.1	32.97	41.405	1.6485
200	650.25	15.33	65.025	1.533
400	321.5	7.5	64.3	1.5
600	195.5	3.6	39.1	0.72
800	85.65	1.5	17.13	0.3
1000	55.1	0	11.02	0
1130	30.2	0	3.926	0
1530	11.5	0	4.6	0
1870	8.5	0	2.89	0
2120	5	0	1.25	0
2580	0	0	0	0
2890	0	0	0	0
3120	0	0	0	0
3560	0	0	0	0
3870	0	0	0	0
4130	0	0	0	0
4580	0	0	0	0
4880	0	0	0	0
5140	0	0	0	0

5900	0	0	0	0
6140	0	0	0	0
6860	0	0	0	0
7160	0	0	0	0
Sum (mg)			**310.296**	**7.901**

Table A113: Carbon measured in the effluent during the second column conditioning process before the adsorption experiment

Volume of D.W (ml)	TOC (mg/l)	IC (mg/l)	Amount of TOC (mg)	Amount of IC (mg)
0	0	0	0	0
50	980	33.5	49	1.675
100	745.1	22.6	37.255	1.13
200	643.5	15.48	64.35	1.548
400	401.3	10.9	80.26	2.18
600	145.5	7.56	29.1	1.512
800	85.5	3	17.1	0.6
1000	45.6	0	9.12	0
1110	34.03	0	3.7433	0
1490	23.13	0	8.7894	0
1840	19.5	0	6.825	0
2120	15.56	0	4.3568	0
2580	11.4	0	5.244	0
2870	9.85	0	2.8565	0
3120	7.25	0	1.8125	0
3530	5.2	0	2.132	0
3840	0	0	0	0
4110	0	0	0	0
4580	0	0	0	0
4870	0	0	0	0
5210	0	0	0	0
5830	0	0	0	0
6210	0	0	0	0
6860	0	0	0	0
7200	0	0	0	0
Sum (mg)			**321.9445**	**8.645**

Tables A114: Adsorption of Cu (II), Zn (II), Cr (VI) and Ni (II) using two columns of cast in seaweed-Hypol foam connected together at series at Cu (II), Zn (II), Cr (VI) and Ni (II) initial concentrations of 6 mgl^{-1}, T 20° C, influent pH 4.98, 4.7 l/hr flow rate and biomass ratio of around 7 % in each column (net dry wt. of biomass in the first column = 3.23 g and in the second column = 3.18 g that makes a total biomass weight of 6.41876g)

Table A114 a: Cu (II)

Volume treated (ml)	**Copper conc. (mg/l)**	**Removal ratio (%)**	Amount of copper in the influent (mg)	approx. amount of copper in the effluent (mg)	approx. copper uptaken at each stage (mg)	approx. amount of adsorbed copper (mg)	**approx. copper uptake by the biomass (mg/g)**
0	**6.813379**	**100**	0	0	0	0	**0**
100	**0.078234**	**98.8517592**	0.6813379	0.0078234	0.6735145	0.6735145	**0.1049293**
280	**0.095285**	**98.6015015**	1.22640822	0.0171513	1.20925692	1.88277142	**0.29332387**
605	**0.139417**	**97.9537759**	2.21434818	0.04531053	2.16903765	4.05180907	**0.63124621**
830	**0.228684**	**96.6436037**	1.53301028	0.0514539	1.48155638	5.53336545	**0.86206331**
1260	**0.439314**	**93.5521861**	2.92975297	0.18890502	2.74084795	8.2742134	**1.28907008**
1820	**0.727175**	**89.3272486**	3.81549224	0.407218	3.40827424	11.6824876	**1.82005763**
2100	**0.869601**	**87.2368615**	1.90774612	0.24348828	1.66425784	13.3467455	**2.07933847**
2760	**1.18354**	**82.6291771**	4.49683014	0.7811364	3.71569374	17.0624392	**2.65822003**
3110	**1.339005**	**80.3474165**	2.38468265	0.46865175	1.9160309	18.9784701	**2.95672552**
3810	**1.605803**	**76.4316208**	4.7693653	1.1240621	3.6453032	22.6237733	**3.52464069**
4125	**1.740205**	**74.4590019**	2.14621439	0.54816458	1.59804981	24.2218231	**3.77360673**
4790	**1.979922**	**70.9406742**	4.53089704	1.31664813	3.21424891	27.436072	**4.27436637**
5140	**2.077213**	**69.5127337**	2.38468265	0.72702455	1.6576581	29.0937301	**4.53261901**
5800	**2.293861**	**66.3329898**	4.49683014	1.51394826	2.98288188	32.076612	**4.99733313**
6230	**2.389146**	**64.9344914**	2.92975297	1.02733278	1.90242019	33.9790322	**5.29371815**
6820	**2.51753**	**63.0501987**	4.01989361	1.4853427	2.53455091	36.5135831	**5.68858514**
7105	**2.56768**	**62.3141469**	1.94181302	0.7317888	1.21002422	37.7236073	**5.87709925**
7840	**2.752232**	**59.6054762**	5.00783357	2.02289052	2.98494305	40.7085504	**6.34213449**
8120	**2.779313**	**59.2080082**	1.90774612	0.77820764	1.12953848	41.8380889	**6.51810943**
8800	**2.89867**	**57.4562049**	4.63309772	1.9710956	2.66200212	44.500091	**6.93283251**
9110	**2.915721**	**57.2059473**	2.11214749	0.90387351	1.20827398	45.708365	**7.12107395**
9810	**3.067174**	**54.9830708**	4.7693653	2.1470218	2.6223435	48.3307085	**7.52961847**
10740	**3.213612**	**52.8337995**	6.33644247	2.98865916	3.34778331	51.6784918	**8.05118192**
11710	**3.431263**	**49.6393346**	6.60897763	3.32832511	3.28065252	54.9591443	**8.56228682**
12150	**3.45032**	**49.3596349**	2.99788676	1.5181408	1.47974596	56.4388902	**8.79282188**
13840	**3.631863**	**46.6951273**	11.5146105	6.13784847	5.37676204	61.8156523	**9.63048737**
14105	**3.68101**	**45.9737966**	1.80554544	0.97546765	0.83007779	62.6457301	**9.75980823**
15980	**3.900667**	**42.7498896**	12.7750856	7.31375063	5.461335	68.1070651	**10.6106497**
16625	**3.932763**	**42.2788164**	4.39462946	2.53663214	1.85799732	69.9650624	**10.9001139**
17140	**3.983916**	**41.5280436**	3.50889019	2.05171674	1.45717345	71.4222358	**11.1271323**
18940	**4.219621**	**38.0686**	12.2640822	7.5953178	4.6687644	76.0910002	**11.8544962**
19700	**4.23266**	**37.8772266**	5.17816804	3.2168216	1.96134644	78.0523467	**12.1600616**
20775	**4.450311**	**34.6827617**	7.32438243	4.78408433	2.5402981	80.5926448	**12.555824**
21610	**4.492437**	**34.0644781**	5.68917147	3.7511849	1.93798657	82.5306313	**12.85775**
22120	**4.514503**	**33.7406153**	3.47482329	2.30239653	1.17242676	83.7030581	**13.0404067**
23900	**4.696046**	**31.0761078**	12.1278146	8.35896188	3.76885274	87.4719108	**13.6275701**
24400	**4.721121**	**30.7080818**	3.4066895	2.3605605	1.046129	88.5180398	**13.7905503**
25660	**4.847499**	**28.8532313**	8.58485754	6.10784874	2.4770088	90.9950486	**14.1764526**

