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DEVELOPMENT OF A MECHANISTIC MODEL TO ASSESS THE DISTRIBUTION OF HEAVY METALS IN MUNICIPAL WASTEWATER TREATMENT

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ABSTRACT

FACULTY OF ENGINEERING AND APPLIED SCIENCE
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Doctor of Philosophy

DEVELOPMENT OF A MECHANISTIC MODEL TO ASSESS THE DISTRIBUTION OF HEAVY METALS IN MUNICIPAL WASTEWATER TREATMENT

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This research advances the understanding of the fate of two heavy metals, copper and zinc, in municipal wastewater treatment systems and is thus valuable to integrated wastewater management. The principal aim of this project was to develop a modelling tool to determine the fate of heavy metals in municipal wastewater treatment plants. This was accomplished using a strategy, which consisted of five stages. The first stage, the literature review, revealed that metal interactions in wastewater treatment processes are complex, with many factors and mechanisms influencing heavy metal removal. However, certain factors appear to be of significant importance with regard to the development of a metals predictive model. Of these factors, the fate of suspended solids in the treatment plant was found to closely influence metal removal. Hence, in the second stage, a model was developed to determine the partitioning of the suspended solids between the sludge and liquid phases in the different wastewater treatment processes.

The third stage focused on the development of a model for the heavy metals. Modelling of the mechanisms of heavy metal removal can be undertaken using a variety of methods, such as equilibrium chemical modelling, use of adsorption isotherms, empirical as well as mechanistic modelling methods. The use and general applicability of these techniques to achieve the objectives of the current research were critically assessed. The most suitable approach for the purpose of this research was found to be a combination of the approaches. The adsorption isotherm approach to modelling describes the physico-chemical mechanisms that are recognised as being important in the removal of heavy metals, while the mechanistic approach allows these mechanisms to be modelled for a range of influencing factors.

In the fourth stage, batch experiments were carried out to determine both the solubility and adsorption of two heavy metals, copper and zinc, under various conditions. The methodology for obtaining model coefficients and correlations with important parameters, such as pH and the solids concentration, was developed. The results of these experiments provide an in-depth understanding of the parameters influencing metal removal and how they interact with each other. The objective of the fifth and final stage was the verification of the model and model coefficients. It was accomplished by carrying out field studies at two wastewater treatment plants in the Southampton area. The Solids Mass Balance and Heavy Metals models are programmed under the Visual Basic Editor of Microsoft Excel 97 to provide a user-friendly interface to aid in the prediction of effluent and sludge concentrations of metals.

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Acknowledgements

In the Name of Allâh, the Most Beneficent, the Most Merciful.
"He sends down water from the sky, and the valleys flow according to their measure...and that which is for the good of mankind remains in the earth."
English Transliteration of Al-Quran, (Chapter: Ar-Ra'd, verse 17)

It is difficult to believe that after three and a half years the ordeal that is doing a Ph.D. is finally over. I could not have accomplished it without the help and support of so many people. Therefore acknowledgements are due to:

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CHAPTER ONE

INTRODUCTION

"As we enter a new millennium, an historical threshold on heavy metals is being crossed - acute effects due to localized pollution problems are giving way to chronic toxicity endpoints associated with globalization of metal pollution...(among) the major scientific achievements pertaining to heavy metals in the environment this century was the development of computer models, which resulted in improved prediction of the fate and effects of metals in the environment"

11th Annual International Conference on Heavy Metals in the Environment (2000)

1.1 Sources and Significance of Heavy Metals in Wastewater

From the point of view of a chemist, there is no precise definition for the term "heavy metals". It is often used as a general term for polluting metal ions, which are persistent and potentially toxic in the environment (ScienceNet 2001). For environmental practitioners, the most commonly encountered definition of heavy metals states that "heavy metals constitute those with specific gravities of approximately $5g/cm^3$ or greater" (Rudd 1987a). This definition includes elements such as arsenic, cadmium, copper, lead, mercury and zinc.

Inputs of heavy metals in the environment as a whole can be divided into two main sources: natural and anthropogenic (man-made). These are discharged to the air, water and soil through a combination of diffuse and point sources. A municipal wastewater treatment system usually has inputs from both domestic and industrial discharges, both of which are point sources. Urban run-off also contributes to the quantity of heavy metals entering the system. The quantity of heavy metals that enter the wastewater treatment network depends on a combination of factors. These can include the location of the wastewater treatment plant, the type of sewerage system served and the presence or absence of domestic and industrial discharges (Stephenson 1987a). It has been found that currently emissions from industrial point sources account for the major sources of pollution to urban wastewaters (IC Consultants 2001).

Due to their potential for long-term accumulation, the presence of heavy metals in wastewater effluents gives rise to concern in terms of:

1. Their possible toxic or inhibitory effect on the efficiency of biological wastewater and sludge treatment processes;
2. Their toxicity to the aquatic environment and possibly to human health;
3. The hazards they pose to the environmental media affected by sludge disposal.

This is of great significance for environmental pollution control. It has been found that as much as 70-90% of the heavy metals in raw sewage is transferred to the sewage sludge, as shown in figure 1.1.

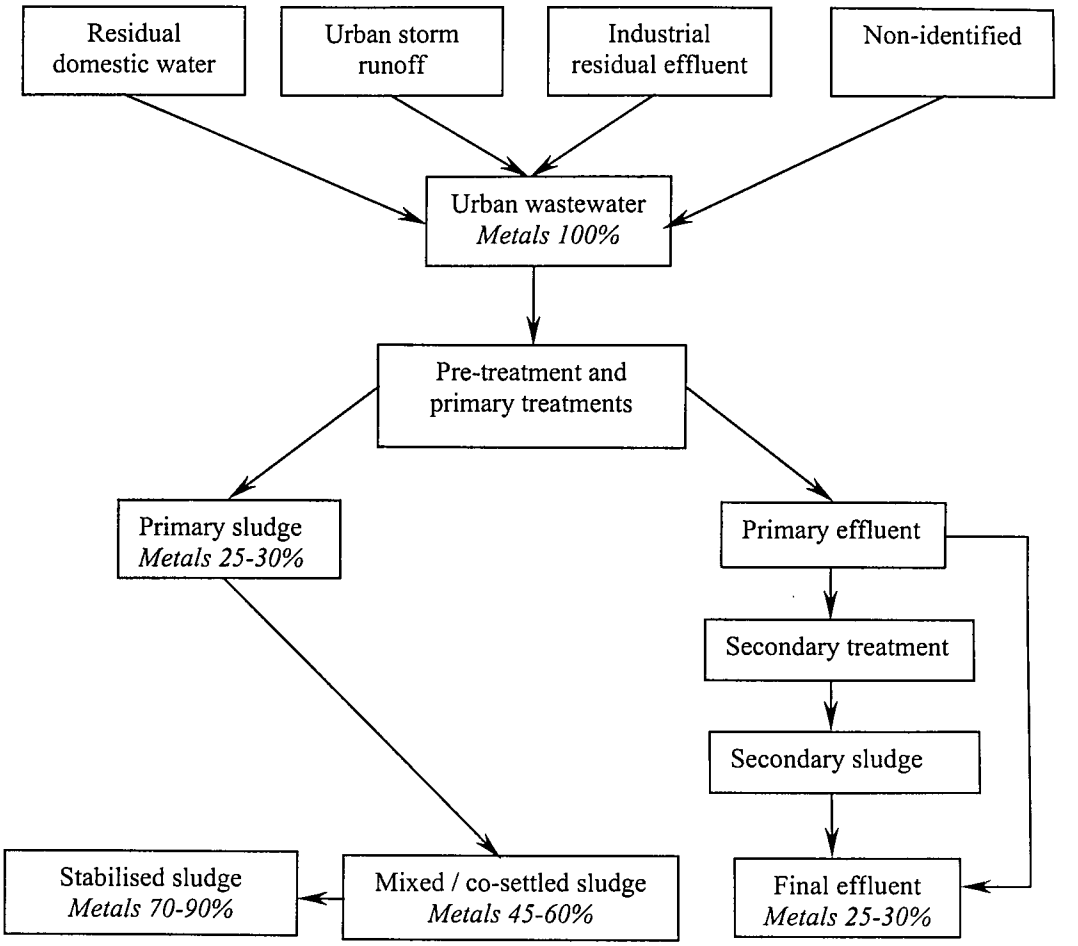


Figure 1.1: *Origin and fate of heavy metals in wastewater treatment (adapted from ADEME 1995)*

Therefore, eventhough wastewater treatment may prevent heavy metals from entering water bodies via the effluent of the works, by removing them from the aqueous phase, they will still have to be disposed of in the resultant sludge, if hazards relating to phytoxicity and the bioaccumulation of metals through the food chain are to be avoided. The toxicity of a metal or a metal compound has been defined as "its intrinsic capacity to cause injury, including potential carcinogenic, mutagenic and teratogenic effects" (Rudd 1987a). The significance of certain heavy metals and the health hazards posed by them are summarised in table 1.1.

Table 1.1: *Sources and significance of heavy metals (Manahan 1991)*

Element	Sources	Effects and significance
Cd	Industrial discharge, mining waste, metal plating, water pipes	Replaces Zn biochemically, causes high blood pressure and kidney damage, destroys testicular tissue and red blood cells, toxic to aquatic biota.
Cr	Metal-plating, cooling tower water additive, normally found as Cr (VI) in polluted water	Essential trace element (glucose tolerance factor), possibly carcinogenic as Cr (VI).
Cu	Metal-plating, industrial and domestic wastes, mining, mineral leaching	Essential trace element, not very toxic to animals, toxic to plants and algae at moderate levels.
Fe	Corroded metal, industrial wastes, acid mine drainage, low pE water in contact with iron minerals	Essential nutrient (component of hemoglobin), not very toxic, damages materials (bathroom fixtures and clothing).
Pb	Industry, mining, plumbing, coal and gasoline	Toxicity (anaemia, kidney disease, nervous system), wildlife destruction
Mn	Mining, industrial waste, acid mine drainage, microbial action on manganese minerals at low pH.	Relatively non-toxic to animals, toxic to plants at higher levels, stains materials (bathroom fixtures and clothing).
Hg	Industrial waste, mining, pesticides, coal	Acute and chronic toxicity
Mo	Industrial waste, natural sources, cooling-tower water additive	Possibly toxic to animals, essential for plants.
Ag	Natural geological sources, mining, electroplating, film-processing wastes, disinfection of water	Causes blue-grey discoloration of skin, mucous membranes and eyes.
Zn	Industrial waste, metal-plating, plumbing	Essential element in many metallo-enzymes, aids wound healing, toxic to plants at higher levels; major component of sewage sludge, limiting land disposal of sludge.

The various factors influencing the toxicity of heavy metals in solution as compiled by Bryan 1976 (in Förstner 1981) are shown in table 1.2.

Table 1.2: *Factors influencing the toxicity of heavy metals in solution (Bryan 1976)*

• Form of a metal in water:	• Inorganic or organic; • Soluble (ion, complex ion, chelate ion, molecule) or Particulate (colloidal, precipitated, adsorbed)
• Presence of other metals or poisons:	• Effect: joint action, no interaction, or antagonism; • More than additive, additive or less than additive.

There is limited information available on the concentration of heavy metals in the influent and effluent from wastewater treatment plants. However, a study carried out by IC Consultants (2001) provides a review of the most up-to-date data on the concentrations of heavy metals in sewage sludge. The results of this survey are summarised in table 1.3.

Table 1.3: *Survey of heavy metal concentrations in sewage sludge (adapted from IC Consultants 2001)*

Metal	**Country (mean concentrations in mg/kg DS)**			**Limit in Sewage Sludge (mg/kg DS)**	
	Denmark	UK	USA	EU	USEPA
Cd	1.4	3.5	38.1	10 1*	39
Cr	33	159.5	589	1000 600*	1200
Cu	284	562	639	1000 50*	1500
Hg	1.29	2.5	3.24	10 0.5*	17
Ni	22.8	58.5	90.6	300 50*	420
Pb	59.9	221.5	204	750 70*	300
Zn	777.2	778	1490	2500 150*	2800

*Notes: *For sludge applied to soil lower and higher limits are allowed for soils with pH in the range 5-6 and >7 respectively*

1.2 Relevant Legislation

1.2.1 EC Law

Due to their non-biodegradability and toxicity, heavy metals are a cause of great environmental concern. In addition, there is an increasing trend of direct or indirect water re-use. This is because surface waters, which are used for the disposal of wastewater effluents, are increasingly being utilised for potable supplies as natural groundwater supplies are depleted (Kirk 1987). Since, heavy metals are ubiquitous in wastewaters, there has been increasing pressure for the development of appropriate water quality criteria to protect potable supply and control the reuse of effluent for a variety of water uses (Kirk 1987).

Several EC directives are addressed to industrial and municipal wastewaters. The Urban Wastewater Treatment Directive (91/271/EEC), which was passed into UK legislation in November 1994, aims to protect surface inland waters and coastal waters by regulating collection and treatment of urban wastewater and discharge of certain biodegradable industrial wastewater (European Commission 1998). It requires sewerage systems and secondary treatment (i.e. biological treatment) for all areas above 2,000 population equivalents. More advanced treatment, such as nutrient removal will be required in sensitive areas. The Directive also required an end to dumping of sewage sludge at sea in 1998.

The earlier directive on dangerous substances discharged to the aquatic environment (76/464/EEC), contains an annexe of List I (black) and List II (grey) substances for which reduction programmes are required. Member states are required to take appropriate steps to eliminate pollution of inland surface waters, territorial waters and internal coastal waters by List I substances and to reduce pollution by the substances in List II. In order to reduce pollution by List II substances, member states are required to adhere to emission standards based on water quality objectives, in accordance with council directives, where they exist (Kirk 1987). Furthermore, emission standards are to be specified for discharges of substances of both lists into sewers, where this is necessary for the implementation of the directive (Kirk 1987). The substances that are included in both lists are shown in the table 1.4.

Table 1.4: *Metals and metal compounds included in Lists I and II of the 'Dangerous Substances Directive' 76/464/EEC (adapted from Kirk 1987)*

List I: • Organotin compounds. • Substances whose carcinogenic activity is exhibited in or by the intervention of the aquatic environment. • Mercury and its compounds. • Cadmium and its compounds.
List II: • The following metalloids and metals and their compounds: Zn, Cu, Ni, Cr, Pb, Se, As, Sb, Mo, Ti, Sn, Ba, Be, B, U, V, Co, Tl, Te, Ag. • Substances which have a deleterious effect on the taste and/or smell of products for human consumption derived from the aquatic environment and compounds liable to give rise to such substances in water.

1.2.2 UK Law

Currently the treatment and disposal of wastewater is the responsibility of the 10 water and sewerage companies. They also operate the regulatory system for discharge of waste to sewers under the legislation contained in the Water Industry Act 1991. Under section 118 of the Water Industry Act 1991, it is a criminal offence to discharge any 'trade effluent' from 'trade premises' into sewers unless a trade effluent consent is obtained from the sewerage undertaker. A trade effluent consent is granted subject to conditions, on such matters as the place of discharge, the nature, temperature and composition of the discharge (Bell 1997). Metals and other hazardous items are controlled by consent limits. Generally, the consent is set by reference to the receiving capabilities of the sewers and treatment works. A major factor that the operator must take into account is the sewerage undertaker's own potential liability for discharges from the treatment works. The discharges from wastewater treatment plants into surface waters is covered by the discharge consents system, which is operated by the Environment Agency under the Water Resources Act 1991.

The consent limits in both systems, disposal of waste to sewers and discharges from wastewater treatment plants, are based on local emission standards, which are set to

achieve local water quality objectives set by the Environment Agency. Through its discharge consenting power, the Environment Agency will ensure that:

- Treatment standards are met for all discharges from sewage treatment works and directed discharges to controlled waters;
- Sewage sludge is not discharged through pipelines to surface waters after 31 December 1998 and that harmful contaminants are reduced up to then.

The enforcement powers and penalties for any breach of the water pollution legislation are given to the Environment Agency under the Water Resources Act 1991.

The treatment and disposal of sewage sludges are also governed by standards and guidelines to minimise the risks arising from them. The two principal disposal routes for sewage sludges have been agricultural land and the marine environment (Kirk 1987). According to 1998 estimates, 50% of sewage was re-used on land, 15% taken to landfill, 9% incinerated and 17% dumped at sea (HCSC 1998). With the phasing out of sludge disposal to sea, as required by the Urban Wastewater Treatment Directive at the end of 1998, alternative routes for disposal of that 17%, which was bound for sea disposal, have had to be found. Furthermore, the amount of sludge being produced is increasing as a result of stricter controls on effluent quality. In the area of Southern Water, for example, it was estimated that the end of dumping at sea, together with the upgrading of twelve of their works, will result in a 100% increase in the amount of sludge requiring disposal (HCSC 1998). The limited range of options that are listed in the House of Commons Select Committee report are: landfill, incineration and "recycling" (disposal to land).

In general, the option of landfilling was not regarded to be an available option, since it was considered environmentally unsustainable and also due to the lack of landfill space available. Incineration was not favoured because of public fears of the emissions involved. Also, the issue of the ash disposal would have to be addressed. Therefore, sludge recycling to land was found to be the best environmental option (HCSC 1998). The main concerns arising from this option were with respect to the possible presence of potentially toxic elements (PTE's), such as heavy metals and organic chemicals, within the sludge.

Due to the high heavy metal concentrations within sludges, many countries have developed legislation, which specify the maximum concentrations of metals in sludge applied to agricultural land. In the UK, the Environment Agency controls the practice of sewage sludge disposal to agricultural land through the regulations (SI 1989/1263), which implement the EC Directive on Sewage Sludge in Agriculture (86/278/EEC). The regulations require that no-one, including the farmer or the supplier of the sludge, may permit the use of sewage sludge on agricultural land unless certain that the requirements are fulfilled. This is to safeguard, particularly, against the addition of excessive levels of heavy metals to the soil (Environment Agency 1998). The Environment Agency has a duty to make sure that PTE's will not be introduced into the soil through using sludge on land. They do this by monitoring the PTE level in the soil. There is also a limit on the rate at which PTE's can be added in sludge, which is set at an average over ten years. The House of Commons Select Committee report recommends that the Environment Agency's current practice should be replaced by the more widely accepted EU option of monitoring PTE's in the sludge as opposed to the soil (HCSC 1998).

Recently, leading food retailers and the water industry have agreed a strategy for the use of sewage sludge on agricultural land (EDIE 1998). The strategy prohibits any use of sewage sludge on land used for growing fruit and salad crops. A matrix and guidelines have been developed by the environmental consultancy ADAS, which was implemented on the 31 December 1998. Other environmental consultancies have developed systems to ensure safe sludge disposal. These include the STATS (Sludge Treatment and Tracking System) developed by Biwater Treatment (Biwater News 1999) and the BioEDGE sludge to land management system developed by Binnie Black & Veatch (In Progress 2000)

1.2.3 Determination of Acceptable Levels of Heavy Metals Discharged to Sewers

The characteristics of wastewater are extremely complex, consisting of inorganic and organic material, as well as supporting a complex microbial system (Horan 1990). It is necessary to understand how a discharge interacts with its receiving environment before suitable standards can be imposed to limit the discharge of wastewaters. A balance must be achieved between protecting the environment and community served by the receiving water course, and ensuring that unnecessary burden is not placed on the operators of wastewater treatment facilities by placing an excessively strict discharge limit. The wastewater discharge standards must therefore adequately reflect the dangers posed by a certain discharge. As these dangers will vary from one environment to another, the discharge limits should be specified on a site-specific basis. Thus, the ability of a water to receive wastes would be divided among those discharging wastes (Tarzwell 1975). Therefore, effluent limits for each discharge are set to achieve water quality standards for a particular watercourse. While the water quality standards are usually fixed, the discharge limits are kept flexible so as to meet the water quality standards, if the situation changes, such as with the introduction of a new plant or an increase in population.

The final composition of the wastewater effluent discharged to surface waters will depend ultimately on the nature of the wastewaters incoming to the plant via the sewers, and on the treatment processes utilised in the plant. As summarised above, wastewater treatment must be able to treat the incoming waste to a level such that the amount discharged does not exceed the discharge limits imposed on that plant. During wastewater treatment, heavy metals will be removed from the soluble state by precipitation and adsorption onto the biomass. The end product will be sludges laden with heavy metals. The disposal of these sludges will also be bound by standards, which seek to minimise the dangers that these sludges pose to the receiving environment. Therefore to control the amount of metals discharged to the environment through the effluent or the sludge resulting from wastewater treatment, trade effluent standards are set to limit the amount of heavy metals discharged from a plant into the sewer system. These are similar to the discharge limits imposed on the wastewater treatment plant and other plants that discharge directly into a watercourse.

Arundel (1995) notes that the UK Water Plc's are noticeably tightening the current metal limits in trade effluent consents. He states that although there are regional variations depending on dilution, past history and type of receiving works, the general trend for limits is ever downwards. Table 1.5 shows typical limits for metal-containing trade effluents discharging to the sewer in the UK.

Table 1.5: *Typical UK trade effluent consent limits (Arundel 1995)*

pH range	6-11
Settleable solids	300 mg/l
Total cyanide	5 mg/l
Sulphate	1500 mg/l
Total sulphide	1 mg/l
Available chlorine	50 mg/l
Available sulphur dioxide	5 mg/l
Free ammonia	100 mg/l
Grease and oil	500 mg/l
Chromium	10 mg/l
Zinc	10 mg/l
Nickel	3 mg/l
Copper	5 mg/l
Lead	10 mg/l
Silver	1 mg/l
Cadmium	*Subject to EC Directive 76/464/EEC and Environment Agency approval (typically <0.1 mg/l)*
Total iron	100 mg/l

Factors affecting the level of discharge to sewers

WRc (1976b) and Arundel (1995) list the factors that influence the setting of tight metal limits by operating and regulatory bodies:

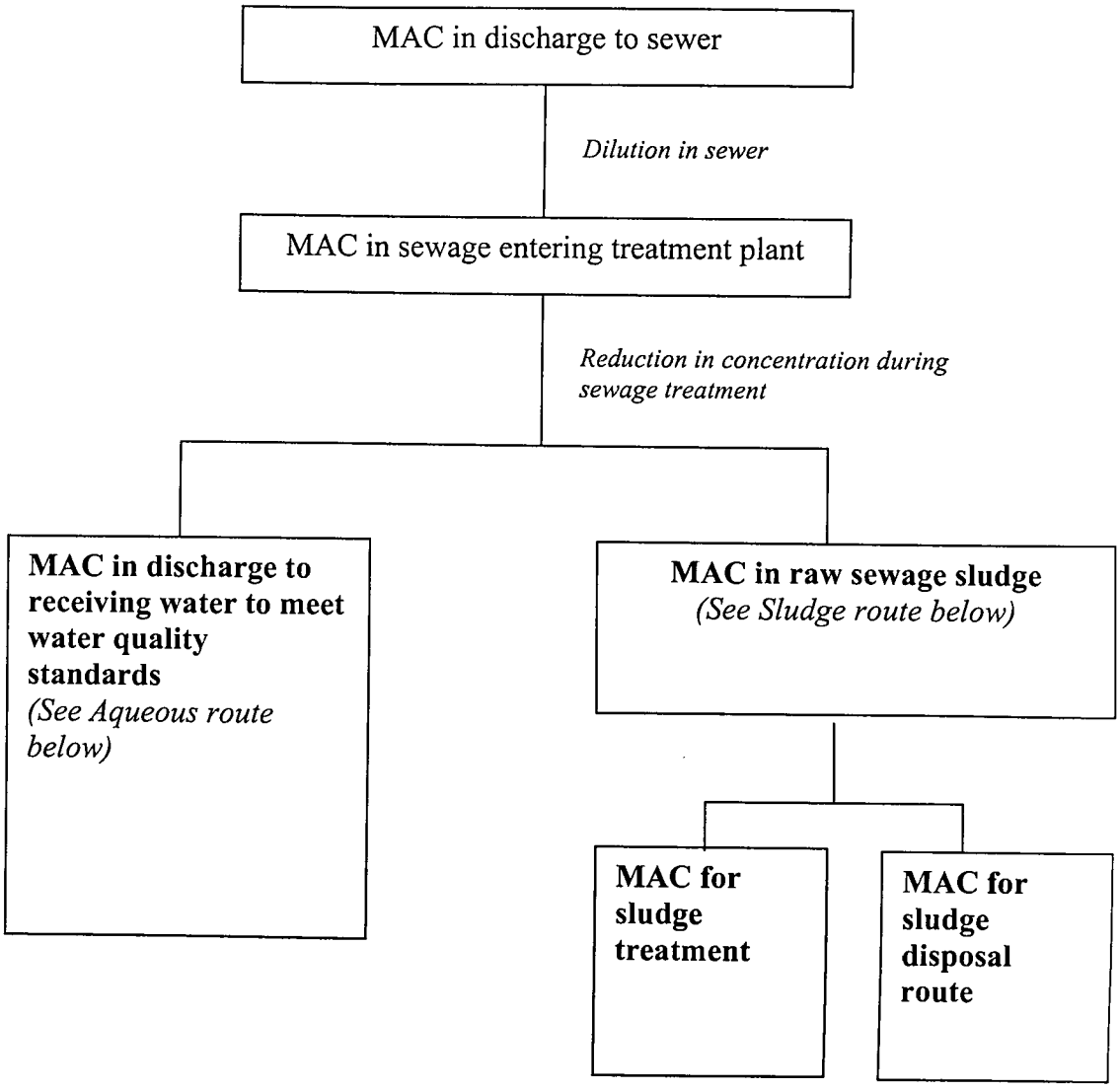
1. To protect the fabric of the sewers and sewer maintenance workers;
2. To protect against loss of treatment works efficiency, especially biological treatments;
3. Restricted sludge disposal routes; and
4. The general toxicity in the aquatic environment and to protect the quality of water abstracted for potable water supply and irrigation.

It is important to know the composition of the wastewater discharged into the sewers, since effluent discharges may cause important effects even if they do not contain metals (WRc 1976a). For example, it was found that the discharge of spent sulphite liquor reduced the concentration of free copper ions by complexation and thus decreased their toxicity. Also, strong complexing and chelating agents can release metals from sediments and hence increase the rate of metal transport.

Determining the Maximum Acceptable Level of Discharge

In practice, the maximum permissible concentration for a trade effluent discharge is determined by looking at critical stages in the wastewater treatment system in relation to all that may be damaging to it. Maximum acceptable concentrations (MAC) are assigned to each stage, taking into account reduction and dilution throughout the system. This is achieved by carrying-out back calculations, starting from the effluent level to satisfy a water quality objective of a particular water course, or, in the case of sludge, the standards associated with the sludge disposal route. This is shown diagrammatically in figure 1.2.

Figure 1.2: *Determining acceptable levels of sewer discharge concentrations (adapted from Banks 1998 and WRc 1976b)*



AQUEOUS ROUTE:

Critical Stages	Critical Concentration Determined By:
• **Water usage of receiving water:** Abstraction for potable water supply; fisheries; shellfisheries; recreation; irrigation.	• Protection of the aquatic environment; • Water quality standards: UK Statutory water quality objectives and EC directives
• **Effluent quality**	• **Treatment plant effluent consent**
• **Secondary biological treatment:** Reduction in concentration through adsorption and biodegradation	• Protection of the process from potentially toxic or inhibitory materials: a)Biomass: e.g. metals, general toxic organics b)Oxygen transfer: e.g. surface active agents, oil
• **Preliminary and primary treatment:** Reduction in concentration through adsorption.	• Protection of the process and equipment: a) Settlement: e.g. surface active agents, oil b) Equipment: e.g. grease
• **Sewer system:** New discharge in relation to existing discharges Dilution	• Protection of the fabric of the sewer: e.g. from acids, sulphates • Protection of the health and safety of the workers: e.g. from solvents, cyanide.

SLUDGE ROUTE:

Critical Stages	Critical Concentration Determined By:
• **Sludge Disposal**	• Protection of the environment and public health Environmental quality standards in relation to disposal route: e.g. Sludge to land regulations and Waste disposal regulations
• **Sludge Treatment**	• Protection of the process: Protecting the biomass from toxic or inhibitory materials: e.g. metal, halogenated hydrocarbons, synthetic detergents

1.3 Aims and Objectives of the Project

The problem of heavy metals discharged to the environment in general and specifically to wastewater treatment systems has been outlined above. Recently, mainly due to the changes in legislation and increased environmental protection measures, the presence of heavy metals in wastewater treatment is receiving more attention. As has been noted previously, the majority of heavy metals are partitioned during wastewater treatment into the sewage sludge or the treated effluent. Thus, due to the ecotoxicological hazards that they might pose and consequently the stricter controls governing their discharge into the environment, it is becoming increasingly important to have a knowledge of the heavy metal content of the effluent and the sludge prior to their disposal.

The principal aim of this project is to produce a computer based simulation model that will predict the partitioning of heavy metals into the solid and liquid phases through the wastewater treatment processes. It is anticipated that the model will have the following practical applications within the water industry:

- As a management tool to trade effluent officers, allowing them to rapidly assess the potential impact of a new discharge on both sludge and effluent quality.
- As a management tool in strategic decision making as to where stricter controls may be necessary in order to achieve increasingly stringent effluent or sludge standards.
- As a modelling tool to assess different operational strategies on a particular works, for example: the import of a sludge, the point of return of sludge liquors, the change in type of chemical conditioning agent, the potential effect of changes in water chemistry (pH, sulphate, organic ligands, etc.).

To achieve this aim, both laboratory-based and field-based studies on the removal of metals from wastewaters will be carried out. The objectives of these studies will be to gain insight into the factors affecting and mechanisms effecting the removal of heavy metals. For the purposes of these studies, the metals that will be investigated are copper and zinc. The environmental significance of these two metals is high, considering both their industrial use and potential pollution impact. While not acutely toxic to humans, copper is toxic to plants and its widespread prevalence in the environment, both due to domestic and industrial sources is a cause for concern. Zinc, on the other hand, is toxic to humans at concentrations of 100-500 mg/day (Chong and Volesky, 1995). Its

sources are even more extensive, ranging from corrosion of plumbing and leaching from paints and water-proofing products on a domestic level to its use in industrial processes such as its use in galvanisation and the production of plastics, tyres and pharmaceutical products (IC Consultants 2001).

1.4 Methodology

The methodology employed in this research project for the development of a predictive model for metals in wastewater treatment follows the basic modelling process described by Olsson and Newell (1999). They proposed a model development process that comprises seven stages. This is shown in figure 1.3.

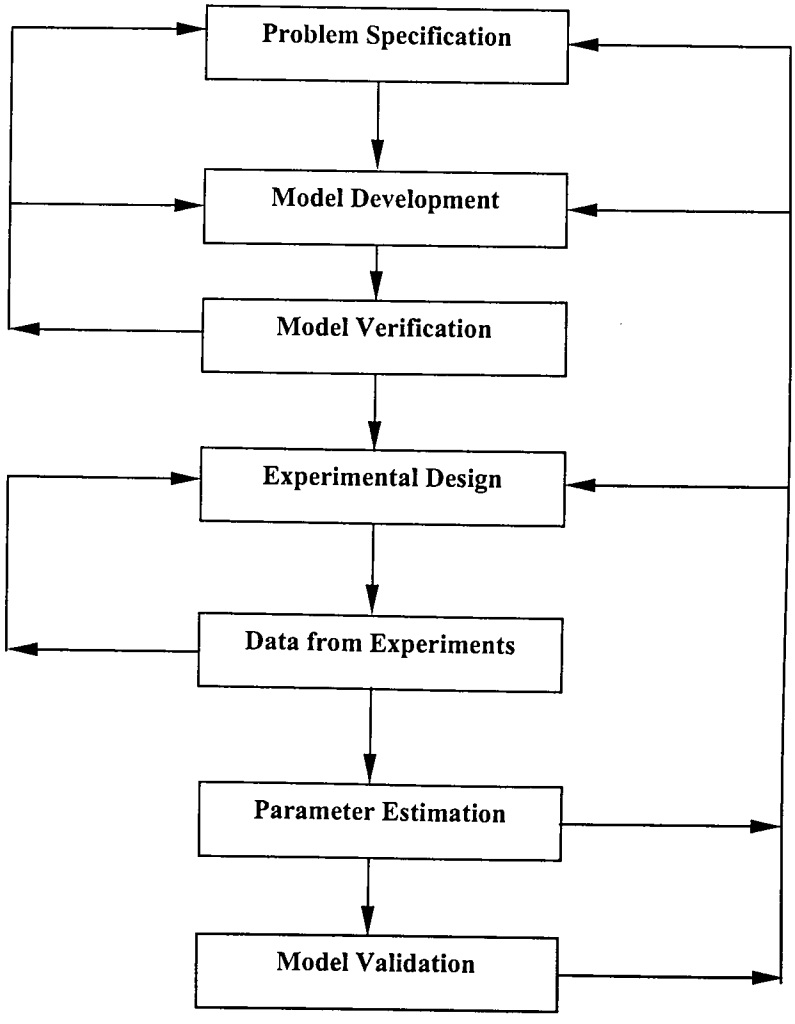


Figure 1.3: *Model Development Process (Olsson and Newell 1999)*

This thesis will describe the application of this methodology to the metals model development. The problem specification and need for this type of model were outlined in this chapter. Chapter 2 provides a thorough examination of the literature surrounding the behaviour of heavy metals during wastewater treatment. Chapters 3 and 4 describe the stages of identifying the most suitable modelling approach and the development of the model equations, with Chapter 3 covering the development of a solids model and Chapter 4 focusing on the metals model development. Chapter 5 details the experimental methods used to derive the model coefficients, using samples from a local wastewater treatment plant. The results from these experiments are also discussed. Chapter 6 covers the sampling procedures used to obtain data from to wastewater treatment plants in the Southampton area to be able to validate the model. The results from these field studies will show the extent to which the model can accurately predict the partitioning of metals in municipal wastewater treatment. Finally, the conclusions of the research and recommendations for future work will be presented.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

The behaviour and significance of heavy metals in wastewater treatment has been the subject of considerable research. As early as the 1930's sewer blockages caused by industrial discharges containing chromium were being investigated. Later, the fate of heavy metals during wastewater treatment, as well as their toxicity to biological treatment, were studied. Subsequently many studies were carried out in order to ascertain the factors and mechanisms influencing the removal of heavy metals from wastewater during the various stages of wastewater treatment. This chapter will review the results of the vast amount of literature concerning the behaviour of heavy metals during the different stages of wastewater treatment.

2.2 Primary Sedimentation

Studies have shown that primary sedimentation has two effects on the metals-laden influent streams before their entry into the aeration tank. According to Barth et al (1965), these are:

(i) It reduces the total metal content since some metal is removed with the primary sludge;

(ii) The physical and chemical characteristics of the sewage alter the form of the metal introduced.

Since high concentrations of certain metals may be toxic to the micro-organisms in biological treatment, primary sedimentation reduces the possibility of impairment of the efficiency of the biological treatment through metals toxicity. It also contributes to the overall removal efficiency of the treatment works (Lester 1987). Due to the physical nature of the primary sedimentation process, the removal of heavy metals during that process is also primarily a physical process. It depends on the settlement of precipitated metals or metals associated with settleable particles. The majority of the metals that are removed are insoluble (Oliver et al 1974). Thus, the proportion of soluble metal to total metal increases in the effluent from the primary tank.

2.2.1 Factors affecting heavy metal removal in primary sedimentation

The three main factors that have been found to affect metal removal in primary sedimentation are the efficiency of suspended solids removal, the chemical species of the metal (Lester 1983) and the sewage matrix characteristics. These three factors are in turn influenced by other factors.

Suspended Solids Removal

Suspended solids removal is affected by operational factors, such as the hydraulic loading, and influent suspended solids concentration (Lester 1983). According to Tebbutt and Christoulas (1975), suspended solids removal is influenced to a greater extent by influent suspended solids concentrations than by overflow rate. The results of Rossin et al (1983) show that the solids removal efficiencies were strongly influenced by influent suspended solids concentrations, and not with hydraulic loading although variable flow conditions resulted in the poorest removal efficiency. The removals of Cd, Cr, Cu and Zn were adversely affected by increasing flow and poorest under variable flow conditions. They suggested that the particulate forms of heavy metals might belong to a class of inorganic particles whose settlability is sensitive to flow rate, while the primary sludge was predominantly organic. Thus they concluded that the distribution of the particulate forms of heavy metals was not related to the distribution of suspended solids and that the removal of heavy metals was not related to the removal of suspended solids. However, the results of a study by Kempton et al (1987a) carried out at a pilot plant indicate that the solids removal efficiency directly increased with increasing solids loading whereas increasing hydraulic loading caused marked reductions in solids removal. A close correlation was also found between the solids loading and the metal removal efficiencies of silver, cadmium, copper, chromium and thallium. Reductions in metal solubility of 50% accompanied increases in suspended solids concentration of approximately 50%. Therefore, the design and operation of the sedimentation tank is critical when considering the efficiency of the solids removal. Yet, with respect to the metals removal, the efficiency will depend mainly on the metal speciation.

Metal Speciation

The chemical species of the metal may depend on influent metal concentration, influent COD, and hardness, alkalinity and pH of the wastewater (Lester 1983). The results of a series of studies at the Oxford Sewage Treatment Works (Lester et al 1979 and Stoveland et al 1979), showed that the chemical species of the metal, which varied on each occasion, was of considerable importance in determining the removal of the metal. This is because the metals that are removed in primary sedimentation are those that exist in insoluble forms or forms that have the capacity for binding to settleable solids. The formation of insoluble hydroxides, carbonates and phosphates by the interaction of

heavy metals with sewage aids the process of removal, but these reactions are influenced by many factors, including pH. Later however, Lester (1987) concluded that the relative importance of the soluble and solid phases of the sewage matrix in determining the removal of individual metals remains to be resolved. In general, it was found that particulate Cu and Ni were removed to a much greater extent than dissolved Cu and Ni. In another study only particulate Cu removal could be significantly correlated to suspended solids removal during primary sedimentation (Ekster and Jenkins 1996).

Sewage Matrix Characteristics

The major subfractions that are present in the raw sewage with which heavy metals may be associated are surface-bound organic ligands, insoluble salts, inorganic solids and soluble organic ligands (Kempton et al 1987b). Although suspended solids fractions were found to be the most important factors in controlling metal removal, the soluble organic ligands may also influence the proportion of metal in the soluble form. The presence of soluble organic ligands in the sewage might bind heavy metals, thus retaining them in solution and preventing their removal during treatment (Stoveland et al 1980). This was demonstrated, with respect to copper by Kempton et al (1987a), who noted that an increase in chemical oxygen demand (COD) was accompanied by an increase in filterable metal concentration. However, copper was the exception, as the other metals studied did not appear to be markedly affected by COD. Thus it was concluded that soluble organic ligands might play a minor role in determining the proportion of metal in the soluble form in raw sewage.

2.2.2 Mechanisms of heavy metal removal in primary sedimentation

The behaviour of a heavy metal during primary sedimentation depends on the metal in question. For some metals, such as manganese, nickel and lead, those fractions that are in particulate or insoluble form and those that are associated with particulates are settled in the primary sedimentation tank, leaving the soluble forms in the primary effluent. On the other hand, particulate forms of some metals, such as cadmium, chromium, copper and zinc, can be found in the primary effluent (Chen et al 1974). For each metal, the removal is generally dominated by one of three mechanisms:

1. Direct precipitation: e.g. lead and bismuth;

2. Adsorption or complexation by the suspended solids: e.g. silver, cadmium, cobalt, copper, chromium, manganese, nickel and thallium;
3. Precipitation followed by the association of the precipitate with the bulk solids fraction: e.g. zinc and molybdenum. (Kempton et al 1987b)

The removal of all particulate fractions does not occur to the same extent. Hence, the unequal association of metals with different particle fractions is a major factor controlling their removal (Kempton 1987b). Chen et al (1974) found that a higher concentration of toxic elements are associated with small-particle-size fractions (0.2 to 0.8 μm) than with larger-particle-size-fractions (>44μm). Lester (1987) concluded that toxic-element removal might be influenced by a critical size of particulate matter, determined by solids distributions. Kempton et al (1987b) found that the critical size varied from 35 to 125 μm, above which size very little particulate matter escaped in the effluent. They suggested that the flow rate was a significant factor and that other variables, such as the influent composition, were influential. Ekster and Jenkins (1996) found that, consistent with the findings of Kempton et al (1987 a &b), Cu and Ni were associated with the smaller particles present in wastewater.

Kempton et al (1987b) concluded that two main groups of elements can be identified. The first group included silver, cobalt and molybdenum, which showed a strong association with the volatile suspended solids (VSS) fraction, suggesting that their partition into the solid phase may be primarily due to adsorption or complexation by organic elements. The second group included copper, manganese, lead and zinc, which were primarily associated with the non-volatile suspended solids (NVSS) fraction. Patterson et al (1983) concluded from their investigations that sedimentation of solids-bound metal is the major removal mechanism for metals during primary sedimentation.

2.2.3 Efficiency of heavy metal removal in primary sedimentation

According to Rossin et al (1983), the efficiency of heavy metal removal during primary sedimentation is dependent on two factors:

1. their existence as settleable particulate forms in the sewage; and
2. the conversion of soluble and non-settleable forms within the process.

There are wide variations in the reported values of metal removals (See Table 2.1). This is due to the factors that influence their removal as presented in section 2.2.2.

Table 2.1: *Metal concentrations in raw sewage and their removal during primary sedimentation (adapted from Lester 1987)*

Reference	Barth et al (1965)		Oliver et al (1974)		Data from 7 studies
Metal	**Influent metal concentration (μg/l)**	**Removal (%)**	**Influent metal concentration (μg/l)**	**Removal (%)**	**Average Removal (%)**
Cd	6	60	24	25	37
Cr	290	55	190	36	38
Co	2	50	ND	ND	ND
Cu	310	33	220	70	45
Hg	7	57	1.3	54	56
Mn	6	33	ND	ND	ND
Ni	330	15	ND	ND	33
Pb	230	66	390	59	58
Zn	2400	54	1050	68	44

Notes: ND: Not detected

Results from several studies showed that Pb, Cu and Zn were the most readily removed metals in primary sedimentation, while Ni was the least readily removed. Cr was also less readily removed than most metals. Although metals removals in primary sedimentation of greater than 50% have frequently been reported by several authors, a few authors have reported relatively low metal removal efficiencies. This could be due to the considerable variations in influent heavy metal loading and heavy metal concentration to primary sedimentation, which have been observed (Roberts et al. 1977). There seems to be some conflicting reports with regards to this point. Oliver et al (1974) reported that 8-10 fold variations in the concentration of some heavy metals in the influent raw sewage over periods of 6 hours did not influence removal efficiencies, which were fairly constant throughout a longer period of study. On the other hand, Brown et al (1973) reported that lower percentage removals of heavy metals during primary sedimentation were observed when anaerobic digester liquors concentrated in heavy metals were recirculated to the primary sedimentation tanks. This implies that the influent concentration may influence removal. Results from studies conducted at the New Works Extension to the Oxford Sewage Treatment Works show that even under similar operational conditions at the same plant, metal removal

varies. Lester (1983) assumes that this phenomenon may be related to variations in influent concentration. However, he further inspected the results, especially by comparing the variation in influent concentration (Cu>Pb>Cr>Cd>Zn>Ni) and the variation in percentage removal (Ni>Cu>Cr>Cd>Pb>Zn). This led to the conclusion that, most likely the chemical species of the metal was variable and of considerable importance in determining the removal of the metal on each occasion.

2.3 Biological Treatment

During primary sedimentation, the only removal of heavy metals is through the settlement of insoluble metals or metals adsorbed to particulates. Little removal of the soluble fractions of heavy metals takes place during primary sedimentation. During activated sludge treatment, a marked reduction in the concentrations of soluble metal occurs as a result of their association with the settleable biomass floc in the aeration tanks with the subsequent settling out of the material in the secondary clarifiers (Oliver et al 1974 and Lawson et al 1984). This section will present the factors that affect heavy metal removal in the activated sludge process as well as the mechanisms that effect it.

2.3.1 Factors affecting heavy metal removal in activated sludge

Overall, Cu and Ni removals by activated sludge have been associated with a variety of factors including the relative concentration of dissolved metals, the concentration of complexing ligands, the nature of the wastewater feed, especially its carbon/ nitrogen or BOD_5/TKN ratio and activated sludge growth, (Ekster and Jenkins 1996). These, and many other factors that have been found to influence the removal of heavy metals in activated sludge, can be divided into three main groups:

1. Operating parameters
2. Physical and chemical factors
3. Biological factors

Operating Parameters:

These affect the metal removal by influencing suspended solids removal or the affinity of the metal for the solid phase.

Sludge Age

Sludge age is the one operational parameter that the operator of an activated sludge plant is best able to control (Neufeld et al 1975). In the experiments conducted by Stephenson et al (1987a), the type of biomass, as determined by the sludge age, was critical. This is because it links many of the other factors (Stoveland et al 1980), e.g. it influences sludge volume index (SVI), mixed liquor suspended solids (MLSS), effluent COD and effluent suspended solids (ESS). Increasing sludge age improves settlability, which leads to increased metal removal. It has been observed that increasing sludge age (from 10 days to 12 days), the concentration of extracellular polymers is increased and that the greatest degree of metal removal coincides with the highest concentration of extracellular material (Stoveland et al 1980).

Lab-scale activated sludge simulations operating at different sludge ages conducted by Stoveland et al (1980) produced the following results:

- Removal of Cd and Cr appear to be independent of sludge age;
- Removal of Cu and Ni would not appear to be directly correlated with sludge age but the highest percentage removed for both metals occurred at the highest sludge age.
- Pb and Zn removals increased with increasing sludge age.

Influence of MLSS concentration on metal removal at different sludge ages (Stoveland et al 1980):

- As MLSS increased, removal of Cd, Cu and Ni increased for all sludge ages
- Cr (VI) removal was only influenced by MLSS concentration at the highest sludge age of 12 days.
- Pb was largely independent of MLSS concentration but was strongly influenced by sludge age.

Four types of responses were observed in a study to assess the effect of sludge age on the removal of metals (Sterritt and Lester 1981):

- Removals of Cu, Ni, Ag and Zn were at their highest when effluent COD was lowest;
- Cr was removed most effectively at sludge ages with the highest MLSS
- Removals of Co, Mn, and Mo were always low and were little influenced by the sludge age.

- Pb removal was at a minimum when ESS were at a minimum.

Therefore, under ideal conditions, since MLSS concentration increases with sludge age, the percentage removal of heavy metals in activated sludge would increase linearly with sludge age (Lawson et al 1984, Stephenson et al 1987a, Ekster and Jenkins 1996). However in practice, due to changes in effluent suspended solids and COD, and shifts in the effluent speciation of metals, this is not the case (Stephenson et al 1987a).

Suspended solids removal:

As in the case of primary sedimentation, suspended solids removal is an important factor influencing metal removal in activated sludge. Results from the study by Brown et al (1973) indicate that secondary treatment has a definite advantage over primary treatment, due to the increased suspended solids removal. It was found that as suspended solids removal increased heavy metals removal increased at an exponential rate, i.e. asymptotically approach completion of heavy metals removal. This phenomenon may be possibly explained by the increased adsorption of heavy metals onto microbial flocs resulting from secondary treatment processes. Lester (1983) also pointed out that increased settling time in the activated sludge plant leads to increased suspended solids removal, which leads to increased removal of the heavy metals that are associated with the suspended solids. Naturally, efficient removal of the metals that are adsorbed onto the sludge flocs and those that form particulates independently can only occur if these settle out efficiently in final sedimentation (Rossin et al 1982). This efficiency is strongly influenced by particle size and effluent solids removal (Stoveland et al 1980).

In the case of Pb and Zn, Stoveland et al (1980) found a considerable proportion of each metal was in an insoluble form; therefore it would be expected that their removal would be related to the effluent suspended solids. However, an increase in the removal of Pb and Zn was observed with increasing sludge age despite an increase in ESS (i.e. a decrease in suspended solids removal). Therefore, they concluded that some other mechanism must have been compensating for the metals lost in the effluent, i.e. direct precipitation.

Volatile suspended solids:

Results of the studies conducted by Cheng et al (1975) clearly indicated that the total amount of metal taken up by the sludge floc increased as the concentration of VSS increased. The only exception was nickel, whose uptake per unit weight of VSS decreased with increasing VSS concentration. The uptake of metal was also found to increase with increasing metal concentration at a constant VSS concentration. The increases in both cases were not linear. Patterson et al (1983) studied the removal of heavy metals in municipal wastewater treatment systems, through conducting a set of experiments on eight pilot treatment plants. They found substantial evidence that the concentration of volatile suspended solids is the dominant factor influencing the distribution of heavy metals. Their results illustrate that:

- As the total metal concentration increases, the amount of sludge-bound metal per unit weight of VSS also increases, at a constant level of VSS.
- At any given total metal concentration, the sludge-bound metal per unit weight of VSS decreases as the VSS concentration increases.
- At low total metal concentrations, the effect of VSS on sludge-bound metal is slight.

These relationships hold for all the eight metals studied. However, in their study, Stephenson et al (1987b) found evidence that suggested that non-settleable precipitates of non-volatile solids rather than biomass associated metal contributed to most of the non-settleable effluent metals. Therefore, they concluded that a model based on high correlations between metal removal and effluent volatile suspended solids found by the other researchers may not apply to all conventional activated sludge plants. Another conclusion that they reached was that a model that would be applicable to a variety of plants would probably have to include a factor to account for other types of non-settleable metals.

Dissolved Oxygen Concentration

Metals-loaded sludges have been found to operate at a decreased oxygen requirement in comparison with a similar metals-free control unit (Neufeld et al 1975). This has an effect on the extracellular polymers in the activated sludge. Dissolved oxygen affects the rate of oxidation of polymers. Where metal ions are adsorbed to extracellular polymers, oxidation of the polymers in activated sludge may result in either the

accumulation of metal ions within cells, or the release of metal ions back into the medium (Lester 1983).

Physical and chemical factors

These factors play an important role in determining the affinity of the metal for biological solids.

Initial Metal Concentration

Besides the possibility of high initial metal concentrations producing toxic effects, the initial metal concentration is an important factor influencing the efficiency of metal removal. High metal inputs have been shown to severely inhibit plant operations, resulting in an inferior effluent of high turbidity (Oliver et al 1974). Brown et al (1973) found that over the range of initial heavy metal loadings utilised in their study (<2000 μg/l), the percentage of heavy metals removed was directly proportional to the initial metals loadings. In another study, the degree of biosorption was found to increase with increasing concentrations of added metal (Stover et al 1976). Experiments were undertaken by Stoveland et al (1980) to investigate the relationships between the heavy metal concentrations in solution and the total heavy metal concentration accumulated in the activated sludge. The results showed that for all the metals, with the possible exception of Pb, the removal efficiency would be maintained despite variations in the influent concentration. The results of the investigations undertaken by Cheng et al (1975) indicate the following mechanisms:

- At lower metal concentrations, metal is taken up by the biofloc through the formation of metal-organic complexes.
- At higher metal concentrations, metal ion precipitation from solution may occur in addition to sludge uptake.

***Metal complexation and speciation*:**

Due to the complex and variable nature of combined wastewater and process supernatants, in addition to the free metal ion, soluble or insoluble complex species involving both organic and inorganic ligands may also exist within the wastewater (Cheng et al 1975). Figure 2.1 shows the possible species that may occur.

Size(nm)	1		10		100		1000
	Soluble			***Colloidal***		***Particulate***	
Metal species	Free metal ions	Inorganic ion pairs; Organic chelates	Organic complexes	Metal species bound to high molecular weight organic material	Metal species adsorbed on colloids	Metals incorporated with organic particles and remains of living organisms	Mineral solids; Metals adsorbed on solids; Precipitates and co-precipitates
Example	Pb^{2+}	$PbHCO^{+}_{3}$ Pb-EDTA	Pb-fulvic acid	Pb-humic acid	Pb-$Fe(OH)_3$ Pb-MnO_2	Pb-organic solids	Pb-clay; $PbCO_3$

Figure 2.1: *The range of forms of heavy metals in water classified according to size association (Harrison and Laxen 1980)*

The most common complexing anions are HCO_3^-/CO_3^{2-}, Cl^-, SO_4^{2-} and organic materials. The relative propensity of the inorganic ligands to form complexes with many metals is: $CO_3^{2-} > SO_4^{2-} > PO_4^{3-} > Cl^-$ (Stumm and Morgan, 1996). The speciation and complexation of a metal are a function of the redox and pH conditions of the wastewater (USEPA 1999). Variations in the speciation of heavy metals may occur as a result of industrial discharges and complexation and chelation by components of the sewage (Rossin et al 1982). These variations in the speciation of the metals markedly influence their affinity to the sludge or the soluble phase, and thus their removal. Metals may form complexes with either soluble ligands or with the wastewater solids. Complexation in the first case would increase the metal in solution while in the second case complexation with the solids will lead to metal remove from solution. The complexation mechanism of the metal thus affects its removal. Stephenson et al (1987c) found that the metal : ligand stoichiometries indicated that the complexation mechanism of Cu was different from that of Cd and Ni. Entrapment of precipitated metal contributed to the overall percentage of Cu removed. On the other hand, extracellular polymers of the activated sludge solids complex soluble metals, and this contributed to the overall amount of metal removed.

Cheng et al (1975) found that the degree to which metal ions associate with the sludge determines the extent of reduction of soluble metal in the supernatant and the consequent effluent metal concentrations. Metals that are largely complexed with organic ligands may only be removed if these complexes dissociate to preferentially

form other metal species that have a greater stability (Lester 1983). The stability of metal complexes depends on:

(i) the affinity of the metal to the soluble phase;

(ii) the affinity of the metal to the biomass;

(iii) the complexation capacity, which is the concentration of the metal that may be maintained in solution by soluble ligands. Thus, a metal with a low complexation capacity has the potential to exist in free ionic form or be converted to other forms (Lester 1983).

Work with bacterial extracellular polymers, conducted by Lester and his co-workers (Lester 1983), has shown that the stability of polymer-Cu complexes is higher than the stability of complexes with Cd, Co and Ni. Thus Cu may dissociate from its soluble complexes to be removed by association with the biomass, whereas Ni, which has an affinity similar to that of Cu for the soluble phase but a weaker affinity for biomass, is removed to lesser extent. Thus the low removal efficiencies in certain metals may be due to a high affinity for soluble ligands rather than a poor affinity for the activated sludge. The variations of the speciation of the metals in the settled sewage could also explain the greater variation in heavy metal removals observed at the lower influent concentrations by Rossin et al (1982).

Rudd (1987a) concludes that the rate and extent of the speciation reactions is controlled by environmental parameters such as pH, ionic strength, the type and concentration of inorganic and organic ligands and the presence of solid surfaces for adsorption.

Redox Reactions

Redox reactions result in the transfer of electrons from one species to another. When an oxidised system is reduced, the order that oxidised species disappear is: O_2, NO_3^-, Mn^{2+}, Fe^{2+}, HS^- and H_2 (USEPA 1999). Lowering the redox status results in an increase in the aqueous phase concentrations of metals. However, the metals released by reduction of iron and manganese are usually readsorbed by solids that are stable at low pE, such as organic solids (USEPA 1999). At a sufficiently low redox status, precipitation of metal sulphides is introduced. Thus the redox status of wastewater may determine the solubility and adsorption potential of metals. However, since many

redox reactions are kinetically slow in natural waters, it would be difficult to accurately predict the removal of redox-sensitive species (USEPA 1999).

pH:

The solution pH, anions (especially complexing agents like cyanide), the concentration of the metal itself and the concentration of the other metals are all factors which affect how the metals entering with the influent are distributed between the solid and liquid phase (Lombraña et al 1995). Nelson et al (1981) stated that the hydrogen ion concentration, or pH, is probably the single most important factor influencing metal adsorption on both organic and inorganic surfaces.

In general, the experimental results agree that metal uptake by activated sludge is highly pH dependent. For all the metals studied, increasing the pH of the system would precipitate the dissolved metals as hydroxides (Oliver et al 1974, Cheng et al 1975 and Lester 1983). The pH of a solution in which interaction between metal ions and organic matter takes place is an important factor in determining the association of metal ions with the organic functional groups. Hydrogen ions will compete with other cations, including the metals for binding sites on the sludge functional groups. As the pH of the solution is increased, resulting in an increase of free binding sites, the formation of metal-organic complexes may also increase (Cheng et al 1975). The hydroxyl ion concentration will also have an effect on the equilibrium of metal ion in solution, acting as a ligand with an affinity for the central metal ion and competing with other ligands for the metal ion. When the pH is increased to a level at which other ligands can no longer successfully compete with the hydroxyl ion, the metal will precipitate from solution as the hydroxide. In general, the complexation capacity of the solution increases with increasing pH, up to a value at which metal hydroxide precipitation occurs.

The pH influences adsorption as well as the solubility of the metals. Increasing pH leads to an increase in the negative surface charge of the solids particles, therefore leading to increased adsorption (USEPA 1999). Also Wang et al (1999) found that as pH and suspended solids increase, organic matter dissolution also increases, leading to increased competition between the solution and the solids for complexation of the metal.

Metal Solubilities

The partitioning of metals between soluble and insoluble phases is important in determining the extent of removal during the activated sludge process (Stephenson et al 1987c). Heavy metals entering the wastewater from industrial sources are largely in the dissolved form, but when they react with municipal sewage, some of the metal is converted into an insoluble state (Oliver et al 1974). The exceptions seem to be metals such as Ni and Mn, which react less extensively with the sewage and enter the treatment plant largely in a dissolved form. The removal efficiencies of these two are poor. Stephenson et al (1987c) stated that metals that are most soluble in the influent settled sewage are least well-removed. This supports the findings of Rossin et al (1982), who found that the high solubility of Ni reflected its poor removal, indicating that it had a very low affinity for particulates. Therefore, the removal efficiencies of a metal seem to be related to the dissolved/insoluble metal ratio in the raw sewage as well as the solubility of the metal (Oliver et al 1974). The solubilities of some complexes of heavy metals are shown in Table 2.2.

Table 2.2: *Solubility of some heavy metal compounds (Rudd 1987a).*

Anion	OH^-	S^{2-}	Cl^-	CO_3^{2-}	NO_3^-	SO_4^{2-}
Cd^{2+}	SS	SS	1400	SS	1500	760
Cr^{3+}	SS	Dec	SS		S	Dec
Co^{2+}	SS	SS	640	SS	VS	362
Cu^{2+}	SS	SS	730	SS	1220	205
Fe^{2+}	SS	SS	644	0.06	S	S
Fe^{3+}	SS	Dec	Dec		S	Dec
Hg_2^{2+}		SS	0.002	SS	Dec	0.6
Hg^{2+}		SS	69	SS	VS	Dec
Mn^{2+}	SS	SS	723[a]	0.0065	VS	630
Ni^{2+}	SS	SS	642	0.09	VS	370
Zn^{2+}	SS	SS	4320[a]	0.01[b]	1170	540

Notes: Solubilities are given as 10^3 times the mass of the anhydrous solute per mass of water at 293 K. VS: very soluble. S: soluble. SS: sparingly soluble. Dec.: decomposes on addition to water.

From this table, it is apparent that the nature of the metal complexes formed with different ligands can influence the solubility of a compound and hence the potential bioavailability and toxicity of the constituent metal.

In the study by Stephenson et al (1987c), the high percentage removals of insoluble metals was found to be mainly due to the interaction of particulate-associated metal with the settleable mixed liquor flocs with an insignificant amount of direct settlement

of insoluble metal. Soluble metal removal also occurs, for example in the Stephenson et al (1987c) study, binding of Cu in the presence of mixed liquor was strongest, although quantitatively of little significance.

It has been found that for most metals, the proportion of dissolved to total metal increases as they pass through the system (Oliver et al 1974 and Rossin et al 1982). This is due to removal of the insoluble forms of the metals during treatment. This shows that an equilibrium between the insoluble and dissolved states of the metal does not exist, since such an equilibrium would require a proportionate removal of the dissolved metal (Oliver et al 1974). However, Rossin et al (1982) accounted for the decline in metal removal efficiency with increasing heavy metal concentrations, which was found in their results, by hypothesising that it might be due to an equilibrium between soluble and adsorbed metal concentrations.

Stephenson et al (1987b) found that the insoluble forms of Ag, Bi, Cr, Cu, Pb and Zn would account for greater than 80% of the non-settleable metal concentration in the effluent discharge to receiving streams and the effluent would probably contain only a small soluble proportion of these metals at whatever sludge age the process was operated. In contrast, the soluble concentrations of the other six metals, which they studied (Cd, Co, Mn, Mo, Ni, Tl) would form a major proportion of the effluent metal discharge and would also be more dependent on the operation of the activated sludge plant. It was concluded that the proportion of insoluble metals in the effluent was dependent on the metal and was likely to exist as non-biomass non-settleable solids.

The differing solubilities of the various metals may be demonstrated by calculating their stability constants in aqueous solution (Lester 1983). The order of solubilities of four metals was found by Cheng et al (1975) to be: Pb < Cu < Cd < Ni. The solubilities and solubility products of heavy metals, as reported in the literature vary markedly. This is because in a dynamic and complex system such as that of the activated sludge process, metal solubilities are greatly affected by all other factors as previously listed. Therefore in practice direct application of those theoretical solubility products may not be appropriate, and it is only possible to make a crude estimation of the expected solubility of any one metal (Cheng et al 1975 and Lester 1983). This is explored further in section 4.3.3.1.

***Composition of the wastewater: concentration of complexing agents and concentration of the substrate*:**

The chemical matrix of the sewage is one factor influencing the forms of the metals and hence the metal balance at a sewage treatment works. It controls the extent of solubility of sparingly soluble salts of the metal, and the degree of enhanced solubility due to formation of ion pairs and complexes (Stoveland et al 1979). Studies have shown that high ligand concentration will both prevent metal precipitation and interfere with sludge uptake, thereby increasing effluent metal levels (Cheng et al 1975). Strong chelating agents, such as EDTA, NTA, oxalate and glycine, have a higher affinity for metal ions than the biomass. The strength of competition was found to be in the order of: sludge < glycine< oxalate< NTA< EDTA (Cheng et al 1975). Natural chelates such as fulvic and humic acids and synthetic chelates such as the detergent builder NTA have also been reported to enhance metal solubility, i.e. reduce the metal removal (Stoveland et al 1979).

The studies carried out by Stoveland et al (1980) to assess the influence of effluent COD concentration on metal removal yielded the following results:

- Cd and Cr were largely unaffected by the organic matrix of this synthetic sewage.
- The solubilities of Cu and Ni appeared to be influenced in an exponential manner by increasing organic concentration.
- The solubilities of Pb and Zn were subject to a small linear increase with increasing COD.
- At increased sludge ages, there was a decrease in the concentrations of soluble organics in the effluent. This may be of considerable significance since many soluble organic ligands compete with the activated sludge for the heavy metals in solution.

Wang et al (1999) conclude that the influence of the composition of the wastewater is mostly to do with the concentration of dissolved organic matter (DOM). Their results show that as pH and suspended solids increase, so does the concentration of DOM. Thus the influence of DOM on heavy metal removal can be regarded as a result of the competition for metals ions between the DOM and the sludge solids.

Metal Valency:

The valency or oxidation states of a metal also have considerable influence on its solubility and thus bioavailability (Rudd 1987a). This can be illustrated in the case of Hg, where mercurous salts (I) are less soluble and consequently less toxic than the mercuric salts (II). Also, for Cr, the hexavalent form is more toxic than the trivalent form. In the case of Cr, the valency has been found to affect removal efficiency. Cr (III) is more efficiently removed than Cr (VI). While most of Cr that enters the plant is Cr (III), this is converted to Cr (VI) during wastewater treatment (Lester 1983).

Competition among metals:

Competition among the heavy metals present in the wastewater influences the relative affinity of the metal ions for the sludge. This competition depends on the number and concentration of different metal ions present in the system (Cheng et al 1975). The order of stabilities of metal-sludge complexes found in the Cheng et al (1975) study was found to be the same as that of the efficiency of metal uptake by the sludge in single metal-mixed liquor experiments. Thus the preferred order of uptake by the activated sludge was found to be in the sequence of Pb > Cu > Cd > Ni. Rossin et al (1982) also noted that the introduction of different chemical species of metals to those normally occurring in the sewage might reduce the availability for uptake by the biomass. Kasan (1993) also points out that while the investigations of Rudd et al (1984) revealed that combined metal addition reduced the overall quantity of each metal bound, the affinity series based on the proportion of each metal ion adsorbed to extracellular polymer showed that metal-ions separately and in combination did not affect relative positions of the metals in the affinity series. Kasan (1993) explains the controlling factors governing the competition between metals for adsorption. The electronegativity of an ion causes it to be attracted more strongly toward a site of opposite charge on the surface of the adsorbent. For ions of equal charge, molecular size determines the order of preference of adsorption, the smaller ion being able to accomplish a closer approach to the adsorption site and thus being favoured in adsorption.

The affinity series for metals biosorption studies on *A.niger* by Chong and Volesky (1996) is Cu > Cd > Zn > Ni. The same results were found by Artola et al (2000), in their experiments on anaerobically digested sludge. The same affinity order was

maintained when multi-metal experiments at equilimolar concentrations of the different metals were performed. Furthermore, it was found that Cu also has the capacity to desorb Zn and Cd previously bound to the sludge to a similar extent to that obtained using HCl at pH 2 as the desorbing agent. Another observation made was that the total sludge adsorption capacity obtained for the four metal system was higher than the maximum adsorption capacity achieved in a single metal system. They concluded that this could be due to the existence of a variety of binding sites on the sludge that are partially specific for individual metal species.

Biological Factors:

Extracellular polymers:

Studies concerning the microbiological aspects of the activated sludge have shown that the settleable activated sludge organisms exist as discrete cells enmeshed in a web of insoluble or slightly soluble extracellular, polysaccharide, polymer fibrils. They contain many functional groups such as phosphoryl, carboxyl, sulphydryl and hydroxyl, which act as adsorption sites (Huang et al 2000). These polymers have a certain affinity for various heavy metals. The microbial polymer acts as an adsorbing agent and causes the metals to be removed from solution (Neufeld et al 1975, Forster 1983). Thus this factor is important with respect to the mechanism of heavy metal removal. Some researchers have found that there is a limit to the amount of metals that can be removed by the sludge. Consequently, it has been proposed that activated sludge has a fixed capacity for the uptake of heavy metals such that if an extra load were introduced, the sludge would have no available adsorption sites (Kodukula et al 1994, Banks 1997, USEPA 1999). However, Rossin et al (1982) anticipated that a decline in metal removal efficiency with increasing heavy metal concentration might also be due to equilibrium between soluble and adsorbed metal concentration rather than saturation of the biomass.

2.3.2 Mechanisms of heavy metal removal in activated sludge

Several possible mechanisms of heavy metal removal in activated sludge have been proposed in the literature. These have been compiled by Brown and Lester (1979) as follows:

(i) Physical trapping of precipitated metals in the sludge floc matrix;
(ii) Binding of soluble metal to bacterial extracellular polymers;
(iii) Accumulation of soluble metal by the cell;
(iv) Volatilisation of metal to the atmosphere.

Physical trapping of precipitated metals in the sludge floc matrix

Precipitation is more likely to be the key mechanism where chemical non-equilibrium exists, or where steep pH or redox gradients occur (USEPA 1999). The literature sources covering this mechanism do not provide a distinction between those metals that settle independently and those that have become entrapped in the floc matrix and settled with the flocs. For example, precipitation appears to be important in the removal of some metals notably Pb and Cr (III). Yet, it is not evident whether their final removal is dependent on their settlement alone or entrapment in the sludge flocs. In the absence of biological cells precipitation might be the most important mechanism, but in the presence of biological cells, other mechanisms may predominate (Lester 1983).

As demonstrated by Sterritt et al (1981), the mechanism, by which metals are removed, is concentration-dependent for certain metals, notably Pb and Cr (III). Other types of behaviour noted by their experiments are (Lester 1983):

- Cd, Cr (VI), Mn and Ni were almost completely soluble in the mixed liquor filtrate and removal was therefore almost entirely due to adsorption onto the biological solids,
- Co was predominantly soluble and its precipitation did not appear to be concentration-dependent. Thus the formation of insoluble salts may have been limited by the concentration of a species able to co-precipitate.
- The relative contributions of adsorption and precipitation to copper removal appeared to be dependent on concentration.

Although the influent settled sewage to full-scale activated sludge plants contains metal as precipitates, Stephenson et al (1987b) found that direct settlement of precipitated metals is of minor importance for well-removed metals and is significant only for poorly removed metals such as Co and Ni. On the other hand, they found that the interaction of particulate-associated metal with the settleable biological solids is the major removal mechanism. However, while keeping these observations in mind, it is important to note that regardless of the mechanism of their settlement, the efficiency of the removal of metals will depend on the removal efficiency of the final clarifier.

Binding of soluble metal to bacterial extracellular polymers (adsorption)

Adsorption is defined as "the net accumulation of matter at the interface between a solid phase and an aqueous phase" and it is likely to be the key mechanism where chemical equilibrium exists (USEPA 1999). The extent of adsorption is controlled by the electrostatic surface charge of the solid phase. The magnitude and polarity of the net surface charge is influenced by a number of factors, including pH. As the pH increases, the surface becomes increasingly negatively charged, thus leading to increased adsorption (USEPA 1999). The paper by Brown and Lester (1979) provides an excellent and in depth explanation of the role of bacterial extracellular polymers in metals removal in activated sludge. Polymers produced by bacteria may be in the form of loose slime or capsules and microcapsules. Their production is affected by growth conditions, especially dissolved oxygen concentration and temperature. Another factor controlling the quantity of extracellular polymers present in activated sludge is the oxidation of extracellular polymers and it has been proposed that dissolved oxygen concentration plays an important part in determining the rate of oxidation. In activated sludge, the slime polymers remain in the dissolved and colloidal phases of an effluent, while capsular polymers remain attached to flocs and hence settle with the sludges. It was observed that different polymers differed in their affinities for metals. Where metal ions are adsorbed to extracellular polymers, oxidation of the polymers in activated sludge may result in either the accumulation of metal ions within cells, or the release of metal ions back into the medium. Brown and Lester (1979) concluded that the evidence that they presented in the paper showed that "different metal adsorption sites exist on neutral polysaccharides and anionic polysaccharides" and that "metal ions of different valencies or with different charges may also bind at different sites".

There are three types of adsorption phenomena (Lawson et al 1984, Kasan 1993): electrical attraction of the solute to the adsorbent, physical adsorption, and chemisorption.

Ion Exchange

Involving the concentration of ionic species on a solid phase as a result of electrostatic attraction to charged sites at the surface, this is one of the most common types of adsorption (Kasan 1993, USEPA 1999). The charge on the ion is the determining factor for adsorption (Kasan 1993).

Physical adsorption

Physical adsorption occurs as a result of weak van der Waals forces. In this type of adsorption, the adsorbate is not fixed to the adsorbent, rather it is free to move within the interface and thus is readily desorbed. Physical adsorption usually occurs at low temperatures and may result in multi-layer adsorption (Lawson et al 1984, Kasan 1993).

Chemisorption

Chemisorption occurs at higher temperatures and involves the formation of covalent bonds between the adsorbate and the adsorbent, leading to the formation of a monolayer. Chemical processes are characterised by high energies of adsorption and thus the adsorbed layer is difficult to desorb (Lawson et al 1984, Kasan 1993).

The investigations of Lawson et al (1984) revealed that the type of adsorption that occurs is dependent on the metal in question. Cu adsorption was found to be as a result of both physical adsorption and chemisorption, while Cd and Mn were predominantly adsorbed through physical adsorption. They concluded that not all metals are removed to the same extent by the mixed liquor solids due to their differing physicochemical behaviour.

Accumulation of soluble metal by the cell (absorption)

Some activated sludge bacteria do not produce capsules or extracellular material. In these bacteria, metals may be accumulated either in the cytoplasm or by adsorption

onto the cell wall (Brown and Lester 1979). Metal uptake by activated sludge involves a two-stage process (Lester 1983):

(i) The first passive phase is considered to be adsorption of cations to negatively charged sites on the cell surface. This uptake is reversible by isotopic exchange; the metal is also easily washed from cells using strong chelating agents. Moreover, the process is independent of temperature.

(ii) The second phase is irreversible, inhibited by metabolic poisons and temperature dependent.

The uptake of the metal was shown to be time-dependent for an active sludge and independent of time for a non-active sludge. The non-active sludge does not have the second slow phase of uptake.

The metabolism of elements occurs in many species of bacteria. The four major types of metal transformations in organisms have been identified by Jernelov and Martin (1975):

(i) Chelate formation by the binding of metals to organic ligands;

(ii) Shifts in metal valencies;

(iii) Substitution of one metal for another; and

(iv) biomethylation of metals by microorganisms.

However, Neufeld et al (1975) concluded that in the case of mercury, metal uptake is not a function of metal concentration or organism viability. They proposed that metal uptake is not a biological phenomenon, but a physicochemical one involving the surface properties of the sludge flocs. Artola et al (2000) also agree that biological uptake is negligible when compared with adsorption, thus biosorption is considered mainly a physico-chemical process, independent of metabolic activity.

Stephenson et al (1987b) found that for the accumulation of metals by the settleable solids, the MLSS concentration would be the major factor influencing insoluble metal accumulation in the activated sludge process, and not changes in the microbial population as controlled by alterations in the sludge age. They also found that some removal of soluble metal occurred. It was concluded that the removal of soluble metal

was unlikely to be a metabolic process, but probably the result of uptake by bacterial extracellular polymers.

Volatilisation of metals to the atmosphere

This mechanism is possible during the activated sludge process following transformation, in particular aerobic biomethylation, for post-transition metals such as Pb (Stephenson et al 1987b). However, Lester (1983) states that it is unlikely that volatilisation would account for the removal of a significant amount of metal in activated sludge since:

- Metals can largely be accounted for by a mass balance between the sludges and effluents produced;
- The majority of biomethylation process are anaerobic;
- Batch studies using enhanced metal concentrations have demonstrated biomethylation to be a relatively minor process.

2.3.3 Efficiency of heavy metal removal in biological treatment

The results of the study by Brown et al (1973) indicate that Cr, Cu and Pb were more efficiently removed in secondary treatment processes than in primary processes. Cr is reduced during aeration in the secondary process. Cu is strongly adsorbed by the microbial floc and Pb is removed more efficiently because of increased settling time and larger particle size in secondary treatment. Zn was removed equally well from all plant types. It was concluded that the results indicated that a definite advantage of a secondary treatment plant over a primary treatment plant in heavy metals removal is the increased suspended solids removal. It has also been proposed that adsorbed metal ions enhance the floc structure and thus the settlement characteristics of suspended solids (Forster 1983)

Although in the study by Oliver et al (1974) there were wide variations in the input concentrations of the various metals for both the short and long term study and within segments of the long term study, the efficiency of the activated sludge process in removing several heavy metals was fairly constant throughout the period of study. For Cu, Mn, Ni and Zn, almost all of the metal in the final effluent is in the dissolved form. Therefore, longer settling periods or the addition of flocculating agents will be of little

use in removing these metals from the effluent. Methods that were proposed to improve the removal efficiency included:

1. Chemical treatment such as lime addition to the raw sewage: This would raise the pH of the system and precipitate the dissolved metals as hydroxides. They would then settle out in the primary clarifiers before reaching the aeration tanks.
2. Physical methods, such as ion exchange, activated carbon adsorption or electrolysis: these would best be employed after primary clarifiers to minimise equipment clogging. This would again inhibit the metals from reaching aerobic micro-organisms.

The results presented in the literature review conducted by Lester (1987) shows that there is considerable variation in the removal efficiency of metals in activated sludge treatment, as shown in table 2.3.

Table 2.3: *Metal removal efficiencies during activated sludge treatment in full scale wastewater treatment plants (adapted from Lester 1987)*

Metal	Activated Sludge Effluent (μg/l)	Average removal efficiency (%)
Al	500-1750	92
Cd	3-120	7-84
Cr	10-38000	24-88
Cu	10-660	25-93
Fe	457-2950	72-97
Pb	20-1100	30-91
Mn	20-100	6-28
Hg	0.6-9	17-62
Ni	30-1600	<0-61
Zn	200-8940	10-93

Another review of the literature was conducted by Stephenson et al (1987a). They stated that studies on the removal of heavy metals in wastewater treatment plants revealed several facts:

1. In general, the removals of Cd, Cu, Cr, Pb and Zn were highest at >50% and Co, Mn and Ni were lowest at < 30%.

2. The percentage removal of any one metal can vary considerably from plant to plant. Therefore, the extent of removal is highly dependent on local conditions.

Yet, the percentage removals for some metals observed in their own study were at the upper end of the range of mean removal efficiencies for activated sludge systems that were quoted in the literature. This was attributed to the fact that the pilot plant that they employed produced a good quality effluent low in suspended solids and COD; both factors can affect metal removals, as described above.

Thus as Lawson et al (1984) concluded, for most metals the predominant mechanism is passive uptake, with the mixed liquor solids acting as particulates for which surface area has an important effect. Furthermore, other factors such as the soluble ligands present and other components of the bacterial cell also affect the overall metal removal efficiency.

2.3.4 Toxic effects of heavy metals on the biological treatment processes

The toxicity of heavy metals to bacteria and inhibition of the oxidation of organics was the subject of early work on heavy metals in activated sludge (Lester 1987). Manifestations of this toxicity may vary from changes in the communities of organisms to ruinous effects on the activated sludge system associated with shock loadings (Lester 1983). In the study by Barth et al (1965), it was shown that for each phase of treatment, aerobic, anaerobic and discharge of final effluent, there are different bases for judging the concentration of metals acceptable in the influent sewage. The aeration phase exhibits a plateau type response, that is, a certain concentration of the metal is required to produce a significant reduction in treatment efficiency, higher concentrations do not cause a significant decrease in the efficiency. Cheng et al (1975) suggested that a strong affinity between the sludge and metal, resulting in accumulation of metal within the sludge, may enhance toxic effects that are not easily alleviated if the metal is tightly bound into the sludge. These toxic properties may carry over to the digestion process receiving excess sludge.

2.4 Sludge Treatment

The sludges produced, through sedimentation and biological treatment, in the first stage of the wastewater treatment process are treated, using a variety of processes in the sludge treatment stage, before disposal. Approximately 1% of the total flow entering a

wastewater treatment plant is ultimately produced as sludge (Rudd 1987b). Thus, depending on the efficiency of the plant in metal removal, there could be considerable concentration of metals within the sludge.

During the sludge treatment stage, the type and combination of processes used will affect the distribution of metals in the sludge. The types of processes usually employed include thickening, stabilisation, conditioning and dewatering. Of all the treatment methods available, a stabilisation process, anaerobic digestion, is the most widely used. Changes in the practices of sludge use and disposal brought on by the phasing out of sludge disposal at sea and increasing pressure from the EC to restrict the practice of land application of sewage sludges largely to stabilised forms, have further increased the importance of anaerobic digestion. However, as a biological process, it is more susceptible to intoxication by heavy metals than the other, primarily physical sludge treatment processes. Sludge thickening is usually accomplished in sedimentation basins through gravity or flotation. Therefore, the factors and mechanisms influencing heavy metals removal in sedimentation would also apply to thickening.

Thus, due to the importance of anaerobic digestion and its susceptibility to metals toxicity, the majority of the literature written on the subject of heavy metals in sludge treatment has focused on this process.

2.4.1 Speciation and distribution of heavy metals in anaerobic digestion

Knowledge of the speciation and distribution of the heavy metals in sludges is important for estimating their mobility and bioavailability and hence their impacts on the anaerobic digestion process. The impact of heavy metals is not only determined by the total metal concentration but also by the metal forms that are present (Lake et al 1985). Heavy metals may occur in anaerobically digested sludges in:

- Soluble forms;
- Complexed with organic compounds;
- Adsorbed;
- Precipitated;
- Co-precipitated with metal oxides, ex. sulphides; and
- In association with biological residues. (Lake et al 1985).

The distribution of these forms varies widely according to the chemical properties of the sludge, which in turn are functions of the physical and chemical properties imposed by the particular sludge treatment process (Alibhai et al 1985). Insoluble metal forms, and especially those that are bound as complexes or precipitates, pose less toxicological hazards than soluble/ ionic species (Lake et al 1985; Gould and Genetelli 1978). Furthermore, there is evidence that suggests that heavy metals associated with the organic fraction of the sludge are less available than inorganic precipitates (Hayes and Theis 1978).

Complexation:

Results of the investigations conducted by Gould and Genetelli (1978) showed that the complexation behaviour differed for each metal and was strongly influenced by pH. Increases in pH increased the degree of complexation and complexation stability at the same solute concentration, while a decrease of pH lead to solubilisation of metals. The order of complexation of the metals studied, on a molar basis, was Cu> Zn> Cd> Ni. Chelation of an added reagent can make a particular metal either more or less available for microbial uptake. It will be more available if the organism has a metal binding component stronger than the added chelating agent, but otherwise it will be less available (Callander 1983). Lake et al (1985) concluded that the observed influence of both total metal concentration and sludge characteristics on metal speciation, particularly with respect to Cd and Ni, emphasises the necessity for consideration of all three factors in the safe disposal of sewage sludge.

In their paper, MacNicol and Beckett (1989) state that before studying its chemistry, the sludge must be fractionated as far as possible into its main components. After reviewing the literature written on this subject and conducting their own fractionation experiments, they concluded that it would be impossible to separate all the components of the digested sludge, since "too many of them are coatings on or embedded in each other". They devised a division that is simple and practical. The heavy metals in the sludge can be separated into three fractions:

1. Particulate: in mineral grains; as exchangeable cations on clays; in discrete crystals or grains of secondary precipitates; or in coatings of biofloc/ colloids;
2. Biofloc/ colloid-bound: as inter-cellular or extra-cellular uptake by bacteria; may contain finely disseminated inorganic precipitates;

3. Soluble: free metal ions, soluble complexes with organic and inorganic ligands.

A review of the results presented in the literature indicated that heavy metals present in sludges showed a strong association with the solids fraction (Gould and Genetelli 1975; Gould and Genetelli 1978; Hayes and Theis 1978; MacNicol and Beckett 1989). Gould and Genetelli (1975) found that 90% of the heavy metals were found in the particulate fraction. Another important observation made was that the heavy metal content had a higher correlation with the volatile solids fractions than the inert solids. Hayes and Theis (1978) found that the major portion of the heavy metals was distributed between the precipitated (insoluble) and intracellular components of the digesters.

Lake et al (1985) carried out experiments to investigate the effect of increasing total metal concentration on metal distribution in two types of sludges, digested primary sludge and digested mixed primary sludge. They found that both sludge types exhibited similar significant transitions in metal distributions following anaerobic digestion. The more-easily-extractable forms, which predominated in the raw sludge were replaced by the less-easily-extractable forms after digestion. The carbonate forms of Cd and Pb and the sulphide form of Cu predominated in the digested sludges. On the other hand, for Zn there was a redistribution towards sulphide and organically bound fractions and Ni was distributed evenly among all the fractions.

With respect to the changes exhibited due to the increase in total metal concentrations, the observations varied depending on the metal. The distribution patterns observed for Cu, Pb and Zn during anaerobic digestion of both sludge types were little affected by the increase in metal concentration. On the other hand, increased percentages of Ni present in the soluble/ exchangeable fraction in both digested sludge types and increased percentages of Cd in the digested mixed primary sludge were observed. In the case of Cd, the widely differing results observed between the two types of sludges suggest that the Cd binding characteristics of the two sludges differ.

2.4.2 Mechanisms of heavy metal removal in anaerobic digestion

The mechanisms controlling the removal of heavy metals in anaerobic digestion are similar to those functioning in aerobic systems, namely (Rudd 1987; Alibhai et al 1985):

1. Direct precipitation;
2. Intracellular uptake;
3. Adsorption;
4. Entrapment of insoluble metals in the biomass;
5. Complexation of soluble metal by both the organic and inorganic ligands.

Precipitation and Precipitation systems:

Precipitation has been shown to be an important mechanism effecting metal removal during anaerobic digestion (Gould and Genetelli 1975; Callander 1983; Lester 1987; MacNicol and Beckett 1989). Results of the various studies also show that the precipitate compounds grow with time (MacNicol and Beckett 1989). The main species capable of precipitating metals in anaerobic digesters are sulphide, carbonate and less importantly, phosphate (Callander 1983).

Of the various precipitation systems, which may function during anaerobic digestion, sulphide precipitation is the most important. Sulphide in a digester is derived from sulphide, sulphate and sulphur-containing organic compounds in the feed. The sulphide ion has a great affinity for many heavy metals (Manahan 1991) and the sulphide salts of the majority of heavy metals, with the notable exception of Cr, are largely insoluble and have the potential to be removed from solution via precipitation (Rudd 1987b). If the total metals are less than the total feed sulphide, then the metals will be totally precipitated (Callander 1983).

The other relatively important precipitation system is that of carbonate. It is controlled by digester pH and the levels of dissolved carbon dioxide (Rudd 1987b). At high pH values (e.g. greater than 7.7 for Zn and greater than 6.4 for Fe), the carbonate salts of some metals are poorly soluble and may precipitate upon formation (Gould and Genetelli 1975; Rudd 1987b). Under atmospheric equilibrium conditions, carbonate precipitates should dissolve and a new equilibrium controlled by organometallic complexation may result (Rudd 1987b).

Sorption Mechanisms (Entrapment, Adsorption, Intracellular uptake):

According to Hayes and Theis (1978), it appears that microbial uptake actively competes with precipitation in the removal of heavy metals from the digester supernatant. However, in addition to precipitate formation, metal ions can be removed by becoming complexed with organic or inorganic ligands. Gould and Genetelli (1975) state that the predominate mechanism observed may be an organometallic type. This can be simple complex formation and/or chelation, and involve oxygen and nitrogen containing groups. Furthermore, metals chelated by organic ligands may be more or less available for microbial uptake, depending on the relative strength of the metal-sequestering mechanisms of the microorganisms (Rudd 1987b).

Results of the studies carried out by Gould and Genetelli (1978) indicate that a sorption-like behaviour takes place until certain metal concentrations are reached, after which all further additions went into the solid phase as a result of precipitation. This 'sorption-like behaviour' is further confirmed by Alibhai et al (1985), who also found that the binding capacity depends both on the metal and the nature of the sludge. The pH, temperature, oxidation-reduction potential and the presence of complexing agents are listed as some of the physicochemical properties, which may be considered significant to the binding of metals. Chemisorption through ion-exchange has been found to be one of the major mechanisms of heavy metal binding to digester biomass (Alibhai et al 1985; Rudd 1987b). The results of the Alibhai et al (1985) study show that the complexation of Cr, Pb and Zn does not depend upon the temperature. Thus knowing that ion reactions are fast reactions and as such are not affected by temperature, they concluded that the binding of Zn, Cr or Pb to digested sludge is a sorption process involving cation exchange. Rudd (1987b) noted that the equilibrium between free and bound is distributed by pH changes and the presence of other metals, which implied that ion exchange mechanisms are involved. Also, according to Gould and Genetelli (1984), adsorption isotherm modelling has indicated that a competition exists between hydrogen and heavy metal ions for the available binding sites, thereby suggesting an ion exchange mechanism. Chemisorption through ion exchange is a function of the ionic valency and ionic radius of the metal. Therefore, the charge, size and nature will decide the overall ionic exchange process (Alibhai et al 1985).

The nature of the sludge:

Alibhai et al (1985) state that due to the rigorously controlled environment in the digester, the microbial ecology will not vary greatly from one digester to another. Therefore, the mechanism of adsorption could be independent of the source of the sludge. However, in a study by Lake et al (1985), it was found that digesters operating on primary sludges achieved greater reductions in volatile solids than the mixed primary and activated sludge digesters, despite virtually identical volatile solids loadings. They proposed that this could be related to the refractability of the organic fraction of the waste-activated sludge, which is reported to be only 30-45% digestible in conventional anaerobic digestion. It is also possible that the presence of an unidentified inhibitory agent, such as ammonia gas may have reduced the efficiency of the mixed primary digesters. With respect to the influence on metal distribution, the presence of chelating agents will be the most significant property of the sludge since they can either exacerbate or ameliorate metal toxicity (Rudd 1987b).

Competition and reversibility

The results of the Gould and Genetelli (1984) study on competition between metals indicated an order of binding capacity of Cu>Cd≥Zn>Ni on both a gravimetric and equivalents basis. In every case when a competing metal was present, the degree of binding of the other metal was decreased. The magnitude of the decrease caused by the competing metal was also in the same order as the binding capacity. Thus Cu had the highest binding capacity and exerted the greatest competitive effect. Ni was the only metal that showed site-specificity. Ni may not be able to compete with metals for sites that are not specific for Ni and likewise other metals may not compete effectively with Ni for sites that are specific for it. If site specificity were confirmed for Ni, it would be a minor effect especially when complexation stability and pH effects are considered.

Their results also indicated that the metals could be reversibly removed by salting them out with solutions containing competing ions. Although the competing metal displaced the original metal, the overall capacity increased, with the exception of Cu. Increasing the concentration of the salting-out ion resulted in increasing the amount of desorption of the first metal.

2.4.3 Availability and the effects of heavy metals in anaerobic digestion

As previously stated, of the various wastewater treatment processes, anaerobic digestion appears to be the most vulnerable to heavy metal toxicity. However, just the presence of heavy metals in sludge does not mean that toxic effects will occur. The concentration of the heavy metal must reach a threshold level and be available (Gould and Genetelli 1975). Callander et al (1983) found that the bioavailability of metals is determined by:

1. the total concentration of metal in the substrate;
2. metal precipitation, principally by sulphide, carbonate and phosphate;
3. metal chelation or complexing with both inorganic species (ion pairs) and organic ligands (chelates), including those synthesised by organisms to assist metal uptake; and
4. the kinetics of precipitation and chelation reactions.

In general, it was found that all cations could produce toxicity in any organism at some level, but the relative toxicity of the cations varied where compared on a weight-weight basis (Hayes and Theis 1978). Depending on the combinations and concentrations of metals present, the resulting effect could be:

- stimulation at low metal concentration;
- toxicity at elevated concentrations; or
- antagonism, where one cation decreases the toxicity of another (Rudd 1987b).

Stimulation

Stimulatory effects of cations at concentrations below those where toxicity was produced have been recognised. According to Hayes and Theis (1978), it was reported that very low concentrations of extremely toxic cations, such as Hg and Pb, could produce a stimulatory effect in the growth rate of various bacterial cultures. Furthermore, there is increasing evidence that deficiencies of certain essential metals, particularly Ni, can severely limit anaerobic digester performance and that metal supplementation may substantially increase digester performance (Callander 1983; Rudd 1987b).

Toxicity

Factors

On the whole, the toxicity of a heavy metal in anaerobic digestion depends upon the various chemical forms which that metal may assume under anaerobic conditions and near-neutral pH (Hayes and Theis 1978). Metals in the soluble state generally exert a higher degree of inhibition than insoluble forms; this is ultimately associated with the relative ease of uptake of various metal species exhibited by the digester microflora (Rudd 1987b). The concentrations of precipitating or chelating agents present, which vary from one system to another, can affect the tolerance of individual digester populations to different concentrations of heavy metals (Rudd 1987b). Thus as stated by one researcher (Hayes and Theis 1978), although low concentrations of some heavy metals have relatively high toxicity to biological systems, high concentrations could be tolerated if sufficient sulphide could be provided to act as a precipitant. Variable operating parameters such as feed composition and concentration, temperature and retention times within the system can also affect the resistance of the microorgansims (Rudd 1987b).

Effects

Toxic inhibition of anaerobic digesters takes place after a particular threshold level has been reached (Barth et al 1965; Rudd 1987b). This inhibition is manifested by a reduction in biogas production and an increase in volatile acids concentrations, with a concomitant decrease in pH (Rudd 1987b). In the study by Hayes and Theis (1978), shock loadings in the form of pulsed addition resulted in lower toxic limits than the continuously added metal, with the exception of Ni and possibly Zn. The results of their study show that the order of decreasing toxicity on a weight-weight basis or molar basis was Ni> Cu> Pb> Cr> Zn. Toxic effects were also found to coincide with the near maximum uptake of metals by bacteria (Hayes and Theis 1978). However, relevant comparisons between the degrees of toxicity of heavy metal ions and metal compounds or complexes are difficult to establish, since toxic limits for various compounds of the same metal, as noted above, are frequently found to differ widely (Rudd 1987b).

Antagonism, where the toxicity of a cation was decreased due to the presence of other cations in the medium, has been observed. However, it was also noted that metal

mixtures caused inhibition at lower total metal concentrations than that caused by individual metals (Rudd 1987b).

The disruption of the digestion process by heavy metals or other toxicants does not affect this process alone. The dewatering may be hampered, the sludge produced may be malodorous, and both its disposal and the restarting of the digester may be problematical (Rudd 1987b).

Efficiency

In general, heavy metal removal from digester supernatant was greater than 95% (Hayes and Theis 1978).

2.5 Conclusions of the Literature Review

The review of the literature shows metal interactions in wastewater treatment processes to be complex. However, certain factors appear to be common and to be of significant importance with regard to the development of a metals predictive model. The following findings need to be taken in consideration the development of the Metals Model, which will be described in Chapter 4.

Primary sedimentation:

- Heavy metal removal efficiencies appear to be strongly associated with solids removal processes.
- Metals that are removed in primary sedimentation are those that exist in insoluble forms or those that have the capacity for binding to settleable solids.
- Formation of insoluble hydroxides, carbonates and phosphates aids the process of removal.
- Soluble organic ligands in the sewage might bind heavy metals, thus retaining them in solution and thus preventing their removal.
- For each metal, there is a dominant mechanism:

(i) Direct precipitation: e.g. Pb and Bi;

(ii) Adsorption or complexation by suspended solids: e.g. Ag, Cd, Co, Cu, Cr, Mn, Ni and Tl;

(iii) Precipitation followed by association of the precipitate with the bulk solids fraction: e.g. Zn and Mo.

- There are two main groups of elements:

(i) Strong association with the VSS (e.g. Ag, Co, Mo); their partition into the solid phase may be primarily due to adsorption or complexation by organic elements;

(ii) Primarily associated with NVSS (e.g. Cu, Mn, Pb, Zn).

- Pb, Cu and Zn are the most readily removed metals in primary sedimentation. Ni and Cr are the least readily removed.

Biological Treatment:

- Under ideal conditions, the percentage removal of heavy metals in activated sludge would increase linearly with the sludge age. However, in practice, due to the changes in ESS and effluent COD, and shifts in the effluent speciation of metals, this is not the case.
- As suspended solids removal increases, heavy metal removal increases at an exponential rate.
- Total metal uptake by the sludge floc increases with increasing VSS concentration. Also, at constant VSS, increasing the influent metal concentration increases the total metal uptake. Therefore, the concentration of VSS is the dominant factor influencing the distribution of heavy metals.
- Uptake by activated sludge is highly pH dependent.
- Increasing pH would precipitate the metals.
- At lower metal concentrations, metal is taken up by the biofloc through the formation of metal organic complexes.
- At higher metal concentrations, metal ion precipitation from solution may occur in addition to sludge uptake.
- Variations in the speciation of the metals markedly influence their affinity to the sludge or the soluble phase, and thus, their removal.
- The composition of the wastewater influences the forms of the metals present. Strong chelating agents might have a higher affinity for metal ions than the biomass, thus enhancing metal solubility and reducing metal removal.
- Direct settlement of precipitated metals is of minor importance for well-removed metals and is significant only for poorly removed metals such as Co and Ni.
- For the accumulation of metals by the settleable solids, the MLSS concentration would be the major factor influencing insoluble metal accumulation in the activated sludge process.
- Results indicate that a definite advantage of a secondary treatment plant over a primary treatment plant in heavy metals removal is the increased suspended solids removal.
- The percentage removal of any one metal can vary considerably from plant to plant. Therefore the extent of removal is highly dependent on local conditions.

Anaerobic Digestion:

- Distribution of the various forms varies widely according to the chemical properties of the sludge, which in turn are functions of the physical and chemical properties imposed by the particular sludge treatment process.
- The complexation behaviour differs depending on the metal and is strongly influenced by pH. Increases in pH increase the degree of complexation stability at the same solute concentration.
- Heavy metal content has a higher correlation with the volatile solids fractions than the inert solids.
- The major portion of the heavy metals is distributed between the precipitated (insoluble) and intracellular components of the digesters.
- Effect of anaerobic digestion: the more easily-extractable forms in raw sewage were replaced by less-easily-extractable forms.
- Heavy metal chemistry is controlled not only by the solubility of inorganic precipitates but also by sorption onto and subsequent incorporation of metals into digester biomass.
- The most important precipitation system is that of sulphide.
- If the total metals are less than the total feed sulphide then the metals will be totally precipitated.
- The pH, temperature, oxidation-reduction potential and the presence of complexing agents are some of the physicochemical properties, which may be considered significant to the binding of metals.

CHAPTER THREE

SOLIDS MODEL DEVELOPMENT

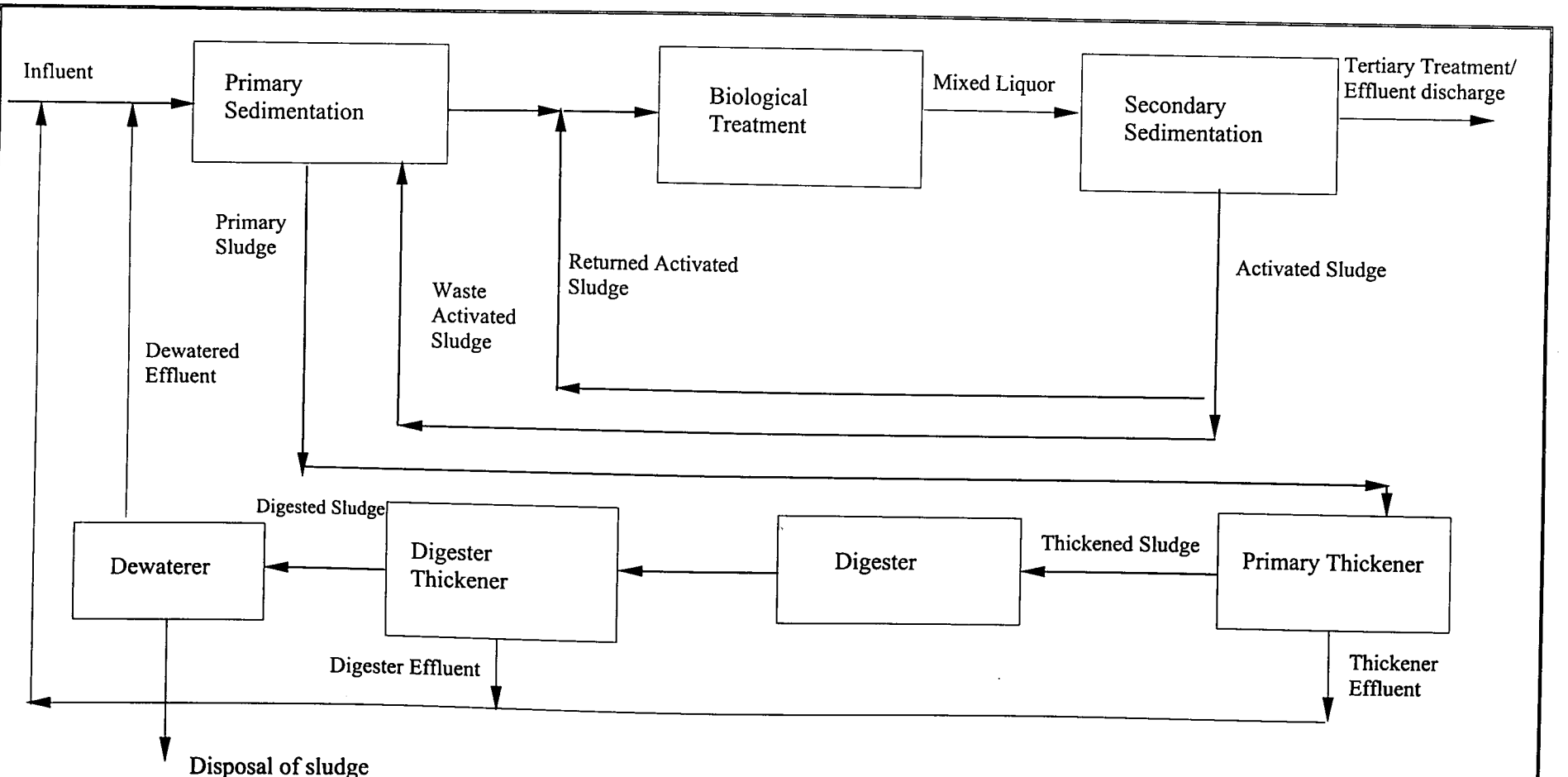


Figure 3.1: *Typical Flowsheet of a Biological Wastewater and Sludge Treatment Plant*

3.2 Set-up of the Computer Program

The computer program utilises the Visual Basic Editor feature of **Microsoft™ Excel 97** software to set-up the equations used in the model. The program consists of three parts:

- Inputs needed at the beginning of the program to perform the calculations;
- Equations on which the calculations are based;
- Outputs.

The program is able to carry out the calculations for an infinite number of iterations.

3.2.1 Symbols and Abbreviations

For each process, three main parameters are used: flow, total suspended solids, and volatile suspended solids. The system of symbols and abbreviations, used to describe the flows and solids concentrations, is similar to that used by Ioannidis (1993) and Clements (1995). This system is as follows:

- **F** at the start of the term denotes a flow, **X** at the start of the term denotes a volatile solids concentration and **C...TS** denote a total suspended solids concentration (**C** being at the start of the term and **TS** at the end).
- Following these letters are two or three letters to describe the nature of the flow. For example **PE** stands for *primary effluent* and **DWS** stands for *dewatered sludge*.
- Therefore **FPE** is the *flow of primary effluent* and **CDWSTS** is the *total suspended solids concentration in the dewatered sludge*.
- Other symbols include **Tsrem%**, which stands for total suspended solids removal percentage and **V/T**, which stands for the volatile to total solids ratio.
- The units for the flows are litres per hour (l/h), and the units for the solids concentrations are milligrams per litre (mg/l). Since the units for the flows are litres per hour, each iteration in the program represents an hour. The program was set to run for 24 iterations, thus representing 24 hours.