26290	**4.891631**	**28.2055057**	4.29242877	3.08172753	1.21070124	92.2057499	**14.3650722**
27650	**5.020015**	**26.321213**	9.26619544	6.8272204	2.43897504	94.6447249	**14.7450491**
28120	**5.054117**	**25.8206978**	3.20228813	2.37543499	0.82685314	95.4715781	**14.8738676**
29810	**5.123324**	**24.8049463**	11.5146105	8.65841756	2.85619295	98.327771	**15.3188444**
30755	**5.174477**	**24.0541734**	6.43864316	4.88988077	1.54876239	99.8765334	**15.5601317**
31210	**5.214597**	**23.465332**	3.10008745	2.37264164	0.72744581	100.603979	**15.6734632**
32700	**5.254717**	**22.8764905**	10.1519347	7.82952833	2.32240638	102.926386	**16.0352794**
33130	**5.273774**	**22.5967908**	2.92975297	2.26772282	0.66203015	103.588416	**16.1384195**
34970	**5.327936**	**21.8018549**	12.5366174	9.80340224	2.73321512	106.321631	**16.5642371**
35790	**5.377083**	**21.0805241**	5.58697078	4.40920806	1.17776272	107.499394	**16.7477251**
36990	**5.534554**	**18.7693214**	8.1760548	6.6414648	1.53459	109.033984	**16.9868045**
37770	**5.591725**	**17.9302223**	5.31443562	4.3615455	0.95289012	109.986874	**17.1352588**
38110	**5.614794**	**17.5916385**	2.31654886	1.90902996	0.4075189	110.394393	**17.1987476**
39790	**5.641875**	**17.1941705**	11.4464767	9.47835	1.96812672	112.362519	**17.5053693**
40750	**5.714091**	**16.1342559**	6.54084384	5.48552736	1.05531648	113.417836	**17.669781**
41780	**5.740169**	**15.7515089**	7.01778037	5.91237407	1.1054063	114.523242	**17.8419963**
42110	**5.775274**	**15.2362726**	2.24841507	1.90584042	0.34257465	114.865817	**17.8953672**
43790	**5.822415**	**14.5443839**	11.4464767	9.7816572	1.66481952	116.530636	**18.1547356**
44420	**5.891622**	**13.5286324**	4.29242877	3.71172186	0.58070691	117.111343	**18.245206**
45680	**5.919706**	**13.1164434**	8.58485754	7.45882956	1.12602798	118.237371	**18.4206341**
46200	**5.970859**	**12.3656705**	3.54295708	3.10484668	0.4381104	118.675482	**18.4888889**
47750	**6.015994**	**11.7032239**	10.5607375	9.3247907	1.23594675	119.911428	**18.6814416**
48870	**6.023015**	**11.6001767**	7.63098448	6.7457768	0.88520768	120.796636	**18.8193513**
49760	**6.113285**	**10.2752834**	6.06390731	5.44082365	0.62308366	121.41972	**18.9164238**
50800	**6.153405**	**9.68644193**	7.08591416	6.3995412	0.68637296	122.106093	**19.0233564**
51770	**6.216594**	**8.75901663**	6.60897763	6.03009618	0.57888145	122.684974	**19.1135424**
52840	**6.253705**	**8.21433829**	7.29031553	6.69146435	0.59885118	123.283825	**19.2068397**
53140	**6.277777**	**7.86103342**	2.0440137	1.8833331	0.1606806	123.444506	**19.2318727**
54950	**6.316894**	**7.286913**	12.332216	11.4335781	0.89863785	124.343144	**19.3718748**
55620	**6.319903**	**7.24274989**	4.56496393	4.23433501	0.33062892	124.673773	**19.4233847**
56210	**6.371056**	**6.49197704**	4.01989361	3.75892304	0.26097057	124.934743	**19.4640422**
57850	**6.406161**	**5.97674076**	11.1739416	10.506104	0.66783752	125.602581	**19.5680871**
58150	**6.418197**	**5.80008833**	2.0440137	1.9254591	0.1185546	125.721135	**19.5865571**
59950	**6.463332**	**5.13764169**	12.2640822	11.6339976	0.6300846	126.35122	**19.6847203**
60730	**6.516491**	**4.35742676**	5.31443562	5.08286298	0.23157264	126.582793	**19.7207979**
61210	**6.520503**	**4.29854262**	3.27042192	3.12984144	0.14058048	126.723373	**19.7426994**
62760	**6.554605**	**3.79802738**	10.5607375	10.1596378	0.4010997	127.124473	**19.8051882**
63120	**6.576671**	**3.47416458**	2.45281644	2.36760156	0.08521488	127.209688	**19.8184642**
64920	**6.598737**	**3.15030178**	12.2640822	11.8777266	0.3863556	127.596043	**19.8786559**
65150	**6.618797**	**2.85588105**	1.56707717	1.52232331	0.04475386	127.640797	**19.8856283**

Table A114 b: Zn (II)

Volume treated (ml)	**Zn conc. (mg/l)**	**Removal ratio (%)**	Amount of Zn in the influent (mg)	approx. amount of Zn in the effluent (mg)	approx. Zn uptaken at each stage (mg)	approx. amount of adsorbed Zn (mg)	**approx. Zn uptake by the biomass (mg/g)**
0	**6.834442**	**100**	0	0	0	0	**0**
100	**0.05015**	**99.2662166**	0.6834442	0.005015	0.6784292	0.6784292	**0.10569498**
280	**0.212636**	**96.8887584**	1.23019956	0.03827448	1.19192508	1.87035428	**0.29138936**
605	**0.990964**	**85.5004403**	2.22119365	0.3220633	1.89913035	3.76948463	**0.58726185**
830	**1.47441**	**78.4267684**	1.53774945	0.33174225	1.2060072	4.97549183	**0.77515014**
1260	**2.14642**	**68.594071**	2.93881006	0.9229606	2.01584946	6.99134129	**1.08920672**

1820	**3.221636**	**52.8617552**	3.82728752	1.80411616	2.02317136	9.01451265	**1.40440401**
2100	**3.513509**	**48.5911359**	1.91364376	0.98378252	0.92986124	9.94437389	**1.54927051**
2760	**4.165459**	**39.0519519**	4.51073172	2.74920294	1.76152878	11.7059027	**1.82370554**
3110	**4.42323**	**35.2803053**	2.3920547	1.5481305	0.8439242	12.5498269	**1.95518359**
3810	**5.029042**	**26.4162019**	4.7841094	3.5203294	1.26378	13.8136069	**2.15207252**
4125	**5.137366**	**24.8312298**	2.15284923	1.61827029	0.53457894	14.3481858	**2.23535653**
4790	**5.392128**	**21.1036102**	4.54490393	3.58576512	0.95913881	15.3073246	**2.38478429**
5140	**5.47638**	**19.8708541**	2.3920547	1.916733	0.4753217	15.7826463	**2.4588364**
5800	**5.551605**	**18.770179**	4.51073172	3.6640593	0.84667242	16.6293187	**2.59074261**
6230	**5.628836**	**17.6401526**	2.93881006	2.42039948	0.51841058	17.1477293	**2.67150769**
6820	**5.728133**	**16.1872615**	4.03232078	3.37959847	0.65272231	17.8004516	**2.7731977**
7105	**5.875574**	**14.0299384**	1.94781597	1.67453859	0.27327738	18.073729	**2.81577258**
7840	**5.976877**	**12.5476959**	5.02331487	4.3930046	0.63031028	18.7040393	**2.91397094**
8120	**6.137357**	**10.1995891**	1.91364376	1.71845996	0.1951838	18.8992231	**2.94437934**
8800	**6.226624**	**8.89345465**	4.64742056	4.23410432	0.41331624	19.3125393	**3.00877139**
9110	**6.275771**	**8.17434693**	2.11867702	1.94548901	0.17318801	19.4857273	**3.03575299**
9810	**6.319903**	**7.52861755**	4.7841094	4.4239321	0.3601773	19.8459046	**3.09186633**
10740	**6.382089**	**6.61872615**	6.35603106	5.93534277	0.42068829	20.2665929	**3.1574069**
11710	**6.424215**	**6.00234811**	6.62940874	6.23148855	0.39792019	20.6645131	**3.21940035**
12150	**6.474365**	**5.26856472**	3.00715448	2.8487206	0.15843388	20.822947	**3.24408335**
13840	**6.522509**	**4.56413267**	11.550207	11.0230402	0.52716677	21.3501138	**3.32621259**
14105	**6.577674**	**3.75697094**	1.81112713	1.74308361	0.06804352	21.4181573	**3.33681334**
15980	**6.602749**	**3.39007925**	12.8145788	12.3801544	0.43442438	21.8525817	**3.40449391**
16625	**6.638857**	**2.86175521**	4.40821509	4.28206277	0.12615233	21.978734	**3.42414764**
17140	**6.682989**	**2.21602583**	3.51973763	3.44173934	0.0779983	22.0567323	**3.43629928**
18940	**6.723109**	**1.62899912**	12.3019956	12.1015962	0.2003994	22.2571317	**3.46752024**
19700	**6.765235**	**1.01262107**	5.19417592	5.1415786	0.05259732	22.309729	**3.47571457**
20775	**6.807361**	**0.39624303**	7.34702515	7.31791308	0.02911207	22.3388411	**3.48025005**
21610	**6.823409**	**0.16143235**	5.70675907	5.69754652	0.00921256	22.3480536	**3.48168531**
22120	**6.833439**	**0.01467567**	3.48556542	3.48505389	0.00051153	22.3485652	**3.481765**
23900	**6.835445**	**0**	12.1653068	12.1670921	0	22.3485652	**3.481765**
24400	**6.888604**	**0**	3.417221	3.444302	0	22.3485652	**3.481765**
25660	**6.847481**	**0**	8.61139692	8.62782606	0	22.3485652	**3.481765**
26290	**6.822406**	**0**	4.30569846	4.29811578	0	22.3485652	**3.481765**
27650	**6.9207**	**0**	9.29484112	9.412152	0	22.3485652	**3.481765**
28120	**6.921703**	**0**	3.21218774	3.25320041	0	22.3485652	**3.481765**
29810	**6.845475**	**0**	11.550207	11.5688528	0	22.3485652	**3.481765**
30755	**6.834442**	**0**	6.45854769	6.45854769	0	22.3485652	**3.481765**
31210	**6.855505**	**0**	3.10967111	3.11925478	0	22.3485652	**3.481765**
32700	**6.833439**	**0**	10.1833186	10.1818241	0	22.3485652	**3.481765**
33130	**6.832436**	**0**	2.93881006	2.93794748	0	22.3485652	**3.481765**
34970	**6.834442**	**0**	12.5753733	12.5753733	0	22.3485652	**3.481765**
35790	**6.921703**	**0**	5.60424244	5.67579646	0	22.3485652	**3.481765**
36990	**6.9207**	**0**	8.2013304	8.30484	0	22.3485652	**3.481765**
37770	**6.922706**	**0**	5.33086476	5.39971068	0	22.3485652	**3.481765**
38110	**6.917691**	**0**	2.32371028	2.35201494	0	22.3485652	**3.481765**
39790	**6.913679**	**0**	11.4818626	11.6149807	0	22.3485652	**3.481765**
40750	**6.914682**	**0**	6.56106432	6.63809472	0	22.3485652	**3.481765**
41780	**6.915685**	**0**	7.03947526	7.12315555	0	22.3485652	**3.481765**
42110	**6.855505**	**0**	2.25536586	2.26231665	0	22.3485652	**3.481765**
43790	**6.865535**	**0**	11.4818626	11.5340988	0	22.3485652	**3.481765**
44420	**6.875565**	**0**	4.30569846	4.33160595	0	22.3485652	**3.481765**

45680	**6.851493**	**0**	8.61139692	8.63288118	0	22.3485652	**3.481765**
46200	**6.835445**	**0**	3.55390984	3.5544314	0	22.3485652	**3.481765**
47750	**6.839457**	**0**	10.5933851	10.6011584	0	22.3485652	**3.481765**
48870	**6.834442**	**0**	7.65457504	7.65457504	0	22.3485652	**3.481765**
49760	**6.84046**	**0**	6.08265338	6.0880094	0	22.3485652	**3.481765**
50800	**6.841463**	**0**	7.10781968	7.11512152	0	22.3485652	**3.481765**
51770	**6.84046**	**0**	6.62940874	6.6352462	0	22.3485652	**3.481765**
52840	**6.839457**	**0**	7.31285294	7.31821899	0	22.3485652	**3.481765**
53140	**6.833439**	**0**	2.0503326	2.0500317	0	22.3485652	**3.481765**
54950	**6.835445**	**0**	12.37034	12.3721555	0	22.3485652	**3.481765**
55620	**6.819397**	**0**	4.57907614	4.56899599	0	22.3485652	**3.481765**
56210	**6.83043**	**0**	4.03232078	4.0299537	0	22.3485652	**3.481765**
57850	**6.835445**	**0**	11.2084849	11.2101298	0	22.3485652	**3.481765**
58150	**6.837451**	**0**	2.0503326	2.0512353	0	22.3485652	**3.481765**
59950	**6.839457**	**0**	12.3019956	12.3110226	0	22.3485652	**3.481765**
60730	**6.84046**	**0**	5.33086476	5.3355588	0	22.3485652	**3.481765**
61210	**6.84046**	**0**	3.28053216	3.2834208	0	22.3485652	**3.481765**
62760	**6.835445**	**0**	10.5933851	10.5949398	0	22.3485652	**3.481765**
63120	**6.841463**	**0**	2.46039912	2.46292668	0	22.3485652	**3.481765**
64920	**6.84046**	**0**	12.3019956	12.312828	0	22.3485652	**3.481765**
65150	**6.841463**	**0**	1.57192166	1.57353649	0	22.3485652	**3.481765**

Table A114 c: Cr (VI)