Appendix A provides a complete list of the symbols and abbreviations used as well as the model equations developed. Using a mass balance approach, the model equations employ a critical parameter, which describes the partitioning of solids within the process. Using a set of typical values from the literature as inputs to the program, the program was run and the outputs obtained are shown in Appendix A. The following sections will describe for each process, the development of the model equations.

3.3 Preliminary treatment

Preliminary treatment of wastewater serves the purpose of removing the floating material, heavy solids and large suspended solids, which are delivered with the raw influent to the treatment works. However, while preliminary treatment will remove the majority of large solid and floating material, the wastewater will still contain a high concentration of suspended solids that range in size from 0.05 to 10 mm. Thus, it can be seen that preliminary treatment has a negligible effect on the removal of fine suspended solids and thus heavy metals. It is worth noting, that in developing their fate model for metals in municipal wastewater treatment, Parker et. al. (1994) included grit removal as a unit process that contributes to the removal of metals. It is possible that since metals may become adsorbed to the solids in the raw sewage prior to entering the plant, the removal of grit during preliminary treatment may also remove some associated metals. However, since at wastewater treatment plants, samples of raw sewage may be taken after preliminary treatment, this process can be considered to be outside the mass balance of the system and thus will not be included in the mass balance model.

3.4 Primary Sedimentation

3.4.1 Process Characteristics and Significant Parameters

Primary sedimentation represents the first major unit process in the solids model. The amount of sludge produced during primary settling will depend on the through-flow, the total suspended solids and the efficiency of solids removal (Kiely 1997). The suspended solids removal efficiency, which is usually around 70-80% is influenced mainly by the retention time, surface loading rate and influent suspended solids.

Several properties of the water and its suspended solids content also influence sedimentation. Of the properties of the water, the temperature was found to be a very important design criterion due to the observation that it affects basin overflow rates (ASCE 1990); the surface overflow rates of cold waters would be lower than those of warmer waters. Important properties of the suspended solids include the specific gravity of the materials as well as their size and shape. In addition, random environmental factors such as heat flux and wind action may also cause major variations in suspended solids removal (Christoulas et al. 1998).

The critical parameter in this process is thus the suspended solids removal efficiency and the two main factors influencing it are the surface overflow rate and influent suspended solids. Ramalho (1983) demonstrated the relationship between the solids removal efficiency and retention time as well as surface overflow rate through a laboratory test-based example. Calculating the suspended solids removal at different retention times and surface overflow rates he plotted the resulting functions. He stated that if similar calculations were performed for other values of the concentration of suspended solids, the data plotted would yield families of curves as shown in figure 3.2.

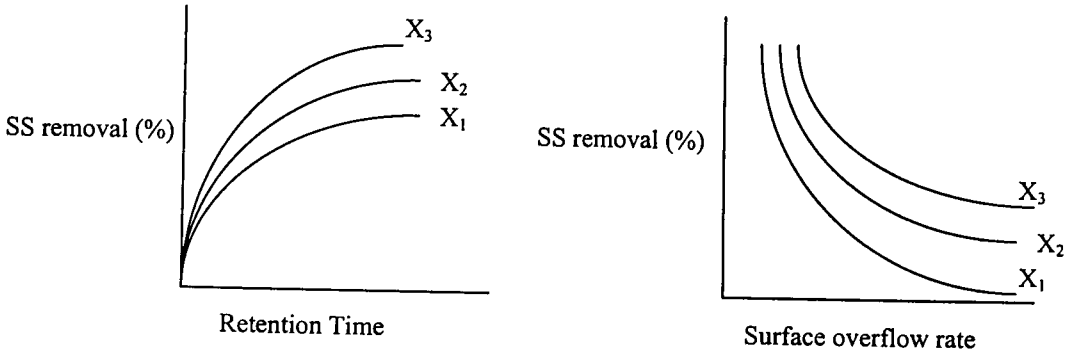


Figure 3.2: *Suspended solids removal versus retention time and overflow rate for different SS concentrations (X), ($X_1<X_2<X_3$).* (after Ramalho 1983)

Christoulas et al (1998) found that empirically-derived models offer a more valid practical approach to the design of sedimentation tanks. Based on data from a pilot plant, they proposed an empirical model, which describes the solids removal efficiency based on the surface overflow rate and the influent suspended solids. The general model takes the form of:

$$E_s = a^{(-\frac{b}{S_i} - cq)}$$

where, E_s denotes the suspended solids removal efficiency, q is the surface overflow rate (m/d), S_i is the influent suspended solids concentration (mg/l) and a, b and c are constants. Studies at pilot plants in Birmingham (England) and Athens (Greece) revealed that the constants a and b are temperature dependent according to equations: a= 1.71-0.03t and b=683.6-21.13T (where T is temperature in °C) and valid for temperatures in the range 15-26 °C. The constant c was found to be 0.0035 d/m.

3.4.2 Mathematical Modelling Expressions

The total influent flow into the primary sedimentation process consists of raw wastewater flow, wastage sludge flow from the biological treatment and flow of the effluents returning from the sludge treatment processes, the latter two flows being zero at the start of the program. The corresponding volatile and total suspended solids concentrations are either known at the start of the program (as in the case of the raw wastewater flow) or subsequently calculated by the program (as in the case of the wastage sludge and returning effluent flows).

The crucial operational factor in this process is the solids removal efficiency of the primary sedimentation tanks. As discussed above, the efficiency can be calculated using the empirical model derived by Christoulas et al (1998). This will require the temperature, surface overflow rate and influent suspended solids to be known. The total solids concentration in the primary sludge must also be input by the operator in order for a corresponding flow value to be calculated. As for the volatile solids concentration, equal removals of volatile and total suspended solids may be assumed and thus, it can be expected that the volatile to total solids ratio remains the same as that of the total influent flow (Clements 1995). The outputs from this process, the primary sludge and primary effluent values can thus be calculated using simple mass balance equations as follows.

```
Primary Sedimentation Equations
Total influent flow: q = fin + fws + fre
Total influent volatile solids: xinn = ((xin*fin)+(fre*xre)+(fws*xws))/q
Total influent total solids: tsin = ((cints*fin)+(fre*crets)+(fws*cwsts))/q
VSS:TSS ratio in influent: vt = xinn / tsin
Primary sludge flow: fps = (tsin*q*tsrem)/cpsts
If fps = 0 Then
cpsts = 0
xps = 0
Else:
Primary sludge total solids: cpsts = as input
Primary sludge volatile solids: xps = cpsts * vt
End If
Primary effluent flow: fpe = q - fps
Primary effluent total solids: cpets = ((tsin * q) - (cpsts * fps)) / fpe
Primary effluent volatile solids: xpe = ((xinn * q) - (xps * fps)) / fpe
```

3.5 Aerobic Biological Treatment

3.5.1 Process Characteristics

The two main types of aerobic biological treatment are activated sludge and biological filters. The solids mass balance model developed in this project will focus only on activated sludge treatment. The conventional activated sludge process as shown in figure 3.3 can be characterised by three types of concentrations:

- Substrate food concentration, which is a measure of the organic matter concentration as BOD, COD, TOC, etc.;
- Volatile suspended solids concentration (VSS), which corresponds to the biological sludge, constituted by the heterogeneous population of micro-organisms;
- Non-volatile suspended solids concentration (NVSS), which is constituted of non-living matter of both an organic and inorganic nature.

In this solids mass balance model, complete mixing conditions are assumed to exist in the reactor, thus the entire contents are homogeneous at every point and as a result of this, the composition of the effluent is identical to the tank contents. Mixed liquor volatile suspended solids are produced continuously in the reactor, owing to the synthesis of biological matter. The concentration of non-volatile solids, on the other hand, is equal to that of the feed influent into the reactor, since there is no production of NVSS in the reactor.

The reactor is also assumed to be a continuous reactor, as opposed to being a batch reactor. This assumption has the following consequences:

- The soluble substrate concentration of the wastewater remains constant. This corresponds generally to a low substrate concentration since the biological reactor is usually designed for removing a high percentage of the influent organic matter.
- The concentration of MLVSS in the continuous reactor is kept constant. (Ramalho 1983).

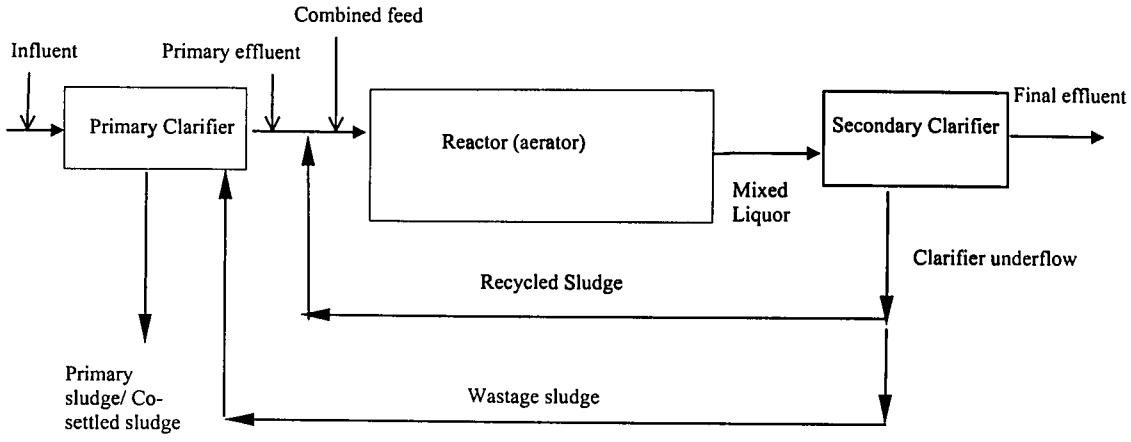


Figure 3.3: *Conventional activated sludge process*

3.5.2 Mathematical Modelling Expressions:

In terms of a solids model, the production of volatile solids (i.e. biological sludge) in activated sludge treatment is of crucial importance, since heavy metals have been shown to have a strong association to volatile suspended solids (Kempton et al 1987a&b and Patterson et. al. 1983).

3.5.2.1 Theoretical Basis

A theoretical expression for calculating volatile suspended solids can be found in many of the textbooks on wastewater treatment processes. This expression is as follows (Ramalho 1983):

$$MLVSS = \frac{1}{t}\frac{\left[Y\theta_c(S_f - S_e)\right]}{1 + k_d\theta_c},$$

where, t = hydraulic retention time (= the volume of the reactor divided by the flow), θ_c = sludge age, Y = yield coefficient, S_f = soluble substrate concentration of influent, S_e = soluble substrate concentration of effluent, and k_d = decay coefficient.

Some textbooks substitute the MLSS (total suspended solids) for the MLVSS. As a result, there was a need to establish whether this equation is for the total or volatile suspended solids in the mixed liquor. Experimental values of MLVSS, MLSS and S_e for different values of sludge age were given by Saunders et. al. (1981). The values for MLVSS and MLSS were plotted against the sludge age. Using the given value of S_f

and t, and the measured S_e values, the theoretical values (from the above equation) were plotted for assumed values of Y and k_d against the sludge age. The resulting graph was found to be more similar to that of the experimental MLSS graph (figure 3.4). Therefore, the above equation should be taken to represent an expression of the MLSS. The ratio of the MLVSS to MLSS will thus be required. It can be easily determined experimentally or a typical value of 80% may be used.

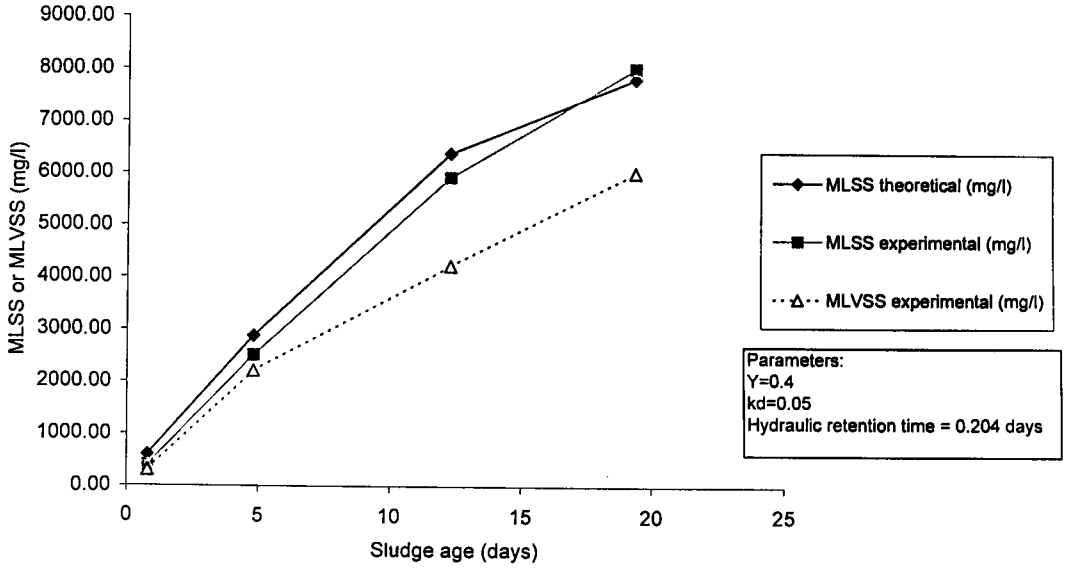


Figure 3.4: *Comparison between theoretical and experimental values of MLSS and MLVSS*

Having established the objective of the equation, to be able to use this expression, the parameters must be known. The hydraulic retention time (t), influent and effluent soluble substrate concentrations (S_f and S_e) may be easily calculated or determined. As for the yield and decay coefficients (Y and k_d), Lovett et. al. (1983) observed that the reported values of Y was relatively constant 'for substrates as different as glucose and yeast and abattoir wastewater'. They noted that this result is surprising in view of the variety of factors that may influence the value of Y. Comparing experimental data from various literature sources (given in Table 3.1) with the theoretical values using the MLSS equation above for different values of Y and k_d, it was also found that the theoretical values generated by the above expression most closely matched the experimental values when Y = 0.4 and k_d = 0.05 approximately.

Thus, these values of Y (0.4) and k_d (0.05) can be taken to be used as the default values in the model.

Table 3.1: *Literature sources used in finding values of Y and k_d*

Authors	Substrate composition
• Bisogni et al (1971)	• Domestic sewage
• Stoveland et al (1980)	• Synthetic sewage
• Saunders et al (1981)	• Domestic wastewater and synthetic sewage (similar composition)
• Rossin et al (1981)	• Settled sewage
• Lovett et al (1983)	• Meat concentrate solution
• Rudd et al (1984)	• Domestic sewage
• Stephenson et al (1987)	• Domestic sewage

The calculation of the final required parameter, the sludge age (θ_c), may pose a problem if this method is used. If the value for sludge age were not known at the plant in question, then it would need to be calculated. However, calculating the sludge age requires the MLSS to be known, which in fact is the value that we are trying to calculate.

3.5.2.2 Alternative Method

An alternative method of depicting the mass balance of solids in activated sludge would involve the use of the MLSS as an input parameter. This is valid since the MLSS is usually continually measured at the plant. Next, in order to calculate the volatile solids production in the reactor, the net sludge yield coefficient (Yn), which incorporates both the yield coefficient and the decay coefficient, is used. The following expression shows the relationship between the net sludge yield coefficient (Yn) and the yield (Y) and decay (k_d) coefficients and sludge age (θ_c).

$$Yn = \frac{Y}{1 + k_d \theta_c}$$

The net sludge yield coefficient, also known as the observed yield, is defined as the excess sludge produced (kg) per soluble substrate removed (kg). Typical values for it can be found in the standard literature. However these values are directly applicable only under the conditions (sludge age and temperature range) of their determination (USEPA 1979). Table 3.2 shows some typical values.

Table 3.2: *Comparison of loading and operational parameters for different activated sludge treatment rates (adapted from Hawkes 1983)*

Treatment rate	*Retention Period (h)*	*Sludge Loading (kg BOD/kg d)*	*Sludge age (d)*	*Net Sludge Yield, Yn (kg dry sludge per kg BOD removed)*
Conventional	5-14	0.2-0.5	3-4	0.5-0.8
High	1-2	>1	0.2-0.5	0.8-1.0
Low	24-72	<0.1	>5-6	0.4

Note: the values given in table 3.2 are not exclusive.
Sludge age values may vary from 4 - 15 days for conventional activated sludge plants and 20-30 days for extended aeration

The amount of VSS produced (given the term **"xmlinc"** in the model) can be calculated by multiplying Yn with the amount of BOD removed (kg/h). To obtain the MLVSS concentration resulting from the biological treatment, the **xmlinc** is added to the volatile solids that are entering the process, i.e. from the primary effluent and the recycled sludge. The model iteratively calculates the solids concentration across the plant on an hourly basis. Since for the first iteration the recycled sludge is assumed to be zero, the concentration of the MLVSS which is initially in the aeration tank must be known. Subsequently, the recycled sludge, which is required to maintain a constant concentration of microorganisms in the aeration tank, would be calculated and used for the next iterations. For the total solids concentration in the reactor, the increase is accounted for by the increase in volatile solids only, since there is no production of non-volatile solids in the aeration tank. The calculation for the total solids concentration thus follows a similar pattern to that for the volatile solids, with the concentration of total solids initially in the aeration tank needed for the first iteration.

3.5.3 Secondary Sedimentation

The equations in the secondary sedimentation process follow a similar pattern to those used for primary sedimentation. Once again, the efficiency of the clarifier for removal of solids will need to be known, as will the solids concentration of the secondary

3.5.4 Partitioning of Secondary Sludge to Wastage and Recycled Sludge

The amount of sludge that must be wasted is equivalent to the amount of sludge that is produced due to the removal of BOD in the reactor, less the amount of solids that go out in the final effluent. The recycled sludge flow can be calculated using the recycle ratio, an operational parameter that is usually known at the wastewater treatment plant. The equations to calculate the solids mass balance in biological treatment are thus as follows:

```
Activated Sludge Equations
Mixed liquor flow: fml = fpe + frs
BOD removed: BODrem = (Sf * fpe) - (Se * fml)
Increase in mixed liquor volatile solids: xmlinc = Yn * BODrem
If j = 4 Then
Mixed liquor volatile solids: xml = (xmlinc+(xml1*fml)+(fpe*xpe) ) / fml
Mixed liquor total solids: cmlts = (xmlinc+(cmlts1*fml)+(fpe*cpets) ) / fml
Else
xml = (xmlinc + (fpe * xpe) + (frs * xrs)) / fml
cmlts = (xmlinc + (fpe * cpets) + (frs * crsts)) / fml
End If
VSS:TSS ratio in mixed liquor: vt2 = xml / cmlts
Secondary Sedimentation Equations
VSS:TSS ratio in final effluent and secondary sludge: vt3 = vt2
Secondary sludge total solids: as input
Secondary sludge volatile solids: xses = csests * vt3
Partitioning of Secondary sludge to wastage and recycle sludge
Wastage sludge
Wastage sludge volatile solids: xws = xses
Wastage sludge total solids: cwsts = csests
Flow of wastage sludge: fws = ((fpe * cpets) + xmlinc - (cmlts * fml * (1 -
tsrem2))) / cwsts
Recycled sludge
Flow of recycled sludge: frs = r * fpe
Recycled sludge volatile solids: xrs = xses
Recycled sludge total solids: crsts = csests
Flow of secondary sludge: fses = fws + frs
Final effluent flow: ffe = fml - fses
Final effluent total solids: cfets = ((cmlts * fml) - (csests * fses)) / ffe
Final effluent volatile solids: xfe = ((xml * fml) - (xses * fses)) / ffe
```

3.6 Sludge production

In wastewater treatment, sludge is produced in the primary sedimentation tank and in the final sedimentation tank after activated sludge treatment. The primary sludges have different characteristics from the sludge produced in biological treatment. Primary sludges consist of solid particles, mainly organic in nature. Secondary sludges consist predominantly of excess biomass produced in the biological process. Primary sludges are readily dewatered and better solids capture can be achieved than for most chemical and biological sludges (USEPA 1979). The quantities and characteristics of biological sludges vary with metabolic and growth rates of various organisms present in the sludge. The concentrations and therefore the volumes of the waste biological sludge are also affected by the method of operation of the clarifiers (USEPA 1979).

A common practice in the UK is for the primary and secondary sludges to be co-settled in the primary sedimentation tank prior to sludge treatment. The supernatants from the sludge treatment processes are also recycled back into the primary sedimentation tank. Since both the waste-secondary sludge and the sludge treatment supernatants have very high waste strengths, recycling them back into the primary sedimentation tank greatly increases the amount of sludge withdrawn from the primary sedimentation tank.

3.7 Sludge Treatment

3.7.1 Thickening

For the solids mass balance model, the performance of the thickener will depend on the unit process used. Average values for the solids concentrations before and after thickening and for the solids capture efficiencies obtained from the literature will be used as default values (see table 3.3), which the user could change according to information of the particular plant in question. The solids capture efficiencies are typically around 80-90% for dissolved air flotation, 95% for gravity thickening (USEPA 1979) or 91-97% for centrifugation (IWPC 1979).

Table 3.3: *The typical increase in solids content for different unit processes*

Process	Sludge Type	Solids Concentration Before Thickening (%)	Solids Concentration After Thickening (%)	Reference
Gravity	P	6	9	IWPC 1979
	P+A	4.5	7	IWPC 1979
	P+H	5.5	8	IWPC 1979
	A	0.5	3	IWPC 1979
	H	2.5	4	IWPC 1979
	AD	3.5	5	IWPC 1979
	P	2-7	5-10	USEPA 1979
	P+A	2.5-4.0	4-7	USEPA 1979
	P+H	2-6	5-9	USEPA 1979
	A	0.5-1.5	2-3	USEPA 1979
	H	1-4	3-6	USEPA 1979
	AD	4	8	USEPA 1979
Centrifugation (depending on feed rate)	A	0.9	8.4	IWPC 1979
	A	1.02	8.9	IWPC 1979
Dissolved air flotation	P+H	0.5	4.5-5.0	USEPA 1979
	A	0.8	4	USEPA 1979
	P+A	2.3	7.1	USEPA 1979

Notes:
P = Primary sludge
A = Waste activated sludge
H = Trickling filter humus sludge
AD = Anaerobically digested sludge
1% solids concentration = 10,000 mg/l dry solids

The stream entering the primary thickening process is the flow of co-settled sludge from the primary sedimentation tanks. The procedure for calculating the outputs of this process is similar to that used in the primary and secondary sedimentation calculations. A value for the solids concentration after thickening is entered by the user of the program; 'TABLE 1' in the program (See section 3.9) gives typical values of solids

concentration for different thickening processes. A value for the removal efficiency is also needed. It is usually within the range of 80-97%, depending on the process employed. Thus the flow of the thickened sludge can be calculated. The VSS:TSS ratio in the thickened sludge is the same as that in the co-settled sludge, hence the volatile solids concentration can be calculated. The values for the thickener effluent can be calculated by simple mass balance equations.

```
Primary Thickening Equations:
VSS:TSS ratio in primary sludge: vt4 = xps / cpsts
Thickened sludge flow: fts = (cpsts * fps * tsrem3) / ctsts
If fts = 0 Then
Thickened sludge total solids: ctsts = 0
Thickened sludge volatile solids: xts = 0
Else:
ctsts = as input
xts = ctsts * vt4
End If
Thickener effluent flow: fte = fps - fts
If fte = 0 Then
Thickener effluent total solids: ctets = 0
Thickener effluent volatile: xte = 0
Else:
ctets = ((fps * cpsts) - (fts * ctsts)) / fte
xte = ((fps * xps) - (fts * xts)) / fte solids
End If
```

3.7.2 Sludge Digestion

The main consequence of anaerobic sludge digestion on the solids mass balance is the destruction of volatile solids. Volatile solids reduction in anaerobic digesters usually ranges from 35-60%. The character of the sludge determines the upper limit for volatile solids reduction achieved at any particular plant (USEPA 1979). The operating parameters of the digestion system also greatly affect the microbial growth rate and thus the reduction of volatile solids. In this respect, the solids retention time and the digestion temperature are the two most important operating parameters.

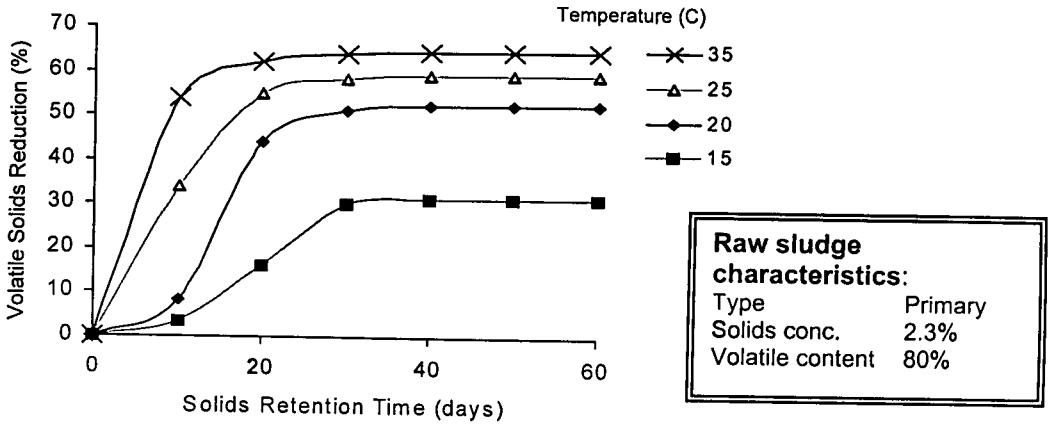


Figure 3.5: *Effect of solids retention time and temperature on volatile solids reduction in a laboratory scale anaerobic digester (O'Rourke 1968)*

As shown in figure 3.5, at 35°C (the temperature usually employed in conventional anaerobic digesters), the volatile solids reduction climbs rapidly to 50-60% as the SRT is increased. After an SRT of 10 days, further solids reduction is minimal, even with substantial increases in SRT. The temperature strongly influences the shape of the curve and the point at which it levels out.

In a paper by Bhattacharya et al (1996), studies were conducted on wastewaters of varying composition, using conventional digesters at a solids retention time of 10.4-12 days and a temperature of 35±1°C. The results, as shown in table 3.4, indicated that the factors that affect the volatile solids reduction were:

1. The composition of the raw influent wastewater (especially the percent and type of industrial input);
2. The type of sludge being treated (i.e. primary, waste activated sludge, humus, mixed, co-settled, etc.).

Table 3.4: *Results of studies on conventional anaerobic digestion (Bhattacharya et.al. 1996)*

Wastewater composition	Sludge composition	Solids Retention Time (days)	Volatile Solids Reduction (%)
50% industrial; 50% domestic	Primary + waste activated sludge	10.4	26.0
10% industrial; 90% domestic	Primary + waste activated sludge	12.5	49.1
15% industrial; 85% domestic	Primary + waste activated sludge	12	50.3
15% industrial; 85% domestic	Primary + waste activated sludge	12	48.3
15% industrial; 85% domestic	Waste activated sludge	12	34.0

Thus, for mixed primary and waste activated sludge, where the wastewater composition is mainly domestic, the volatile solids reduction is usually around 50%. Hence in the solids mass balance model, there will be a default value of 50% volatile solids reduction. Ideally, at plants where there is a high level of industrial input into the wastewater, or where potentially inhibitory substances (such as heavy metals, halogenated hydrocarbons and anionic detergents) are present, batch studies should be carried out to determine the percentage of volatile solids reduction.

The thickened sludge is usually pumped onto the stabilisation process, which is typically achieved through anaerobic digestion, before dewatering. As mentioned previously, the anaerobic digestion process generally results in volatile solids destruction (given the term "vsd") of 50%. Since the non-volatile solids are not affected, the total suspended solids concentration after digestion can be calculated by adding the non-volatile fraction of the thickened sludge to the volatile solids concentration after digestion.

```
Anaerobic digestion Equations:
Flow of sludge between digester and digester thickener: fts2 = fts
Volatile solids content of sludge after digestion: xts2 = xts * vsd
Total solids content of sludge after digestion: ctsts2 = (ctsts - xts) + xts2
```

Digester Thickening

After digestion, the sludge is further concentrated in the digester thickening process. The calculations in this stage follow the same procedure as for the primary thickening. Again values for the solids concentration after thickening of anaerobically digested sludge can be obtained from 'TABLE1'. The VSS:TSS ratio in the sludge and effluent of the digester thickener is the same as that of the sludge produced from the digester.

```
Digester Thickening Equations:
VSS:TSS ratio after digestion: vt5 = xts2 / ctsts2
Digester sludge flow: fds = (fts2 * ctsts2 * tsrem4) / cdsts
If fds = 0 Then
Digester sludge total solids: cdsts = 0
Digester sludge volatile solids: xds = 0
Else:
cdsts = as input
xds = cdsts * vt5
End If
Flow of digester effluent: fde = fts2 - fds
If fde = 0 Then
Digester effluent total solids: cdets = 0
Digester effluent volatile solids: xde = 0
Else:
cdets = ((fts2 * ctsts2) - (fds * cdsts)) / fde
xde = ((fts2 * xts2) - (fds * xds)) / fde
End If
```

3.7.3 Sludge Dewatering

As for thickening, the two variables that are needed in the model in terms of dewatering are the typical solids increase and the solids removal efficiency. Both values are dependent on the method of dewatering employed.

Filtration Dewatering Systems

Factors that affect their performance include (IWPC 1981):

- *Nature of feed sludge:* Primary sludges produce a thicker and drier cake than secondary and digested sludges, which produce a cake with a lower solids content and reduced yield.
- *Condition of filtration medium:* The efficiency will be reduced unless the filtration medium is routinely cleaned.
- *Age of Sludge:* Fresh sludges are more amenable to dewatering than older sludges.

Centrifugal Dewatering Systems

Variables that affect the performance of the centrifuge are (IWPC 1981):

- *Nature of feed sludge:* Raw sludges are easier to dewater because of their high fibrous matter content. However, high levels of grease in the sludge can cause operating problems.
- *Solids content of feed sludge:* A thicker feed sludge reduces the amount of polyelectrolyte needed and increases the solids throughput.

Experimental results using digested sludge showed that the typical range of increase in solids content is 4.7-6.7, with an average of 5.3. The solids recovery (%) ranged from 96.8 to 99.5, with an average of 98.6 (Bettesworth in IWPC 1981).

Table 3.5: *Typical performance values of various types of filters (adapted from IPWC 1981):*

Method	**Type of Sludge**	**Feed Sludge (% dry solids)**	**Cake (% dry solids)**	**Suspended Solids Capture Efficiency (%)**
Filter-Press	Primary/ mixed sludge	4-8	30-40	Not available
	Digested sludge	3-6	30-40	Not available
Rotary-Drum Vacuum Filter	Primary and digested	5	19	94
	Primary and humus	7	25	98
	Primary	6	27	95
Vacuum Disk Filter	Mixed	2.9	15	Not available
Filter Belt Press (conventional)	Raw primary/humus	3.2-11.2	17.6-32.6	97-99
	Raw primary/activated	2.4-4.6	16.8-20.7	96-99
	Cold digested	6.3-7.7	21.1-29.1	95-98
	Heated digested	1.9-4.1	17.9-25.7	99
	Surplus activated	1.4-2.3	12.6-15.9	99

Again the same procedure followed above is used at this stage. Values for the solids concentration after dewatering and the solids capture efficiency for various dewatering processes are given in 'TABLE 2' (See section 3.9).

```
Dewaterer Equations:
VSS:TSS ratio in dewaterer: vt6 = vt5
Dewatered sludge flow: fdws = (fds * cdsts * tsrem5 / cdwsts)
If fdws = 0 Then
Dewatered sludge total solids: cdwsts = 0
Dewatered sludge volatile solids: xdws = 0
Else:
cdwsts = as input
xdws = vt6 * cdwsts
End If
Dewaterer effluent flow: fdwe = fds - fdws
If fdwe = 0 Then
Dewaterer effluent total solids: cdwets = 0
Dewaterer effluent volatile solids: xdwe = 0
Else:
cdwets = ((fds * cdsts) - (fdws * cdwsts)) / fdwe
xdwe = ((fds * xds) - (fdws * xdws)) / fdwe
End If
```

The supernatants resulting from the sludge treatment processes are combined and returned to the primary sedimentation process. The dewatered sludge is taken away for disposal.

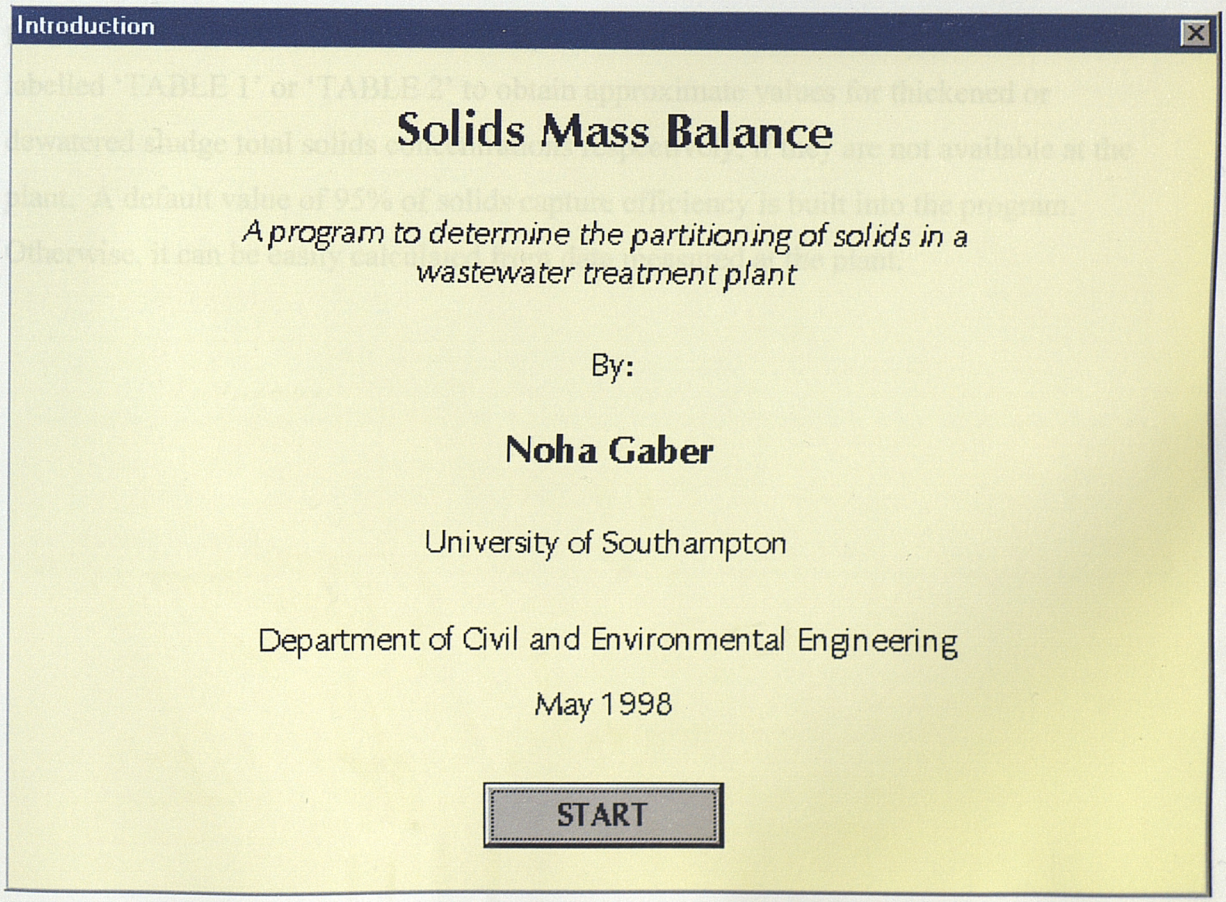
```
Effluents returning to top of works:
Flow of returning effluent stream: fre = fdwe + fde + fte
If fre = 0 Then
Total solids in returning effluent stream: crets = 0
Volatile solids in returning effluent stream: xre = 0
Else:
crets = ((fdwe * cdwets) + (fde * cdets) + (fte * ctets)) / fre
xre = ((fdwe * xdwe) + (fde * xde) + (fte * xte)) / fre
End If
```

3.8 Overall Assumptions

The International Association on Water Pollution Research and Control (IAWPRC) developed a model for simulating the activated sludge system, which they called "The Activated Sludge No.1 Model". It incorporates phenomena such as carbon oxidation, nitrification and denitrification. The report that describes this model stated that: *"When a wastewater treatment system is to be modelled, a certain number of simplifications and assumptions must be made to make the model tractable. Some of these are associated with the physical system itself, while others concern the mathematical model."* (IAWPRC 1986). The main assumption used in developing the current solids mass balance model is that steady state is present. Thus, the system is assumed to have a constant flow and influent solids and metals concentrations.

3.9 User-Interface

A user interface was also developed using the Visual Basic Editor in **Microsoft™ Excel 97** to simplify the process of inputting the necessary data at the beginning and reviewing the outputs. The user interface screens are shown below.



The first screen, introduces the user to the program and when the **'START'** is pressed, the input spread sheet appears:

Solids Mass Balance
Inputs needed at beginning of Solids Mass Balance Program

Note that the units for flows are l/hr, for concentr

Raw influent flow (FIN)	41,667.000	
Raw influent total solids (CINTS)	500.000	
Raw influent volatile solids (XIN)	400.000	
Primary sludge total solids (CPSTS)	20,000.000	
Percentage removal of total solids in primary clarifier (Tsrem%)	0.800	
Concentration of mixed liquor total solids initially in reactor (cmlts1)	3,000.000	
Concentration of mixed liquor volatile solids initially in reactor (xml1)	2,400.000	
Percentage removal of total solids in secondary clarifier (TSrem2%)	0.985	
Secondary sludge total solids (CSESTS)	9,000.000	
Recycle ratio (R)	0.520	
Net SludgeYield (Yn)	0.500	Depends on process (conventional=0.5, high aeration=1
Soluble substrate of primary effluent (Sf)	150.000	
Soluble substrate of reactor effluent (Se)	10.000	
Thickened sludge total solids (CTSTS)	70,000.000	See Table 1
Percentage removal of total solids in primary thickener (Tsrem3%)	0.950	
Percentage reduction of volatile solids in digester (VSD%)	0.500	
Digester sludge total solids (CDSTS)	80,000.000	See Table 1
Percentage removal of total solids in digester thickener (Tsrem4%)	0.960	
Dewatered sludge total solids (CDWSTS)	300,000.000	See Table 2
Percentage removal of total solids in dewaterer (Tsrem5%)	0.980	

To run the Solids Mass Balance program:
Input data into spreadsheet and press "Start Program" button

Start Program

There are 19 values, which the user must input at the beginning, in order for the program to carry out all the necessary calculations. The user may press the tabs labelled 'TABLE 1' or 'TABLE 2' to obtain approximate values for thickened or dewatered sludge total solids concentrations respectively, if they are not available at the plant. A default value of 95% of solids capture efficiency is built into the program. Otherwise, it can be easily calculated from data measured at the plant.

Table 1:

Typical Solids Content Achieved Using Different (Thickening) Unit Process

PROCESS	SLUDGE TYPE	Solids Content After Thickening(%)
Gravity	P	5-10
	P+A	4-7
	P+H	5-9
	A	2-3
	H	3-6
	AD	5-8
Centrifugation	A	8.4
Dissolved Air Flotation	P+H	4.5-5
	A	4
	P+A	7

Notation:
A: Waste activated sludge P: Primary sludge
H: Humus sludge AD: Anaerobically digested sludge

NB: 1% solids= 10,000mg/l

Table 2:

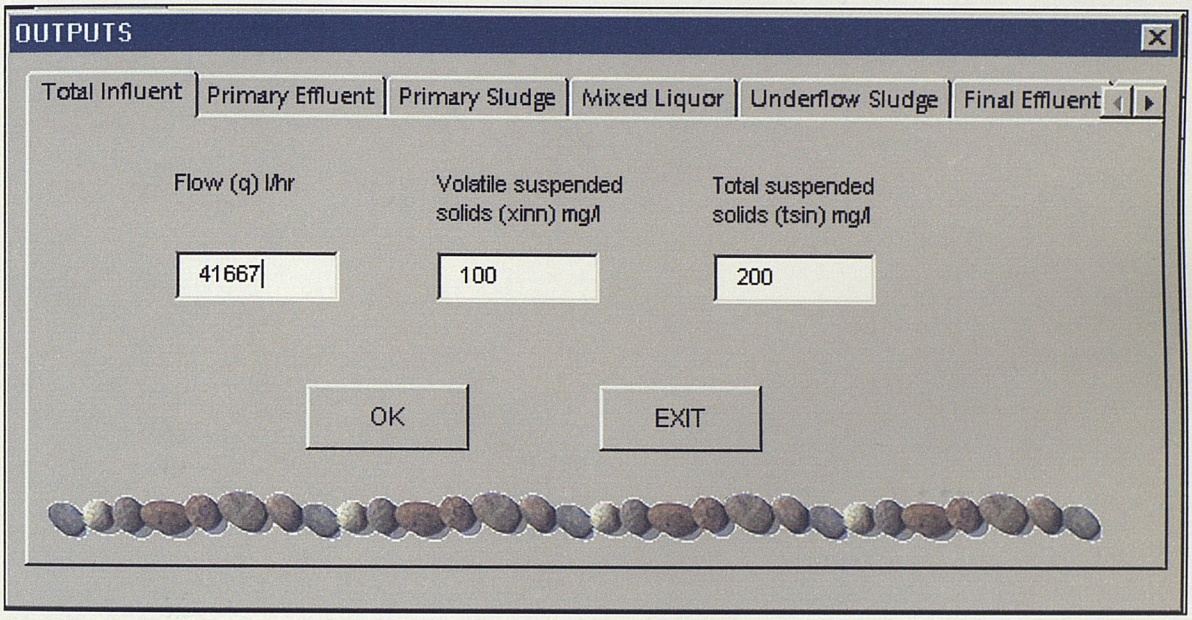
Typical Solids Content Achieved Using Different (Dewatering) Unit Process

Process	Sludge Type	Cake (% Dry Solids)	Suspended Solids Capture Efficiency (%)
Filter-Press	P/Mixed	30-40	Not available
	AD	30-40	Not available
Rotary-Drum Vacuum Filter	P+AD	19.00	94
	P+H	25.00	98
	P	27.00	95
Vacuum Disk Filter	Mixed	15.00	Not available
Filter Belt Press (conventional)	Raw P+H	17.6-32.6	97-99
	Raw P+A	16.8-20.7	96-99
	Cold digested	21.1-29.1	95-98
	Heated digested	17.9-25.7	99
	Surplus Activated	12.6-15.9	99

Notation:
A: Waste activated sludge P: Primary sludge
H: Humus sludge AD: Anaerobically digested sludge

NB: 1% solids= 10,000mg/l

After all the values required have been entered, the user presses the "Start Program" button, this starts the program calculations and the OUPUTS screen immediately appears. The OUTPUTS are grouped in terms of the type of flow, so for example, all the values for primary effluent are grouped together. Pressing the OK button shows the values for the next iteration, until 24 iterations (i.e. 24 hours) are reached. The outputs may be viewed in tabulated form by pressing the "OUT-LIST" tab at the bottom of the screen.



Chapter Four

Metals Model Development

4.1 Behaviour of metals in wastewater treatment

Having considered the partitioning of solids it is next necessary to understand how the metals themselves associate with the solid fraction at each stage of wastewater treatment. For the purposes of the model development in this project, two main metal fractions are of interest. These are: soluble metal fraction (which includes free metal ions and metals complexed with soluble organic and inorganic ligands); and solids-associated fraction (which includes metals adsorbed onto the solid particles as well as precipitated metals). Studies on the partitioning of metals between the different fractions have shown that the two main mechanisms of metal removal from solution are precipitation and adsorption onto the solids. Kodukula et al (1994) proposed a conceptual model for the activated sludge system to define the distribution of metal between soluble and solid phases. Their model shows that as soluble metal is added to a sample of activated sludge mixed liquor, "the metal is partially adsorbed to the sludge solids in accordance with the sorption characteristics of the solids until the soluble metal concentration reaches the solubility limit, governed by the soluble phase chemistry of the system". Any increase in the metal concentration after this point would not cause an increase in the soluble metal fraction and would contribute to the solids-associated fraction through adsorption or precipitation. The behaviour of solids bound metal can be similarly described. For each solids concentration, a fixed proportion of soluble metal is adsorbed onto the solids. This proportion, as denoted by the adsorption coefficient, increases with increasing solids concentration. Therefore, as soluble metal is added to the system, the metal is adsorbed onto the solids, according to the adsorption coefficient, up to a point where the sludge capacity is reached. After that point, the metal stays in solution until the solubility limit is reached, after which, the soluble metal concentration stays constant and any further metal additions would go into the solids phase as precipitates. This saturation behaviour has also been noted by other researchers with regards to the saturation of activated sludge solids under varying sludge ages (Banks 1997). The results of Kodukula et al (1994) show that for the conditions encountered in full-scale plants, adsorption was the main mechanism of metal removal. Kunz and Jardim (2000) agree that adsorption and complexation (to soluble ligands) act as competitive mechanisms in copper speciation, and their work shows that complexation is the most important mechanism, i.e. the metals will be complexed in solution and will not precipitate. Figures 4.1 and 4.2 show this conceptual behaviour of soluble and solids associated metal.

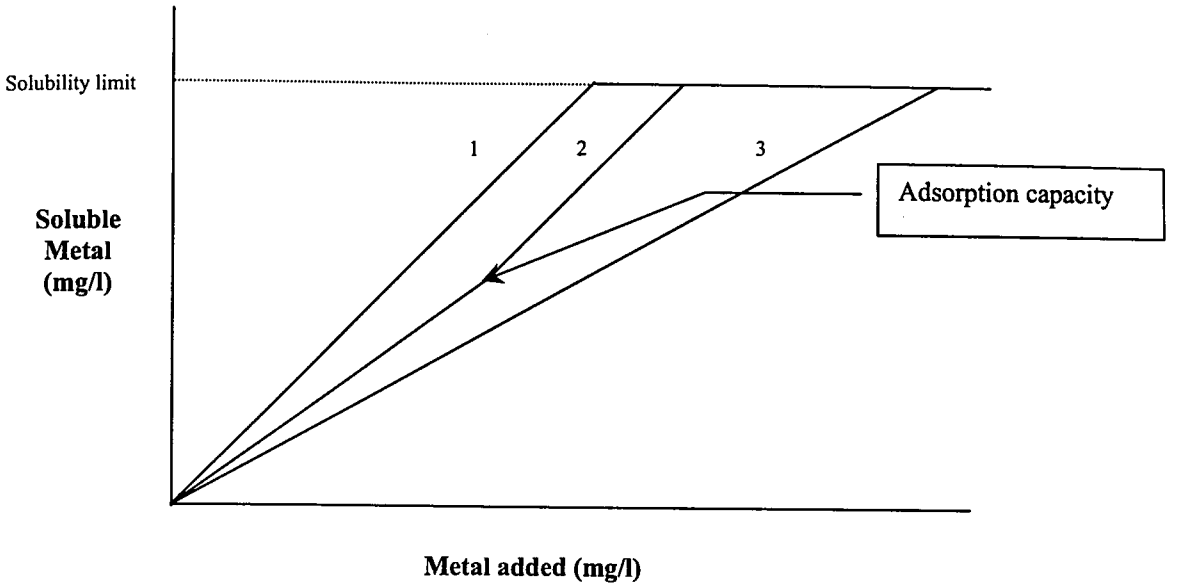
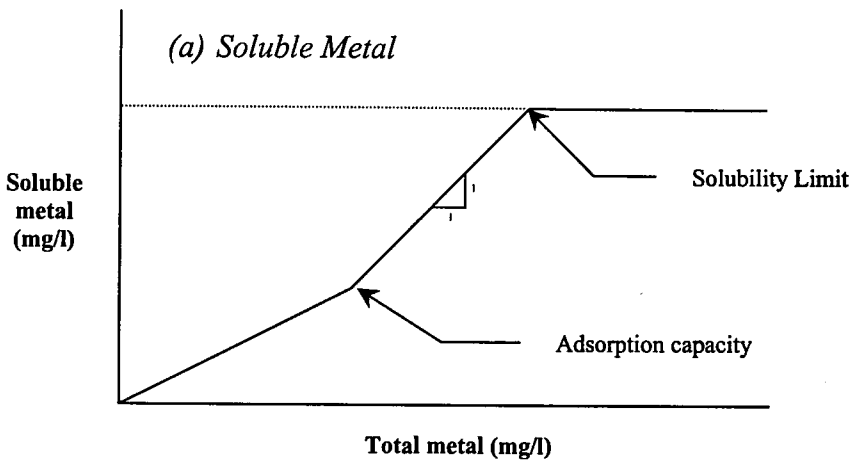


Figure 4.1: *Conceptual model for metal sorption and precipitation mechanisms (1: No solids; 2: low solids; 3: high solids) (after Kodukula et al 1994)*



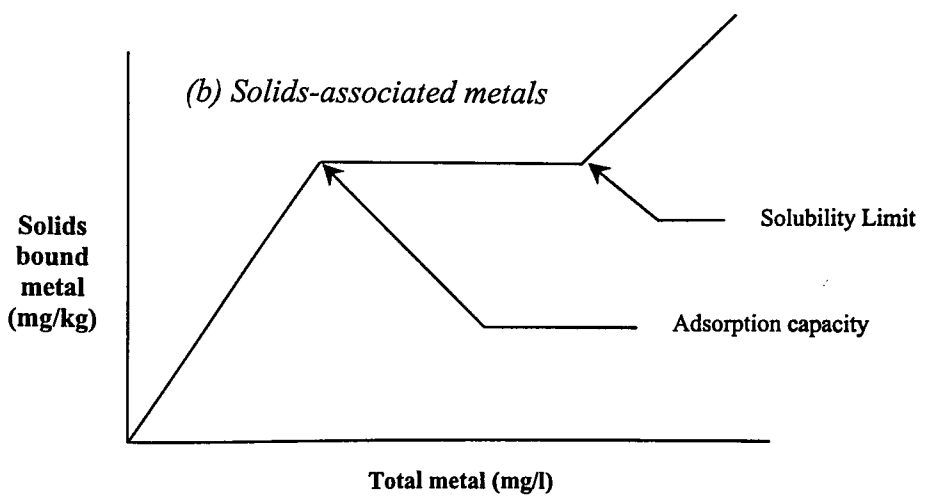
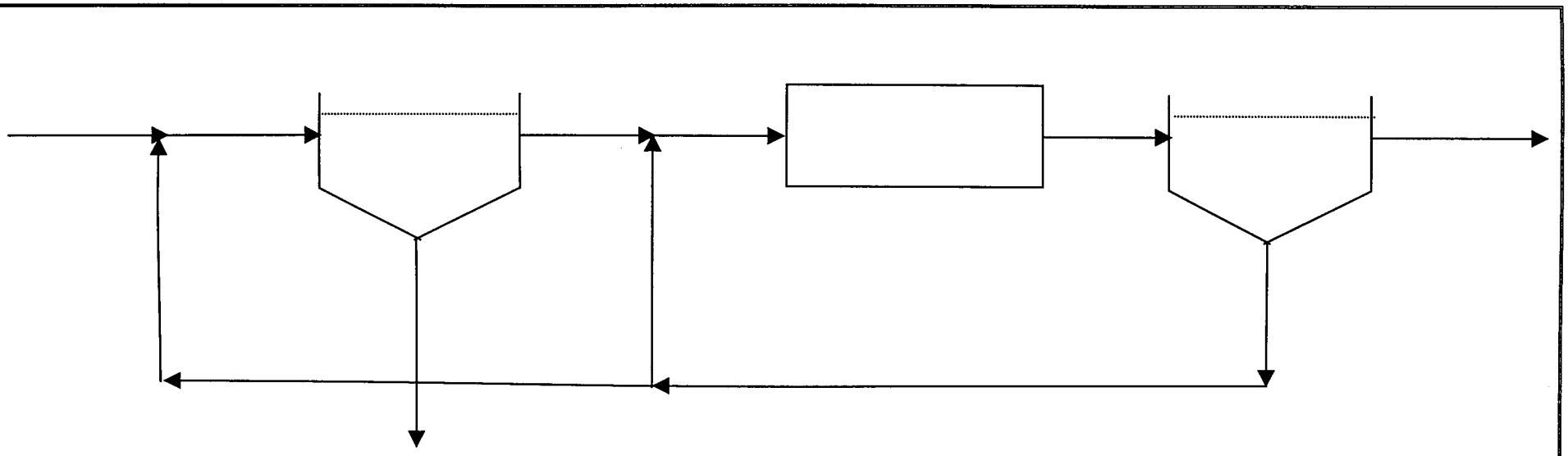


Figure 4.2: *Metal behaviour governed by adsorption capacity and solubility limits*

In actual conditions, the total metal concentration will not increase as shown in figure 4.1. Equilibrium between the different metal fractions will have been reached in the sewer system prior to entry into the wastewater treatment plant. Adsorption onto the solids and complexation with the soluble ligands take place according to the conditions that exist in the sewer system. During treatment, the adsorbed fraction is removed from the wastewater by the settlement of solids, while removal of the soluble fraction during treatment in the plant results from changes in factors that affect the solubility of the metal, for example the pH of the system or the solids concentration. This can be shown schematically in figure 4.3.

Thus for each treatment process, the mechanisms of adsorption onto the wastewater solids and complexation with soluble ligands will form the basis of the predictive model. The types of approaches available for modelling these mechanisms will now be described, with reference to previous studies, which have employed them. The relative merits and limitations of each approach will be discussed, helping to select the most suitable approach, or combination of approaches, for this application.



Raw Sewage
Soluble metal: adsorbed metal equilibrium already established
Fractions:
- Soluble
- Insoluble settleable
- Insoluble non-settleable
- Adsorbed

Primary Sedimentation:
Mechanisms:
- Settling of insoluble settleable metals
- Settling of adsorbed metal along with associated solids

Aeration:
Adsorption of some soluble fractions onto biological solids

Secondary Sedimentation
Same as primary sedimentation

Final Effluent

Fractions:
- Soluble
- Associated with NVSS as well as VSS

Figure 4.3: *Metal Speciation and Behaviour across Treatment Plant*

4.2 Approaches to Modelling

Several modelling approaches are available to describe the adsorption behaviour of metals:

4.2.1 Empirical Models

Empirical or black box models are based on mathematical expressions, which have been formulated through regression analysis to reasonably represent data from the system being modelled. Patterson et al (1983) employed what might be described as an empirical approach to the development of their metals removal model. A series of 49 runs on pilot plant units was conducted varying the influent metals concentration and metals combinations. The data from these tests was used to find the correlation between metals removals and several process parameters. Equations that best fit the experimental data were generated. The regression equation, which best fit the metals and treatment stages examined takes the form of:

$$C_{TM}\left(\frac{VSS}{C_{SM}}\right) = A \bullet VSS + B$$

where,

C_{TM}: concentration of total metal;

C_{SM}: concentration of solid or sludge-bound metal;

VSS: volatile suspended solids;

A and B: model parameters that were computed by multi-variant linear regression.

This equation was arrived at by plotting C_{SM}/VSS vs. C_{TM} for each constant VSS concentration. The resulting linear graph had the following equation:

$$\frac{C_{SM}}{VSS} = mC_{TM}$$

Then by plotting m vs. VSS, the resulting linear graph had the following equation:

$$m = \frac{1}{A * VSS + B}$$

4.2.2 Equilibrium Chemical Modelling

In this approach, the chemical speciation-distribution of heavy metals is described through the formulation of conditional adsorption constants correlating bound metal, free metal and ligand concentrations (Fristoe and Nelson, 1983). From basic chemical principles, the adsorption of metal ions by a bacterial surface may be conceptually represented as the formation of a surface-metal complex:

M + S = MS, with the equilibrium adsorption constant K_A given as:

$$K_{A,M} = \frac{[MS_m]}{[M]\{S_m\}}$$

where:

$K_{A,M}$ = conditional adsorption constant (l/g)

$\{S_m\}$ = adsorbing surface of type m (g/l)

[M] = free metal ion (mol/l)

$[MS_m]$ = metal-surface complex (mol/l)

(Fristoe and Nelson, 1983)

The total bacterial mass (S_T) is the sum of the occupied and unoccupied sites:

$S_T = \{S\} + [MS]/y$

Where y = number of surface sites per unit mass of bacteria (moles charge/g).

Chemical reaction modelling is an example of this type of modelling. A chemical reaction model is defined as "the integration of mathematical expressions describing theoretical concepts and thermodynamic relationships on which the aqueous speciation, oxidation/ reduction, precipitation/ dissolution and adsorption/ desorption calculations are based" (USEPA 1999). Numerous chemical reaction models exist. The MINTEQA2 computer model was developed with funding from the USEPA and is used to calculate complex chemical equilibria between dissolved and adsorbed states. However, some major limitations to this approach must be recognised. There are numerous chemical and biological factors that could influence the value of the conditional adsorption constant. In addition to pH, ionic strength and ionic constituency of the growth medium are important chemical factors. The chemical composition of the water and the bacterial culturing conditions (e.g. sludge age, substrate type and strength and reactor environmental conditions) are also very important (Nelson et al 1981). These constants are thus valid only at the pH and solution conditions specified. Therefore, at best, the chemical modelling based on equilibrium conditions may provide estimates of bounding limits for some processes (USEPA 1999).

Vuceta and Morgan (1978) examined the physical-chemical distribution of trace metals in terms of two chemical models:

- Inorganic systems: factors studied were pH, different adsorbing surface areas.
- Organic systems: the effect of different organic ligands (such as EDTA, citrate) and surface areas was examined.

They found that the chemical modelling of the distribution of trace metals depends on a variety of factors: the metal being studied, the inorganic and organic ligands and the surfaces in the system. Since in many cases the concentrations as well as identities of organic constituents and the stability constants for the metal-ligand and metal surface interactions are poorly known, this approach may not be easily applicable to predictive modelling of the partitioning of metals in wastewaters.

Thus the reliability of this type of model will depend on the availability of extensive knowledge of the composition and characteristics of a given wastewater. Furthermore, since these conditional stability constants attempt to calculate the metal speciation as free metal ions or complexed forms, they are not suitable for a predictive model, which aims to predict the equilibria between soluble phase metal (including free metal and soluble organic and inorganic metal complexes) and solids phase metal (including solids-bound and precipitate metal).

4.2.3 Adsorption Isotherms

Based on physico-chemical processes, adsorption isotherms are the result of a suite of experiments evaluating the effect of contaminant concentration on adsorption (USEPA 1999). They describe metal partitioning (adsorbed vs. soluble) at equilibrium conditions and at discrete temperatures and pH values. Isotherm models explicitly consider the dependency of partitioning on only the solution concentration of the adsorbate. Other solution parameters, which can influence adsorption, are not considered (USEPA 1999). The linear adsorption isotherm is defined as follows:

$C_X = C_S K_p X$,

Where, C_X = solids bound metal conc. (mg/l);

C_S = soluble metal conc. (mg/l);

K_p = partitioning coefficient and

X = volatile suspended solids conc. (mg/l)

The mechanism of adsorption may be represented graphically as shown in figure 4.4.

$$Cx = \frac{mass\_sorbed}{mass\_sorbent}$$

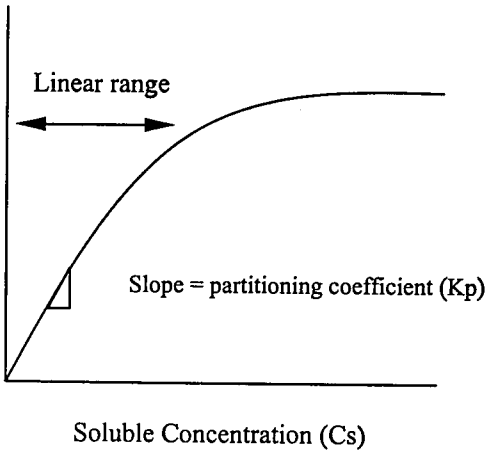


Figure 4.4: *Linear Sorption Isotherm (after Sawyer et al 1994)*

The conditional adsorption equilibrium constant described previously in section 4.2.2 is equivalent to the sorption or partitioning coefficient as shown above. This coefficient is a direct measure of the partitioning of a contaminant between the solid and aqueous phases (USEPA 1999). Its magnitude depends on the characteristics of the adsorbent and adsorbate as well as the pH of the solution, the functional groups on the solid surface (adsorbent) and complexation in solution (Grassi et al 2000). It was noted by Nelson et al (1981) that often the region of interest for adsorption in wastewaters falls in the linear uptake region. Thus only the slope of the linear isotherm needs to be determined. The linear adsorption isotherm curve is a characteristic L-curve. As can be seen, the initial slope of C_X (solute adsorbed per unit mass of solid) versus C_S (soluble concentration of the adsorbate) is large, but the slope decreases as the soluble concentration increases. This is due to the saturation of adsorption sites (USEPA 1999).

Closer comparison between the empirical equation as developed by Patterson et al (1983) and the linear adsorption isotherm model, revealed that they are very similar. Manipulating the linear adsorption isotherm:

$$C_x = C_s * K_P * VSS$$

$$C_{TM} = C_x + \frac{C_x}{K_P * VSS}$$

$$C_x = \frac{C_{TM} * K_P * VSS}{1 + K_P * VSS}$$

$$C_x(1 + K_P * VSS) = C_T * K_P * VSS$$

$$1 + K_P * VSS = \frac{C_T}{C_x} * K_P * VSS$$

$$1 + K_P * VSS = C_T\left(\frac{VSS}{C_x}\right) * K_P$$

$$\frac{1}{K_P} + VSS = C_T\left(\frac{VSS}{C_x}\right)$$

Comparing the resulting equation with the Patterson equation, it is clear that Patterson "B" constant is equivalent to the inverse of the adsorption coefficient Kp in the mechanistic equation and Patterson "A" constant is equivalent to 1.

4.2.3.1 Generic Adsorption Isotherms

Generic adsorption isotherms such as the Freundlich or Langmuir isotherms resulted from extensive studies on the adsorption phenomenon. They are used to interpret data to determine the equilibrium constants that describe the sludge/metal interactions (Kasan 1993). Each of these generic isotherms results in significantly different functional relations. The best isotherm to use in a particular case will depend on which one best describes the data.

The Langmuir Isotherm:

The Langmuir isotherm describes single-layer adsorption and takes the form of:

$$\frac{C_s}{C_x} = \frac{1}{K_a K_L} + \frac{C_s}{K_a}$$

Where:

C_s = concentration of adsorbate in solution (mg/l)

C_x = concentration of adsorbate per adsorbent (mg/kg)

K_a = maximum adsorption capacity (mg/kg)

K_L = Langmuir equilibrium constant (l/g), which gives an indication of the affinity of adsorption.

Other assumptions of the Langmuir isotherm are (Kasan 1993, Daintith 1996):

- There is no interaction between molecules on different sites and each site can only hold one adsorbed molecule.
- The heat of adsorption does not depend on the number of sites and is equal for all sites.

As can be seen, these assumptions limit the applicability of the Langmuir isotherm. Furthermore, since this isotherm was derived for single solutes adsorption on completely homogenous surfaces, there is doubt as to whether a heterogeneous system such as wastewater can be fitted to it (Tsilipakos 1995).

From the chemical modelling equations given in section 4.2.2 above, a Langmuir isotherm can be derived as Nelson et al (1981):

$$\frac{[M]}{[MS]/S_T} = \frac{1}{K_A} + \frac{[M]}{y}$$

Comparing this with the Langmuir isotherm shown above, then:

$$\frac{y}{K_A} = K_L$$

Thus the Langmuir adsorption constant, K_L, is proportional to the reciprocal of the equilibrium constant for adsorption (K_A). Since the Langmuir equilibrium constant gives an indication of the affinity of adsorption, the equilibrium adsorption constants may be used to compare the relative adsorption affinities for different metals, solids concentrations and values of pH.

The BET (Braunauer, Emmett and Teller) isotherm

The BET isotherm is based on the Langmuir isotherm but it takes into account multi-layer adsorption. It assumes that a number of layers accumulate at the surface and that the Langmuir isotherm applies to each layer (Sawyer et al 1994).

The Freundlich isotherm

The Freundlich isotherm model is defined as:

$$C_x = K_F C_s^N$$

Where:

K_F = Freundlich adsorption constant

N = empirical constant

Although the Freundlich model considers heterogeneous adsorption surfaces and the possibility of multi-layer adsorption, it does not account for finite adsorption capacity.

The Redlich-Peterson Isotherm

The Redlich-Peterson isotherm is a more recent development than the above isotherms. It incorporates some refinements, which make it better than the other isotherms. However, eventhough it has been found to better fit experimental data (Artola et al 2000), it has scarcely been applied in the modelling of wastewater adsorption systems. It takes the form of:

$$C_x = \frac{K_a b C_s}{1 + b C_s^B}$$

Where:

b = adsorption energy related constant

B = empirical parameter

The main limitation for use of isotherm models in a predictive model for adsorption is the fact that the equilibrium constant or adsorption coefficient derived using this method is only valid for the set of environmental conditions under which it was derived. Furthermore the applicability of the generic isotherms is dependent on their assumptions.

4.2.4 Mechanistic Models

Mechanistic models describe the actual or believed physical or chemical behaviour in terms of mathematical equations employing experimentally derived coefficients. They explicitly accommodate for the dependency of the adsorption/ partition coefficient values on contaminant concentration, competing ion concentration, variable surface charge on the adsorbent and solute species distribution (USEPA 1999). Thus the use

of mechanistic models renders the predictive models more robust and scientifically defensible.

The TOXCHEM+ computer model, developed in 1991 by ***Enviromega Ltd.*** (Canada), is described as being an example of this type of modelling approach. It predicts the fate of organic chemicals and metals in wastewater collection and treatment systems at steady state (Monteith et al 1993). Based on mass balance calculations and removals through precipitation and sorption onto settleable solids, the model predicts the metal concentrations in primary sludge, return activated sludge, waste activated sludge and secondary settler effluent. Batch experiments were used to obtain values for the adsorption coefficient and solubility limit of each metal. In developing the model equations, the following basic assumptions were made:

1. The system is always at equilibrium with regard to sorption and desorption;
2. Sorption follows a linear isotherm;
3. Precipitation and dissolution are simultaneous
4. Precipitated metals are integrated into the biomass and are removed at the same efficiency as the bulk solids in the primary and secondary settlers.

The equations employed in the TOXCHEM+ model are as follows:

$C_T = C_S + C_X$

$C_X = C_P + K_P X C_S$

where C_T = total metal concentration (mg/l); C_S = soluble metal concentration (mg/l); C_X = solids phase concentration (mg/l); C_P = precipitated metal concentration (mg/l); K_P = linear sorption coefficient (l/mg); X = volatile suspended solids concentration (mg/l).

The soluble, sorbed and precipitated fractions of a metal are calculated by the following expression:

$$C_{test} = \frac{C_{T,o}}{(1 + K_{P,1} X_o)}$$

where $C_{T,o}$ = influent total metal concentration; $K_{P,1}$ = primary clarifier sorption coefficient and; X_o = influent volatile suspended solids (VSS) concentration;

- If C_{test} is less than or equal to the solubility limit in the model's database for the metal in primary effluent ($C_{sol,1}$), the influent soluble metal concentration $C_{s,o}$ is equal to C_{test} and the precipitate concentration, $C_{P,o}$ is zero.

- If C_{test} is greater than the solubility limit, the soluble concentration $C_{s,o}$ equals the solubility limit and the precipitate concentration is given by:

$$C_{P,o} = C_{T,o} - (1 + K_{P,1} X_o) C_{sol,1}$$

The mathematical equations are bound by the following assumptions:

1. Biomass concentration is constant during the experimental run;
2. Influent concentration is constant during each step interval;
3. Sorption follows a linear isotherm;
4. Sorption and desorption are at equilibrium in the system;
5. The aeration tank is a completely mixed reactor.

Thus, it can be seen that the main equation employed in this model is the linear isotherm model and the experimentally derived adsorption coefficients and solubility limits used are based on one set of environmental conditions. Thus it does not accommodate for the dependency of the partition coefficient on the factors that influence it. Furthermore, it is clear that the model does not take into account the saturation of adsorption sites. The adsorption coefficient assigned to each treatment process stays valid regardless of the loading of influent metals. This is a serious limitation of this model, since many researchers have found that sludge has a fixed capacity for the uptake of heavy metals (Rossin et al 1982, Banks 1997).

4.2.5 Most Suitable Approach

As can be seen, the use and general applicability of some of these techniques to achieve the objectives of the current research are limited for several reasons. The linear adsorption isotherm model describes the fundamental adsorption process at work in wastewater treatment and can thus help to predict the distribution of heavy metals during wastewater treatment using adsorption/partitioning coefficients. However, its main limitation stems from the fact that the adsorption/partitioning coefficient is only valid for the particular adsorbate, adsorbent and environmental conditions in which it was derived. Thus it does not address the sensitivity to changing conditions. An improvement on this model will involve the use of empirically derived relationships between the adsorption/ partitioning coefficient and various influencing aqueous and solid phase parameters. These relationships would be derived from the results of a suite of experiments carried out at varying concentrations of adsorbate and adsorbent as well as different pH values. This technique may also be extended to determine the correlations between the adsorption capacity, as derived using a generic adsorption isotherm, and the parameters varied.

Hence, the most suitable approach for the purpose of this research is a combination of the approaches described above. The adsorption isotherm approach to modelling describes the complex physico-chemical and biological mechanisms that are known to be at work within the process of sewage treatment, using equations to mimic the observed reactions. The mechanistic approach allows these mechanisms to be modelled for a range of influencing factors.

4.3 Final Model

4.3.1 Model Assumptions

- Steady state conditions, in terms of influent flow rates and solids concentrations.
- Metals removal is proportional to solids removal due to settlement of solids associated metals.
- Sorption follows a linear isotherm
- Adsorption capacity can be described using a Langmuir isotherm.
- Metals are in equilibrium with respect to their different fractions prior to entering the plant.

- Adsorption takes preference over precipitation as long as there are free adsorption sites.

4.3.2 Model Equations

The model deals with one unit process at a time. The equations used to calculate the metals concentrations in soluble and solids bound fractions for each unit process are the same; the only variations are the values of the coefficients. The model coefficients are the solubility limit of the metal, the adsorption/ partitioning coefficient and the adsorption capacity.

From the linear adsorption model, and assuming no precipitation, the solids bound metal can be calculated by:

$$C_T = C_s + C_x$$

$$C_x = C_s KpX$$

$$C_T = \frac{C_x}{KpX} + C_x$$

$$C_x = \frac{C_T KpX}{1 + KpX}$$

A flowchart showing the equations and the logic used in the calculations (for raw sewage) is shown in Figure 4.5.

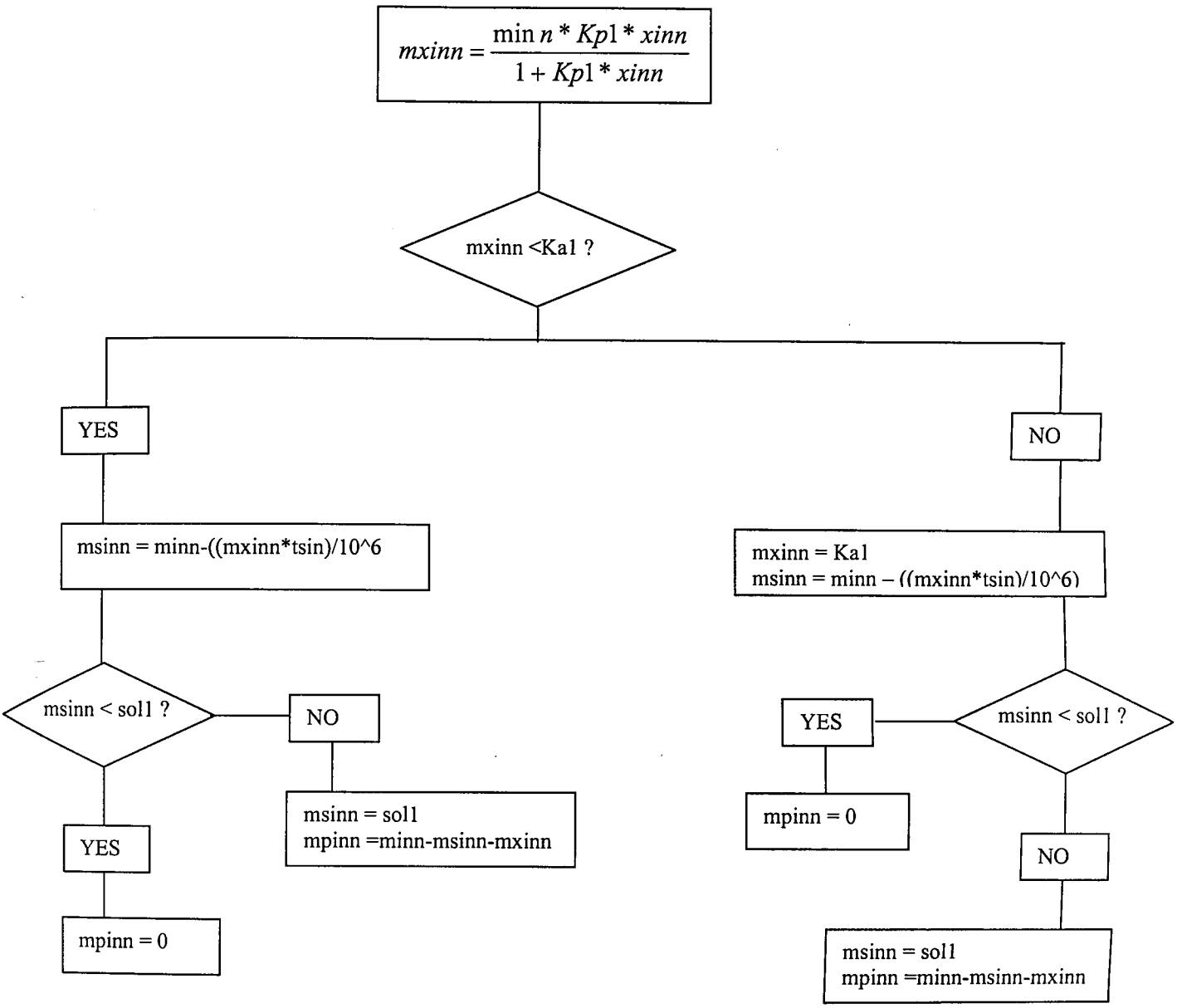


Figure 4.5: *Flow Chart of Model Calculations for Metals in Raw Sewage*

Notes:

mx = solids bound metal; ms = soluble metal; mp = precipitated metal

Kp = adsorption coefficient; Ka = adsorption capacity; sol = solubility limit

x = volatile suspended solids

The model tests for both mechanisms for metal removal from solution: precipitation and adsorption. Starting with the total metal concentration in the influent, the model calculates the solids bound metal concentration, using the adsorption coefficient determined for that process stream. If the calculated value of the solids bound metal is less than the value for the adsorption capacity input in the model database, then the

soluble metal concentration may be calculated. Otherwise, the solids bound concentration will be taken to be equal to the adsorption capacity value. In calculating the soluble metal concentration, a test is carried out for precipitation. If the calculated soluble metal concentration is greater than the solubility limit given in the model database, the soluble metal may be taken to be equal to the solubility limit value and the excess attributed to precipitated metal. During sedimentation, removal of metals may take place through adsorption of soluble metal species onto the solids and the subsequent settlement of the solids. The extent of this adsorption is calculated using the adsorption coefficient of the effluent. The efficiency of removal of solids bound metal fractions is assumed to be the same as the efficiency of solids removal.

The complete set of model equations is given in Appendix B.

4.3.3 Model Coefficients

It is important to note that the coefficients and constants employed in this model are conditional, since their value is dependent on operational conditions, such as pH, ionic strength, concentration of complexing organic and inorganic ligands and concentration of other competing surfaces (Nelson et al 1981). In the batch experiments carried out in this research, identification of the correlations between some of these important factors will be attempted. The experimental procedure used to calibrate the model will be fully described in Chapter 5.

4.3.3.1 Solubility Limits:

In solution, the metals may exist as free metal ions or as organic and inorganic complexes. Precipitation of metals will occur when the soluble metal concentration exceeds the solubility limit. The metals may precipitate as hydroxides, carbonates, phosphates, sulphates or sulphides. In addition to the many organic complexing ligands that may bind metals in solution, Kunz and Jardim (2000) found that inorganic species such as carbonate and bicarbonate may also form soluble metal complexes. Solubility product constants, which are used to relate the solubility of the metal complexes, can be found in most chemistry textbooks. However, there are considerable variations in the figures quoted from different sources. Stumm and Morgan (1996) outline the various reasons for these discrepancies:

1. "The formation of a sparingly soluble phase and its equilibrium with the solution is a more complicated process than equilibration reactions in a homogenous solution;
2. The composition and properties, that is, the reactivity, of the solids vary from different modifications (disordered) forms of the same modifications;
3. Species influencing the solubility equilibrium (e.g. species formed by hydrolysis, ion-pair or complex formation) have been overlooked in defining the solubility product."

Also, each solubility product relates to one single metal species. It can rarely be assumed that the solid phase is of a single species, or even of a consistent composition. Another limitation on the theoretical solubility constants is the formation of metal complexes with soluble ligands, which may inhibit metal precipitation. Also, co-precipitation or adsorption of metals with other precipitates or suspended solids may result in residual metal concentration less than the theoretical predicted values. Thus, due to the variable and complex nature of wastewaters and the limitations on the use of theoretical solubility constants, their direct application may not be appropriate. According to Eilbeck and Mattock (1987), "the most that can be said for hydroxide solubility product data (and to some extent those of oxides as well) is that they give a semi-quantative indication as to the level of metal ion concentrations that may apply in given pH conditions."

In terms of the predictive model being developed in this project, solubility limits are needed to calculate the soluble metal concentration and predict the metal removal due to precipitation. Due to inherent limitations on their application to wastewaters, theoretical solubility products, which might otherwise be used to derive solubility limits are not appropriate. Thus batch tests experiments, which test the effect of related factors, such as TSS (total suspended solids), VSS (volatile suspended solids), SOC (soluble organic carbon) and pH on the solubility limits in different process liquids, prove to be the most useful.

4.3.3.2 Adsorption Coefficients

Section 4.2 above stressed the fact that the value of the adsorption coefficient is dependent on the conditions under which it was derived. Additionally, developing relationships between the values of the adsorption coefficient and the factors that affect

it will increase the reliability of this method for predicting the distribution of metals in wastewaters. However, it was noted that the experimental procedure employed in determining the adsorption/ partitioning coefficient varied in the literature; batch tests, pilot plant tests or field tests were used. Monteith et al (1993) attempted to derive the coefficients using batch tests and pilot plant experiments. The results show that there are significant differences between the values of the coefficients derived using the different methods. As the pilot plant-derived values were verified against field data, this could mean that the batch tests are not as reliable as pilot plant tests and consequently using field data would be even more reliable.

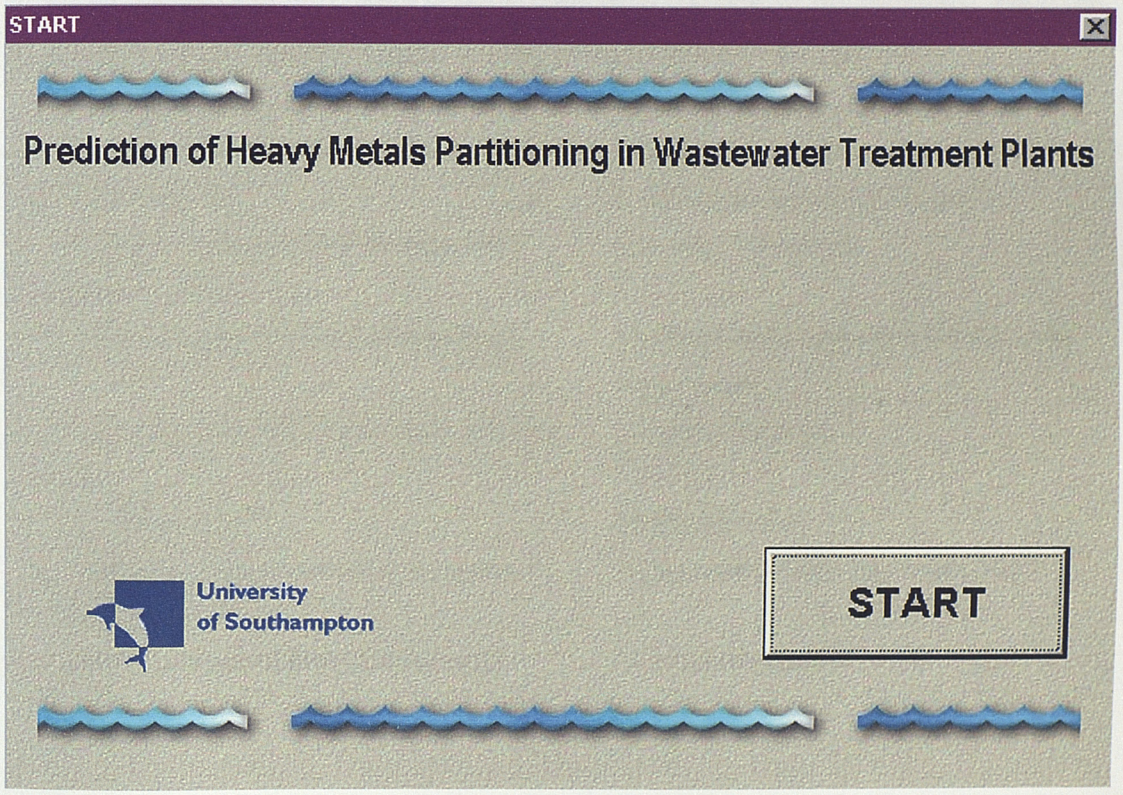
The work by Parker et al (1994) was a continuation of the studies conducted by Monteith et al (1993). They experimentally-derived partitioning coefficients for input into their model. But when the field verification was carried out, many of the observed values were significantly different from the predicted ones. The results of their study suggests that the model should be calibrated for each metal at a given wastewater treatment plant. They suggested that calibration should be performed by regression of the model predictions against data measured at the plant influent, the primary clarifier effluent and the final clarifier effluent.

An alternative to calibrating the model at each plant using field data would be to obtain sufficient field data to enable regression analysis to be carried out correlating the different metal fractions and factors affecting metal partitioning. This in turn would require variations in the metal concentrations to allow a regression analysis to be conducted. However, field data collected at Millbrook wastewater treatment plant in July-August 1999 indicated that the concentrations of the metals being studied are very low. Therefore it would be too difficult to obtain data sufficient to perform regression analysis. However, the results of Wang et al (1999) indicated that sludge activity and aeration condition, which are the most important factors influencing organic matter degradation in wastewater treatment processes, do not significantly affect metal uptake under the experimental conditions used in their study. They concluded that it is possible to determine metal uptake characteristics using batch metal uptake experiments in the laboratory and that results from batch experiments can be readily applied to wastewater treatment processes in the field.

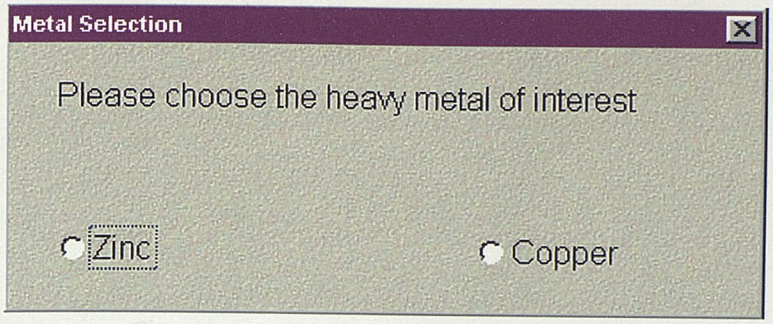
4.4 Computer Program and User-Interface

Building on from the Solids Mass Balance program developed using the Visual Basic editor in **Microsoft™ Excel 97**, a program was compiled for the metals predictive model. It consists of a userform for input of the required data, modules for calculating the partitioning of metals in the plant and output forms for presentation of the calculated values. The full code for the program is given in Appendix B. In addition a trial run-through of the model calculations can found in Appendix E.

A start page introduces the program:



After pressing the "START" button, the user is asked to select the metal to be modelled. In this case, the only metals that can be modelled are Zn and Cu.



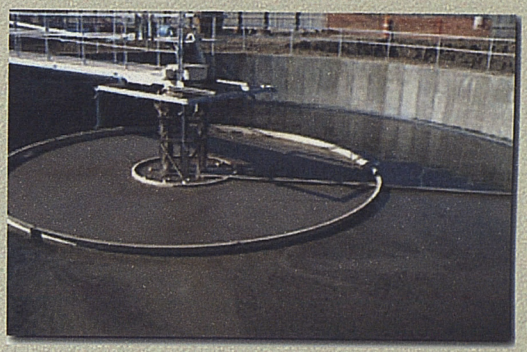
A userform facilitates the input of data required at the start of the program. Each tab represents a main treatment process. The inputs needed at the start are:

1. Raw influent flow (l/hr)
2. Raw influent total solids (mg/l)
3. Raw influent volatile solids (mg/l)
4. Raw influent metal concentration (mg/l)
5. Raw Sewage pH
6. Primary sludge total solids (mg/l)
7. Efficiency of solids removal during primary sedimentation (0-1)
8. Primary Effluent pH
9. Soluble substrate of primary effluent (mg/l)
10. Mixed liquor total solids initially in the reactor (mg/l)
11. Mixed liquor volatile solids initially in reactor (mg/l)
12. Mixed liquor pH
13. Net sludge yield
14. Recycle ratio
15. Efficiency of solids removal in secondary sedimentation (0-1)
16. Secondary sludge total solids (mg/l)
17. Soluble substrate of final effluent (mg/l)
18. Final effluent pH

Inputs Zn

Inputs | Raw Sewage | Primary Treatment | Aeration | Secondary Sedimentation

Please enter values for the following parameters:



Please note that the unit for flows is l/hr

and for solids and metals concentrations mg/l

Inputs Zn

Inputs | Raw Sewage | Primary Treatment | Aeration | Secondary Sedimentation

Raw sewage flow

Raw sewage total solids

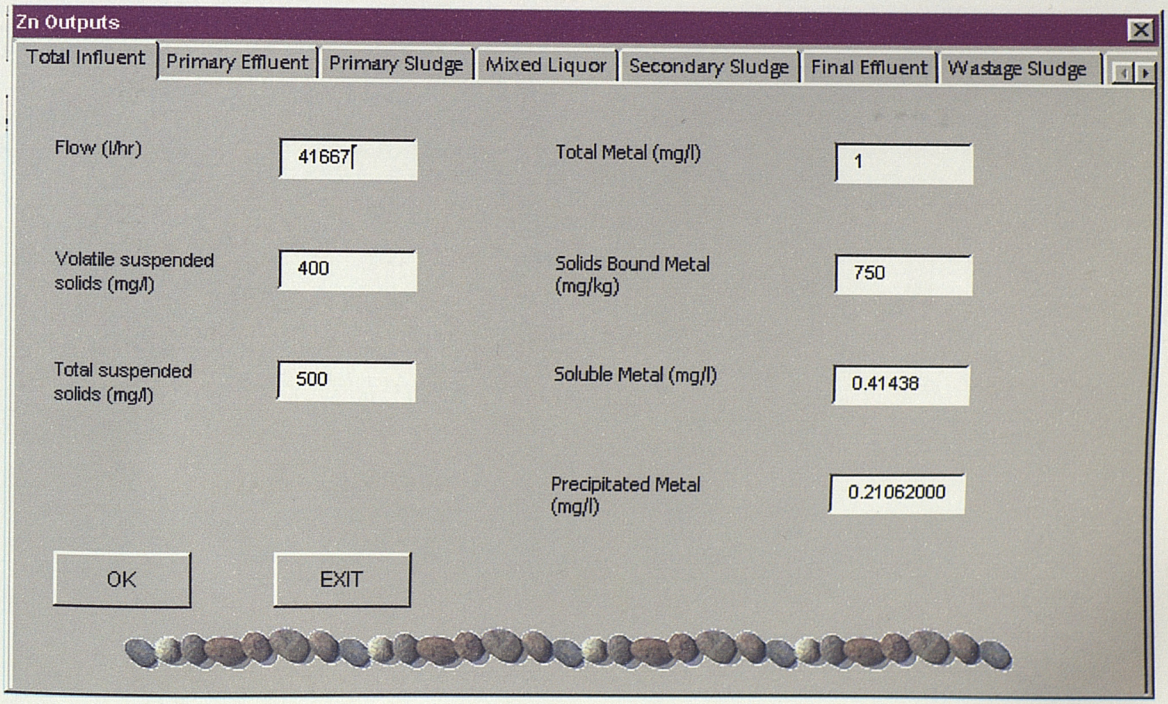
Raw sewage volatile solids

Raw sewage metal concentration

Raw sewage pH

Two modules, one for each metal, are compiled to calculate the partitioning of the metals into soluble, sorbed and precipitated fractions during wastewater treatment using the model equations developed in section 4.3.2 above. For the calculation of the model coefficients, correlation equations, relating the adsorption coefficient (Kp) and the pH and total solids concentration; solubility limit (sol) and pH; and adsorption capacity (Ka) are required and will be derived from the experiments carried out as part of the model calibration in chapter 5.

The calculated values for both the partitioning of solids and metals are presented on output forms, where each tab represents a process stream (raw sewage, primary effluent, primary sludge, mixed liquor, final effluent, secondary sludge, wastage sludge and recycled sludge).



4.5 Comparison with state of the art model

The most recent model developed to predict the fate and transport of heavy metals in wastewater treatment was developed by a research team at the University of Delaware, USA (Huang et al 2000). Their investigations adopted a "multi-pronged approach" by carrying out both laboratory experiments and field studies.

The objective of the initial field studies, carried out at four wastewater treatment plants, was to characterise the wastewater chemistry (pH, alkalinity, major cations and anions) and to determine the characteristics of the dissolved organic matter (DOM) and the sludge particulates. The conclusions of these studies state that wastewater samples containing less than 5 g/l suspended solids have similar characteristics, independent of sampling type, date or location. They also stated that these parameters, with the exception of pH, were linearly correlated to the concentration of suspended solids. Their results also showed no correlation between the wastewater characteristics and heavy metal distribution. Yet, they do not give any explanations for their findings nor do they give information on the type of wastewater treated at the treatment plants that they investigated. Considerable variation in the composition of raw sewage in terms of silt content, and concentrations of organic and inorganic ligands would be expected, especially if industrial wastewaters are also treated at the wastewater treatment plant. Furthermore the correlations between the wastewater parameters and the suspended solids concentrations were not very convincing, as there was considerable scatter on the plots produced.

The next stage of the study covered the equilibrium aspects of metal interaction with sludge particulates. A general model equation, based on chemical stability constants was developed. This took the form of:

$$R = \left[1 + \frac{M_D \left\{ 1 + \alpha_H K_S \dfrac{\alpha_a K_L (M_D - L_T) - 1 + \sqrt{[\alpha_a K_L (M_D - L_T) - 1]^2 + 4\alpha_a K_L M_D}}{2\alpha_a K_L} \right\}}{\alpha_H K_S \Gamma_m SS \dfrac{\alpha_a K_L (M_D - L_T) - 1 + \sqrt{[\alpha_a K_L (M_D - L_T) - 1]^2 + 4\alpha_a K_L M_D}}{2\alpha_a K_L}} \right]^{-1}$$

Where,

R = percentage of metal uptake;

M_D = total dissolved metal concentration;

$\alpha_H = K_H/([H^+]+K_H)$;

K_H = acidity constant of surface site = $([H^+]\{SO^-\})/\{SOH\}$;

SO^- = deprotonated surface site;

SOH = protonated surface site;

$\alpha_a = K_a/([H^+]+K_a)$;

K_a = acidity constant of DOM = $([H^+][L^-])/[HL]$;

L^- = deprotoanted acid site in DOM;

HL = protonated acid site in DOM;

K_S = stability constant of metal-sludge complex = $\{SOM^+\}/([M^{2+}]\{SO^-\})$;

M^{2+} = free metal ion;

SOM^+ = metal-surface site complex;

K_L = stability constant of metal-DOM complex = $[ML^+]/([M^{2+}][L^-]$;

ML^+ = metal-DOM complex

L_T = total dissolved ligands;

Γ_m = maximum adsorption density.

Note: [ ] denotes moles/litre; { } denotes grams/litre

In addition, simplified model equations were also developed for special cases, for example, where metal binding sites in the DOM is much lower than that in the sludge particulates or if the metal loading is outside the linear adsorption range or linear metal-DOM complexation range. However, it is clear that this model does not take into account removal of metals through precipitation.

Batch experiments were performed under various suspended solids and pH conditions, using a continuously mixed continuous flow reactor. The data obtained was plotted as graphs of pH vs. metal uptake (%) and was fit using the general and simplified models to enable the stability constants to be determined. The researchers made an assumption that the COD concentration is a function of pH. Consequently the term related to COD concentration in the general equation was replaced by an empirically-derived relationship between the two parameters. While it is agreed that the COD concentration may be influenced by pH, due to the dissolution of organic matter at alkaline pH values, it is questionable that the concentration of COD is entirely dependent on the pH.

It was found that the results of the batch experiments carried out on sludge samples collected from different wastewater treatment plants yielded similar values for the stability constants. Yet it was observed that these experiments were not conducted under the same suspended solids or metal added concentrations.

They concluded that metal type is the most important factor determining the magnitude of the stability constants and that the sludge type, location and sampling time are relatively unimportant. Furthermore, they state that since pH field conditions are rarely above pH 8.0, the dissolved organic matter effect on metal uptake can be neglected and the generalised K_s stability constant derived as part of their study can be applied to the field. This stability constant is used for all wastewater treatment processes.

As can be seen, the complex form of the general model originally developed by this study (Huang et al 2000) has been greatly diminished by the use of wide-ranging generalisations. Moreover, the authors do not provide any discussion of the limitations of the model. Therefore, it can be concluded that this model is of limited use in

practice. It relies on the use of a single stability constant, which was derived and tested under limited conditions and using unsubstantiated assumptions.

The approach utilised in developing the metals fate model in this Ph.D. project was based on a fundamental understanding of the physico-chemical processes influencing metal removal through adsorption and precipitation reactions. It also provides a practical means of calibrating the model to produce accurate predictions for the fate of heavy metals in wastewater treatment systems.

CHAPTER FIVE

MODEL CALIBRATION

5.1 Preparations for experiments and analysis

5.1.1 Preparation of Glassware and Standards

Experimental design and chemical analyses were carried out according to Standard Methods (APHA et al 1995) and took into account the recommendations of Hunt and Wilson (1986). All apparatus used (flasks, vials, tests tubes, pipette tips, etc.) was soaked in 10% nitric acid and subsequently rinsed with purified water before use. Water for the final rinsing of glassware was provided using the Elix® Water Purification system (Millipore Corporation, MA, USA) while the high purity water used in the preparation of blanks and other standard solutions was obtained from a Milli-Q® Ultra Pure Water system (Millipore Corporation, MA, USA). Metal solutions were prepared as stock solutions of 1000 mg/l in volumetric flasks using Analar grade sulphate salts (BDH Ltd., Poole, England) and acidified to less than pH 2 with HNO_3 to maintain the stability of the metals. The test vessels were either made of borosilicate glass (solubility tests) or polyethylene or polypropylene (adsorption tests), as recommended in Standard Methods (APHA et al 1995).

5.1.2 Collection and Storage of Samples

Samples of wastewater or sludge were obtained from Millbrook Wastewater Treatment Plant (WWTP) or Portswood WWTP, both in Southampton, on the day of the experiment. The wastewater samples were obtained by immersing the sample collection container at the sampling point and rinsing the sample container with the sample before being filled. The collected samples were stored at 4°C until the commencement of the experiment. Samples of activated sludge were also aerated until the start of the experiment.

After the development of a suitable methodology for the solubility limit and adsorption experiments, the samples were subsequently only collected from Portswood WWTP. These were subdivided into aliquots for each experiment and frozen until needed. This procedure minimised any variability in the composition of the samples used for experimentation.

5.1.3 Routine Analyses

Total Suspended Solids (TSS):

As per Standard Methods (APHA et al 1995), TSS concentrations were determined by filtering a 100ml homogenised sample through a pre-dried and pre-weighed Whatman™ GF/C filter. After filtration, the filter was placed in an oven (ELE International Ltd., England) set at 105°C until constant weight was obtained.

Volatile Suspended Solids (VSS):

The filters used for the TSS determination were ignited in a furnace (Thermolyne 62700, Iowa , USA) at 550°C for 20 minutes, cooled, re-weighed and the weight lost on ignition taken to represent the volatile solids fraction. This thus offers a rough approximation of the organic matter present in the solids fraction of wastewater (APHA et al 1995).

Filtration for soluble metal analysis:

It was found during the course of the tests that the filtered samples contained more zinc than the unfiltered samples. It was suspected that the filter paper being used (Whatman™ GF/C) was contributing to the increase in zinc in the filtered samples. Tests carried out on the filter paper did indeed show that the filter paper contained a considerable amount of zinc (up to 0.8 mg/l per filter washed through with 100 ml of MilliQ water). When the technical assistance team at Whatman Corporation, USA was contacted to inquire about this, they revealed that zinc oxide was in fact a component of the GF/C filter paper and suggested that another type of filter such as the hardened ashless cellulose paper filters was used. However these have a pore size of 8 μm and thus would not be suited to soluble metal analysis. Hence, it was decided to use Millipore HA 0.45 μm membrane filters for soluble metal analysis.

Acid digestion for metal extraction:

For the determination of non-soluble or solids-bound metal, a modification of the UK Standing Committee of Analysts (DoE 1986) standard method for the determination of acid soluble metals in sewage sludge by atomic absorption spectrophotometry following a digestion with a hydrochloric and nitric acid mixture was used. According to Method C, 0.5g of dried sludge is digested with 6ml of hydrochloric acid, 2 ml of

nitric acid and 6ml of water in a 50 ml calibrated borosilicate glass boiling tube heated on a temperature controlled heating mantle for approximately 1.5 hours. According to the method guide, this does not determine the total metal content. Only some 70-90% of the total contents of Cd, Cr, Cu, Fe, Pb, Mn and Zn are extracted from uncontaminated top soils although an even greater proportion is extractable from sludge contaminated soils (DoE 1986).

However, as the Techne block digester available in the laboratory was only suitable for 16mm ϕ tubes, which hold a maximum volume of 10 ml, the method was altered to allow the digestion to take place in these smaller size tubes. The final modified method used a 0.1g sample of the dried sludge to which 1.2 ml of hydrochloric acid, 0.4 ml nitric acid and 1.2 ml water were added. The digestion was carried out a temperature of 120°C for approximately 4 hours until a clear solution was obtained.

5.1.4 Heavy Metal Analysis

Analysis using Atomic Absorption Spectrophotometery (AAS)

Analysis of the soluble metal samples was carried out using an atomic absorption spectrophotomer (SpectraAA-200, Varian Ltd. Australia), with an air-acetylene flame and hollow cathode lamps for Cu and Zn (Varian Ltd. Australia). The machine has a detection range of 0.01-2 mg/l for Zn and 0.03-10 mg/l for Cu.

Analysis using Ion Chromatography (IC)

Ion chromatography (Dionex Corp., DX-500 system, Sunnyvale, CA, USA), using the transition metals analytical column (IonPac CS5A), was also used for metals analysis. Using this method, transition metals are separated as both cationic and anionic complexes using an oxalate or PDCA-based eluents obtained from Dionex Corp. The metals are detected by measuring the absorbance at 530nm of the complex formed with the post-column PAR reagent (Dionex Corp.). Other operating conditions included using an injected sample volume of 50µl, an eluent flowrate of 1.2 ml/min and reagent flowrate of 0.7 ml/min.

In the initial analysis trials carried out using the IC, it was observed that in the chromatograms, there was an initial peak, dip and peak at the beginning of the analysis

of each sample. This initial dip affected the integration of the peaks by lowering the baseline. A test was conducted to determine the cause of this peak-dip-peak behaviour (See figure 5.1).

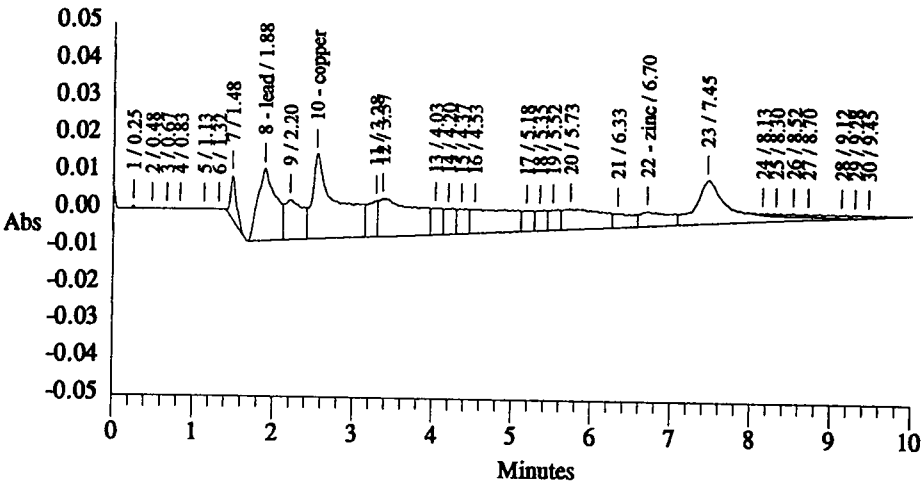


Figure 5.1: *Sample IC chromatogram showing the problematic drop in the baseline*

Standards of single metals (unacidified) were run in addition to a sample with only comprising MilliQ water and a sample with only 2% HNO_3. It was found that all the samples produced a small dip in the beginning, but the 2%HNO_3 caused the problematic peak and dip behaviour. Another test was run to determine if using other acids (2% of sulphuric acid, acetic acid and hydrochloric acid) also produced the same behaviour. The chromatograms produced showed that hydrochloric acid produced the most level baseline. Therefore subsequently, a final concentration of 2% HCl was used in the preservation of the samples and standards.

Comparison of the AAS analysis and the IC analysis showed that both analytical techniques yielded very similar results, as shown in figure C.162 (in Appendix C). The regression equation obtained is: $y=0.9996x$ ($R^2=0.9979$), where y = IC reading (mg/l) and x = AAS reading (mg/l).