Volume treated (ml)	**Cr conc. (mg/l)**	**Removal ratio (%)**	Amount of Cr in the influent (mg)	approx. amount of Cr in the effluent (mg)	approx. uptaken Cr at each stage (mg)	approx. amount of adsorbed Cr (mg)	**approx. Cr uptake by the biomass (mg/g)**
0	**6.410173**	**100**	0	0	0	0	**0**
100	**0.012036**	**99.812236**	0.6410173	0.0012036	0.6398137	0.6398137	**0.09967892**
280	**0.086258**	**98.6543577**	1.15383114	0.01552644	1.1383047	1.7781184	**0.27701959**
605	**3.3238417**	**48.1473948**	2.08330623	1.08024855	1.00305767	2.78117607	**0.43328963**
830	**4.608785**	**28.1020185**	1.44228893	1.03697663	0.4053123	3.18648837	**0.49643472**
1260	**4.801361**	**25.0977938**	2.75637439	2.06458523	0.69178916	3.87827753	**0.60421109**
1820	**5.013997**	**21.780629**	3.58969688	2.80783832	0.78185856	4.66013609	**0.72601971**
2100	**5.139372**	**19.8247536**	1.79484844	1.43902416	0.35582428	5.01596037	**0.78145488**
2760	**5.361035**	**16.3667658**	4.23071418	3.5382831	0.69243108	5.70839145	**0.88933126**
3110	**5.548596**	**13.4407761**	2.24356055	1.9420086	0.30155195	6.0099434	**0.93631114**
3810	**5.772265**	**9.95149429**	4.4871211	4.0405855	0.4465356	6.456479	**1.00587856**
4125	**5.859526**	**8.59020498**	2.0192045	1.84575069	0.17345381	6.62993281	**1.03290157**
4790	**5.889616**	**8.12079487**	4.26276505	3.91659464	0.34617041	6.97610321	**1.08683273**
5140	**5.916697**	**7.69832577**	2.24356055	2.07084395	0.1727166	7.14881981	**1.11374088**
5800	**5.941772**	**7.30715068**	4.23071418	3.92156952	0.30914466	7.45796447	**1.16190366**
6230	**5.964841**	**6.9472696**	2.75637439	2.56488163	0.19149276	7.64945723	**1.19173702**
6820	**5.985904**	**6.61868252**	3.78200207	3.53168336	0.25031871	7.89977594	**1.23073509**
7105	**6.006967**	**6.29009545**	1.82689931	1.7119856	0.11491371	8.01468965	**1.24863792**
7840	**6.030036**	**5.93021436**	4.71147716	4.43207646	0.2794007	8.29409035	**1.29216678**
8120	**6.083195**	**5.10092317**	1.79484844	1.7032946	0.09155384	8.38564419	**1.30643029**
8800	**6.126324**	**4.42810202**	4.35891764	4.16590032	0.19301732	8.57866151	**1.33650117**
9110	**6.163435**	**3.84916289**	1.98715363	1.91066485	0.07648878	8.65515029	**1.34841763**
9810	**6.203555**	**3.22328274**	4.4871211	4.3424885	0.1446326	8.79978289	**1.37095048**
10740	**6.221609**	**2.94163668**	5.96146089	5.78609637	0.17536452	8.97514741	**1.39827116**
11710	**6.255711**	**2.40963855**	6.21786781	6.06803967	0.14982814	9.12497555	**1.42161343**
12150	**6.355008**	**0.8605852**	2.82047612	2.79620352	0.0242726	9.14924815	**1.42539495**

13840	**6.420203**	**0**	10.8331924	10.8501431	0	9.14924815	**1.42539495**
14105	**6.418197**	**0**	1.69869585	1.70082221	0	9.14924815	**1.42539495**
15980	**6.408167**	**0**	12.0190744	12.0153131	0	9.14924815	**1.42539495**
16625	**6.430233**	**0**	4.13456159	4.14750029	0	9.14924815	**1.42539495**
17140	**6.416191**	**0**	3.3012391	3.30433837	0	9.14924815	**1.42539495**
18940	**6.40917**	**0**	11.5383114	11.536506	0	9.14924815	**1.42539495**
19700	**6.410173**	**0**	4.87173148	4.87173148	0	9.14924815	**1.42539495**
20775	**6.411176**	**0**	6.89093598	6.8920142	0	9.14924815	**1.42539495**
21610	**6.317897**	**0**	5.35249446	5.275444	0	9.14924815	**1.42539495**
22120	**6.4192**	**0**	3.26918823	3.273792	0	9.14924815	**1.42539495**
23900	**6.42923**	**0**	11.4101079	11.4440294	0	9.14924815	**1.42539495**
24400	**6.420203**	**0**	3.2050865	3.2101015	0	9.14924815	**1.42539495**
25660	**6.421206**	**0**	8.07681798	8.09071956	0	9.14924815	**1.42539495**
26290	**6.418197**	**0**	4.03840899	4.04346411	0	9.14924815	**1.42539495**
27650	**6.417194**	**0**	8.71783528	8.72738384	0	9.14924815	**1.42539495**
28120	**6.416191**	**0**	3.01278131	3.01560977	0	9.14924815	**1.42539495**
29810	**6.4192**	**0**	10.8331924	10.848448	0	9.14924815	**1.42539495**
30755	**6.420203**	**0**	6.05761349	6.06709184	0	9.14924815	**1.42539495**
31210	**6.421206**	**0**	2.91662872	2.92164873	0	9.14924815	**1.42539495**
32700	**6.422209**	**0**	9.55115777	9.56909141	0	9.14924815	**1.42539495**
33130	**6.417194**	**0**	2.75637439	2.75939342	0	9.14924815	**1.42539495**
34970	**6.415188**	**0**	11.7947183	11.8039459	0	9.14924815	**1.42539495**
35790	**6.416191**	**0**	5.25634186	5.26127662	0	9.14924815	**1.42539495**
36990	**6.417194**	**0**	7.6922076	7.7006328	0	9.14924815	**1.42539495**
37770	**6.413182**	**0**	4.99993494	5.00228196	0	9.14924815	**1.42539495**
38110	**6.430233**	**0**	2.17945882	2.18627922	0	9.14924815	**1.42539495**
39790	**6.411176**	**0**	10.7690906	10.7707757	0	9.14924815	**1.42539495**
40750	**6.40917**	**0**	6.15376608	6.1528032	0	9.14924815	**1.42539495**
41780	**6.408167**	**0**	6.60247819	6.60041201	0	9.14924815	**1.42539495**
42110	**6.4192**	**0**	2.11535709	2.118336	0	9.14924815	**1.42539495**
43790	**6.418197**	**0**	10.7690906	10.782571	0	9.14924815	**1.42539495**
44420	**6.418197**	**0**	4.03840899	4.04346411	0	9.14924815	**1.42539495**
45680	**6.417194**	**0**	8.07681798	8.08566444	0	9.14924815	**1.42539495**
46200	**6.408167**	**0**	3.33328996	3.33224684	0	9.14924815	**1.42539495**
47750	**6.4192**	**0**	9.93576815	9.94976	0	9.14924815	**1.42539495**
48870	**6.4192**	**0**	7.17939376	7.189504	0	9.14924815	**1.42539495**
49760	**6.411176**	**0**	5.70505397	5.70594664	0	9.14924815	**1.42539495**
50800	**6.412179**	**0**	6.66657992	6.66866616	0	9.14924815	**1.42539495**
51770	**6.411176**	**0**	6.21786781	6.21884072	0	9.14924815	**1.42539495**
52840	**6.417194**	**0**	6.85888511	6.86639758	0	9.14924815	**1.42539495**
53140	**6.416191**	**0**	1.9230519	1.9248573	0	9.14924815	**1.42539495**
54950	**6.417194**	**0**	11.6024131	11.6151211	0	9.14924815	**1.42539495**
55620	**6.420203**	**0**	4.29481591	4.30153601	0	9.14924815	**1.42539495**
56210	**6.4192**	**0**	3.78200207	3.787328	0	9.14924815	**1.42539495**
57850	**6.411176**	**0**	10.5126837	10.5143286	0	9.14924815	**1.42539495**
58150	**6.412179**	**0**	1.9230519	1.9236537	0	9.14924815	**1.42539495**
59950	**6.411176**	**0**	11.5383114	11.5401168	0	9.14924815	**1.42539495**
60730	**6.414185**	**0**	4.99993494	5.0030643	0	9.14924815	**1.42539495**
61210	**6.417194**	**0**	3.07688304	3.08025312	0	9.14924815	**1.42539495**
62760	**6.416191**	**0**	9.93576815	9.94509605	0	9.14924815	**1.42539495**
63120	**6.4192**	**0**	2.30766228	2.310912	0	9.14924815	**1.42539495**
64920	**6.412179**	**0**	11.5383114	11.5419222	0	9.14924815	**1.42539495**
65150	**6.4192**	**0**	1.47433979	1.476416	0	9.14924815	**1.42539495**

Table AI14 d: Ni (II)

Volume treated (ml)	**Ni conc. (mg/l)**	**Removal ratio (%)**	Amount of Ni in the influent (mg)	approx. amount of Ni in the effluent (mg)	approx. uptaken Ni at each stage (mg)	approx. amount of adsorbed Ni (mg)	**approx. Ni uptake by the biomass (mg/g)**
0	**6.6198**	**100**	0	0	0	0	**0**
100	**0.05015**	**99.2424242**	0.66198	0.005015	0.656965	0.656965	**0.10235099**
280	**0.161483**	**97.5606061**	1.191564	0.02906694	1.16249706	1.81946206	**0.28346067**
605	**1.034093**	**84.3787879**	2.151435	0.33608023	1.81535478	3.63481684	**0.56628146**
830	**1.698079**	**74.3484848**	1.489455	0.38206778	1.10738723	4.74220406	**0.73880538**
1260	**2.644911**	**60.0454545**	2.846514	1.13731173	1.70920227	6.45140633	**1.00508827**
1820	**3.506488**	**47.030303**	3.707088	1.96363328	1.74345472	8.19486105	**1.27670748**
2100	**3.743196**	**43.4545455**	1.853544	1.04809488	0.80544912	9.00031017	**1.40219136**
2760	**4.295849**	**35.1060606**	4.369068	2.83526034	1.53380766	10.5341178	**1.64114888**
3110	**4.468365**	**32.5**	2.31693	1.56392775	0.75300225	11.2871201	**1.75846187**
3810	**4.668965**	**29.469697**	4.63386	3.2682755	1.3655845	12.6527046	**1.97121129**
4125	**4.917709**	**25.7121212**	2.085237	1.54907834	0.53615867	13.1888632	**2.05474142**
4790	**5.240675**	**20.8333333**	4.402167	3.48504888	0.91711813	14.1059814	**2.19762262**
5140	**5.401155**	**18.4090909**	2.31693	1.89040425	0.42652575	14.5325071	**2.26407263**
5800	**5.501455**	**16.8939394**	4.369068	3.6309603	0.7381077	15.2706148	**2.37906514**
6230	**5.531545**	**16.4393939**	2.846514	2.37856435	0.46794965	15.7385645	**2.45196873**
6820	**5.603761**	**15.3484848**	3.905682	3.30621899	0.59946301	16.3380275	**2.54536127**
7105	**5.672968**	**14.3030303**	1.886643	1.61679588	0.26984712	16.6078746	**2.58740174**
7840	**5.744181**	**13.2272727**	4.865553	4.22197304	0.64357997	17.2514546	**2.68766743**
8120	**5.901652**	**10.8484848**	1.853544	1.65246256	0.20108144	17.452536	**2.71899465**
8800	**5.9177**	**10.6060606**	4.501464	4.024036	0.477428	17.929964	**2.79337491**
9110	**5.946787**	**10.1666667**	2.052138	1.84350397	0.20863403	18.138598	**2.82587877**
9810	**6.099243**	**7.86363636**	4.63386	4.2694701	0.3643899	18.5029879	**2.88264841**
10740	**6.132342**	**7.36363636**	6.156414	5.70307806	0.45333594	18.9563239	**2.95327528**
11710	**6.236654**	**5.78787879**	6.421206	6.04955438	0.37165162	19.3279755	**3.01117625**
12150	**6.257717**	**5.46969697**	2.912712	2.75339548	0.15931652	19.487292	**3.03599675**
13840	**6.277777**	**5.16666667**	11.187462	10.6094431	0.57801887	20.0653109	**3.12604843**
14105	**6.316894**	**4.57575758**	1.754247	1.67397691	0.08027009	20.145581	**3.13855401**
15980	**6.330936**	**4.36363636**	12.412125	11.870505	0.54162	20.687201	**3.22293497**
16625	**6.373062**	**3.72727273**	4.269771	4.11062499	0.15914601	20.846347	**3.24772892**
17140	**6.394125**	**3.40909091**	3.409197	3.29297438	0.11622263	20.9625696	**3.26583566**
18940	**6.431236**	**2.84848485**	11.91564	11.5762248	0.3394152	21.3019848	**3.3187144**
19700	**6.517494**	**1.54545455**	5.031048	4.95329544	0.07775256	21.3797374	**3.33082776**
20775	**6.561626**	**0.87878788**	7.116285	7.05374795	0.06253705	21.4422744	**3.34057064**
21610	**6.656911**	**0**	5.527533	5.55852069	0	21.4422744	**3.34057064**
22120	**6.695025**	**0**	3.376098	3.41446275	0	21.4422744	**3.34057064**
23900	**6.667944**	**0**	11.783244	11.8689403	0	21.4422744	**3.34057064**
24400	**6.6198**	**0**	3.3099	3.3099	0	21.4422744	**3.34057064**
25660	**6.620803**	**0**	8.340948	8.34221178	0	21.4422744	**3.34057064**
26290	**6.621806**	**0**	4.170474	4.17173778	0	21.4422744	**3.34057064**
27650	**6.618797**	**0**	9.002928	9.00156392	0	21.4422744	**3.34057064**
28120	**6.640863**	**0**	3.111306	3.12120561	0	21.4422744	**3.34057064**
29810	**6.63986**	**0**	11.187462	11.2213634	0	21.4422744	**3.34057064**
30755	**6.638857**	**0**	6.255711	6.27371987	0	21.4422744	**3.34057064**
31210	**6.637854**	**0**	3.012009	3.02022357	0	21.4422744	**3.34057064**
32700	**6.6198**	**0**	9.863502	9.863502	0	21.4422744	**3.34057064**
33130	**6.636851**	**0**	2.846514	2.85384593	0	21.4422744	**3.34057064**
34970	**6.636851**	**0**	12.180432	12.2118058	0	21.4422744	**3.34057064**
35790	**6.620803**	**0**	5.428236	5.42905846	0	21.4422744	**3.34057064**
36990	**6.621806**	**0**	7.94376	7.9461672	0	21.4422744	**3.34057064**
37770	**6.618797**	**0**	5.163444	5.16266166	0	21.4422744	**3.34057064**