5.1.5 Carbon Analysis

Analyses of the soluble organic carbon concentrations in the experimental samples were carried out using a high temperature catalytic oxidation analyser (Dohrmann DC-190, Ohio, USA). The samples were prepared for analysis by membrane filtration and

acidified with HCl. A 100 mg/l carbon standard was prepared from glycine. Two readings for each sample were taken.

5.1.6 Quality Control of Metals Analysis

Experimental and analytical errors due to operating procedures were minimised by the use of automatic finpippettes (relative error 0.5-0.65%) for all sample and reagent transfers. Duplicate samples were analysed on the AAS and the IC and the relative standard deviations calculated. Standards were also analysed during the analysis of the samples, at intervals of one standard per 10 samples, to ensure that the machines were reading with precision throughout the analysis. The mean results and standard deviations and standard errors of the analysis were calculated. The standard error of the analysis, taking into account random and systematic errors is ±3% unless otherwise stated. All results are expressed as mg/l.

5.2 Equilibrium Time Experiments

5.2.1 Cu Uptake in Primary Sedimentation

To simulate Cu uptake during primary sedimentation, a sample of primary sludge was obtained from Millbrook WWTP. Five hundred millilitre flasks were used to test samples made up to a total volume of 250ml by adding various proportions of the sludge, metal solution and MilliQ water. For this experiment, three solids concentrations representative of the solids concentrations likely to be encountered during primary sedimentation were made up. To each flask, a Cu^{2+} spike was added to ensure that the Cu^{2+} concentration in the flask was at least 2 mg/l. The contents of the flasks were then mixed on an orbital shaker (Lab-Line Instruments, Model.3521, Illinois, USA) and 1.5ml samples were taken from each flask at 5 minute intervals for the first half hour and then at half hour intervals for the next two and a half hours. The experiment was carried out at approximately 20°C. These samples were centrifuged (Eppendorf, 5417C) and the supernatant diluted and analysed on the AAS. It appears from figure 5.2 that the equilibrium time for metal uptake during primary sedimentation was approximately 90 minutes.

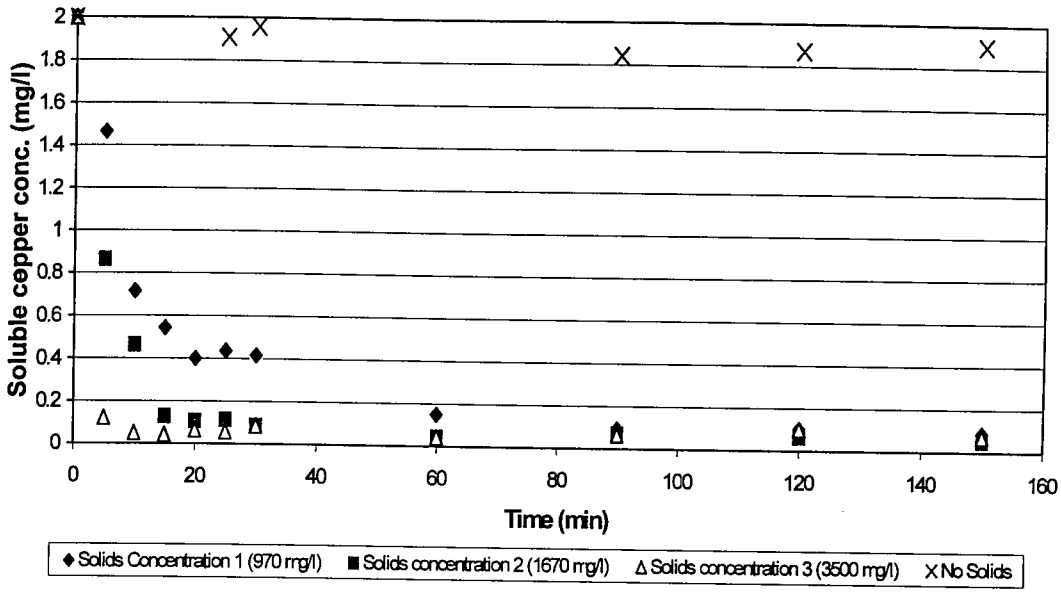


Figure 5.2: *Soluble Copper concentration in primary sedimentation as a function of time showing the time taken to reach equilibrium*

5.2.2 Cu Uptake in Activated Sludge Treatment

The same experimental procedure was employed as in section 5.2.1. Portions of activated sludge (obtained from Millbrook WWTP) were resuspended in distilled water to simulate mixed liquor. To this, a copper solution was added to obtain a final concentration of 5 mg/l in the test vessels. The flasks were placed on the orbital shaker and 1.5ml samples taken at 5 minute intervals for the first half an hour and subsequently at half hour intervals for the next two and a half hours. The samples were centrifuged at 20800 g and the supernatant diluted and analysed by AAS.

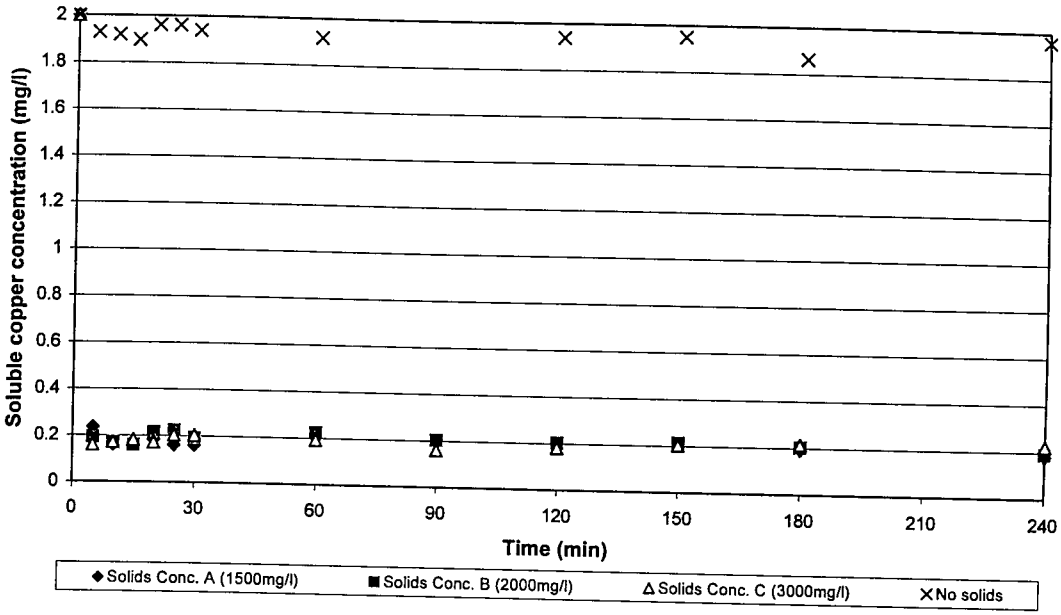


Figure 5.3: *Soluble Copper concentration in activated sludge as a function of time showing the time taken to reach equilibrium*

The results show that after 5 minutes the metal was removed from solution to a baseline value of 0.2mg/l. This agrees with the findings of other researchers. Cheng et al (1975) found that under aerobic conditions metal uptake by the biomass is characterised by a rapid phase of 3 to 10 minutes from the start of the experiment. Nelson et al (1981), on the other hand found that equilibrium times in the activated sludge process were reached generally in the 5 minute to 1 hour range from the start of the experiment. Wang et al (1999) also found that the metal uptake process was rapid and that equilibrium conditions are reached after one hour. It was decided to use an equilibrium time of 90 minutes for all further adsorption equilibrium experiments on biological material eventhough equilibrium could be attained more rapidly than this.

5.3 Solubility Limit Experiments

5.3.1 Introduction

The objective of these experiments was to investigate the effect of the concentration of suspended solids, and most importantly pH, on the solubility limits of metals in the four main process streams in wastewater treatment, namely raw sewage, primary effluent, mixed liquor and final effluent.

Previous attempts to determine the solubility limit of metals in wastewaters were undertaken by Monteith et al (1993). They applied a single dose of a solution containing seven metals (Al, Cd, Cr, Cu, Ni, Pb, Zn) to filtered and whole samples of primary and final effluent. The solubility tests were run over the pH range 6.0-8.0, at increments of 0.5 pH units. It can be seen that this methodology does not take into account competition between metals for adsorption sites. This is important since competition between the different metals for complexation with the finite concentration of soluble ligands would be expected (Buffle 1990). Therefore, experiments using single metals would be more appropriate. Also, adding one single dose of metals and measuring the soluble metal left after equilibrium time is reached does not necessarily give an indication of whether or not the solubility limit had been exceeded. Patterson et al (1983) carried out single metal experiments, however their methodology involved continually adding metal to a pH-adjusted test liquid until a visible precipitate formed and stayed for one minute. This however does not appear to be a robust and scientifically sound method, since a precipitate may not always be immediately visible, especially in wastewaters with high solids concentrations. Therefore the methodology for determining solubility limits in this research was designed to obtain a more fundamental picture of the behaviour of soluble metal under various conditions. The methodology of the experiment was continually assessed and improved as results dictated.

5.3.2 Trials and Problems

Experiment to determine the solubility of Zn^{2+} in Raw Sewage Using Different Solids Concentrations

Three solids concentrations were tested in this experiment and at each solids concentration, 6 different pH levels were studied (pH 5.5-8.0 in increments of 0.5 pH units). The three different solids concentrations were achieved by diluting or concentrating the original sample. The pH was adjusted by addition of 10% HNO_3 or IM NaOH. Addition of the stock metal solution resulted in a final concentration of 0.5 mg/l of zinc ion solution being added to each flask. The flasks were placed on the orbital shaker at 20°C for 90 minutes for equilibration. After equilibration, 1.5 ml samples were taken from each flask. These samples were then centrifuged for 5 minutes at a speed of 20800 g. After centrifuging, the supernatants were decanted into sample vials, diluted and preserved by acidification to a pH less than 2. After each

equilibriation period, a further spike, which resulted in another 0.5mg/l of metal was added to the flask. In total, four metal spikes were added to each flask, resulting in a cumulative metal addition of 2 mg/l.

pH Adjustment

The original pH of the raw sewage was around 7.8. After the addition of the acidified stock metal solution, the pH of the sample was found to decrease considerably. In order to achieve the desired pH values for experimentation, 1M NaOH was then added in varying amounts to readjust the pH to values between pH 5.5 and 8.5. It was observed that after pH adjustment with 1M NaOH additions, and shaking for the equilibrium time (90 minutes), the pH in the flask had changed from the original adjusted value. Flasks with pH adjusted to less than pH 8.0 had their pH values increased whilst those with pH adjusted to pH greater than 8.0 decreased in value, with both sets attaining values close to 8.3.

It was hypothesised that this phenomenon was due to the carbon dioxide escaping from the flasks during shaking, leading to an increase in pH. When trial experiments were conducted with flasks sealed with parafilm, the increase in the pH was still observed. This increase was less than occurred when the flasks were not sealed. Patterson et al (1983) also noted this phenomenon. In their studies, they had sealed the test flasks with parafilm prior to placing them on the shaker, the pH of the samples were noted to shift with time towards a pH of value of 8.0. They concluded that the test liquids (tap water, raw sewage and mixed liquor) were well buffered, probably by the carbonate-bicarbonate system. It has been shown that the most significant buffering system in natural waters is due to carbon dioxide and its related species (Droste 1997). Quek et al (1998) also noted that reactions, which occurred during the adsorption process, caused some slight increases in the solution pH. Other researchers have noted that it is very difficult to adjust and maintain pH under experimental conditions (Shi et al 1996). Nelson et al (1981) stated that in their experiments, pH adjustment was achieved by trial and error additions. Furthermore, the use of buffer solutions to adjust the pH to predefined values introduces complications for metal speciation studies. Buffers, such as citrate, or polydentate ligands forming amino acids, may form complexes with metal ions that can reduce the effective concentration of these ions in solution (Beynon and Easterby 1996).

pH adjustment was complicated further by the fact that sequential addition of acidified stock metal solutions were made to each flask in these studies, thus requiring pH readjustment with 1M NaOH additions after each metal addition. Furthermore, the volume of NaOH required to achieve a certain pH was different each time. Therefore the pH adjustment and readjustment process became labour intensive.

5.3.3 New Procedure for solubility limit experiments

Due to the problems encountered with pH adjustment, a new approach to determine the solubility limits of metals was developed. Instead of using a single flask (for each pH value), to which sequential metal solution additions were made, it was decided to use one test vessel for each metal concentration added. Each test vessel would be set at the required pH value by adding a known amount of 1M NaOH, which had been determined by titration experiments to give the required pH. The set-up of the experiment is shown schematically in figure 5.4.

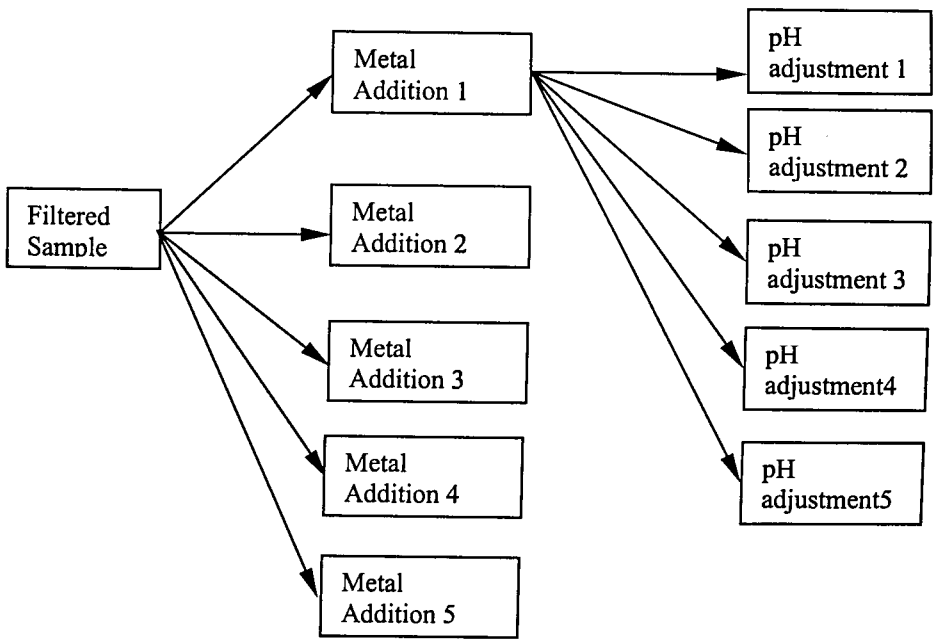
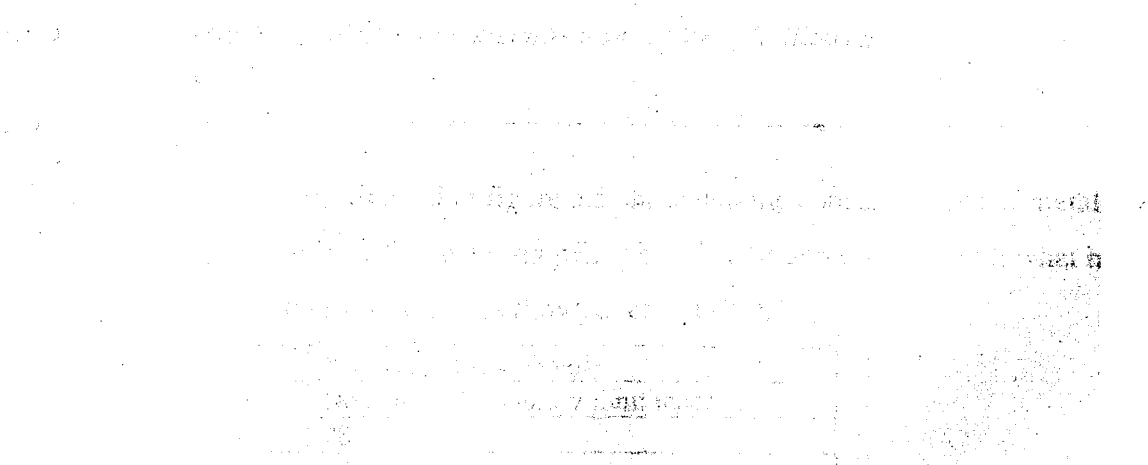


Figure 5.4: *Schematic for the set-up of the solubility limit batch tests*

Since this procedure resulted in a much greater number of test vessels being used (25), a decision was made to use test tubes (20 ml volume) instead of flasks. The test tubes were made up to constant volume ± 1%. The volume of filtered wastewater sample used in all test tubes was 9 ml. To obtain a required metal added concentration of 10mg/l, 0.1 ml of the 1000 mg/l metal stock solution was added with 0.9 ml of MilliQ

water. The proportion of metal stock solution to MilliQ water added was adjusted to obtain the other metal added concentration required. Therefore to obtain a metal added concentration of 20 mg/l, the volume of metal stock solution used was increased to 0.2 ml and the volume of MilliQ water used decreased to 0.8 ml. The pH adjustment was accomplished by additions of 1M NaOH ranging from 5 μl to 85 μl to obtain the required pH variation. Mixing of the contents of the test tubes was accomplished by placing them on a test tube rack, on an orbital shaker. After shaking for 90 minutes, 0.25 ml samples were taken from each test tube, placed in sample vials and diluted to 5 ml with 2% HCl for soluble metal analysis. The final pH was measured with the remaining contents of the test tubes.

This procedure was used to carry out the solubility limit experiments for Zn^{2+}, Cu^{2+} and Pb^{2+} in filtered raw sewage and final effluent. It may be assumed that the main difference between filtered samples of raw sewage, primary effluent and mixed liquor would be the concentration of soluble organic ligands; soluble organics would have been removed in the final effluent.



5.3.4 Results

Zn in Raw Sewage

Two experiments were conducted on the solubility of Zn^{2+} in raw sewage. In the first experiment, metal additions of 10, 20 30, 40 and 50 mg/l were added. Each group of metal addition consisted of 5 test tubes, with all the test tubes in that group receiving the same metal addition, but different NaOH additions to result in 5 different pH adjustments. After the 90 minutes equilibration period, the final pH values were in the range of pH 6.5-9.0. In the second experiment, the metal additions were 20, 30, 40, 50, 60 mg/l and the resultant pH values were in the range of pH 7.0-9.0. The results from both experiments were combined as shown in figure 5.5.

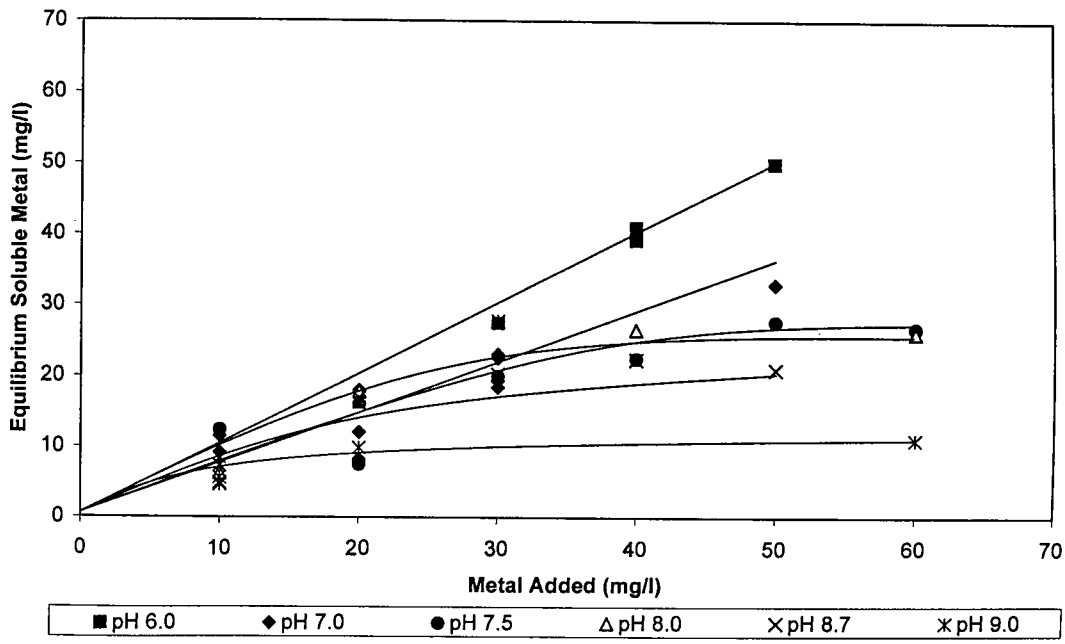


Figure 5.5: *Equilibrium concentrations of Zn^{2+} in filtered raw sewage at different pH values*

The trendlines represented in figure 5.5 show that the concentrations of metal in solution decreased with increasing pH. This observation concurs with what has been observed by other investigators (Sawyer et al 1994).

pH	Solubility Limit (mg/l)
6.0 and 7.0	No apparent solubility limit reached
7.5	28
8.0	25
8.7	22
9.0	12

Cu in Raw Sewage

To determine the solubility of Cu^{2+} in raw sewage, two experiments were also carried out. Both experiments had metal additions of 10, 20, 30, 40 and 50 mg/l and the resultant pH's were within the range of pH 6.3-9. Combining the results of the two experiments, figure 5.6 was obtained.

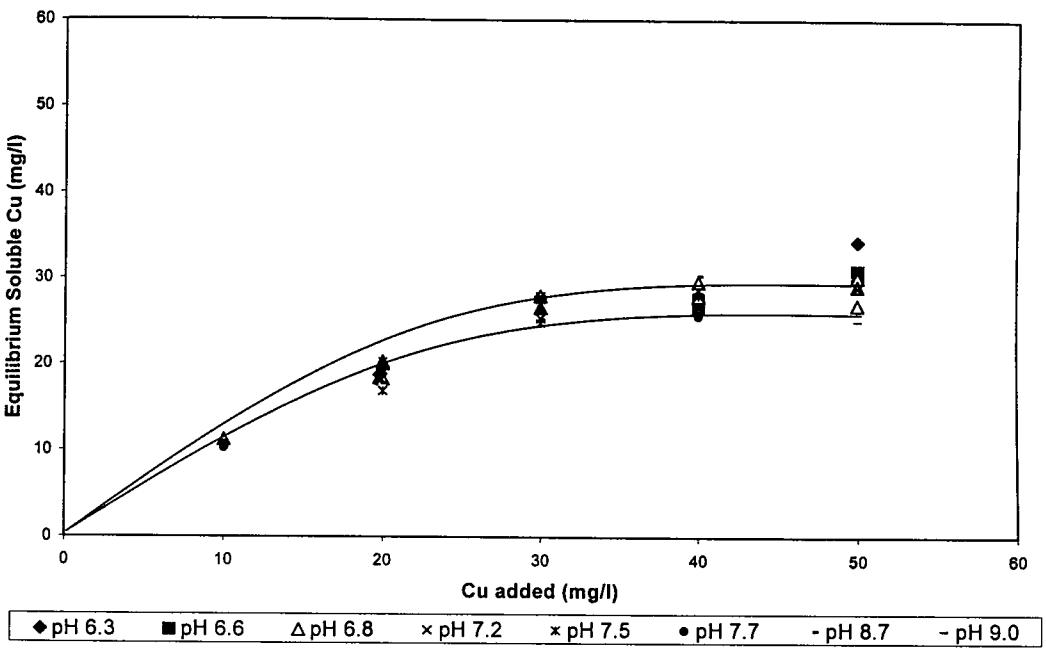


Figure 5.6: *Equilibrium concentrations of Cu^{2+} in filtered raw sewage at different pH values*

It can be observed that the trend for all pH's was the same. The solubility limits obtained were within the range of 25-30 mg/l.

Pb in Raw Sewage

Using the same filtered sample of raw sewage that was used for the copper and zinc solubility limit experiments, and employing the same method, the solubility of Pb^{2+} in raw sewage was tested. The results are shown in figure 5.7.

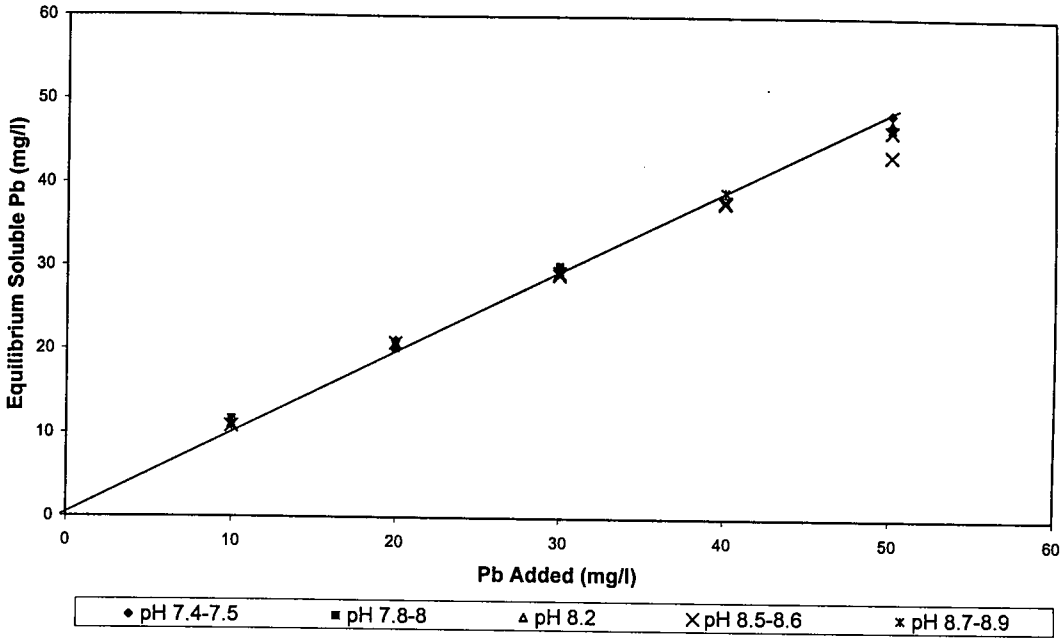


Figure 5.7: *Equilibrium concentrations of Pb^{2+} in filtered raw sewage at different pH values*

It can be seen from the results that over the pH ranges studied (pH 7.5-8.9) and the metal concentrations added (10-50 mg/l), no solubility limits were reached.

Zn, Cu and Pb in Final Effluent

To determine the solubility of the three metals in final effluent, the same procedures were followed. The same filtered sample of final effluent, to which metal was added at 10, 20, 30, 40 and 50 mg/l concentrations, was used in all three experiments. The pH ranges achieved pH 7.4-9.3 (Zn), pH 7.0-8.0 (Cu) and pH 7.3-8.9 (Pb). The results are shown in figures 5.8, 5.9 and 5.10.

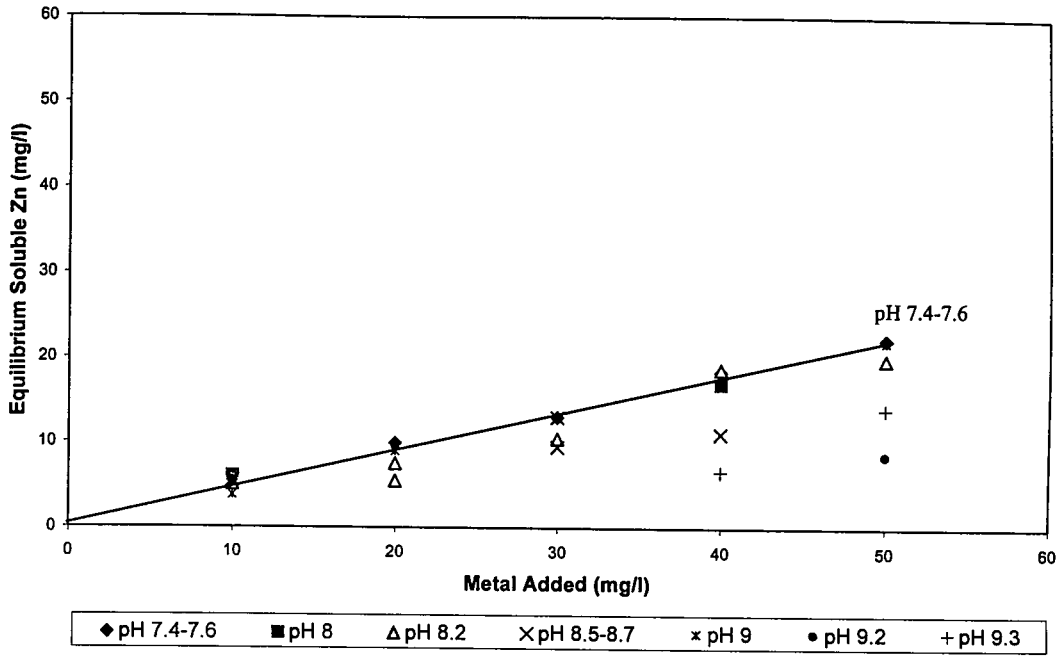


Figure 5.8: *Equilibrium concentrations of soluble Zn^{2+} in filtered final effluent at different pH*

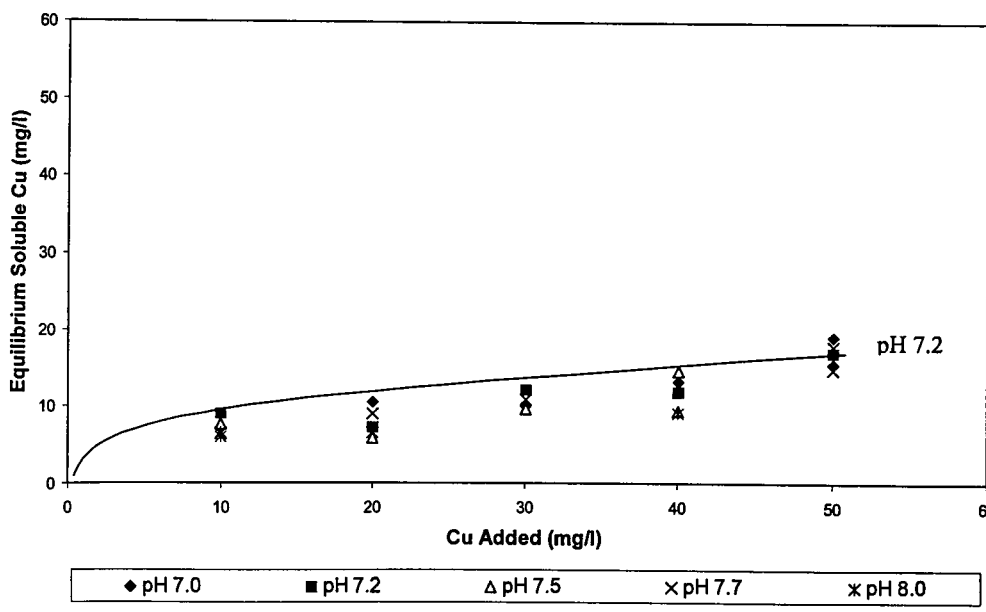


Figure 5.9: *Equilibrium concentrations of soluble Cu^{2+} in filtered final effluent at different pH*

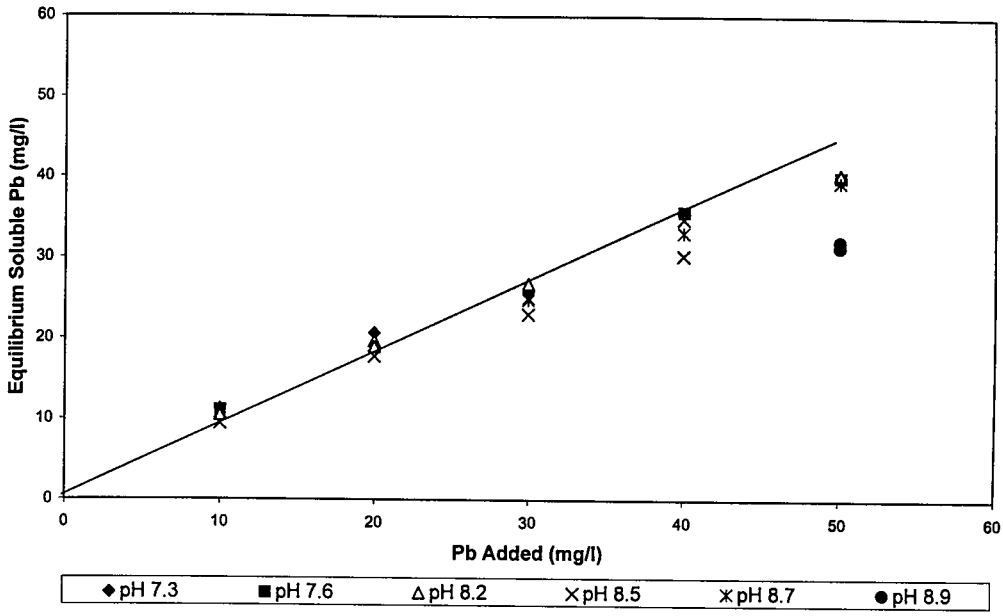


Figure 5.10: *Equilibrium concentrations of soluble Pb^{2+} in filtered final effluent at different pH*

For Zn^{2+} (figure 5.8), the results show that soluble metal concentrations increased with increasing metal addition for all the pH levels studied. However this increase was not proportional. The soluble metal concentrations were not equivalent to the metal concentrations added. This was not expected since the test sample was filtered and theoretically free from any solids, which might remove the metals from solution by sorption. Also the results were obtained from analysis using the AAS, which should theoretically determine all fractions of the metal ions in solution, whether bound to inorganic and organic soluble ligands or as hydrated metal ions. One explanation to account for this uptake of metal from solution could be the presence of colloidal solids, which after binding a proportion of the metals and effectively removing them from solution, had coagulated and settled. While theoretically colloidal solids are not easily settleable, the samples used in these experiments had been frozen and thawed and hence the hydrophobic colloidal solids properties may have been destroyed, leading to their coagulation during the experiment. It has been noted that the use of 0.45-μm membrane filters would not exclude all colloidal matter and furthermore freezing has been identified as leading to the destruction of the colloidal character of solids (Sawyer et al 1994). The measured solubility limits of Zn^{2+} were thus approximately 10 mg/l for

pH 8.5-8.7 and 8 mg/l for pH 9.2-9.3. For Pb^{2+} (figure 5.10) similar observations were made, however, a solubility limit does not appear to have been reached at the pH ranges studied. For Cu^{2+} (figure 5.9), a solubility limit appears to have been reached at approximately 15 mg/l.

Investigation into the effect of different proportions of final effluent on the solubility of Cu^{2+}

This experiment was carried out to determine the effect of the constituents of the final effluent on the solubility of copper. The proportions of final effluent used were 90%, 67.5%, 45% and 22.5% (diluted with MilliQ water). Copper solution was added at concentrations of 10, 20, 30, 40 and 50 mg/l to each set. The resultant pH's were in the range of pH 6-7.5. The results are shown in figure 5.11 and indicate that increasing the percentage of final effluent used decreases the equilibrium soluble metal concentration. This may indicate that the final effluent contains a substance, most likely to be colloidal solids, which binds the metal and then settles. The likelihood of this hypothesis was substantiated by the fact that fine light blue material had settled in the test tubes at high concentrations of added metals.

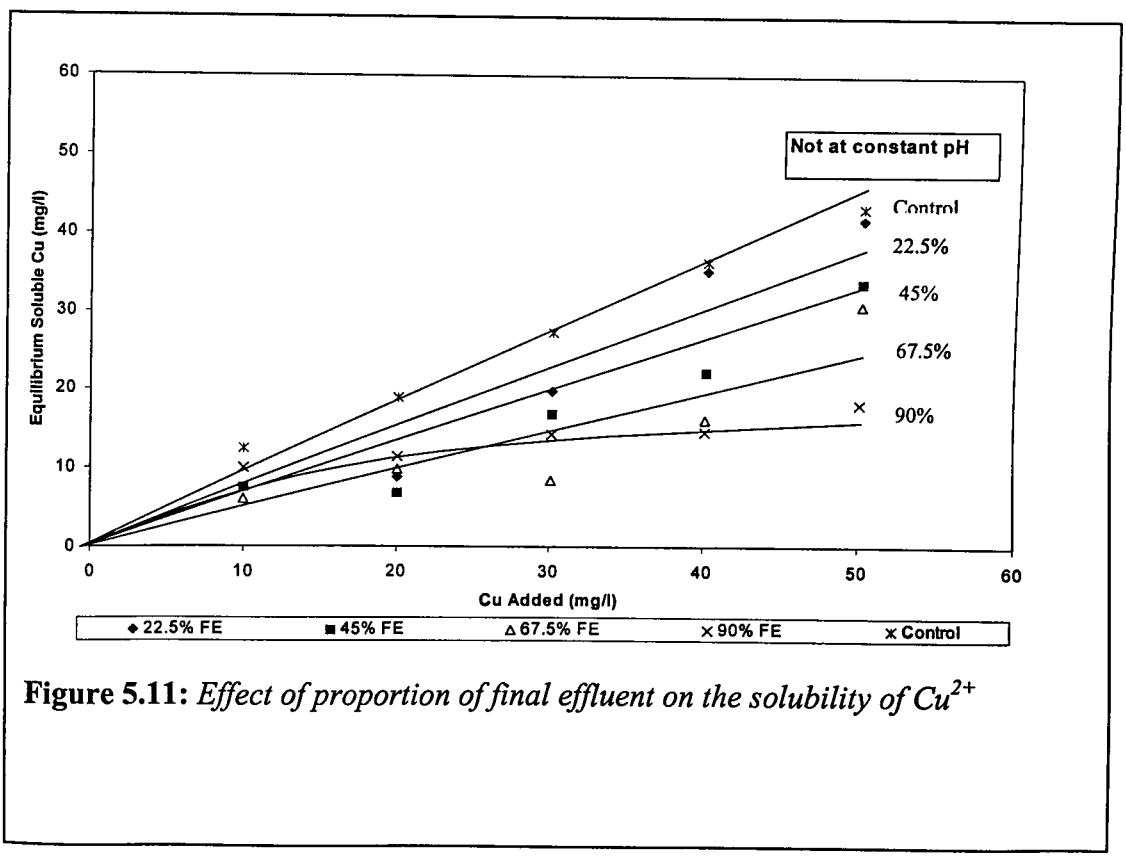


Figure 5.11: *Effect of proportion of final effluent on the solubility of Cu^{2+}*

5.3.5 Discussion

The measured solubility limit values derived from these experiments are considerably higher than the solubility limit values obtained from experiments on distilled water (as shown in figure 5.12).

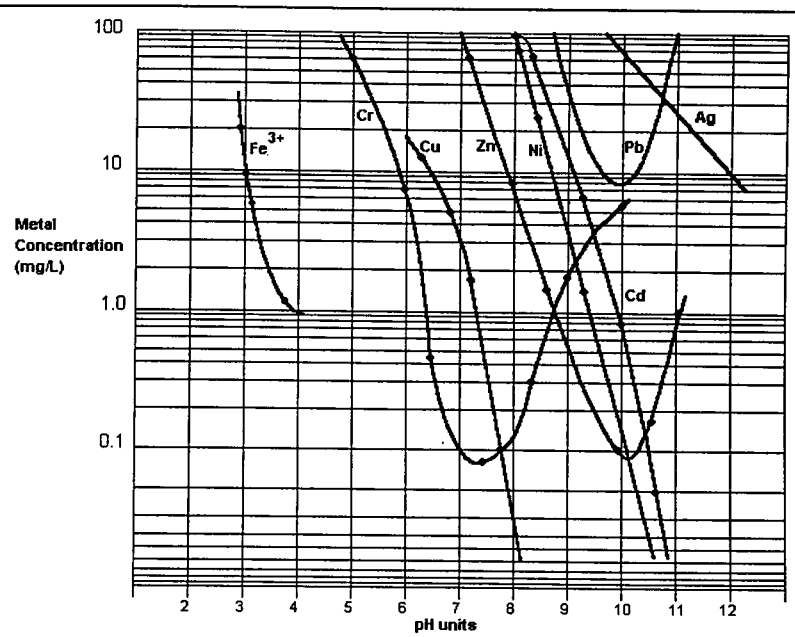


Figure 5.12: *Effect of pH on the solubility of metal hydroxides (after Hoffland Environmental, Inc. 2001)*

The results presented above show that the filtered portion of wastewater is capable of complexing considerable amounts of Zn^{2+}, Cu^{2+} and Pb^{2+}, without saturating the soluble ligands present, as shown by the absence of solubility limits. It has also been shown that final effluent may contain a high concentration of unfilterable colloidal solids. While these solids bind metals and technically remove them from solution, these solids are not settleable under field conditions, therefore metals bound to colloidal solids should be considered as remaining in solution. The experiments show that the methodology developed in this research is easy to carry out and overcomes the problems of pH fluctuations during experimentation. It allows the solubility of metals to be tested over a range of pH values. In this respect, it is an improvement on the methods previously employed in wastewater.

The results of the solubility limit experiments are tabulated in Appendix C (tables C.3-C.9)

5.4 Adsorption Experiments

5.4.1 Objectives

In order to study the uptake or removal of metals from solution by solids in the four process streams of interest, isotherm adsorption experiments were carried out. The main objective of these experiments was to obtain data on the uptake of metals at different metals and solids concentrations to allow adsorption/ partitioning coefficients and adsorption capacities needed for the metals model to be derived. The experiments were also carried out over a range of different pH values to allow a correlation, between the adsorption coefficients and the pH of the system, to be obtained. The experiments were first run for a single metal and then subsequently two metals at the same time, to determine the uptake of the metals under competitive conditions.

5.4.2 Methodology

The adsorption experiments were carried out using a similar set-up to that used for the solubility experiments. Centrifuge tubes of 10ml volume (polyethylene) were used as the test vessels. Centrifuge tubes, as opposed to test tubes, were used in these experiments to allow samples to be centrifuged after the experiment, to obtain the supernatant for soluble metal analysis. Metals were added at concentrations less than the solubility limits previously determined to ensure that no precipitation occurred and to ensure that metal removal from the solution was only due to adsorption onto the solids. All the experiments for each process stream were carried out on the same sample, which had been previously frozen in aliquots for each experiment. Five litre samples of raw sewage, primary effluent, mixed liquor and final effluent were obtained from Portswood sewage works. Each sample was divided into three solids concentrations:

A: original SS;

B: diluted SS (original sample diluted with supernatant of original sample that had been left to settle and MilliQ water, to give 40% dilution); and

C: concentrated SS (original sample left to settle and supernatant decanted off to give 30% concentration, i.e. 130% of original volume).

The only exception to this was the final effluent, which could not be diluted or concentrated using its supernatant because it was not settleable. Each solids concentration was then divided into aliquots sufficient to carry out each experiment.

These were placed in plastic bottles and frozen. For each experiment, a bottle of each solids concentration was defrosted. For raw sewage and final effluent, the same sample that was used for the solubility limit experiments was additionally used for the adsorption experiments.

Table 5.1: *Suspended solids concentrations used in the adsorption experiments*

Process Stream	Sample	Total Suspended Solids (mg/l)
Raw Sewage	*Original*	474
	Diluted	322
	Concentrated	668
Primary Effluent	*Original*	94
	Diluted	86
	Concentrated	125
Mixed Liquor	*Original*	1800
	Diluted	1058
	Concentrated	2500
Final Effluent	*Original*	32
	Diluted	31

As for the solubility limit experiments, the test tubes in the adsorption experiments were made up to constant volume using 9 ml of wastewater sample and 0.1-0.4 ml of 100 mg/l Zn^{2+} stock solution (or 0.1-0.4 ml of 250 mg/l Cu^{2+} stock solution) and volumes made up to 10ml with MilliQ water. The metal concentrations added were 1, 2, 3 and 4mg/l for zinc and 2.5, 5, 7.5 and 10mg/l for copper. Each set of metal addition consisted of four tubes, each adjusted to a different pH level using different volumes of 1M NaOH. After shaking for the equilibrium time (taken to be 90 minutes for all the process streams), the tubes were centrifuged for 5 minutes at 10000 g. Then 5ml of the centrate was taken and preserved by acidification to less than pH 2 (with HCl) for later analysis on the AAS and IC. The pH of the remaining centrate was then measured. The soluble and total metal concentrations initially in the original samples were also analysed. The non-soluble / adsorbed metal concentration at the end of each experiment was taken to be the difference between the total metal (initial and added) and the soluble metal concentrations.

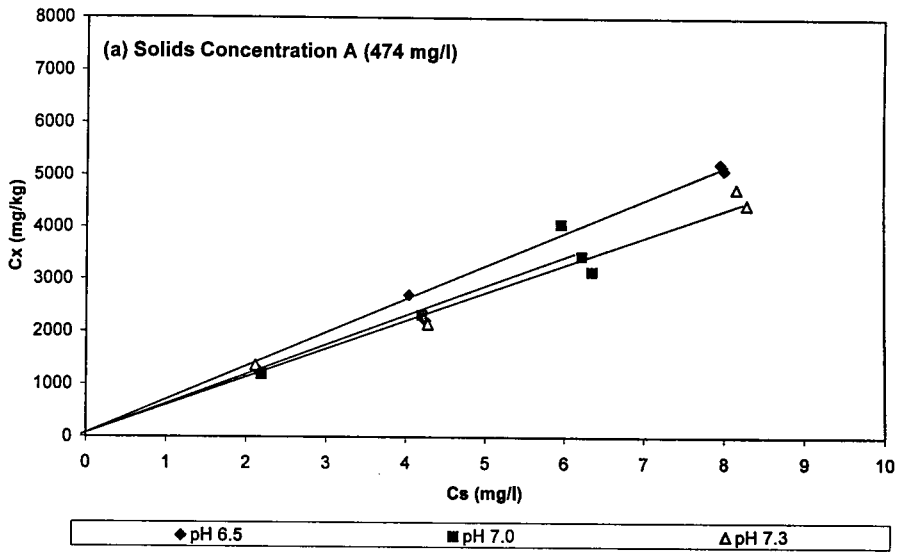
5.4.3 Results and Observations

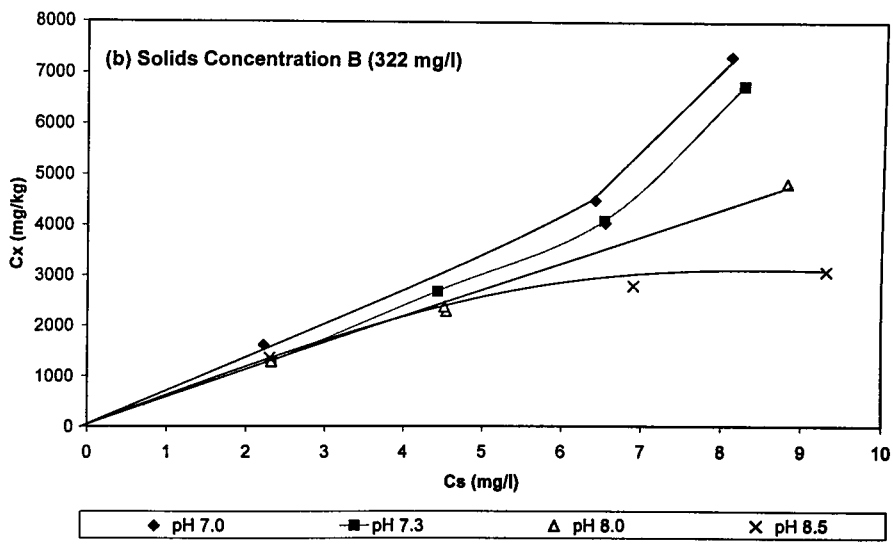
The results of the adsorption experiments are presented as a series of graphs showing the relationship between soluble (C_s) and non-soluble metal concentrations (C_{NS}) and the total metal concentration (C_T). In addition, adsorption isotherms are shown in the usual format, where the soluble metal concentrations (C_s) and solids bound metal concentrations (C_x) are plotted on the x- and y- axes respectively. Finally, graphs were also plotted showing the relationship between metal removal (%) and pH. Where possible, the results were also plotted according to the Langmuir isotherm, to enable the derivation of the adsorption capacities. The trendlines for these graphs are shown for illustrative purposes. The regression equations for data in the linear range of the adsorption isotherm graphs (C_s vs.C_x) are of importance to the calibration of the model as they allow the adsorption coefficient to be derived (the slope of the linear range of the graph = adsorption coefficient). The data derived from these graphs are tabulated in tables 5.2 (Cu) and 5.3 (Zn). The statistical significance of the regression coefficients were obtained using a t-test analysis in Microsoft Excel 97™. These significance values and the correlation coefficients (R^2) are also presented in tables 5.2-5.3. The graphs presented in this section are used to show the main observations revealed in each experiment. For some graphs, trendlines for all pH ranges could not be plotted due to the limited number of data points resulting from the difficulty of precisely adjusting pH values to fall within specific ranges for all experiments conducted. A full set of graphs can be found in Appendix C (figure C.1-C.81). The results are also tabulated in Appendix C, tables C.10-C.21.

<u>Cu in Raw Sewage</u>

It is apparent from the C_S vs. C_x graphs (figure 5.13 a-c) that the experimental results do not follow the typical L-curve isotherm expected for metal adsorption. However, they depict what can be termed as a C-curve isotherm. This type of isotherm indicates that there is a constant rate of adsorption and that the number of available sorption sites remains constant throughout the whole range of solute concentrations studied (USEPA 1999). Therefore since the Langmuir isotherm can only be applied for an L-curve isotherm, it is not possible to predict the adsorption capacity under the concentrations studied. It is also apparent that for some pH ranges, steeper slopes (indicative of increased adsorption) occur after a specific solute concentration. This is especially evident at solids concentration B (322 mg/l).

Increasing the solids concentration slightly increased the adsorption of Cu. However, adsorption did not seem to be affected by increasing metal addition. It is also apparent that pH affects the slope of the graph, i.e. the adsorption / partitioning coefficient. Overall Cu removal was in the range of 10-25% over the pH ranges studied. It is shown in the graph of pH vs. metal removal % (see Appendix C) that increasing the pH slightly decreased the removal of Cu in raw sewage.





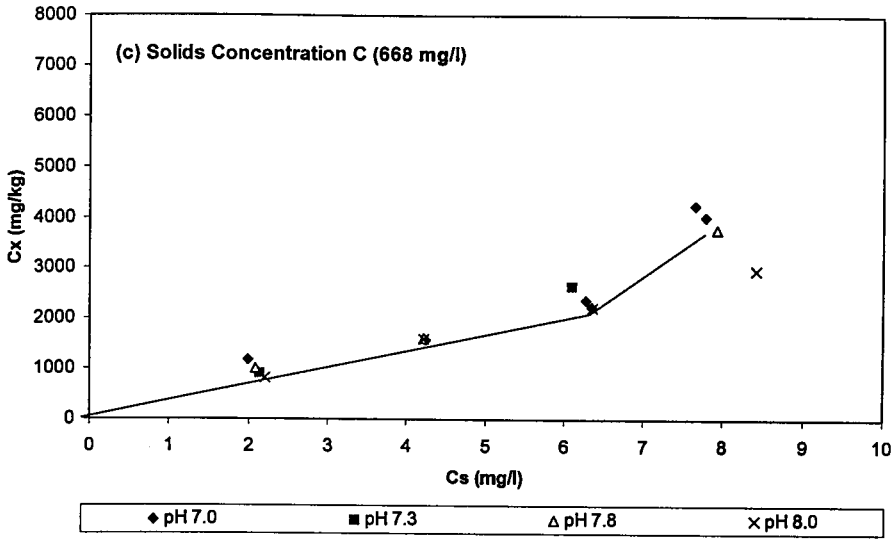
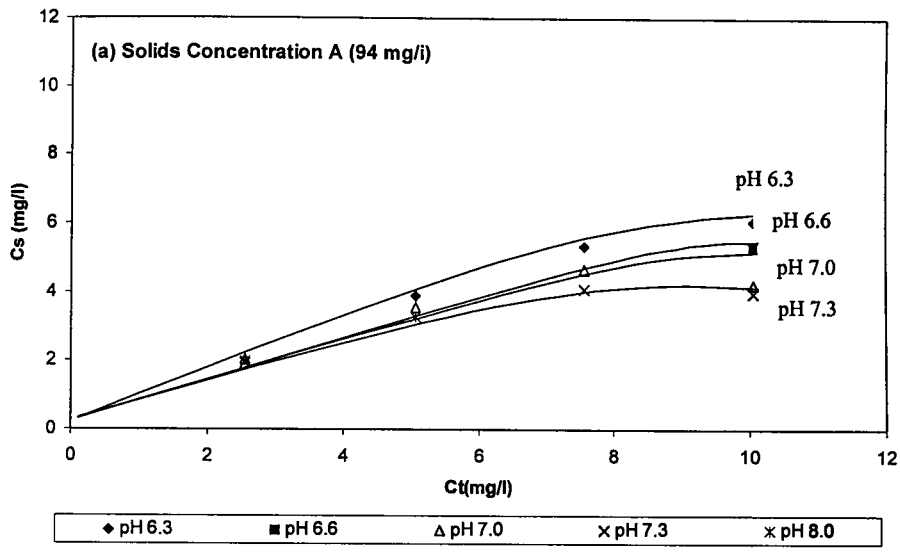
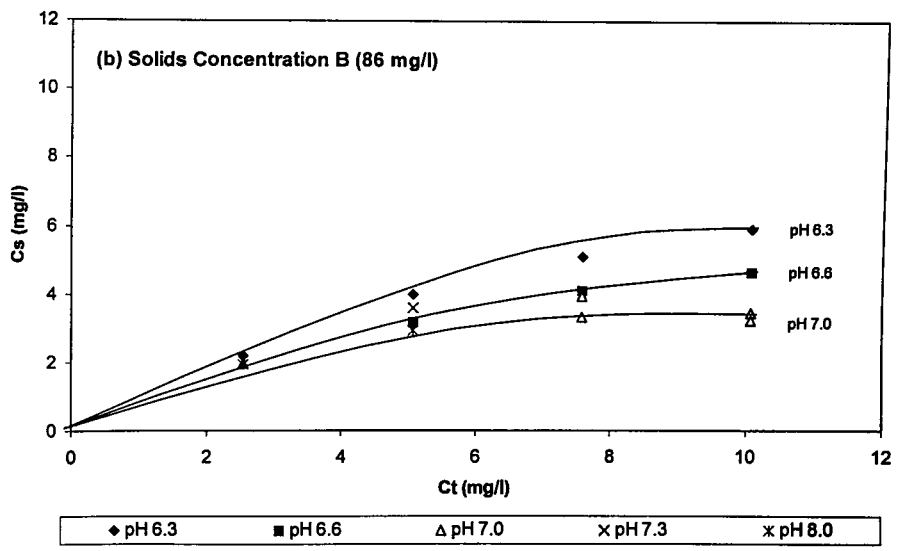


Figure 5.13: *Cu adsorption in Raw Sewage*

Cu in Primary Effluent

The C_T vs. C_s graphs (figure 5.14 a-c) show that pH slightly increases Cu adsorption in primary effluent. The graphs also show that for pH values above 6.6, above a total metal concentration of approximately 7.5 mg/l, an increase in total metal does not result in any further increase in the soluble metal concentration. Comparing the results for the different solids concentrations shows that adsorption slightly decreased with increasing solids concentration. Overall the removal of Cu in primary effluent was within the range of 20-70%.





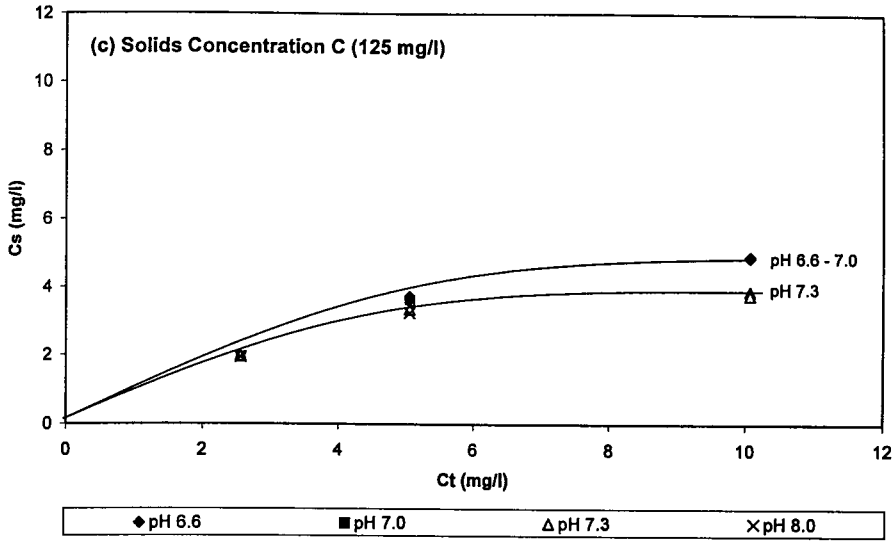
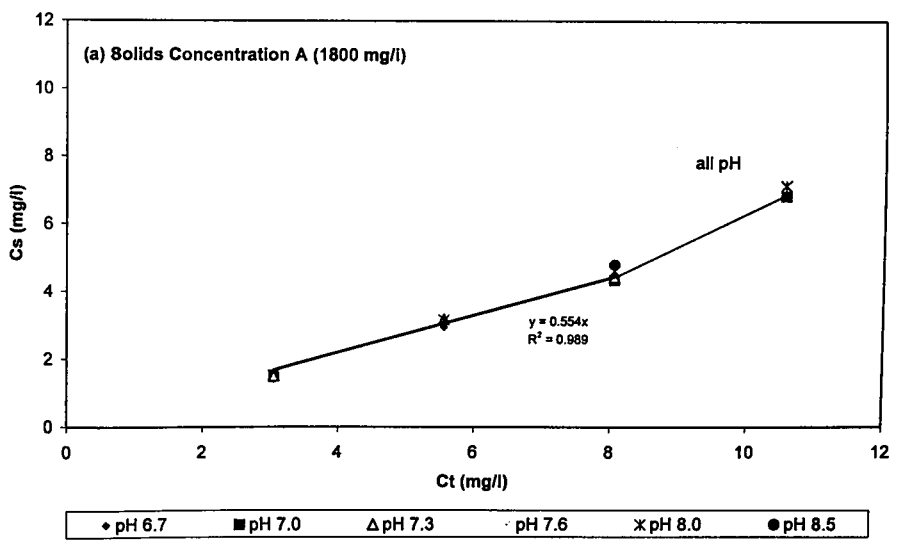
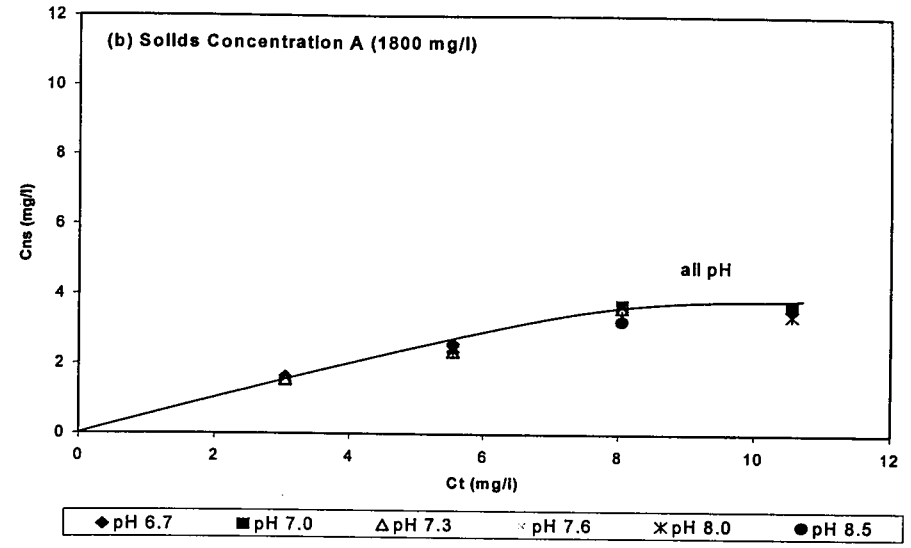


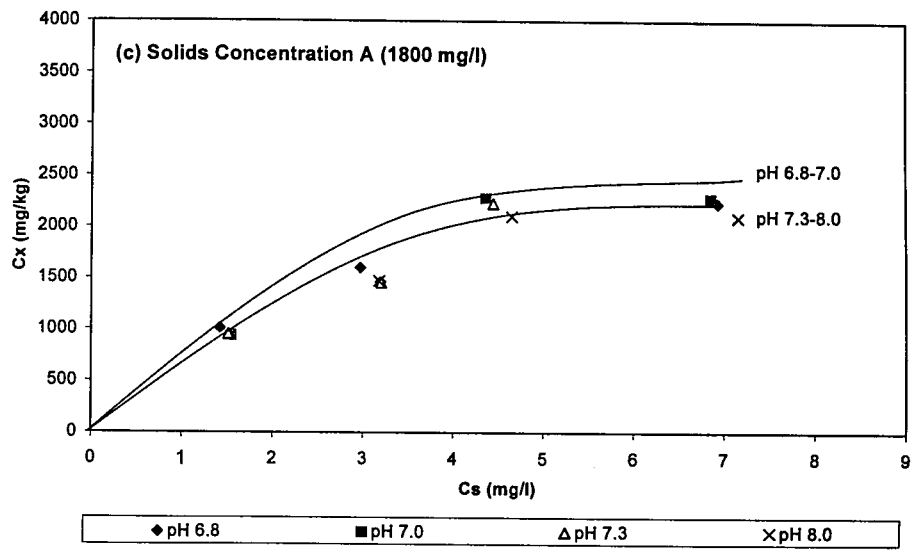
Figure 5.14: *Cu adsorption in primary effluent*

Cu in Mixed Liquor

For all solids concentrations, the C_T vs. C_s graphs (figure 5.15a) show a constant proportion of metal adsorbed, with only minor differences being attributed to differences in pH. This trend was consistent up until a total metal concentration of approximately 8 mg/l, where further increases in total metal concentration resulted in equivalent increases in soluble metal, implying that no further adsorption had occurred. This is also shown in the graphs of C_T vs. C_{NS} (figure 5.15b). The adsorption of Cu in mixed liquor was shown to increase with increasing solids concentration. The adsorption capacity was also shown to increase with increasing solids concentration. It is apparent from the C_s vs. C_x graphs (figure 5.15c) that a characteristic L-curve isotherm applies for all three solids concentrations tested in this experiment. Thus the Langmuir model applies. Overall the removal of Cu in mixed liquor was found to be in the range of 30-60%. The graphs of pH vs. removal % (figure 5.15d) on the other hand shows only a very slight decrease in removal with increasing pH. A decrease in adsorption with increasing added metal concentrations is also shown.







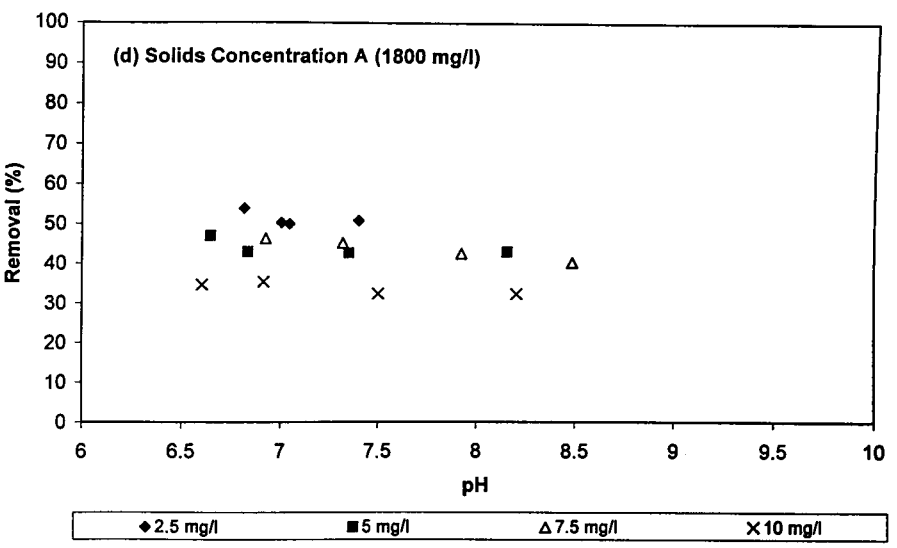
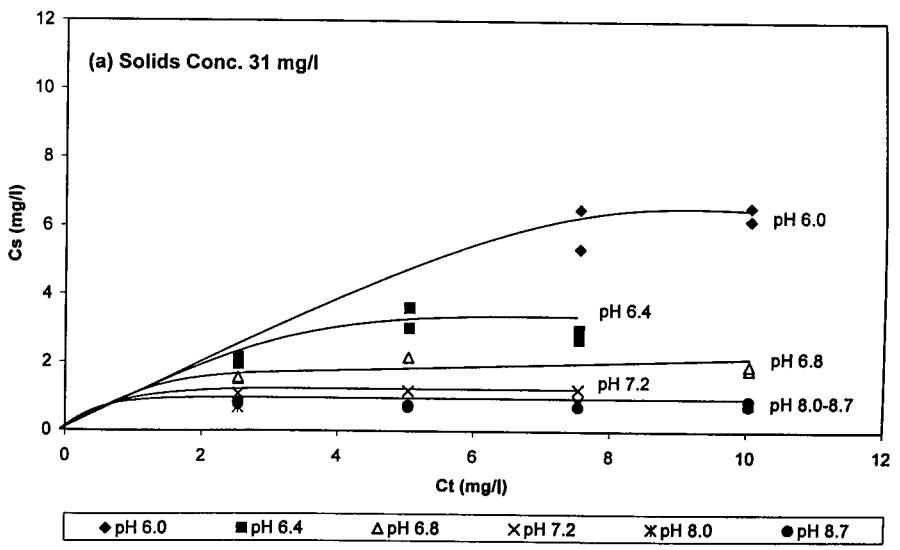
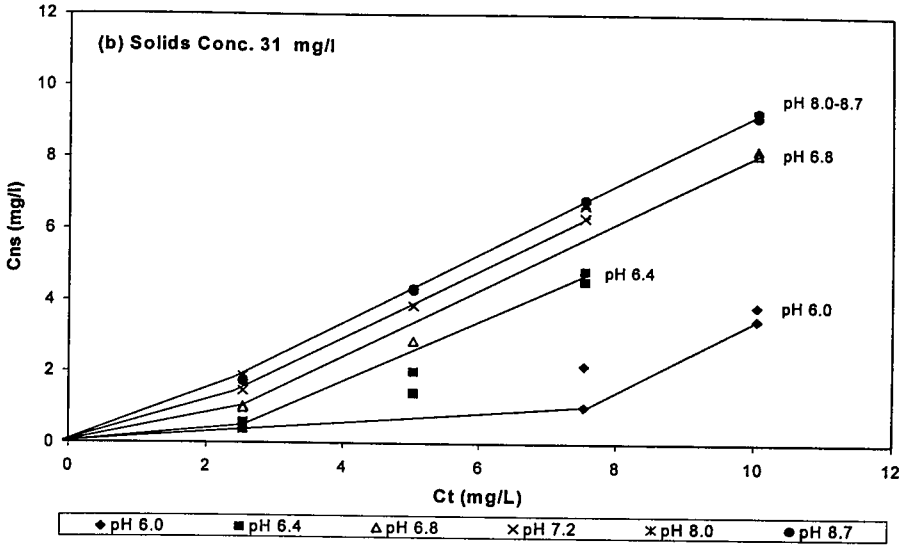


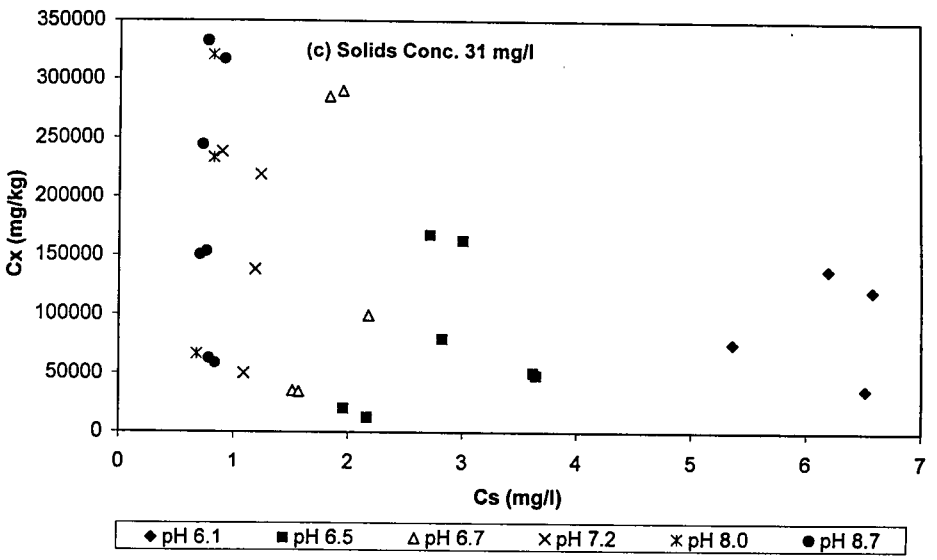
Figure 5.15: *Cu adsorption in mixed liquor*

Cu in Final Effluent

Since dilution of the final effluent with the supernatant did not result in a significantly different suspended solids concentration, the results of both solids concentrations were combined for the analysis of the results. The graph of C_T vs. C_s (figure 5.16a) shows that for pH values greater than 6, a point occurs where the soluble metal concentration does not increase with increasing total metal concentration. This is also shown in the C_T vs. C_{NS} graph (figure 5.16b) where the slope of the graph in this range equals 1 and in the graph of C_s vs. C_x where the slope of the graph was equal to infinity (figure 5.16c). The graph of pH vs. removal % (figure 5.16d) shows increasing removal with increasing added metal concentration. The increased uptake was also shown to be due to increases in pH. However a plateau, where no further increase in adsorption is shown, occurs at approximately pH 7.5. This plateau increases with increasing metal concentration and is at a maximum of approximately 91% for a total metal concentration of 10.0 mg/l.







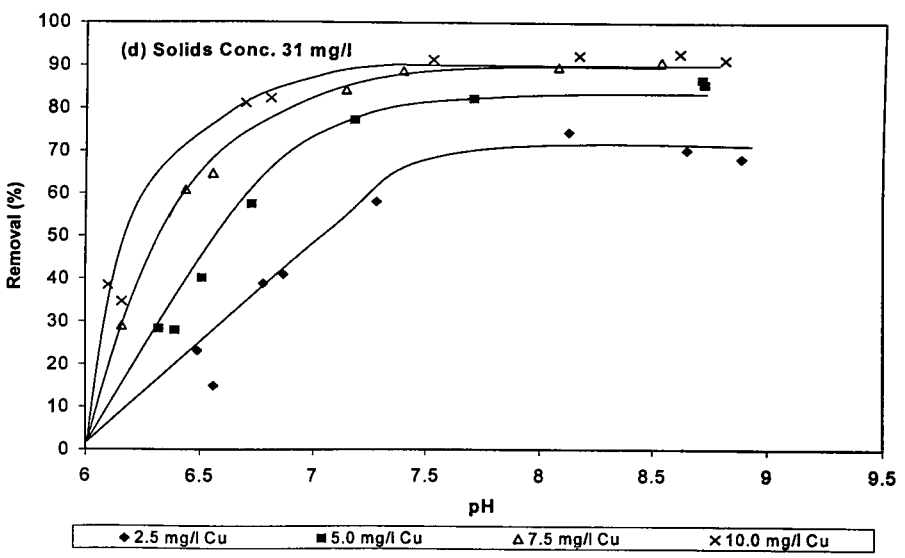
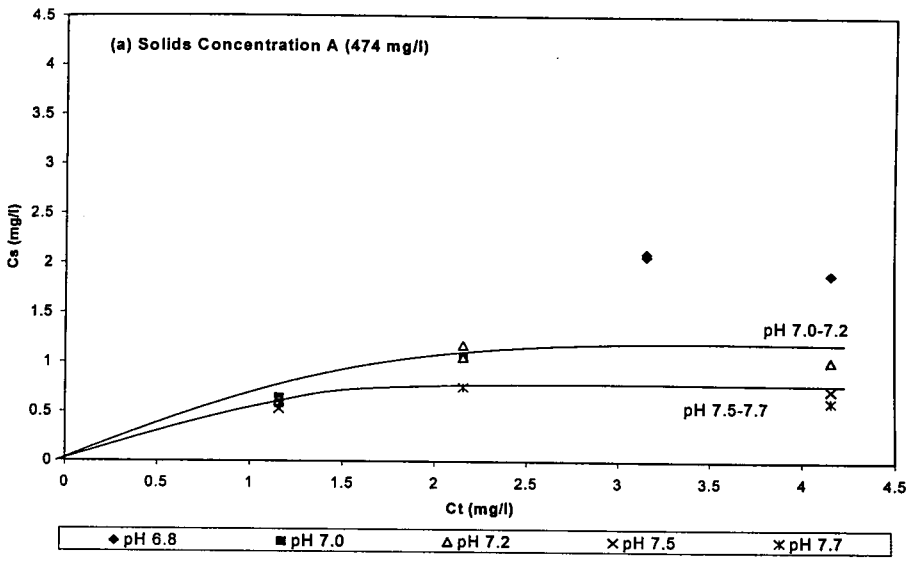
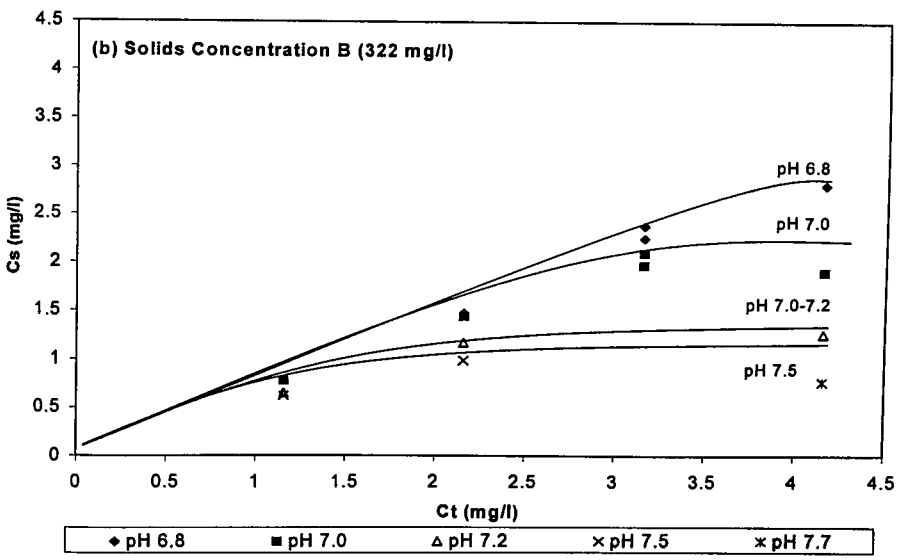


Figure 5.16: *Cu adsorption in Final Effluent*

Zn in Raw Sewage

The graphs generated from this experiment show that at pH values greater than 6.8, no increase in soluble metal with increasing total metal concentration, greater than 2 mg/l, was evident. The graphs of C_T vs. C_S (figure 5.17 a-c) also indicated increasing adsorption with both increasing solids concentration and increasing pH. Overall removal of Zn in raw sewage was found to be in the range of 30-90%.





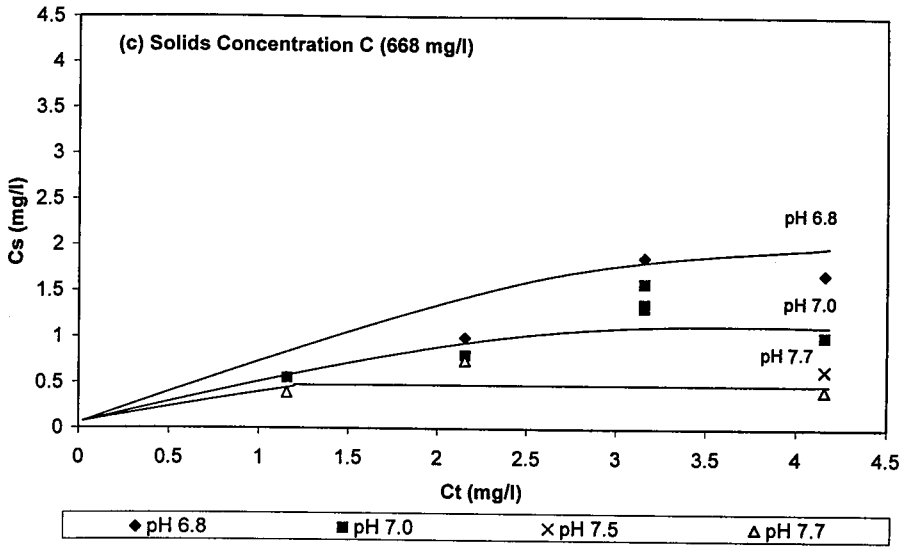
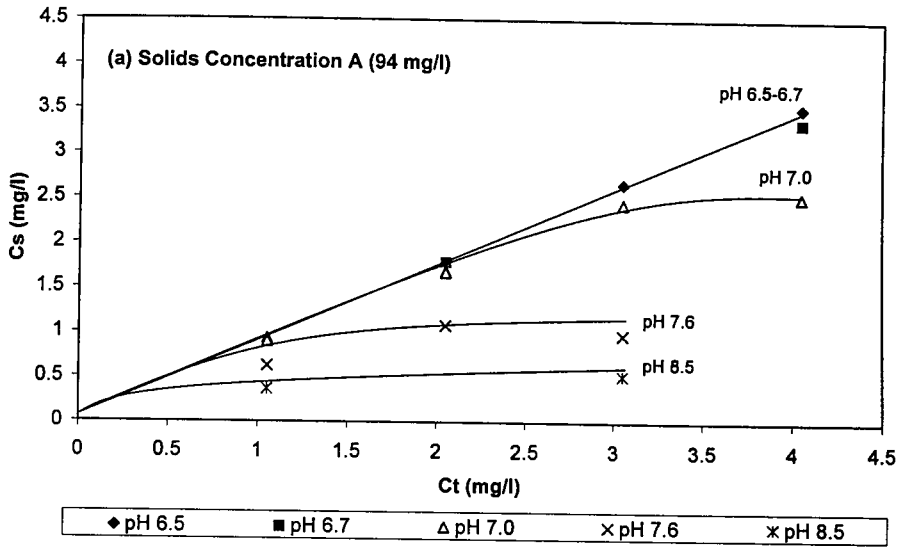
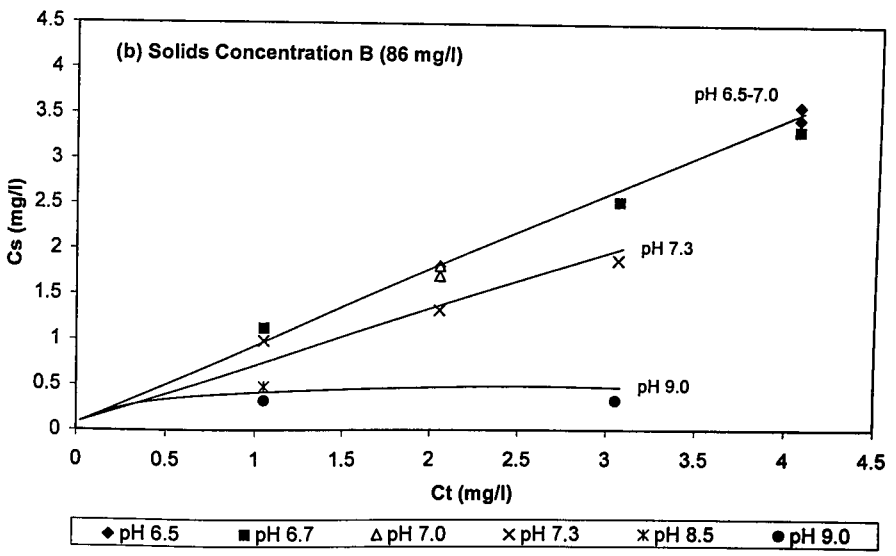


Figure 5.17: *Zn adsorption in raw sewage*

Zn in Primary Effluent

The graphs of C_T vs. C_S (figure 5.18 a-c) generated by the results of this experiment also indicate that at some concentrations no increase in soluble metal with increasing total metal concentration occurs. Increases in solids concentration as well as increases in pH cause increased adsorption. The graph of pH vs. removal % (in Appendix C) also shows that the increase in removal with increasing pH was similar for all added metal concentrations. The maximum removal (%) encountered was 90%.





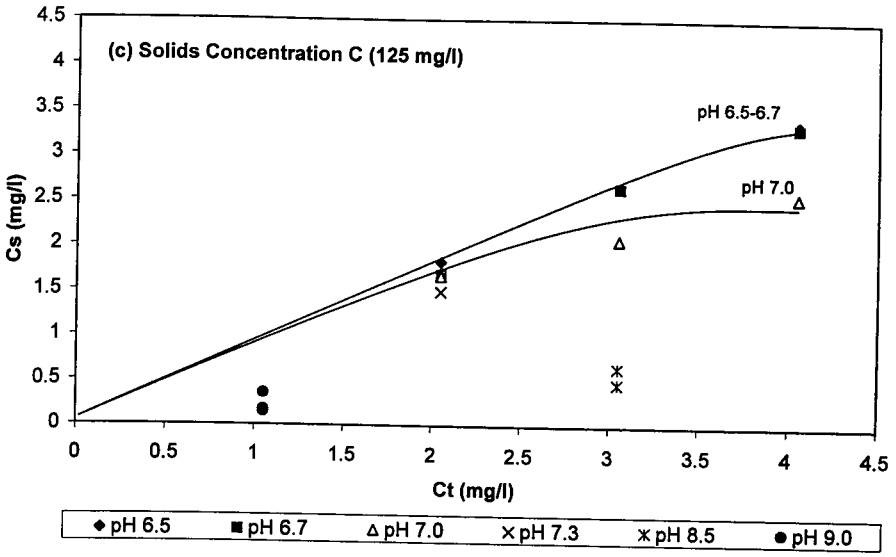
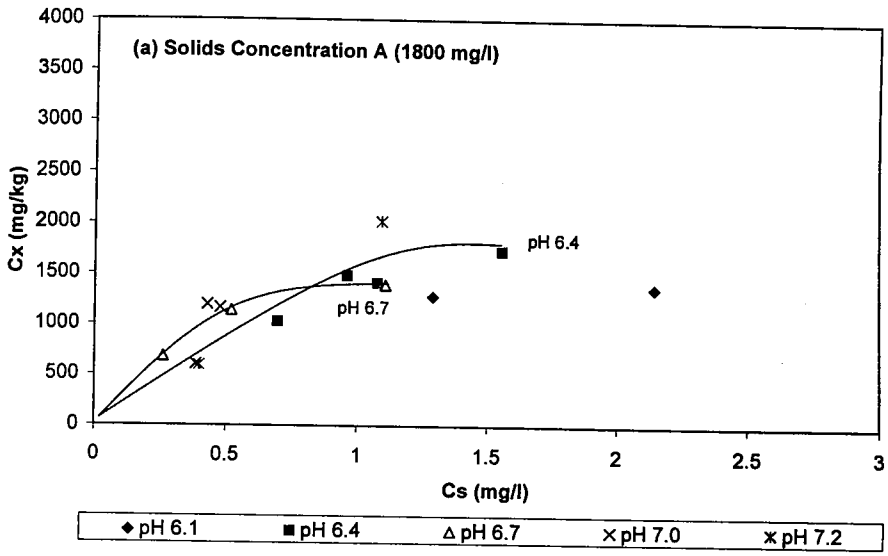
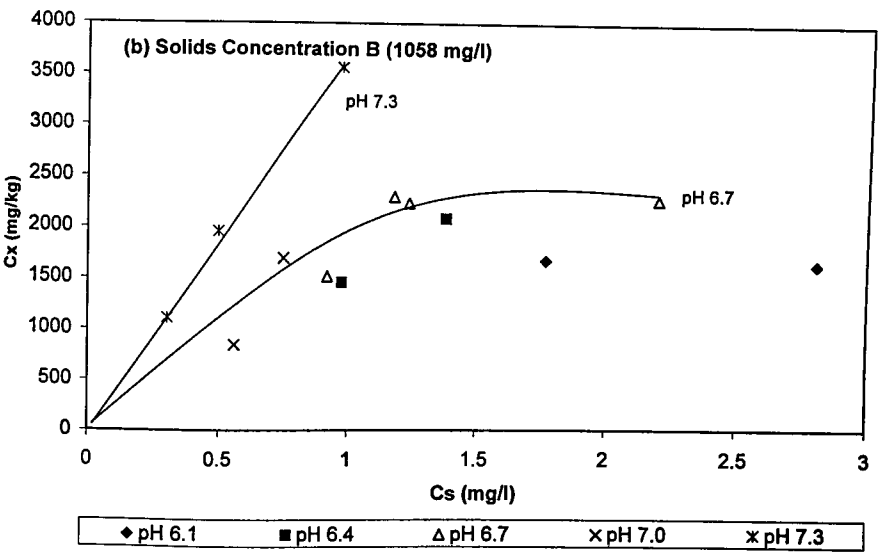


Figure 5.18: *Zn in Primary Effluent*

Zn in Mixed Liquor

The graphs of C_s vs. C_x (figure 5.19 a-c) show that for pH values less than 7.0, an L-curve isotherm is exhibited. The adsorption of Zn in mixed liquor is also positively influenced by increasing pH and solids concentrations, as shown by increased values of the adsorption coefficient. However, the adsorption capacities achieved increased with decreasing solids concentration. The removal (%) was greatly influenced by pH. The maximum removal (approximately 80%) was similar for all three solids concentrations.





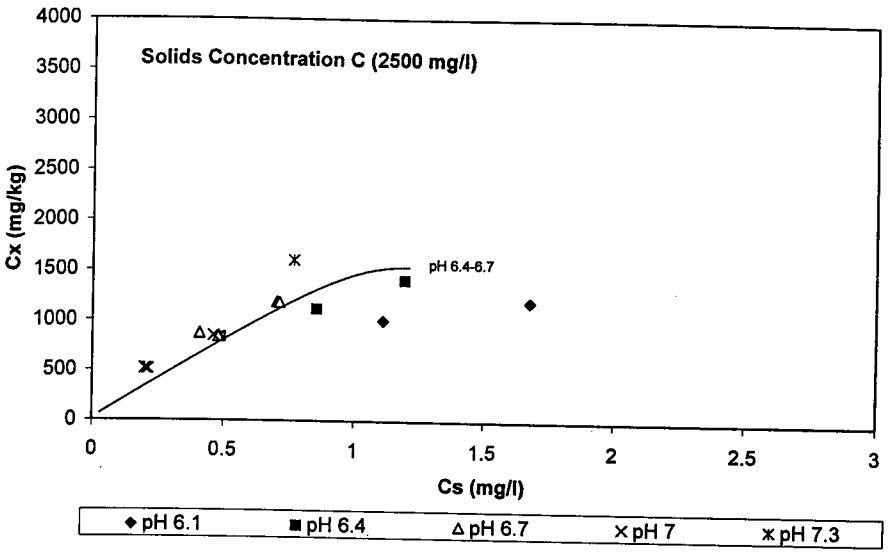
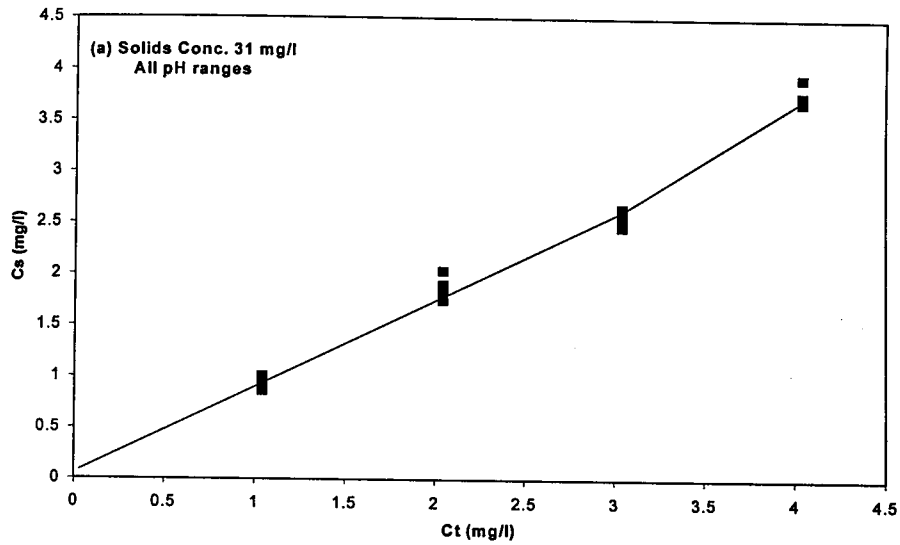
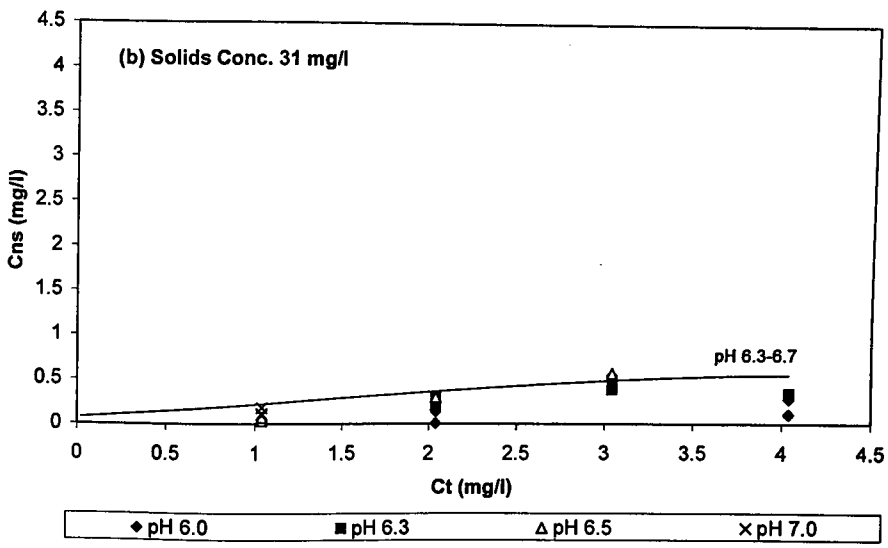


Figure 5.19: *Zn in Mixed Liquor*

Zn in Final Effluent

The results of this experiment show that adsorption increased with increasing pH. The graphs of C_T vs. C_S (figure 5.20 a) and C_T vs. C_{NS} (figure 5.20 b) show that the adsorption capacity was reached at low metal concentrations for pH values lower than 6.5. The graph of pH vs. removal % (figure 5.20c) also shows an increase in removal with both increasing added metal concentration and pH, reaching a maximum of approximately 85% removal at pH 8.4.





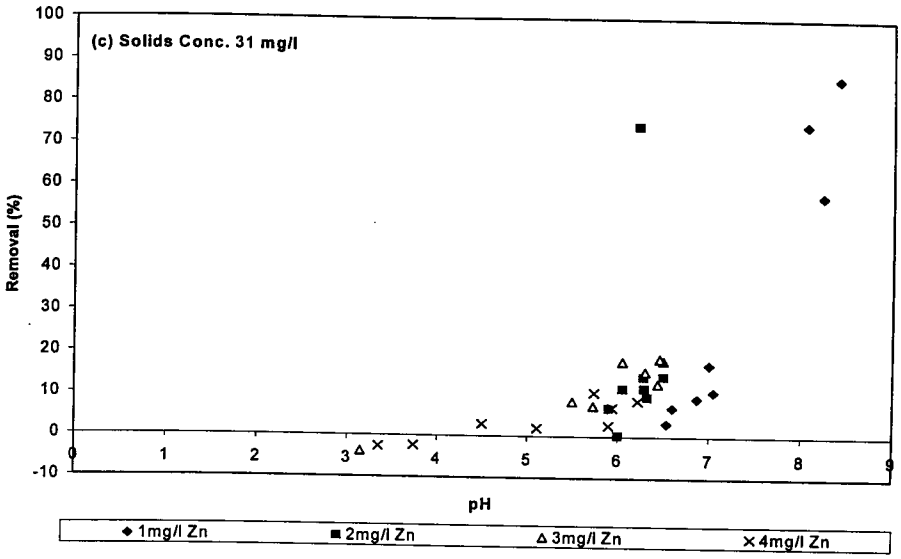


Figure 5.20: *Zn in Final Effluent*

Using this data, the values for the model coefficients shown in tables 5.2 and 5.3 can be derived. The adsorption coefficient value (Kp) is calculated from the initial slope of the C_s vs. C_x graphs. The solubility limits are derived from the C_T vs. C_S graphs, where the graphs show no increase in soluble metal concentrations with increasing total metal concentrations.

As can be seen from tables 5.2 and 5.3, the statistical significance of the adsorption coefficients derived from the experimental data is high. This shows that the method used for the derivation of this model coefficient is sufficiently reliable. While these adsorption coefficients are significant they are only applicable to the experimental conditions under which they were derived.

Table 5.2: *Experimentally-derived model coefficients for copper*

Process Stream	Total Suspended Solids (mg/l)	pH	Solubility Limit (mg/l)	Kp (l/kg)	Ka (mg/kg)	Langmuir-derived Ka, (mg/kg)	Significance of Kp value	R^2 of Kp
Raw Sewage	474	6.5	Not reached	634	Not reached		99%	0.98
		7.0	Not reached	569	Not reached		99%	0.91
		7.3	Not reached	555	Not reached		99%	0.98
	322	7.0	Not reached	663	Not reached		95%	0.97
		7.3	Not reached	615	Not reached		98%	0.99
		8.0	Not reached	536	Not reached		99%	1.00
		8.5	Not reached	524	Not reached			
	668	7.0	Not reached	376	Not reached		99%	0.79
		7.3	Not reached	433	Not reached		99%	1.00
		7.8	Not reached	456	Not reached		95%	0.97
		8.0	Not reached	353	Not reached		99%	0.99
Primary Effluent	94	6.3	6.10	4482	Not reached		90%	0.79
		7.0	4.70	6382	Not reached		99%	0.81
		7.3	4.00	8966	Not reached		80%	0.80
		8.0		5675	Not reached		80%	0.75
	86	6.3	5.90	5663	Not reached		80%	0.84
		6.6	4.60	9703	Not reached		90%	0.69
		7.0	3.50	12644	Not reached		80%	0.64
		7.3	3.30	5167	Not reached		95%	0.96
		7.7	2.80		Not reached			
	125	6.6	5.00	3095	Not reached		95%	0.97
		7.3	3.75	4093	Not reached		80%	0.80
Mixed Liquor	1800	6.8	Not reached	516	2132	3333	90%	0.4
		7.0	Not reached	541	2280		95%	0.98
		7.3	Not reached	495	Not reached		95%	0.93
		8.0	Not reached		2090	3333		
	1058	6.8	Not reached	750	Not reached	5000	90%	0.5
		7.0	Not reached	723	3464	5000	90%	0.9
		7.3	Not reached	668	3321	5000	80%	0.14
		7.6	Not reached		3125	5000		
		8.0	Not reached		3000			
		8.5	Not reached		2878	5000		
	2500	6.7	Not reached	503	2100	3333	95%	0.95
		7.0	Not reached	448	1900	3333	99%	0.61
		7.6	Not reached	389	1695	3333	95%	0.90
Final Effluent	31	6.0	6.70		Not reached			
		6.4	3.60		Not reached			
		6.8	2.10	34130	Not reached		80%	0.5
		7.2	1.20		Not reached			
		8.0	0.80		Not reached			
		8.7	0.70		Not reached			

Notes: Kp = adsorption coefficient

Ka = adsorption capacity

Table 5.3: *Experimentally-derived model coefficients for zinc*

Process Stream	Total Suspended Solids (mg/l)	pH	Solubility Limit (mg/l)	Kp (l/kg)	Ka (mg/kg)	Langmuir derived Ka (mg/kg)	Significance of Kp value	R^2 of Kp
Raw Sewage	474	6.8	2.10		Not reached			
		7.0	1.75		Not reached			
		7.2	1.10		Not reached			
		7.5	0.70		Not reached			
	322	6.8	3.30	1425	Not reached		99%	0.68
		7.0	2.00	1833	Not reached		99%	0.94
		7.2	1.30	2836	Not reached		99%	0.99
		7.5	1.00	3733	Not reached		90%	0.86
		7.7	0.65		Not reached			
	668	6.8	1.80		Not reached			
		7.0	1.40		Not reached			
		7.7	0.60		Not reached			
Primary Effluent	94	6.7	Not reached	2270	Not reached		90%	0.91
		7.0	2.60	2655	Not reached		99%	0.91
		7.6	1.15	9980	Not reached		90%	0.91
		8.5	0.60		Not reached			
	86	6.5	Not reached	1867	Not reached		90%	0.77
		6.7	Not reached	2702	Not reached		98%	0.98
		7.3	Not reached	7710			95%	0.95
		9.0	0.40		Not reached			
	125	6.5	Not reached	1683	Not reached		80%	0.85
		6.7	Not reached	1761	Not reached		90%	0.77
		7.0	Not reached	4853	Not reached		90%	0.74
Mixed Liquor	1800	6.1	Not reached		1280	1429		
		6.4	Not reached	1362	17520	5000	95%	0.86
		6.7	Not reached	2269	Not reached	2500	95%	0.91
	1058	6.1	Not reached		1650	1667		
		6.4	Not reached	1502	1680	5000	99%	1.0
		6.7	Not reached	1817	Not reached		95%	0.87
		7	Not reached	1982	Not reached		95%	0.69
		7.2	Not reached	3709	Not reached		99%	1.0
	2500	6.1	Not reached		1040	2000		
		6.4	Not reached	1269	1360	2500	90%	0.65
		6.7	Not reached	1733	Not reached	2500	99%	0.72
		7.0	Not reached	2013	Not reached	1667	90%	0.65
		7.3	Not reached	2114	Not reached	5000	95%	0.98
Final Effluent	31	All	Not reached	6854	Not reached		99%	0.79

Notes: Kp = adsorption coefficient

Ka = adsorption capacity

5.4.3.1 Association between model coefficients and critical parameters

Correlation relationships linking the coefficients derived from the adsorption experiments and the two main parameters, pH and solids concentration were examined. The derivation of these correlation relationships was limited by the fact that solubility limits and adsorption capacities were not reached in all of the experiments. Therefore for Cu, correlating pH and the solubility limit was only possible for the primary and final effluents. Correlation between pH and adsorption coefficients (Kp) was only possible for raw sewage samples. In general it was found that Kp values were in the range of 388-970 l/kg for solids concentrations greater than 300 mg/l and in the range of 8200-15000 l/kg for solids concentrations less than 300 mg/l. The adsorption capacities (Ka) were only reached for mixed liquor samples. Correlations between Ka values and pH showed a decrease in adsorption capacity with increasing pH. Ka values were also found to decrease with increasing TSS concentration.

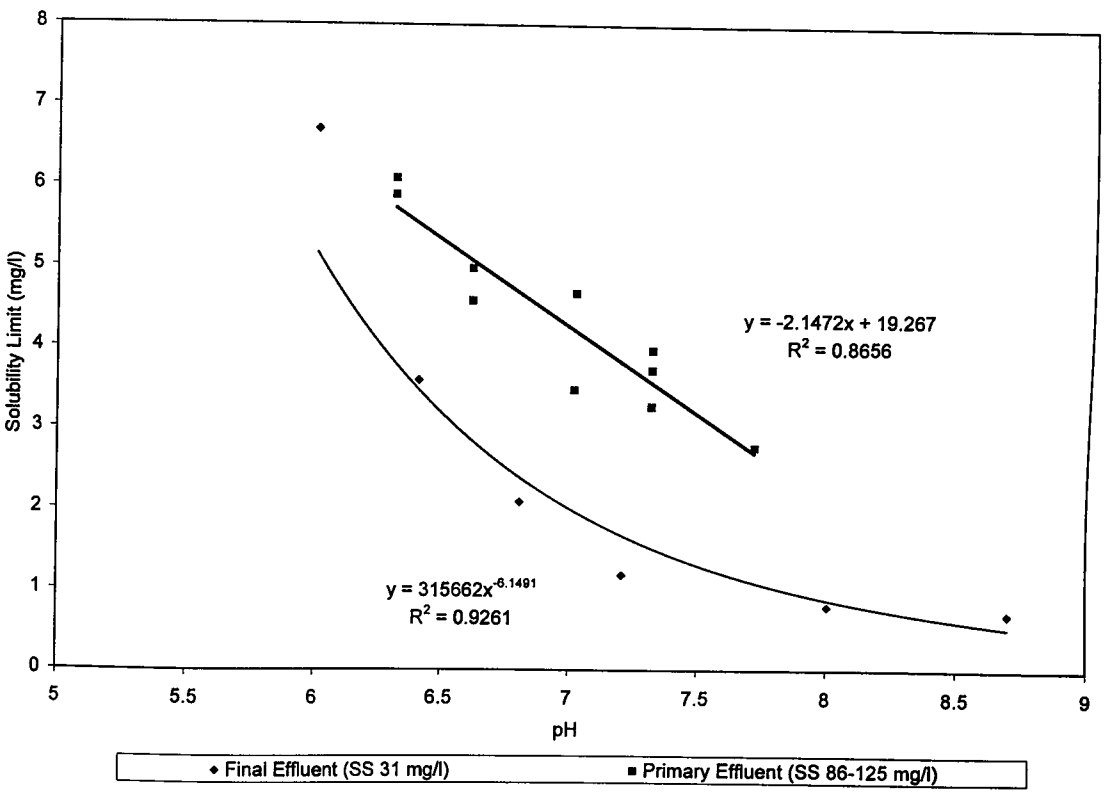


Figure 5.21: *Relationship between pH and the solubility limit of Cu in Primary Effluent and Final Effluent*

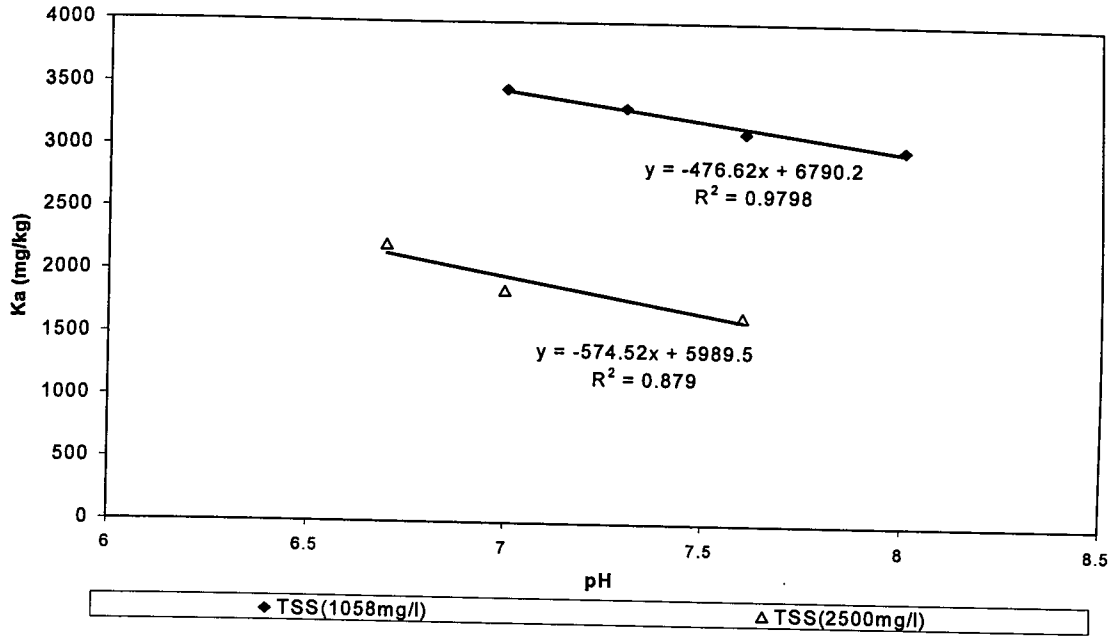


Figure 5.22: *Relationship between pH and adsorption capacity of Cu in mixed liquor*

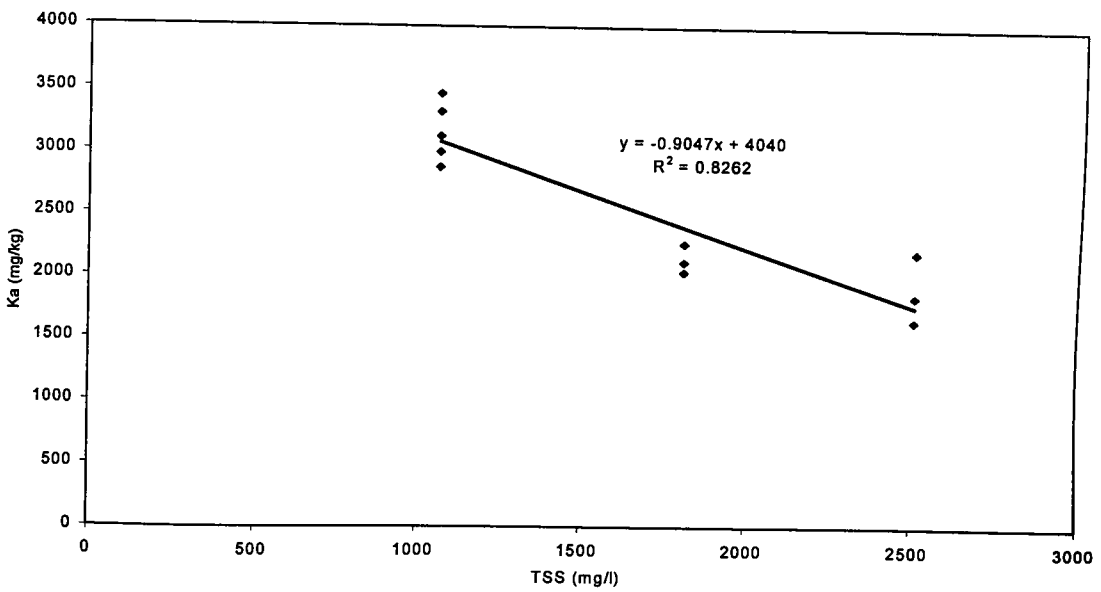


Figure 5.23: *Relationship between TSS and adsorption capacity of Cu at pH 7.0-8.0*

Correlating pH and the solubility limit for Zn was only possible for raw sewage and the primary effluent. It was found that Kp values were between 1330-9980 l/kg for all experimental results, with the average and median being 2473 and 1871 l/kg

respectively. The values for the adsorption capacity were in the range of 1250-1680 mg/kg in mixed liquor.

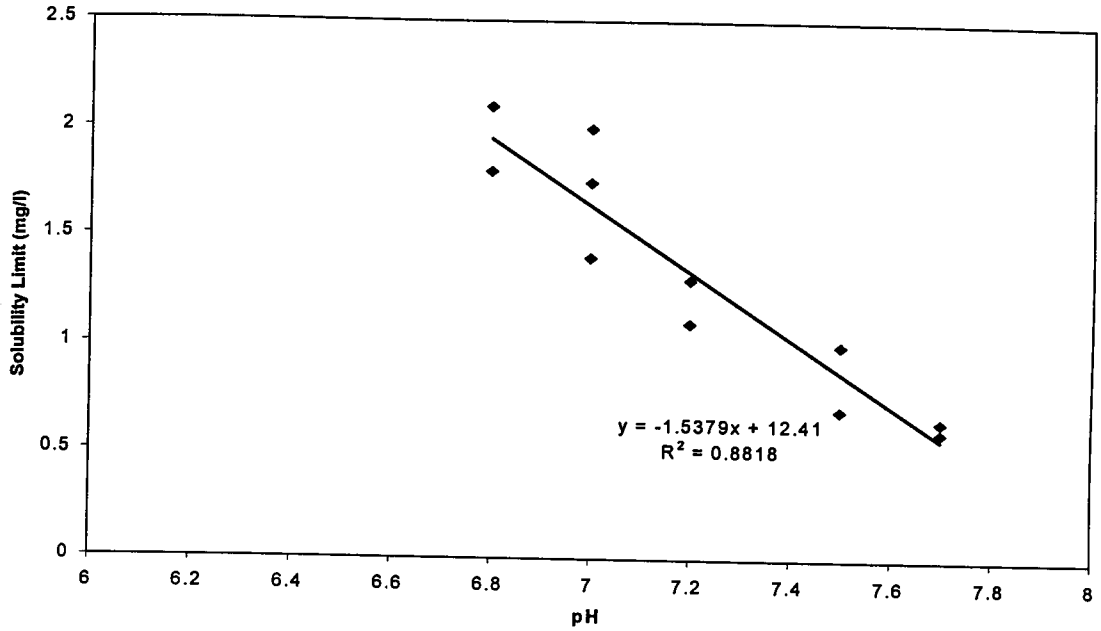


Figure 5.24: *Relationship between pH and solubility limit of Zn in Raw Sewage*

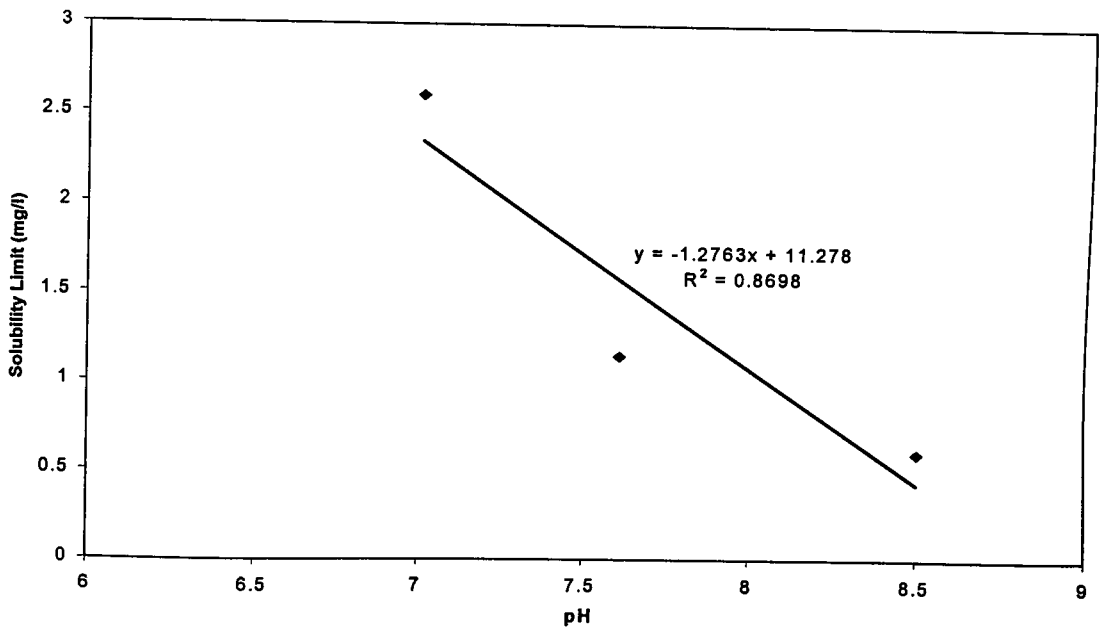


Figure 5.25: *Relationship between pH and solubility limit of Zn in primary effluent*

5.4.4 Competition Adsorption Experiments

In addition to the adsorption experiments carried out on a single metal, competition experiments were conducted. These experiments examined the effect on adsorption of each metal in the presence of another metal in solution. Mixed metal solutions were added in the same concentrations as those used in the single-metal adsorption experiments (namely, 2.5, 5.0, 7.5 and 10.0 mg/l for Cu and 1.0,2.0,3.0 and 4.0 mg/l for Zn). These experiments were carried out using aliquots of the same sample material, which had been used for the solubility and adsorption experiments. Analysis of the results was carried out using the same method as was used for the single metal adsorption experiments. The graphs generated can be found in Appendix C (figures C.82-C.161). The model coefficients derived as a result of these experiments are shown in tables 5.4 and 5.5. In some cases, the results obtained are not sufficient to make general statements as to what effect the presence of one metal has on the adsorption of the other metal. The observations presented are thus subject to the limitations posed by the results obtained.

5.4.4.1 Results and Observations

Cu and Zn in Raw Sewage

The adsorption of Cu in this experiment exhibited a C-type adsorption isotherm. Adsorption was slightly increased with increased solids concentration. While increasing pH did not greatly affect the level of adsorption, it was slightly decreased with increasing metal concentration. Zinc adsorption, however, increased with increasing pH. There was also some precipitation of Zn at higher pH values. Generally Zn removal (40-95%) was greater than that of Cu (10-30%).

In comparison to the results of the single metal adsorption experiments, the solubility limits for Zn were similar in both experiments. The adsorption coefficients for Cu decreased by up to 8% in comparison to those obtained from the single metal experiments. On the other hand, Zn adsorption coefficients increased by 60-100% in the mixed metal system compared to the single metal system.

Cu and Zn in Primary Effluent

In this experiment, both Cu and Zn exhibited some precipitation. For both metals, increased pH resulted in increased removal and the increase in removal with pH

increased with increasing added metal concentration. However, again in general, Zn removals (10-90%) were higher than Cu removals (10-70%).

Comparison of the results of the single metal and competition experiments shows that for both Cu and Zn the solubility limits reached at specific pH values were greater in the single metal experiments. The solubility limits for Cu showed a decrease on average of 25% in the competition experiments. Zinc solubility at pH 7 in solids concentration 94 mg/l was decreased by 40% in the competition experiments. It was found that the values for the adsorption coefficients were difficult to obtain to for both metals.

Cu and Zn in Mixed Liquor

The results show that Cu adsorption follows a C-type isotherm. The pH of the solution had a slightly negative effect on the adsorption of Cu, yet had a positive effect on the adsorption of Zn. Increasing solids concentration increased the adsorption of both metals.

The competition experiments also showed a decrease (35%) in adsorption coefficients for Cu while no discernible trend could be found for the change in the Zn adsorption coefficients.

Cu and Zn in Final Effluent

The adsorption of both metals followed a C-type isotherm, while showing some precipitation. Adsorption also increased with increasing pH.

5.4.4.2 Correlation Relationships

The results of the competition adsorption experiments were also used to derive relationships between the model coefficients and the critical parameters. Due to the limitations of the data, only relationships between pH and the solubility limit of both metals were obtained. These are shown in figures 5.26 and 5.27.

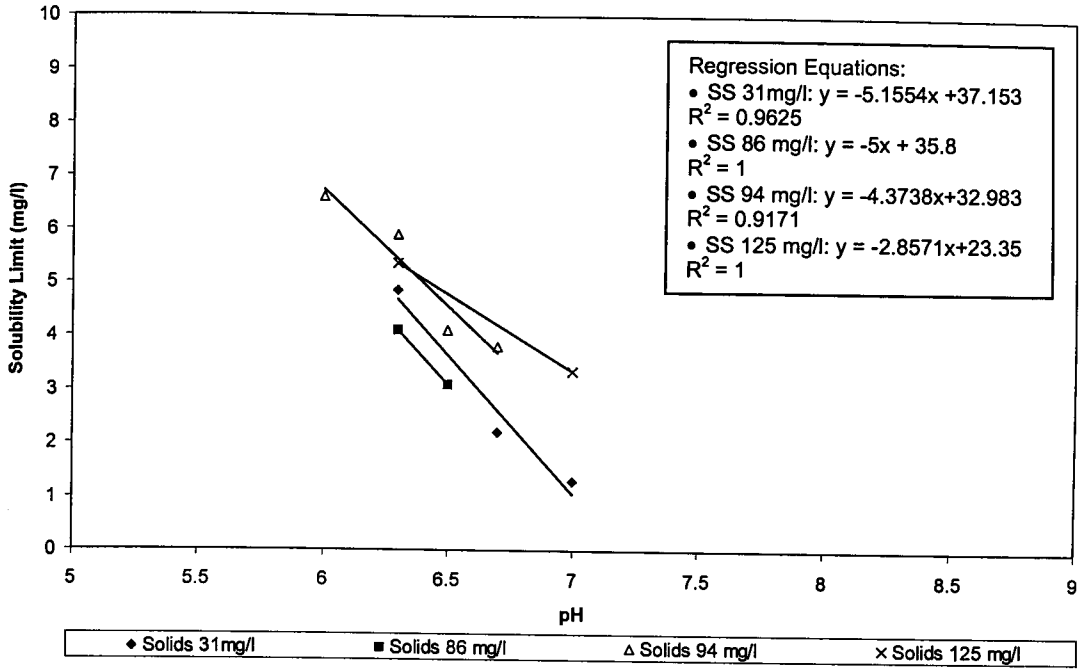


Figure 5.26: *Relationship between pH and the solubility limit of Cu in the presence of Zn*

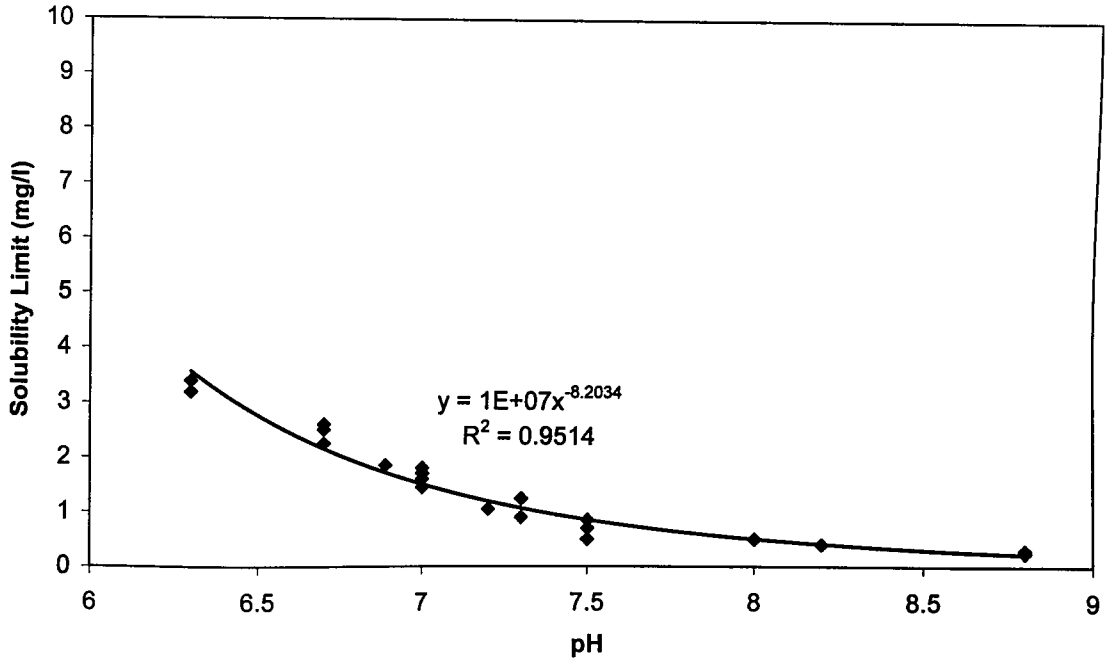


Figure 5.27: *Relationship between pH and the solubility limit of Zn in the presence of Cu*

Table 5.4: *Results of competition adsorption experiments (Cu)*

Process Stream	Total Suspended Solids (mg/l)	pH	Solubility Limit (mg/l)	Adsorption Coefficient Kp (l/kg)	Significance of Kp value	R^2 of Kp
Raw Sewage	474	6.4	Not reached	614	90%	0.88
		6.7	Not reached	537	99%	0.41
		7.0	Not reached	525	90%	0.83
		7.3	Not reached	486	99%	1.0
		8.0	Not reached	494	90%	
	322	6.4	Not reached	577	98%	0.96
		7.0	Not reached	678	90%	0.95
		8.3	Not reached	445	90%	0.90
	668	7.0	Not reached	383	90%	0.95
		7.3	Not reached	360	90%	0.83
		8.2	Not reached	254	95%	0.98
Primary Effluent	94	6.0	6.60			
		6.3	5.90			
		6.5	4.10			
		6.7	3.80			
	86	6.3	4.10			
		6.5	3.10			
	125	6.3	5.35			
		7.0	3.35			
Mixed Liquor	1800	6.3	Not reached	381	95%	0.85
		6.6	Not reached	377	90%	0.89
		7.0	Not reached	352	99%	0.79
		7.2	Not reached	429	80%	0.26
	1058	6.6	Not reached	522	99%	0.48
		7.0	Not reached	460	99%	0.72
		7.2	Not reached	458	99%	0.60
	2500	6.3	Not reached	346	90%	0.82
		6.6	Not reached	334	99%	0.80
		7.0	Not reached	325	99%	0.80
		7.2	Not reached	308	80%	0.46
Final Effluent	31	6.3	4.85			
		6.7	2.20			
		7.0	1.30			

Notes: Kp = adsorption coefficient

Ka = adsorption capacity

Table 5.5: *Results of competition adsorption experiments (Zn)*

Process Stream	Total Suspended Solids (mg/l)	pH	Solubility Limit (mg/l)	Adsorption Coefficient Kp (l/kg)	Significance of Kp value	R^2 of Kp
Raw Sewage	474	6.7	2.60			
		7.0	1.85	2763	80%	0.41
		7.3	0.90	4988	80%	0.51
		7.5	0.50			
	322	7.0	Not reached	3651	90%	0.94
		7.3	1.85	4773	95%	0.97
		7.5	0.70			
		8.0	0.50			
		8.2	0.40			
		8.8	0.25			
	668	7.0	1.60			
		7.2	1.05			
		7.5	0.85	6371	95%	0.99
		8.2	0.40			
		8.8	0.30			
Primary Effluent	94	6.7	2.25			
		7.0	1.45			
	86	6.3	3.20			
	125	6.7	2.50			
		7.0	1.70			
		7.3	0.90			
Mixed Liquor	1800	6.3	Not reached	1485	95%	0.96
		6.6	Not reached	1762	90%	0.89
		7.0	Not reached	2258	99%	0.86
		7.2	Not reached	3538	95%	0.98
	1058	6.6	Not reached	1674	99%	0.26
		7.0	Not reached	2105	98%	0.61
		7.2	Not reached	3950	99%	0.99
	2500	6.3	Not reached	1288	80%	0.49
		6.6	Not reached	1667	99%	0.85
		7.0	Not reached	1951	99%	0.92
		7.2	Not reached	2346	90%	0.91
Final Effluent	31	6.3	3.40			
		6.7	2.50			
		7.0	1.80			

Notes: Kp = adsorption coefficient

Ka = adsorption capacity

5.4.5 Overall Discussions

5.4.5.1 Conceptual Idea:

As previously mentioned in section 4.2.3, it is generally thought that adsorption of metals onto solids follows a linear isotherm with a characteristic L-curve. The slope of the curve is the adsorption / partitioning coefficient. As shown in figure 5.28, the initial amount adsorbed is large, this being the linear region of adsorption. The slope, and therefore the value of the adsorption/ partitioning coefficient, decreases as binding sites become saturated. The asymptotic line to this plot is the adsorption capacity of the adsorbate. The Langmuir isotherm can be applied to this type of behaviour. However, the Langmuir isotherm cannot be used to determine the adsorption capacity if the experimental data does not fall within the range where decrease of adsorption occurs.

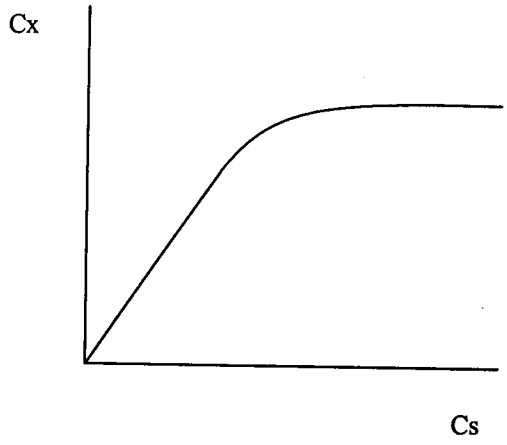


Figure 5.28: *L-type adsorption isotherm*

Another type of adsorption isotherm is the S-form, as shown in figure 5.29.

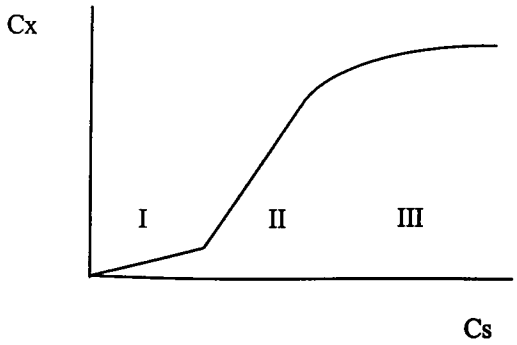


Figure 5.29: *S-type adsorption isotherm*

In this case, adsorption is progressively increased due to intermolecular attraction (Lawson et al 1984; USEPA 1999). In the first region of the graph (I), surface coverage is so sparse that adsorbed molecules cannot interact. Subsequently (II), adsorption is enhanced by the already bound molecules, until the binding sites start to get saturated and the slope starts to decrease again (III). Another explanation for the increased adsorption behaviour is associated with the competition between soluble ligands and the solids surfaces for binding of the metal ions. In the first region of the graph (I), adsorption occurs with competition from soluble ligands for complexation of metal ions. Thereafter (II), saturation of the soluble ligands leads to decreased competition for the metal ions, leading to increases in adsorption. Finally, saturation of the solids binding sites will result in a decrease in adsorption, until the adsorption capacity is finally reached (III).

However, if precipitation occurs before adsorption capacity, then the plot will have the following shape (figure 5.30).

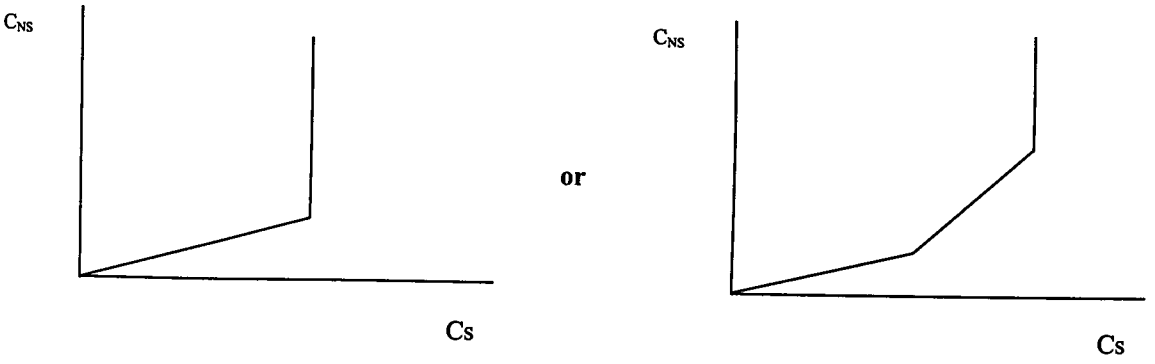


Figure 5.30: *Precipitation occurring before adsorption capacity is reached*

An alternative method of plotting these isotherms uses the values of non-soluble metal concentration and total metal concentration. In case 1, shown in figure 5.31(a) the solubility limit is reached before the adsorption capacity occurs. Thus if the adsorption capacity is reached, it will not be distinguishable since the precipitates are not differentiated from the adsorbed fraction. Figure 5.31(b) represents case 2, where the adsorption capacity is reached before precipitation occurs.

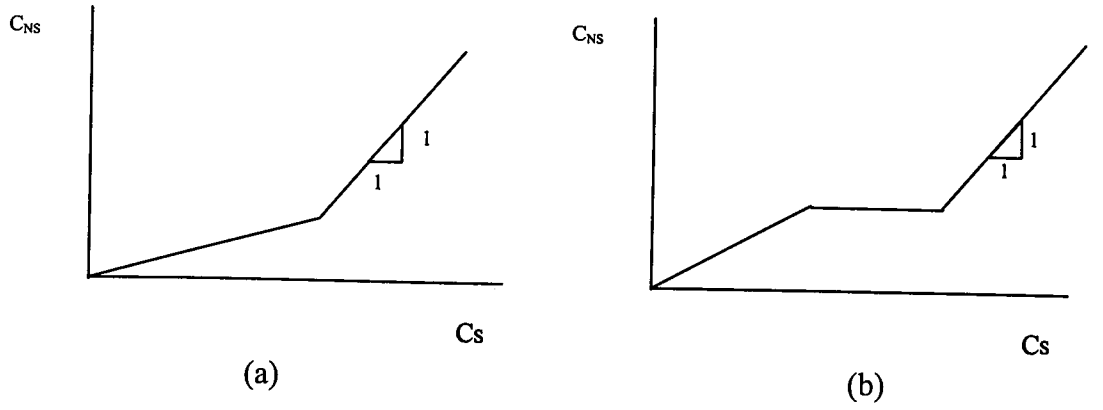


Figure 5.31: *(a) Case 1: solubility limit occurring before adsorption capacity*
(b) Case 2: adsorption capacity occurring before solubility limit

The parameter that most influences which case occurs is the pH. At lower pH values, the solubility limit is expected to be high and thus the adsorption capacity may occur before precipitation. While at higher pH values, the solubility limit may occur at quite low concentrations and thus before adsorption capacity is reached.

5.4.5.2 Parameters affecting metal removal from wastewater

The most important parameters affecting the processes of metal removal from wastewater have been found to be:

1. pH
2. solids concentration
3. the metal in question and its concentration as well as the presence of other metals
4. organic matter

The following discussion will provide an examination of how these parameters influence metal removal both singularly and interactively, with reference to the results of the adsorption experiments carried out in this research project as well as to the work of previous researchers.

pH:

The pH of the zero-point-of-charge of an adsorbant is the pH at which the surface of a material has a net surface charge of zero (USEPA 1999). In theory, an increase in pH results in more negative charge on the solids, thereby increasing cation adsorption

(McLean and Bledsoe 1992; USEPA 1999). Most of the results of the adsorption experiments agree with this, with the exception of the experiment on Cu in raw sewage. Adsorption was found to decrease with increasing pH (figure 5.12). However, this behaviour may be explained by the dissolution of dissolved organic matter at high pH. Enhanced concentrations of dissolved organic matter increasingly compete with the solids for complexation of the metals (Wang et al 1999, Grassi et al 2000). Another explanation of this phenomenon was given by McLean and Bledsoe (1992). They stated that at low pH, H^+ ions compete with the metal ion for complexation with the organic matter. As the pH increases, more of the metal can be complexed with dissolved organic matter and less was therefore adsorbed by the solids.

In the experiment studying Cu in final effluent, increased pH was shown to enhance adsorption, until a plateau was reached, where no further adsorption occurred with increases in pH (figure 5.15d). The plateau-type behaviour was also shown by Quek et al (1998) and Wang et al (1999). The level of the plateau reached also increased with increasing metal added concentration (from 70% at 2.5 mg/l Cu added to 90% at 10 mg/l Cu added). Thus the maximum adsorption ratio increases with increasing metal concentration.

Solids characteristics and concentration:

The size, nature and concentration of the solids determine the rates of adsorption and the resulting equilibrium conditions. More importantly, since adsorption is a surface phenomena, the rate and extent of adsorption are functions of the surface area of the solids used. For example, due to their high cation exchange capacity and high specific surface areas, increasing clay or organic matter content leads to an increase in adsorption. More rapid adsorption also takes place with smaller particles (O'Connor and Connolly 1980). The functional groups on the solid surface are also an important characteristic of the solids (Grassi et al 2000).

It would be expected that the concentration of solids in a solution would positively influence adsorption. The experiment on adsorption of Cu in primary effluent is the only exception to this principle (figure 5.13). Although there is no fundamental basis for this behaviour, O'Connor and Connolly (1980) also found that the results of a vast number of laboratory studies demonstrated an inverse relationship between

concentration of adsorbing solids and the adsorption / partitioning coefficient. Possible explanations for this unexpected behaviour have been given in the 1999 USEPA report on partitioning coefficients:

1. Particle interactions in systems with high solids content may result in blocking of some adsorption sites and thus cause a decrease in adsorption.
2. Individual particles in a solution with a high solids concentration may have a tendency to coagulate and flocculate into larger particles, which have less available adsorption sites than individual particles.
3. Adsorption onto colloidal solids and insufficient separation techniques, resulting in the colloidal particles staying in solution and thus the adsorbate associated with them is included in the analysis of the soluble phase.
4. Complexing agents (organic matter) may desorb or dissociate from the solids and in turn compete with the adsorbate for the available sorption sites. *However, in my view it is more likely that the dissociated organic matter competes with the solids for complexation of the adsorbate.*
5. The use of short-term laboratory measurements that do not allow sufficient time for the adsorbate to diffuse to the internal surface adsorption sites, and thus a final equilibrium state is not reached.

Another observation that has been made in many of the adsorption experiments (Cu in raw sewage, Cu in final effluent, Zn in raw sewage, Zn in primary effluent), shows that at a certain point for various pH values, any further increase in total metal does not cause an increase in soluble metal. This behaviour could indicate that either:

1. the solubility limit for Cu at that pH had been reached and thus precipitation is occurring; or that
2. the adsorption by the solids had suddenly reached 100%.

It is most likely that possibility (1) is occurring. However, these solubility limits are approximately 10 times less than those previously determined by the solubility limit experiments (section 5.3.4). In their studies, Nelson et al (1981) observed that for copper, precipitation in the unfiltered experimental reactors was observed (blue precipitate) during isotherm determinations at lower soluble concentrations than those observed in the filtered effluent experiments, for example at pH 7.0, Cu solubility in the unfiltered reactor effluent was found to be 6.6mg/l in comparison to 15 mg/l in the filtered samples. They concluded that nucleation sites on the solids and floc

enmeshment led to lower soluble values, although remaining supersaturated. Assuming that precipitation is occurring, the partitioning/adsorption coefficients can thus be derived by studying the first portion of the graph, where adsorption was the only mechanism for removal. However, the Langmuir model cannot be applied for these results.

Another possibility to account for the precipitation occurring at low metal concentrations could be due to the use of sulphate metal salts in the preparation of the stock metal solutions used in the experiments. If anaerobic conditions had occurred during the experiments, the metal sulphates would have been reduced to the highly insoluble metal sulphides and caused precipitation of the metals. However, to test this possibility, measurements of the redox potentials during the experiment would have been required. It may be beneficial to test this possibility in future experiments.

Metal concentration

Within the linear adsorption isotherm range, an increase in metal concentration increases adsorption. However, beyond the linear range, adsorption decreases with increasing metals concentration. Chen et al (1998) gave two explanations for this behaviour. Firstly, efficiency of metal ion sorption decreases as the metal ion concentration increases, since by increasing metal concentration, the total amount of sites available for sorption decreases. Also, the higher surface charge coverage enhances the activation energy for the sorption reactions, thereby making it more difficult for the surface to bind metal ions.

The only experiment, which shows a decrease in adsorption with increasing metal concentration is that of Cu in mixed liquor (figure 5.14). This could be attributed to the fact that metal concentrations were beyond the linear range of adsorption and that increasing metal concentration would result in decreased adsorption due to the decrease in binding sites available.

The results of some experiments (Cu in raw sewage and Cu in primary effluent) show two regions of adsorption rates, one low adsorption rate and one higher adsorption rate (figures 5.12 and 5.13 respectively). This increased adsorption at high metal

concentrations may be due to the saturation of dissolved organics binding sites, leading to increased complexation with the solids.

Metal in question

Metal characteristics also influence the removal behaviour. The extent to which a metal ion binds to a ligand largely depends on the chemistry of the metal ion and its preference to form ionic or covalent bonds. The strength of interaction between divalent transition metals and donor ligands is given by the Irving-Williams series, as follows: Mn(II)< Fe(II)< Co(II)< Ni(II)< Cu(II) > Zn (II) (Hughes and Poole 1991). Metals such as Co, Ni, Hg, Cu and Zn showed a preference for the N/S ligand group (Al-Hakawati 1998). It has also been noted that metals such as Cd and Zn do not form highly stable complexes with the dissolved organic matter, while Cu, Pb and Hg do (McLean and Bledsoe 1992). Therefore when competing with the solids for metal complexation, since Cu has a high affinity to soluble organics, the dissolved organic matter will preferentially complex with Cu and result in its desorption from the solids, but the same cannot be true for Zn. This can also explain the observation that in the experiments carried out in this research project the solubility limits of Cu were higher than those of Zn.

Competition between metals

Atkinson et al (1998) stated that speciation plays a significant role in adsorption processes in a mixed metal system. Ions with lower ionic radii are more easily adsorbed. While ions with similar ionic radii but higher ionic charge are more strongly attracted to the biomass. For ions of similar charge, the hydrated radius determines the order of preference, where ions with smaller radii being more easily adsorbed (Bux et al 1994).

It has been reported that the presence of Cu interfered with the adsorption of Zn and Cd in soils, while the adsorption of Cu was not affected significantly by added Zn (Kuo and Baker 1980 in McLean and Bledsoe 1992). The study by Sánchez et al (1999) showed that Zn uptake by a brown alga (*Cymodocea nodosa*) decreased in the presence of Cu. Similarly, Chong and Volesky (1995) showed that in the Cu-Zn system, the biosorbent (*Ascophyllum nodosum*) exhibited a net preference for the Cu ion over Zn and the presence of Zn did not significantly interfere with Cu adsorption. Other studies

(McBride and Blasiak 1979) found that Cu was ineffective in competing for Zn adsorption sites and thus it was concluded that Zn and Cu were preferentially adsorbed at different sites (McLean and Bledsoe 1992). Atkinson et al (1998) showed that adsorption of heavy metals by activated sludge in mixed metal streams occurs in a non-specific fashion, with preference shown towards those metals that are present in the greatest concentrations. However the method that they used for comparing adsorption of different metals is questionable. They compared the adsorbed metal concentrations of a range of metals as opposed to comparing the adsorption coefficients or percentages of removal. Since in their experiments Zn was originally added at the highest concentration, and exhibited the highest adsorbed concentration, they concluded that the competitive adsorption seemed to be more dependent on loading than on the chemical characteristics of the metals. The applicability of the results of the studies named above are limited for several reasons. Firstly, it can be seen that with the exception of the study by Atkinson et al (1998), the studies were carried out on non-wastewater adsorbents. These studies also focused on just one type of adsorbent. Wastewaters contain many different types of living matter, e.g. bacteria, fungi and algae, each containing different functional groups and thus different metal binding properties. Furthermore, these studies did not consider the effect of metal complexation with soluble ligands, which may be significant in the removal of metals from solution.

Due to the limitations of the experimental data in the competition experiments carried out in this research project, it was difficult to reach a definite conclusion as to the effect of each of the metals studied on the adsorption of the other.

Organic matter

The presence of complexing ligands (organic matter) on solids enhances adsorption onto the solids, whereas complexing ligands in solution form non-adsorbable metal complexes and hence keep the metal in solution. The organic matter associated with the solids fraction can be related to the volatile suspended solids (VSS) concentration. The dissolved organic matter (DOM) can be represented by two fractions:

(1) DOM initially in raw sewage, either from organic pollutants such as detergents, etc. or biological waste; and

(2) (2) DOM that was originally associated with the solids.

The amount of DOM can be expected to decrease through the action of biological treatment processes. However, at the same time, the volatile suspended solids concentration increases due to the formation of biomass. An increase in pH can then lead to dissociation of some of the organic matter from the solids, resulting in an increase in DOM, which will then be able to compete with the solids fraction for complexation of the metal ions. Therefore the DOM must be related to the influent soluble substrate concentration as measured by COD/ TOC, pH and the VSS concentration. Samples of the filtered process streams used in the solubility and adsorption experiments had been acidified and refrigerated for soluble organic carbon analysis. These included samples of the original unfrozen samples and samples that had been frozen and thawed for use in the experiments.

Table 5.6: *Results of Soluble Organic Carbon Analysis*

Sample	Average Soluble Organic Carbon (mg/l)
Raw Sewage Initial (16/6)	47.23
Raw Sewage thawed (19/6)	34.17
Raw Sewage thawed (20/6)	36.99
Raw Sewage thawed (21/6)	34.23
Raw Sewage thawed (23/6)	32.50
Raw Sewage thawed (27/6)	64.49
Raw Sewage thawed (28/6)	75.31
Raw Sewage thawed (30/6)	77.92
Primary Effluent (4/7)	22.27
Mixed Liquor (4/7)	13.55
Final Effluent (4/7)	8.92
Final Effluent thawed (5/7)	9.14
Final Effluent thawed (6/7)	8.44
Final effluent thawed (11/7)	31.57
Primary Effluent (20/11)	156.10
Mixed Liquor (20/11)	0.64

The results show that there are significant variations in the concentrations of soluble organic carbon from the same sample used at different times. This most likely indicates that the original sample had not been homogenised well. However, in general it can be seen that the concentrations of soluble organic carbon in mixed liquor and final effluent are lower than those for raw sewage and primary effluent. Thus as expected, metal precipitation in final effluent samples occurs at lower concentrations than in the other process streams.

It is recognised that freezing of the samples may cause cell lysis, which results in the release of cellular material into solution (Hunt and Wilson 1986). This could account for the increase in the concentration of soluble organic carbon in the thawed samples. Yet, it was necessary to freeze the samples used in these experiments to ensure consistency in the composition of the samples and reduce the variability associated with sampling at different times. Since all samples that were used for experimentation were previously frozen and thawed, this reduces the variation in the dissolved organic matter content since all samples will have undergone some degree of cell lysis. This is considered a limitation of the experimental technique, since it results in a higher concentration of DOM than would normally occur and may thus result in a higher estimate of metal complexation with the DOM. This could in turn lead to the prediction of solubility limits that are higher than those that occur under natural conditions. Likewise, it may also lead to an under-estimation of the degree of adsorption, since during the experiments there is enhanced competition with the DOM.

5.4.6 Summary

The results of the experiments on the solubility and adsorption of metals in wastewater carried out as part of this project provide an in depth understanding of the processes and parameters affecting the fate of metals in municipal wastewater treatment. In the solubility limit experiments, it has been shown that due to the presence of soluble ligands, considerable amounts of metals may be present in solution without precipitating. However, due to the presence of suspended solids, metals are removed from solution both by sorption onto the solids and by precipitation induced by the nucleation provided by the solids. The extent of metal removal from solution is governed by critical parameters as described above. These interactions are shown schematically in figure 5.32.

Calibration of the metals model was another purpose of the experiments carried out in this study. It was anticipated that correlation relationships would be derived to enable the model coefficients to be calculated for a given set of conditions. While, it was possible to obtain some of these relationships, it is recommended that further studies be carried out to determine a complete set of relationships for a given WWTP.

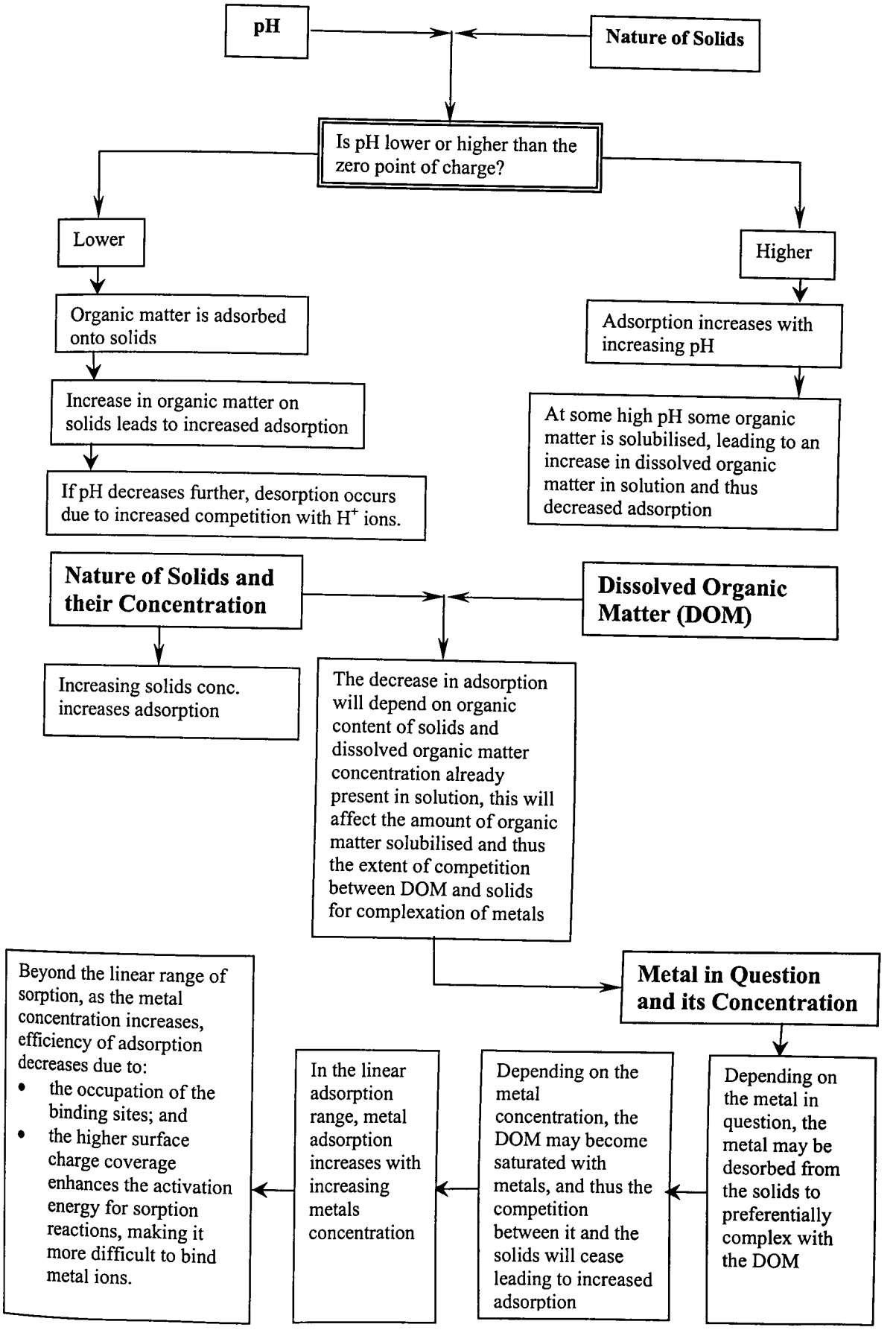


Figure 5.32: *Interactions between parameters affecting metal removal from wastewaters*

CHAPTER SIX

MODEL VERIFICATION

6.1 Introduction

The previous chapters have shown the stages of the development and calibration of the predictive metals model. This chapter will detail the field data collection studies carried out to verify the model set-up and outputs. The aim of the field studies carried-out as part of this project was to collect data on the partitioning of metals and solids throughout an actual wastewater treatment plant (WWTP). This data would be used to compare the values generated by the developed mechanistic model, given the plant's operating conditions. In addition, this data would be used to derive the correlations between the solids removal and flow, metals removal and flow, metals removal and influent metals concentration and metals removal and solids removal.

6.2 Millbrook WWTP Field Study

The first field study was carried out at Millbrook wastewater treatment plant. Millbrook WWTP is the major treatment works in the city of Southampton, England. It receives and treats wastewater from a domestic population of 138,000 plus trade effluents equivalent to a population of 20,000. At the works, the wastewater undergoes screening, grit removal, primary settlement and biological treatment (activated sludge). The sludge produced from the treatment processes, as well as sludge imported from other wastewater treatment plants in the area, is then treated in the new on-site sludge treatment centre, where it undergoes thickening, anaerobic digestion, centrifuge dewatering and thermal drying. The final product is an organic-based fertiliser and soil conditioner. The liquors from the sludge treatment processes are treated in a sequencing batch reactor (SBR) before being returned to the head of the works. The flow diagram for the WWTP is shown in figure 6.1

This study took place in July-August 1999.

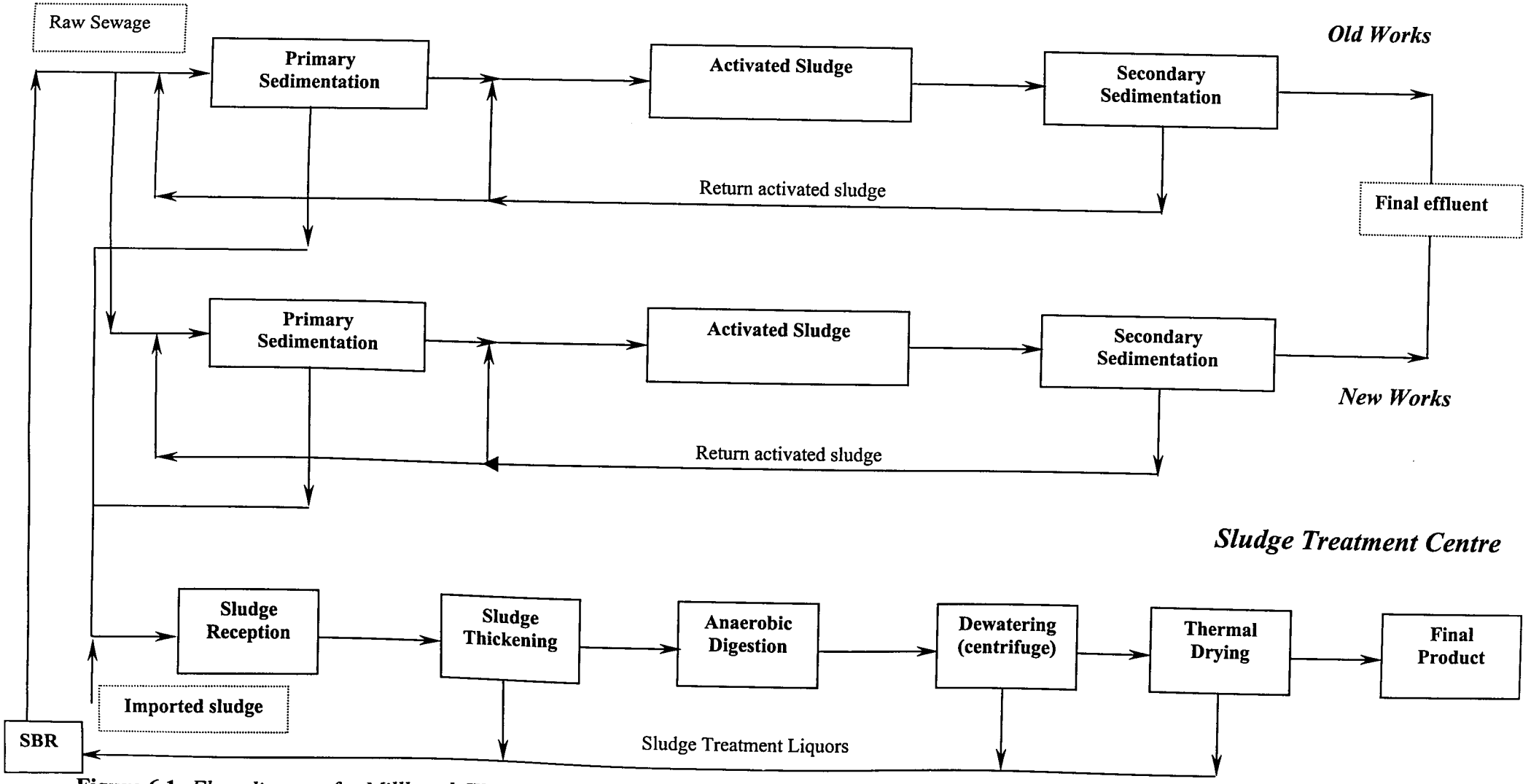


Figure 6.1: *Flow diagram for Millbrook WWTP*

6.2.1 Procedure

The field study at Millbrook WWTP was originally intended to provide mass balance data for the solids and metals (Cu, Zn and Pb) throughout the WWTP, in order to allow the development of an empirically-based model, similar to that developed by Patterson et al (1983). Using two portable autosamplers (American Sigma Corp. Streamline 800SL, USA), the procedure for sampling involved taking hourly samples (250ml) for a period of 24 hours at the inlet and outlet of one treatment process at a time. Subsequently the autosamplers would be placed at the outlet of the process and the inlet of the next treatment process. Sample preservation during the sampling process was achieved by placing 1 ml of concentrated HNO_3 into the 250 ml sampling bottle, so that the sample would be acidified as soon as it was collected. The next day, the samples were be emptied into other bottles and taken back to the lab for filtration. Spot samples were also taken from sludge treatment processes at the following points:

1. Indigenous primary/ co-settled sludge
2. Imported Slowhill sludge
3. Thickened sludge
4. Digested sludge
5. Centrifuge cake
6. Final Product.

These samples were placed in crucibles and dried in an oven at 105°C overnight.

6.2.2 Problems Encountered

Two weeks after starting this field study, the objectives were re-assessed and the procedure altered. This was due to the problems that were encountered; namely, major faults with the auto-sampling equipment and problems with obtaining accurate flow data from the on-site flow meters. Therefore, it was decided that instead of attempting a mass balance, the aim of the field study would be to collect data to allow a correlation to be derived between the metal and VSS concentrations throughout the plant. This would eliminate the need for flow data. Therefore, the new procedure involved taking spot samples (250ml) from each process influent and effluent in both the new and old works on a daily basis for 10 days. In addition, sludge and supernatant samples from the Sludge Treatment Centre, were also taken. Each day the samples were collected from 8:30-9:30 A.M. In the laboratory, the pH of each sample was measured and each sample was divided into 100 ml (for TSS and VSS analysis and soluble metal analysis using the AAS, see section 5.1.3 and 5.1.4) and 150ml (centrifugation and acid digestion of the resultant solids for total metal analysis). The filtration was carried out

using Whatman™ GF/C filters. The filtrates were acidified to a pH <2 by adding HNO_3 and analysed on the AAS. The sludge samples were dried and acid digested using the closed tube method.

1. Crude sewage + Returned sludge liquors
2. Influent into primary tank (old works)
3. Primary effluent (old works)
4. Influent into aeration tanks (old works)
5. Mixed liquor (old works)
6. Final effluent (old works)
7. Influent into primary tank (new works)
8. Primary effluent (new works)
9. Influent into aeration tanks (new works)
10. Mixed liquor (new works)
11. Final effluent (new works)
12. Return Activated Sludge (old works)
13. Return Activated Sludge (new works)
14. Thickener supernatant
15. Centrifuge supernatant
16. SBR influent
17. SBR supernatant
18. Primary sludge
19. Slowhill Sludge
20. Inlet to thickeners
21. Thickened sludge
22. Digested sludge
23. Centrifuge cake

6.2.3 Results & Findings

Soluble Metal Concentrations

The results from this two-week field study are shown in Appendix D (table D.1). However, it can be seen that the concentrations of the metals being considered are extremely low. The measurements of Cu and Pb were in the range of 0.002-0.005 mg/l, which is outside the operating range of the AAS. Only the soluble concentration of Zn was within the range of determination of the AAS. However, it later transpired that even for Zn, the samples had been contaminated, since the samples were filtered using GF/C paper, which was discovered to severely contaminate samples with Zn (May 2000), see section 5.1.3. Therefore only the data for solids can be used from this field study. The Zn concentrations in the acid-digested samples of sludge were also of value.

Results from Sludge Treatment Centre Samples:

Sludge samples were taken across the Sludge Treatment Centre. Closed-tube acid extractions were carried out on these samples to determine the total metal concentrations as shown in table 6.1.

Table 6.1: *Total concentrations of Zn (mg/kg) in Sludge Treatment Centre samples*

Day	Millbrook Primary Sludge	Imported Slowhill Sludge	Inlet to Sludge Thickeners	Thickened Sludge	Digested Sludge	Centrifuge Cake
09-Aug	492.59	41034.97	637.22	903.76	2539.25	927.66
10-Aug	644.24	26362.16	714.96	819.06	1368.47	707.14
11-Aug	728.90	37406.19	1105.87	721.39	1547.68	753.23
12-Aug	559.95	37826.48	919.96	860.75	1563.74	736.92
13-Aug	678.25	48185.22	704.26	645.55	1362.07	718.44
16-Aug	594.11	42575.25	807.35	843.82	897.74	819.60
17-Aug	606.50	44131.86	764.99	850.25	1483.68	868.25
18-Aug	814.93	48233.11	583.66	625.34	2752.90	773.69
19-Aug	1064.56	31673.43	666.94	704.04	1629.38	Not determined
20-Aug	757.95	56730.27	701.81	833.63	1644.42	791.82
Average	694.20	41415.89	760.70	780.76	1678.93	788.53

Slowhill Copse Sludge

The most important observation obtained from these results related to the concentrations of Zn in the imported Slowhill sludge. It was found that the concentrations of Zn within these samples were consistently within the range of 26000-57000 mg/kg, with an average concentration of 41416 mg/kg. It was decided to investigate the origin of these exceedingly high levels of Zn. The Slowhill sludge consists of sludge generated by Slowhill Copse WWTP in Marchwood, as well as sludge from Portswood and Woolston WWTPs and sludge from plants serving mainly residential areas in the New Forest. All these sludges are consolidated at Slowhill Copse WWTP before being pumped via pipeline to Millbrook Sludge Treatment Centre. Portswood and Woolston WWTPs are the only two plants, which receive a relatively high proportion of industrial effluent. A site visit to each of these plants was carried out at the end of September and the beginning of October 1999. Samples taken at these two site visits did not show any high concentrations of Zn. However, the records obtained from the trade effluent group at Southern Water Plc, showed that over the period of a year (1998), levels of Zn at Portswood WWTP ranged from 395-17600

mg/kg. The Ford Motor Company at Eastliegh is one of the major industrial dischargers to Portswood WWTP. Their Environmental Officer was contacted to see if he could offer any explanation as to the high levels of Zn. I was informed that throughout the year, the effluent from the Ford plant is continuously discharged during working hours, however this discharge is limited to 4 mg/l for Zn. However, the Zn sludge tanks are cleaned 2-3 times a year, and according to him, this may cause a peak in the concentrations of Zn being discharged. Therefore, it was concluded that Portswood WWTP is the plant that receives a high concentration of Zn. This was important in terms of our work since variations in the influent metal concentrations are needed in order to produce correlations between the metal concentrations and factors affecting its behaviour, such as VSS concentration and pH. Liasing with Ford Motor Company, it was found that the Zn sludge tanks were due to be cleaned in the week of 31 July 2000. It was thus decided to carry out the field study at Portswood WWTP at that time.

6.3 Portswood WWTP Field Study

Portswood WWTP serves a population equivalent of approximately 70,000, of which, 7000 is trade effluent. At the works, two primary tanks and two aeration lanes (followed by 4 secondary sedimentation tanks) are used to treat the wastewater. Figure 5.2 shows the flow diagram of plant.

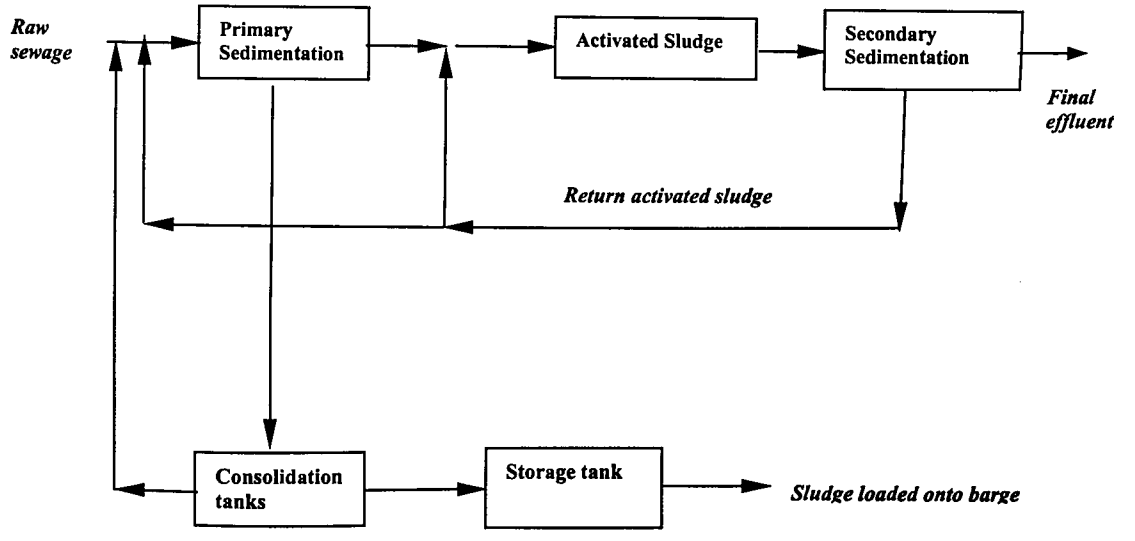


Figure 5.2: *Flow Diagram for Portswood WWTP*

6.3.1 Preparations:

Flow Measurement:

Ultrasonic sensors (Massa Corporation,MassaSonic M-5000/95, USA) , which measure depth, were installed at the inlet flume of one of the aeration tanks as well as at the returned activated sludge flume for that aeration tank. Figure 6.3 shows the placement of the ultrasonic sensor in the flume. The measurements taken by these sensors was downloaded on to a portable PC and converted to flow readings by calibrating the sensor against a flow sensor already installed at the plant, as shown in figure 6.4.

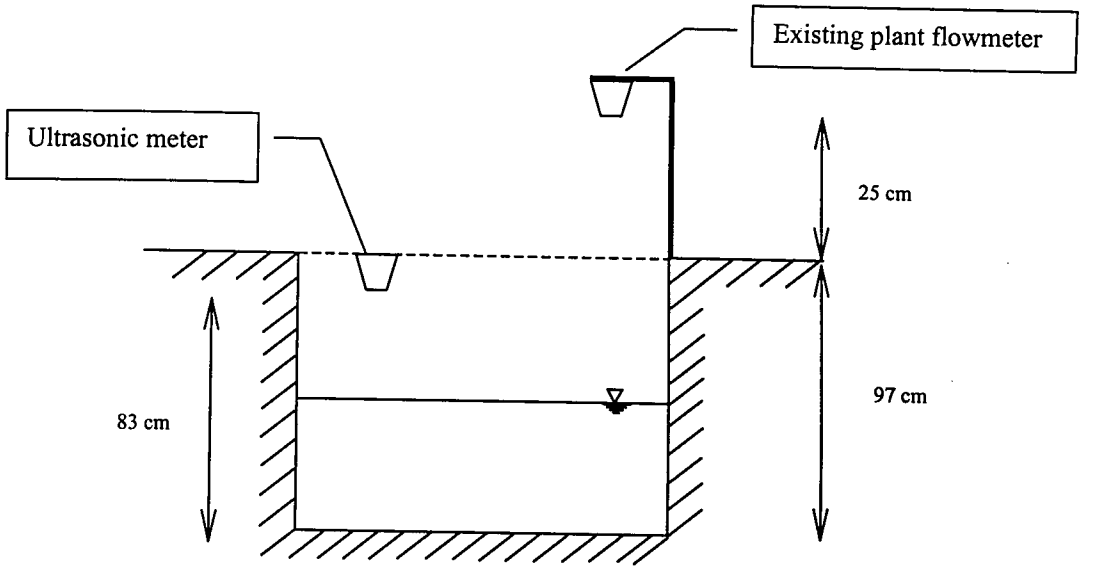


Figure 6.3: *Placement of ultrasonic sensor in flume*

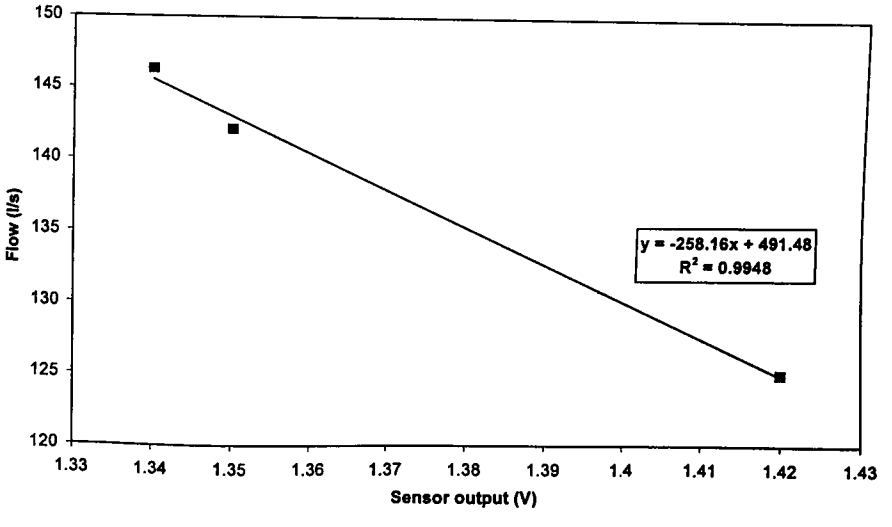


Figure 6.4: *Calibration of ultrasonic sensor*

Background Metal Concentrations:

A week before the actual expected slug discharge was due, samples were taken across the plant over a 24-hour period using the portable autosamplers. This was to determine the metal content in the plant prior to the discharge. After the samples were collected, they were filtered (for TSS analysis) and centrifuged (to obtain solids for acid digestion to determine the total metal content). Due to problems again with the autosamplers and problems with the drying of the centrifuged samples, only a few of the mixed liquor samples could be analysed for total metal content. A sample of primary sludge was also obtained and dried for acid digestion to determine the total metal content. The average concentration of Zn in the sludge was found to be 392 mg/kg, while the average concentration of Cu was 358 mg/kg.

6.3.2 Field Study 31 July-3 August 2000

6.3.2.1 Sample Collection

The retention times were calculated using the dimensions of the tanks and the average dry weather flows provided by the plant operators. These were used to develop the following timetable for manual sampling.

Table 6.2: *Sampling timetable for Portswood Field Study*

Time	Sample
8:30	RS
9:30	RS
10:30	RS
11:30	RS, PE
12:30	RS, PE
13:30	RS, PE
14:30	RS, PE, ML
15:30	RS, PE, ML
16:30	RS, PE, ML
17:30	PE, ML
18:30	PE, ML
19:30	PE, ML
20:30	ML, RAS, FE

Notes:
RS: raw sewage, sampled from the detritor tank
PE: primary effluent, sampled from the effluent weir of primary sedimentation tank No. 2
ML: mixed liquor, sampled from aeration lane No.2
RAS: returned activated sludge, sampled from the activated sludge channel on aeration lane No. 2
FE: final effluent, sampled from the effluent weir of one of the secondary sedimentation tanks

In addition to the manual sampling, carried out for 12 hours, auto-sampling was also used to obtain samples of mixed liquor and final effluent, over the time period when manual sampling was not possible (from 21:30-7:30). These samples were acid digested to determine the total metal concentrations in them. This was done mainly to track the expected slug of Zn across the treatment plant.

Preparation of the sampling equipment was conducted per the recommendations of the UK Standing Committee of Analysts' General Principles for Sampling Waters (DoE 1996) and the recommendations of Hunt and Wilson (1986). In particular, the recommendations with respect of the following aspects were adhered to:

1. Choice of locations to obtain representative samples of the wastewater streams of interest.
2. Choice and preparation of sample containers to avoid any contamination of the sample.
3. Sample preservation and treatment techniques, to prevent any chemical, physical or biological processes, which can lead to changes in the composition of the samples.

The objective of this field study was to collect data regarding the partitioning of Zn and Cu in different wastewater process streams. Therefore the concentration of soluble vs. solids bound metal at different total metal and VSS concentrations would need to be known. It was recommended that where dissolved forms of metals were to be determined, the sample should be filtered through a 0.45-μm membrane filter and acidified to pH< 2, by adding HCl, to prevent any adsorption of metals by the containers. Acidification was carried out after filtration to prevent the dissolution of colloidal and particulate metals, thus resulting in invalid data for the soluble metals.

A mini-lab was set-up on-site to preserve the samples collected for later analysis. After sampling from the required points, the samples were taken back to the mini-lab for treatment as follows:

- For soluble metal analysis: Filter 50 ml through membrane filter, acidify filtrate with 0.1ml HCl.
- For total metal analysis: Acidify 250ml of sample with 0.5ml HCl.
- For TSS analysis: Filter 100ml of sample through pre-weighed GF/C filter.

In addition, samples of primary sludge, from the storage tank, were taken on 31 July and 4 August. In the Departmental laboratory, the mixed liquor and return activated sludge samples were centrifuged and placed in crucibles for drying in the oven. These samples and the liquid samples were set aside for total metal analysis after acid digestion.

6.3.2.2 Sample Analysis

Soluble Metal

The soluble samples were analysed directly on both the AAS and the HPLC. However, it was found that the concentrations in the samples were considerably lower than expected. For Zn, the range of concentrations was 0.03-0.2 mg/l. Full results are shown in Appendix D (tables D.2-D4).

Acid Extraction of Sludge-Bound Metals:

Extraction of total metals in the dry solid samples and the liquid samples was achieved using a microwave assisted acid digestion method (CEM Corporation, MARS-X, Matthews, NC, USA). For the soluble samples, an acid leach of the metals was accomplished by adding 5 ml of HNO_3 to 45 ml of the liquid sample and heating the sample for 35 minutes at 90°C using 50 ml polypropylene high-throughput vessels (Corning, USA). If there was any loss due to evaporation, the sample was brought back up to 50ml with deionised water. Acid extraction of the metals from the dry solid samples was also carried out using the high-throughput vessels. In this case, 0.1-0.2g of the dried solids was acid digested using 10ml of HNO_3 and ramping the temperature to 105°C over a 15 minute period and holding for a further 20 minutes. To determine the percentage of metals extracted using this method and comparing it with the closed tube acid digestion method previously used (as described in chapter 5), a standard reference material of activated sludge with known concentrations of metals (LGC6136) was acid digested using the two methods. The acid digestion was carried out in triplicate using both methods. The results and statistical analysis are shown in table 6.3.

Table 6.3: *Comparison of two acid extraction methods using a standard reference material (LGC6136)*

Acid Extraction	**Cu (mg/kg)**				
Sample	1	2	3	Average	Std Dev (%)
Closed tube method	567.36	519.51	553.49	546.79	4.50
Microwave-assisted method	564.87	576.56	589.04	576.82	2.10
Reference material total concentration	480				

Acid Extraction	**Zn (mg/kg)**				
Sample	1	2	3	Average	Std Dev (%)
Closed tube method	854.09	907.88	884.89	882.29	3.06
Microwave-assisted method	872.94	952.82	1004.50	943.4	7.03
Reference material total concentration	850				

6.4 Results and Discussions

6.4.1 Analysis of results

The results for each process stream taken over the four days of sampling were combined. The solids bound metal concentration was taken to be the difference between the total extracted metal concentration and the soluble metal concentration. Based on these analyses and calculations, plots of C_T (mg/kg) vs. C_X (mg/l) and Langmuir plots were produced. These are shown in figures 6.5-6.10.

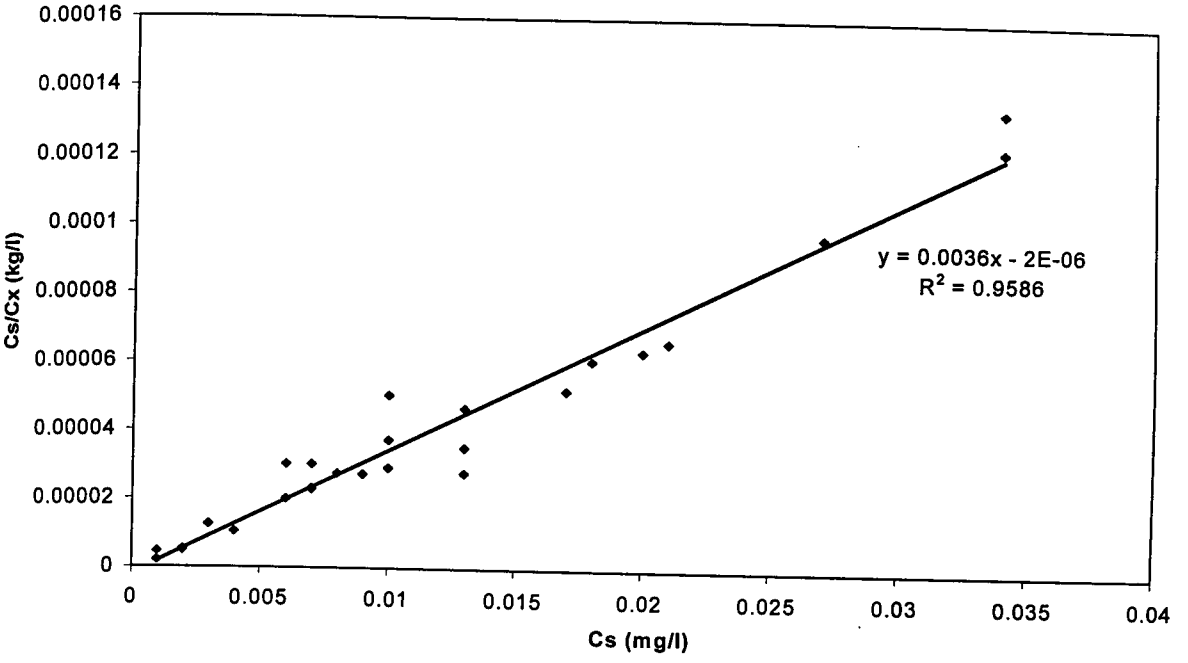


Figure 6.5: *Langmuir isotherm for Cu in raw sewage at Portswood WWTP*

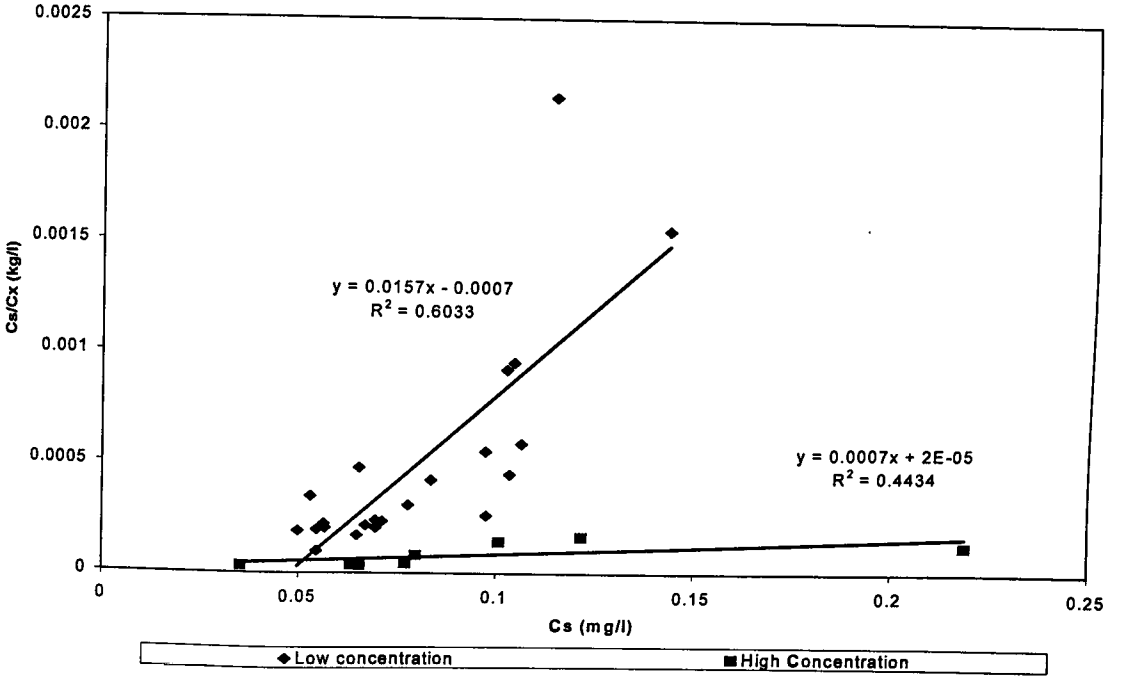


Figure 6.6: *Langmuir isotherm for Zn in raw sewage at Portswood WWTP*

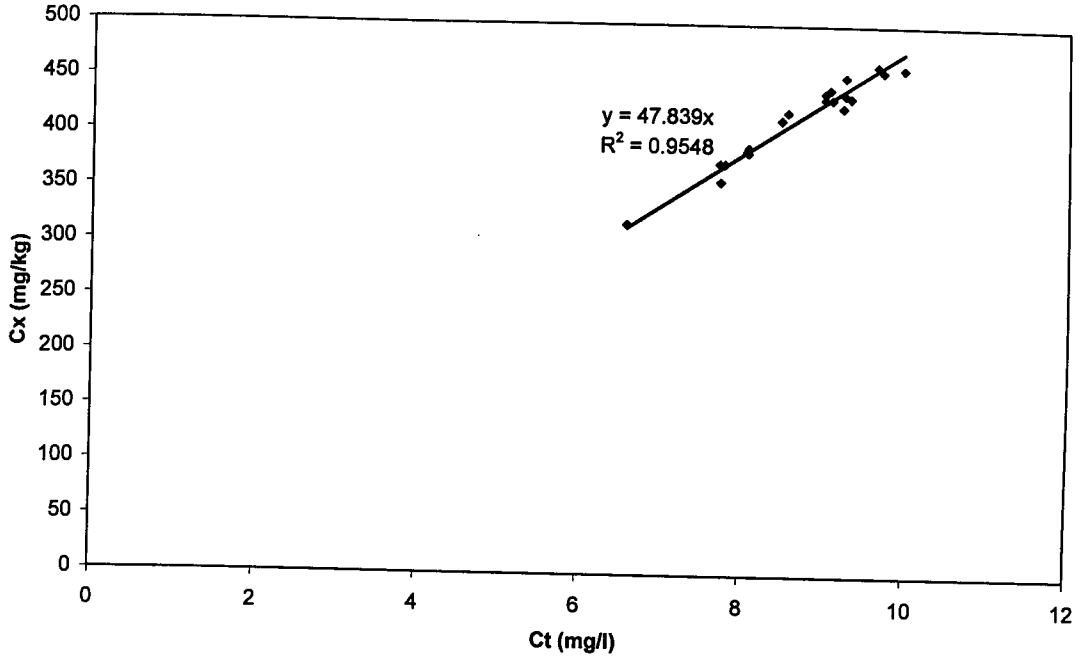


Figure 6.7: *Cu concentrations in mixed liquor at Portswood WWTP*

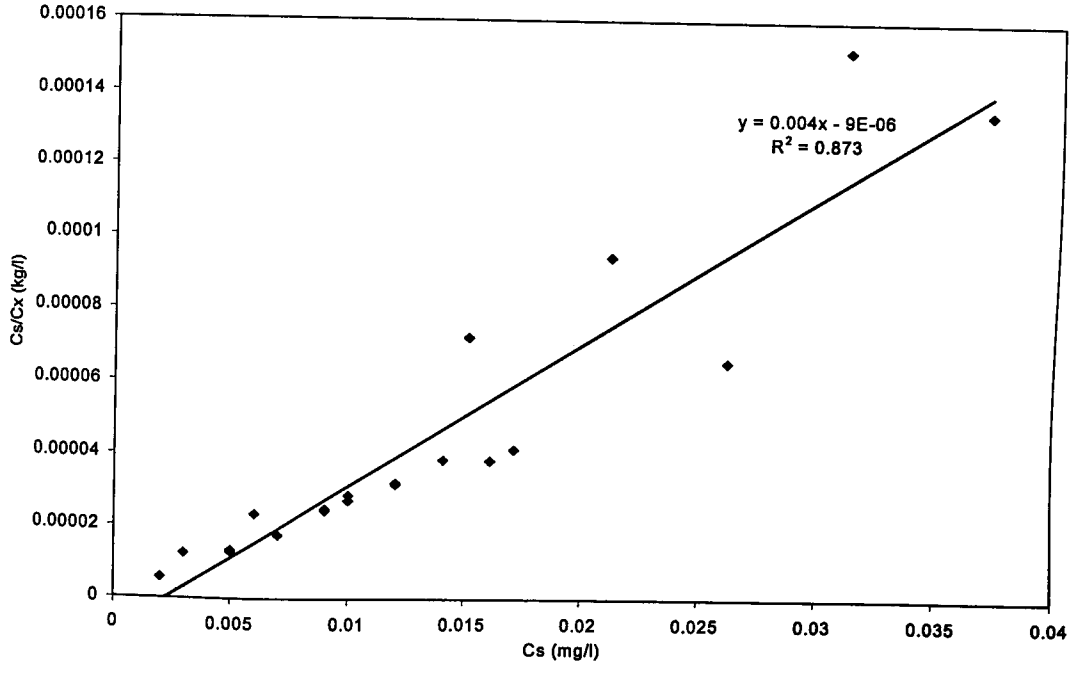


Figure 6.8: *Langmuir isotherm for Cu in mixed liquor at Portswood WWTP*

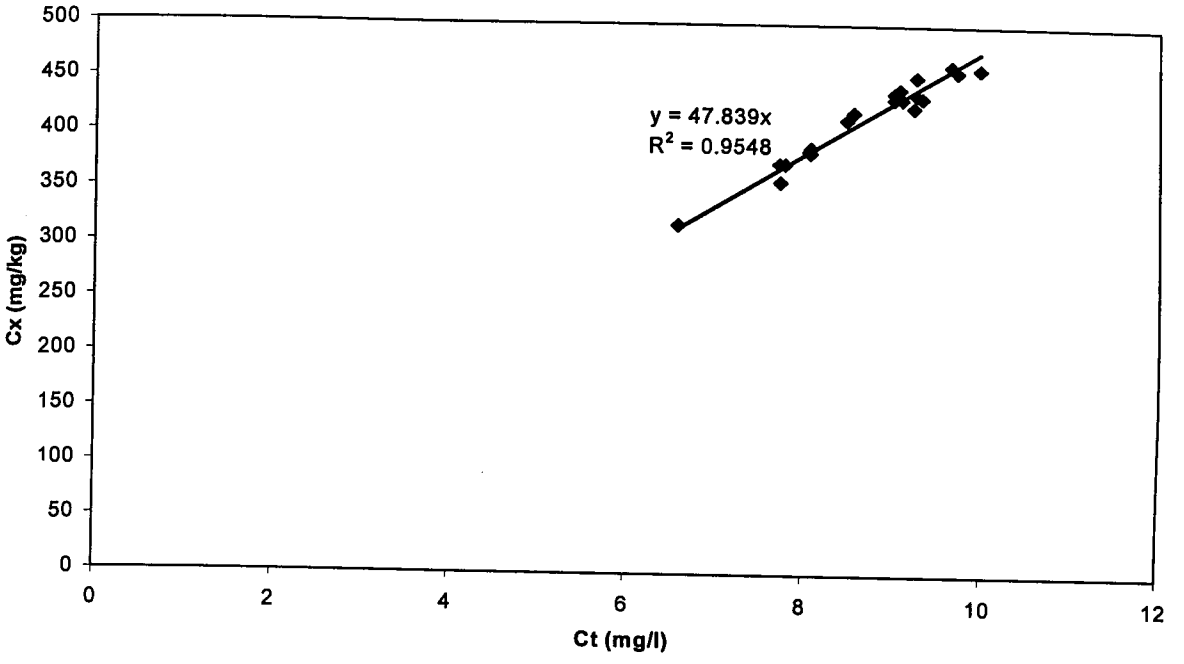


Figure 6.9: *Zn concentrations in mixed liquor at Portswood WWTP*

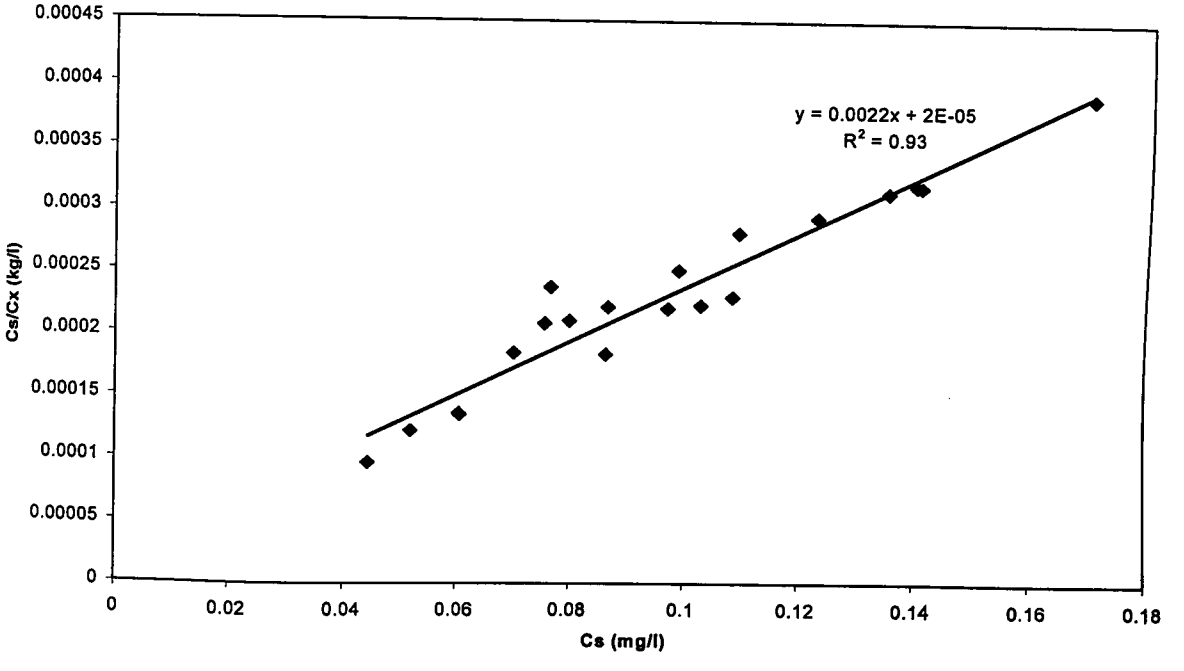


Figure 6.10: *Langmuir isotherm for Zn in mixed liquor at Portswood WWTP*

The Langmuir plots (figure 6.5, 6.6, 6.8 and 6.10) can be used to predict the adsorption capacities of Cu and Zn in both raw sewage and mixed liquor. These are shown in table 6.4.

Table 6.4: *Adsorption capacities derived by applying the Langmuir Isotherm to field data*

Process Stream	Cu adsorption capacity (mg/kg)	Zn adsorption capacity (mg/kg)
Raw Sewage	278	Low conc.: 81 High conc.: 1430
Mixed Liquor	250	455

The adsorption coefficients in each process stream were calculated using the following equation:

$$Kp = \frac{\frac{C_T}{C_S} - 1}{X}$$

where,

K_P = adsorption coefficient (l/mg); X = volatile suspended solids concentration (mg/l)

C_S = soluble metal concentration (mg/l); C_T = total metal concentration (mg/l)

The adsorption coefficients in each process stream were found to be highly variable. Table 6.5 shows the average values.

Table 6.5: *Adsorption coefficients of Cu and Zn (l/kg) derived from the field data*

Process Stream	Cu	Zn
Raw Sewage	181000	61000
Primary Effluent	51232	2100
Mixed Liquor	557300	59300
Final Effluent	11837	8815

Comparison between experimental and field model coefficients

It can be seen from the values in table 6.4 that the adsorption capacities derived from the field data are considerably lower than those derived from the laboratory batch experiments, while on the other hand the field adsorption coefficients (shown in table 6.5) were markedly higher than the experimentally-derived ones, as shown in tables 5.2 and 5.3. A possible explanation of this discrepancy may be the fact that the batch

experiments were conducted on wastewater samples, which had been frozen and thawed. It has been discussed in section 5.4.5.2 that sample preservation through freezing changes the nature of the suspended solids in the original wastewater sample. The freezing process may cause cell lysis, with the subsequent release of organic matter into solution. This increases the DOM concentration during experimentation, which can lead to an overestimation of the solubility limit as well as an underestimation of adsorption due to enhanced competition with the DOM for complexation with the metal ions. Freezing may also cause the suspended solids to separate into smaller sized particles, thereby increasing the surface area available for adsorption. This could account for the higher adsorption capacities derived from the experimental data compared to the field data.

Moreover, in the analysis of the field data it was impossible to differentiate between metals bound to solids through adsorption and precipitated metal, which had become associated with the solids. Thus both fractions were taken into account in the derivation of the field adsorption coefficients.

6.4.2 Mass Balance Calculations

In this study, the retention times at each process in the treatment plant were calculated using the plant data provided by Southern Water Plc. These were calculated to be:

- Primary sedimentation: 3.5 hrs
- Aeration: 6 hrs
- Final sedimentation: 2 hrs

Thus, it was found that one mass balance of the solids and metals across the whole plant may be carried out on the samples collected each day. The concentration in the sample taken at 8:30 can be related to the concentration in the primary effluent in the sample taken at 11:30, the mixed liquor samples taken at 17:30 and the sample in the final effluent taken at 20:30.

The calculations for the mass balance of Cu and Zn in primary and secondary treatment are shown in tables 6.6-6.8. The load in the influent and effluent of each treatment process were compared to determine the removal of the total, soluble and solids-bound fraction of each metal. A final mass balance calculation was carried out on the secondary treatment data by comparing the primary effluent metal load (as an influent stream) and the load in the final effluent and waste activated sludge, WAS (as the effluent streams).

Table 6.6: *Removal of Cu and Zn in primary sedimentation at Portswood WWTP*

(a) Total Metal Concentrations:

Cu:

Day	Flow at 8:30 (l/sec)	Raw Sewage total Cu (mg/l)	Load into primary sedimentation (mg/sec)	Flow at 11:30 (l/sec)	Primary Effluent total Cu (mg/l)	Load in Primary Effluent (mg/sec)	Removal during primary sedimentation (%)
31-7-00	106.822	2.08	222.186	137.80	0.065	8.957	95.97
1-8-00	106.822	0.121	12.925	124.89	0.018	2.248	82.61
2-8-00	106.822	0.129	13.780	127.47	0.073	9.306	32.47

Zn:

Day	Flow at 8:30 (l/sec)	Raw Sewage total Zn (mg/l)	Load into primary sedimentation (mg/sec)	Flow at 11:30 (l/sec)	Primary Effluent total Zn (mg/l)	Load in Primary Effluent (mg/sec)	Removal during primary sedimentation (%)
31-7-00	106.822	7.18	766.967	137.80	0.090	12.457	98.38
1-8-00	106.822	0.191	20.435	124.89	0.091	11.377	44.32
2-8-00	106.822	0.206	22.026	127.47	0.087	11.090	49.65

(b) Soluble metal concentrations:

Cu:

Day	Flow at 8:30 (l/sec)	Raw Sewage soluble Cu (mg/l)	Load into primary sedimentation (mg/sec)	Flow at 11:30 (l/sec)	Primary Effluent soluble Cu (mg/l)	Load in Primary Effluent (mg/sec)	Removal during primary sedimentation (%)
31-7-00	106.822	0.027	2.884	137.80	0.029	3.996	-38.56
1-8-00	106.822	0.007	0.748	124.89	0.018	2.248	-200.64
2-8-00	106.822	0.010	1.068	127.47	0.016	2.040	-90.94

Zn:

Day	Flow at 8:30 (l/sec)	Raw Sewage soluble Zn (mg/l)	Load into primary sedimentation (mg/sec)	Flow at 11:30 (l/sec)	Primary Effluent soluble Zn (mg/l)	Load in Primary Effluent (mg/sec)	Removal during primary sedimentation (%)
31-7-00	106.822	0.080	8.503	137.80	0.070	12.457	-13.93
1-8-00	106.822	0.057	6.035	124.89	0.062	11.377	-27.26
2-8-00	106.822	0.056	6.003	127.47	0.076	11.090	-61.80

(c) Solids-bound metal concentrations

Cu:

Day	Flow at 8:30 (l/sec)	Raw Sewage solids bound Cu (mg/l)	Load into primary sedimentation (mg/sec)	Flow at 11:30 (l/sec)	Primary Effluent solids bound Cu (mg/l)	Load in Primary Effluent (mg/sec)	Removal during primary sedimentation (%)
31-7-00	106.822	2.053	219.302	137.80	0.036	4.961	97.74
1-8-00	106.822	0.114	12.178	124.89	0.054	6.744	44.62
2-8-00	106.822	0.119	12.718	127.47	0.057	7.266	42.84

Zn:

Day	Flow at 8:30 (l/sec)	Raw Sewage solids bound Zn (mg/l)	Load into primary sedimentation (mg/sec)	Flow at 11:30 (l/sec)	Primary Effluent solids bound Zn (mg/l)	Load in Primary Effluent (mg/sec)	Removal during primary sedimentation (%)
31-7-00	106.822	7.100	758.465	137.80	0.020	2.770	99.64
1-8-00	106.822	0.135	14.400	124.89	0.030	3.697	74.33
2-8-00	106.822	0.150	16.023	127.47	0.011	1.377	91.41

Table 6.7: *Removal of Cu and Zn in secondary treatment at Portswood WWTP*

(a) Total Metal Concentrations:

Cu:

Day	Flow at 20:30 (l/sec)	Final Effluent total Cu (mg/l)	Load in final effluent (mg/sec)	Removal during secondary sedimentation (%)
31-7-00	130.506	0.008	1.040	88.38
1-8-00	124.893	0.022	2.748	-22.23
2-8-00	215.249	0.006	1.291	86.12

Zn:

Day	Flow at 20:30 (l/sec)	Final Effluent total Zn (mg/l)	Load in final effluent (mg/sec)	Removal during secondary sedimentation (%)
31-7-00	130.506	0.025	3.212	74.21
1-8-00	124.893	0.048	5.982	47.42
2-8-00	215.249	0.045	9.751	12.08

(b) Soluble metal concentrations:

Cu:

Day	Flow at 20:30 (l/sec)	Final Effluent soluble Cu (mg/l)	Load in final effluent (mg/sec)	Removal during secondary sedimentation (%)
31-7-00	130.506	0	0	100
1-8-00	124.893	0.008	0.999	55.55
2-8-00	215.249	0.002	0.430	78.89

Zn:

Day	Flow at 20:30 (l/sec)	Final Effluent soluble Zn (mg/l)	Load in final effluent (mg/sec)	Removal during secondary sedimentation (%)
31-7-00	130.506	0	0	100
1-8-00	124.893	0.040	4.983	35.12
2-8-00	215.249	0.044	9.557	1.61

(c) Solids-bound metal concentrations

Cu:

Day	Flow at 20:30 (l/sec)	Final Effluent solids-bound Cu (mg/l)	Load in final effluent (mg/sec)	Removal during secondary sedimentation (%)
31-7-00	130.506	0.008	1.040	79.03
1-8-00	124.893	0.014	1.748	74.07
2-8-00	215.249	0.006	1.291	82.23

Zn:

Day	Flow at 20:30 (l/sec)	Final Effluent solids-bound Zn (mg/l)	Load in final effluent (mg/sec)	Removal during secondary sedimentation (%)
31-7-00	130.506	0.025	3.212	-15.98
1-8-00	124.893	0.008	0.999	72.97
2-8-00	215.249	0.001	0.194	85.93

Table 6.8: *Mass balance calculations for Cu and Zn in secondary treatment at Portswood WWTP*

(a) Total Metal Concentrations:

Cu:

Day	WAS Flow at 20:30 (l/sec)	WAS total Cu (mg/l)	Load in WAS (mg/sec)	Mass Balance
31-7-00	5.25	8.48	44.52	-36.60
1-8-00	5.25	4.04	21.21	-21.71
2-8-00	5.25	7.68	40.32	-33.31

Zn:

Day	WAS Flow at 20:30 (l/sec)	WAS total Zn (mg/l)	Load in WAS (mg/sec)	Mass Balance
31-7-00	5.25	10.30	54.05	-44.81
1-8-00	5.25	6.8	35.7	-30.41
2-8-00	5.25	8.68	45.55	-44.21

(b) Soluble metal concentrations:

Cu:

Day	WAS Flow at 20:30 (l/sec)	WAS soluble Cu (mg/l)	Load in WAS (mg/sec)	Mass Balance
31-7-00	5.25	0.007	0.037	3.96
1-8-00	5.25	0.01	0.053	1.20
2-8-00	5.25	0.093	0.488	1.12

Zn:

Day	WAS Flow at 20:30 (l/sec)	WAS soluble Zn (mg/l)	Load in WAS (mg/sec)	Mass Balance
31-7-00	5.25	0.029	0.154	9.53
1-8-00	5.25	0.093	0.488	2.21
2-8-00	5.25	0.094	0.495	-0.34

(c) Solids-bound metal concentrations

Cu:

Day	WAS Flow at 20:30 (l/sec)	WAS solids-bound Cu (mg/l)	Load in WAS (mg/sec)	Mass Balance
31-7-00	5.25	8.473	44.48	-40.56
1-8-00	5.25	4.03	21.16	-16.16
2-8-00	5.25	7.59	39.83	-33.86

Zn:

Day	WAS Flow at 20:30 (l/sec)	WAS solids-bound Zn (mg/l)	Load in WAS (mg/sec)	Mass Balance
31-7-00	5.25	10.27	53.90	-54.34
1-8-00	5.25	6.71	35.21	-32.51
2-8-00	5.25	8.582	45.05	-43.87

The concept of mass balance calculations is commonly accepted as a method for determining the fate of contaminants in wastewater treatment using field collected samples. Nevertheless, they are subject to limitations due to the problems associated with obtaining representative samples and consequently it has been shown that small errors in measurement may lead to large errors in the mass balance (Goldstone and Lester 1991).

The results of the mass balance calculations in this study show that in primary sedimentation, removal of both Cu and Zn were greater than the average removals reported in the literature (as shown in chapter2). The average removal of Cu in primary sedimentation was reported to be 45%, while in this study total copper removal ranged from 32.5-96%. Likewise, the average removal of Zn in primary sedimentation was given as 44%, and this study showed up to 98% removal of total zinc. On the other hand, the soluble metal concentrations of both metals showed an increase during primary sedimentation. This is not believed to be due to solubilisation of the metals, since previous researchers have shown that the waste activated sludge and return sludge liquors returned to the primary sedimentation tank resulted in more soluble metal becoming adsorbed onto the solids (Goldstone et al 1990). It can be seen that the soluble metal concentrations are very near the detection limit of the analytical equipment used, thus the reliability of these measurements is questionable.

The results of this study also show that during activated sludge treatment, the average removal of Cu was higher (87.25%) than the values reported by other researchers (62.25%), while average removal of Zn was slightly lower (44.57%) than the reported average (54.67%).

6.4.3 Model Verification

The field data was also used to verify the model's ability to accurately predict the partitioning of heavy metals. The values of the adsorption coefficients and adsorption capacities derived from the field data were entered into the model code and the model was run using the flow, suspended solids and pH data encountered at the plant during the field data collection. The soluble metal concentrations in the actual samples were used as a guide to assess the solubility limit of the samples. The calculated values of total, soluble and solids bound metal were compared with measured values. The input values are shown in table 6.9 and the calculated values and the measured values are shown in table 6.10.

Table 6.9: *Input values for model simulation*

Parameter	Value
Raw sewage flow (l/hr)	490973
Raw sewage total solids (mg/l)	476
Raw sewage volatile solids (mg/l)	380.8
Raw sewage total metal (mg/l)	2.1 (Cu); 7.1 (Zn)
Raw sewage pH	7.8
Primary sludge total solids (mg/l)	25000
Efficiency of solids removal in primary sedimentation	0.6
Primary effluent pH	7.8
Soluble substrate of primary effluent (mg/l)	150
Initial mixed liquor total solids (mg/l)	1740
Initial mixed liquor volatile solids (mg/l)	1392
Mixed liquor pH	7.0
Net sludge yield	0.50
Recycle ratio	1.4
Efficiency of solids removal in secondary sedimentation	0.985
Secondary sludge total solids (mg/l)	3000
Soluble substrate of final effluent (mg/l)	10
Final effluent pH	7.0

Table 6.10: *Comparison between measured and predicted values of Cu and Zn using data from first day of sampling*

Parameter	**Cu**		**Zn**	
	Predicted value	*Measured value*	*Predicted value*	*Measured value*
Raw sewage total metal (mg/l)	2.1	2.1	7.1	7.1
Raw sewage solids bound metal (mg/kg)	278	278.18	1430	961
Raw sewage soluble metal (mg/l)	0.03	0.027	0.10	0.088
Raw sewage precipitated metal (mg/l)	1.94		6.32	
Primary effluent total metal (mg/l)	0.05	0.065	0.19	0.090
Primary effluent solids-bound metal (mg/kg)	117.21	246.58	646.6	167.12
Primary effluent soluble metal (mg/l)	0.03	0.029	0.07	0.066
Primary effluent precipitated metal (mg/l)	0.78		2.2	
Primary sludge total metal (mg/kg)	278	257.00	1430.00	766.00
Mixed liquor total metal (mg/kg)	378.58	367.13	608.3	443.44
Mixed liquor solids bound metal (mg/kg)	250	366.65	455.00	436.28
Mixed liquor soluble metal (mg/l)	0.02	0.01	0.1	0.149
Mixed liquor precipitated metal (mg/l)	0.21		0.19	
Secondary sludge total metal (mg/kg)	500	404.77	455	491.46
Final effluent total metal (mg/l)	0.004	0.008	0.05	0.016
Final effluent soluble metal (mg/l)	0		0	
Final effluent solids bound metal (mg/kg)	126.2	246.94	47.2	390.44
Final effluent precipitated metal (mg/l)	0		0	

The model output shows that model predictions closely match the measured concentrations. The relatively small errors encountered suggest that the model is reasonably robust. The exception was the solids bound metal concentration in the final effluent. It would be expected that the adsorption coefficient in the final effluent is similar to that of the mixed liquor. However, as can be seen, it was calculated to be considerably lower. This leads to the calculated value of the solids bound metal to be lower than the real value. A possible explanation for this difference may be due to the extremely low metal concentrations encountered. It is suggested that the adsorption of metals in the final effluent be investigated further to enable accurate determination of the adsorption coefficient.

Although the field study had been designed expressly to circumvent this problem, by timing the sampling period with an expected high concentration discharge, this did not occur. Since the metal concentrations in the samples were in many cases below or very near the detection limit of the analytical instruments, this renders the measurements unreliable.

6.4.4 Limitations of the model

Quantifying the uncertainties in mathematical models is essential for making reliable predictions in complex systems. The uncertainties and limitations associated with modelling may be divided into three categories (Willems 2000):

- Uncertainties of the model input variables (input uncertainties);
- Uncertainties of the model parameter values (parameter uncertainties);
- Uncertainties originating from the imperfect description of the physical reality by a limited number of mathematical relations (model-structure uncertainties).

These are shown in figure 6.11.

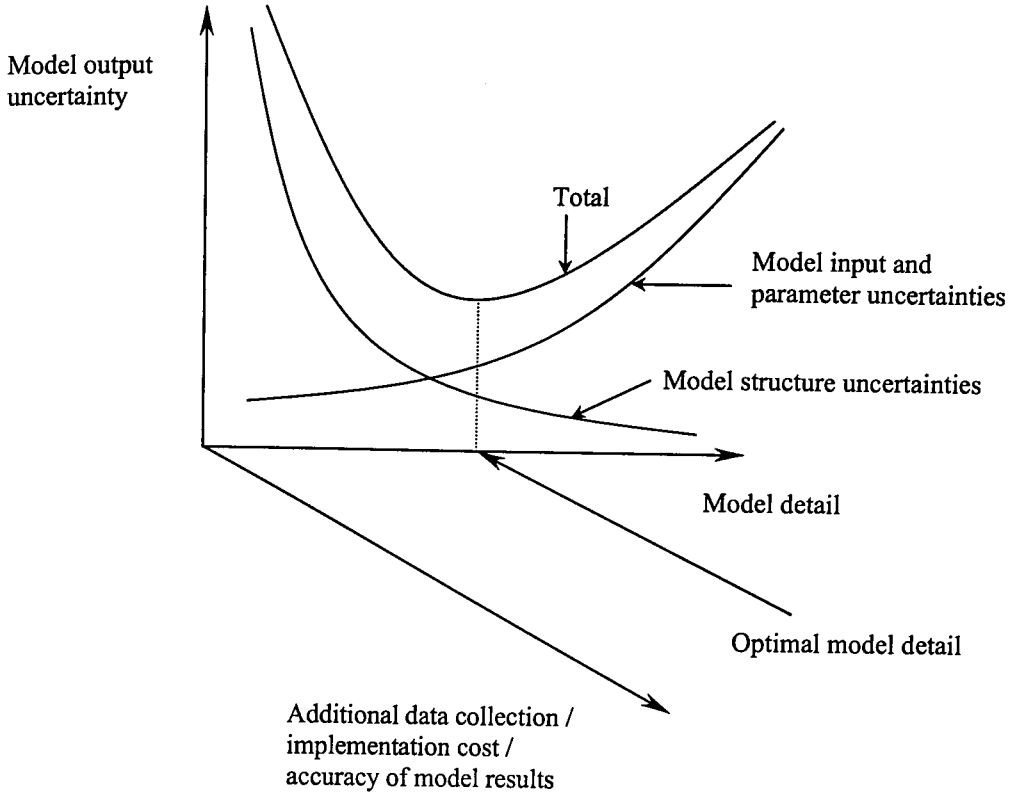


Figure 6.11: *Balancing different types of uncertainties to determine the optimal model-structure detail (after Willems 2000)*

Since the model developed in this project is based on the fundamental chemical and physical processes widely recognised as being important in the removal of heavy metals from wastewater, uncertainties related to the model structure are not relevant. Hence, application of the model is subject mainly to input and parameter uncertainties. The "input uncertainties" are associated with the collection and input of data by the user of the model. Many of the input data required (such as mixed liquor suspended solids concentration) are routinely measured at most wastewater treatment plants. The remaining parameters required are also easily measured. This minimises the input-related uncertainties. The "parameter uncertainties" relate to the calibration of the model with respect to the development of relationships correlating the model coefficients with the input parameters. Further statistical analyses on the model prediction errors will need to be performed to ascertain the model's sensitivity.