38110	**6.631836**	**0**	2.250732	2.25482424	0	21.4422744	**3.34057064**
39790	**6.620803**	**0**	11.121264	11.122949	0	21.4422744	**3.34057064**
40750	**6.6198**	**0**	6.355008	6.355008	0	21.4422744	**3.34057064**
41780	**6.632839**	**0**	6.818394	6.83182417	0	21.4422744	**3.34057064**
42110	**6.618797**	**0**	2.184534	2.18420301	0	21.4422744	**3.34057064**
43790	**6.620803**	**0**	11.121264	11.122949	0	21.4422744	**3.34057064**
44420	**6.617794**	**0**	4.170474	4.16921022	0	21.4422744	**3.34057064**
45680	**6.640863**	**0**	8.340948	8.36748738	0	21.4422744	**3.34057064**
46200	**6.7201**	**0**	3.442296	3.494452	0	21.4422744	**3.34057064**
47750	**6.711073**	**0**	10.26069	10.4021632	0	21.4422744	**3.34057064**
48870	**6.621806**	**0**	7.414176	7.41642272	0	21.4422744	**3.34057064**
49760	**6.650893**	**0**	5.891622	5.91929477	0	21.4422744	**3.34057064**
50800	**6.632839**	**0**	6.884592	6.89815256	0	21.4422744	**3.34057064**
51770	**6.6198**	**0**	6.421206	6.421206	0	21.4422744	**3.34057064**
52840	**6.632839**	**0**	7.083186	7.09713773	0	21.4422744	**3.34057064**
53140	**6.62983**	**0**	1.98594	1.988949	0	21.4422744	**3.34057064**
54950	**6.632839**	**0**	11.981838	12.0054386	0	21.4422744	**3.34057064**
55620	**6.631836**	**0**	4.435266	4.44333012	0	21.4422744	**3.34057064**
56210	**6.6198**	**0**	3.905682	3.905682	0	21.4422744	**3.34057064**
57850	**6.632839**	**0**	10.856472	10.877856	0	21.4422744	**3.34057064**
58150	**6.633842**	**0**	1.98594	1.9901526	0	21.4422744	**3.34057064**
59950	**6.6198**	**0**	11.91564	11.91564	0	21.4422744	**3.34057064**
60730	**6.632839**	**0**	5.163444	5.17361442	0	21.4422744	**3.34057064**
61210	**6.631836**	**0**	3.177504	3.18328128	0	21.4422744	**3.34057064**
62760	**6.62983**	**0**	10.26069	10.2762365	0	21.4422744	**3.34057064**
63120	**6.6198**	**0**	2.383128	2.383128	0	21.4422744	**3.34057064**
64920	**6.632839**	**0**	11.91564	11.9391102	0	21.4422744	**3.34057064**
65150	**6.617794**	**0**	1.522554	1.52209262	0	21.4422744	**3.34057064**

Table A115: pH changes during the adsorption experiment

Volume treated (ml)	pH	Volume treated (ml)	pH	Volume treated (ml)	pH
0	4.98	21150	4.11	46150	4.67
1150	3.59	26150	4.25	51250	4.73
6150	3.76	31150	4.36	56150	4.79
11150	3.87	36150	4.46	61150	4.84
16350	3.99	41150	4.57		

Table A116: Determination of the accuracy and precision of copper measurement by Atomic Absorption Spectrophotometer (Spectre AA-200, Varian, Australia)

	Cu standards read by the machine						
Nominal concentration	**1 mg/l**	**2 mg/l**	**4 mg/l**	**10 mg/l**	**20 mg/l**	**40 mg/l**	**60 mg/l**
first reading (mg/l)	1.1	2.11	4.024	9.985	19.875	40.3	59.815
second reading (mg/l)	0.945	1.995	3.991	9.995	20	39.855	60.2
third reading (mg/l)	1.063	1.988	3.976	10.025	20.011	39.955	59.945
fourth reading (mg/l)	0.977	1.99	3.984	9.875	19.858	40.015	60.155
fifth reading (mg/l)	0.945	2.115	4.03	9.889	19.898	40.025	59.935
sixth reading (mg/l)	1.019	2.12	4.112	9.955	20.21	39.915	60.15
seventh reading (mg/l)	0.989	1.985	3.998	10.215	19.855	39.895	59.845
eighth reading (mg/l)	1.011	1.992	4.215	9.985	19.915	39.855	60.105
average	**1.0061**	**2.037**	**4.041**	**9.9905**	**19.9528**	**39.977**	**60.0188**
accuracy	**0.0061**	**0.037**	**0.041**	**0.0095**	**0.04725**	**0.0231**	**0.01875**
Stdv (precision)	**0.0546**	**0.065**	**0.082**	**0.1046**	**0.12**	**0.1458**	**0.1513**

Table A117: Determination of the accuracy and precision of the carbon machine (Dohrmann DC-190, USA) (measuring TC for a standard of 200 mgl^{-1})

Readings	**Sample1**	**Sample2**	**Sample3**	**Sample4**	**Sample5**	**Sample6**	**Sample7**	**Sample8**	**Sample9**
Reading1	226.5	224.9	218.3	217.4	218.7	224.8	222	225.8	230.7
Reading2	200.6	196	191.6	189.8	190.5	194.3	192	201.9	199.8
Reading3	196.2	199.3	191.3	189.6	192.4	193.8	191.3	208.6	199.4
Reading4	195.5	194.7	191.2	193.5	193.1	192.6	192.8	200.4	200.1
Reading5	193.7	196.5	191.3	189.9	193.8	201.2	191.3	199	199.3
Average ± Std dev	202.5 ± 13.67	202.3 ± 12.76	196.70 ± 12.09	196.00 ± 12.05	197.70 ± 11.83	201.30 ± 13.55	197.90 ± 13.50	207.1 ± 11.06	205.9 ± 13.89
% Std dev	6.753	6.31	6.144	6.144	5.981	6.731	6.819	5.341	6.747
Overall average ± Std dev			200.83 ± 12.14		**% Std dev**		6.044914		

Appendix B: Analytical instruments used in the study

B1: Measurement of heavy metals using Atomic Absorption Spectrophotometer

Atomic spectroscopy is used for the qualitative and quantitative determination of perhaps 70 elements. Advantages of using these methods are high sensitivities (parts-per-million to parts per billion), speed, convenience, unusually high selectivity and moderate instrument costs (skoog et al., 1988).

Atomic spectroscopy gives information about the identity and concentration of atoms in a sample regardless of how these atoms are combined. Atomic spectroscopy is based on absorption, fluorescence and emission phenomena. These methods are limited to ultraviolet, visible and X-ray frequencies because only such radiation is energetic enough to cause electronic transitions. The first step in all atomic spectroscopic procedures is "atomization"; a process in which a sample is volatilized and decomposed in such a way as to produce an atomic gas.