The results of this study highlight the difficulty in applying batch experimental data to a highly dynamic system such as wastewater. The difficulty in obtaining accurate data

for the calibration or verification of this type of model is also shown. Therefore, in addition to calibrating the model at each given WWTP, care must be taken to ensure that the process of calibration is representative of the actual conditions at the plant. It can be concluded from the model verification results that the model configuration is correct and that it is possible to accurately predict the partitioning of metals in wastewater treatment, given that the model calibration is conducted under conditions that meticulously represent those that actually occur in the field.

CHAPTER SEVEN

CONCLUSIONS & RECOMMENDATIONS

7.1 Conclusions

- A review of the literature examined the main factors and mechanisms influencing the fate of heavy metals in wastewater and sludge treatment processes. Based on the finding that the fate of suspended solids was crucial to the distribution of heavy metals, a model was developed to calculate the mass balance of solids in a wastewater treatment plant.
- The dominant mechanisms influencing metals partitioning are complexation with soluble ligands and adsorption onto the suspended solids. Thus metal removal during wastewater treatment takes place through direct precipitation or adsorption onto the wastewater solids.
- It was judged that a mechanistic approach to modelling would offer the most suitable approach for the development of a predictive model for heavy metals. Combined with the general adsorption isotherm, which employs the concept of the adsorption / partitioning coefficient, this type of approach allowed the model coefficients (adsorption coefficient, adsorption capacity and solubility limit) to be determined for a range of significant factors.
- The model coefficients were greatly influenced by factors such as pH, suspended solids concentration, metals concentration, and soluble organic ligand concentration. General theoretical values, such as solubility and stability products, available in the literature were not suitable and these values must be derived experimentally.
- Previous research had shown the difficulties associated with the adjustment of pH for experiments dealing with wastewaters. The experimental methods provided in the literature were found to be ineffective, prompting an experimental methodology to be developed.
- The results of experiments carried out on filtered samples of raw sewage and final effluent show that the filtered portion of wastewater is capable of complexing considerable amounts of copper and zinc, without saturating the soluble ligands present. The complexing of metals by soluble ligands is believed to increase the solubility of the metals by rendering them less likely to precipitate if bound in this manner.
- The results showed that the final effluent might contain a high concentration of unfilterable colloidal solids. While these solids bind metals and technically remove

them from solution, these solids are not settleable under field conditions and thus metals bound to colloidal solids should be considered as remaining in the aqueous phase.

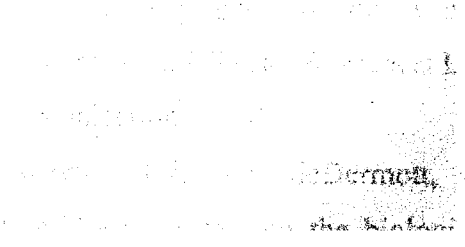
- Laboratory experiments provided data, which enabled the derivation of some of the model coefficients. The correlations between these coefficients and the crucial parameters influencing them, together with the results from the adsorption experiments provided an in-depth understanding of the parameters influencing metal removal and the way they interact with each other. In conclusion, the interactions of these parameters may be summarised as follows:
  - At low pH values, organic matter is adsorbed onto solids, thereby increasing metal adsorption. If metal loading is increased, both dissolved and solids bound metal concentrations will increase. Initially these increases will be proportional to metal loading, however, if metal loading increases further, more and more surface sites will become occupied by metal ions. Once the metal concentration is beyond the linear adsorption range, adsorption will decrease.
  - At high pH values, desorption of some of the organic matter on the solids will occur. Thus competition between the dissolved organic matter (DOM) and the solids will result in a decrease in adsorption. If metal loading is increased, saturation of DOM sites will take place (usually binding sites on DOM are less than those on solids). Once DOM sites are saturated, increased uptake by the solids will take place. The pH also affects the solubility of the metal.
  - Thus at lower pH values, the solubility limit is expected to be high, and consequently the adsorption capacity may be reached before precipitation occurs. While at higher pH values, the solubility limit is expected to be low and thus precipitation may occur before the adsorption capacity is reached.
- In terms of providing a full calibration of the model, the laboratory experimental results could not be used to derive all the coefficients and correlations needed. Likewise, a complete set of empirical equations correlating the model coefficients with pH and suspended solids concentrations could not be derived.
- It was possible to obtain some estimates of the adsorption coefficients and adsorption capacities for both metals in raw sewage, primary effluent, mixed liquor and final effluent under field conditions.

- Comparison of the model coefficients derived from the batch experimental tests and the field study revealed that the field adsorption coefficients were considerably higher than the experimental adsorption coefficients, while the field adsorption capacities were much lower than the experimental ones. It is hypothesised that this could be due to the sample preservation technique used in the experiments. Consequently, this resulted in the overestimation of the solubility limits and adsorption capacities as well as the underestimation of the adsorption coefficients.
- In the analysis of the field samples, the difference between precipitated metal and solids-bound (adsorbed) metal could not be discerned. Thus the adsorption coefficients derived from the field data are based on both precipitated and adsorbed metal fractions.
- Verification of the model's ability to accurately predict the partitioning of heavy metals, using the field-derived model coefficients, showed that the predicted values calculated by the model closely matched the measured values. This indicated that the model equations and configuration are correct.
- Since the model developed in this project is based on the fundamental chemical and physical processes widely recognised as being important in the removal of heavy metals from wastewater, uncertainties related to the model structure are not relevant. Hence, application of the model is subject mainly to input and parameter uncertainties.
- The "input uncertainties" are associated with the collection and input of data by the user of the model. Many of the input data required (such as mixed liquor suspended solids concentration) are routinely measured at most wastewater treatment plants. The remaining parameters required are also easily measured. This minimises the input-related uncertainties.
- The "parameter uncertainties" relate to the calibration of the model with respect to the development of relationships correlating the model coefficients with the input parameters. This project has shown the difficulties relating to the model calibration. To ensure that the experimentally-derived model coefficients accurately predict the partitioning of heavy metals in the field, it must be ensured that the experimental conditions closely represent the field conditions.
- The work described in this thesis has addressed the need for a greater understanding of the factors and mechanisms affecting heavy metal partitioning in wastewater

treatment. It presents a predictive model, which has been shown to accurately predict the fate of heavy metals.

7.2 Recommendations

- To obtain a fully workable model, further adsorption experiments will need to be carried out, using the methodology developed in this project. The objective of these experiments would be to verify the model coefficients obtained in this project and develop further correlations between the model coefficients and crucial parameters that affect metal partitioning.
- Modelling of the anaerobic sludge digestion process also needs to be considered.
- The resulting metals predictive model may be used as a module for the existing integrated sewer, wastewater treatment plants, receiving water system models such as the UPM model SIMPOL (Foundation for Water Research) or Hydroworks (Wallingford Software).
- Using the methodology developed, metals modelling may also be performed on any water in the urban wastewater system, for example to model metals removal from raw sewage during sewer transport and also in the modelling of the metals in the watercourse receiving a wastewater treatment effluent or combined sewer overflow. In these cases other important factors, such as flow, need to be taken into account.
- Thus further research will need to address fully calibrating the model as well as examining the suitability/ feasibility of integrating the metals model into existing integrated urban wastewater simulation models. The resulting model will be a valuable management tool, aiding in the establishment of heavy metal trade effluent standards.



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APPENDICES

APPENDIX A

SOLIDS MODEL

Equations for Solids Mass Balance Model

```
' This step is for the inputs
fin = Worksheets(2).Cells(4, 2) 'Raw influent flow
cints = Worksheets(2).Cells(5, 2) 'Raw influent total solids
xin = Worksheets(2).Cells(6, 2) 'Raw influent volatile solids
cpsts = Worksheets(2).Cells(7, 2) 'Primary sludge total solids
tsrem = Worksheets(2).Cells(8, 2) 'Percentage removal of total solids in primary sedimentation
cmlts1 = Worksheets(2).Cells(9, 2) 'Concentration of mixed liquor total solids initially in reactor
xml1 = Worksheets(2).Cells(10, 2) 'Concentration of mixed liquor volatile solids initially in reactor
tsrem2 = Worksheets(2).Cells(11, 2) 'Percentage removal of total solids in secondary clarifier
csests = Worksheets(2).Cells(12, 2) 'Secondary sludge total solids
r = Worksheets(2).Cells(13, 2) 'Recycle ratio
Yn = Worksheets(2).Cells(14, 2) 'Net Sludge Yield
Sf = Worksheets(2).Cells(15, 2) 'Soluble substrate of primary effluent
Se = Worksheets(2).Cells(16, 2) 'Soluble substrate of reactor effluent
ctsts = Worksheets(2).Cells(17, 2) 'Thickened sludge total solids
tsrem3 = Worksheets(2).Cells(18, 2) 'Percentage removal of total solids in primary thickener
vsd = Worksheets(2).Cells(19, 2) 'Percentage reduction of volatile solids in digester
cdsts = Worksheets(2).Cells(20, 2) 'Digester sludge total solids
tsrem4 = Worksheets(2).Cells(21, 2) 'Percentage removal of total solids in digester thickener
cdwsts = Worksheets(2).Cells(22, 2) 'Dewatered sludge total solids
tsrem5 = Worksheets(2).Cells(23, 2) 'Percentage removal of total solids in dewaterer


'This step is for the equations
'Primary Sedimentation equations:
q = fin + fws + fre 'Total influent flow
xinn = ((xin * fin) + (fre * xre) + (fws * xws)) / q 'Total influent volatile solids
tsin = ((cints * fin) + (fre * crets) + (fws * cwsts)) / q  'Total influent total solids
vt = xinn / tsin 'VSS:TSS ratio in influent
fps = (tsin * q * tsrem) / cpsts 'Primary sludge flow

  If fps = 0 Then
  cpsts = 0
  xps = 0
```

```
    Else:
    cpsts = Worksheets(2).Cells(7, 2) 'Primary sludge total solids
    xps = cpsts * vt 'Primary sludge volatile solids
    End If

fpe = q - fps 'Primary effluent flow
cpets = ((tsin * q) - (cpsts * fps)) / fpe 'Primary effluent total solids
xpe = ((xinn * q) - (xps * fps)) / fpe 'Primary effluent volatile solids


'Biological Treatment Equations:
fml = fpe + frs 'Mixed liquor flow
BODrem = (Sf * fpe) - (Se * fml) 'BOD removed
xmlinc = Yn * BODrem  'Increase in mixed liquor volatile solids
If j = 4 Then
xml = (xmlinc + (xml1 * fml) + (fpe * xpe)) / fml  'Mixed liquor volatile solids
cmlts = (xmlinc + (cmlts1 * fml) + (fpe * cpets)) / fml 'Mixed liquor total solids
Else
xml = (xmlinc + (fpe * xpe) + (frs * xrs)) / fml 'Mixed liquor volatile solids
cmlts = (xmlinc + (fpe * cpets) + (frs * crsts)) / fml 'Mixed liquor total solids
End If

vt2 = xml / cmlts 'VSS:TSS ratio in mixed liquor

'Secondary Sedimentation
vt3 = vt2 'VSS:TSS ratio in final effluent and secondary sludge

xses = csests * vt3 'Secondary sludge volatile solids


'Partitioning of Secondary sludge to wastage and recycle sludge

'Wastage sludge
xws = xses 'Wastage sludge volatile solids
cwsts = csests 'Wastage sludge total solids
'fws = fses - frs
```

```
fws = ((fpe * cpets) + xmlinc - (cmlts * fml * (1 - tsrem2))) / cwsts 'Flow of wastage sludge
'Recycled sludge
frs = r * fpe 'Flow of recycled sludge
xrs = xses 'Recycled sludge volatile solids
crsts = csests 'Recycled sludge total solids

fses = fws + frs

'Final Effluent
ffe = fml - fses 'Final effluent flow
cfets = ((cmlts * fml) - (csests * fses)) / ffe  'Final effluent total solids
xfe = ((xml * fml) - (xses * fses)) / ffe 'Final effluent volatile solids

'Primary Thickening:
'Thickened sludge
vt4 = xps / cpsts 'VSS:TSS ratio in primary sludge
fts = (cpsts * fps * tsrem3) / ctsts 'Thickened sludge flow

  If fts = 0 Then
  ctsts = 0
  xts = 0
  Else:
  ctsts = Worksheets(2).Cells(17, 2) 'Thickened sludge total solids
  xts = ctsts * vt4 'Thickened sludge volatile solids
  End If

'Thickener effluent
fte = fps - fts 'Thickener effluent flow

  If fte = 0 Then
  ctets = 0
  xte = 0
  Else:
  ctets = ((fps * cpsts) - (fts * ctsts)) / fte 'Thickener effluent total solids
  xte = ((fps * xps) - (fts * xts)) / fte 'Thickener effluent volatile solids
  End If
```

```
'Anaerobic digestion:
fts2 = fts 'Flow of sludge between digester and digester thickener
xts2 = xts * vsd 'Volatile solids content of sludge between digester and digester thickener
ctsts2 = (ctsts - xts) + xts2 'Total solids content of sludge between digester and digester thickener

'Digester Thickening:
'Digester sludge
vt5 = xts2 / ctsts2 'VSS:TSS ratio after digestion
fds = (fts2 * ctsts2 * tsrem4) / cdsts 'Digester sludge flow

  If fds = 0 Then
  cdsts = 0
  xds = 0
  Else:
  cdsts = Worksheets(2).Cells(20, 2) 'Digester sludge total solids
  xds = cdsts * vt5 'Digester sludge volatile solids
  End If

'Digester effluent
fde = fts2 - fds 'Flow of digester effluent

  If fde = 0 Then
  cdets = 0
  xde = 0
  Else:
  cdets = ((fts2 * ctsts2) - (fds * cdsts)) / fde 'Digester effluent total solids
  xde = ((fts2 * xts2) - (fds * xds)) / fde 'Digester effluent volatile solids
  End If

'Dewaterer:
'Dewaterer sludge:
vt6 = vt5 'VSS:TSS ratio in dewaterer
fdws = (fds * cdsts * tsrem5 / cdwsts) 'Dewatered sludge flow

  If fdws = 0 Then
```

```
    cdwsts = 0
    xdws = 0
    Else:
    cdwsts = Worksheets(2).Cells(22, 2) 'Dewatered sludge total solids
    xdws = vt6 * cdwsts 'Dewatered sludge volatile solids
    End If

'Dewaterer effluent:
fdwe = fds - fdws 'Dewaterer effluent flow

    If fdwe = 0 Then
    cdwets = 0
    xdwe = 0
    Else:
    cdwets = ((fds * cdsts) - (fdws * cdwsts)) / fdwe 'Dewaterer effluent total solids
    xdwe = ((fds * xds) - (fdws * xdws)) / fdwe 'Dewaterer effluent volatile solids
    End If

'Effluents returning to top of werks:
fre = fdwe + fde + fte 'Flow of returning effluent stream

    If fre = 0 Then
    crets = 0
    xre = 0
    Else:
    crets = ((fdwe * cdwets) + (fde * cdets) + (fte * ctets)) / fre 'Total solids in returning effluent stream
    xre = ((fdwe * xdwe) + (fde * xde) + (fte * xte)) / fre 'Volatile solids in returning effluent stream
    End If
```

Outputs

	Total Influent			Primary Effluent			Primary Sludge			Mixed Liquor		
Iteration	q	xinn	tsin	fpe	xpe	cpets	fps	xps	cpsts	fml	xml	cmlts
1	41667.00	400.00	500.00	40833.66	81.63	102.04	833.34	16000.00	20000.00	40833.66	2551.63	3172.04
2	43035.23	506.48	634.63	41942.78	103.93	130.23	1092.46	15961.51	20000.00	63176.28	2547.06	3156.15
3	43309.36	515.07	645.72	42190.74	105.74	132.57	1118.62	15953.27	20000.00	64000.98	2589.28	3198.85
4	43341.83	516.93	647.76	42218.83	106.14	133.00	1123.00	15960.64	20000.00	64158.01	2605.33	3209.47
5	43346.67	517.40	647.98	42223.17	106.23	133.04	1123.50	15969.88	20000.00	64176.96	2613.45	3210.61
6	43347.25	517.72	648.00	42223.69	106.30	133.05	1123.55	15979.15	20000.00	64179.74	2620.52	3210.80
7	43347.31	518.01	647.99	42223.77	106.36	133.05	1123.54	15988.16	20000.00	64180.09	2627.23	3210.82
8	43347.31	518.28	647.98	42223.78	106.41	133.04	1123.53	15996.84	20000.00	64180.14	2633.68	3210.82
9	43347.30	518.55	647.97	42223.78	106.47	133.04	1123.51	16005.23	20000.00	64180.15	2639.90	3210.82
10	43347.29	518.80	647.96	42223.79	106.52	133.04	1123.50	16013.31	20000.00	64180.16	2645.90	3210.82
11	43347.28	519.05	647.96	42223.80	106.57	133.04	1123.48	16021.11	20000.00	64180.17	2651.68	3210.82
12	43347.27	519.29	647.95	42223.80	106.62	133.04	1123.47	16028.64	20000.00	64180.17	2657.27	3210.81
13	43347.26	519.52	647.94	42223.81	106.67	133.04	1123.46	16035.90	20000.00	64180.18	2662.65	3210.81
14	43347.26	519.74	647.93	42223.81	106.71	133.03	1123.45	16042.90	20000.00	64180.19	2667.85	3210.81
15	43347.25	519.95	647.93	42223.82	106.76	133.03	1123.43	16049.65	20000.00	64180.20	2672.86	3210.81
16	43347.24	520.16	647.92	42223.82	106.80	133.03	1123.42	16056.17	20000.00	64180.20	2677.69	3210.81
17	43347.23	520.35	647.91	42223.82	106.84	133.03	1123.41	16062.45	20000.00	64180.21	2682.35	3210.81
18	43347.23	520.55	647.91	42223.83	106.88	133.03	1123.40	16068.51	20000.00	64180.22	2686.85	3210.81
19	43347.22	520.73	647.90	42223.83	106.92	133.03	1123.39	16074.36	20000.00	64180.22	2691.19	3210.81
20	43347.22	520.91	647.90	42223.84	106.95	133.03	1123.38	16080.00	20000.00	64180.23	2695.38	3210.81
21	43347.21	521.08	647.89	42223.84	106.99	133.03	1123.37	16085.44	20000.00	64180.24	2699.41	3210.81
22	43347.20	521.25	647.88	42223.84	107.02	133.02	1123.36	16090.69	20000.00	64180.24	2703.31	3210.81
23	43347.20	521.41	647.88	42223.85	107.06	133.02	1123.35	16095.75	20000.00	64180.25	2707.06	3210.80
24	43347.19	521.56	647.87	42223.85	107.09	133.02	1123.34	16100.64	20000.00	64180.25	2710.69	3210.80

Solids Mass Balance

Outputs

	Secondary Sludge			Final Effluent			Wastage Sludge			Recycled Sludge			Thi
Iteration	fses	xses	csests	ffe	xfe	cfets	fws	xws	cwsts	frs	xrs	crsts	fts
1	21798.19	7239.72	9000.00	19035.47	-2816.86	-3501.76	564.69	7239.72	9000.00	21233.50	7239.72	9000.00	226.19
2	22399.27	7263.14	9000.00	40777.01	-43.54	-53.95	589.02	7263.14	9000.00	21810.24	7263.14	9000.00	296.52
3	22535.46	7284.97	9000.00	41465.52	37.29	46.07	596.28	7284.97	9000.00	21939.18	7284.97	9000.00	303.63
4	22550.67	7305.87	9000.00	41607.34	57.70	71.07	596.88	7305.87	9000.00	21953.79	7305.87	9000.00	304.81
5	22553.01	7326.02	9000.00	41623.95	60.05	73.77	596.96	7326.02	9000.00	21956.05	7326.02	9000.00	304.95
6	22553.28	7345.44	9000.00	41626.46	60.56	74.20	596.96	7345.44	9000.00	21956.32	7345.44	9000.00	304.96
7	22553.31	7364.18	9000.00	41626.78	60.75	74.25	596.95	7364.18	9000.00	21956.36	7364.18	9000.00	304.96
8	22553.30	7382.26	9000.00	41626.83	60.91	74.26	596.94	7382.26	9000.00	21956.36	7382.26	9000.00	304.96
9	22553.30	7399.70	9000.00	41626.85	61.05	74.26	596.93	7399.70	9000.00	21956.37	7399.70	9000.00	304.95
10	22553.29	7416.52	9000.00	41626.86	61.19	74.26	596.92	7416.52	9000.00	21956.37	7416.52	9000.00	304.95
11	22553.29	7432.74	9000.00	41626.88	61.32	74.26	596.92	7432.74	9000.00	21956.37	7432.74	9000.00	304.95
12	22553.29	7448.39	9000.00	41626.89	61.45	74.26	596.91	7448.39	9000.00	21956.38	7448.39	9000.00	304.94
13	22553.28	7463.49	9000.00	41626.90	61.58	74.26	596.90	7463.49	9000.00	21956.38	7463.49	9000.00	304.94
14	22553.28	7478.05	9000.00	41626.91	61.70	74.26	596.90	7478.05	9000.00	21956.38	7478.05	9000.00	304.94
15	22553.27	7492.10	9000.00	41626.92	61.81	74.26	596.89	7492.10	9000.00	21956.38	7492.10	9000.00	304.93
16	22553.27	7505.65	9000.00	41626.94	61.93	74.26	596.88	7505.65	9000.00	21956.39	7505.65	9000.00	304.93
17	22553.26	7518.72	9000.00	41626.95	62.03	74.26	596.88	7518.72	9000.00	21956.39	7518.72	9000.00	304.93
18	22553.26	7531.33	9000.00	41626.96	62.14	74.26	596.87	7531.33	9000.00	21956.39	7531.33	9000.00	304.92
19	22553.26	7543.50	9000.00	41626.97	62.24	74.26	596.86	7543.50	9000.00	21956.39	7543.50	9000.00	304.92
20	22553.25	7555.23	9000.00	41626.98	62.34	74.26	596.86	7555.23	9000.00	21956.40	7555.23	9000.00	304.92
21	22553.25	7566.55	9000.00	41626.99	62.43	74.26	596.85	7566.55	9000.00	21956.40	7566.55	9000.00	304.91
22	22553.25	7577.47	9000.00	41626.99	62.52	74.26	596.85	7577.47	9000.00	21956.40	7577.47	9000.00	304.91
23	22553.24	7588.00	9000.00	41627.00	62.61	74.26	596.84	7588.00	9000.00	21956.40	7588.00	9000.00	304.91
24	22553.24	7598.16	9000.00	41627.01	62.69	74.26	596.84	7598.16	9000.00	21956.40	7598.16	9000.00	304.91

Solids Mass Balance

Outputs

	Thickened Sludge		Thickener Effluent			Flow between digester and digester thicke			Digester Sludge			Digester Effluer	
Iteration	xts	ctsts	fte	xte	ctets	fts2	xts2	ctsts2	fds	xds	cdsts	fde	xde
1	56000.00	70000.00	607.15	1098.04	1372.55	226.19	28000.00	42000.00	114.00	53333.33	80000.00	112.19	2258.06
2	55865.30	70000.00	795.93	1095.40	1372.55	296.52	27932.65	42067.35	149.69	53119.86	80000.00	146.84	2256.31
3	55836.44	70000.00	815.00	1094.83	1372.55	303.63	27918.22	42081.78	153.33	53074.22	80000.00	150.30	2255.93
4	55862.24	70000.00	818.19	1095.34	1372.55	304.81	27931.12	42068.88	153.88	53115.03	80000.00	150.94	2256.27
5	55894.57	70000.00	818.55	1095.97	1372.55	304.95	27947.28	42052.72	153.89	53166.19	80000.00	151.06	2256.69
6	55927.04	70000.00	818.59	1096.61	1372.55	304.96	27963.52	42036.48	153.84	53217.63	80000.00	151.13	2257.11
7	55958.54	70000.00	818.58	1097.23	1372.55	304.96	27979.27	42020.73	153.78	53267.56	80000.00	151.19	2257.53
8	55988.96	70000.00	818.57	1097.82	1372.55	304.96	27994.48	42005.52	153.72	53315.81	80000.00	151.24	2257.92
9	56018.30	70000.00	818.56	1098.40	1372.55	304.95	28009.15	41990.85	153.66	53362.38	80000.00	151.29	2258.30
10	56046.60	70000.00	818.55	1098.95	1372.55	304.95	28023.30	41976.70	153.61	53407.34	80000.00	151.34	2258.67
11	56073.90	70000.00	818.54	1099.49	1372.55	304.95	28036.95	41963.05	153.56	53450.74	80000.00	151.39	2259.02
12	56100.23	70000.00	818.53	1100.00	1372.55	304.94	28050.12	41949.88	153.51	53492.63	80000.00	151.43	2259.37
13	56125.64	70000.00	818.52	1100.50	1372.55	304.94	28062.82	41937.18	153.46	53533.06	80000.00	151.48	2259.70
14	56150.14	70000.00	818.51	1100.98	1372.55	304.94	28075.07	41924.93	153.41	53572.08	80000.00	151.52	2260.01
15	56173.78	70000.00	818.50	1101.45	1372.55	304.93	28086.89	41913.11	153.37	53609.75	80000.00	151.56	2260.32
16	56196.58	70000.00	818.49	1101.89	1372.55	304.93	28098.29	41901.71	153.32	53646.10	80000.00	151.60	2260.62
17	56218.58	70000.00	818.48	1102.33	1372.55	304.93	28109.29	41890.71	153.28	53681.19	80000.00	151.64	2260.90
18	56239.79	70000.00	818.48	1102.74	1372.55	304.92	28119.90	41880.10	153.24	53715.05	80000.00	151.68	2261.17
19	56260.26	70000.00	818.47	1103.14	1372.55	304.92	28130.13	41869.87	153.20	53747.73	80000.00	151.72	2261.44
20	56280.00	70000.00	818.46	1103.53	1372.55	304.92	28140.00	41860.00	153.17	53779.27	80000.00	151.75	2261.69
21	56299.05	70000.00	818.45	1103.90	1372.55	304.91	28149.52	41850.48	153.13	53809.71	80000.00	151.78	2261.94
22	56317.42	70000.00	818.45	1104.26	1372.55	304.91	28158.71	41841.29	153.09	53839.08	80000.00	151.82	2262.18
23	56335.14	70000.00	818.44	1104.61	1372.55	304.91	28167.57	41832.43	153.06	53867.43	80000.00	151.85	2262.41
24	56352.23	70000.00	818.43	1104.95	1372.55	304.91	28176.12	41823.88	153.03	53894.79	80000.00	151.88	2262.63

Solids Mass Balance

Outputs

	ıt	Dewatered Sludge			Dewaterer Effluent			Returning Effluent		
Iteration	cdets	fdws	xdws	cdwsts	fdwe	xdwe	cdwets	fre	xre	crets
1	3387.10	29.79	200000.00	300000.00	84.21	1444.04	2166.06	803.55	1296.26	1736.98
2	3398.07	39.12	199199.47	300000.00	110.57	1438.26	2166.06	1053.34	1293.22	1738.20
3	3400.42	40.07	199028.34	300000.00	113.26	1437.03	2166.06	1078.56	1292.57	1738.47
4	3398.31	40.21	199181.35	300000.00	113.66	1438.13	2166.06	1082.79	1293.15	1738.23
5	3395.68	40.22	199373.20	300000.00	113.67	1439.52	2166.06	1083.29	1293.88	1737.94
6	3393.03	40.20	199566.10	300000.00	113.63	1440.91	2166.06	1083.35	1294.61	1737.64
7	3390.47	40.19	199753.36	300000.00	113.59	1442.26	2166.06	1083.36	1295.33	1737.35
8	3387.99	40.17	199934.27	300000.00	113.55	1443.57	2166.06	1083.36	1296.01	1737.08
9	3385.61	40.16	200108.93	300000.00	113.51	1444.83	2166.06	1083.36	1296.67	1736.81
10	3383.31	40.14	200277.53	300000.00	113.47	1446.05	2166.06	1083.36	1297.31	1736.55
11	3381.09	40.13	200440.27	300000.00	113.43	1447.22	2166.06	1083.36	1297.93	1736.31
12	3378.96	40.12	200597.35	300000.00	113.39	1448.36	2166.06	1083.35	1298.52	1736.07
13	3376.90	40.10	200748.97	300000.00	113.36	1449.45	2166.06	1083.35	1299.10	1735.83
14	3374.91	40.09	200895.31	300000.00	113.32	1450.51	2166.06	1083.35	1299.65	1735.61
15	3373.00	40.08	201036.56	300000.00	113.29	1451.53	2166.06	1083.35	1300.18	1735.40
16	3371.15	40.07	201172.88	300000.00	113.26	1452.51	2166.06	1083.35	1300.70	1735.19
17	3369.37	40.06	201304.45	300000.00	113.22	1453.46	2166.06	1083.35	1301.20	1734.99
18	3367.66	40.05	201431.44	300000.00	113.20	1454.38	2166.06	1083.35	1301.67	1734.80
19	3366.01	40.04	201553.99	300000.00	113.17	1455.26	2166.06	1083.35	1302.14	1734.61
20	3364.41	40.03	201672.26	300000.00	113.14	1456.12	2166.06	1083.35	1302.58	1734.43
21	3362.87	40.02	201786.41	300000.00	113.11	1456.94	2166.06	1083.35	1303.01	1734.26
22	3361.39	40.01	201896.56	300000.00	113.09	1457.74	2166.06	1083.35	1303.43	1734.09
23	3359.96	40.00	202002.86	300000.00	113.06	1458.50	2166.06	1083.35	1303.83	1733.93
24	3358.58	39.99	202105.45	300000.00	113.04	1459.25	2166.06	1083.35	1304.21	1733.77

Solids Mass Balance

APPENDIX B

METALS MODEL

Equations for Metals Model

```
'Zn Calculations
'This step is for the inputs
fin = UserForm1.TextBox1.Text 'Raw influent flow
cints = UserForm1.TextBox2.Text 'Raw influent total solids
xin = UserForm1.TextBox3.Text 'Raw influent volatile solids
mint = UserForm1.TextBox4.Text 'Raw influent total metal concentration
pH1 = UserForm1.TextBox5.Text 'Raw sewage pH
cpsts = UserForm1.TextBox6.Text 'Primary sludge total solids
tsrem = UserForm1.TextBox7.Text 'Percentage removal of total solids in primary sedimentation
pH2 = UserForm1.TextBox8.Text 'Primary effluent pH
Sf = UserForm1.TextBox9.Text 'Soluble substrate of primary effluent
cmlts1 = UserForm1.TextBox10.Text 'Concentration of mixed liquor total solids initially in reactor
xml1 = UserForm1.TextBox11.Text 'Concentration of mixed liquor volatile solids initially in reactor
pH3 = UserForm1.TextBox12.Text 'Mixed Liquor pH
Yn = UserForm1.TextBox13.Text 'Net Sludge Yield
r = UserForm1.TextBox14.Text 'Recycle ratio
tsrem2 = UserForm1.TextBox15.Text 'Percentage removal of total solids in secondary clarifier
csests = UserForm1.TextBox16.Text 'Secondary sludge total solids
Se = UserForm1.TextBox17.Text 'Soluble substrate of reactor effluent
pH4 = UserForm1.TextBox18.Text 'Final Effluent pH


'This step is for the equations
'Raw Sewage Equations
q = fin + fws  'Total influent flow
xinn = ((xin * fin) + (fws * xws)) / q  'Total influent volatile solids
tsin = ((cints * fin) + (fws * cwsts)) / q  'Total influent total solids
vt = xinn / tsin 'VSS:TSS ratio

'Calculating model coefficients in raw sewage
kp1 = 1500 / (10 ^ 6) 'Adsorption coefficient for Zn in raw sewage
sol1 = -1.5379 * pH1 + 12.41 'Solubility limit of Zn in Raw Sewage
ka1 = 5000 'Adsorption Capacity for Zn in Raw Sewage
```

```
'Metals in Raw Sewage
minn = ((mint * fin) + (fws * mws * cwsts / 10 ^ 6)) / q  'Total influent metals
mxinn = ((minn * kp1 * xinn) / (1 + (kp1 * xinn))) * (10 ^ 6 / tsin) 'Influent solids bound metal
If mxinn < ka1 Then
msinn = minn - ((mxinn * tsin) / 10 ^ 6) 'Influent soluble metal
   If msinn < sol1 Then
   mpinn = 0
   Else
   msinn = sol1
   mpinn = minn - msinn - ((mxinn * tsin) / 10 ^ 6)
   End If
Else:
mxinn = ka1
msinn = minn - ((mxinn * tsin) / 10 ^ 6) 'Influent soluble metal
   If msinn < sol1 Then
   mpinn = 0
   Else
   msinn = sol1
   mpinn = minn - msinn - ((mxinn * tsin) / 10 ^ 6)
   End If
End If

'Primary sedimentation equations
fps = (tsin * q * tsrem) / cpsts 'Primary sludge flow
If fps = 0 Then
cpsts = 0
xps = 0
Else:
cpsts = UserForm1.TextBox6.Text 'Primary sludge total solids
xps = cpsts * vt 'Primary sludge volatile solids
End If
fpe = q - fps 'Primary effluent flow
cpets = ((tsin * q) - (cpsts * fps)) / fpe 'Primary effluent total solids
xpe = ((xinn * q) - (xps * fps)) / fpe 'Primary effluent volatile solids

'Calculating Model Coefficients in Primary Sedimentation
```

```
kp2 = 1800 / (10 ^ 6) 'Adsorption coefficient for Zn in Primary effluent
sol2 = -1.2763 * pH2 + 10.5 'Solubility limit in primary effluent
ka2 = 4000 'Adsorption capacity for Zn in Primary effluent

'Metals in Primary sedimentation
tmrem = tsrem  'Total metal removal in primary sedimentation
mxp = msinn * kp2 * xpe 'Influent soluble metal adsorbed during primary treatment
mxpe = (((mxp * q * ((10 ^ 6) / cpets)) + (mxinn * q)) * (1 - tmrem)) / fpe
If mxpe < ka2 Then
mspe1 = msinn - mxp  'Soluble metal in primary effluent
   If mspe1 < 0 Then
   mspe = 0
   mppe = (mpinn * q * (1 - tmrem)) / fpe
   Else
   If mspe1 < sol2 Then
   mspe = mspe1
   mppe = (mpinn * q * (1 - tmrem)) / fpe
   Else
   mspe = sol2
   mppe = mspe1 - sol2 + ((mpinn * q * (1 - tmrem)) / fpe)
   End If
   End If
Else
mxpe = ka2
mspe1 = msinn - mxp
   If mspe1 < 0 Then
   mspe = 0
   mppe = (mpinn * q * (1 - tmrem)) / fpe
   Else
   If mspe1 < sol2 Then
   mspe = mspe1
   mppe = (mpinn * q * (1 - tmrem)) / fpe
   Else
   mspe = sol2
   mppe = mspe1 - sol2 + ((mpinn * q * (1 - tmrem)) / fpe)
   End If
```

```
    End If
  End If

  If mppe < 0 Then
  mppe = 0
  End If

  mpe = mspe + mppe + (mxpe * cpets / 10 ^ 6)

  mps = (((minn * q) - (mpe * fpe)) / fps) * (10 ^ 6 / cpsts) 'Primary sludge metat concentration



  'Activated Sludge Treatment Equations
  fml = fpe + frs 'Mixed Liquor Flow
  BODrem = (Sf * fpe) - (Se * fml) 'BOD removed
  xmlinc = Yn * BODrem 'Increased in mixed liquor volatile solids
  If j = 4 Then
  xml = (xmlinc + (xml1 * fml) + (fpe * xpe)) / fml 'Mixed liquor volatile solids
  cmlts = (xmlinc + (cmlts1 * fml) + (fpe * cpets)) / fml 'Mixed liquor total solids
  Else
  xml = (xmlinc + (fpe * xpe) + (frs * xrs)) / fml 'Mixed liquor volatile solids
  cmlts = (xmlinc + (fpe * cpets) + (frs * crsts)) / fml 'Mixed liquor total solids
  End If
  vt2 = xml / cmlts 'VSS:TSS ratio in mixed liquor

  'Calculating model coefficients in mixed liquor
  kp3 = 2500 / (10 ^ 6) 'Adsorption coefficient for Zn in mixed liquor
  sol3 = -1.2763 * pH3 + 9 'Solubility limit for Zn in mixed liquor
  ka3 = 1700 'Adsorption coefficient for Zn in mixed liquor

  'Metals in Mixed Liquor
  mml = ((mpe * fpe * ((10 ^ 6) / cpets)) + (mrs * frs)) / fml 'Influent metals to mixed liquor
  mxml = ((mml * (cmlts / (10 ^ 6)) * kp3 * xml) / (1 + (kp3 * xml))) * (10 ^ 6 / cmlts) 'Mixed liquor soltds bound metal
  If mxml < ka3 Then
  msml = mml - mxml * (cmlts / (10 ^ 6)) 'Mixed liquor soluble metal
```

```
    If msml < 0 Then
    msml = 0
    Else
    If msml < sol3 Then
    mpml = mppe
    Else
    msml = sol3
    mpml = ((mml * cmlts) / (10 ^ 6)) - msml - ((mxml * cmlts) / 10 ^ 6)
    End If
    End If
Else
mxml = ka3
msml = (mml - mxml) * (cmlts / (10 ^ 6)) 'Mixed liquor soluble metal
    If msml < 0 Then
    msml = 0
    Else
    If msml < sol3 Then
    mpml = mppe
    Else
    msml = sol3
    mpml = ((mml * cmlts) / (10 ^ 6)) - msml - ((mxml * cmlts) / 10 ^ 6)
    End If
    End If
End If

If mpml < 0 Then
mpml = 0
End If

'Secondary Sedimentation Equations
vt3 = vt2 'VSS:TSS ratio in final effluent and secondary sludge
xses = csests * vt3 'Secondary sludge volatile solids


'Partitioning of secondary sludge to wastage and recycle sludge
'Wastage sludge
```

```
 xws = xses 'Wastage sludge volatile solids
 cwsts = csests 'Wastage sludge total solids
 fws = ((fpe * cpets) + xmlinc - (cmlts * fml * (1 - tsrem2))) / cwsts 'Flow of wastage sludge
 'Recycled sludge
 frs = r * fpe 'Flow of recycled sludge
 xrs = xses 'Recycled sludge volatile solids
 crsts = csests 'Recycled sludge total solids
 fses = fws + frs 'Secondary sludge flow
 ffe = fml - fses 'Final effluent flow
 cfets = ((cmlts * fml) - (csests * fses)) / ffe 'Final effluent total solids
 xfe = ((xml * fml) - (xses * fses)) / ffe 'Final effluent volatile solids

 'Calculating model coefficients in final effluent
 kp4 = 4500 / (10 ^ 6) 'Adsorption coefficient for Zn in final effluent
 sol4 = -1.2763 * pH4 + 9.5
 ka4 = 4000

 'Metals in Secondary sedimentation
 tmrem2 = tsrem2  'Total metal removal in final sedimentation
 mxf = msml * kp4 * xfe 'Mixed liquor soluble metal adsorbed during final sedimentation
 mxfe = (((mxml * fml) + (mxf * fml * ((10 ^ 6) / cfets))) * (1 - tmrem2)) / ffe 'Solids bound metal in final effluent
 If mxfe < ka4 Then
 msfe1 = msml - mxf 'Soluble metal in final effluent
    If msfe1 < 0 Then
    msfe = 0
    mpfe = (mpml * fml * (1 - tmrem2)) / ffe
    Else
    If msfe1 < sol4 Then
    msfe = msfe1
    mpfe = (mpml * fml * (1 - tmrem2)) / ffe
    Else
    msfe = sol4
    mpfe = msfe1 - sol4 + ((mpml * fml * (1 - tmrem2)) / ffe)
    End If
    End If
 Else
```

```
 mxfe = ka4
 msfe1 = msml - mxf 'Soluble metal in final effluent
    If msfe1 < 0 Then
    msfe = 0
    mpfe = (mpml * fml * (1 - tmrem2)) / ffe
    Else
    If msfe1 < sol4 Then
    msfe = msfe1
    mpfe = (mpml * fml * (1 - tmrem2)) / ffe
    Else
    msfe = sol4
    mpfe = msfe1 - sol4 + ((mpml * fml * (1 - tmrem2)) / ffe)
    End If
    End If
End If

If mpfe < 0 Then
mpfe = 0
End If

mfe = msfe + mpfe + (mxfe * cfets / 10 ^ 6)

mses = (((mml * fml) - (mfe * ffe)) / fses) * (10 ^ 6 / csests) 'Secondary sludge metal concentration



'Partitioning of secondary sludge to wastage and recycle sludge
'Wastage sludge
mws = mses 'Wastage sludge metal concentration
'Recycled sludge
mrs = mses 'Recycled sludge metal concentration
```

```
'Cu Calculations
Sub Inputscalc2()
j = 4
Do
'This step is for the inputs
fin = UserForm5.TextBox1.Text 'Raw influent flow
cints = UserForm5.TextBox2.Text 'Raw influent total solids
xin = UserForm5.TextBox3.Text 'Raw influent volatile solids
mint = UserForm5.TextBox4.Text 'Raw influent total metal concentration
pH1 = UserForm5.TextBox5.Text 'Raw sewage pH
cpsts = UserForm5.TextBox6.Text 'Primary sludge total solids
tsrem = UserForm5.TextBox7.Text 'Percentage removal of total solids in primary sedimentation
pH2 = UserForm5.TextBox8.Text 'Primary effluent pH
Sf = UserForm5.TextBox9.Text 'Soluble substrate of primary effluent
cmlts1 = UserForm5.TextBox10.Text 'Concentration of mixed liquor total solids initially in reactor
xml1 = UserForm5.TextBox11.Text 'Concentration of mixed liquor volatile solids initially in reactor
pH3 = UserForm5.TextBox12.Text 'Mixed Liquor pH
Yn = UserForm5.TextBox13.Text 'Net Sludge Yield
r = UserForm5.TextBox14.Text 'Recycle ratio
tsrem2 = UserForm5.TextBox15.Text 'Percentage removal of total solids in secondary clarifier
csests = UserForm5.TextBox16.Text 'Secondary sludge total solids
Se = UserForm5.TextBox17.Text 'Soluble substrate of reactor effluent
pH4 = UserForm5.TextBox18.Text 'Final Effluent pH


'This step is for the equations
'Raw Sewage Equations
q = fin + fws + fre 'Total influent flow
xinn = ((xin * fin) + (fre * xre) + (fws * xws)) / q 'Total influent volatile solids
tsin = ((cints * fin) + (fre * crets) + (fws * cwsts)) / q 'Total influent total solids
vt = xinn / tsin 'VSS:TSS ratio

'Calculating model coefficients in raw sewage
kp1 = 500 / (10 ^ 6)
sol1 = -1.9904 * pH1 + 18.18
ka1 = 4000
```

```
'Metals in Raw Sewage
minn = ((mint * fin) + (fws * mws * cwsts / 10 ^ 6)) / q  'Total influent metals
mxinn = ((minn * kp1 * xinn) / (1 + (kp1 * xinn))) * (10 ^ 6 / tsin) 'Influent solids bound metal
If mxinn < ka1 Then
msinn = minn - ((mxinn * tsin) / 10 ^ 6) 'Influent soluble metal
   If msinn < sol1 Then
   mpinn = 0
   Else
   msinn = sol1
   mpinn = minn - msinn - ((mxinn * tsin) / 10 ^ 6)
   End If
Else:
mxinn = ka1
msinn = minn - ((mxinn * tsin) / 10 ^ 6) 'Influent soluble metal
   If msinn < sol1 Then
   mpinn = 0
   Else
   msinn = sol1
   mpinn = minn - msinn - ((mxinn * tsin) / 10 ^ 6)
   End If
End If

'Primary sedimentation equations
fps = (tsin * q * tsrem) / cpsts 'Primary sludge flow
If fps = 0 Then
cpsts = 0
xps = 0
Else:
cpsts = UserForm5.TextBox6.Text 'Primary sludge total solids
xps = cpsts * vt 'Primary sludge volatile solids
End If
fpe = q - fps 'Primary effluent flow
cpets = ((tsin * q) - (cpsts * fps)) / fpe 'Primary effluent total solids
xpe = ((xinn * q) - (xps * fps)) / fpe 'Primary effluent volatile solids
```

```
'Calculating Model Coefficients in Primary Sedimentation
kp2 = 8000 / (10 ^ 6)
sol2 = -1.9904 * pH2 + 17
ka2 = 5000

'Metals in Primary sedimentation
tmrem = tsrem  'Total metal removal in primary sedimentation
mxp = msinn * kp2 * xpe 'Influent soluble metal adsorbed during primary treatment
mxpe = (((mxp * q * ((10 ^ 6) / cpets)) + (mxinn * q)) * (1 - tmrem)) / fpe
If mxpe < ka2 Then
mspe1 = msinn - mxp  'Soluble metal in primary effluent
   If mspe1 < 0 Then
   mspe = 0
   mppe = (mpinn * q * (1 - tmrem)) / fpe
   Else
   If mspe1 < sol2 Then
   mspe = mspe1
   mppe = (mpinn * q * (1 - tmrem)) / fpe
   Else
   mspe = sol2
   mppe = mspe1 - sol2 + ((mpinn * q * (1 - tmrem)) / fpe)
   End If
   End If
Else
mxpe = ka2
mspe1 = msinn - mxp
   If mspe1 < 0 Then
   mspe = 0
   mppe = (mpinn * q * (1 - tmrem)) / fpe
   Else
   If mspe1 < sol2 Then
   mspe = mspe1
   mppe = (mpinn * q * (1 - tmrem)) / fpe
   Else
   mspe = sol2
   mppe = mspe1 - sol2 + ((mpinn * q * (1 - tmrem)) / fpe)
```

```
    End If
    End If
End If

If mppe < 0 Then
mppe = 0
End If

mpe = mspe + mppe + (mxpe * cpets / 10 ^ 6)
mps = (((minn * q) - (mpe * fpe)) / fps) * (10 ^ 6 / cpsts) 'Primary sludge metal concentration



'Activated Sludge Treatment Equations
fml = fpe + frs 'Mixed Liquor Flow
BODrem = (Sf * fpe) - (Se * fml) 'BOD removed
xmlinc = Yn * BODrem 'Increased in mixed liquor volatile solids
If j = 4 Then
xml = (xmlinc + (xml1 * fml) + (fpe * xpe)) / fml 'Mixed liquor volatile solids
cmlts = (xmlinc + (cmlts1 * fml) + (fpe * cpets)) / fml 'Mixed liquor total solids
Else
xml = (xmlinc + (fpe * xpe) + (frs * xrs)) / fml 'Mixed liquor volatile solids
cmlts = (xmlinc + (fpe * cpets) + (frs * crsts)) / fml 'Mixed liquor total solids
End If
vt2 = xml / cmlts 'VSS:TSS ratio in mixed liquor

'Calculating model coefficients in mixed liquor
kp3 = 800 / (10 ^ 6)
sol3 = 315662 * pH3 ^ (-6.1491)
ka3 = 3000

'Metals in Mixed Liquor
mml = ((mpe * fpe * ((10 ^ 6) / cpets)) + (mrs * frs)) / fml 'Influent metals to mixed liquor
mxml = ((mml * (cmlts / (10 ^ 6)) * kp3 * xml) / (1 + (kp3 * xml))) * (10 ^ 6 / cmlts) 'Mixed liquor solids bound metal
If mxml < ka3 Then
msml = mml - mxml * (cmlts / (10 ^ 6)) 'Mixed liquor soluble metal
```

```
    If msml < 0 Then
    msml = 0
    Else
    If msml < sol3 Then
    mpml = mppe
    Else
    msml = sol3
    mpml = ((mml * cmlts) / (10 ^ 6)) - msml - ((mxml * cmlts) / 10 ^ 6)
    End If
    End If
Else
mxml = ka3
msml = (mml - mxml) * (cmlts / (10 ^ 6)) 'Mixed liquor soluble metal
    If msml < 0 Then
    msml = 0
    Else
    If msml < sol3 Then
    mpml = mppe
    Else
    msml = sol3
    mpml = ((mml * cmlts) / (10 ^ 6)) - msml - ((mxml * cmlts) / 10 ^ 6)
    End If
    End If
End If

If mpml < 0 Then
mpml = 0
End If

'Secondary Sedimentation Equations
vt3 = vt2 'VSS:TSS ratio in final effluent and secondary sludge
xses = csests * vt3 'Secondary sludge volatile solids


'Partitioning of secondary sludge to wastage and recycle sludge
'Wastage sludge
```

```
 xws = xses 'Wastage sludge volatile solids
 cwsts = csests 'Wastage sludge total solids
 fws = ((fpe * cpets) + xmlinc - (cmlts * fml * (1 - tsrem2))) / cwsts 'Flow of wastage sludge
 'Recycled sludge
 frs = r * fpe 'Flow of recycled sludge
 xrs = xses 'Recycled sludge volatile solids
 crsts = csests 'Recycled sludge total solids
 fses = fws + frs 'Secondary sludge flow
 ffe = fml - fses 'Final effluent flow
 cfets = ((cmlts * fml) - (csests * fses)) / ffe 'Final effluent total solids
 xfe = ((xml * fml) - (xses * fses)) / ffe 'Final effluent volatile solids

 'Calculating model coefficients in final effluent
 kp4 = 14000 / (10 ^ 6) 'Adsorption coefficient for Zn in final effluent
 sol4 = -1.2763 * pH4 + 11.278
 ka4 = 10000

 'Metals in Secondary sedimentation
 tmrem2 = tsrem2  'Total metal removal in final sedimentation
 mxf = msml * kp4 * xfe 'Mixed liquor soluble metal adsorbed during final sedimentation
 mxfe = (((mxml * fml) + (mxf * fml * ((10 ^ 6) / cfets))) * (1 - tmrem2)) / ffe 'Solids bound metal in final effluent
 If mxfe < ka4 Then
 msfe1 = msml - mxf 'Soluble metal in final effluent
    If msfe1 < 0 Then
    msfe = 0
    mpfe = (mpml * fml * (1 - tmrem2)) / ffe
    Else
    If msfe1 < sol4 Then
    msfe = msfe1
    mpfe = (mpml * fml * (1 - tmrem2)) / ffe
    Else
    msfe = sol4
    mpfe = msfe1 - sol4 + ((mpml * fml * (1 - tmrem2)) / ffe)
    End If
    End If
 Else
```

```
 mxfe = ka4
 msfe1 = msml - mxf 'Soluble metal in final effluent
    If msfe1 < 0 Then
    msfe = 0
    mpfe = (mpml * fml * (1 - tmrem2)) / ffe
    Else
    If msfe1 < sol4 Then
    msfe = msfe1
    mpfe = (mpml * fml * (1 - tmrem2)) / ffe
    Else
    msfe = sol4
    mpfe = msfe1 - sol4 + ((mpml * fml * (1 - tmrem2)) / ffe)
    End If
    End If
End If

If mpfe < 0 Then
mpfe = 0
End If

mfe = msfe + mpfe + (mxfe * cfets / 10 ^ 6)

mses = (((mml * fml) - (mfe * ffe)) / fses) * (10 ^ 6 / csests) 'Secondary sludge metal concentration



'Partitioning of secondary sludge to wastage and recycle sludge
'Wastage sludge
mws = mses 'Wastage sludge metal concentration
'Recycled sludge
mrs = mses 'Recycled sludge metal concentration
```

Outputs

Zn	Total Influent							Primary Effluent						
Iteration	q	xinn	tsin	minn	mxinn	msinn	mpinn	fpe	xpe	cpets	mpe	mxpe	mspe	mppe
1	41667.000	400.000	500.000	1.000	750.000	0.414	0.211	40833.660	81.633	102.041	0.425	274.838	0.353	0.043
2	43399.167	480.550	599.781	1.164	812.679	0.414	0.262	42357.967	98.472	122.905	0.430	288.991	0.341	0.054
3	43718.319	495.419	617.303	1.192	823.474	0.414	0.270	42638.821	101.592	126.586	0.431	291.618	0.339	0.055
4	43772.612	498.481	620.259	1.197	825.791	0.414	0.271	42686.599	102.233	127.208	0.431	292.299	0.338	0.056
5	43781.662	499.485	620.750	1.198	826.644	0.414	0.271	42694.562	102.441	127.311	0.431	292.630	0.338	0.055
6	43783.162	500.104	620.832	1.198	827.212	0.414	0.270	42695.882	102.568	127.328	0.431	292.883	0.338	0.055
7	43783.410	500.620	620.845	1.198	827.697	0.414	0.270	42696.101	102.674	127.331	0.430	293.107	0.338	0.055
8	43783.451	501.085	620.848	1.198	828.136	0.414	0.270	42696.137	102.769	127.332	0.430	293.311	0.338	0.055
9	43783.458	501.509	620.848	1.198	828.536	0.414	0.269	42696.143	102.856	127.332	0.430	293.498	0.338	0.055
10	43783.459	501.898	620.848	1.198	828.902	0.414	0.269	42696.144	102.936	127.332	0.430	293.669	0.338	0.055
11	43783.459	502.254	620.848	1.198	829.238	0.414	0.269	42696.144	103.009	127.332	0.430	293.826	0.338	0.055
12	43783.459	502.581	620.848	1.198	829.545	0.414	0.269	42696.144	103.076	127.332	0.430	293.969	0.337	0.055
13	43783.459	502.880	620.848	1.198	829.827	0.414	0.269	42696.144	103.137	127.332	0.430	294.101	0.337	0.055
14	43783.459	503.154	620.848	1.198	830.085	0.414	0.268	42696.144	103.194	127.332	0.430	294.221	0.337	0.055
15	43783.459	503.405	620.848	1.198	830.321	0.414	0.268	42696.144	103.245	127.332	0.430	294.331	0.337	0.055
16	43783.459	503.636	620.848	1.198	830.537	0.414	0.268	42696.144	103.292	127.332	0.430	294.432	0.337	0.055
17	43783.459	503.847	620.848	1.198	830.735	0.414	0.268	42696.144	103.336	127.332	0.430	294.525	0.337	0.055
18	43783.459	504.040	620.848	1.198	830.917	0.414	0.268	42696.144	103.375	127.332	0.430	294.610	0.337	0.055
19	43783.459	504.217	620.848	1.198	831.083	0.414	0.268	42696.144	103.412	127.332	0.430	294.688	0.337	0.055
20	43783.459	504.380	620.848	1.198	831.236	0.414	0.268	42696.144	103.445	127.332	0.430	294.759	0.337	0.055
21	43783.459	504.528	620.848	1.198	831.375	0.414	0.268	42696.144	103.475	127.332	0.430	294.824	0.337	0.055
22	43783.459	504.665	620.848	1.198	831.503	0.414	0.268	42696.144	103.503	127.332	0.430	294.884	0.337	0.055
23	43783.459	504.790	620.848	1.198	831.620	0.414	0.268	42696.144	103.529	127.332	0.430	294.939	0.337	0.055
24	43783.459	504.904	620.848	1.198	831.728	0.414	0.267	42696.144	103.552	127.332	0.430	294.989	0.337	0.055

Outputs

Zn	Primary Sludge				Mixed Liquor						
Iteration	fps	xps	cpsts	mps	fml	xml	cmlts	mml	mxml	msml	mpml
1	833.340	16000.000	20000.000	1459.926	40833.660	1331.633	1652.041	4160.295	1700.000	0.066	3.999
2	1041.200	16024.168	20000.000	1550.267	63591.470	904.662	1115.216	2898.624	1700.000	0.066	1.271
3	1079.498	16051.075	20000.000	1563.652	64664.963	927.185	1136.593	2823.153	1700.000	0.066	1.211
4	1086.013	16073.325	20000.000	1566.078	64858.785	935.091	1140.479	2810.094	1700.000	0.066	1.200
5	1087.099	16092.952	20000.000	1566.691	64891.593	939.970	1141.139	2807.370	1700.000	0.066	1.198
6	1087.279	16110.759	20000.000	1566.985	64897.055	944.035	1141.249	2806.411	1700.000	0.066	1.197
7	1087.309	16127.041	20000.000	1567.210	64897.959	947.693	1141.267	2805.788	1700.000	0.066	1.196
8	1087.314	16141.954	20000.000	1567.409	64898.109	951.034	1141.270	2805.260	1700.000	0.066	1.195
9	1087.315	16155.619	20000.000	1567.590	64898.134	954.094	1141.271	2804.782	1700.000	0.066	1.195
10	1087.315	16168.142	20000.000	1567.756	64898.138	956.897	1141.271	2804.346	1700.000	0.066	1.194
11	1087.315	16179.618	20000.000	1567.908	64898.139	959.467	1141.271	2803.947	1700.000	0.066	1.194
12	1087.315	16190.135	20000.000	1568.047	64898.139	961.821	1141.271	2803.581	1700.000	0.066	1.194
13	1087.315	16199.773	20000.000	1568.174	64898.139	963.979	1141.271	2803.246	1700.000	0.066	1.193
14	1087.315	16208.605	20000.000	1568.291	64898.139	965.956	1141.271	2802.939	1700.000	0.066	1.193
15	1087.315	16216.699	20000.000	1568.398	64898.139	967.768	1141.271	2802.657	1700.000	0.066	1.193
16	1087.315	16224.117	20000.000	1568.496	64898.139	969.429	1141.271	2802.399	1700.000	0.066	1.192
17	1087.315	16230.915	20000.000	1568.585	64898.139	970.951	1141.271	2802.163	1700.000	0.066	1.192
18	1087.315	16237.144	20000.000	1568.668	64898.139	972.346	1141.271	2801.947	1700.000	0.066	1.192
19	1087.315	16242.853	20000.000	1568.743	64898.139	973.624	1141.271	2801.748	1700.000	0.066	1.191
20	1087.315	16248.085	20000.000	1568.812	64898.139	974.795	1141.271	2801.567	1700.000	0.066	1.191
21	1087.315	16252.879	20000.000	1568.875	64898.139	975.868	1141.271	2801.400	1700.000	0.066	1.191
22	1087.315	16257.273	20000.000	1568.933	64898.139	976.852	1141.271	2801.248	1700.000	0.066	1.191
23	1087.315	16261.299	20000.000	1568.987	64898.139	977.754	1141.271	2801.108	1700.000	0.066	1.191
24	1087.315	16264.989	20000.000	1569.035	64898.139	978.580	1141.271	2800.980	1700.000	0.066	1.191

Outputs

Zn	Secondary Sludge				Final Effluent							Wastage Sludge		
Iteration	fses	xses	csests	mses	ffe	xfe	cfets	mfe	mxfe	msfe	mpfe	fws	xws	cwsts
1	22965.670	2418.159	3000.000	1700.000	17867.990	-64.877	-80.487	0.217	66.469	0.085	0.137	1732.167	2418.159	3000.000
2	24077.462	2433.597	3000.000	1700.000	39514.008	-26.979	-33.258	0.103	46.845	0.074	0.031	2051.319	2433.597	3000.000
3	24277.799	2447.274	3000.000	1700.000	40387.165	13.419	16.449	0.092	46.639	0.062	0.029	2105.612	2447.274	3000.000
4	24311.693	2459.731	3000.000	1700.000	40547.093	20.929	25.526	0.090	46.624	0.060	0.029	2114.662	2459.731	3000.000
5	24317.334	2471.135	3000.000	1700.000	40574.259	22.298	27.070	0.089	46.643	0.059	0.029	2116.162	2471.135	3000.000
6	24318.269	2481.584	3000.000	1700.000	40578.786	22.605	27.327	0.089	46.666	0.059	0.029	2116.410	2481.584	3000.000
7	24318.423	2491.160	3000.000	1700.000	40579.536	22.727	27.370	0.089	46.689	0.059	0.029	2116.451	2491.160	3000.000
8	24318.449	2499.935	3000.000	1700.000	40579.660	22.813	27.377	0.089	46.710	0.059	0.029	2116.458	2499.935	3000.000
9	24318.453	2507.977	3000.000	1700.000	40579.681	22.888	27.378	0.089	46.729	0.059	0.029	2116.459	2507.977	3000.000
10	24318.454	2515.347	3000.000	1700.000	40579.684	22.955	27.378	0.089	46.746	0.059	0.029	2116.459	2515.347	3000.000
11	24318.454	2522.100	3000.000	1700.000	40579.685	23.017	27.378	0.089	46.762	0.059	0.029	2116.459	2522.100	3000.000
12	24318.454	2528.290	3000.000	1700.000	40579.685	23.073	27.378	0.089	46.777	0.059	0.029	2116.459	2528.290	3000.000
13	24318.454	2533.962	3000.000	1700.000	40579.685	23.125	27.378	0.089	46.790	0.059	0.029	2116.459	2533.962	3000.000
14	24318.454	2539.160	3000.000	1700.000	40579.685	23.172	27.378	0.089	46.803	0.059	0.029	2116.459	2539.160	3000.000
15	24318.454	2543.923	3000.000	1700.000	40579.685	23.216	27.378	0.089	46.814	0.059	0.029	2116.459	2543.923	3000.000
16	24318.454	2548.288	3000.000	1700.000	40579.685	23.256	27.378	0.089	46.824	0.059	0.029	2116.459	2548.288	3000.000
17	24318.454	2552.289	3000.000	1700.000	40579.685	23.292	27.378	0.089	46.834	0.059	0.029	2116.459	2552.289	3000.000
18	24318.454	2555.955	3000.000	1700.000	40579.685	23.326	27.378	0.089	46.843	0.059	0.029	2116.459	2555.955	3000.000
19	24318.454	2559.315	3000.000	1700.000	40579.685	23.356	27.378	0.089	46.851	0.059	0.029	2116.459	2559.315	3000.000
20	24318.454	2562.393	3000.000	1700.000	40579.685	23.385	27.378	0.089	46.858	0.059	0.029	2116.459	2562.393	3000.000
21	24318.454	2565.215	3000.000	1700.000	40579.685	23.410	27.378	0.089	46.865	0.059	0.029	2116.459	2565.215	3000.000
22	24318.454	2567.801	3000.000	1700.000	40579.685	23.434	27.378	0.089	46.871	0.059	0.029	2116.459	2567.801	3000.000
23	24318.454	2570.170	3000.000	1700.000	40579.685	23.455	27.378	0.089	46.876	0.059	0.029	2116.459	2570.170	3000.000
24	24318.454	2572.342	3000.000	1700.000	40579.685	23.475	27.378	0.089	46.881	0.059	0.029	2116.459	2572.342	3000.000

Outputs

Zn		Recycled Sludge			
Iteration	mws	frs	xrs	crsts	mrs
1	1700.000	21233.503	2418.159	3000.000	1700.000
2	1700.000	22026.143	2433.597	3000.000	1700.000
3	1700.000	22172.187	2447.274	3000.000	1700.000
4	1700.000	22197.031	2459.731	3000.000	1700.000
5	1700.000	22201.172	2471.135	3000.000	1700.000
6	1700.000	22201.859	2481.584	3000.000	1700.000
7	1700.000	22201.972	2491.160	3000.000	1700.000
8	1700.000	22201.991	2499.935	3000.000	1700.000
9	1700.000	22201.994	2507.977	3000.000	1700.000
10	1700.000	22201.995	2515.347	3000.000	1700.000
11	1700.000	22201.995	2522.100	3000.000	1700.000
12	1700.000	22201.995	2528.290	3000.000	1700.000
13	1700.000	22201.995	2533.962	3000.000	1700.000
14	1700.000	22201.995	2539.160	3000.000	1700.000
15	1700.000	22201.995	2543.923	3000.000	1700.000
16	1700.000	22201.995	2548.288	3000.000	1700.000
17	1700.000	22201.995	2552.289	3000.000	1700.000
18	1700.000	22201.995	2555.955	3000.000	1700.000
19	1700.000	22201.995	2559.315	3000.000	1700.000
20	1700.000	22201.995	2562.393	3000.000	1700.000
21	1700.000	22201.995	2565.215	3000.000	1700.000
22	1700.000	22201.995	2567.801	3000.000	1700.000
23	1700.000	22201.995	2570.170	3000.000	1700.000
24	1700.000	22201.995	2572.342	3000.000	1700.000

Outputs
Cu

	Total Influent							Primary Effluent						
Iteration	q	xinn	tsin	minn	mxinn	msinn	mpinn	fpe	xpe	cpets	mpe	mxpe	mspe	mppe
1	41667.000	400.000	500.000	1.000	333.333	0.833	0.000	40833.660	81.633	102.041	0.407	1156.463	0.289	0.000
2	43399.167	480.550	599.781	1.319	426.129	1.064	0.000	42357.967	98.472	122.905	0.408	1484.452	0.226	0.000
3	43718.319	495.419	617.303	1.375	442.334	1.102	0.000	42638.821	101.592	126.586	0.402	1542.011	0.206	0.000
4	43772.612	498.481	620.259	1.385	445.446	1.109	0.000	42686.599	102.233	127.208	0.399	1553.049	0.202	0.000
5	43781.662	499.485	620.750	1.386	446.318	1.109	0.000	42694.562	102.441	127.311	0.398	1556.119	0.200	0.000
6	43783.162	500.104	620.832	1.387	446.785	1.109	0.000	42695.882	102.568	127.328	0.397	1557.753	0.199	0.000
7	43783.410	500.620	620.845	1.387	447.158	1.109	0.000	42696.101	102.674	127.331	0.397	1559.055	0.198	0.000
8	43783.451	501.085	620.848	1.387	447.491	1.109	0.000	42696.137	102.769	127.332	0.396	1560.215	0.197	0.000
9	43783.458	501.509	620.848	1.387	447.794	1.109	0.000	42696.143	102.856	127.332	0.395	1561.272	0.196	0.000
10	43783.459	501.898	620.848	1.387	448.072	1.109	0.000	42696.144	102.936	127.332	0.395	1562.240	0.196	0.000
11	43783.459	502.254	620.848	1.387	448.326	1.108	0.000	42696.144	103.009	127.332	0.394	1563.126	0.195	0.000
12	43783.459	502.581	620.848	1.387	448.559	1.108	0.000	42696.144	103.076	127.332	0.394	1563.938	0.194	0.000
13	43783.459	502.880	620.848	1.387	448.772	1.108	0.000	42696.144	103.137	127.332	0.393	1564.682	0.194	0.000
14	43783.459	503.154	620.848	1.387	448.968	1.108	0.000	42696.144	103.194	127.332	0.393	1565.364	0.193	0.000
15	43783.459	503.405	620.848	1.387	449.147	1.108	0.000	42696.144	103.245	127.332	0.392	1565.988	0.193	0.000
16	43783.459	503.636	620.848	1.387	449.311	1.108	0.000	42696.144	103.292	127.332	0.392	1566.560	0.192	0.000
17	43783.459	503.847	620.848	1.387	449.461	1.108	0.000	42696.144	103.336	127.332	0.392	1567.085	0.192	0.000
18	43783.459	504.040	620.848	1.387	449.599	1.108	0.000	42696.144	103.375	127.332	0.391	1567.565	0.192	0.000
19	43783.459	504.217	620.848	1.387	449.725	1.108	0.000	42696.144	103.412	127.332	0.391	1568.005	0.191	0.000
20	43783.459	504.380	620.848	1.387	449.841	1.107	0.000	42696.144	103.445	127.332	0.391	1568.409	0.191	0.000
21	43783.459	504.528	620.848	1.387	449.947	1.107	0.000	42696.144	103.475	127.332	0.390	1568.778	0.191	0.000
22	43783.459	504.665	620.848	1.387	450.044	1.107	0.000	42696.144	103.503	127.332	0.390	1569.117	0.190	0.000
23	43783.459	504.790	620.848	1.387	450.133	1.107	0.000	42696.144	103.529	127.332	0.390	1569.427	0.190	0.000
24	43783.459	504.904	620.848	1.387	450.215	1.107	0.000	42696.144	103.552	127.332	0.390	1569.711	0.190	0.000

Outputs

Cu	Primary Sludge				Mixed Liquor						
Iteration	fps	xps	cpsts	mps	fml	xml	cmlts	mml	mxml	msml	mpml
1	833.340	16000.000	20000.000	1502.551	40833.660	1331.633	1652.041	3989.796	2057.978	2.007	1.184
2	1041.200	16024.168	20000.000	1919.249	63591.470	904.662	1115.216	3213.935	1349.411	2.007	0.072
3	1079.498	16051.075	20000.000	1991.866	64664.963	927.185	1136.593	3113.866	1326.084	2.007	0.025
4	1086.013	16073.325	20000.000	2005.757	64858.785	935.091	1140.479	3092.323	1323.333	2.007	0.010
5	1087.099	16092.952	20000.000	2009.606	64891.593	939.970	1141.139	3084.688	1323.997	2.007	0.002
6	1087.279	16110.759	20000.000	2011.648	64897.055	944.035	1141.249	3079.727	1325.125	2.007	0.000
7	1087.309	16127.041	20000.000	2013.271	64897.959	947.693	1141.267	3075.523	1326.232	2.007	0.000
8	1087.314	16141.954	20000.000	2014.718	64898.109	951.034	1141.270	3071.728	1327.248	2.007	0.000
9	1087.315	16155.619	20000.000	2016.036	64898.134	954.094	1141.271	3068.261	1328.169	2.007	0.000
10	1087.315	16168.142	20000.000	2017.242	64898.138	956.897	1141.271	3065.086	1329.003	2.007	0.000
11	1087.315	16179.618	20000.000	2018.347	64898.139	959.467	1141.271	3062.178	1329.759	2.007	0.000
12	1087.315	16190.135	20000.000	2019.360	64898.139	961.821	1141.271	3059.514	1330.444	2.007	0.000
13	1087.315	16199.773	20000.000	2020.287	64898.139	963.979	1141.271	3057.073	1331.067	2.007	0.000
14	1087.315	16208.605	20000.000	2021.137	64898.139	965.956	1141.271	3054.836	1331.632	2.007	0.000
15	1087.315	16216.699	20000.000	2021.916	64898.139	967.768	1141.271	3052.787	1332.146	2.007	0.000
16	1087.315	16224.117	20000.000	2022.629	64898.139	969.429	1141.271	3050.910	1332.613	2.007	0.000
17	1087.315	16230.915	20000.000	2023.283	64898.139	970.951	1141.271	3049.189	1333.039	2.007	0.000
18	1087.315	16237.144	20000.000	2023.882	64898.139	972.346	1141.271	3047.613	1333.426	2.007	0.000
19	1087.315	16242.853	20000.000	2024.431	64898.139	973.624	1141.271	3046.169	1333.779	2.007	0.000
20	1087.315	16248.085	20000.000	2024.934	64898.139	974.795	1141.271	3044.845	1334.100	2.007	0.000
21	1087.315	16252.879	20000.000	2025.395	64898.139	975.868	1141.271	3043.633	1334.394	2.007	0.000
22	1087.315	16257.273	20000.000	2025.817	64898.139	976.852	1141.271	3042.521	1334.661	2.007	0.000
23	1087.315	16261.299	20000.000	2026.204	64898.139	977.754	1141.271	3041.503	1334.906	2.007	0.000
24	1087.315	16264.989	20000.000	2026.558	64898.139	978.580	1141.271	3040.570	1335.128	2.007	0.000

Outputs

Cu	Secondary Sludge				Final Effluent					
Iteration	fses	xses	csests	mses	ffe	xfe	cfets	mfe	mxfe	msfe
1	22965.670	2418.159	3000.000	3000.000	17867.990	-64.877	-80.487	3.803	847.071	2.344
2	24077.462	2433.597	3000.000	3000.000	39514.008	-26.979	-33.258	2.748	582.907	2.344
3	24277.799	2447.274	3000.000	3000.000	40387.165	13.419	16.449	1.640	582.448	1.630
4	24311.693	2459.731	3000.000	3000.000	40547.093	20.929	25.526	1.434	584.624	1.419
5	24317.334	2471.135	3000.000	3000.000	40574.259	22.298	27.070	1.397	587.107	1.381
6	24318.269	2481.584	3000.000	3000.000	40578.786	22.605	27.327	1.388	589.466	1.372
7	24318.423	2491.160	3000.000	3000.000	40579.536	22.727	27.370	1.385	591.642	1.369
8	24318.449	2499.935	3000.000	3000.000	40579.660	22.813	27.377	1.383	593.638	1.366
9	24318.453	2507.977	3000.000	3000.000	40579.681	22.888	27.378	1.380	595.467	1.364
10	24318.454	2515.347	3000.000	3000.000	40579.684	22.955	27.378	1.379	597.143	1.362
11	24318.454	2522.100	3000.000	3000.000	40579.685	23.017	27.378	1.377	598.679	1.361
12	24318.454	2528.290	3000.000	3000.000	40579.685	23.073	27.378	1.375	600.086	1.359
13	24318.454	2533.962	3000.000	3000.000	40579.685	23.125	27.378	1.374	601.376	1.357
14	24318.454	2539.160	3000.000	3000.000	40579.685	23.172	27.378	1.373	602.558	1.356
15	24318.454	2543.923	3000.000	3000.000	40579.685	23.216	27.378	1.371	603.640	1.355
16	24318.454	2548.288	3000.000	3000.000	40579.685	23.256	27.378	1.370	604.633	1.354
17	24318.454	2552.289	3000.000	3000.000	40579.685	23.292	27.378	1.369	605.542	1.353
18	24318.454	2555.955	3000.000	3000.000	40579.685	23.326	27.378	1.368	606.375	1.352
19	24318.454	2559.315	3000.000	3000.000	40579.685	23.356	27.378	1.368	607.138	1.351
20	24318.454	2562.393	3000.000	3000.000	40579.685	23.385	27.378	1.367	607.838	1.350
21	24318.454	2565.215	3000.000	3000.000	40579.685	23.410	27.378	1.366	608.479	1.349
22	24318.454	2567.801	3000.000	3000.000	40579.685	23.434	27.378	1.365	609.067	1.349
23	24318.454	2570.170	3000.000	3000.000	40579.685	23.455	27.378	1.365	609.605	1.348
24	24318.454	2572.342	3000.000	3000.000	40579.685	23.475	27.378	1.364	610.098	1.348

Outputs

Cu

		Wastage Sludge				Recycled Sludge			
Iteration	mpfe	fws	xws	cwsts	mws	frs	xrs	crsts	mrs
1	1.527	1732.167	2418.159	3000.000	3000.000	21233.503	2418.159	3000.000	3000.000
2	0.423	2051.319	2433.597	3000.000	3000.000	22026.143	2433.597	3000.000	3000.000
3	0.001	2105.612	2447.274	3000.000	3000.000	22172.187	2447.274	3000.000	3000.000
4	0.000	2114.662	2459.731	3000.000	3000.000	22197.031	2459.731	3000.000	3000.000
5	0.000	2116.162	2471.135	3000.000	3000.000	22201.172	2471.135	3000.000	3000.000
6	0.000	2116.410	2481.584	3000.000	3000.000	22201.859	2481.584	3000.000	3000.000
7	0.000	2116.451	2491.160	3000.000	3000.000	22201.972	2491.160	3000.000	3000.000
8	0.000	2116.458	2499.935	3000.000	3000.000	22201.991	2499.935	3000.000	3000.000
9	0.000	2116.459	2507.977	3000.000	3000.000	22201.994	2507.977	3000.000	3000.000
10	0.000	2116.459	2515.347	3000.000	3000.000	22201.995	2515.347	3000.000	3000.000
11	0.000	2116.459	2522.100	3000.000	3000.000	22201.995	2522.100	3000.000	3000.000
12	0.000	2116.459	2528.290	3000.000	3000.000	22201.995	2528.290	3000.000	3000.000
13	0.000	2116.459	2533.962	3000.000	3000.000	22201.995	2533.962	3000.000	3000.000
14	0.000	2116.459	2539.160	3000.000	3000.000	22201.995	2539.160	3000.000	3000.000
15	0.000	2116.459	2543.923	3000.000	3000.000	22201.995	2543.923	3000.000	3000.000
16	0.000	2116.459	2548.288	3000.000	3000.000	22201.995	2548.288	3000.000	3000.000
17	0.000	2116.459	2552.289	3000.000	3000.000	22201.995	2552.289	3000.000	3000.000
18	0.000	2116.459	2555.955	3000.000	3000.000	22201.995	2555.955	3000.000	3000.000
19	0.000	2116.459	2559.315	3000.000	3000.000	22201.995	2559.315	3000.000	3000.000
20	0.000	2116.459	2562.393	3000.000	3000.000	22201.995	2562.393	3000.000	3000.000
21	0.000	2116.459	2565.215	3000.000	3000.000	22201.995	2565.215	3000.000	3000.000
22	0.000	2116.459	2567.801	3000.000	3000.000	22201.995	2567.801	3000.000	3000.000
23	0.000	2116.459	2570.170	3000.000	3000.000	22201.995	2570.170	3000.000	3000.000
24	0.000	2116.459	2572.342	3000.000	3000.000	22201.995	2572.342	3000.000	3000.000

APPENDIX C

EXPERIMENTAL RESULTS

Table C.1: *Equilibrium Time Experiment: Copper in Primary Sedimentation*

Time (min)	SS conc 970 mg/l	SS conc 1670 mg/l	SS conc 3500 mg/l	No Solids
0	2.00000	2.00000	2.00000	2.00000
5	1.46429	0.86429	0.12143	2.12857
10	0.71429	0.46429	0.05000	2.24286
15	0.54286	0.12857	0.04286	2.27143
20	0.40000	0.10714	0.06429	2.19286
25	0.43571	0.11429	0.05714	1.90714
30	0.41429	0.08571	0.08571	1.95714
60	0.15000	0.04286	0.04286	2.13571
90	0.09286	0.07143	0.06429	1.84286
120	0.10000	0.06429	0.10000	1.87143
150	0.08571	0.05000	0.07143	1.90000

Table C.2: *Equilibrium Time Experiment Copper in Activated Sludge*

Time (min)	SS Conc 1500 mg/l	SS Conc 2000 mg/l	SS Conc 3000 mg/l	No solids
0	2.00000	2.00000	2.00000	2.00000
5	0.21429	0.17143	0.13929	1.95000
10	0.13393	0.16607	0.15000	1.96071
15	0.13393	0.13393	0.15536	1.85893
20	0.14464	0.17143	0.13929	1.90714
25	0.12857	0.20893	0.16071	1.92857
30	0.11786	0.16607	0.16607	1.88571
60	0.15536	0.17679	0.15000	1.88036
90	0.16071	0.16607	0.13929	1.96071
120	0.16071	0.17143	0.14464	1.89643
150	0.17143	0.18750	0.17143	1.92857
180	0.15536	0.16607	0.19286	1.82143
240	0.16071	0.16071	0.19286	1.92321

Table C.3: *Results of Solubility Limit for Zn in Raw Sewage*

Zn addition (mg/l)	Soluble Zn (mg/l)	pH
10	9.258	6.59
10	9.146	6.89
10	11.504	6.97
10	9.412	7.25
10	8.444	7.31
10	12.4	7.35
10	8.338	7.91
10	6.224	8.2
10	4.862	8.32
10	4.324	8.44
10	7.306	8.58
10	4.852	8.74
10	4.608	8.86
10	5.586	9.04
10	8.398	9.08
20	16.294	6.05
20	20.421	6.55
20	17.144	6.76
20	16.594	6.78
20	19.31	6.8
20	18.038	7.12
20	12.077	7.12
20	11.066	7.16
20	9.986	7.17
20	7.994	7.4
20	7.502	7.5
20	15.408	7.75
20	17.87	8.09
20	12.243	8.25
20	12.12	8.28
20	13.56	8.36
20	11.636	8.4
20	11.598	8.47
20	16.992	8.7
20	9.85	8.88
30	25.462	3.74
30	27.465	5.93
30	27.433	6.33
30	25.778	6.38
30	27.005	6.5
30	21.508	6.65
30	25.714	6.7
30	27.23	6.71
30	23.068	6.85
30	22.912	6.87
30	19.344	7.05
30	22.556	7.08
30	18.424	7.09
30	16.874	7.17
30	24.094	7.2
30	19.964	7.36
30	20.248	8.58
30	27.73	8.98
30	18.48	9.3

30	15.846	10.05
40	33.894	3.06
40	40.892	3.34
40	39.823	4.26
40	37.636	5.57
40	40.97	5.95
40	39.21	6.18
40	33.626	6.31
40	41.55	6.33
40	30.362	6.44
40	39.426	6.47
40	30.66	6.72
40	28.46	6.77
40	19.334	7.22
40	22.47	7.55
40	29.832	7.67
40	11.912	7.79
40	26.518	7.95
40	11.544	8.56
40	22.336	8.71
40	20.276	9.42
50	50	6.12
50	44	6.51
50	32.854	6.88
50	33.394	7.18
50	27.598	7.5
50	29.676	7.74
50	9.772	7.75
50	20.916	8.75
50	16.028	9.28
50	18.586	9.4
60	26.652	7.58
60	14.352	8.2
60	11.036	9.11
60	13.328	9.7
60	12.806	10.3

Table C.4: *Results of Solubility Limit for Zn in Final Effluent*

Zn addition (mg/l)	Soluble Zn (mg/l)	pH
10	6.022	7.91
10	5.052	8.18
10	5.462	8.72
10	3.764	8.94
10	5.372	9.13
20	9.908	7.35
20	7.498	8.16
20	5.46	8.22
20	6.076	8.36
20	8.966	8.9
30	13.03	7.52
30	9.5	8.52
30	13.002	8.75
30	10.492	8.16
30	7.938	9.67
40	18.394	7.56
40	16.976	8.04
40	18.71	8.16
40	11.08	8.63
40	6.604	9.31
50	22.224	7.47
50	19.848	8.17
50	21.95	9
50	8.506	9.19
50	13.956	9.32

Table C.5 *Results of Solubility Limit for Cu in Raw Sewage*

Cu addition (mg/l)	Soluble Cu (mg/l)	pH
10	11.2	6.94
10	10.645	7.28
10	10.25	7.7
10	10.51	7.72
10	10.655	7.8
19.8	18.705	6.42
19.8	18.42	6.78
19.8	18.03	7.12
19.8	18.385	7.47
19.8	18.33	8.3
20	20.26	6.75
20	18.26	6.89
20	20.025	6.93
20	19.78	7.14
20	19.29	7.3
20	20.25	7.43
20	16.87	7.62
20	18.23	8.21
20	17.78	8.92
20	17.505	9.2
30	27.845	6.36
30	27.96	6.9
30	26.605	6.92
30	25.35	7.1
30	27.59	7.14
30	27.93	7.23
30	24.785	7.58
30	26.42	7.7
30	24.745	8.44
30	25.225	8.67
40	27.92	6.32
40	26.815	6.54
40	27.665	6.7
40	27.95	6.83
40	29.665	6.92
40	28.715	7.19
40	28.055	7.6
40	25.675	7.74
40	28.245	8.74
40	30.395	8.92
50	34.39	6.26
50	30.515	6.55
50	31.045	6.6
50	27.01	6.76
50	30.29	6.85
50	29.21	7.05
50	29.03	7.29
50	21.215	8.17
50	27.04	8.36
50	25.125	9.08

Table C.6 *Results of Solubility Limit for Cu in Final Effluent*

Cu addition (mg/l)	Soluble Cu (mg/l)	pH
10	9.01	7.23
10	7.605	7.37
10	6.515	7.94
10	6.335	7.72
10	5.885	7.91
20	10.46	7.05
20	7.125	7.24
20	5.845	7.54
20	8.97	7.7
20	6.535	7.71
30	10	7.03
30	12.14	7.15
30	9.575	7.46
30	10.93	7.62
30	7.425	8.28
40	13.255	6.92
40	11.82	7.16
40	9.295	7.56
40	14.625	7.45
40	9.1	7.84
50	15.37	6.91
50	18.965	7
50	17.75	7.62
50	14.69	7.7
50	16.905	7.2

Table C.7 *Results of Solubility Limit for Pb in Raw Sewage*

Pb addition (mg/l)	Soluble Pb (mg/l)	pH
10	11.54	7.55
10	11.62	7.79
10	11.04	8.16
10	10.8	8.6
10	10.74	8.78
20	21.08	7.48
20	20.14	7.74
20	20.6	8.15
20	20.78	8.43
20	20.44	8.94
30	29.78	7.56
30	30.12	7.86
30	29.02	8.47
30	29.3	8.56
30	29.52	8.8
40	38.08	7.56
40	38.1	8.06
40	37.72	8.43
40	37.88	8.6
40	39.08	8.83
50	48.42	7.35
50	47.28	8.24
50	43.46	8.49
50	46.4	8.55
50	46.8	8.73

Table C.8 *Results of Solubility Limit for Pb in Final Effluent*

Pb addition (mg/l)	Soluble Pb (mg/l)	0
10	19.76	7.35
10	11.24	7.38
10	11.06	7.74
10	10.44	8.18
10	9.38	8.53
20	23.14	6.9
20	20.66	7.41
20	19.66	8.25
20	18.94	8.28
20	17.76	8.55
30	25.88	7.31
30	26.8	8.17
30	23.04	8.53
30	24.8	8.6
30	25.06	8.65
40	35.64	7.59
40	35.3	8.03
40	34.74	8.39
40	30.24	8.51
40	33.06	8.75
50	40	7.7
50	40.36	8.26
50	39.34	8.67
50	31.28	8.94
50	32	8.95

Table C.9 *Effect of Final Effluent Concentration on Solubility limit of Cu*

Cu addition (mg/l)	Soluble Cu (mg/l)	pH	% FE
10	20.69	4.5	22.5
20	8.725	6.71	22.5
30	19.855	6.18	22.5
40	35.39	5.6	22.5
50	41.875	4.36	22.5
10	7.48	6.94	45
20	6.81	7.19	45
30	16.88	6.86	45
40	22.34	6.39	45
50	33.76	6.18	45
10	5.99	7.07	67.5
20	9.84	7.78	67.5
30	8.43	7.18	67.5
40	16.25	6.8	67.5
50	30.81	6.64	67.5
10	9.925	7.52	90
20	11.35	7.58	90
30	14.33	7.52	90
40	14.655	7.15	90
50	18.12	6.88	90
10	12.34	Acidified	0
20	18.965	Acidified	0
30	27.375	Acidified	0
40	36.43	Acidified	0
50	43.325	Acidified	0

Table C.10 *Cu adsorption in raw sewage*

Date carried out: 23/08/00

Date analysed: 01/09/00

Initial Total Cu (mg/l) 0.2

Sample	TSS (mg/l)	pH	Cu Added (mg/l)	Residual Soluble Cu (mg/l)	Total Adsorbed (mg/l)	Adsorbed (mg/kg)	Total Metal (mg/l)
A-1-1	474	6.58	2.5	2.162	0.538	1261.134552	2.7
A-2-1	474	6.5	5	4.04	1.16	2719.174871	5.2
A-2-2	474	6.71	5	4.249	0.951	2229.254571	5.2
A-4-1	474	6.56	10	7.961	2.239	5248.476324	10.2
A-4-2	474	6.71	10	8.01	2.19	5133.614627	10.2
B-2-1	322	6.55	5	4.302	0.898	3098.688751	5.2
C-2-1	668	6.59	5	4.044	1.156	1922.821025	5.2
A-1-2	474	7.03	2.5	2.185	0.515	1207.219878	2.7
A-1-3	474	7.08	2.5	2.183	0.517	1211.908111	2.7
A-2-3	474	7.06	5	4.204	0.996	2334.739803	5.2
A-3-1	474	6.96	7.5	6.219	1.481	3471.636193	7.7
A-3-2	474	6.78	7.5	5.958	1.742	4083.450539	7.7
A-3-3	474	6.96	7.5	6.346	1.354	3173.933427	7.7
B-1-1	322	6.89	2.5	2.231	0.469	1618.357488	2.7
B-3-1	322	6.85	7.5	6.39	1.31	4520.358868	7.7
B-3-2	322	7.13	7.5	6.521	1.179	4068.322981	7.7
B-4-1	322	6.98	10	8.069	2.131	7353.347136	10.2
C-1-1	668	6.91	2.5	1.991	0.709	1179.308051	2.7
C-2-2	668	6.99	5	4.248	0.952	1583.499667	5.2
C-3-1	668	6.99	7.5	6.274	1.426	2371.922821	7.7
C-3-2	668	6.99	7.5	6.355	1.345	2237.192282	7.7
C-4-1	668	6.84	10	7.648	2.552	4244.843646	10.2
C-4-2	668	7.1	10	7.783	2.417	4020.292748	10.2
A-1-4	474	7.4	2.5	2.112	0.588	1378.340366	2.7
A-2-4	474	7.31	5	4.278	0.922	2161.275199	5.2
A-4-3	474	7.3	10	8.163	2.037	4774.964838	10.2
A-4-4	474	7.4	10	8.292	1.908	4472.57384	10.2
B-1-2	322	7.21	2.5	2.328	0.372	1283.643892	2.7
B-2-2	322	7.22	5	4.417	0.783	2701.863354	5.2
B-3-3	322	7.25	7.5	6.505	1.195	4123.533471	7.7

Sample	TSS (mg/l)	pH	Cu Added (mg/l)	Residual Soluble Cu (mg/l)	Total Adsorbed (mg/l)	Adsorbed (mg/kg)	Total Metal (mg/l)
B-4-2	322	7.24	10	8.235	1.965	6780.538302	10.2
C-1-2	668	7.35	2.5	2.141	0.559	929.8070526	2.7
C-3-3	668	7.16	7.5	6.101	1.599	2659.680639	7.7
A-3-4	474	7.65	7.5	6.634	1.066	2498.827942	7.7
C-1-3	668	7.47	2.5	2.093	0.607	1009.647372	2.7
C-2-3	668	7.7	5	4.224	0.976	1623.419827	5.2
C-4-3	668	7.53	10	7.926	2.274	3782.43513	10.2
B-1-3	322	8.08	2.5	2.325	0.375	1293.995859	2.7
B-2-3	322	8	5	4.532	0.668	2305.037957	5.2
B-2-4	322	8.23	5	4.507	0.693	2391.304348	5.2
B-4-3	322	8.19	10	8.796	1.404	4844.720497	10.2
C-1-4	668	7.92	2.5	2.203	0.497	826.6799734	2.7
C-2-4	668	8.02	5	4.231	0.969	1611.776447	5.2
C-3-4	668	8.05	7.5	6.366	1.334	2218.895542	7.7
C-4-4	668	8.21	10	8.415	1.785	2969.061876	10.2
B-1-4	322	8.5	2.5	2.305	0.395	1363.008972	2.7
B-3-4	322	8.51	7.5	6.883	0.817	2819.185645	7.7
B-4-4	322	8.48	10	9.306	0.894	3084.886128	10.2

Cu adsorption in raw sewage

Figure C.1: ***Cu adsorption in Raw Sewage Solids Concentration A (474 mg/l)***

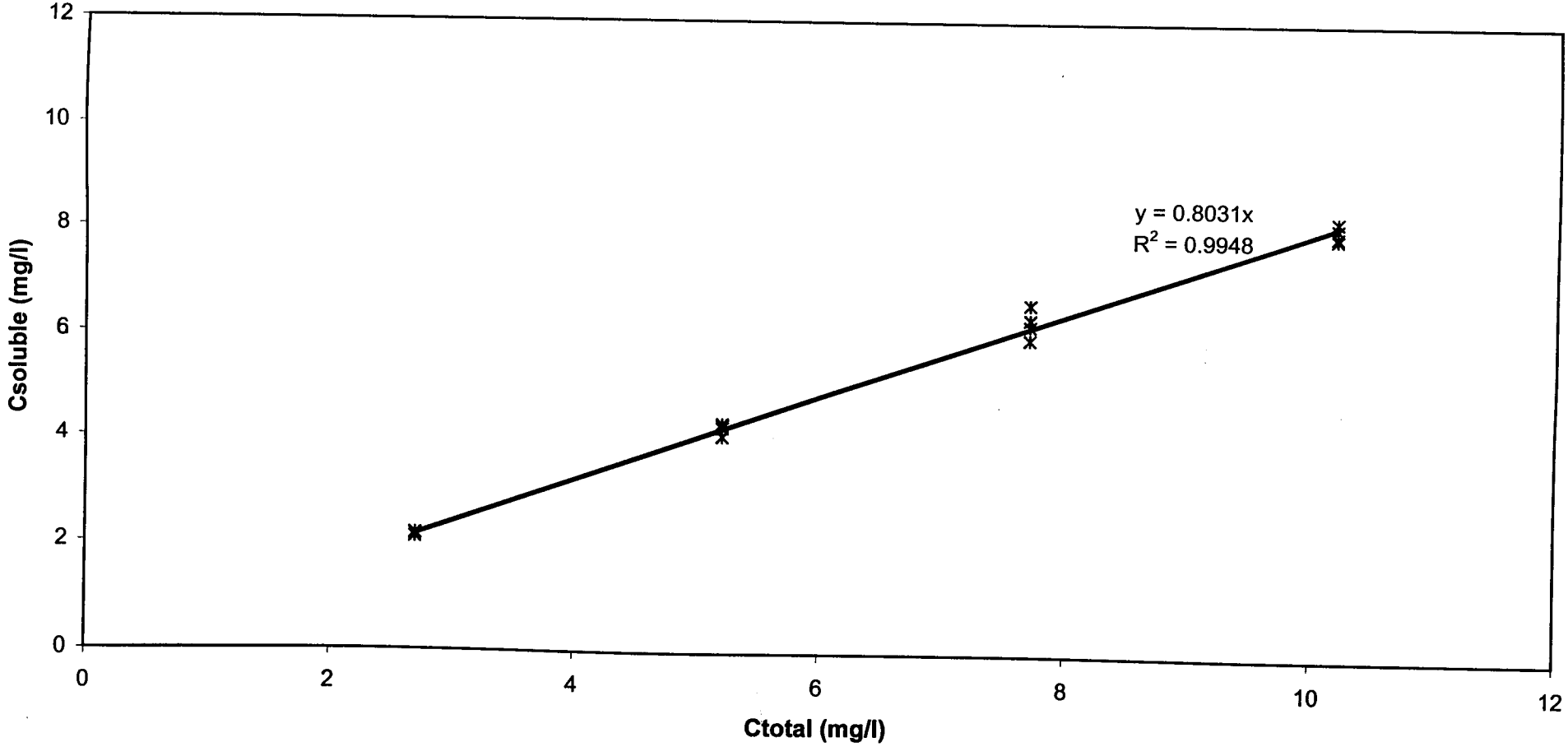


Figure C.2: ***Cu adsorption in Raw Sewage Solids Concentration A (474 mg/l)***

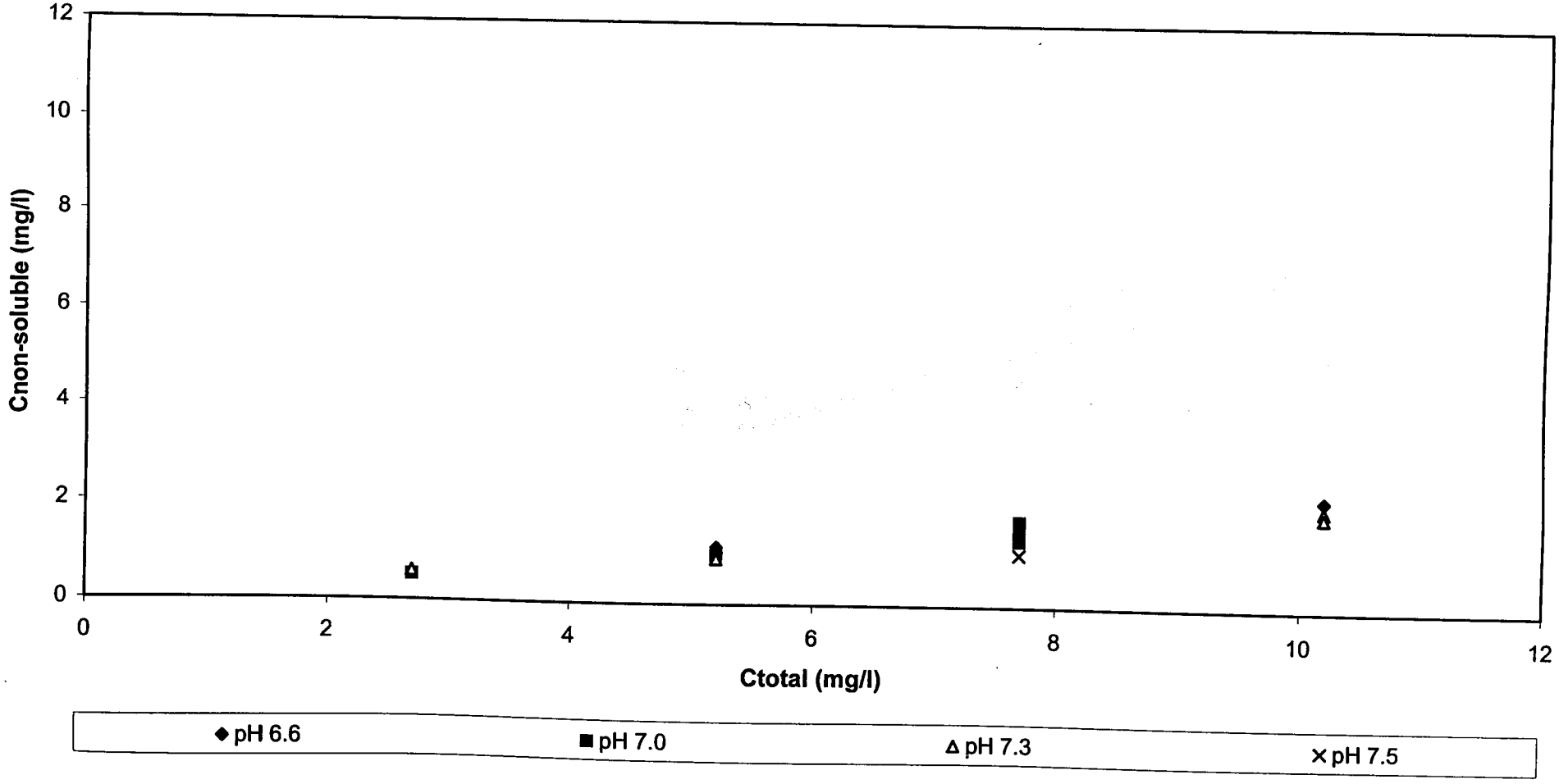


Figure C.3: ***Cu adsorption in Raw Sewage Solids Concentration A (474 mg/l)***

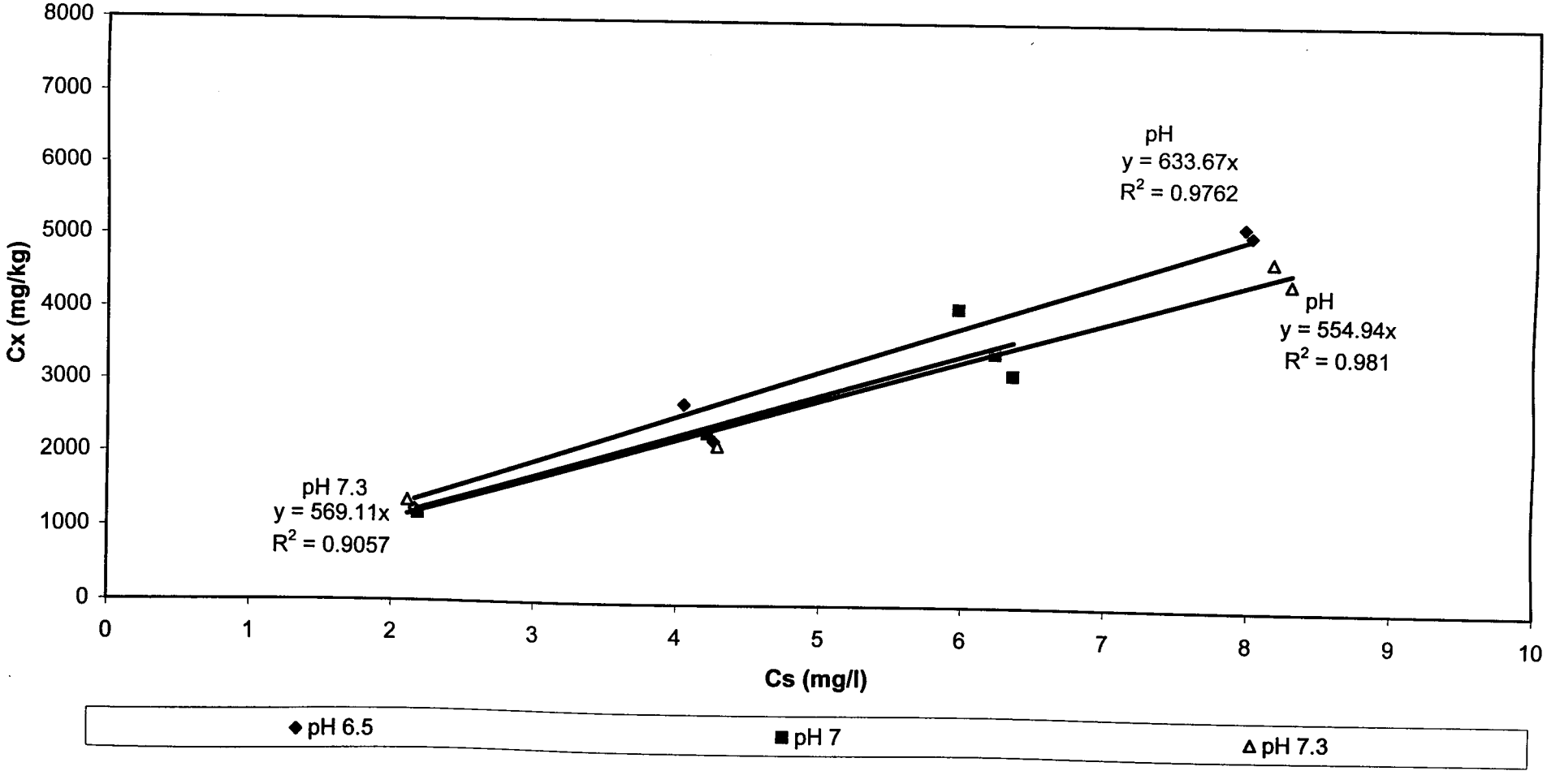


Figure C.4: ***Cu adsorption in Raw Sewage Solids Concentration A (474 mg/l)***

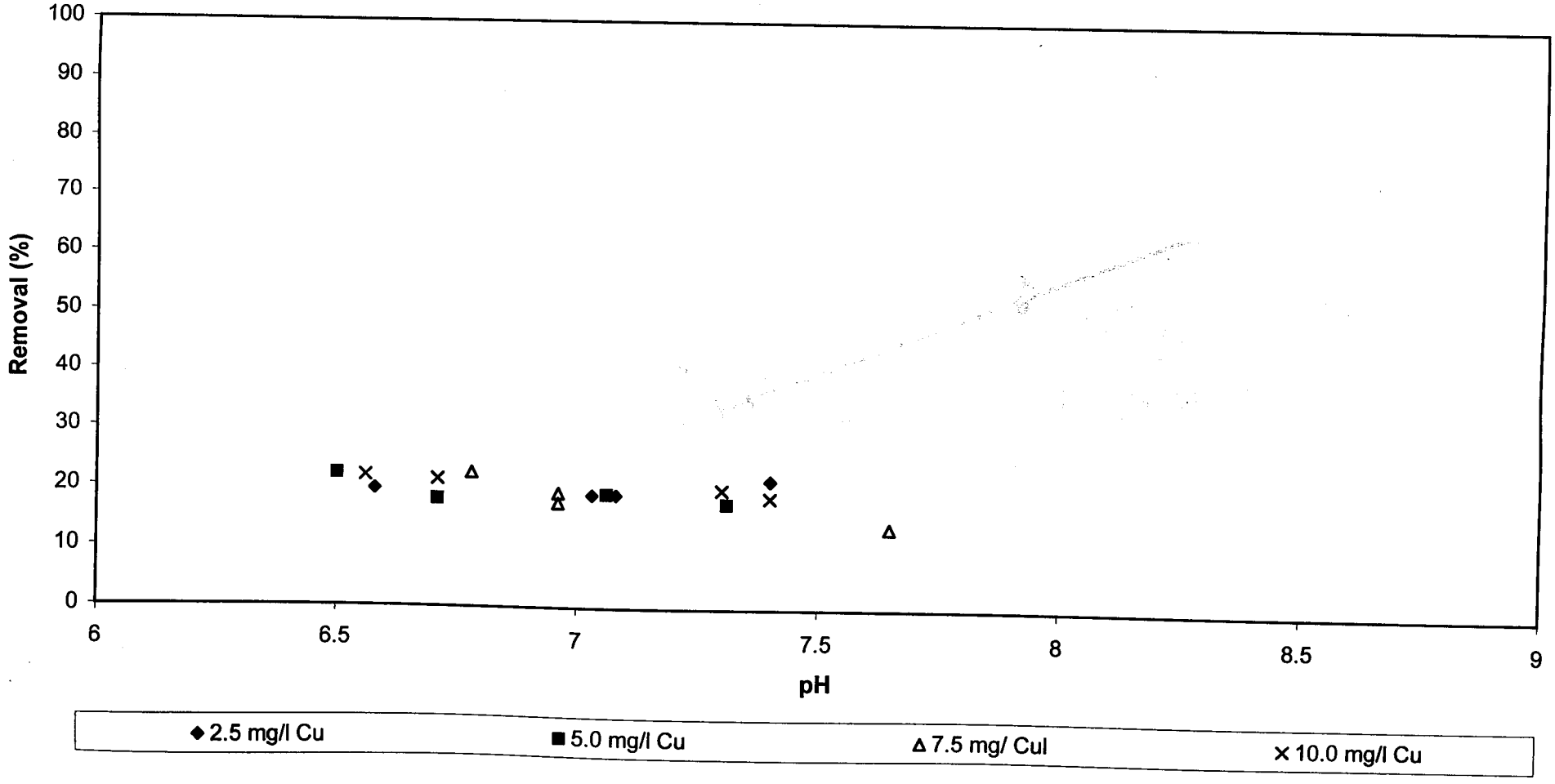


Figure C.5: ***Cu adsorption in Raw Sewage Solids Concentration B (322 mg/l)***

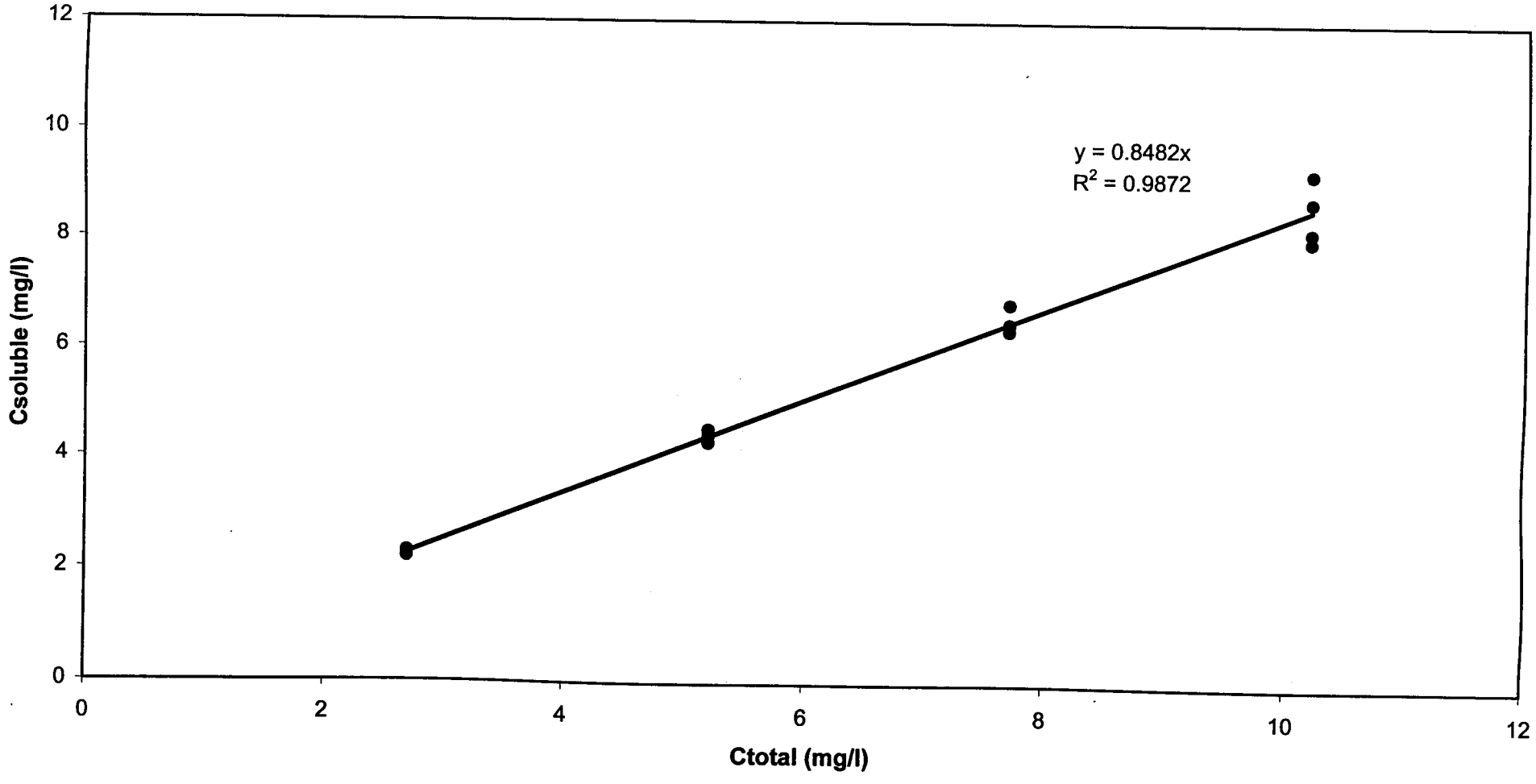


Figure C.6: ***Cu adsorption in Raw Sewage Solids Concentration B (322 mg/l)***

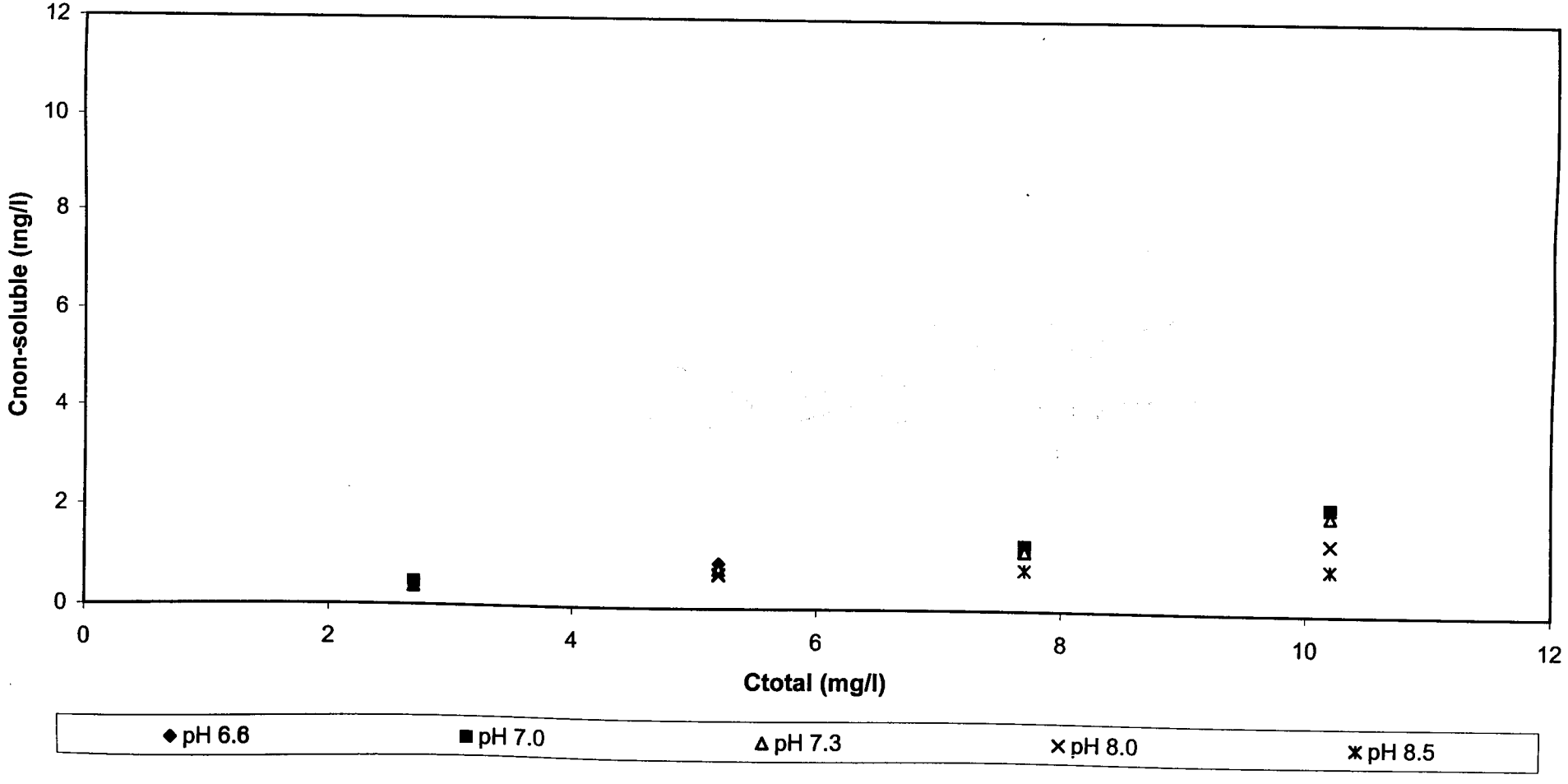


Figure C. 7: ***Cu adsorption in Raw Sewage Solids Concentration B (322 mg/l)***

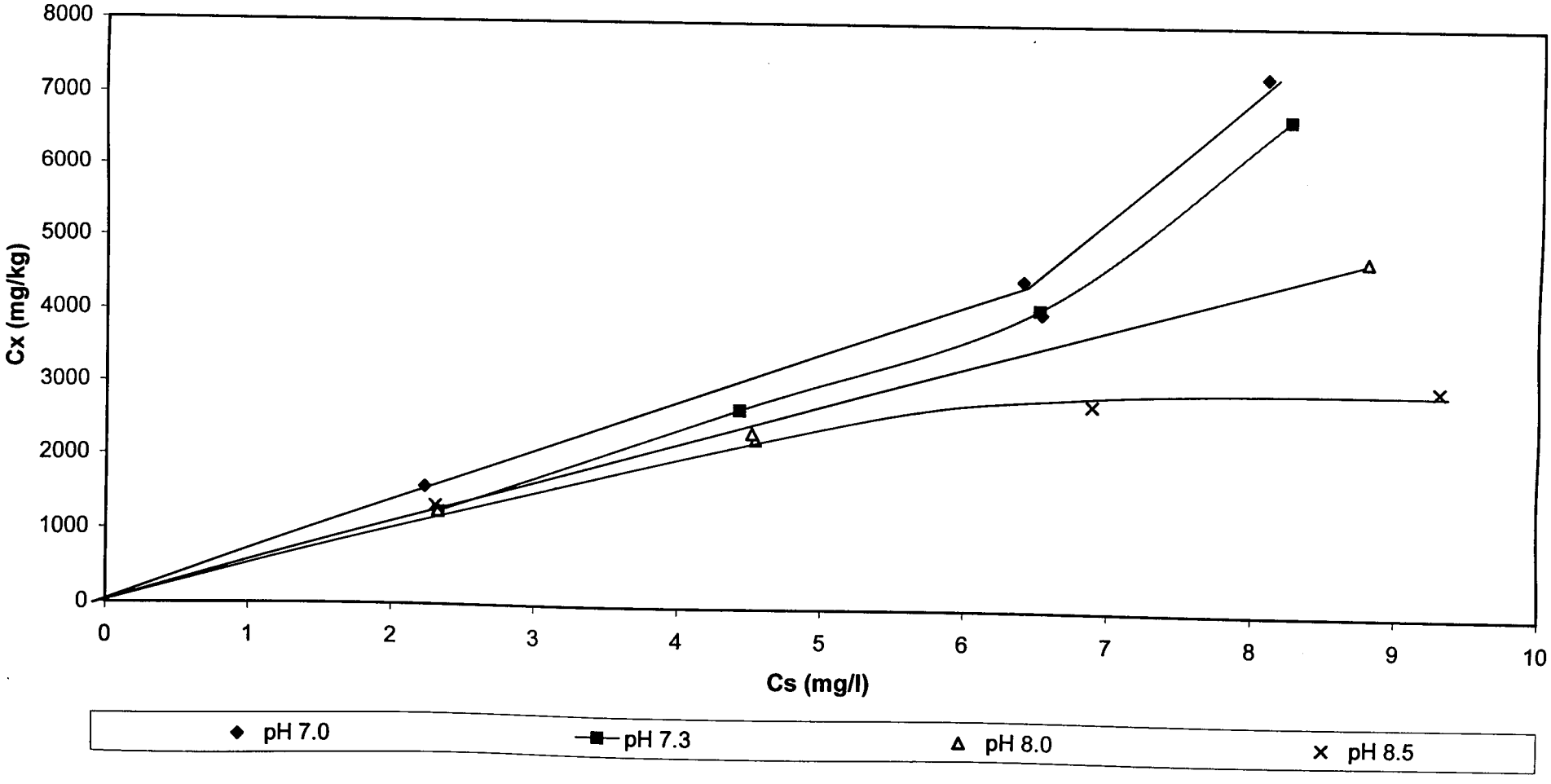


Figure C.8: ***Cu adsorption in Raw Sewage Solids Concentration B (322 mg/l)***

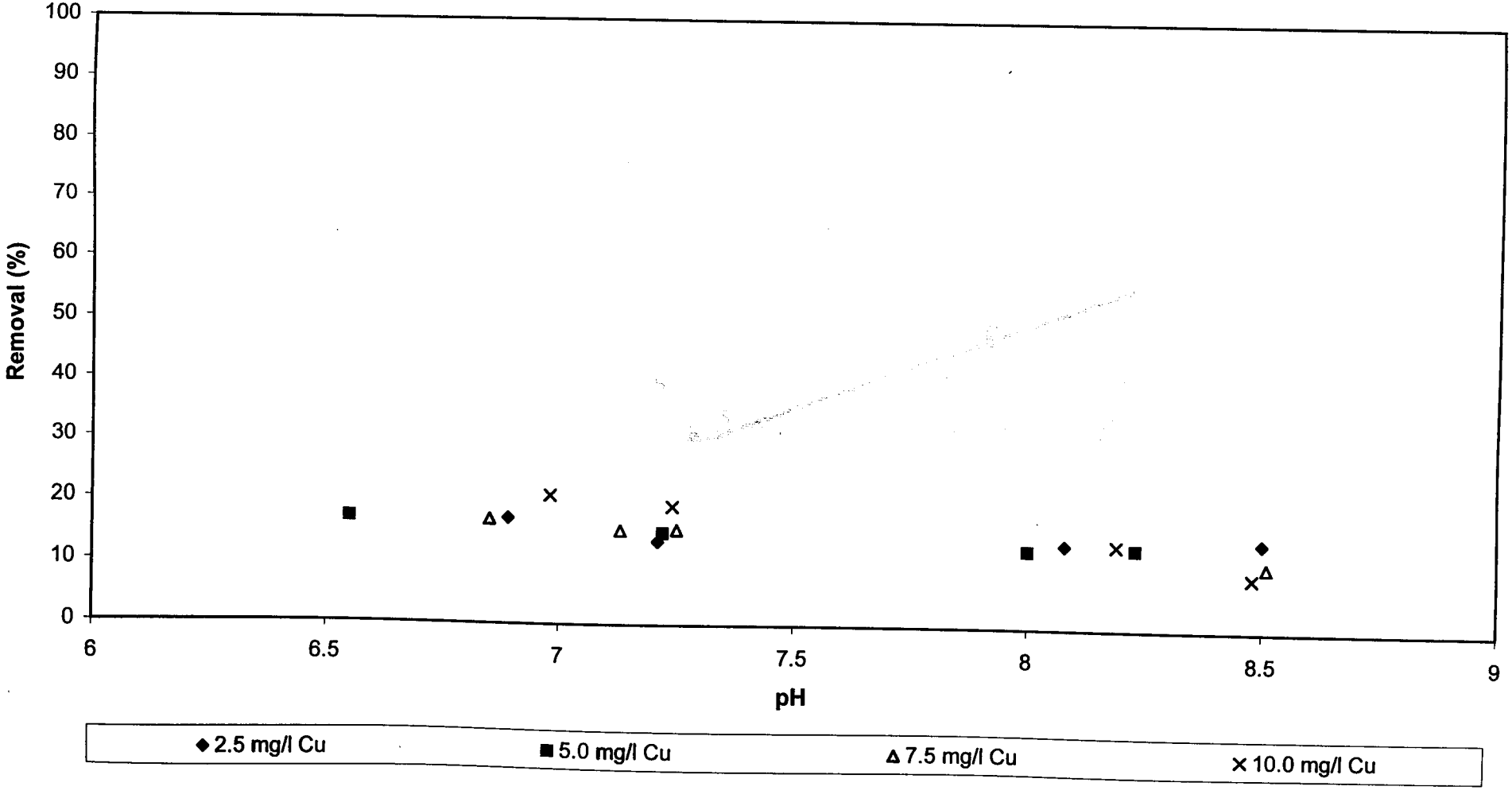


Figure C.9: ***Cu adsorption in Raw Sewage Solids Concentration C (668 mg/l)***

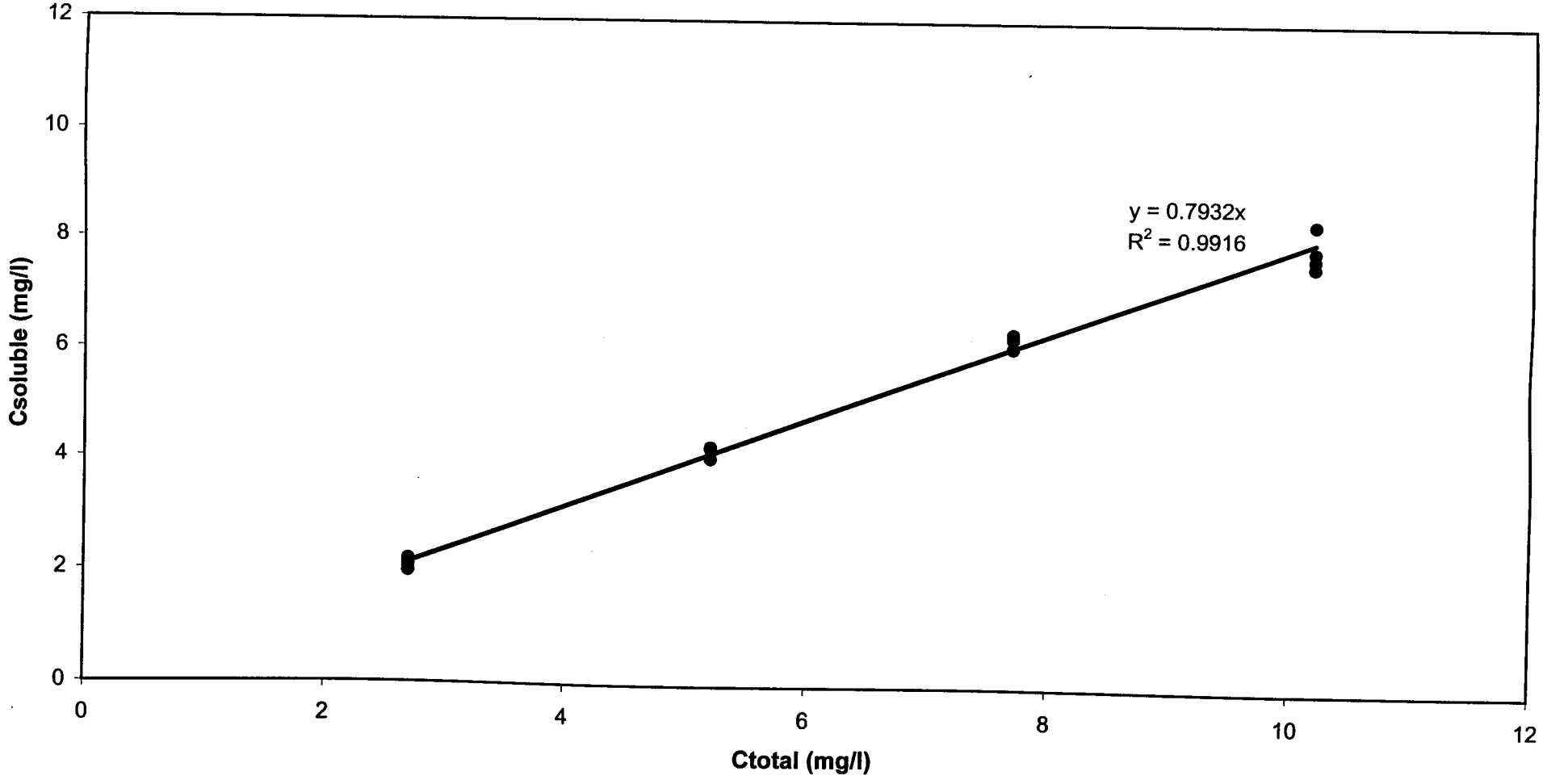


Figure C. 10: ***Cu adsorption in Raw Sewage Solids Concentration C (668 mg/l)***

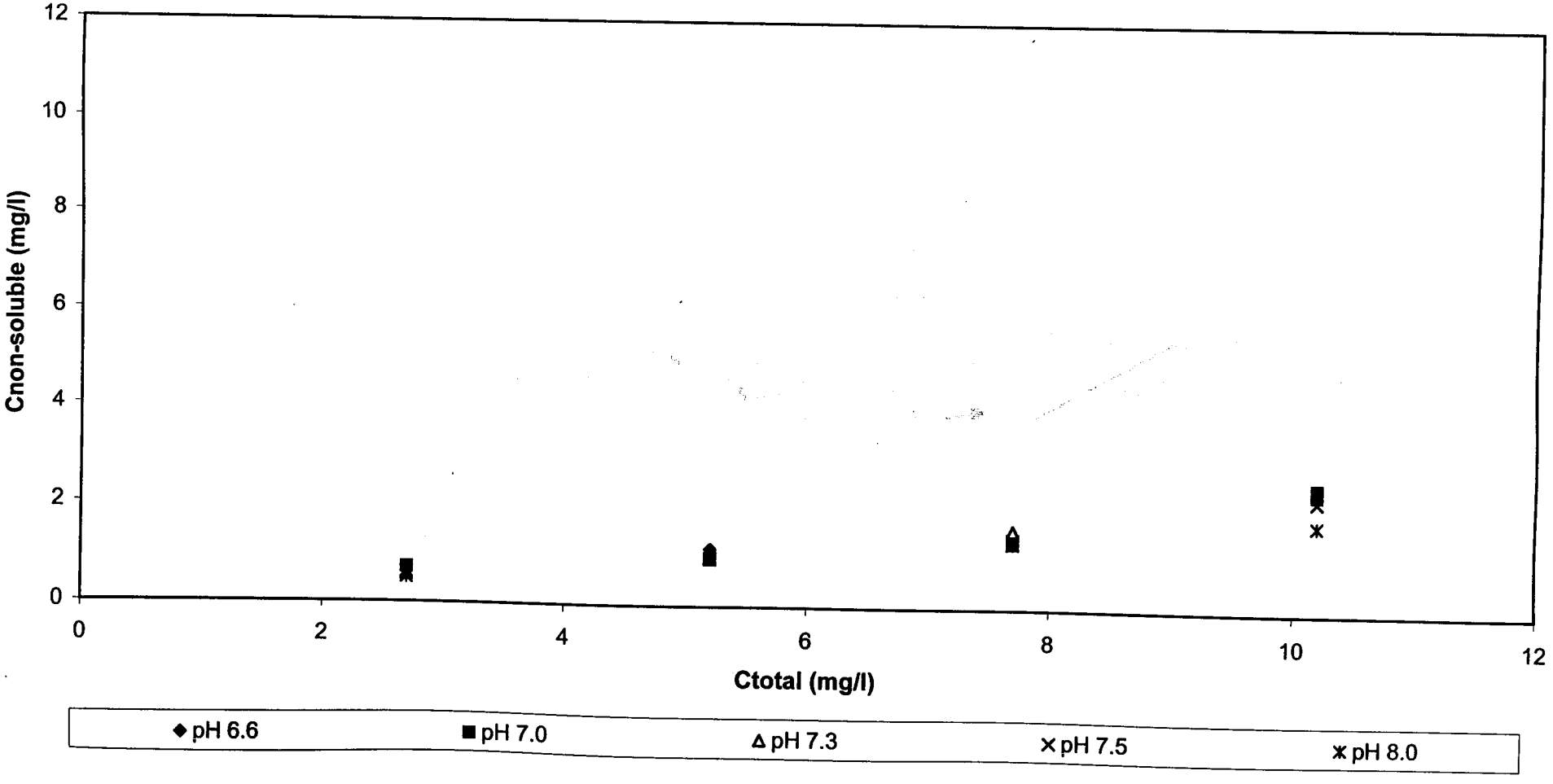


Figure C.11: Cu adsorption in Raw Sewage Solids Concentration C (668 mg/l)

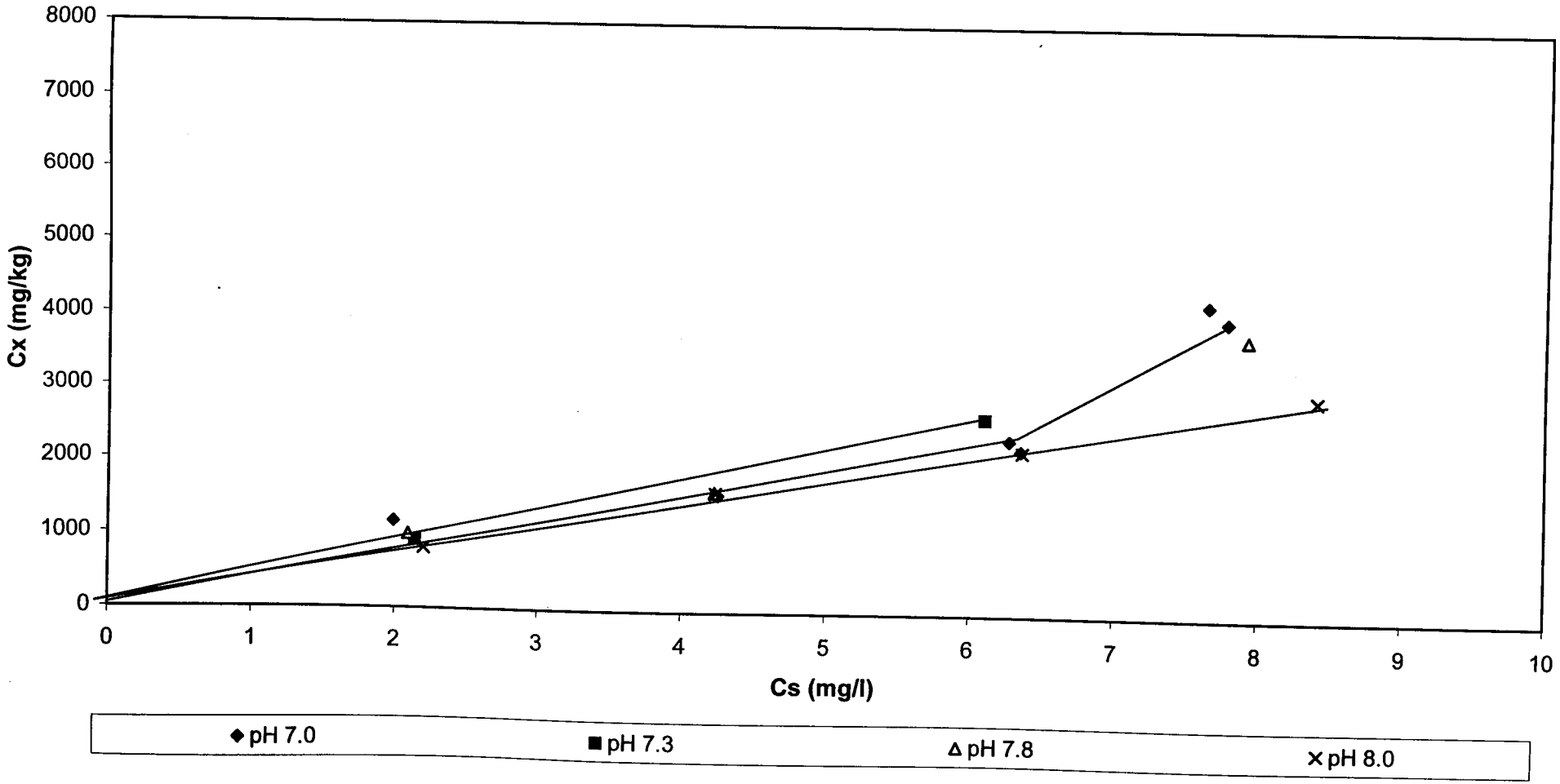


Figure C.12: ***Cu adsorption in Raw Sewage Solids Concentration C (668 mg/l)***

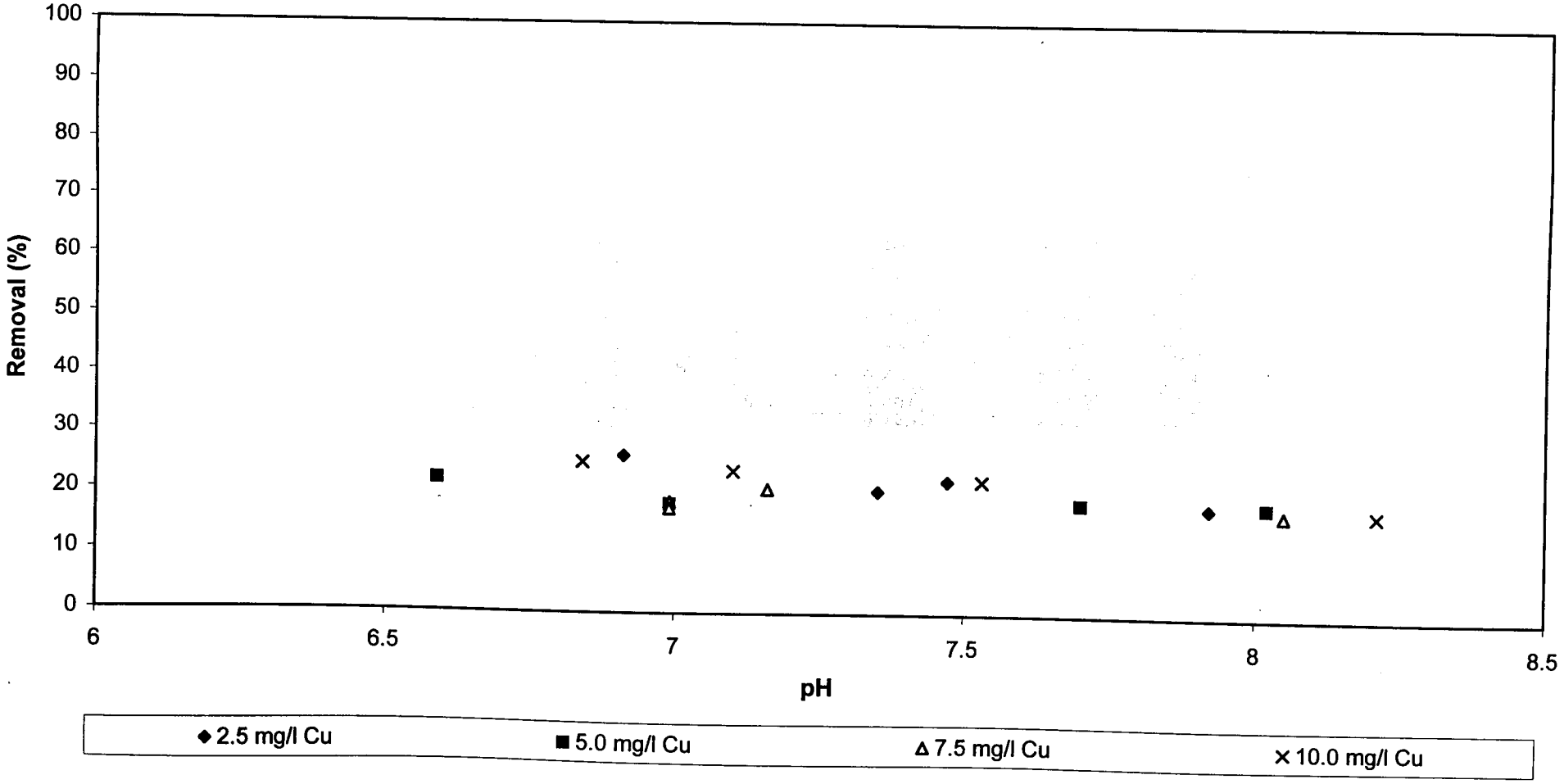


Table C.11 *Cu adsorption in primary effluent*

Date carried out: 24-Aug-00

Date analysed 04-Sep-00

Initial Total Cu (mg/l) 0.06

Actual Sample	TSS (mg/l)	pH	Cu Added (mg/l)	Residual Soluble Cu (mg/l)	Adsorbed (mg/l)	Adsorbed (mg/kg)	Total Cu (mg/l)
A-1-1	94	6.85	2.5	2.024	0.536	6335.6974	2.56
A-1-2	94	7.33	2.5	1.913	0.647	7647.754137	2.56
A-1-3	94	7.03	2.5	2.038	0.522	6170.212766	2.56
A-1-4	94	8.08	2.5	1.98	0.58	6855.791962	2.56
A-2-1	94	6.27	5	3.867	1.193	14101.65485	5.06
A-2-2	94	6.82	5	3.534	1.526	18037.82506	5.06
A-2-3	94	7.75	5	3.267	1.793	21193.85343	5.06
A-2-4	94	8.23	5	3.208	1.852	21891.25296	5.06
A-3-1	94	6.35	7.5	5.338	2.222	26264.77541	7.56
A-3-2	94	6.79	7.5	4.646	2.914	34444.44444	7.56
A-3-3	94	6.83	7.5	4.663	2.897	34243.49882	7.56
A-3-4	94	7.32	7.5	4.085	3.475	41075.65012	7.56
A-4-1	94	6.4	10	6.068	3.992	47186.76123	10.06
A-4-2	94	6.63	10	5.351	4.709	55661.93853	10.06
A-4-3	94	7.02	10	4.227	5.833	68947.99054	10.06
A-4-4	94	7.29	10	3.967	6.093	72021.2766	10.06
B-1-1	86	6.37	2.5	2.156	0.404	5219.638243	2.56
B-1-2	86	7.07	2.5	1.944	0.616	7958.656331	2.56
B-1-3	86	7.45	2.5	1.901	0.659	8514.211886	2.56
B-1-4	86	7.67	2.5	1.899	0.661	8540.05168	2.56
B-2-1	86	6.13	5	3.961	1.099	14198.96641	5.06
B-2-2	86	6.61	5	3.171	1.889	24405.68475	5.06
B-2-3	86	7.27	5	3.576	1.484	19173.12661	5.06
B-2-4	86	7.88	5	2.905	2.155	27842.37726	5.06
B-3-1	86	6.4	7.5	5.097	2.463	31821.70543	7.56
B-3-2	86	6.71	7.5	4.1	3.46	44702.84238	7.56
B-3-3	86	6.86	7.5	3.928	3.632	46925.0646	7.56
B-3-4	86	7.13	7.5	3.312	4.248	54883.72093	7.56
B-4-1	86	6.33	10	5.895	4.165	53811.36951	10.06
B-4-2	86	6.58	10	4.632	5.428	70129.19897	10.06

Actual Sample	TSS (mg/l)	pH	Cu Added (mg/l)	Residual Soluble Cu (mg/l)	Adsorbed (mg/l)	Adsorbed (mg/kg)	Total Cu (mg/l)
B-4-3	86	6.98	10	3.447	6.613	85439.27649	10.06
B-4-4	86	7.07	10	3.211	6.849	88488.37209	10.06
C-1-1	125	6.73	2.5	1.96	0.6	5333.333333	2.56
C-1-2	125	7	2.5	1.957	0.603	5360	2.56
C-1-3	125	7.19	2.5	1.959	0.601	5342.222222	2.56
C-1-4	125	7.84	2.5	1.931	0.629	5591.111111	2.56
C-2-1	125	6.51	5	3.721	1.339	11902.22222	5.06
C-2-2	125	6.8	5	3.617	1.443	12826.66667	5.06
C-2-3	125	7.4	5	3.344	1.716	15253.33333	5.06
C-2-4	125	7.88	5	3.232	1.828	16248.88889	5.06
C-4-1	125	6.69	10	4.886	5.174	45991.11111	10.06
C-4-2	125	6.7	10	4.85	5.21	46311.11111	10.06
C-4-3	125	7.15	10	3.865	6.195	55066.66667	10.06
C-4-4	125	7.28	10	3.75	6.31	56088.88889	10.06

Cu adsorption in primary effluent

Figure C.13: ***Cu adsorption in Primary Effluent Solids Concentration A (94 mg/l)***

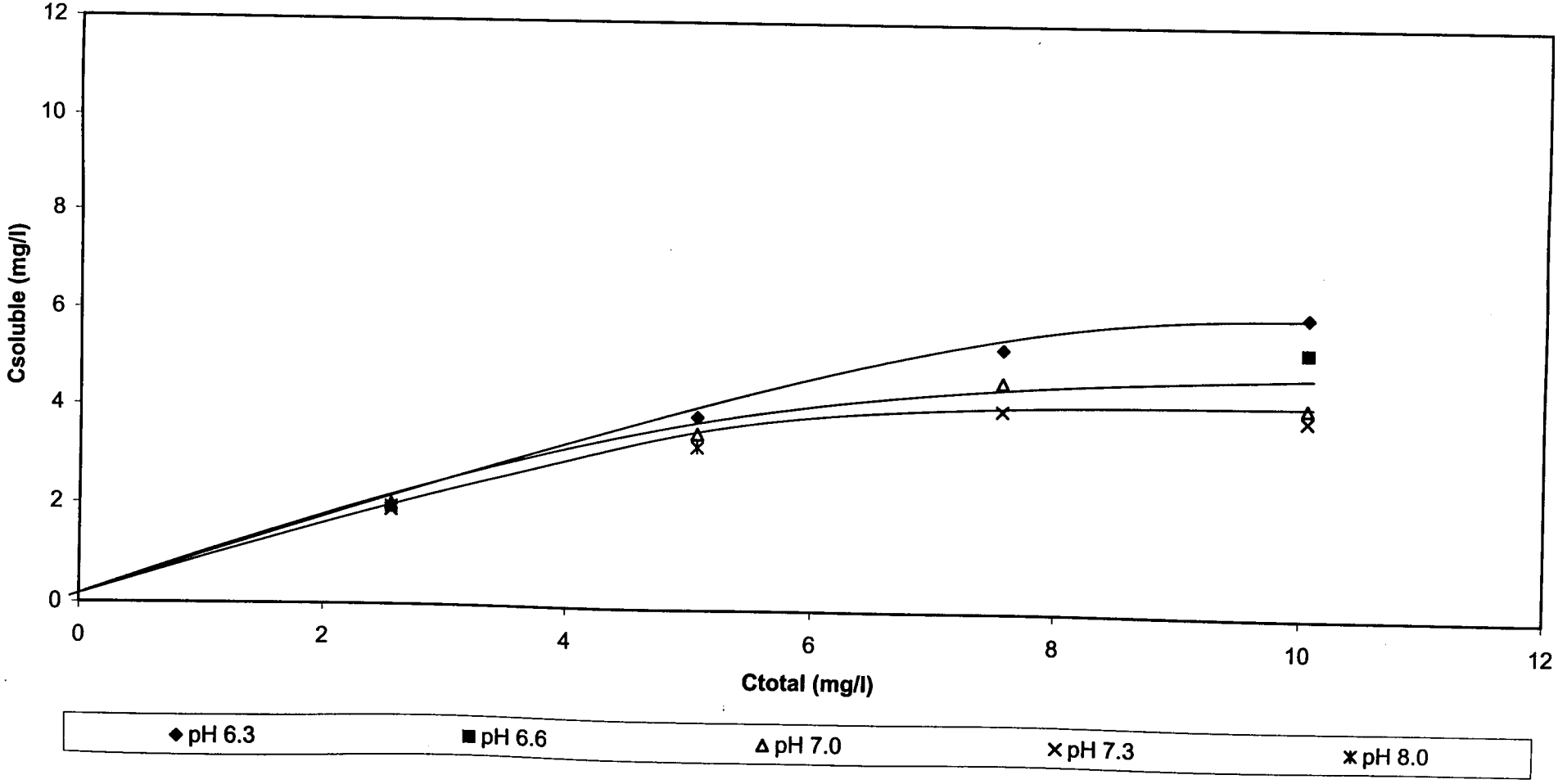


Figure C.14: ***Cu adsorption in Primary Effluent Solids Concentration A (94 mg/l)***

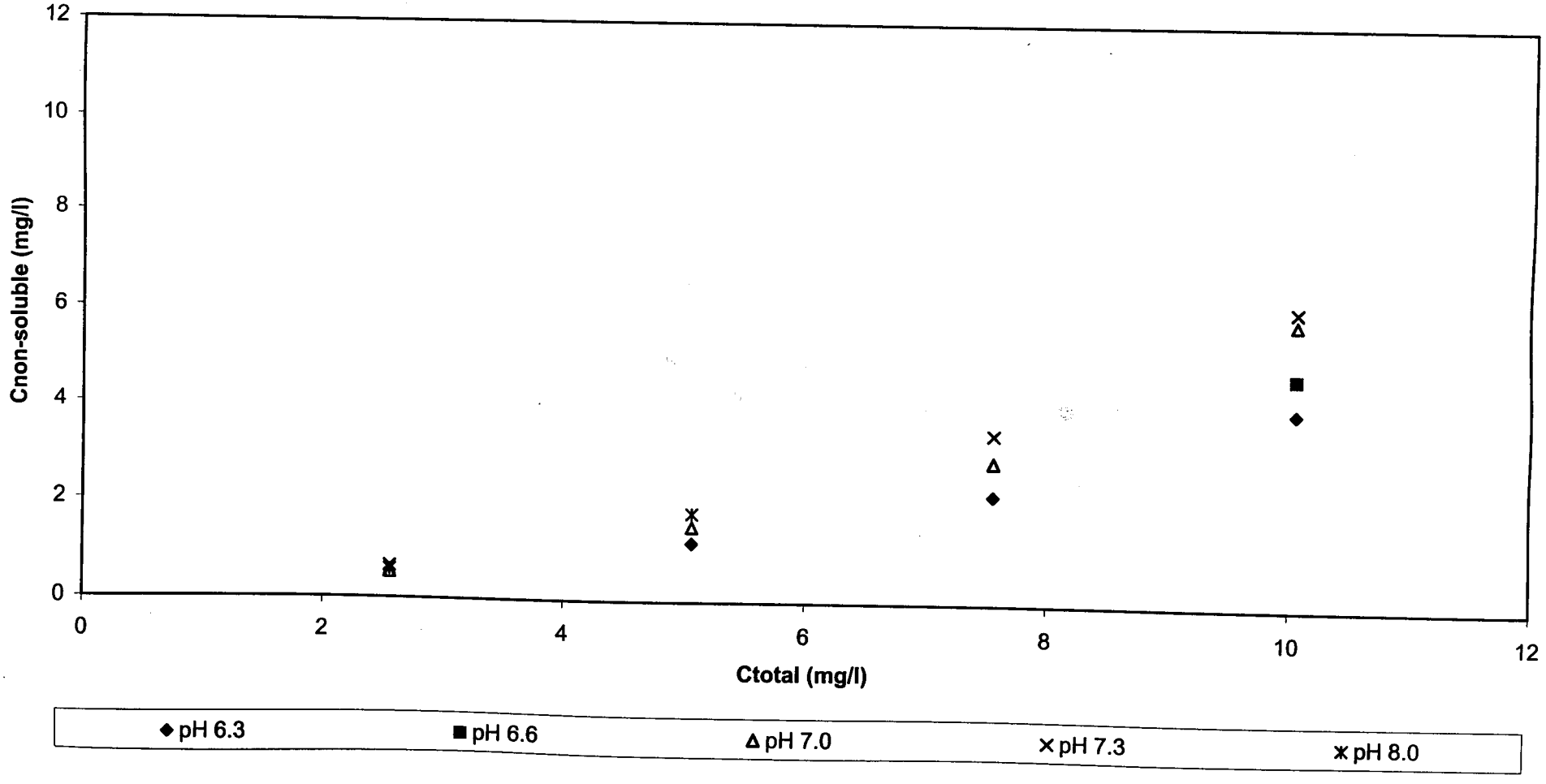


Figure C.15: ***Cu adsorption in Primary Effluent Solids Concentration A (94 mg/l)***

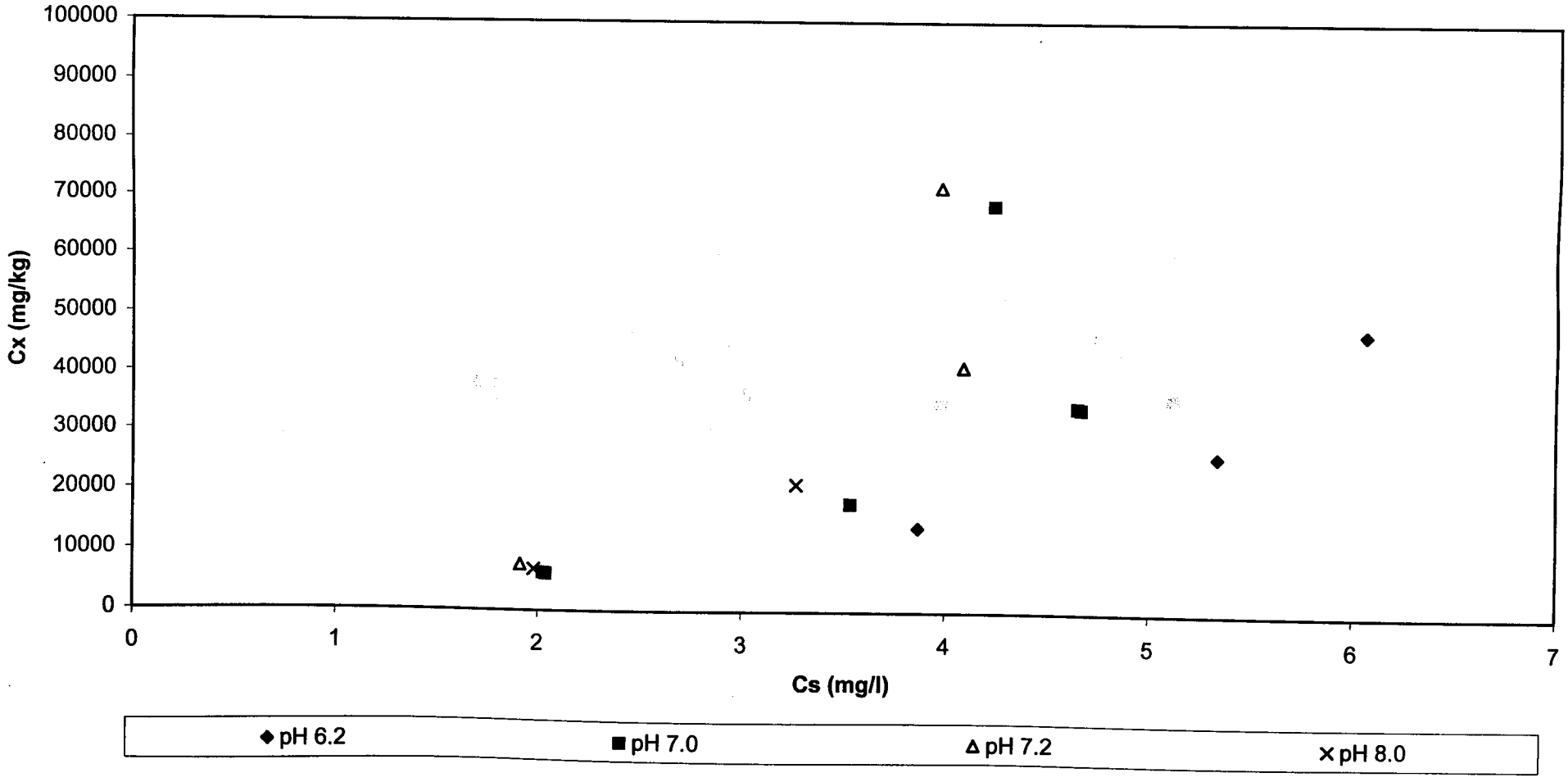


Figure C.16: ***Cu adsorption in Primary Effluent Solids Concentration A (94 mg/l)***

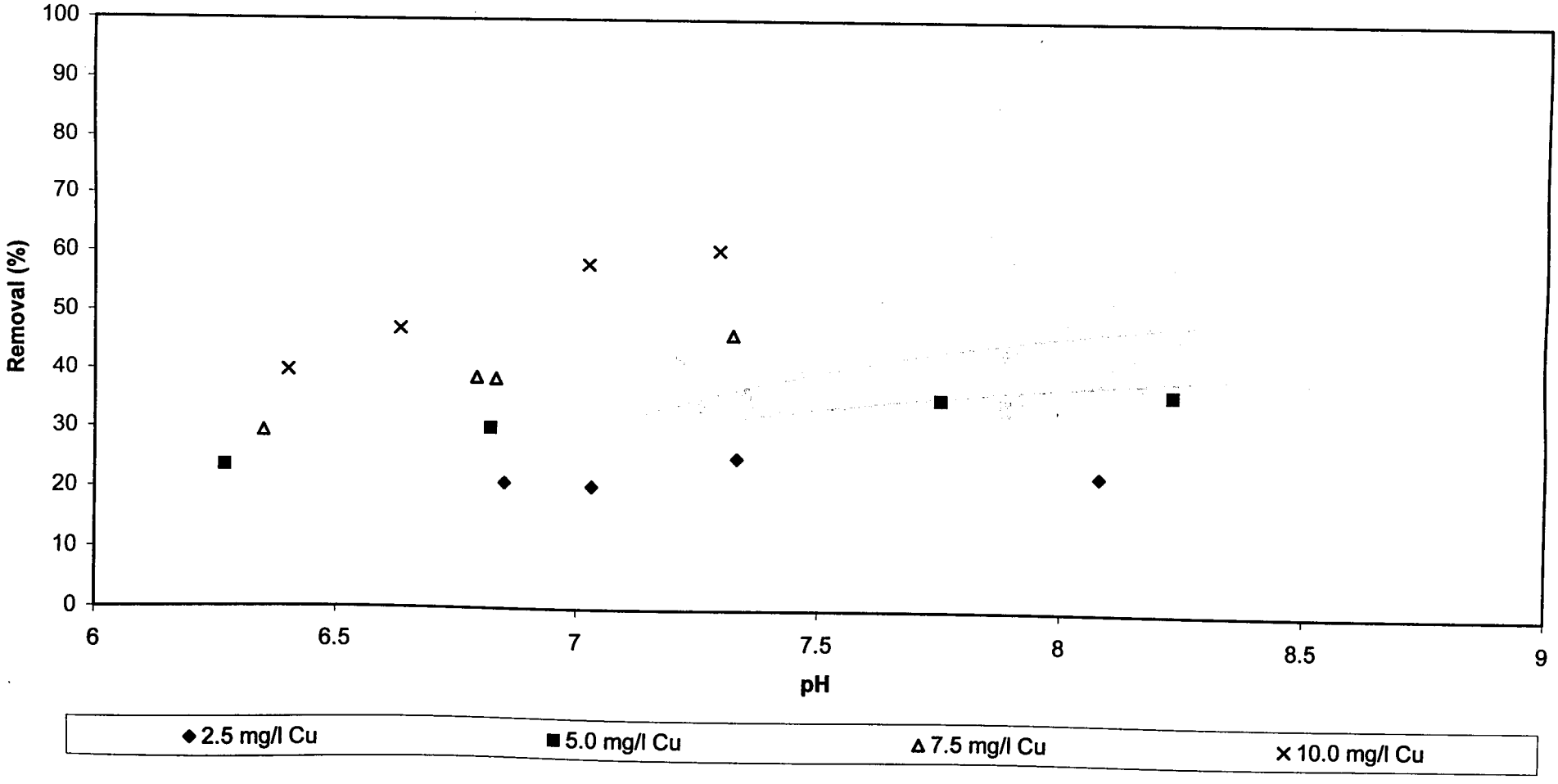


Figure C.17: ***Cu adsorption in Primary Effluent Solids Concentration B (86 mg/l)***

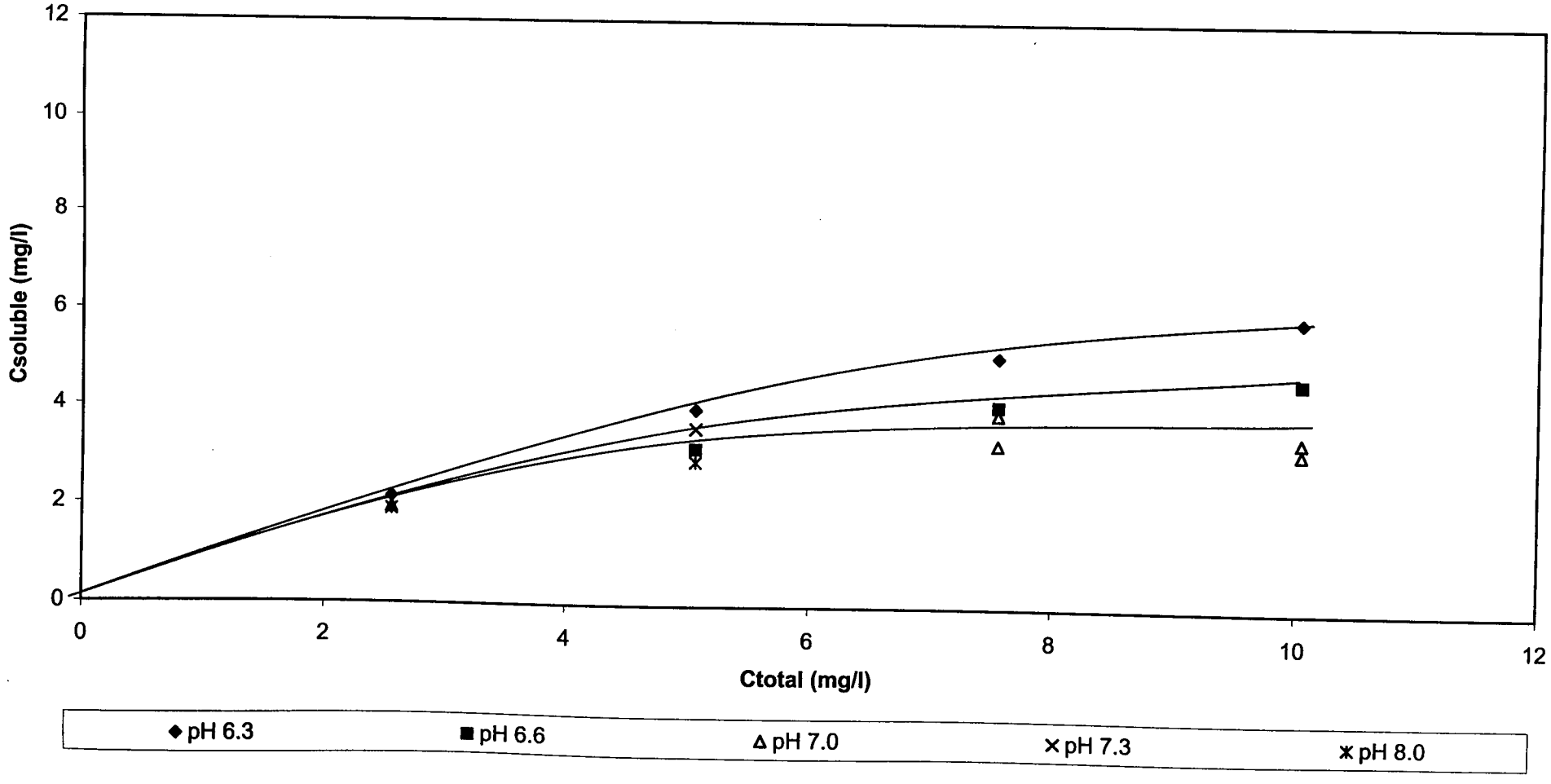


Figure C.18: ***Cu adsorption in Primary Effluent Solids Concentration B (86 mg/l)***

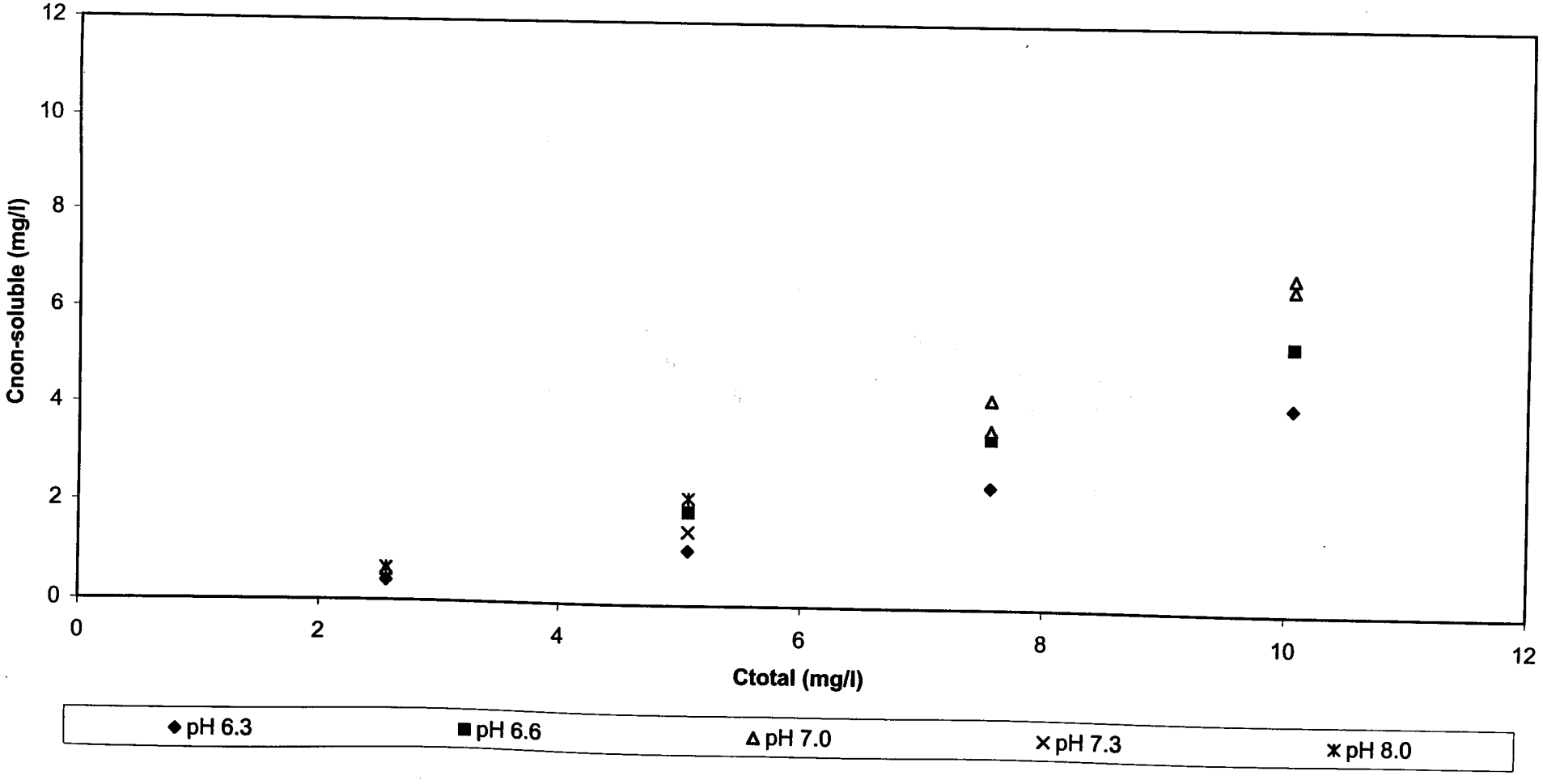


Figure C.19: ***Cu adsorption in Primary Effluent Solids Concentration B (86 mg/l)***

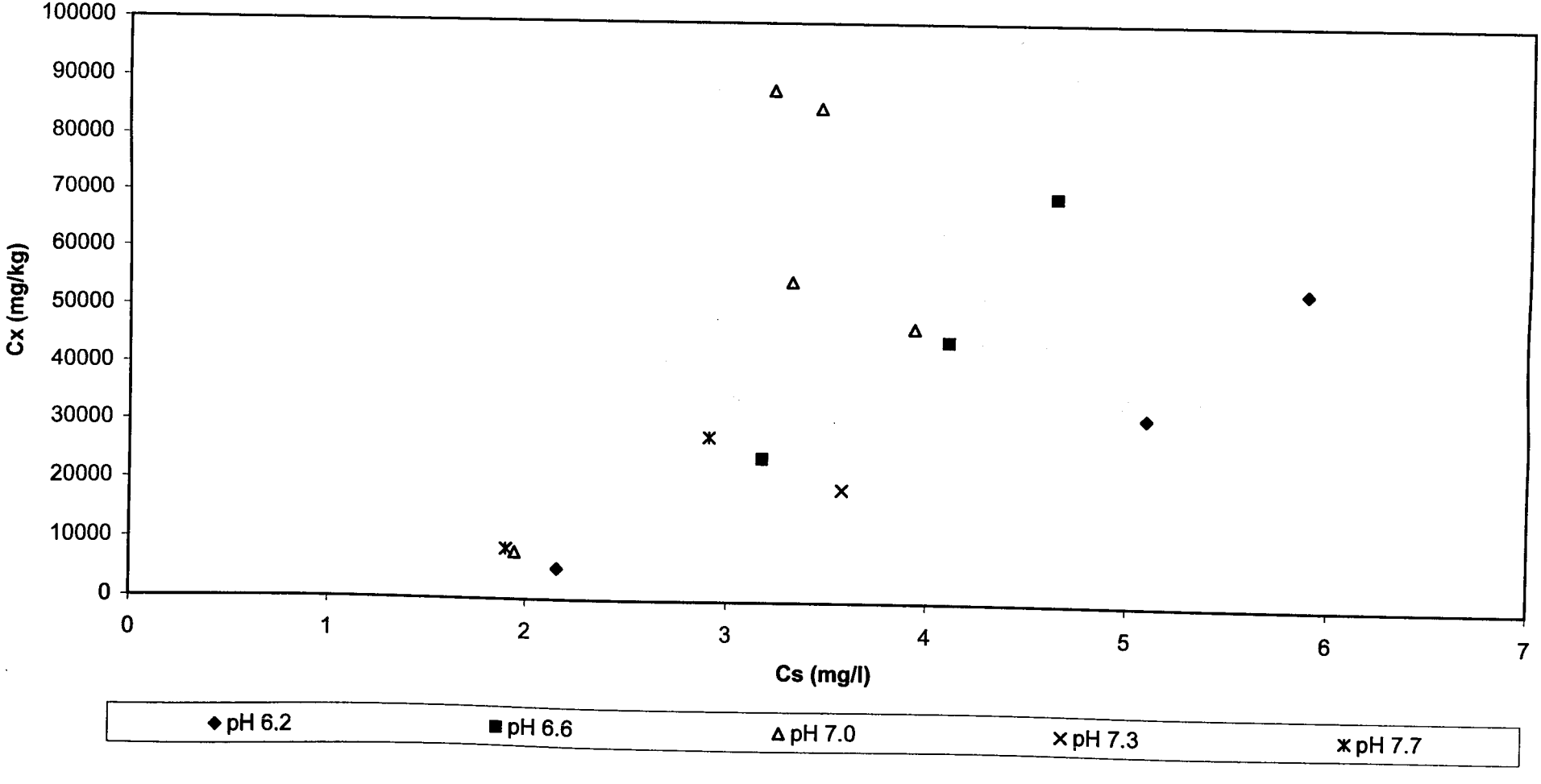


Figure C.20: ***Cu adsorption in Primary Effluent Solids Concentration B (86 mg/l)***

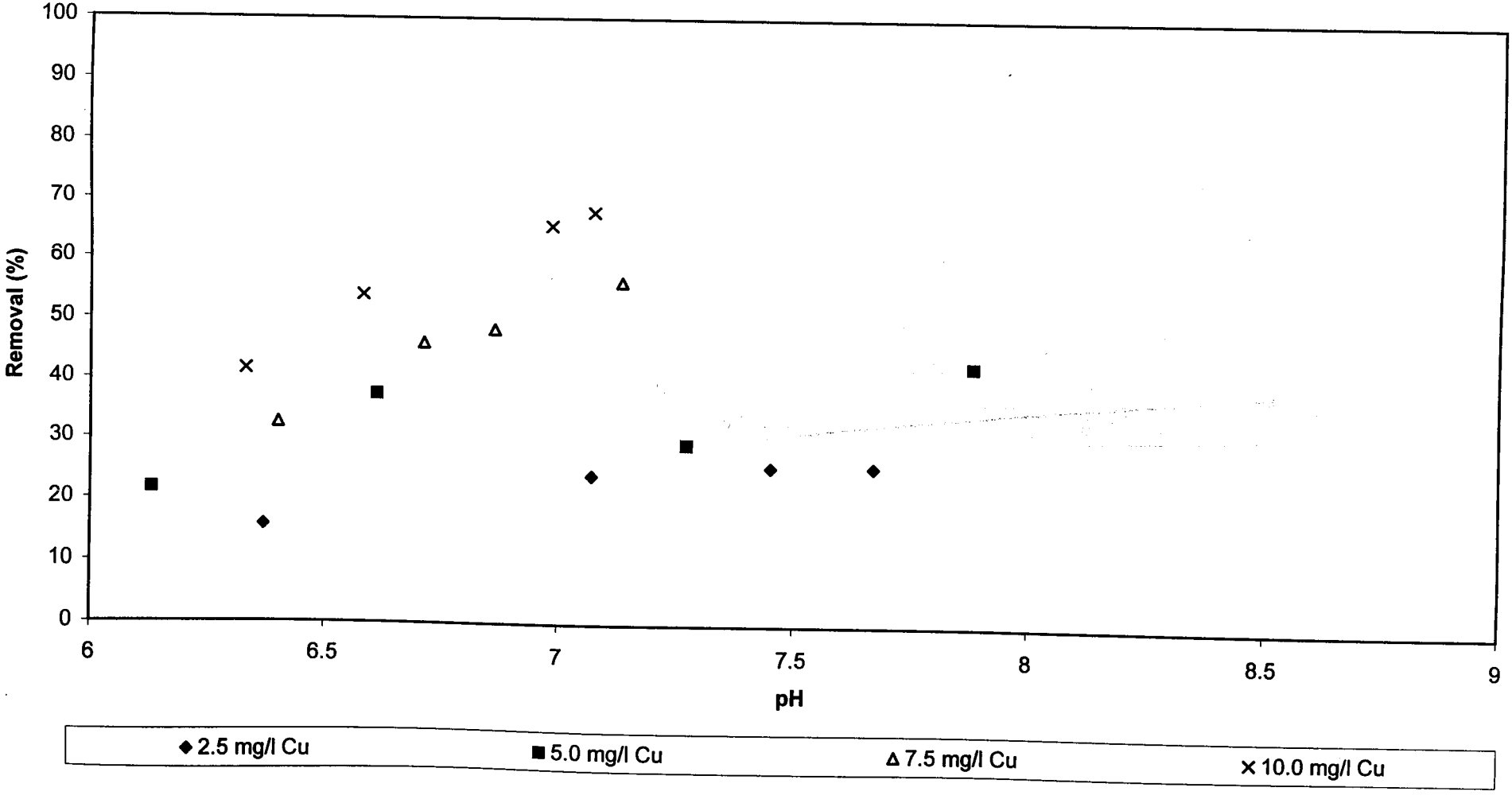


Figure C.21: ***Cu adsorption in Primary Effluent Solids Concentration C (125 mg/l)***

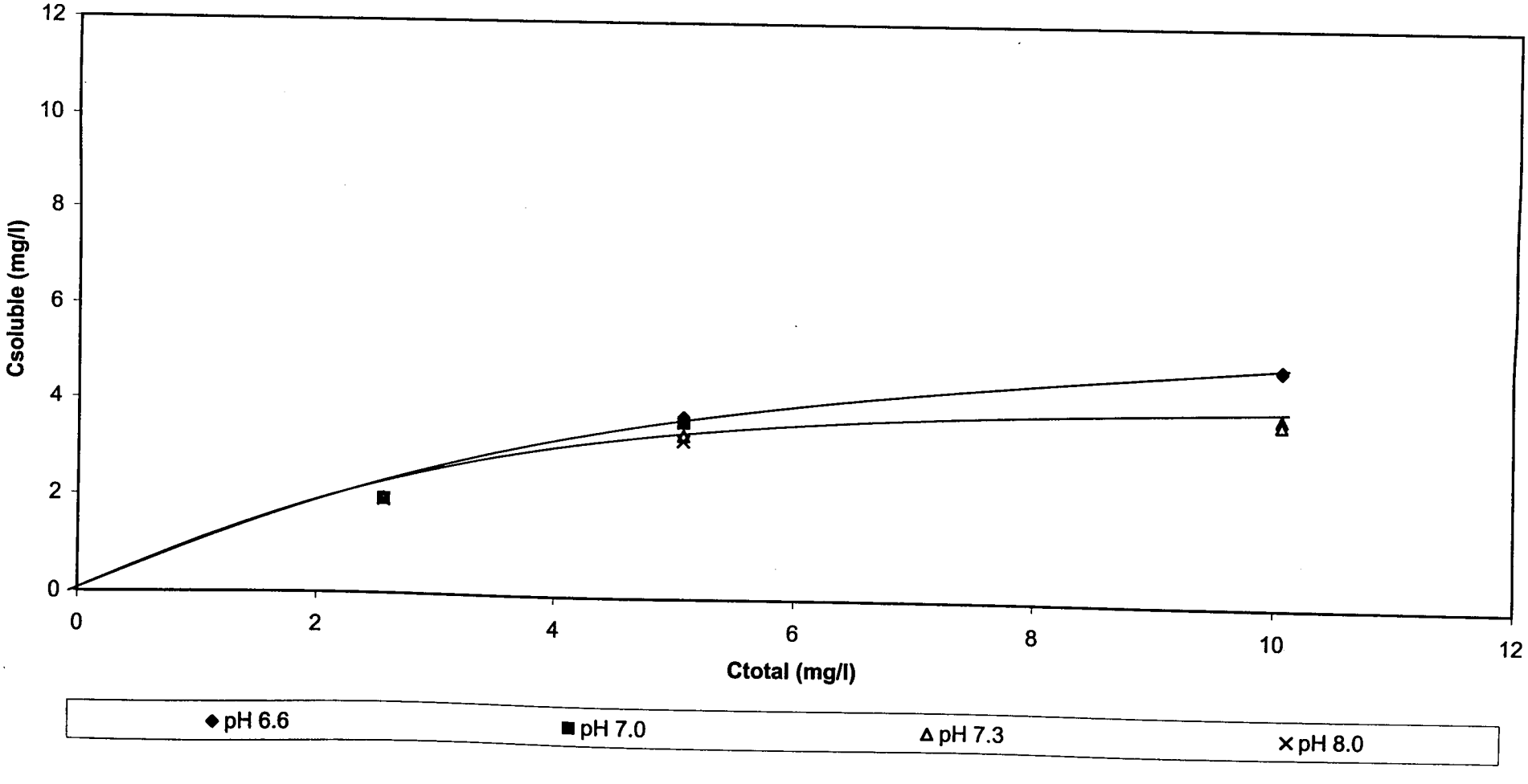


Figure C.22: ***Cu adsorption in Primary Effluent Solids Concentration C (125 mg/l)***

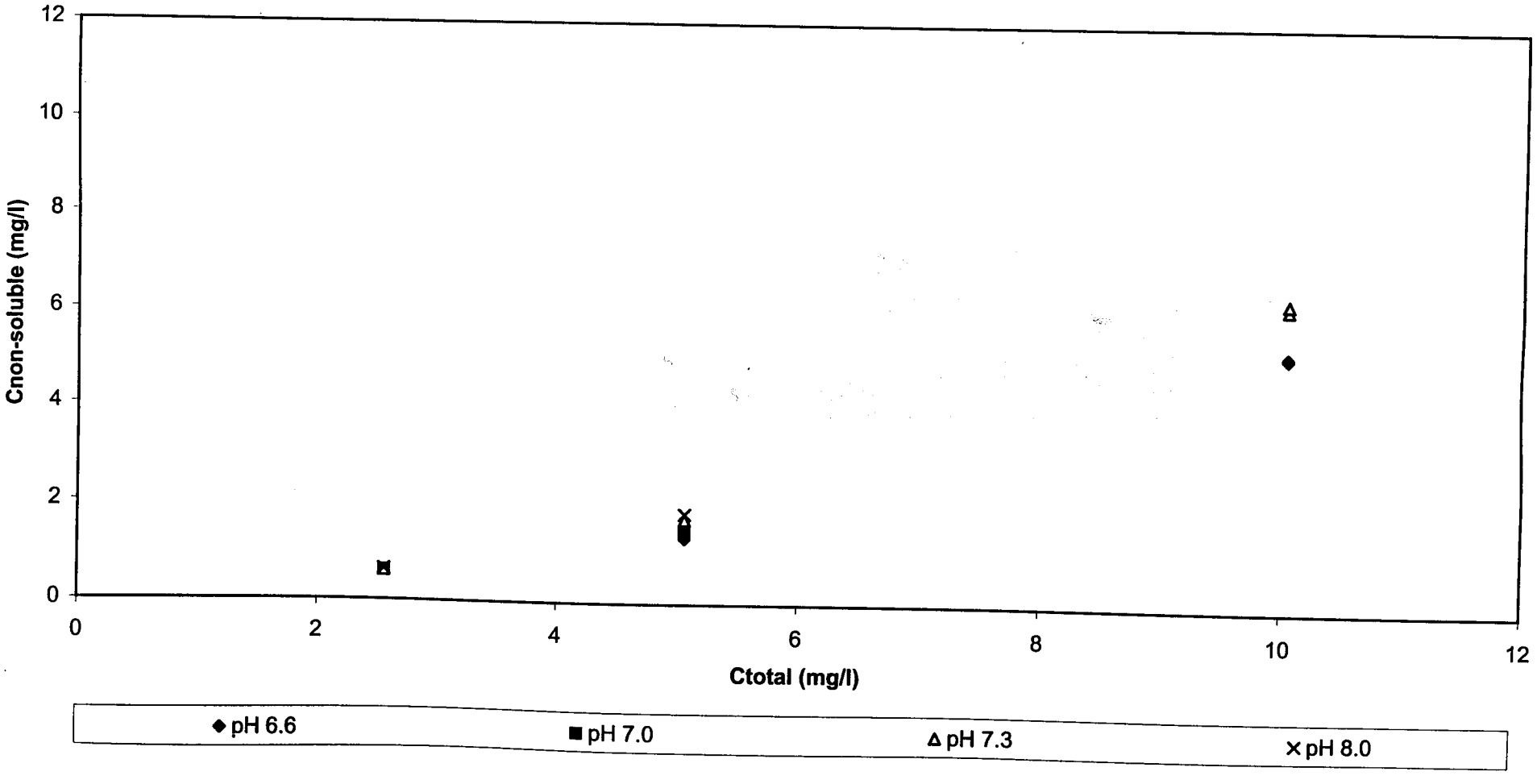


Figure C.23: ***Cu adsorption in Primary Effluent Solids Concentration C (125 mg/l)***

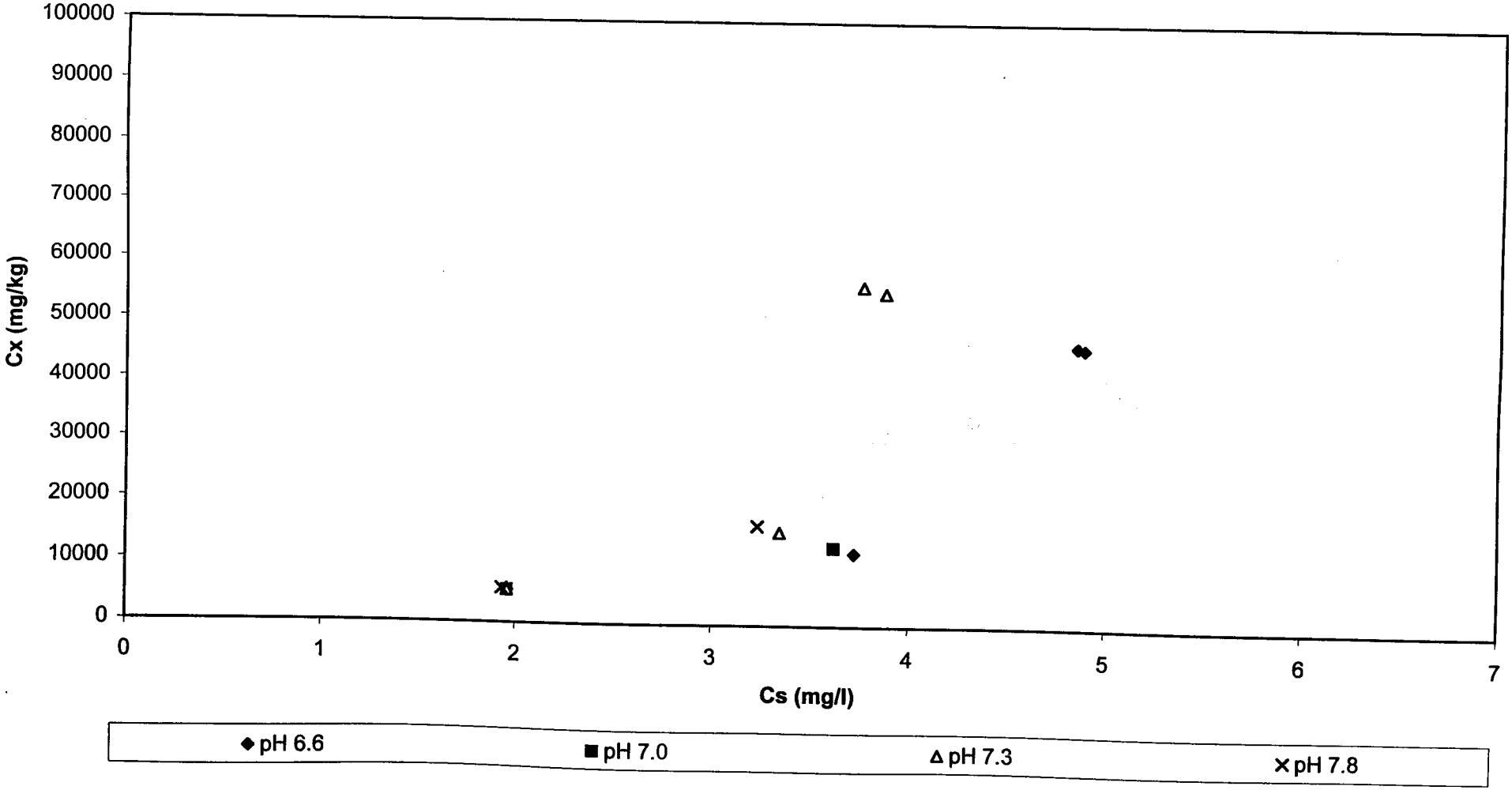


Figure C.24: ***Cu adsorption in Primary Effluent Solids Concentration C (125 mg/l)***

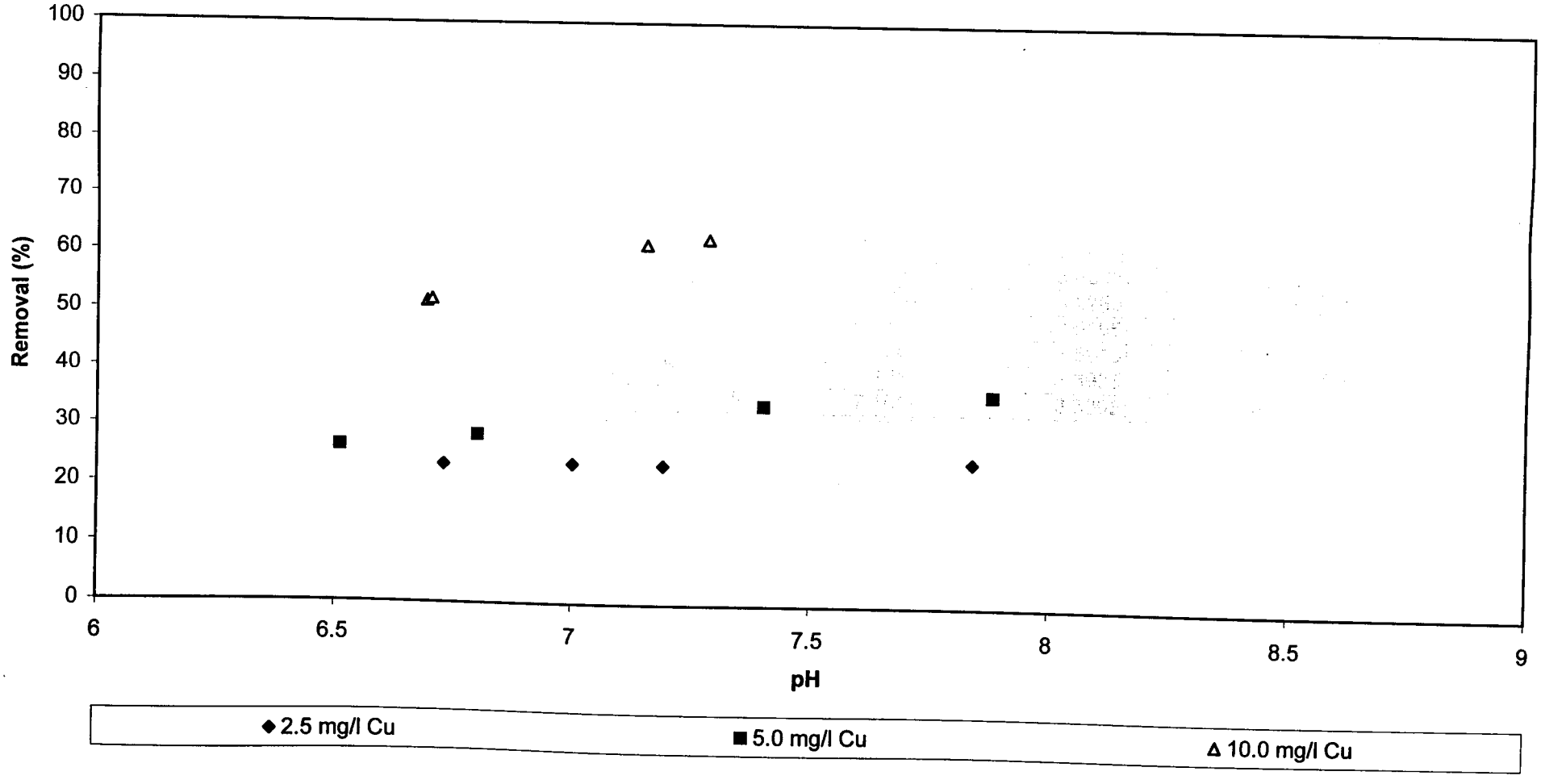


Table C.12 *Cu adsorption in mixed liquor*

Date Carried out 25-Aug-00

Date analysed 05-Sep-00

Initial Total Cu (mg/l) 0.5515

Actual Sample	TSS (mg/l)	pH	Cu Added (mg/l)	Residual Soluble Cu (mg/l)	Adsorbed Cu (mg/l)	Adsorbed Cu (mg/kg)	Total Cu (mg/l)
A-1-1	1800	6.82	2.5	1.419	1.6325	1007.716049	3.0515
A-1-2	1800	7.01	2.5	1.53	1.5215	939.1975309	3.0515
A-1-3	1800	7.05	2.5	1.539	1.5125	933.6419753	3.0515
A-1-4	1800	7.4	2.5	1.511	1.5405	950.9259259	3.0515
A-2-1	1800	6.65	5	2.964	2.5875	1597.222222	5.5515
A-2-2	1800	6.84	5	3.19	2.3615	1457.716049	5.5515
A-2-3	1800	7.35	5	3.199	2.3525	1452.160494	5.5515
A-2-4	1800	8.15	5	3.175	2.3765	1466.975309	5.5515
A-3-1	1800	6.93	7.5	4.357	3.6945	2280.555556	8.0515
A-3-2	1800	7.32	7.5	4.444	3.6075	2226.851852	8.0515
A-3-3	1800	7.92	7.5	4.651	3.4005	2099.074074	8.0515
A-3-4	1800	8.48	7.5	4.823	3.2285	1992.901235	8.0515
A-4-1	1800	6.61	10	6.936	3.6155	2231.790123	10.5515
A-4-2	1800	6.92	10	6.86	3.6915	2278.703704	10.5515
A-4-3	1800	7.5	10	7.161	3.3905	2092.901235	10.5515
A-4-4	1800	8.2	10	7.161	3.3905	2092.901235	10.5515
B-1-1	1058	6.82	2.5	1.584	1.4675	1541.167822	3.0515
B-1-2	1058	6.94	2.5	1.588	1.4635	1536.967024	3.0515
B-1-3	1058	7.16	2.5	1.634	1.4175	1488.657845	3.0515
B-1-4	1058	7.89	2.5	1.711	1.3405	1407.792481	3.0515
B-2-1	1058	6.78	5	3.331	2.2205	2331.968074	5.5515
B-2-2	1058	7.19	5	3.5	2.0515	2154.484352	5.5515
B-2-3	1058	7.49	5	3.649	1.9025	1998.004621	5.5515
B-2-4	1058	8.2	5	3.664	1.8875	1982.251628	5.5515
B-3-1	1058	7	7.5	4.842	3.2095	3370.615417	8.0515
B-3-2	1058	7.86	7.5	5.122	2.9295	3076.559546	8.0515
B-3-3	1058	8.52	7.5	5.227	2.8245	2966.288595	8.0515
B-3-4	1058	9	7.5	5.275	2.7765	2915.879017	8.0515
B-4-1	1058	6.67	10	7.253	3.2985	3464.083176	10.5515
B-4-2	1058	7.07	10	7.408	3.1435	3301.302247	10.5515

Actual Sample	TSS (mg/l)	pH	Cu Added (mg/l)	Residual Soluble Cu (mg/l)	Adsorbed Cu (mg/l)	Adsorbed Cu (mg/kg)	Total Cu (mg/l)
B-4-3	1058	7.8	10	7.701	2.8505	2993.593783	10.5515
B-4-4	1058	8.6	10	7.811	2.7405	2878.071834	10.5515
C-1-1	2500	6.68	2.5	1.33	1.7215	765.1111111	3.0515
C-1-2	2500	6.84	2.5	1.281	1.7705	786.8888889	3.0515
C-1-3	2500	6.97	2.5	1.282	1.7695	786.4444444	3.0515
C-1-4	2500	7.5	2.5	1.395	1.6565	736.2222222	3.0515
C-2-1	2500	6.85	5	2.753	2.7985	1243.777778	5.5515
C-2-2	2500	7.04	5	2.758	2.7935	1241.555556	5.5515
C-2-3	2500	7.12	5	2.886	2.6655	1184.666667	5.5515
C-2-4	2500	7.61	5	2.986	2.5655	1140.222222	5.5515
C-3-1	2500	6.83	7.5	3.862	4.1895	1862	8.0515
C-3-2	2500	7.4	7.5	4.203	3.8485	1710.444444	8.0515
C-3-3	2500	7.83	7.5	4.348	3.7035	1646	8.0515
C-3-4	2500	8.46	7.5	4.198	3.8535	1712.666667	8.0515
C-4-1	2500	6.64	10	5.829	4.7225	2098.888889	10.5515
C-4-2	2500	6.98	10	6.226	4.3255	1922.444444	10.5515
C-4-3	2500	7.4	10	6.798	3.7535	1668.222222	10.5515
C-4-4	2500	7.84	10	6.737	3.8145	1695.333333	10.5515

Cu adsorption in mixed liquor

Figure C.25: ***Cu adsorption in Mixed Liquor Solids Concentration A (1800 mg/l)***

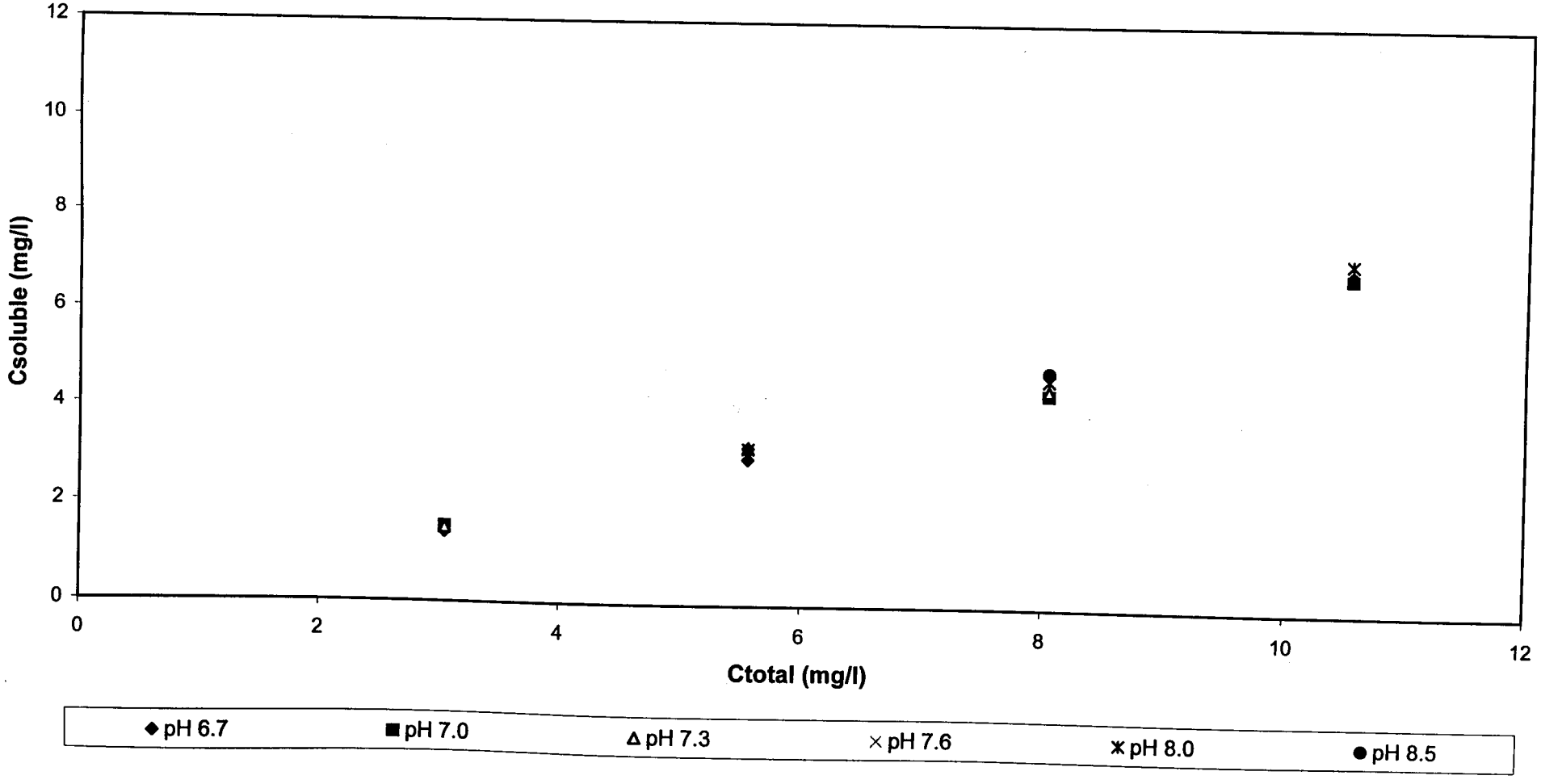


Figure C.26: ***Cu adsorption in Mixed Liquor Solids Concentration A (1800 mg/l)***

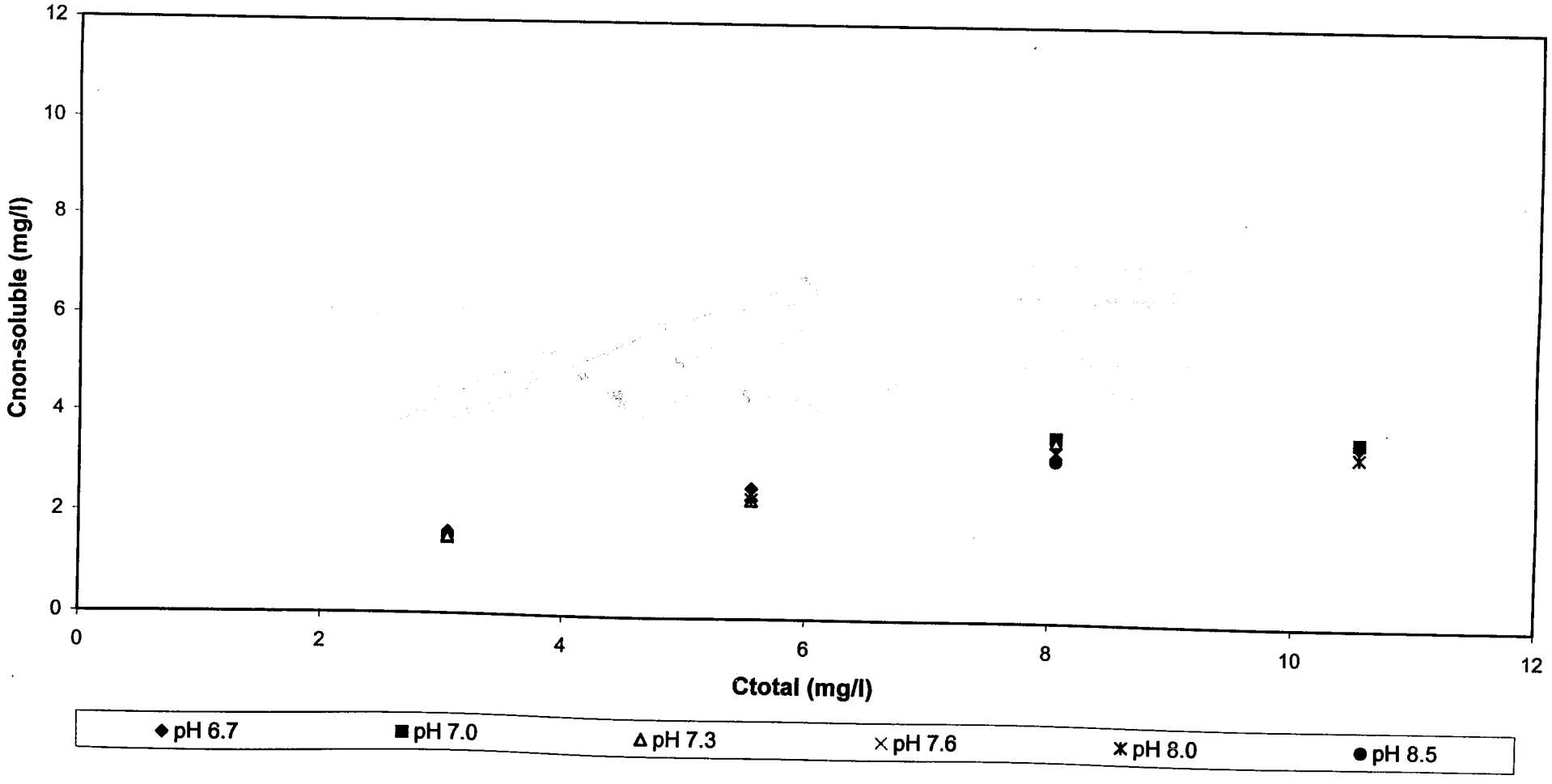


Figure C.27: ***Cu adsorption in Mixed Liquor Solids Concentration A (1800 mg/l)***

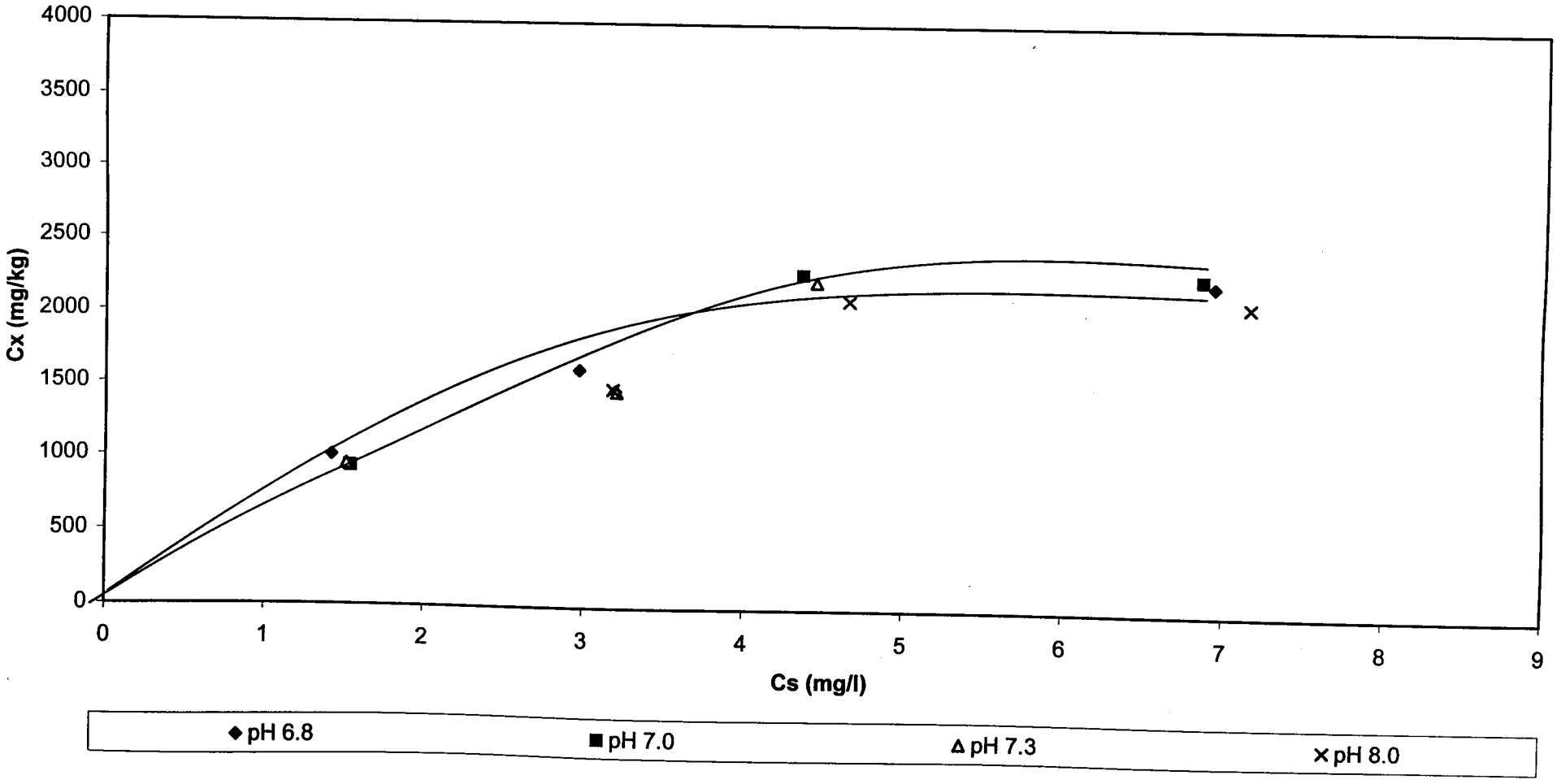


Figure C.28: ***Cu adsorption in Mixed Liquor Solids Concentration A (1800 mg/l)***