The device used in our experiments is an atomic absorption spectrophotometer (Spectre AA-200) manufactured by Varian, Australia. Therefore our brief discussion will be confined only on atomic absorption spectroscopy.

Figure b1.1 shows a simple diagram of the components of a single-beam atomic absorption spectrophotometer.

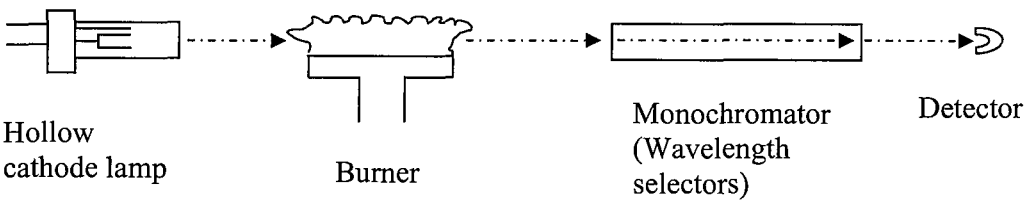


Fig b1.1: Optical paths in a single-beam atomic absorption spectrophotometer

When a beam of polychromatic ultraviolet or visible radiation passes through a medium containing gaseous atoms, only a few frequencies are attenuated (decreases the intensity) by absorption; in other words the atoms will absorb the energy of the photon (particle of electromagnetic stream) and get excited (excitation is the transition of electron or more from their ground state orbital to higher orbital). Under these

circumstances the energy of the photon is transferred to the atom converting it to the higher energy state that has so very short lifetime (10^{-6} to 10^{-9} sec). The excite species, therefore, quickly relaxes to its original or ground state transferring its excess energy to other atoms in the medium.

When a beam of parallel radiation pass through absorbing matter (atoms, ions, or molecules) with a thickness b and a concentration c of an absorbing species, the power of the beam is attenuated from Po to P. Transmittance T of radiation by the solution is often expressed as a percentage:

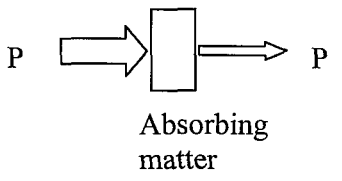


Fig b1.2: Attenuation of a beam of radiation by an absorbing matter

$$T = \frac{P}{P_o}$$

While the absorbance A is defined by:

$$A = -\log T = \log \frac{P_O}{P}$$

The functional relationship between the absorbance A and the analyte concentration c is known as Beer's law, which can be written in the following form:

$$A = \log \frac{P_O}{P} = a \times b \times c$$

Where a: is the absorptivity constant

b: is the path length of the radiation through the absorbing medium

c: is the analyte concentrations

Therefore the relation between radiation absorption by the matter A and the concentration of analyte is linear.

A hollow-cathode lamp is used to provide the radiation. The lamp consists of a tungsten anode and a cylindrical cathode sealed in a glass tube containing an inert gas, such as argon. The cathode is either fabricated from the analyte metal or else serves as a support for a coating of that metal. The application of a potential across the electrodes causes ionization of the argon and generation of a current as the argon cations and electrons migrate to the two electrodes. The argon cations then will strike the cathode to dislodge some of the metal atoms and thereby produce an atomic cloud (sputtering). A fraction of the sputtered metal atoms is in an excited state and emit

their characteristic wavelengths as they return to the ground state. The emitted radiation from the electrically excited atoms, when they return to their ground state in the lamp have wavelengths that are identical to the wavelengths absorbed by the analyte atoms in the flame. The hollow-cathode lamps produce a series of narrow peaks or lines of radiation and not a single line. Beer's law applies only when absorbance is measured with monochromatic radiation. Monochromatic sources, such as laser, are not practical for routine analytical instruments, however a polychromatic continuous source can be employed in conjunction with a monochromator or a filter that isolates a more or less symmetric band of wavelengths around the desired one.

The monochromator can't produce a single wavelength, instead it produces a group of contiguous wavelengths called a band. The monochromator also acts to restrict or eliminate the radiation produced from the flame (i.e. by the analyte). Therefore the atomic absorption device must be able of providing a sufficiently narrow bandwidth to isolate the line chosen for a measurement from other lines that may interfere with or diminish the sensitivity of the device. After the radiation beam pass through the flame and the monochromator, it goes to the surface of radiation detector (transducer) that converts light intensity into electrical signals. The electrical signals then pass through an electronic device that amplifies the signals which can then be registered and displayed.

Table b1.1 provides information on the detection limits for a number of common elements by flame atomic absorption.

Table b1.1: Detection limits of a number of common elements by flame atomic absorption (Skoog et al., 1988)

Element	Detection limit (x 10^{-3} ppm)
Al	30
As	100
Ca	1
Cd	1
Cr	3
Cu	2
Fe	5
Hg	500
Mg	0.1
Mn	2
Mo	30
Na	2
Ni	5
Pb	10
Sn	20
V	20
Zn	2

B2: Carbon measurement using Dohrmann DC-190 carbon and nitrogen analyser

Dohrmann DC-190 machine was used for carbon determination. The DC-190 system features a vertical quartz combustion tube packed with supported platinum catalyst which receives a continuous flow of oxygen or air at 200 cc/min for TOC (Total organic carbon) measurement and 150 cc/min for TON (Total organic nitrogen) measurement. The furnace is normally maintained at 680° C but can be varied to any temperature up to 900° C. Organic containing samples are manually or automatically introduced into the combustion tube via an air-actuated injection port. Through catalytic oxidation, the sample is completely oxidized to CO_2 and H_2O. The gas flow

sweeps the CO_2 containing steam out of the combustion tube and into the IC reactor. It continues through a condenser, a gas liquid separator, and moisture trap. Final H_2O removal is accomplished by permeation dryer. The dried CO_2 containing gas is then passed through a halogen scrubber and to a CO_2 specific non-dispersive infrared detector (NDIR) for peak quantification. Inorganic carbon (IC) samples are manually or automatically introduced into the IC reactor, which contains acidic water solution at room temperature, via an air-operated injection port. In this acidic environment, all forms of IC are purged out of the solution as CO_2 by the continuous flow of gas. The gas then continues through the drying system to the NDIR detector for quantification. The system also provides manual capability to measure purgeable organic carbon (POC) by purging the sample with 200 cc/min of oxygen or air at room temperature. The POC containing gas is passed through a lithium hydroxide scrubber to remove CO_2 then directly to the combustion tube for oxidation. Figure b2.1 shows the system flow diagram