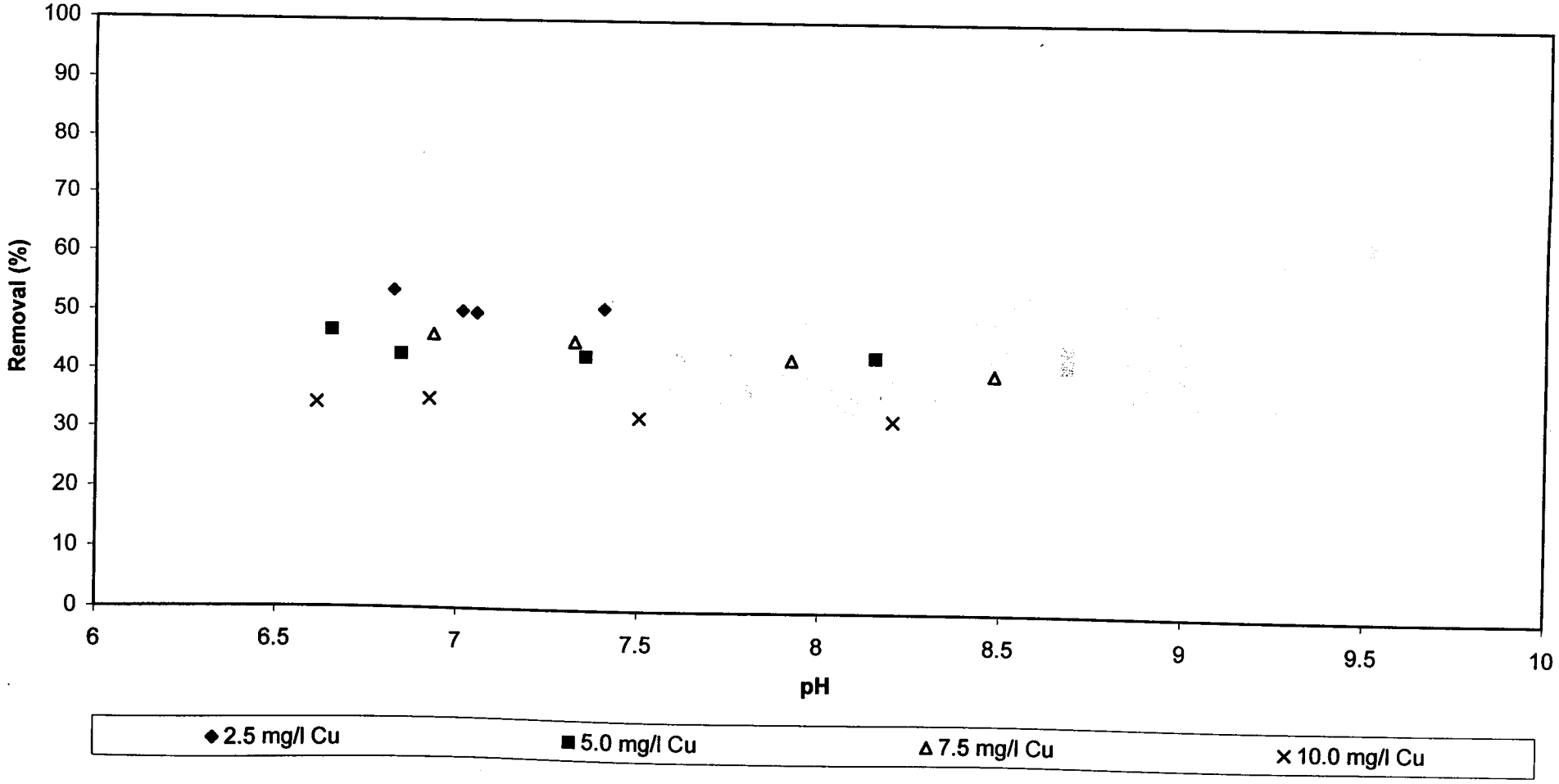


Figure C. 30: ***Cu adsorption in Mixed Liquor Solids Concentration B (1058 mg/l)***

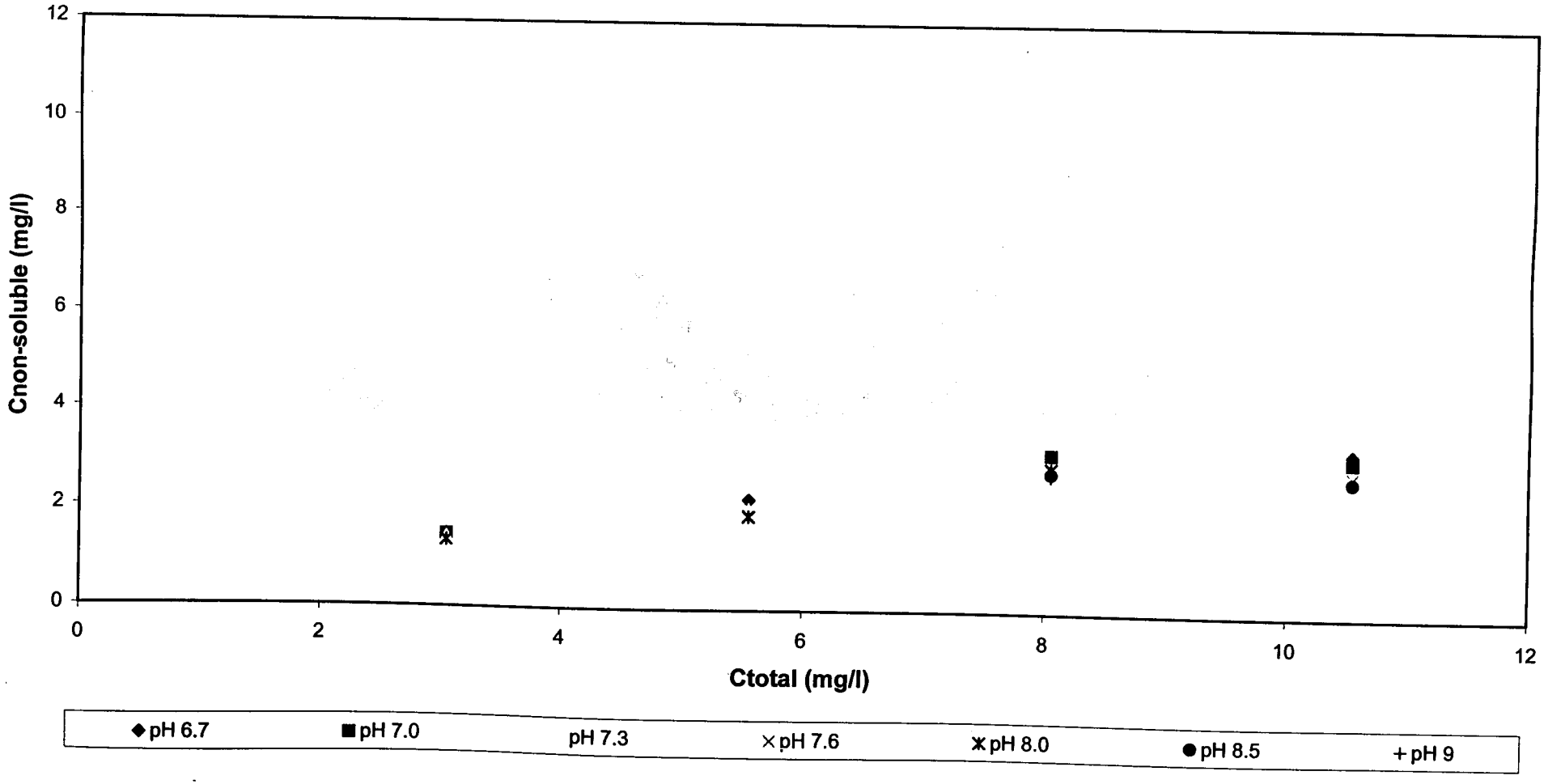


Figure C.31: ***Cu adsorption in Mixed Liquor Solids Concentration B (1058 mg/l)***

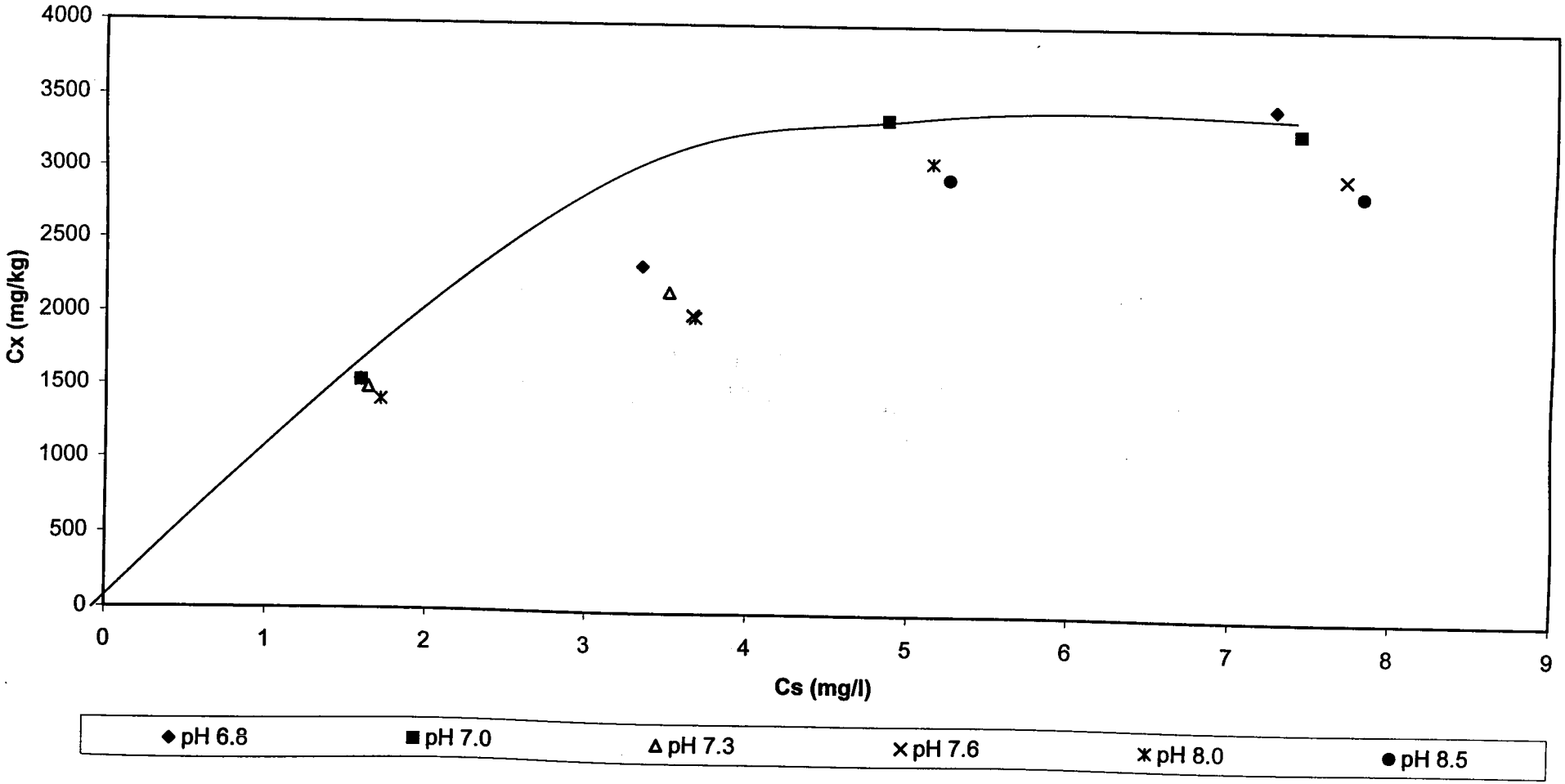


Figure C.32: ***Cu adsorption in Mixed Liquor Solids Concentration B (1058 mg/l)***

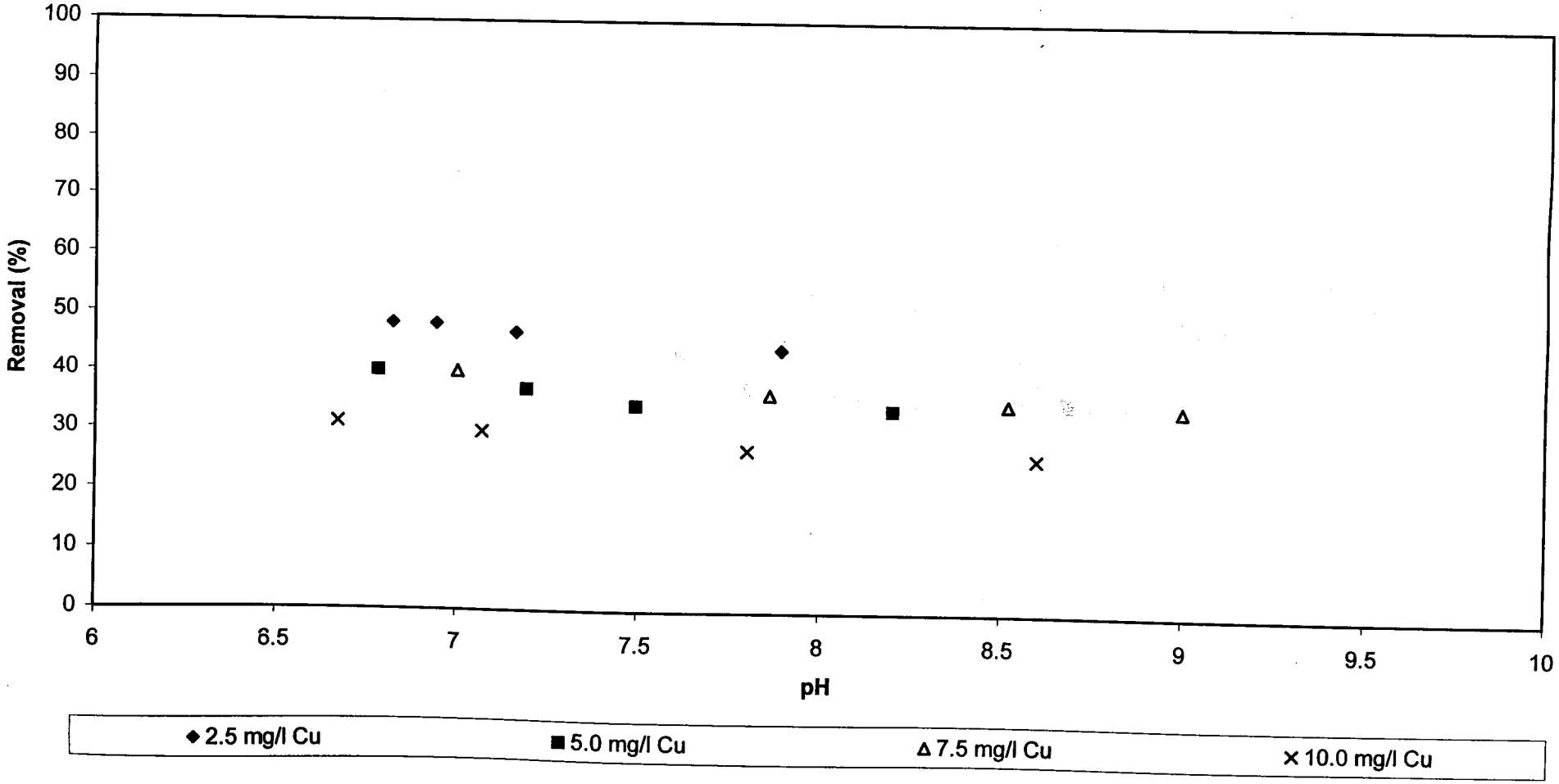


Figure C.33: ***Cu adsorption in Mixed Liquor Solids Concentration C (2500 mg/l)***

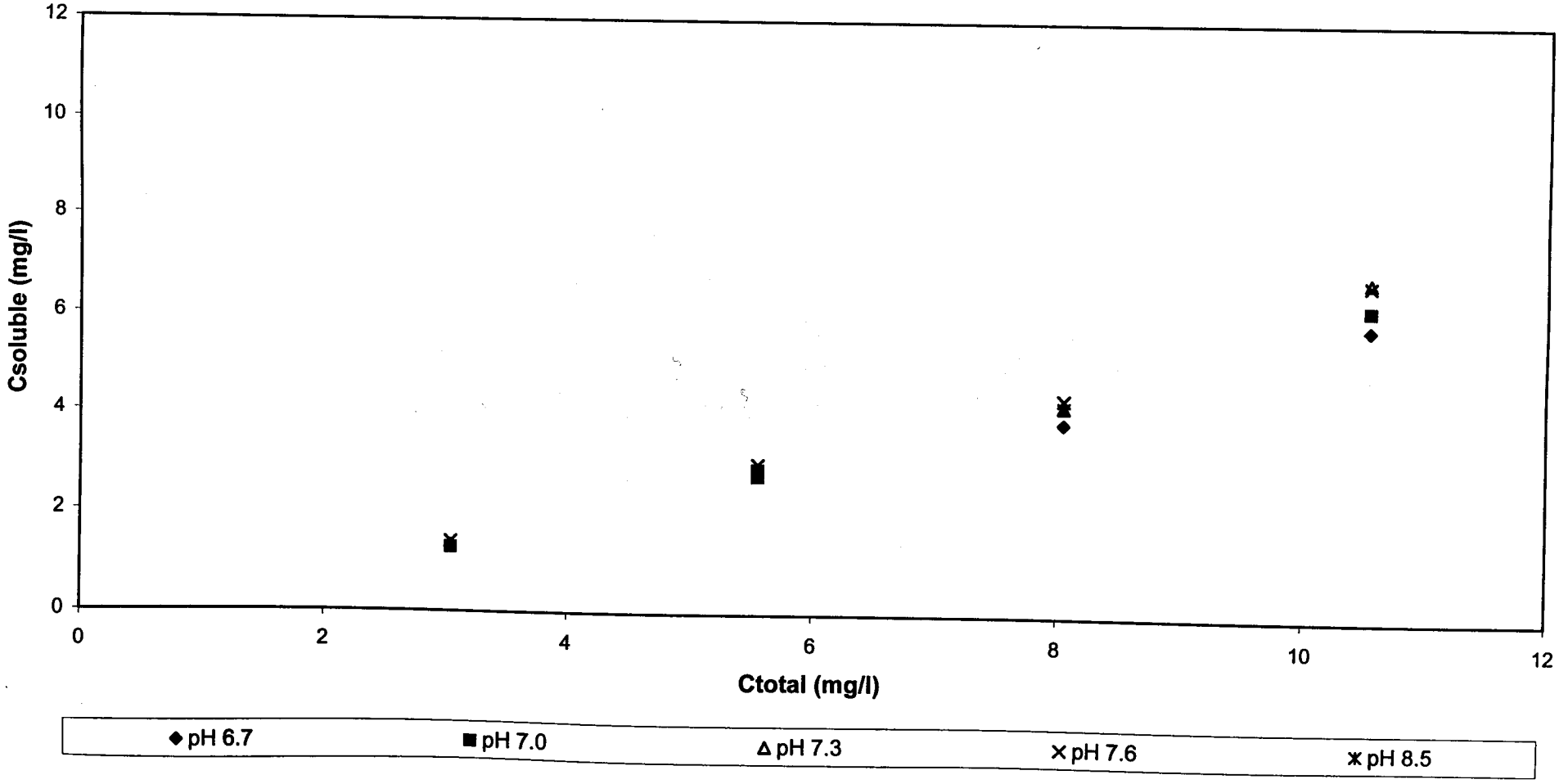


Figure C.34: ***Cu adsorption in Mixed Liquor Solids Concentration C (2500 mg/l)***

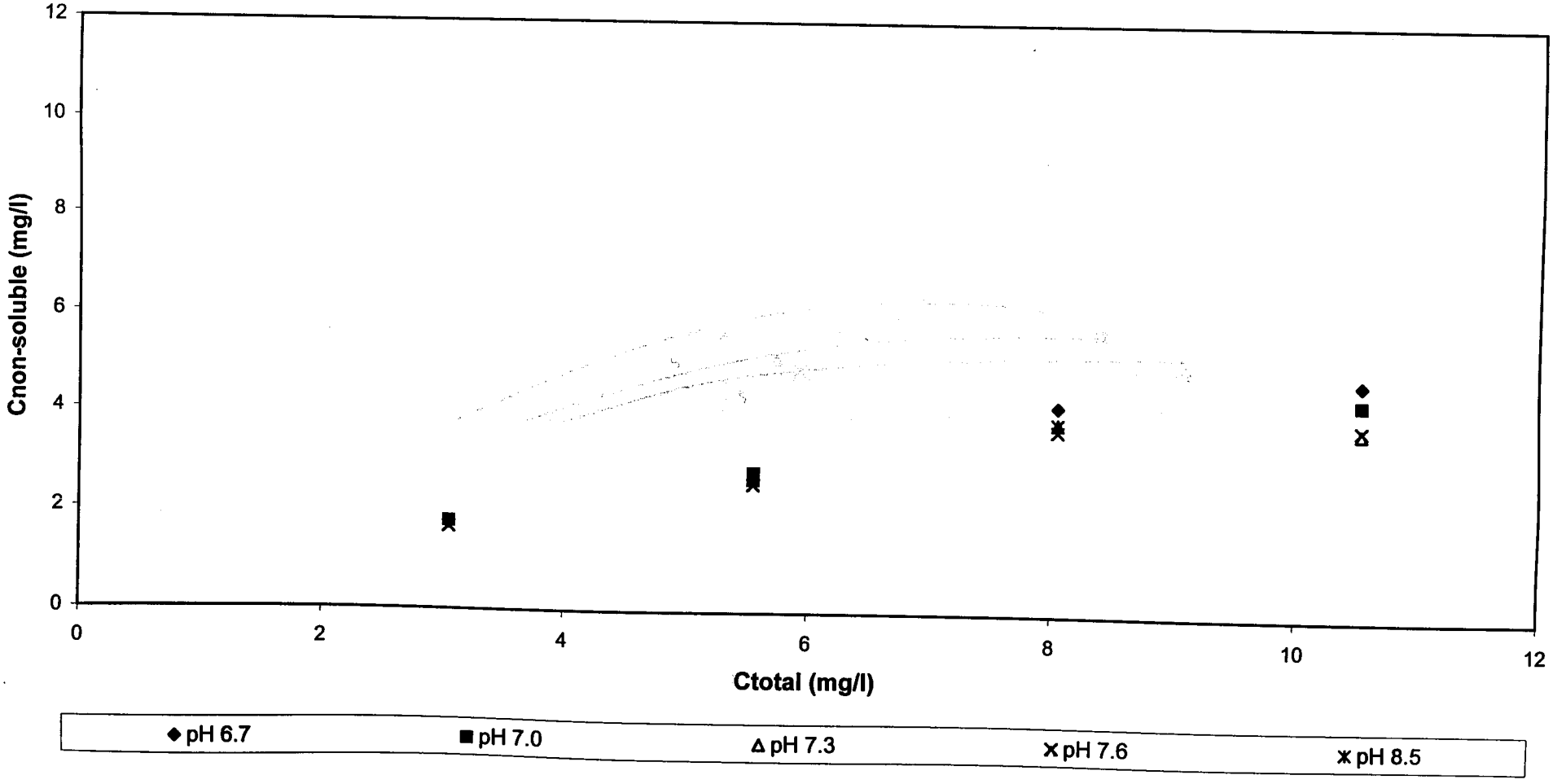


Figure C.35: ***Cu adsorption in Mixed Liquor Solids Concentration C (2500 mg/l)***

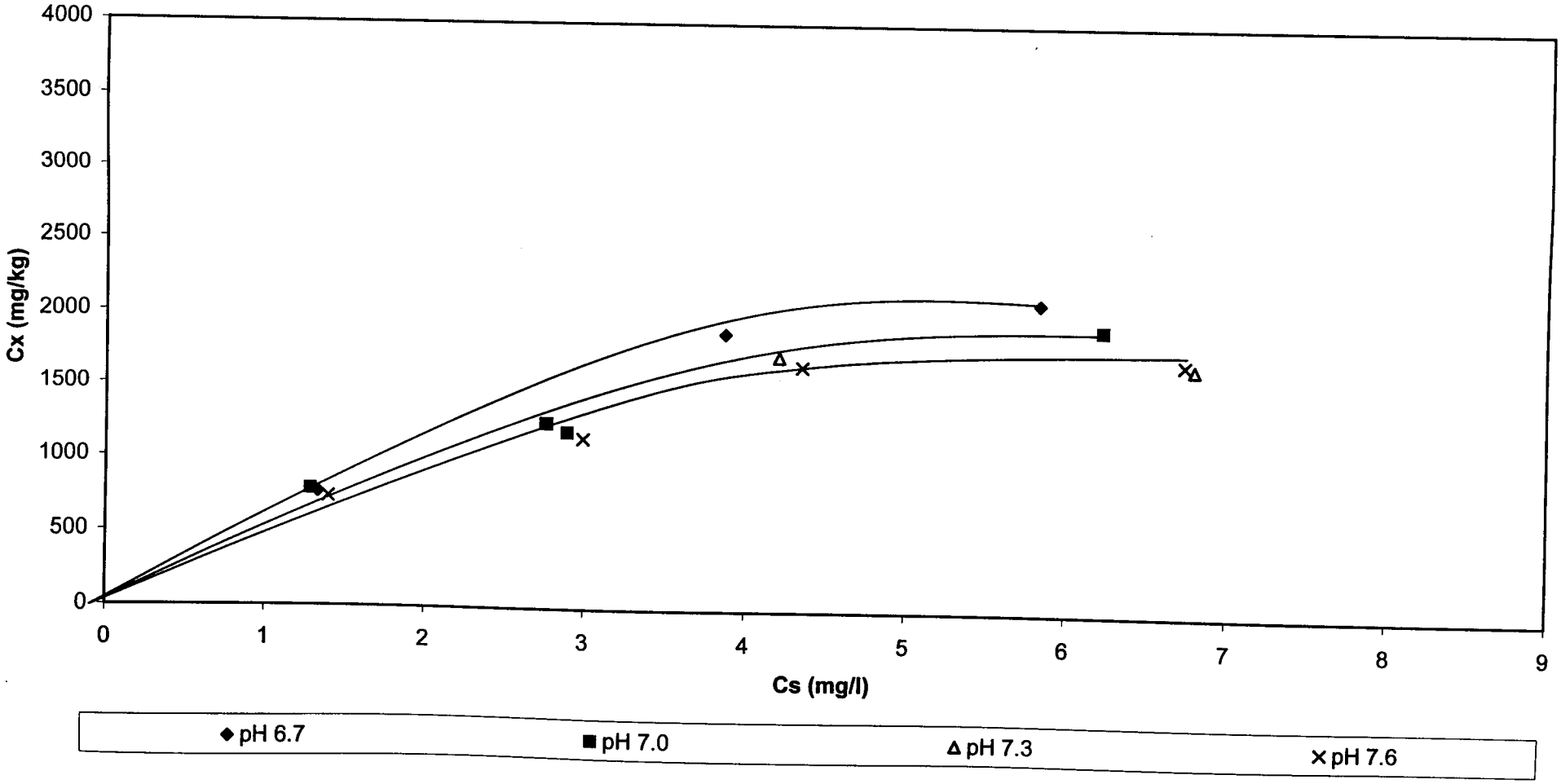


Figure C.36: ***Cu adsorption in Mixed Liquor Solids Concentration C (2500 mg/l)***

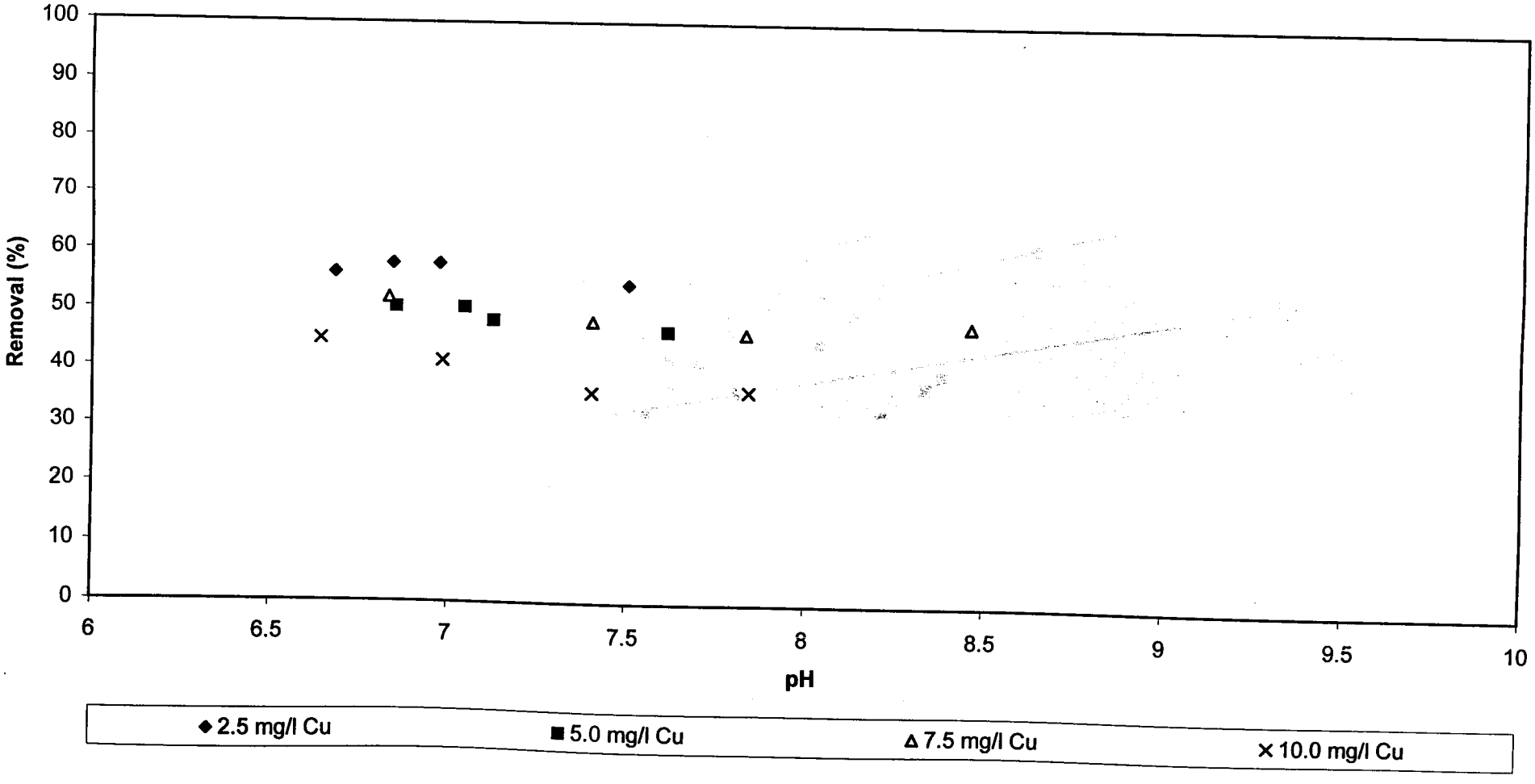


Figure C.37: ***Adsorption of Cu in Mixed Liquor (Fitted to Langmuir Isotherm)***

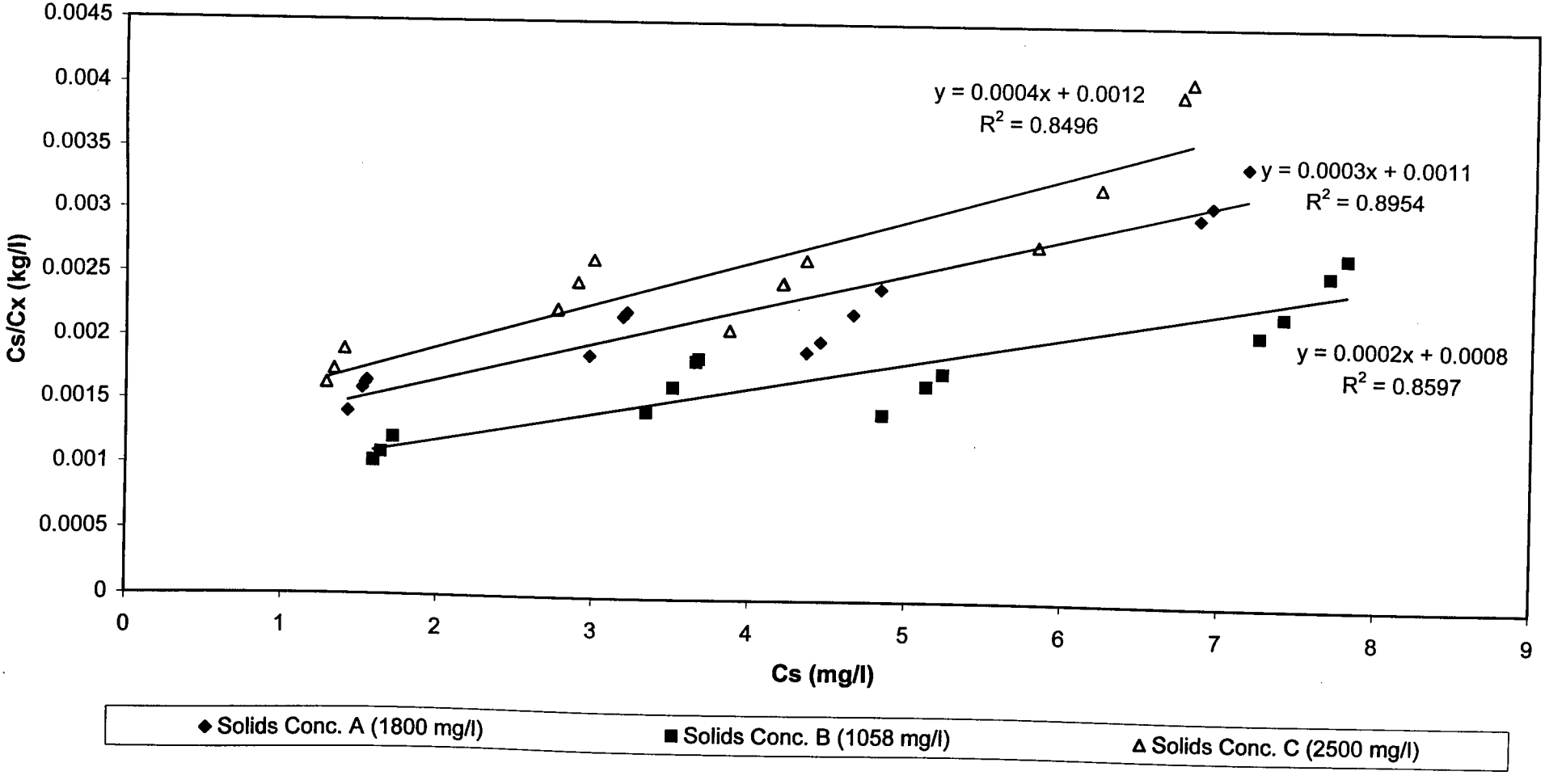


Table C.13 *Cu adsorption in final effluent*

Date Carried out 28-Aug-00

Date analysed 06-Sep-00

Initial Total Cu (mg/l) 0.0355

Actual Sample	TSS (mg/l)	pH	Cu Added (mg/l)	Residual Soluble Cu (mg/l)	Adsorbed Cu (mg/l)	Adsorbed Cu (mg/kg)	Total Cu (mg/l)
A-1-1	32	6.56	2.5	2.164	0.3715	12899.30556	2.5355
A-1-2	32	6.87	2.5	1.516	1.0195	35399.30556	2.5355
A-1-3	32	7.28	2.5	1.09	1.4455	50190.97222	2.5355
A-1-4	32	8.88	2.5	0.837	1.6985	58975.69444	2.5355
A-2-1	32	6.39	5	3.641	1.3945	48420.13889	5.0355
A-2-2	32	6.73	5	2.176	2.8595	99288.19444	5.0355
A-2-3	32	7.7	5	0.93	4.1055	142552.0833	5.0355
A-2-4	32	8.7	5	0.703	4.3325	150434.0278	5.0355
A-3-1	32	6.16	7.5	5.365	2.1705	75364.58333	7.5355
A-3-2	32	6.56	7.5	2.708	4.8275	167621.5278	7.5355
A-3-3	32	7.14	7.5	1.229	6.3065	218975.6944	7.5355
A-3-4	32	8.07	7.5	0.819	6.7165	233211.8056	7.5355
A-4-1	32	6.16	10	6.577	3.4585	120086.8056	10.0355
A-4-2	32	6.81	10	1.827	8.2085	285017.3611	10.0355
A-4-3	32	8.16	10	0.812	9.2235	320260.4167	10.0355
A-4-4	32	8.8	10	0.909	9.1265	316892.3611	10.0355
B-1-1	31	6.49	2.5	1.958	0.5775	20698.92473	2.5355
B-1-2	31	6.78	2.5	1.569	0.9665	34641.57706	2.5355
B-1-3	31	8.12	2.5	0.679	1.8565	66541.21864	2.5355
B-1-4	31	8.64	2.5	0.785	1.7505	62741.93548	2.5355
B-2-1	31	6.32	5	3.62	1.4155	50734.76703	5.0355
B-2-2	31	6.51	5	3.034	2.0015	71738.35125	5.0355
B-2-3	31	7.18	5	1.184	3.8515	138046.595	5.0355
B-2-4	31	8.71	5	0.76	4.2755	153243.7276	5.0355
B-3-1	31	5.83	7.5	6.515	1.0205	36577.06093	7.5355
B-3-2	31	6.44	7.5	2.999	4.5365	162598.5663	7.5355
B-3-3	31	7.39	7.5	0.891	6.6445	238154.1219	7.5355
B-3-4	31	8.52	7.5	0.722	6.8135	244211.4695	7.5355
B-4-1	31	6.1	10	6.197	3.8385	137580.6452	10.0355
B-4-2	31	6.7	10	1.943	8.0925	290053.7634	10.0355

Actual Sample	TSS (mg/l)	pH	Cu Added (mg/l)	Residual Soluble Cu (mg/l)	Adsorbed Cu (mg/l)	Adsorbed Cu (mg/kg)	Total Cu (mg/l)
B-4-3	31	7.52	10	0.906	9.1295	327222.2222	10.0355
B-4-4	31	8.6	10	0.762	9.2735	332383.5125	10.0355

Cu adsorption in final effluent

Figure C.38: ***Cu adsorption in Final Effluent Solids Concentration (31 mg/l)***

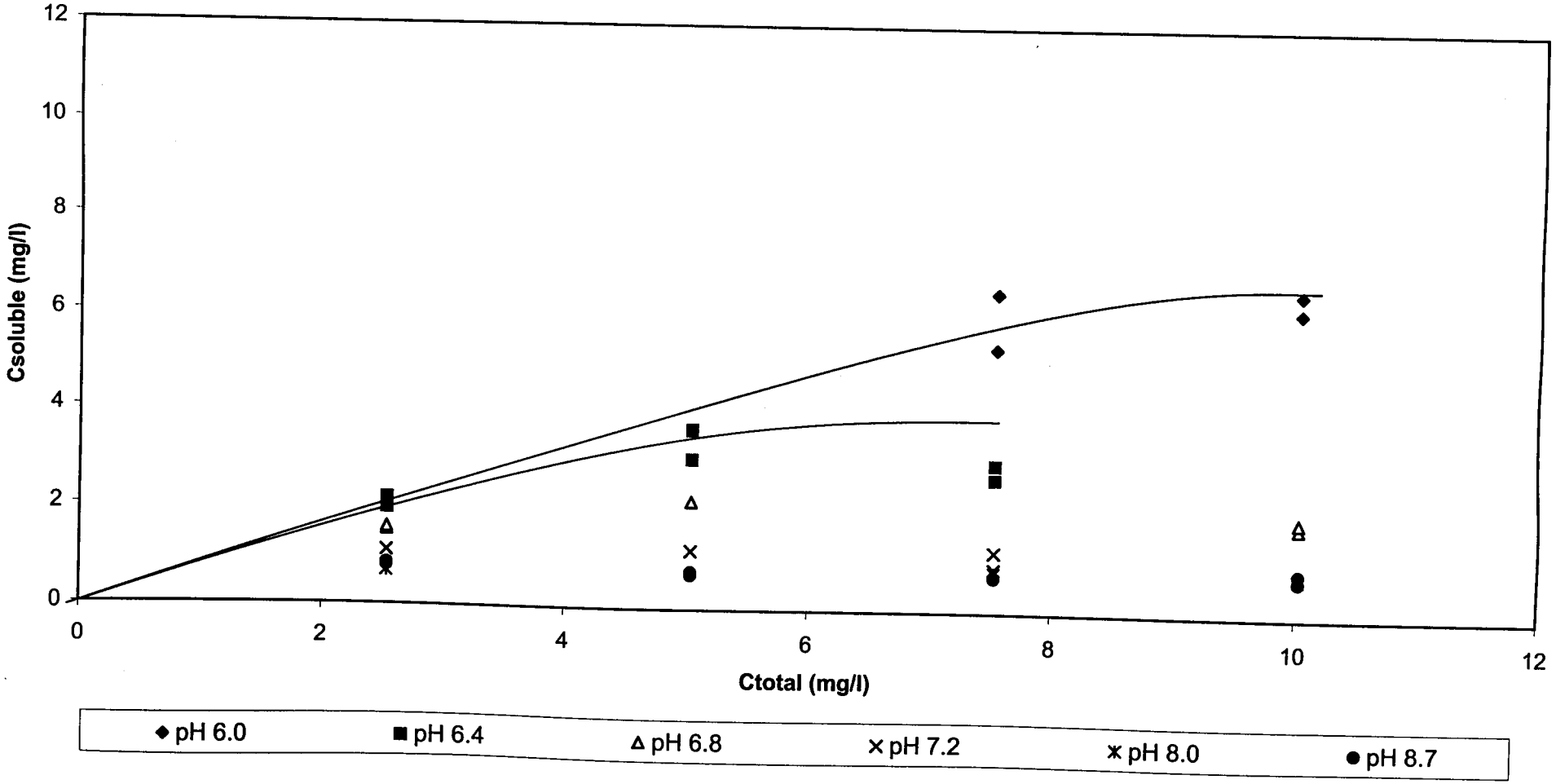


Figure C.39: ***Cu adsorption in Final Effluent Solids Concentration (31 mg/l)***

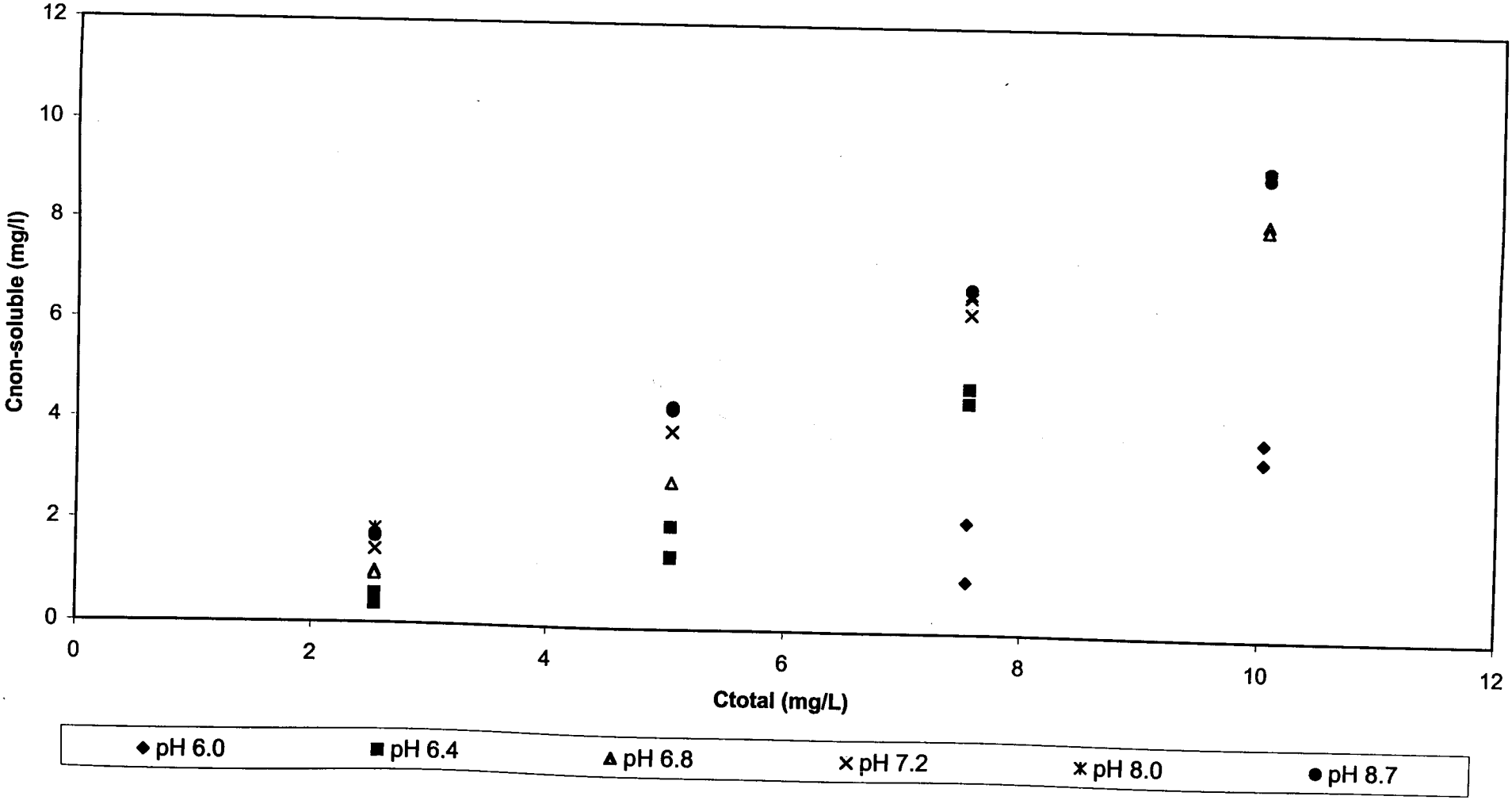


Figure C.40: ***Cu adsorption in Final Effluent Solids Concentration (31 mg/l)***

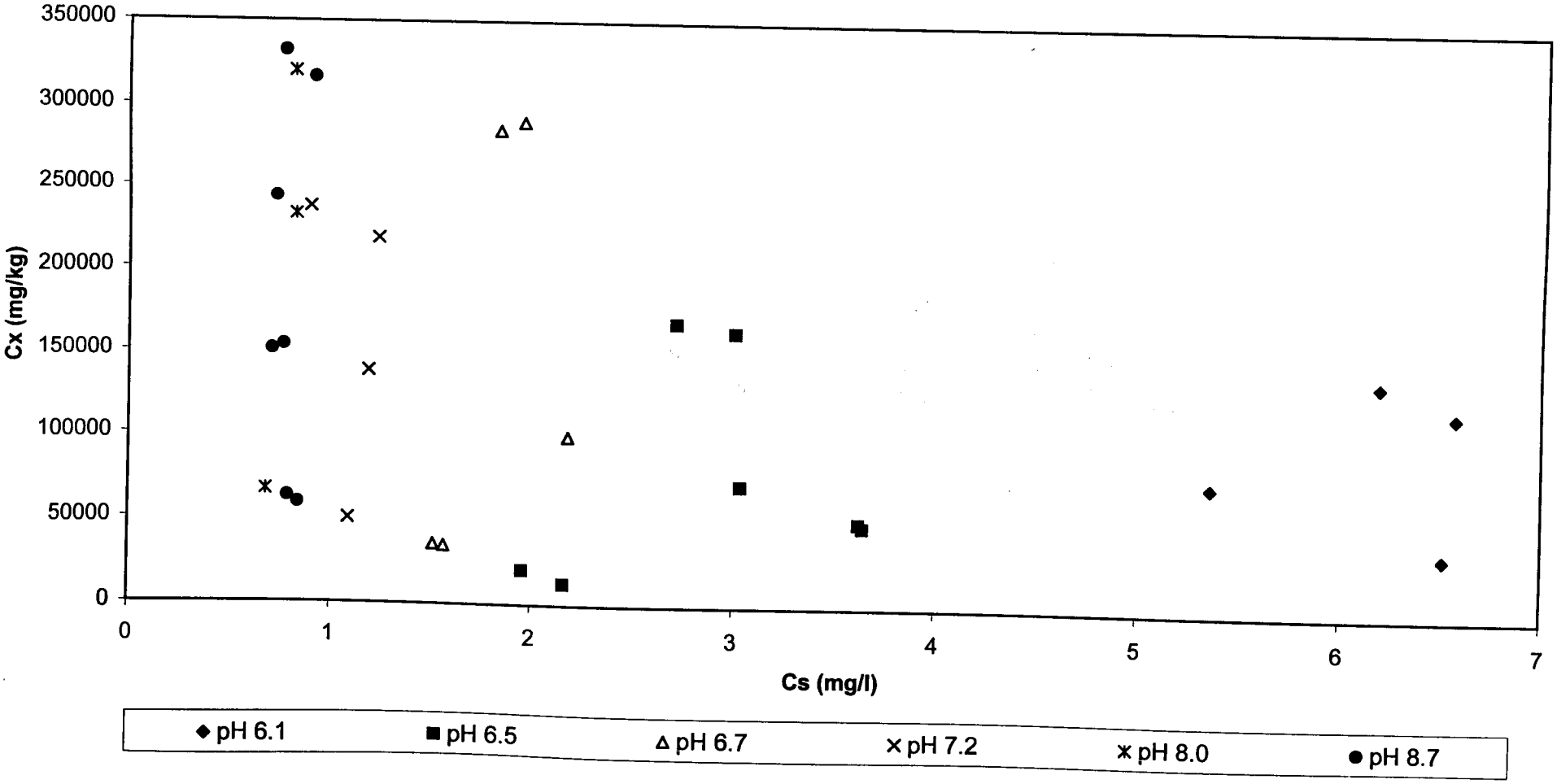


Figure C.41: ***Cu adsorption in Final Effluent Solids Concentration (31 mg/l)***

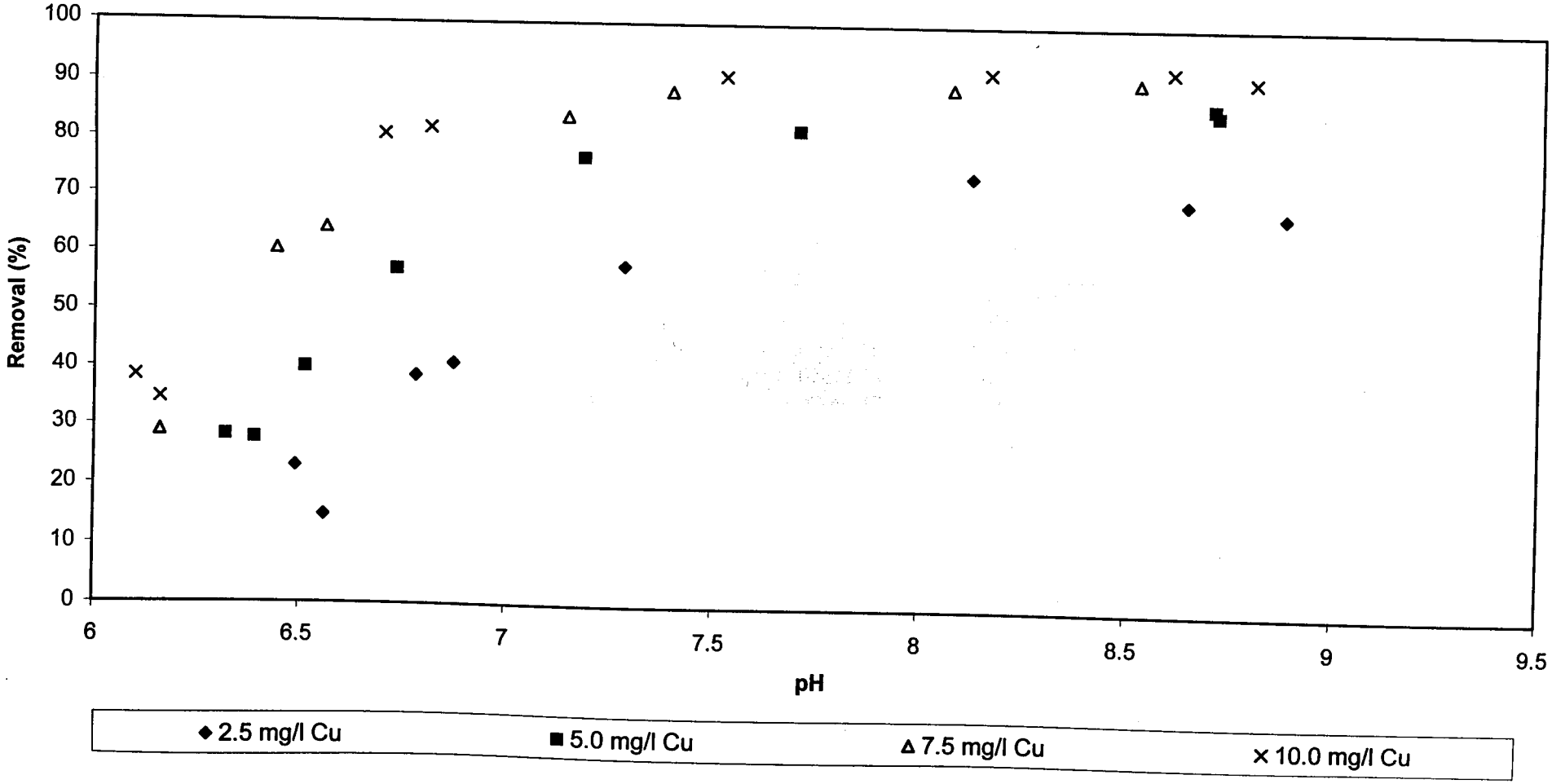


Table C.14 *Zn adsorption in raw sewage*

Date carried out: 21-Aug-00

Date analysed: 30-Aug-00

Initial Total Zn (mg/l) 0.1565

Actual Sample	TSS (mg/l)	pH	Zn Added (mg/l)	Residual soluble Zn (mg/l)	Adsorbed Zn (mg/l)	Adsorbed Zn (mg/kg)	Total Zn (mg/l)
A-1-1	474	7	1	0.57862391	0.57787609	1354.608744	1.1565
A-1-2	474	7.13	1	0.641510539	0.514989461	1207.195173	1.1565
A-1-3	474	7.46	1	0.526117772	0.630382228	1477.689235	1.1565
A-1-4	474	8.34	1	0.394785587	0.761714413	1785.547147	1.1565
A-2-1	474	6.99	2	1.054711688	1.101788312	2582.719906	2.1565
A-2-2	474	7.17	2	1.174067279	0.982432721	2302.936524	2.1565
A-2-3	474	7.2	2	1.049167422	1.107332578	2595.716311	2.1565
A-2-4	474	7.8	2	0.750610422	1.405889578	3295.568631	2.1565
A-3-1	474	6.84	3	2.100045416	1.056454584	2476.452377	3.1565
A-3-2	474	6.7	3	2.070925276	1.085574724	2544.71337	3.1565
A-3-3	474	7.05	3	1.936648655	1.219851345	2859.473382	3.1565
A-3-4	474	7.01	3	1.638767062	1.517732938	3557.74247	3.1565
A-4-1	474	6.84	4	1.896153304	2.260346696	5298.515461	4.1565
A-4-2	474	7.16	4	1.020929309	3.135570691	7350.142266	4.1565
A-4-3	474	7.43	4	0.726766074	3.429733926	8039.695092	4.1565
A-4-4	474	7.76	4	0.60809537	3.54840463	8317.873019	4.1565
B-1-1	322	6.95	1	0.778884208	0.377615792	1303.022058	1.1565
B-1-2	322	7.23	1	0.648511332	0.507988668	1752.893954	1.1565
B-1-3	322	7.36	1	0.623585029	0.532914971	1838.906041	1.1565
B-1-4	322	8.67	1	0.292339236	0.864160764	2981.9212	1.1565
B-2-1	322	6.75	2	1.479732858	0.676767142	2335.290344	2.1565
B-2-2	322	6.9	2	1.446170893	0.710329107	2451.101128	2.1565
B-2-3	322	7.15	2	1.175985119	0.980514881	3383.41919	2.1565
B-2-4	322	7.5	2	0.993180502	1.163319498	4014.214968	2.1565
B-3-1	322	6.58	3	2.256761322	0.899738678	3104.68833	3.1565
B-3-2	322	6.66	3	2.386428089	0.770071911	2657.252972	3.1565
B-3-3	322	6.91	3	2.104052044	1.052447956	3631.635461	3.1565
B-3-4	322	7.01	3	1.979270168	1.177229832	4062.214742	3.1565
B-4-1	322	6.81	4	2.818385564	1.338114436	4617.372106	4.1565
B-4-2	322	7.04	4	1.9110206	2.2454794	7748.376122	4.1565

Actual Sample	TSS (mg/l)	pH	Zn Added (mg/l)	Residual soluble Zn (mg/l)	Adsorbed Zn (mg/l)	Adsorbed Zn (mg/kg)	Total Zn (mg/l)
B-4-3	322	7.3	4	1.268355433	2.888144567	9965.992296	4.1565
B-4-4	322	7.57	4	0.775768089	3.380731911	11665.74158	4.1565
C-1-1	668	7.03	1	0.553637541	0.602862459	1002.765234	1.1565
C-1-2	668	7.34	1	0.024225614	1.132274386	1883.357261	1.1565
C-1-3	668	7.57	1	0.3903919	0.7661081	1274.298237	1.1565
C-1-4	668	8.23	1	0.608088732	0.548411268	912.194392	1.1565
C-2-1	668	6.74	2	0.991270354	1.165229646	1938.173064	2.1565
C-2-2	668	7.05	2	0.804686448	1.351813552	2248.525536	2.1565
C-2-3	668	7.64	2	0.741906431	1.414593569	2352.950048	2.1565
C-2-4	668	7.69	2	0.741906431	1.414593569	2352.950048	2.1565
C-3-1	668	6.6	3	1.862629602	1.293870398	2152.146371	3.1565
C-3-2	668	6.86	3	1.58374981	1.57275019	2616.018279	3.1565
C-3-3	668	7.12	3	1.357428158	1.799071842	2992.468134	3.1565
C-3-4	668	7.08	3	1.31601052	1.84048948	3061.359748	3.1565
C-4-1	668	6.77	4	1.677089079	2.479410921	4124.103328	4.1565
C-4-2	668	7.11	4	1.00389117	3.15260883	5243.860329	4.1565
C-4-3	668	7.45	4	0.635462944	3.521037056	5856.681729	4.1565
C-4-4	668	7.76	4	0.415586897	3.740913103	6222.410351	4.1565

Zn adsorption in raw sewage

Figure C.42: ***Zn adsorption in Raw Sewage Solids Concentration A (474 mg/l)***

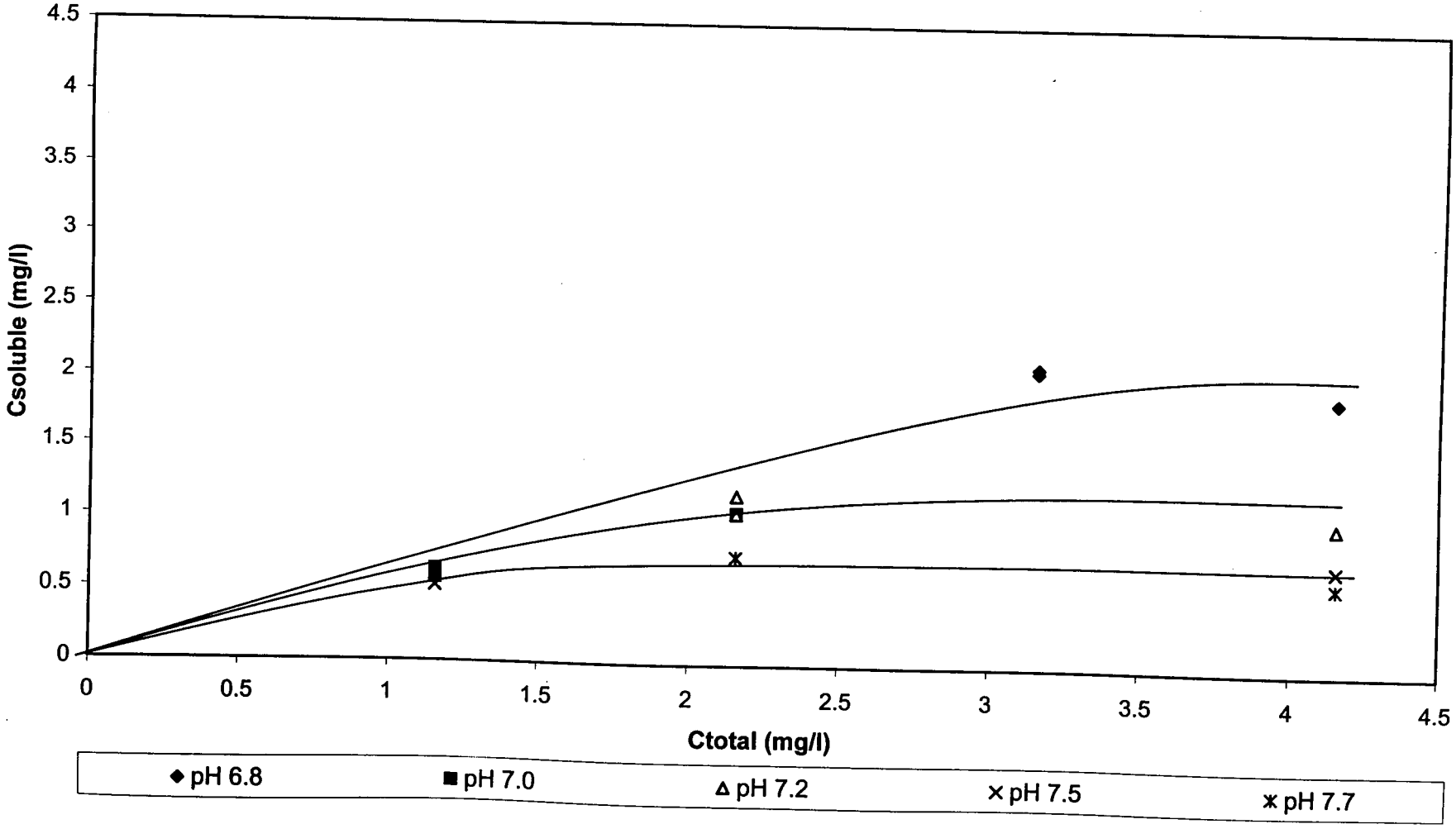


Figure C.43: ***Zn adsorption in Raw Sewage Solids Concentration A (474 mg/l)***

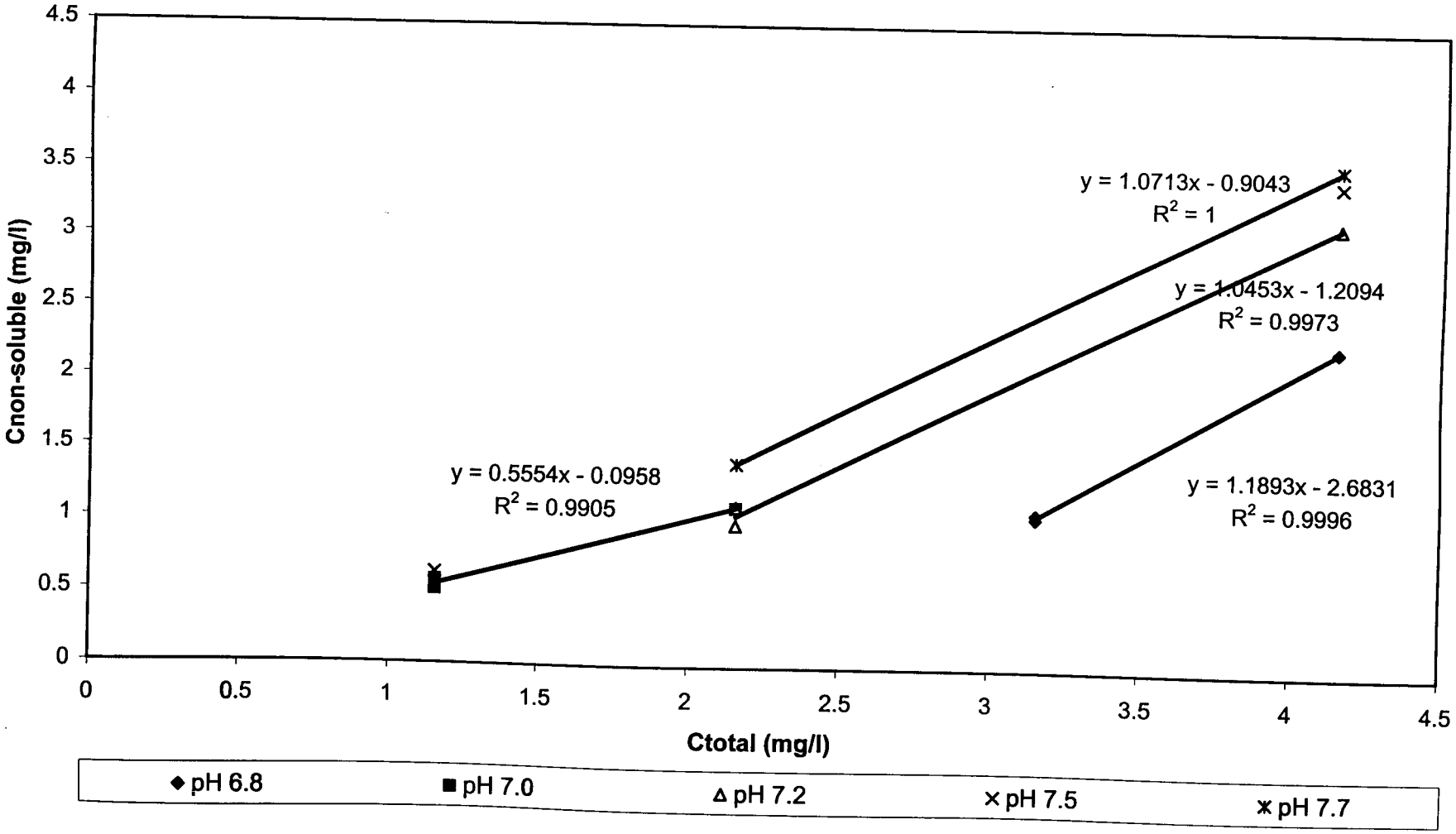


Figure C.44: ***Zn adsorption in Raw Sewage Solids Concentration A (474 mg/l)***

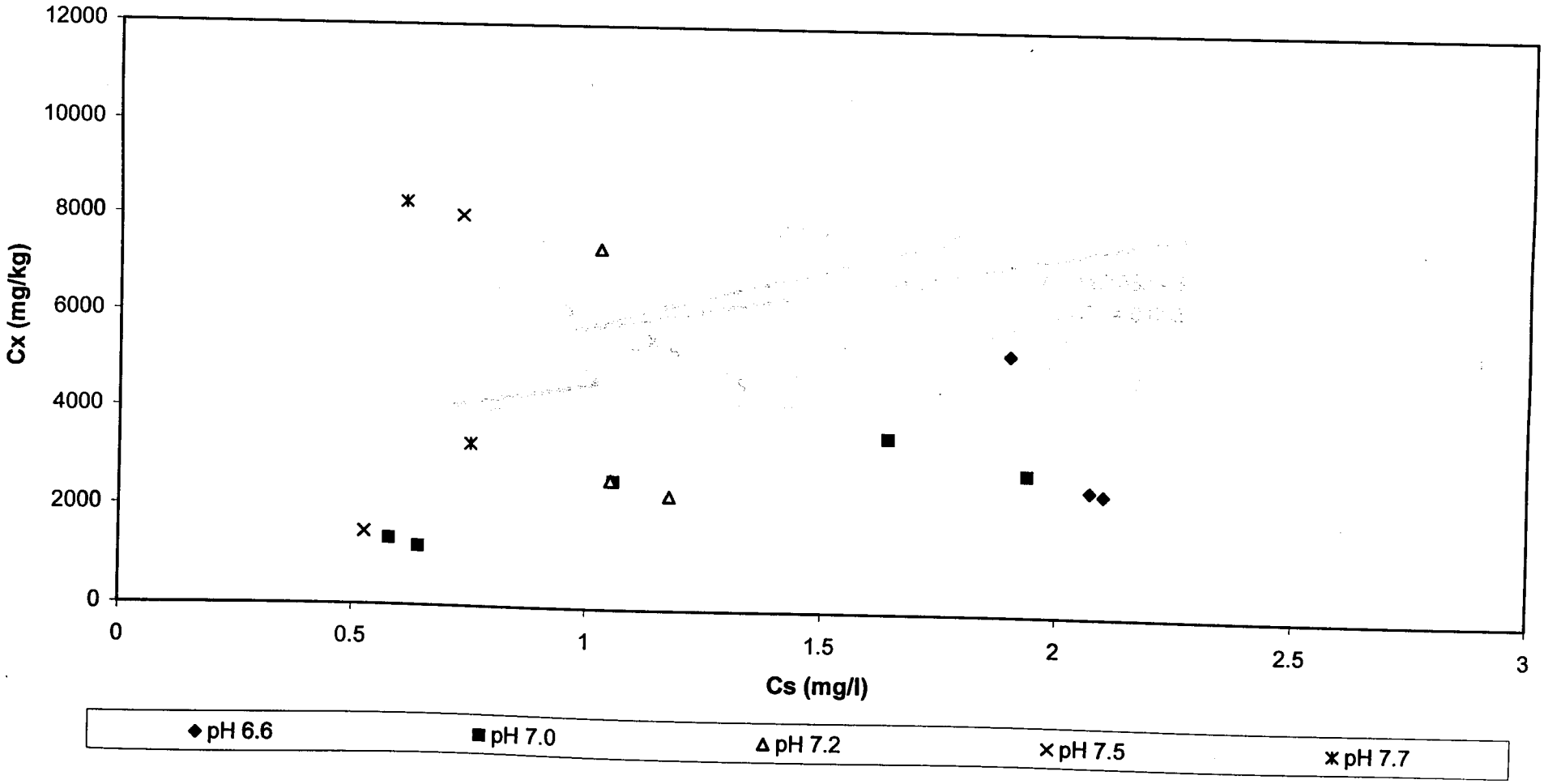


Figure C.45: ***Zn adsorption in Raw Sewage Solids Concentration A (474 mg/l)***

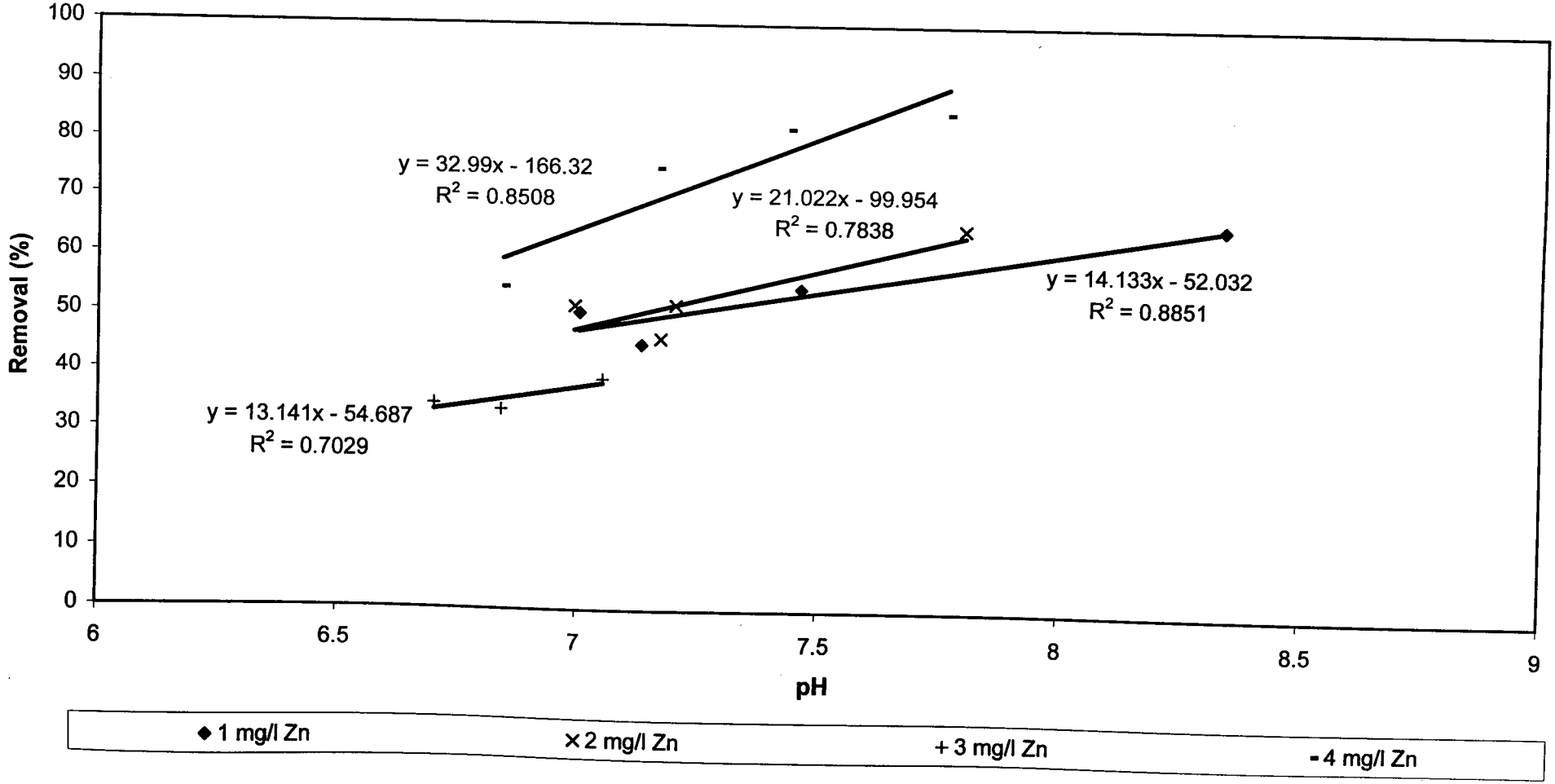


Figure C.46: ***Zn adsorption in Raw Sewage Solids Concentration B (322 mg/l)***

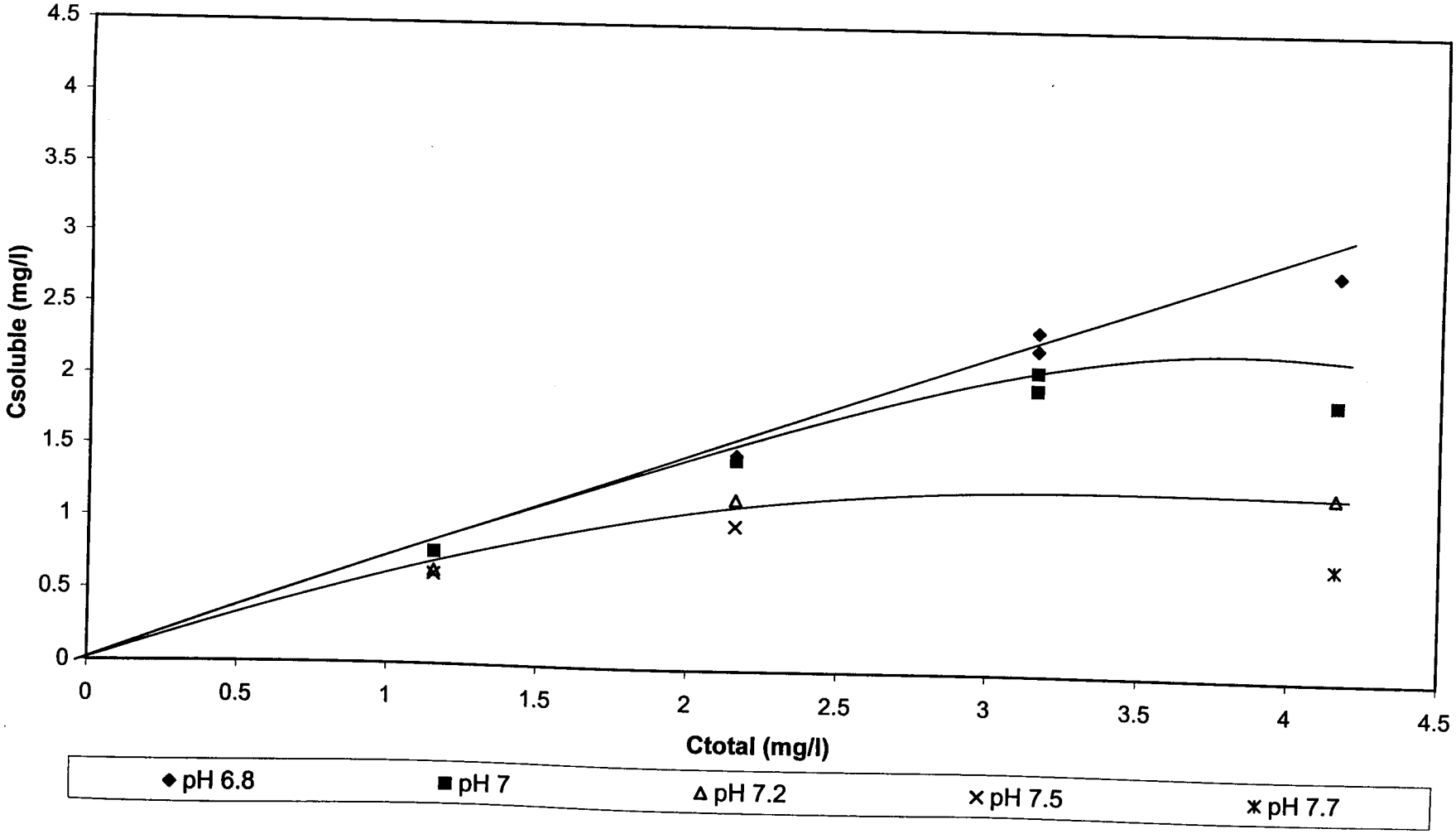


Figure C.47: ***Zn adsorption in Raw Sewage Solids Concentration B (322 mg/l)***

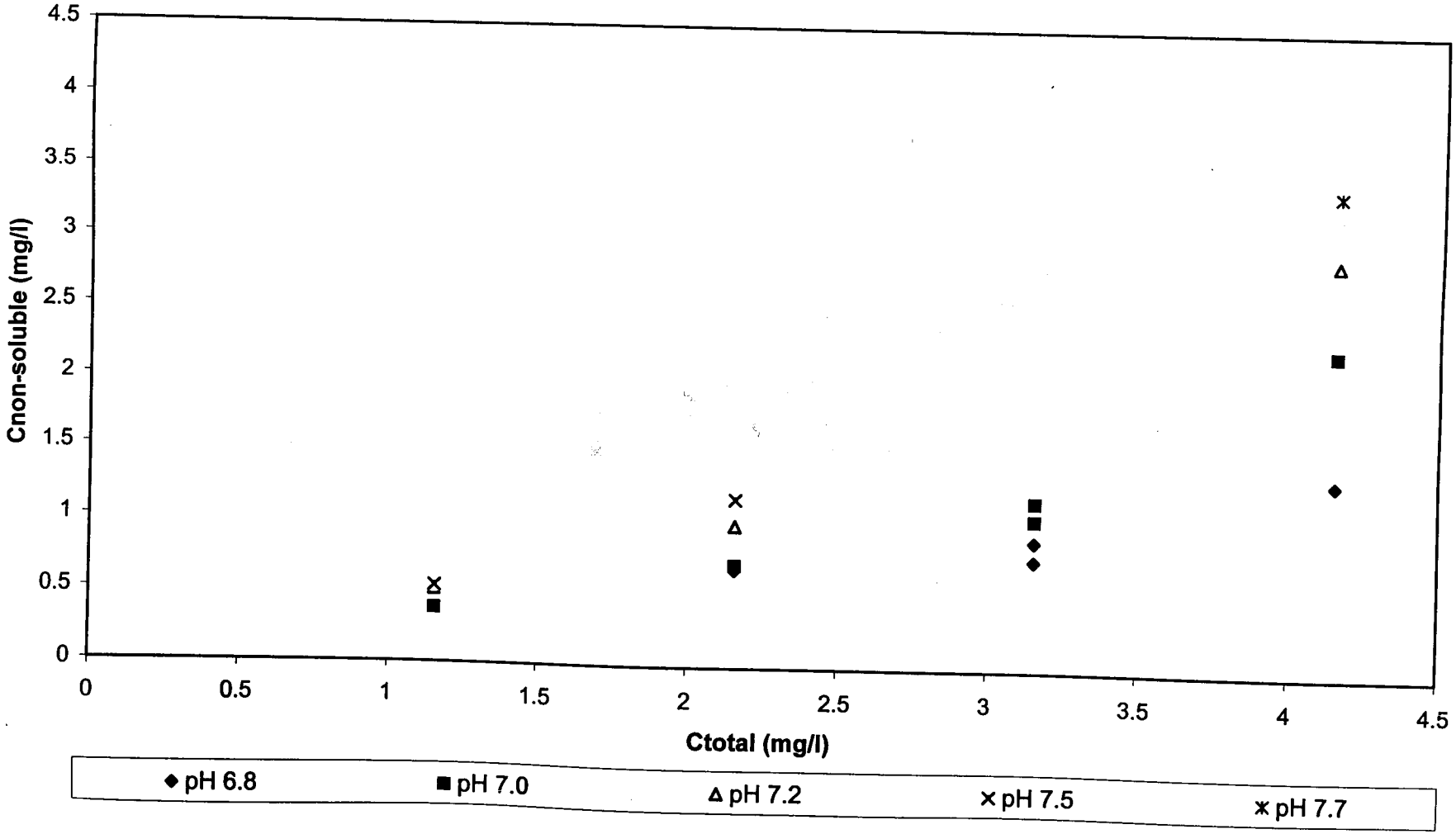


Figure C.48: ***Zn adsorption in Raw Sewage Solids Concentration B (322 mg/l)***

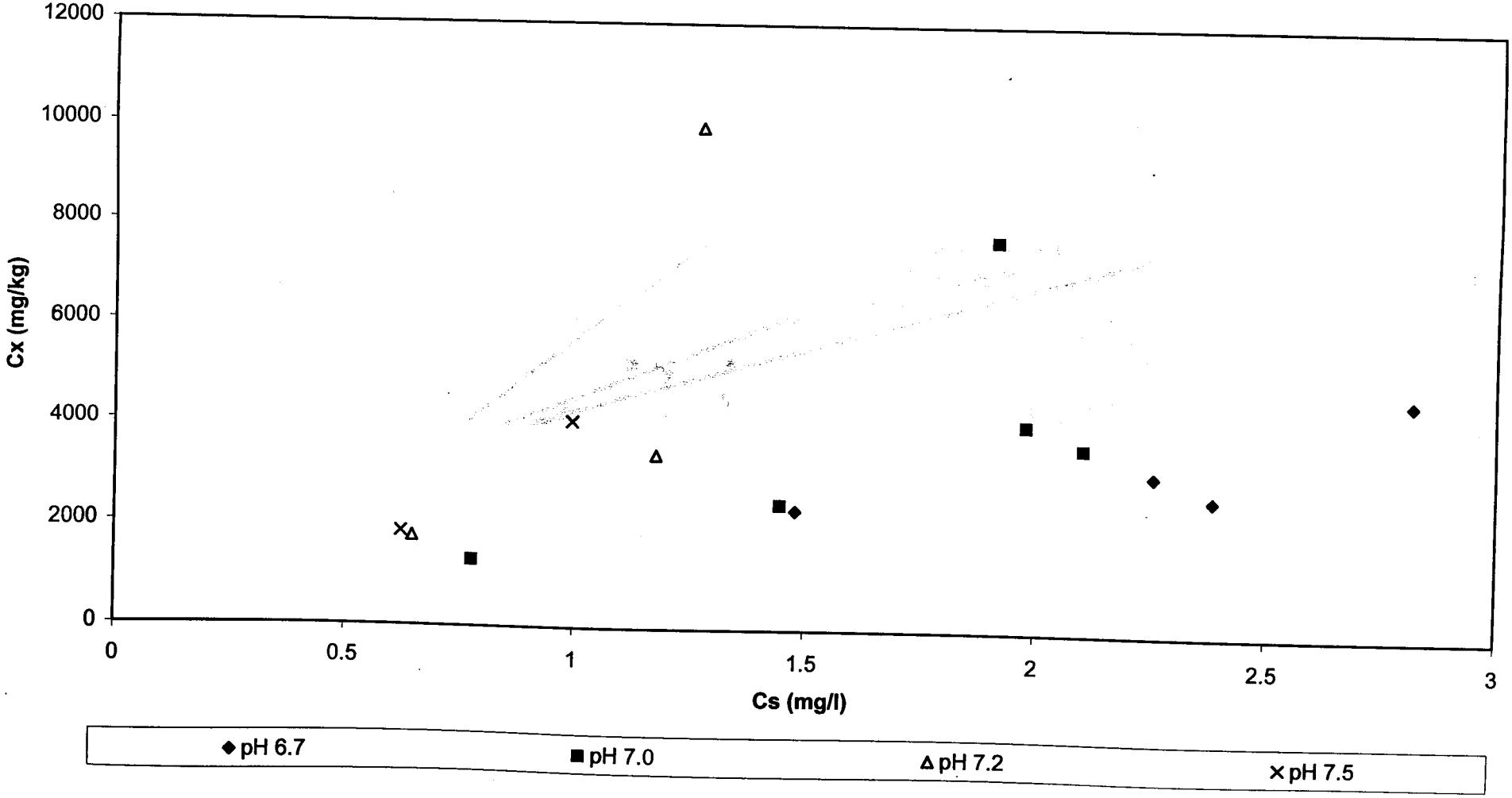


Figure C.49: ***Zn adsorption in Raw Sewage Solids Concentration B (322 mg/l)***

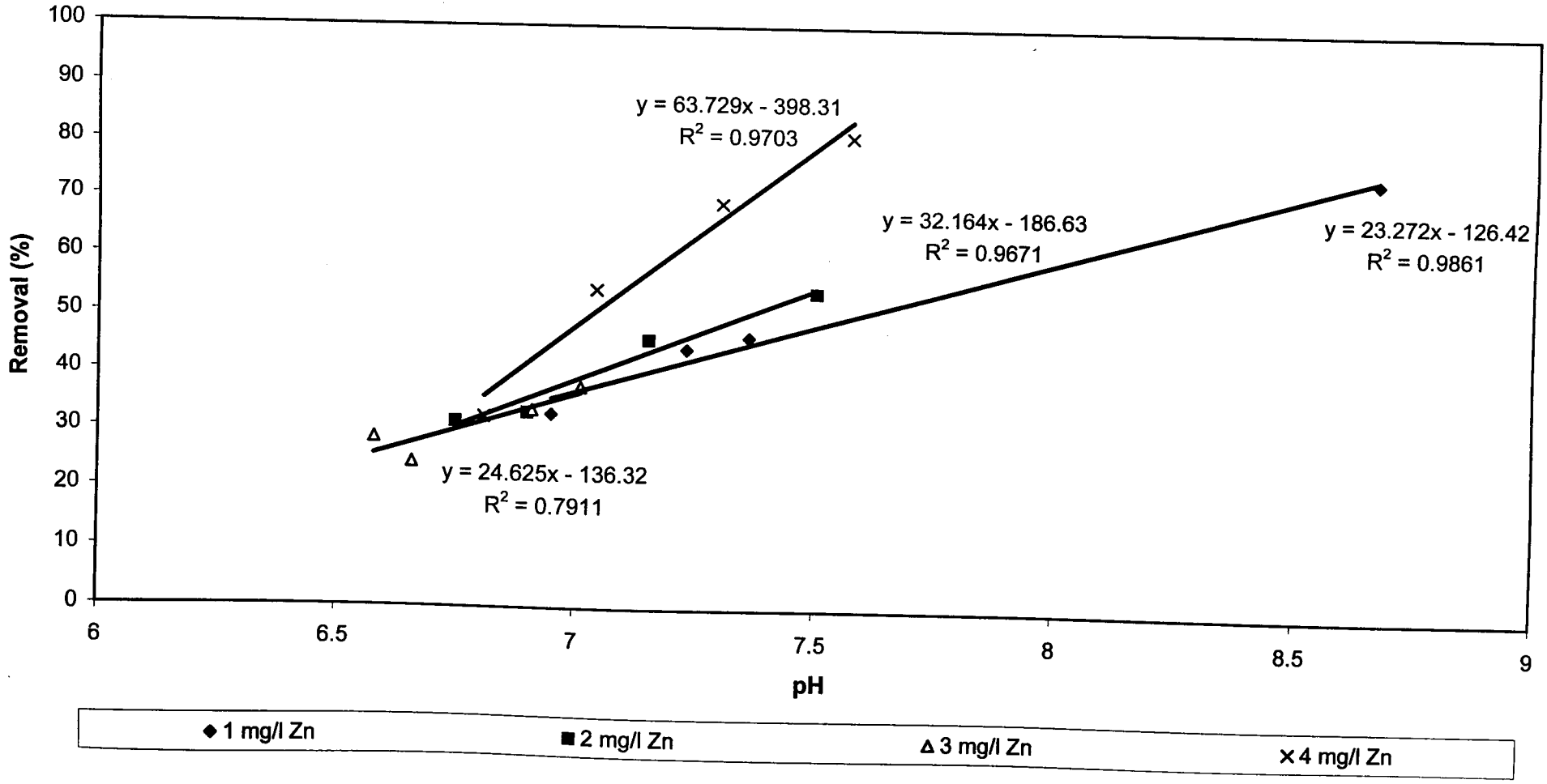


Figure C.50: ***Zn adsorption in Raw Sewage Solids Concentration C (668 mg/l)***

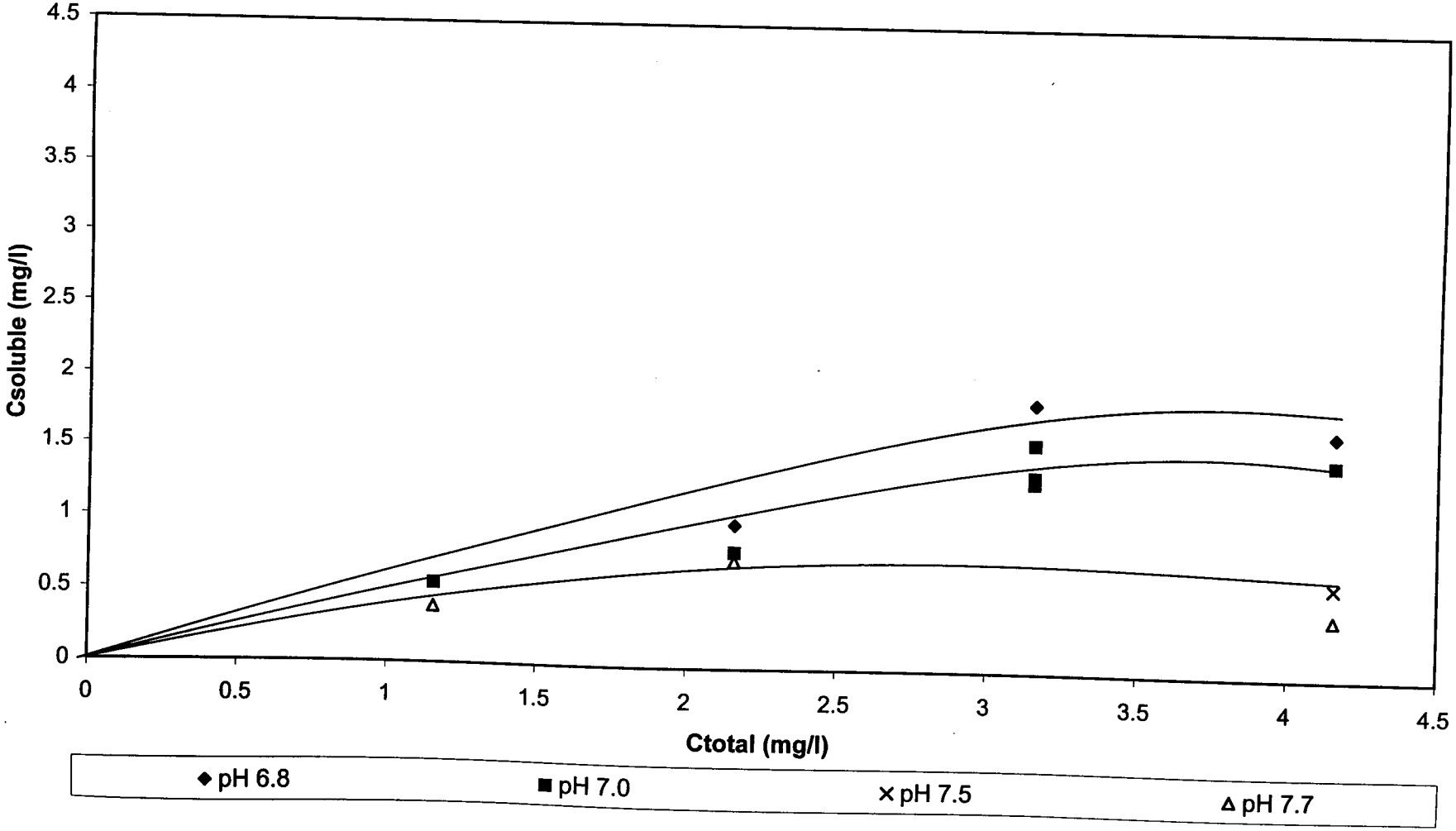


Figure C.51: ***Zn adsorption in Raw Sewage Solids Concentration C (668 mg/l)***

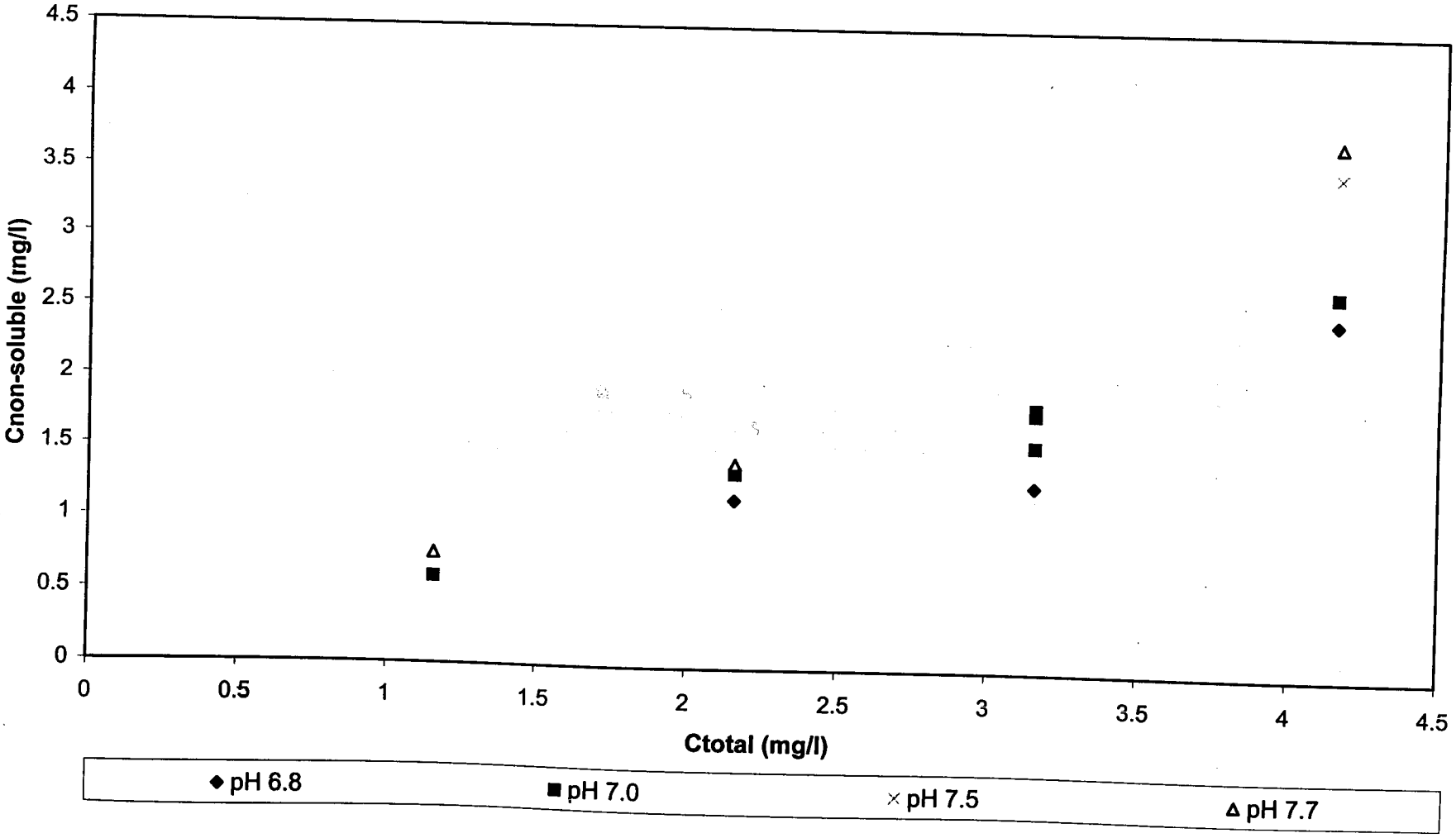


Figure C.52: ***Zn adsorption in Raw Sewage Solids Concentration C (688 mg/l)***

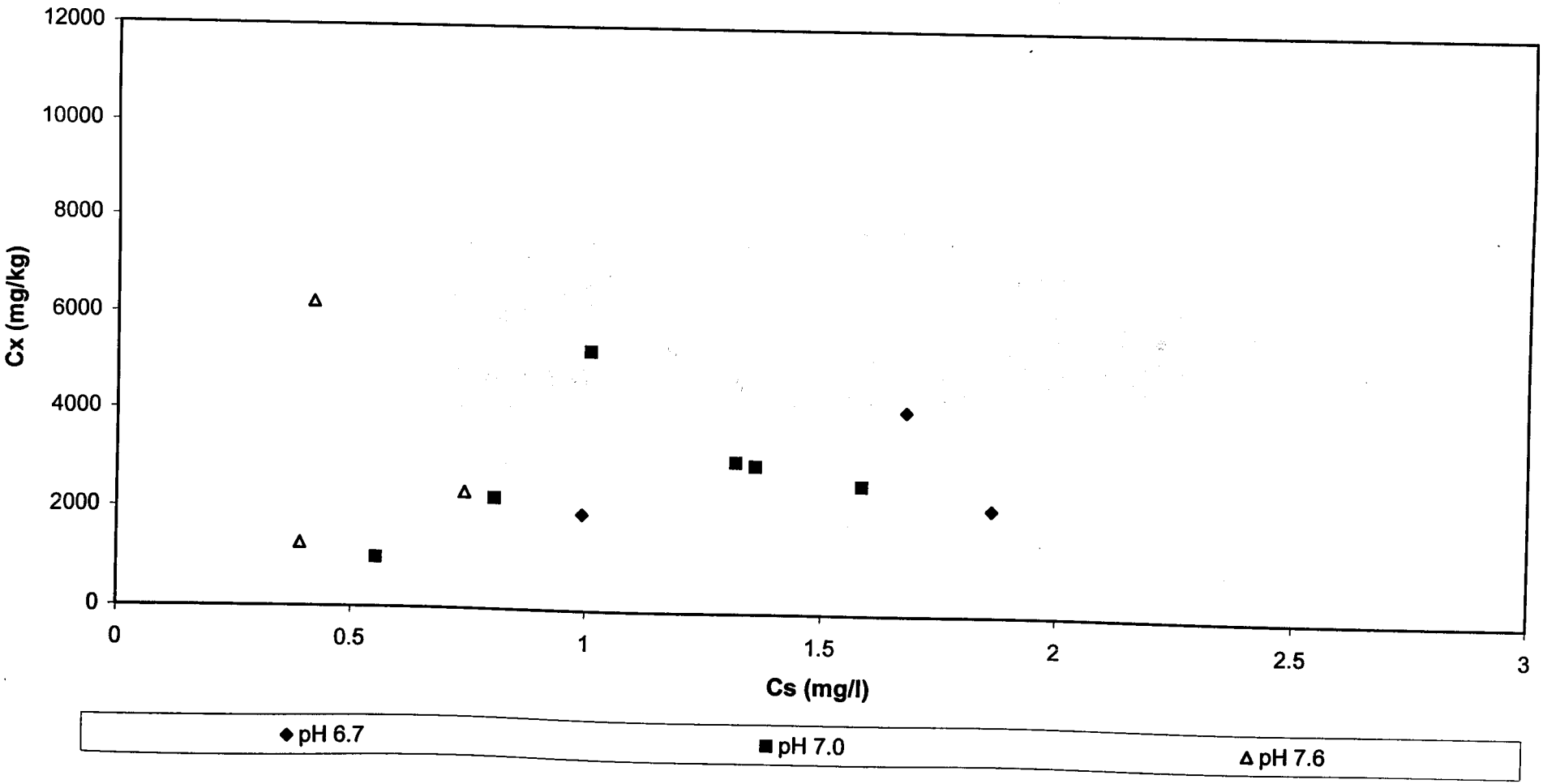


Figure C.53: ***Zn adsorption in Raw Sewage Solids Concentration C (668 mg/l)***

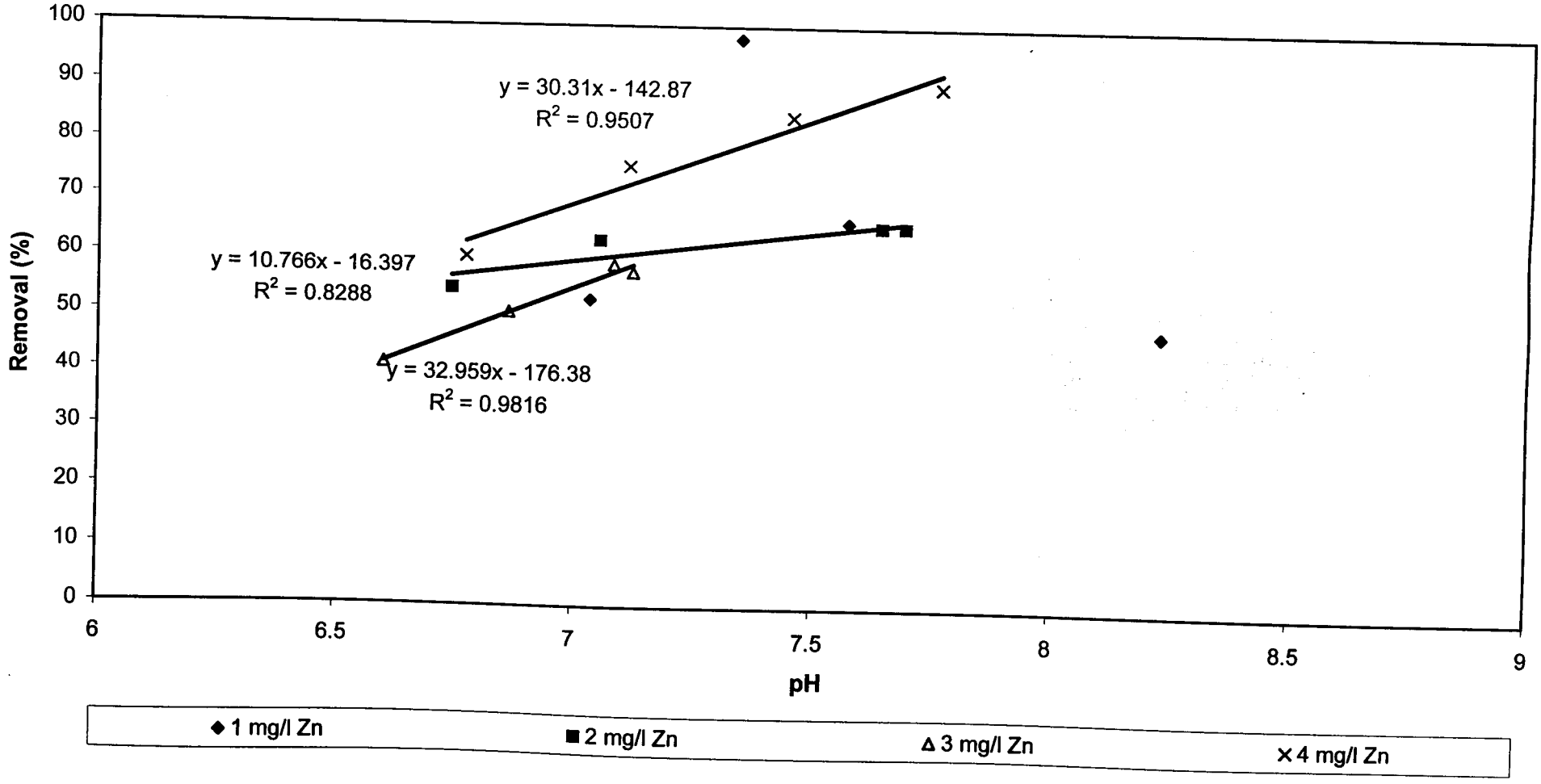


Table C.15 *Zn adsorption in primary effluent*

Date carried out: 14-Aug-00

Date analysed: 15-Aug-00

Initial Total Zn (mg/l) 0.0509

Actual Sample	TSS	pH	Zn Added(mg/l)	Residual soluble Zn (mg/l)	Adsorbed Zn (mg/l)	Adsorbed Zn (mg/kg)	Total Zn (mg/l)
A-1-1	94	7	1	0.93364861	0.11725139	1385.950236	1.0509
A-1-2	94	7.1	1	0.89805158	0.15284842	1806.718913	1.0509
A-1-3	94	7.77	1	0.62463946	0.42626054	5038.540662	1.0509
A-1-4	94	8.4	1	0.36347999	0.68742001	8125.532033	1.0509
A-2-1	94	6.69	2	1.78733589	0.26356411	3115.415012	2.0509
A-2-2	94	7.1	2	1.68611415	0.36478585	4311.88948	2.0509
A-2-3	94	7.63	2	1.08029715	0.97060285	11472.84693	2.0509
A-2-4	94	7.14	2	1.67250371	0.37839629	4472.769385	2.0509
A-3-1	94	6.43	3	2.66518555	0.38571445	4559.272459	3.0509
A-3-2	94	6.91	3	2.44152476	0.60937524	7203.017021	3.0509
A-3-3	94	7.57	3	0.97858221	2.07231779	24495.48215	3.0509
A-3-4	94	8.61	3	0.52293886	2.52796114	29881.33735	3.0509
A-4-1	94	6.26	4	3.48672492	0.56417508	6668.73617	4.0509
A-4-2	94	6.41	4	3.52768194	0.52321806	6184.610638	4.0509
A-4-3	94	6.69	4	3.36244916	0.68845084	8137.716785	4.0509
A-4-4	94	7.08	4	2.52711681	1.52378319	18011.62163	4.0509
B-1-1	86	6.81	1	1.12083301	-0.06993301	-903.527261	1.0509
B-1-2	86	7.4	1	0.980543	0.070357	909.005168	1.0509
B-1-3	86	8.33	1	0.47593189	0.57496811	7428.528553	1.0509
B-1-4	86	8.88	1	0.32297243	0.72792757	9404.748966	1.0509
B-2-1	86	6.58	2	1.80501834	0.24588166	3176.765633	2.0509
B-2-2	86	7.11	2	1.69957828	0.35132172	4539.04031	2.0509
B-2-3	86	7.08	2	1.80929175	0.24160825	3121.553618	2.0509
B-2-4	86	7.42	2	1.32087719	0.73002281	9431.819251	2.0509
B-3-1	86	2.88	3	4.04321698	-0.99231698	-12820.63282	3.0509
B-3-2	86	6.82	3	2.53786269	0.51303731	6628.389018	3.0509
B-3-3	86	7.24	3	1.88512295	1.16577705	15061.71899	3.0509
B-3-4	86	9.24	3	0.32768455	2.72321545	35183.66214	3.0509
B-4-1	86	6	4	3.55903081	0.49186919	6354.899096	4.0509
B-4-2	86	6.4	4	3.60547868	0.44542132	5754.797416	4.0509