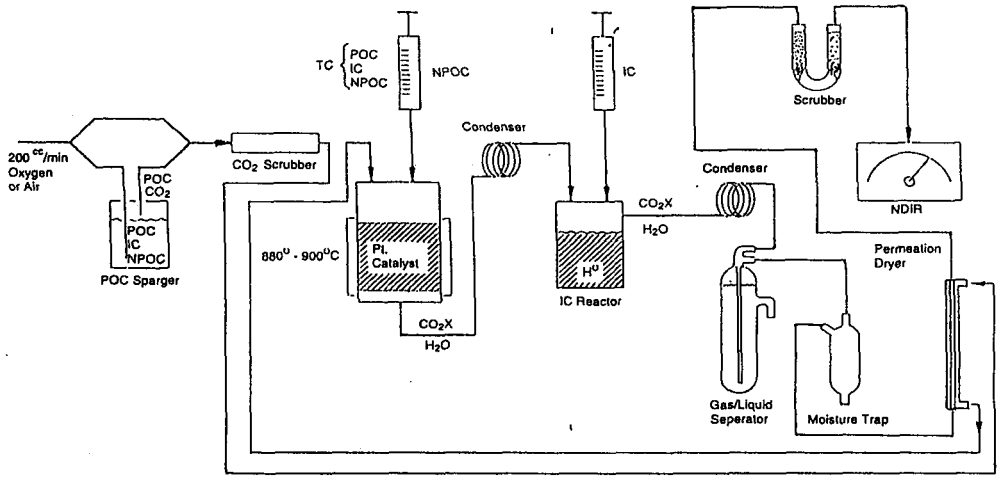


Fig. b2.1: Dohrmann DC-190 system flow diagram

Appendix C: Brief explanation of the statistics used in the study to present the experimental data

Errors, accuracy and precision of the experimental data

Experimental scientists make a fundamental distinction between three types of errors. These are known as **gross, random** and **systematic** errors.

Gross errors are so serious that there is no real alternative to abandoning the experiment and making a completely fresh start. Examples would include a complete instrument breakdown or discovering during the experiment that a supposedly pure reagent was in fact badly contaminated. Such errors are normally very easily recognised.

Systematic (or determinate) errors are those that can be mostly specified and hence controlled, corrected or eliminated. These errors can arise from procedures, apparatus or human bias. Systematic errors affect accuracy (i.e. proximity of the result's average to the true value). Therefore the closer the result's average to the true value, the more accurate the results are and the smaller the systematic error is. Examples of systematic errors in weighings includes adsorption of moisture on the surface of the weighing vessel; failure to allow heated vessels to cool to the same temperature as the balance before weighing; corroded or dust-contaminated weights; and the buoyancy effect of the atmosphere. Poor calibration of instruments and devices introduce systematic errors. Some chemists suffer from colour-blindness which might introduce errors into their readings of instruments and other observations.

Random (or indeterminate) errors are those that cause the individual results to fall on both sides of the average value (Miller and Miller, 1988). These errors affect the precision or reproducibility/repeatability of an experiment. Therefore the closer the individual results to the mean value (i.e. the average), the more precise the results are and the smaller the random error is. Random errors can never be eliminated, though by careful technique we can minimize them, and by making repeated measurements we can measure them and evaluate their significance (Miller and Miller, 1988). Although, for the first glance, reproducibility and repeatability look similar but modern convention makes a careful distinction between them.

If an experiment is repeated several times directly (i.e. at the same time or following each others) using the same stock for solutions preparation, the same glassware, the same procedures and the same instruments and devices set up and calibration and the temperature, humidity and other laboratory conditions would remain the same; in such circumstances the precision measured would be the within-run precision and is called the **repeatability**. On the other hand, if the experiment is repeated at different occasions using different stocks for solutions preparation, different pieces of glassware, different instruments set up and calibration and the laboratory conditions might also change from time to time; in these circumstances the precision measured would reflect the between-run and is termed **reproducibility**, (Miller and Miller, 1988).

If good care is taken to conduct the experiments, we can assume that the systematic errors are absent. Therefore we shall concentrate in the following discussion on how to measure and evaluate the random errors.

When experiment is repeated n times, two criteria are used to evaluate and express the results. The first is the mean which is calculated using the following equation:

$$\bar{x} = \frac{\sum x_i}{n} \qquad (4.1)$$

Where x: is each value of the repeated results

n: is the number of repeat

$\sum$: is the Greek capital sigma (i.e. S) denotes "sum of"

The second criterion is the standard deviation. Standard deviation measures the spread of the results about the mean value or in other words it measures the precision of the repeated results or observations (Standard Methods, 1985). Standard deviation is given by the following equation:

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{(n-1)}} \qquad (4.2)$$

(n-1) is used when we are working with a sample data set, while (n) is used if the data set is known to be the whole population (Internet site a). (n-1) is called the degree of

freedom and a good example to gain an intuitive feel for the meaning of it is to consider choosing a chocolate from a box of n chocolates. Every time we come to choose a chocolate we have a choice, until we come to the last one and then we have no choice. Thus we have (n-1) choices or "degree of freedom" (BMJ.com, 2002).

In our project some experiments were conducted two times and other three times, therefore we are dealing only with samples from the very large number (in theory infinite) of measurements which we could make; this set of measurements called the population. If there are no systematic errors, then the mean of this population, denoted by μ, is the true value of the observations which we are trying to determine. The mean, $\bar{x}$, of the sample gives us an estimate of μ. Similarly, the value of the standard deviation, s, of the sample gives us an estimate of the population standard deviation, σ.

Most of experimental measurements accurately conformed to normal or Gaussian distribution (Meier and Zund, 2000). In this distribution whatever the value of μ and σ, approximately 68% of the population lies within $\pm 1\sigma$ of the mean, approximately 95% of values lie within $\pm 2\sigma$ or more precisely $\pm 1.96\sigma$ of the mean and approximately 99.7% of $\pm 3\sigma$ of the mean (Miller and Miller, 1988).

For example, a result is quoted as having an uncertainty of $\pm 1\sigma$, an equivalent statement would be " the 68.3% confidence limits are given by $\bar{x} \pm 1\sigma$", the reason being that the area under a normal distribution curve between -1σ to $+1\sigma$ is equal to 0.683 (Meier and Zund, 2000).

Confidence limit of the mean

The best way of representing the data is to define a range within which we may reasonably assume the true value, μ, lies. Such a range is known as confidence limits. The term "confidence" implies that we can assert with a given degree of confidence (i.e. a certain probability), that the confidence limits do include the true value.

For a sample of small size we use the following equation:

$$\mu = \bar{x} \pm t\left(\frac{s}{\sqrt{n}}\right) \qquad (4.3)$$

The appropriate value of t depends on both the degree of freedom (n-1) and the degree of confidence required. Values of t are given in table 5.1 (Miller and Miller, 1988).

Table 5.1: Values of t for confidence limits (Miller and Miller, 1988)

Degree of freedom (n-1)	95% confidence limit	99% confidence limit
1	12.71	63.66
2	4.30	9.92
3	3.18	5.84
4	2.78	4.60
5	2.57	4.03
10	2.23	3.17
20	2.09	2.85
30	2.04	2.75
50	2.01	2.68
100	1.98	2.63

Presentation of the results

A common practice in analytical chemistry literature is to quote the mean as the estimate of the quantity measured and the standard deviation as the estimate of the precision (i.e. $\bar{x} \pm$ s). Less commonly, the result is given in the form of the 95% confidence limits of the mean (i.e. $\mu = \bar{x} \pm t(\frac{s}{\sqrt{n}})$), (Miller and Miller, 1988).

Since there is no universal convention it is obviously essential to state the form used and providing the value of n.

In our analysis all graphs were plotted using the mean value of the results with error bars being drawn as ± s. In addition to this the 95% confidence limits of the mean were calculated and reported in the results tables.