Actual Sample	TSS	pH	Zn Added(mg/l)	Residual soluble Zn (mg/l)	Adsorbed Zn (mg/l)	Adsorbed Zn (mg/kg)	Total Zn (mg/l)
B-4-3	86	6.4	4	3.46370061	0.58719939	7586.555426	4.0509
B-4-4	86	6.72	4	3.33918018	0.71171982	9195.346512	4.0509
C-1-1	125	9	1	0.14611333	0.90478667	8042.548178	1.0509
C-1-2	125	9.24	1	0.17001835	0.88088165	7830.059111	1.0509
C-1-3	125	9.28	1	0.35244411	0.69845589	6208.4968	1.0509
C-1-4	125	9.46	1	0.14821073	0.90268927	8023.904622	1.0509
C-2-1	125	6.56	2	1.81789953	0.23300047	2071.115289	2.0509
C-2-2	125	6.89	2	1.6904391	0.3604609	3204.096889	2.0509
C-2-3	125	7	2	1.66478209	0.38611791	3432.1592	2.0509
C-2-4	125	7.27	2	1.4894014	0.5614986	4991.098667	2.0509
C-3-1	125	6.87	3	2.63859219	0.41230781	3664.958311	3.0509
C-3-2	125	7.11	3	2.06738872	0.98351128	8742.322489	3.0509
C-3-3	125	8.52	3	0.6509422	2.3999578	21332.95822	3.0509
C-3-4	125	8.53	3	0.47352475	2.57737525	22910.00222	3.0509
C-4-1	125	6.18	4	3.51978036	0.53111964	4721.063467	4.0509
C-4-2	125	6.6	4	3.35523931	0.69566069	6183.650578	4.0509
C-4-3	125	6.7	4	3.31855273	0.73234727	6509.753511	4.0509
C-4-4	125	7	4	2.54370982	1.50719018	13397.24604	4.0509

Zn adsorption in primary effluent

Figure C.54: ***Zn adsorption in Primary Effluent Solids Concentration A (94 mg/l)***

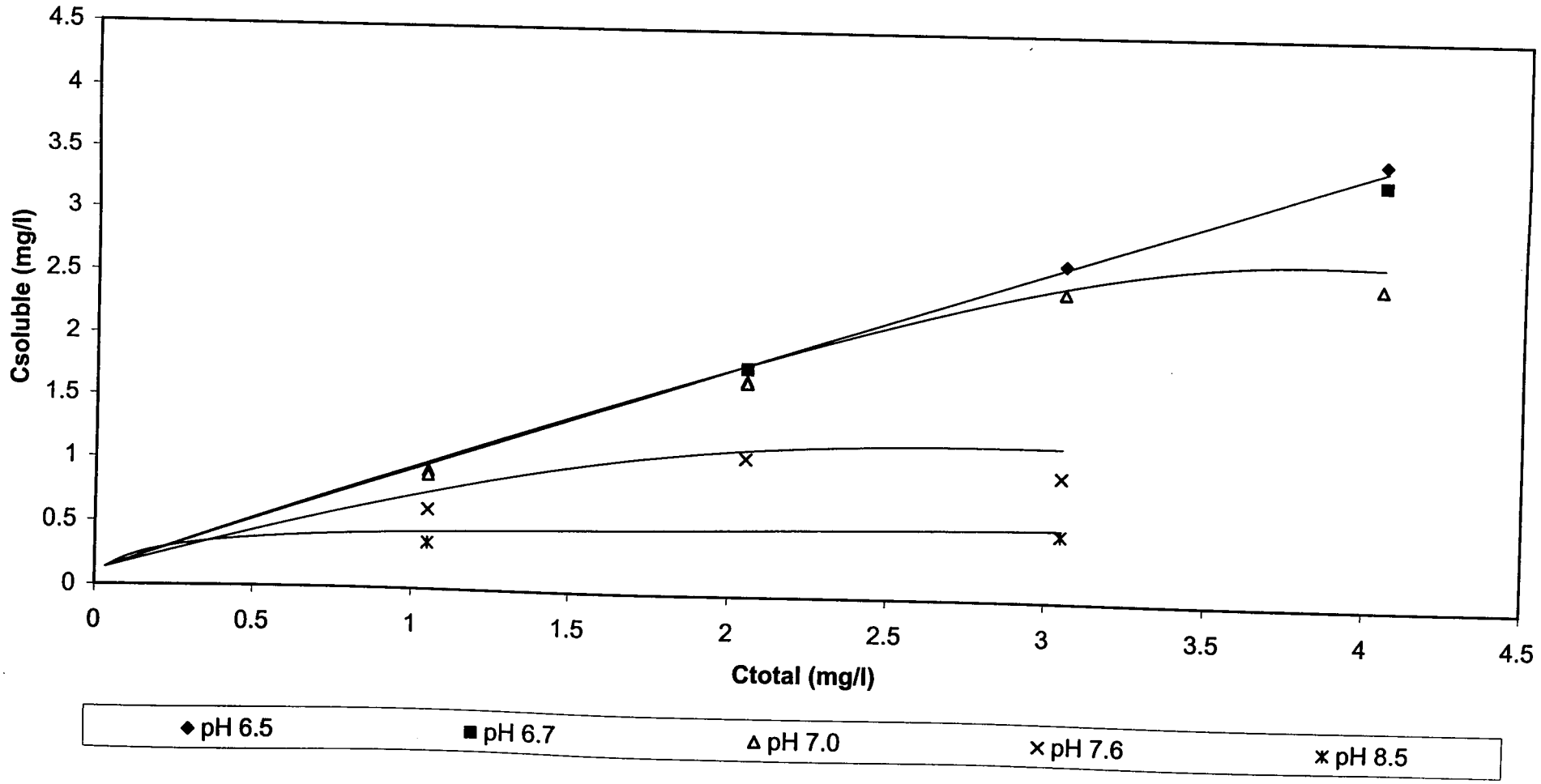


Figure C.55: ***Zn adsorption in Primary Effluent Solids Concentration A (94 mg/l)***

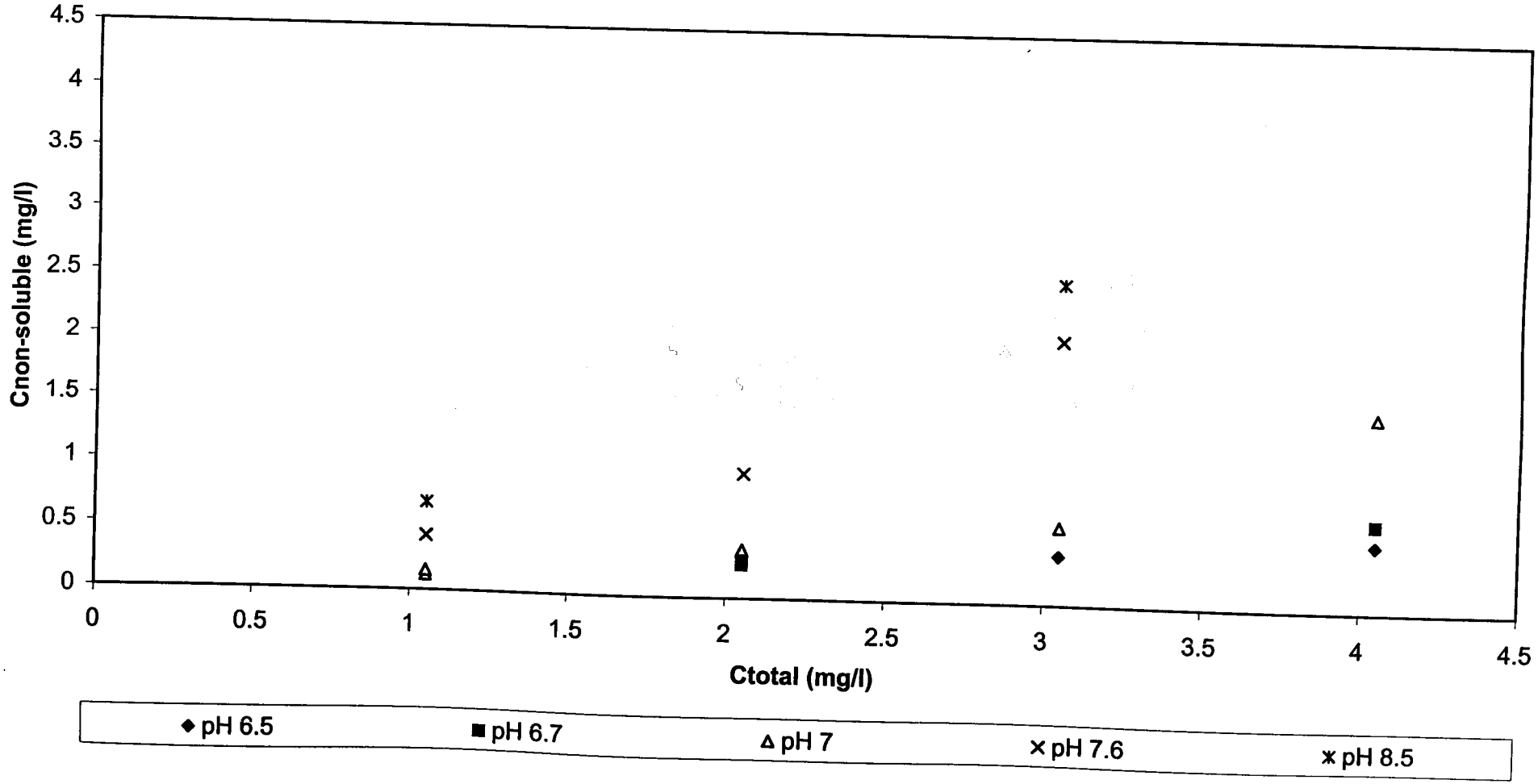


Figure C.56: ***Zn adsorption in Primary Effluent Solids Concentration A (94 mg/l)***

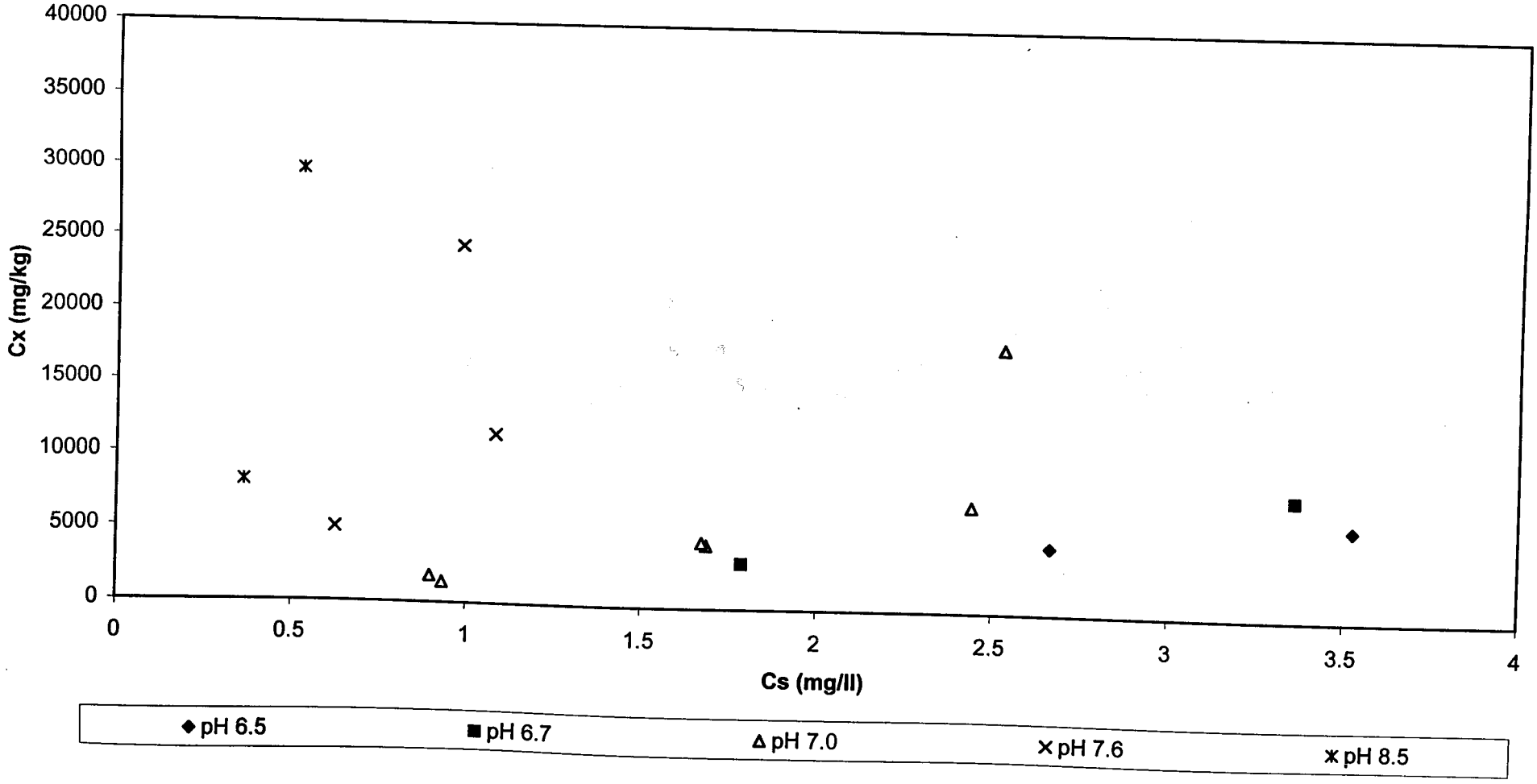


Figure C.57: ***Zn adsorption in Primary Effluent Solids Concentration A (94 mg/l)***

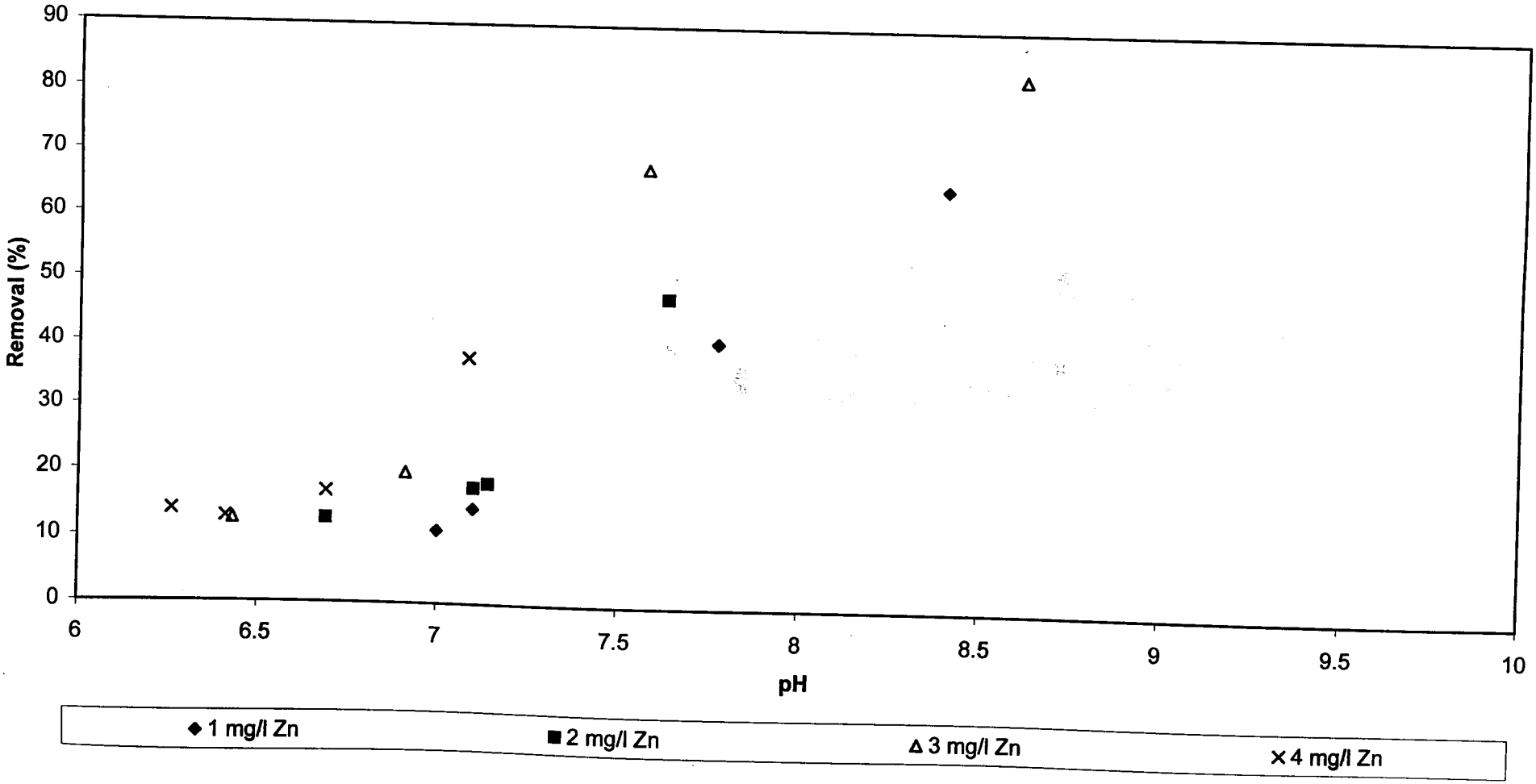


Figure C.58: ***Zn adsorption in Primary Effluent Solids Concentration B (86 mg/l)***

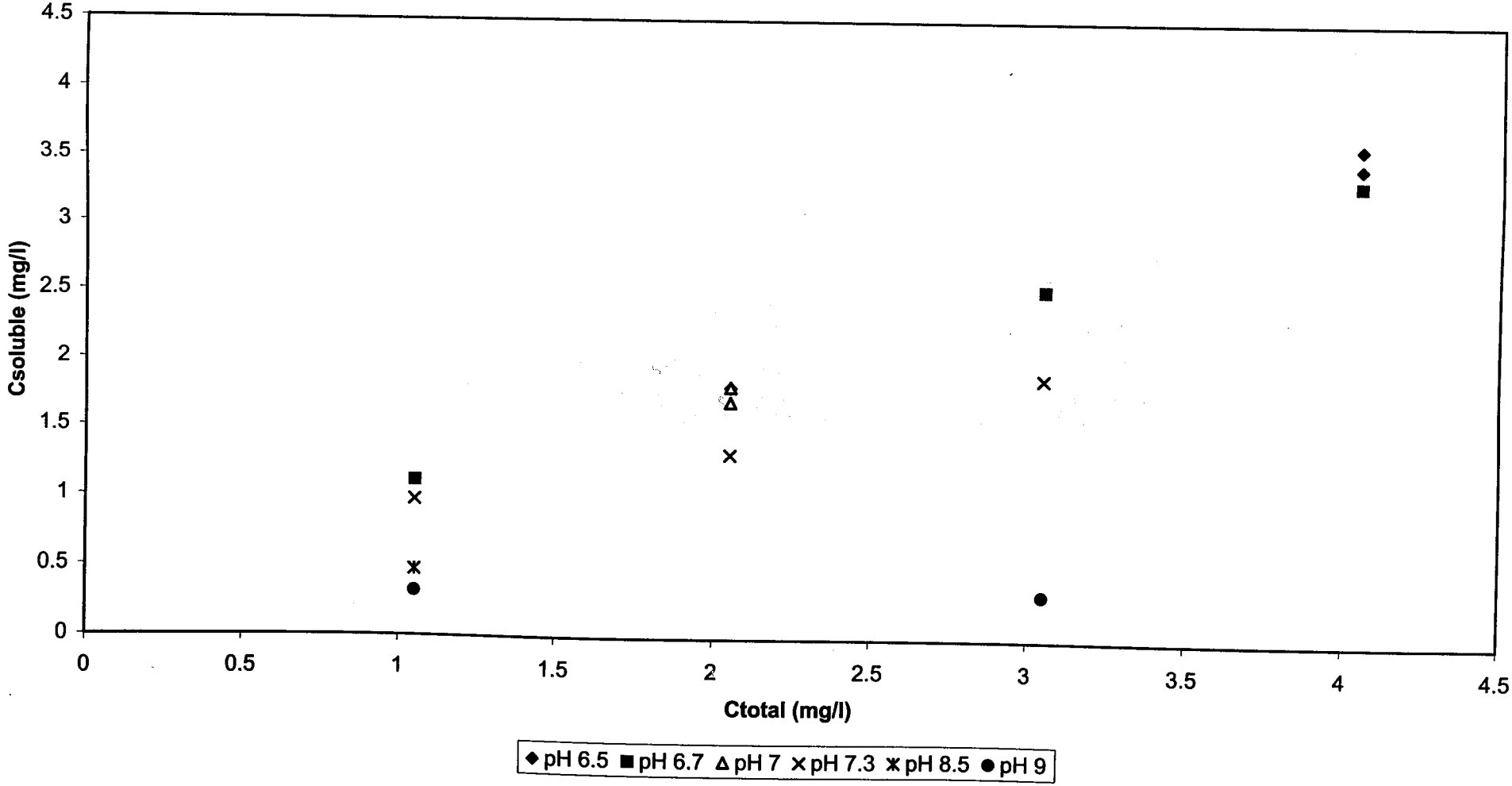


Figure C. 59: ***Zn adsorption in Primary Effluent Solids Concentration B (86 mg/l)***

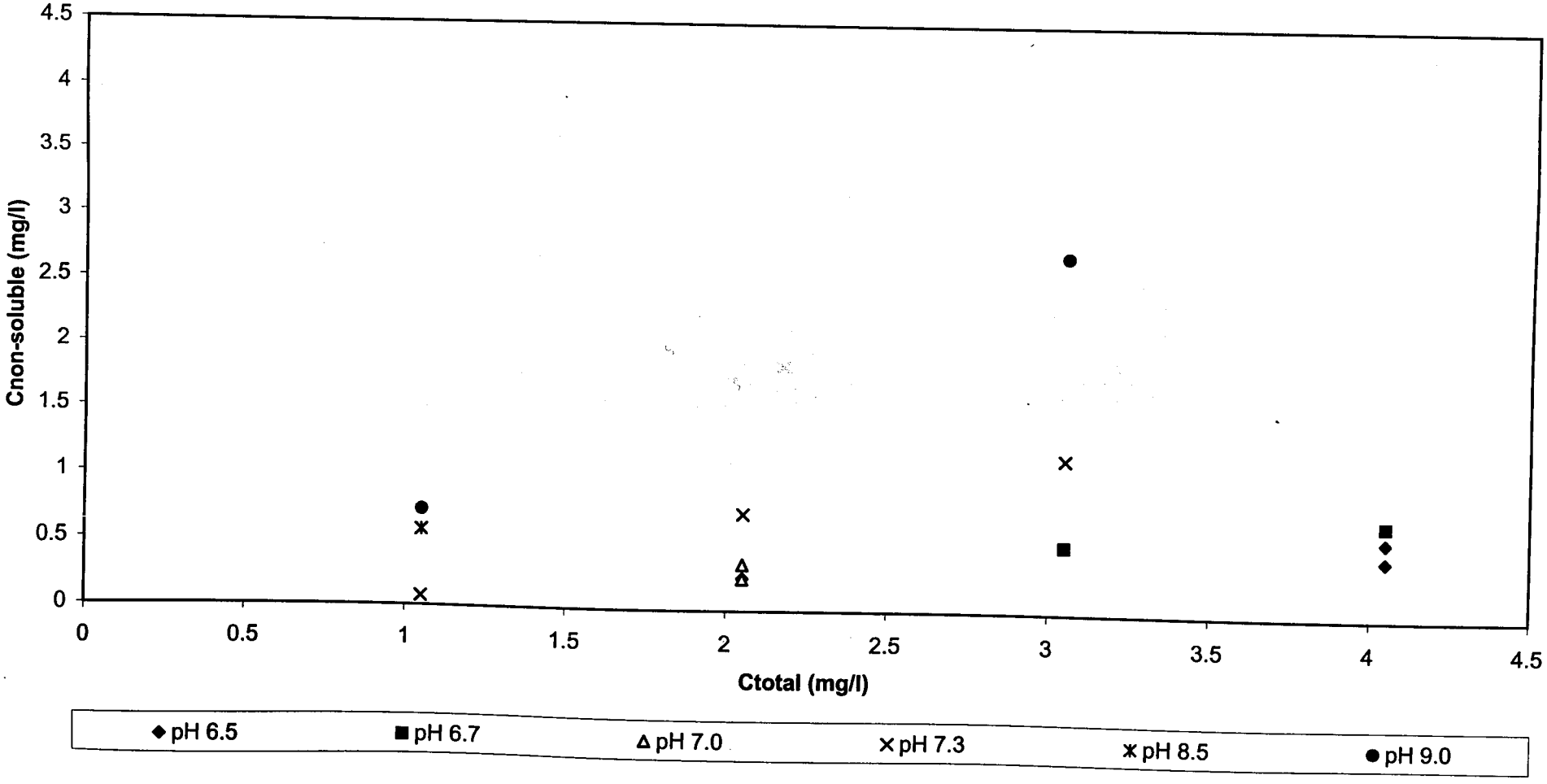


Figure C.60: ***Zn adsorption in Primary Effluent Solids Concentration B (86 mg/l)***

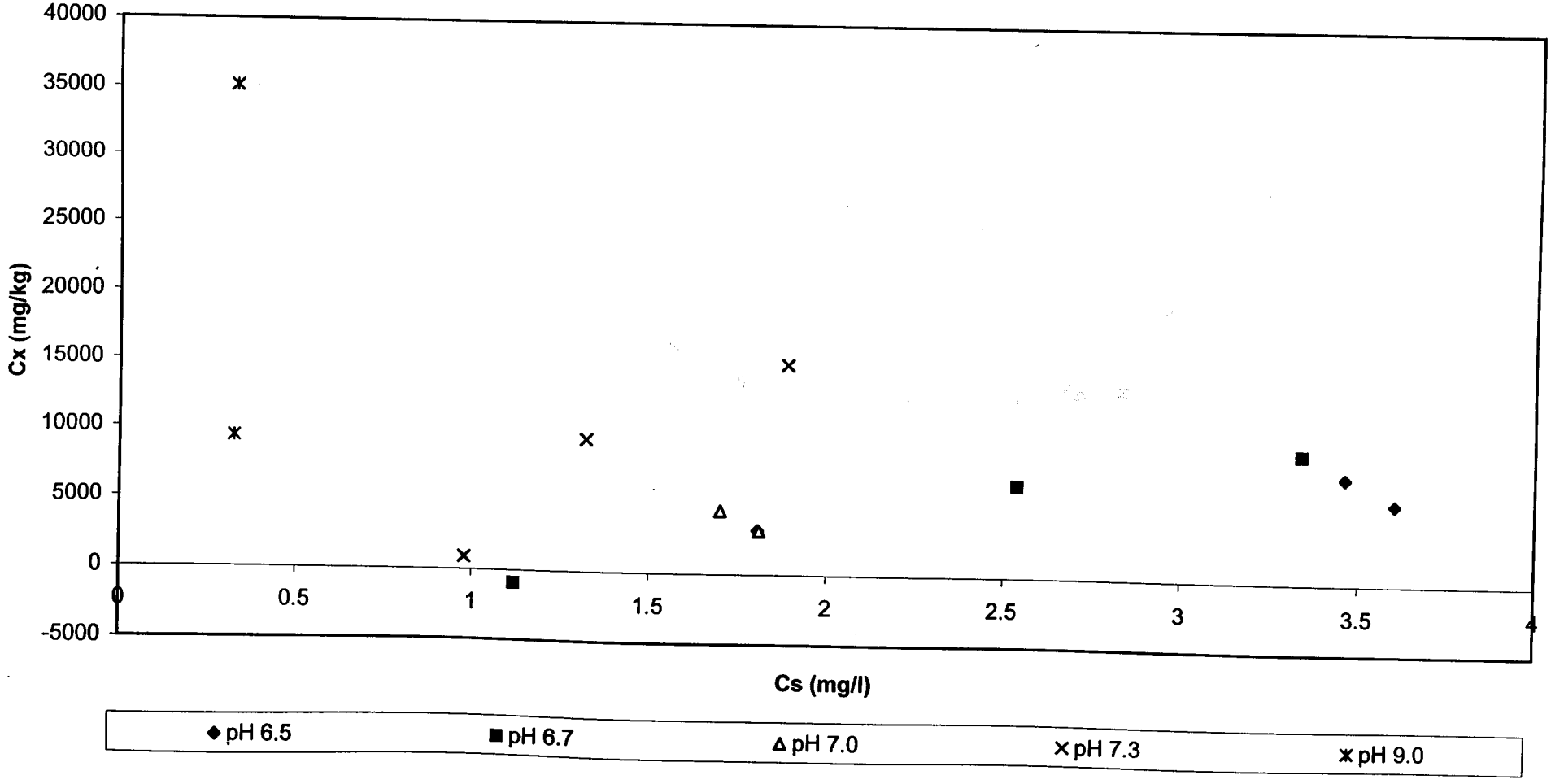


Figure C.61: ***Zn adsorption in Primary Effluent Solids Concentration B (86 mg/l)***

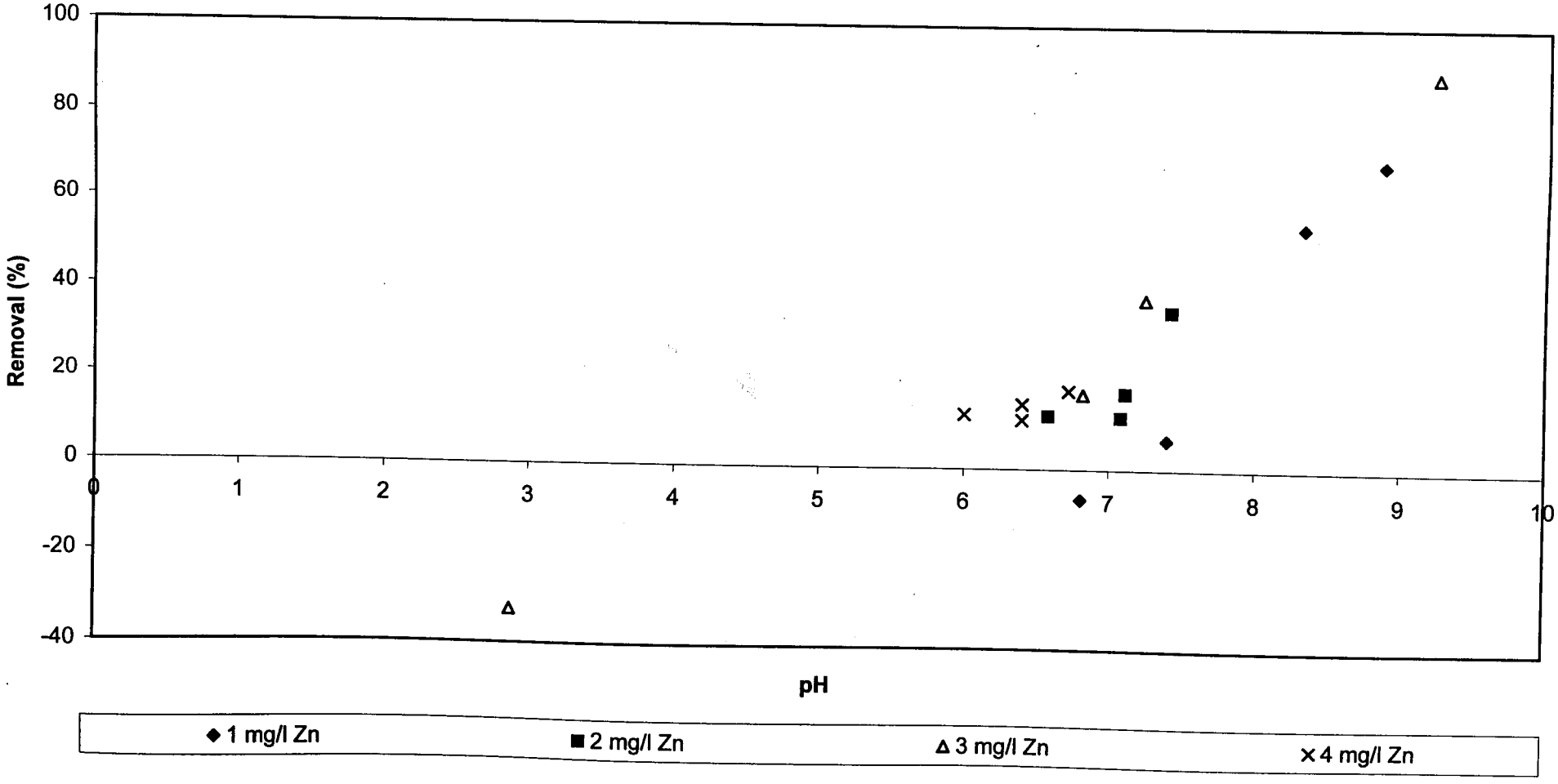


Figure C.62: ***Zn adsorption in Primary Effluent Solids Concentration C (125 mg/l)***

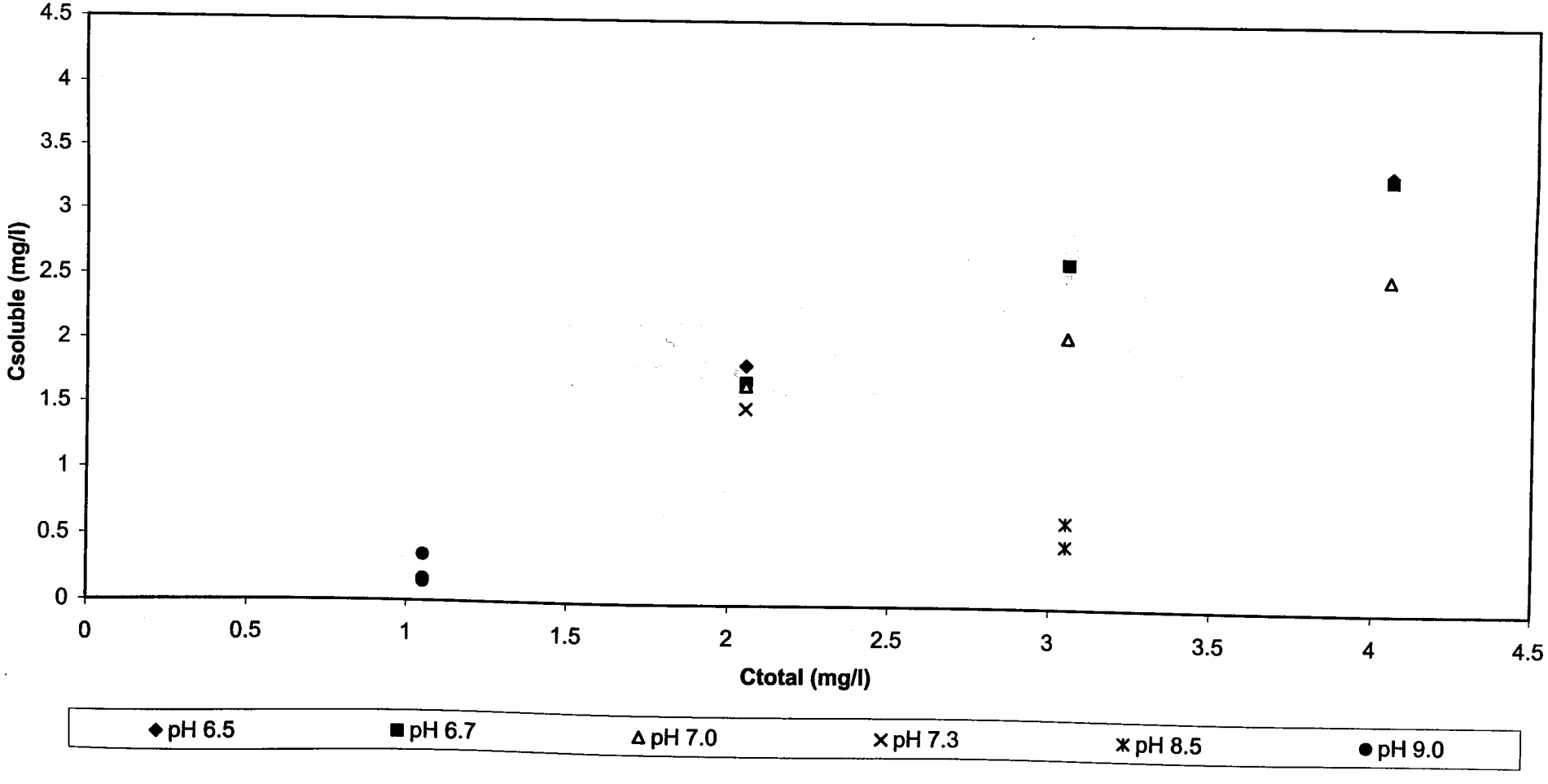


Figure C.63: ***Zn adsorption in Primary Effluent Solids Concentration C (125 mg/l)***

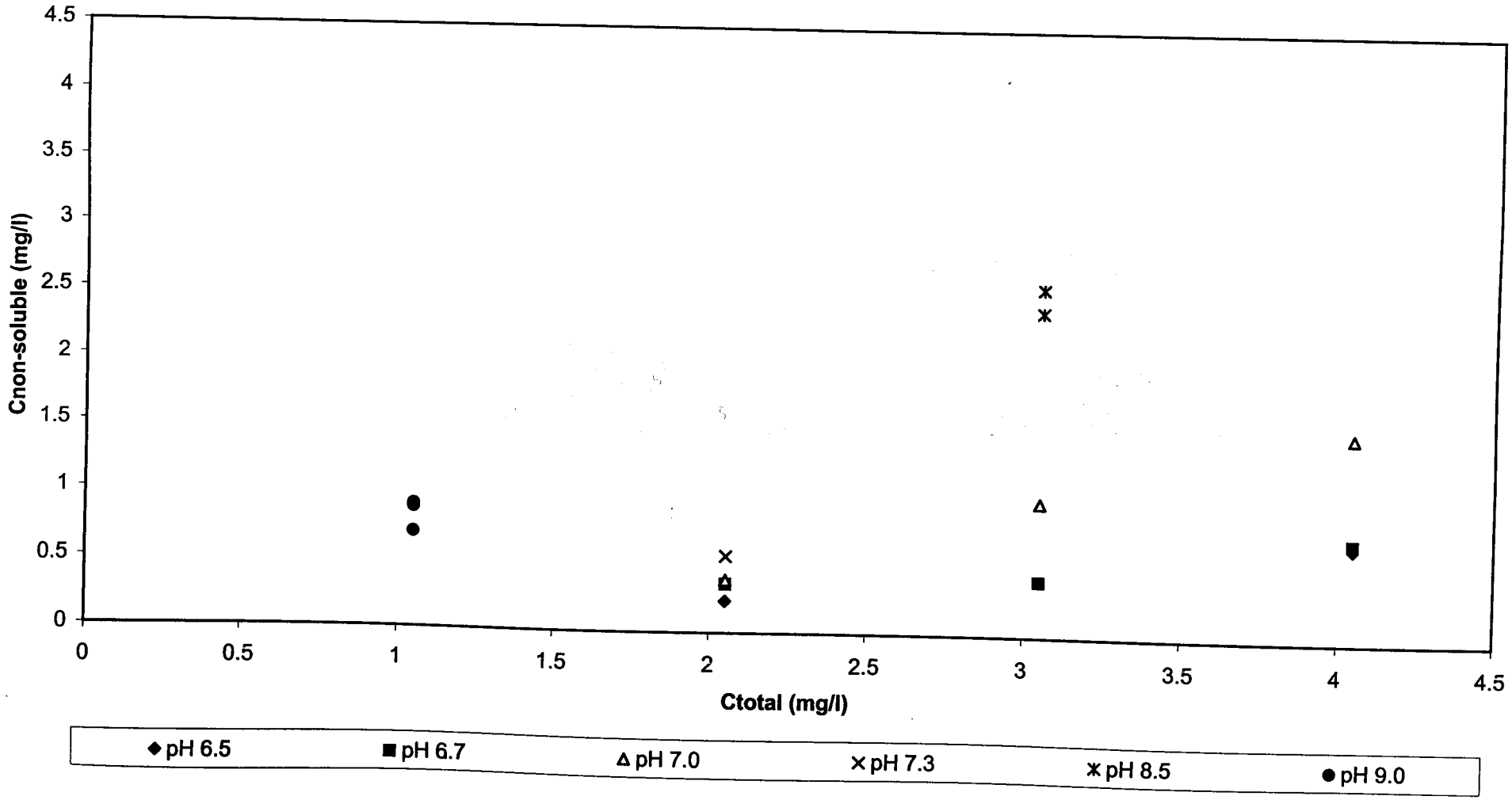


Figure C.64: ***Zn adsorption in Primary Effluent Solids Concentration C (125 mg/l)***

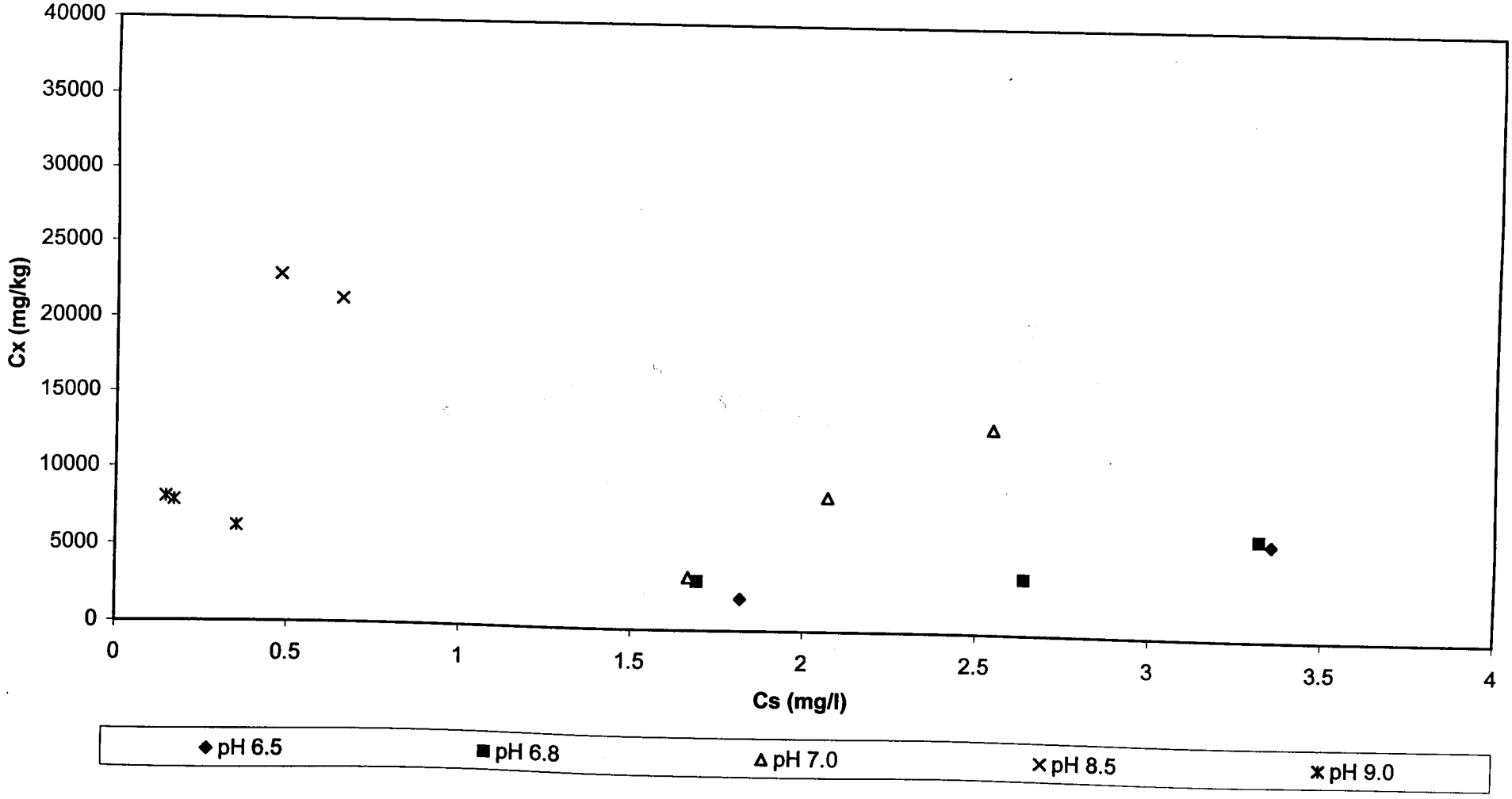


Figure C.65: ***Zn adsorption in Primary Effluent Solids Concentration C (125 mg/l)***

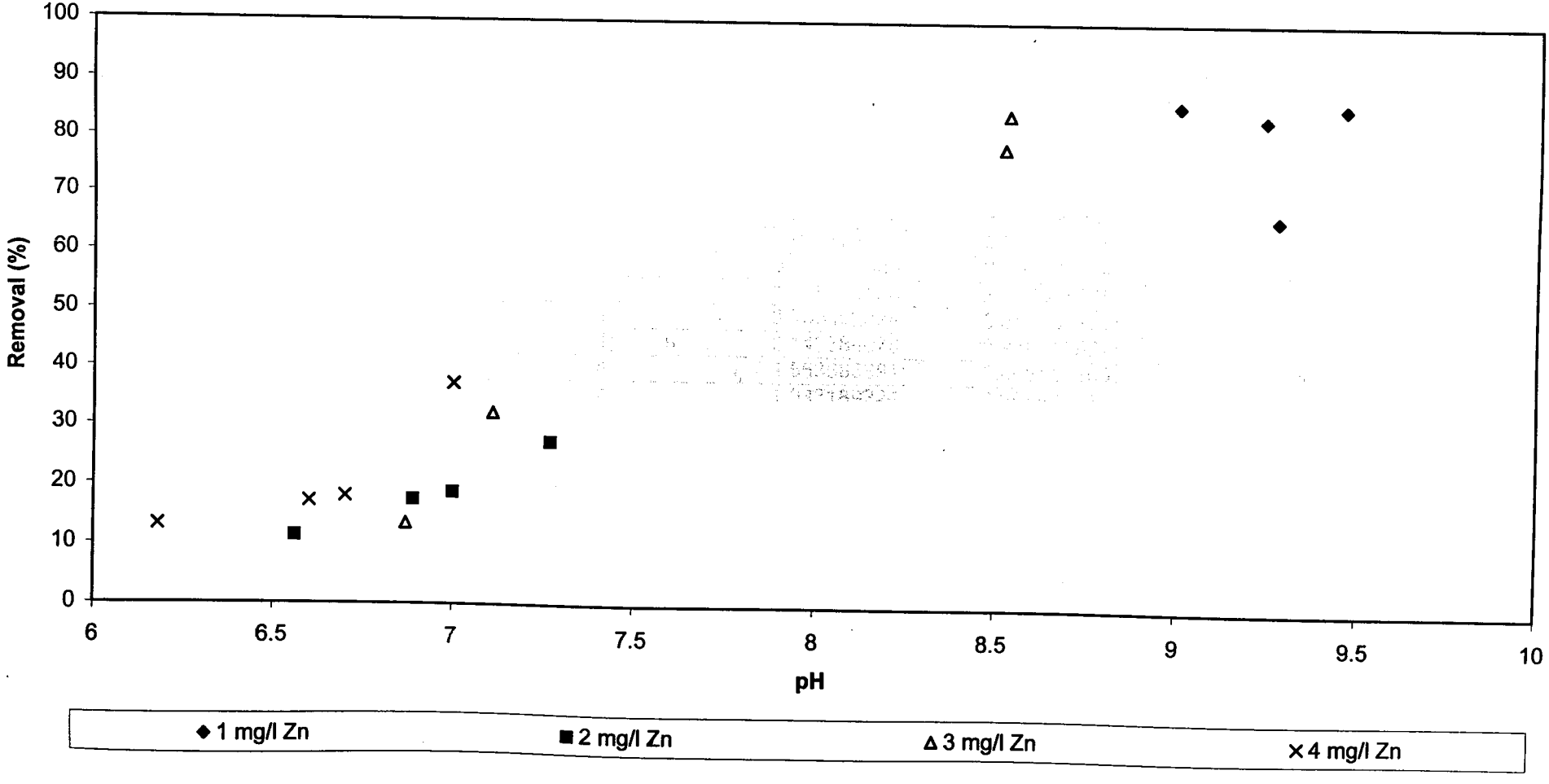


Table C.16 *Zn adsorption in mixed liquor*

Date carried out: 16-Aug-00

Date analysed: 29-Aug-00

Initial Total Zn (mg/l) 0.3621

Actual Sample	TSS (mg/l)	pH	Zn Added (mg/l)	Residual Soluble Zn (mg/l)	Adsorbed Zn (mg/l)	Adsorbed Zn (mg/kg)	Total (mg/l)
A-1-1	1800	6.84	1	0.261848061	1.100251939	679.1678638	1.3621
A-1-2	1800	7.12	1	0.386043684	0.976056316	602.5038986	1.3621
A-1-3	1800	7.3	1	0.398421147	0.963678853	594.8634896	1.3621
A-1-4	1800	7.8	1	0.339816705	1.022283295	631.0390711	1.3621
A-2-1	1800	6.35	2	0.694518372	1.667581628	1029.371375	2.3621
A-2-2	1800	6.68	2	0.520033666	1.842066334	1137.077984	2.3621
A-2-3	1800	6.87	2	0.476858958	1.885241042	1163.729038	2.3621
A-2-4	1800	7.02	2	0.428505988	1.933594012	1193.57655	2.3621
A-3-1	1800	6.14	3	1.290304738	2.071795262	1278.885964	3.3621
A-3-2	1800	6.32	3	1.075823665	2.286276335	1411.281688	3.3621
A-3-3	1800	6.51	3	0.959613486	2.402486514	1483.016367	3.3621
A-3-4	1800	6.59	3	1.108083825	2.254016175	1391.368009	3.3621
A-4-1	1800	5.19	4	3.505402824	0.856697176	528.8254174	4.3621
A-4-2	1800	6.14	4	2.143384076	2.218715924	1369.577731	4.3621
A-4-3	1800	6.51	4	1.553685891	2.808414109	1733.588956	4.3621
A-4-4	1800	7.17	4	1.093189224	3.268910776	2017.846158	4.3621
B-1-1	1058	7.04	1	0.560674184	0.801425816	841.6570218	1.3621
B-1-2	1058	7.35	1	0.304760224	1.057339776	1110.417745	1.3621
B-1-3	1058	7.69	1	0.264568682	1.097531318	1152.626883	1.3621
B-1-4	1058	8.48	1	0.246554344	1.115545656	1171.545532	1.3621
B-2-1	1058	6.44	2	0.977658695	1.384441305	1453.939619	2.3621
B-2-2	1058	6.63	2	0.922661295	1.439438705	1511.697863	2.3621
B-2-3	1058	6.87	2	0.751641103	1.610458897	1691.30319	2.3621
B-2-4	1058	7.4	2	0.498860794	1.863239206	1956.772953	2.3621
B-3-1	1058	6.14	3	1.76652448	1.59557552	1675.672673	3.3621
B-3-2	1058	6.52	3	1.379776966	1.982323034	2081.834734	3.3621
B-3-3	1058	6.64	3	1.237598057	2.124501943	2231.150959	3.3621
B-3-4	1058	6.7	3	1.179825813	2.182274187	2291.823342	3.3621
B-4-1	1058	5.05	4	3.863953037	0.498146963	523.1537108	4.3621
B-4-2	1058	6.1	4	2.806654407	1.555445593	1633.528243	4.3621

B-4-3	1058	6.56	4	2.194139102	2.167960898	2276.791534	4.3621
B-4-4	1058	7.27	4	0.972853348	3.389246652	3559.385268	4.3621
C-1-1	2500	6.87	1	0.212676371	1.149423629	510.8549464	1.3621
C-1-2	2500	7.05	1	0.202628392	1.159471608	515.3207146	1.3621
C-1-3	2500	7.2	1	0.199836741	1.162263259	516.5614484	1.3621
C-1-4	2500	8.25	1	0.280049925	1.082050075	480.9111445	1.3621
C-2-1	2500	6.3	2	0.487761932	1.874338068	833.0391412	2.3621
C-2-2	2500	6.69	2	0.479936494	1.882163506	836.5171137	2.3621
C-2-3	2500	6.73	2	0.408542772	1.953557228	868.2476569	2.3621
C-2-4	2500	6.89	2	0.461863265	1.900236735	844.5496602	2.3621
C-3-1	2500	6.04	3	1.112902342	2.249197658	999.6434037	3.3621
C-3-2	2500	6.42	3	0.855066683	2.507033317	1114.23703	3.3621
C-3-3	2500	6.64	3	0.703056289	2.659043711	1181.797205	3.3621
C-3-4	2500	6.7	3	0.712903369	2.649196631	1177.420725	3.3621
C-4-1	2500	5.47	4	3.141258841	1.220841159	542.5960708	4.3621
C-4-2	2500	6.1	4	1.67813338	2.68396662	1192.874053	4.3621
C-4-3	2500	6.45	4	1.194513665	3.167586335	1407.816149	4.3621
C-4-4	2500	7.2	4	0.767421018	3.594678982	1597.635103	4.3621

Zn adsorption in mixed liquor

Figure C.66: ***Zn adsorption in Mixed Liquor Solids Concentration A (1800 mg/l)***

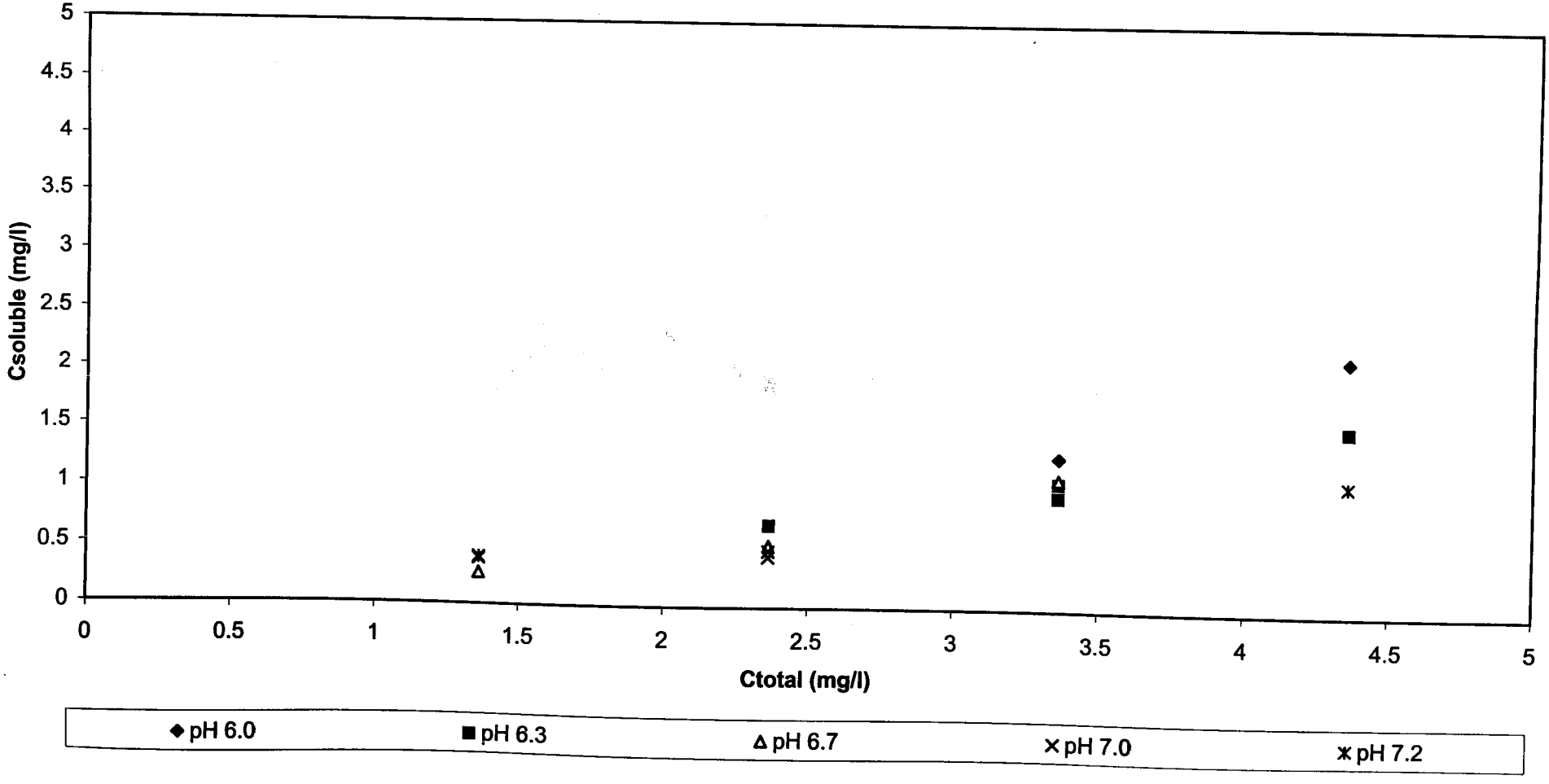


Figure C.67: ***Zn adsorption in Mixed Liquor Solids Concentration A (1800 mg/l)***

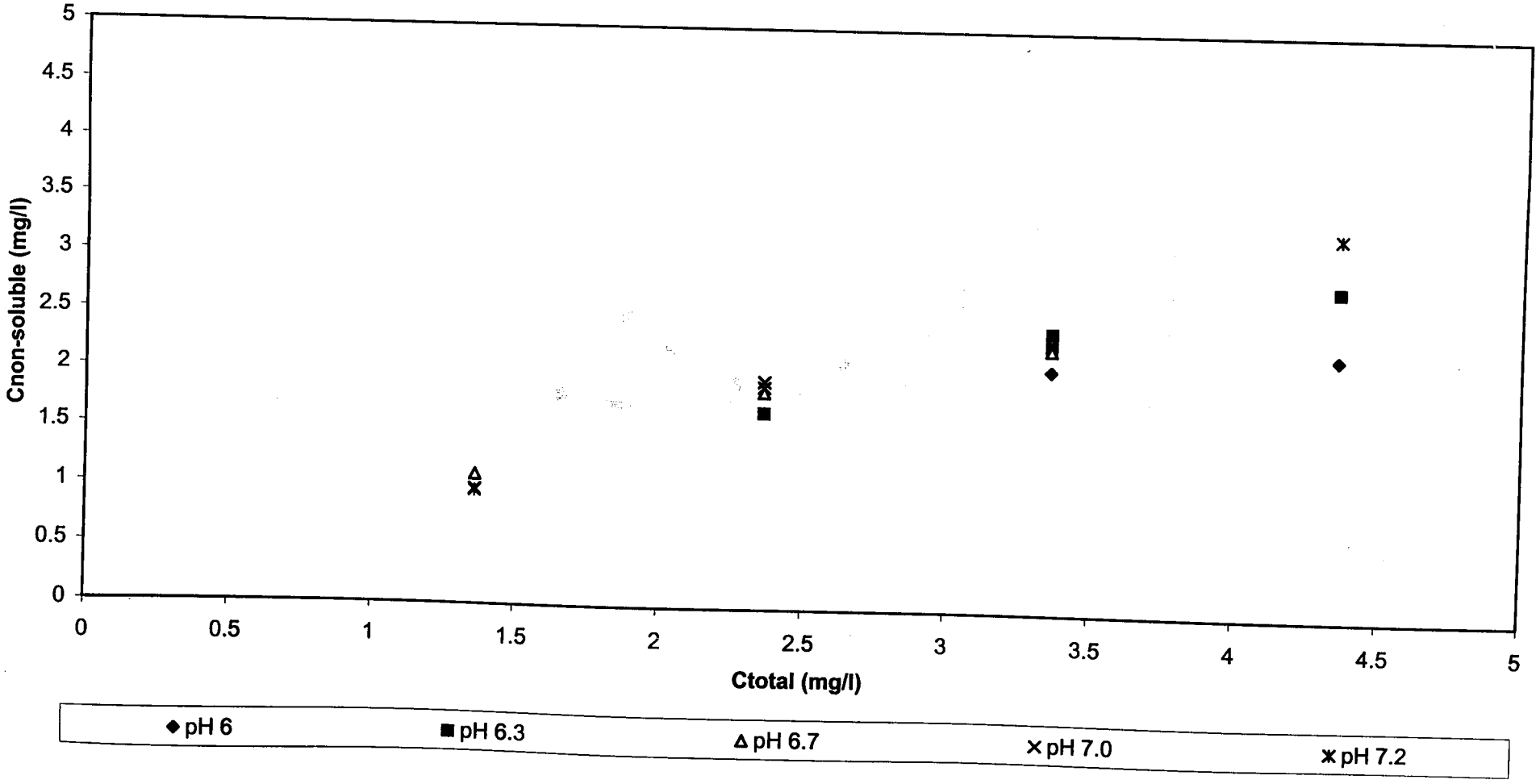


Figure C.68: ***Zn adsorption in Mixed Liquor Solids Concentration A (1800 mg/l)***

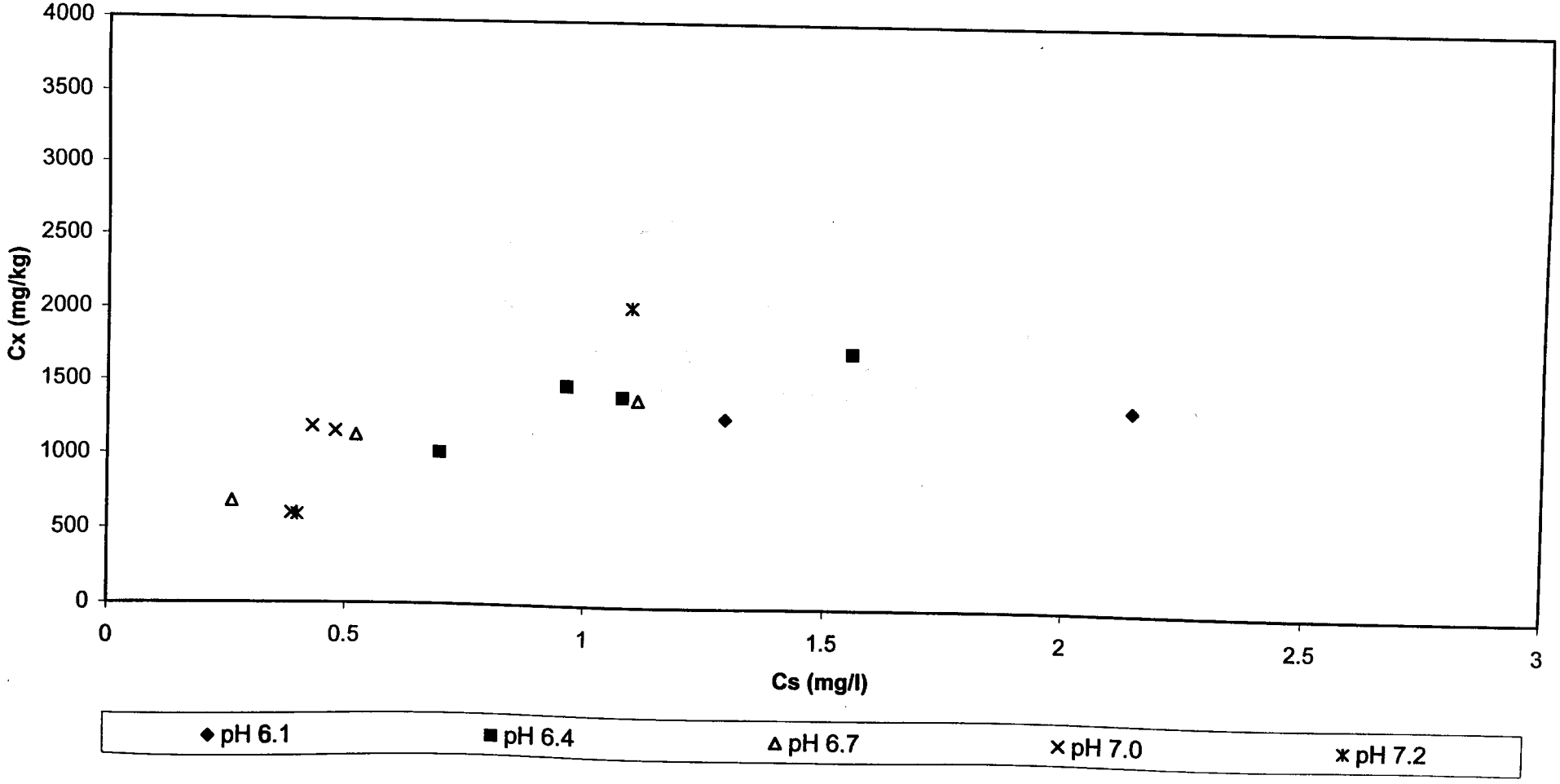


Figure C.69: ***Zn adsorption in Mixed Liquor Solids Concentration A (1800 mg/l)***

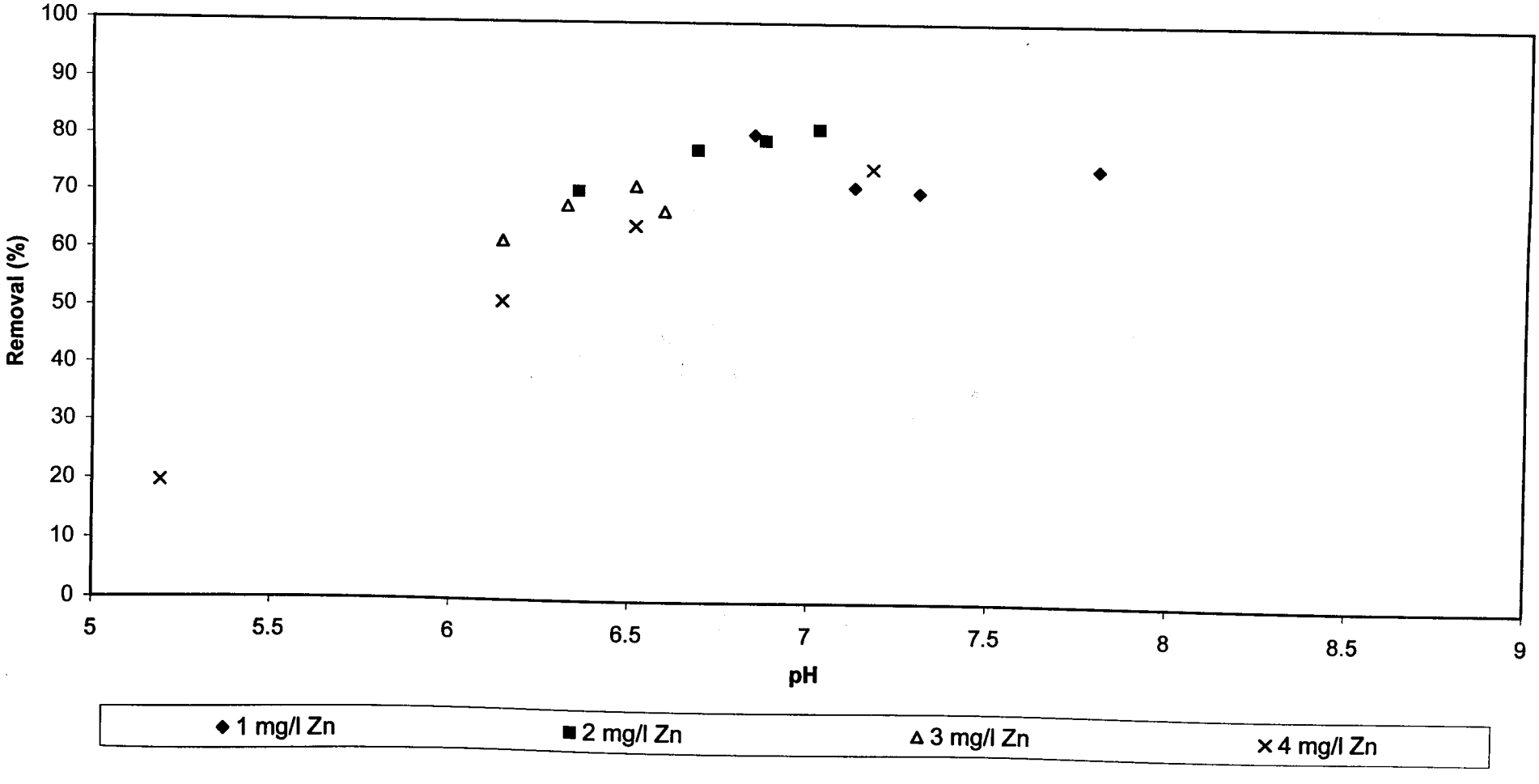


Figure C.70: ***Zn adsorption in Mixed Liquor Solids Concentration B (1058 mg/l)***

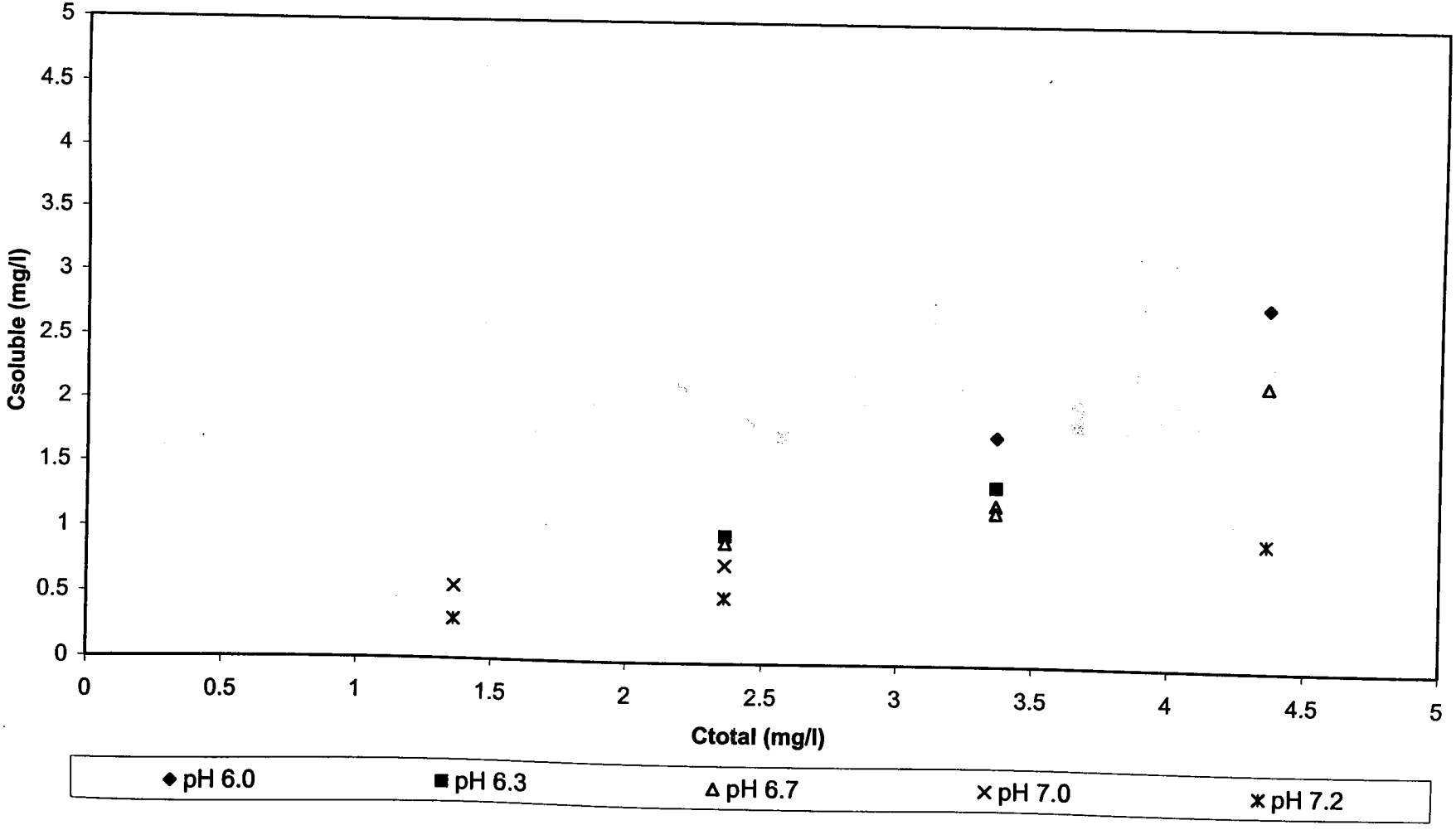


Figure C.71: ***Zn adsorption in Mixed Liquor Solids Concentration B (1058 mg/l)***

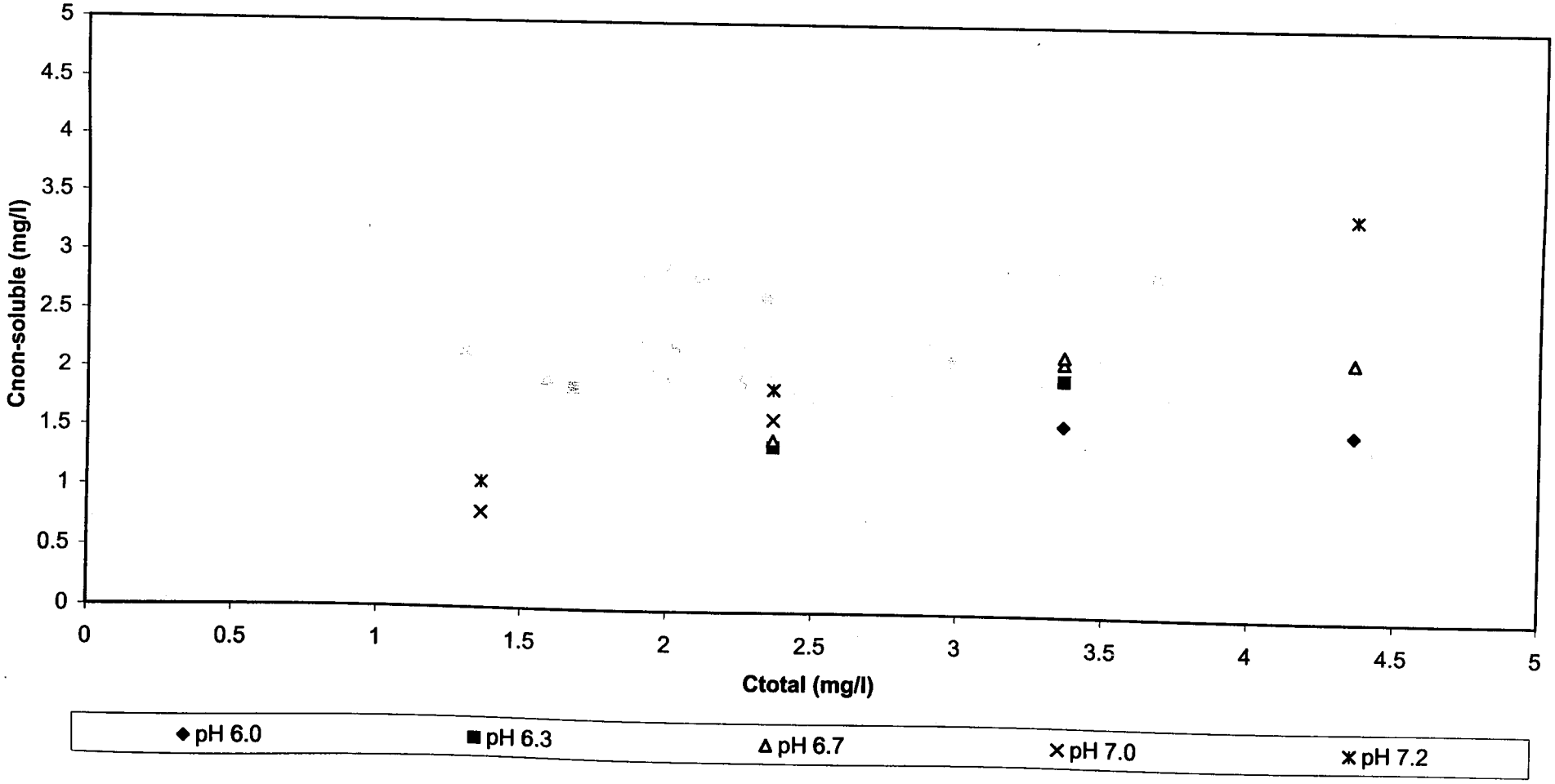


Figure C.72: ***Zn adsorption in Mixed Liquor Solids Concentration B (1058 mg/l)***

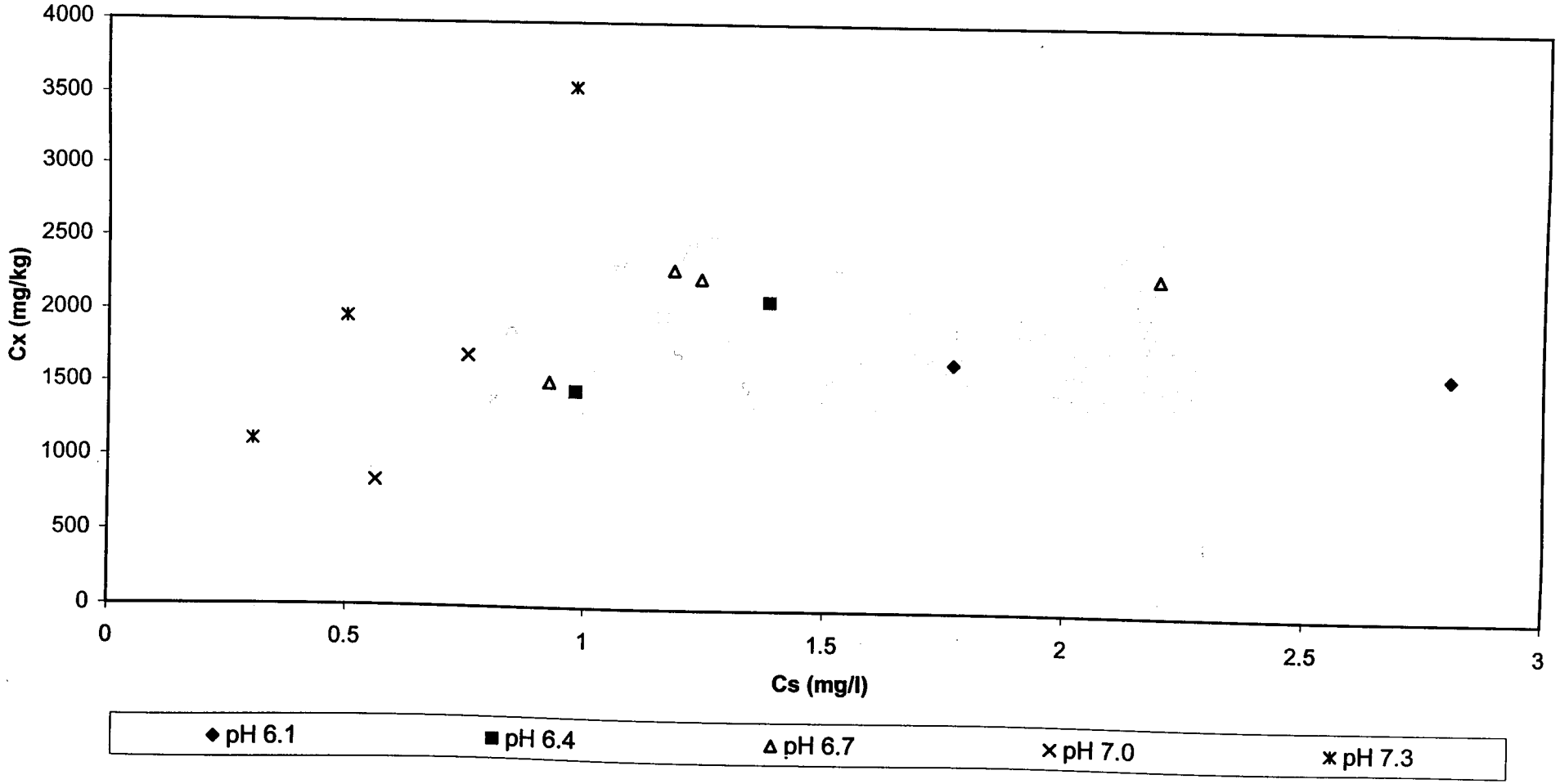


Figure C.73: ***Zn adsorption in Mixed Liquor Solids Concentration B (1058 mg/l)***

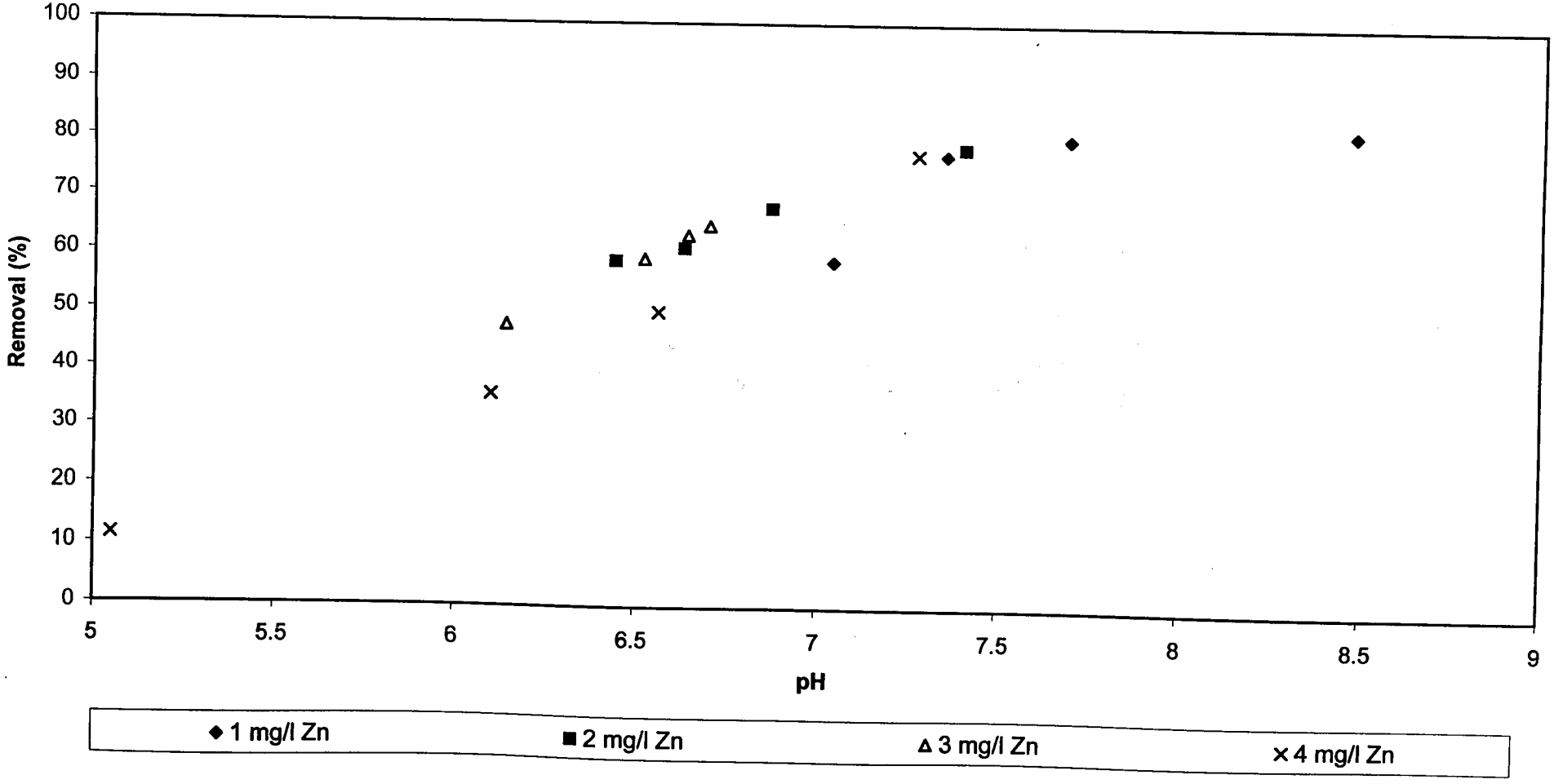


Figure C.74: ***Zn adsorption in Mixed Liquor Solids Concentration C (2500 mg/l)***

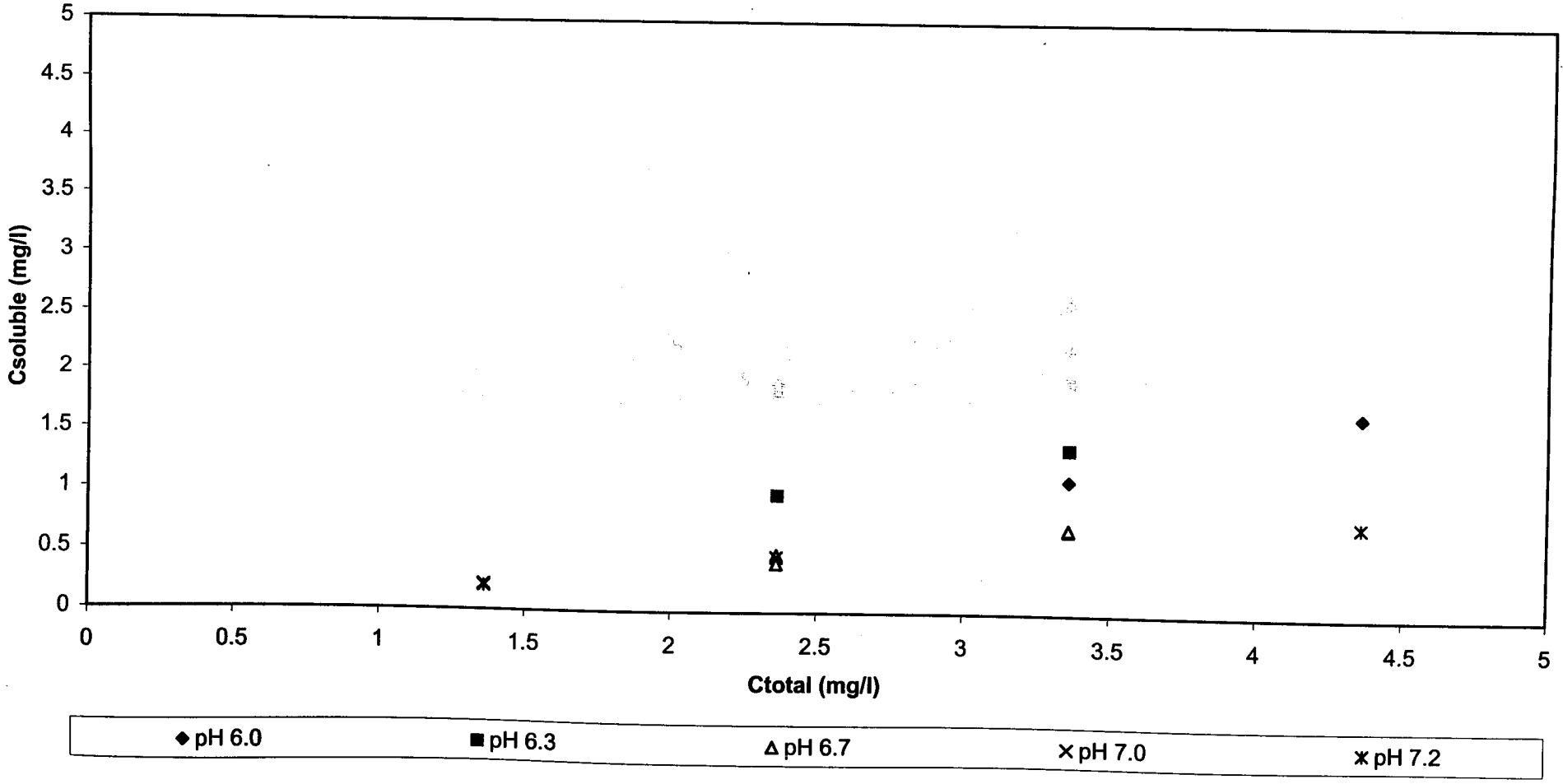


Figure C.75: ***Zn adsorption in Mixed Liquor Solids Concentration C (2500 mg/l)***

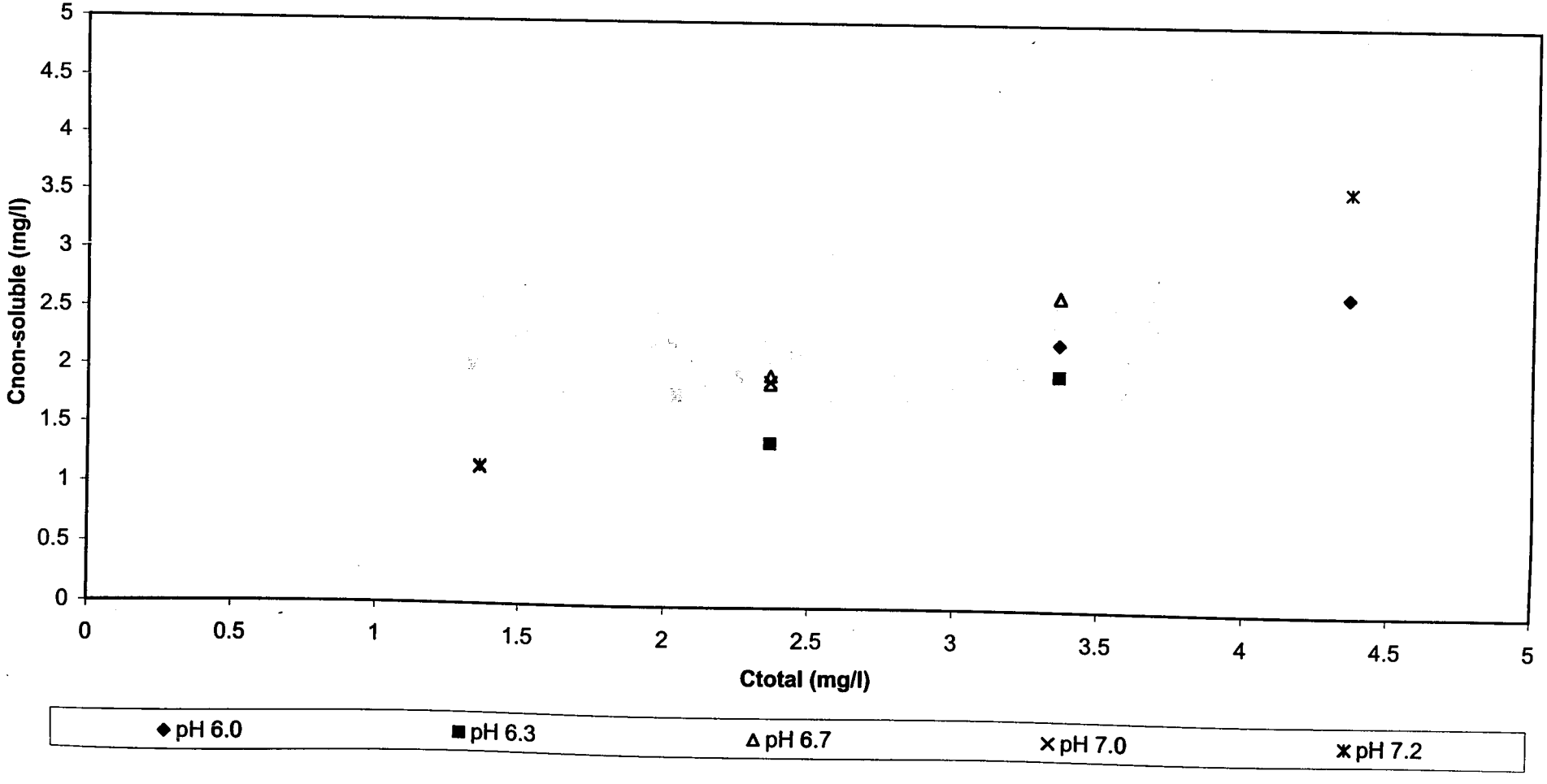


Figure C.76: ***Zn adsorption in Mixed Liquor Solids Concentration C (2500 mg/l)***

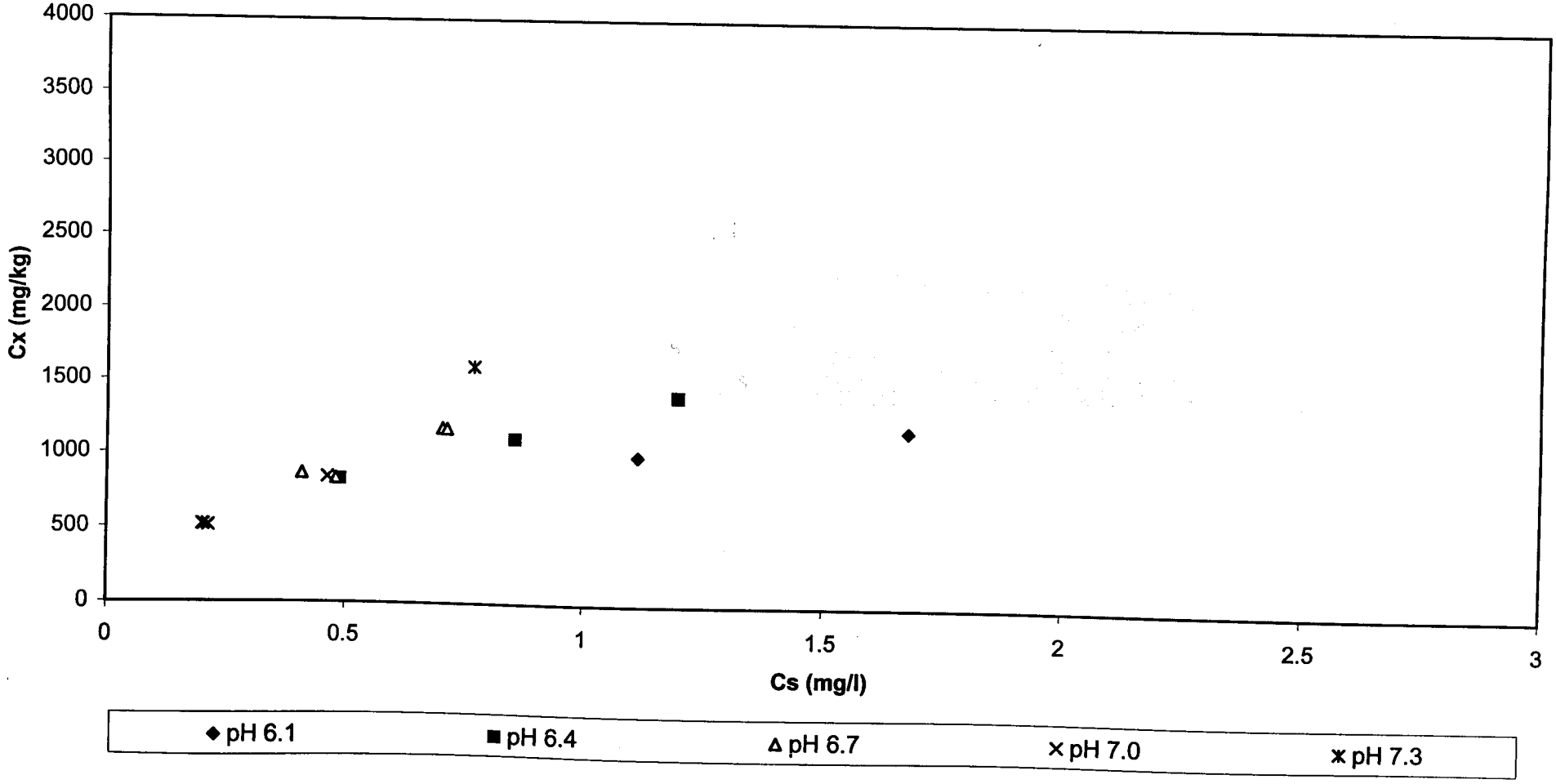


Figure C.77: ***Zn adsorption in Mixed Liquor Solids Concentration C (2500 mg/l)***

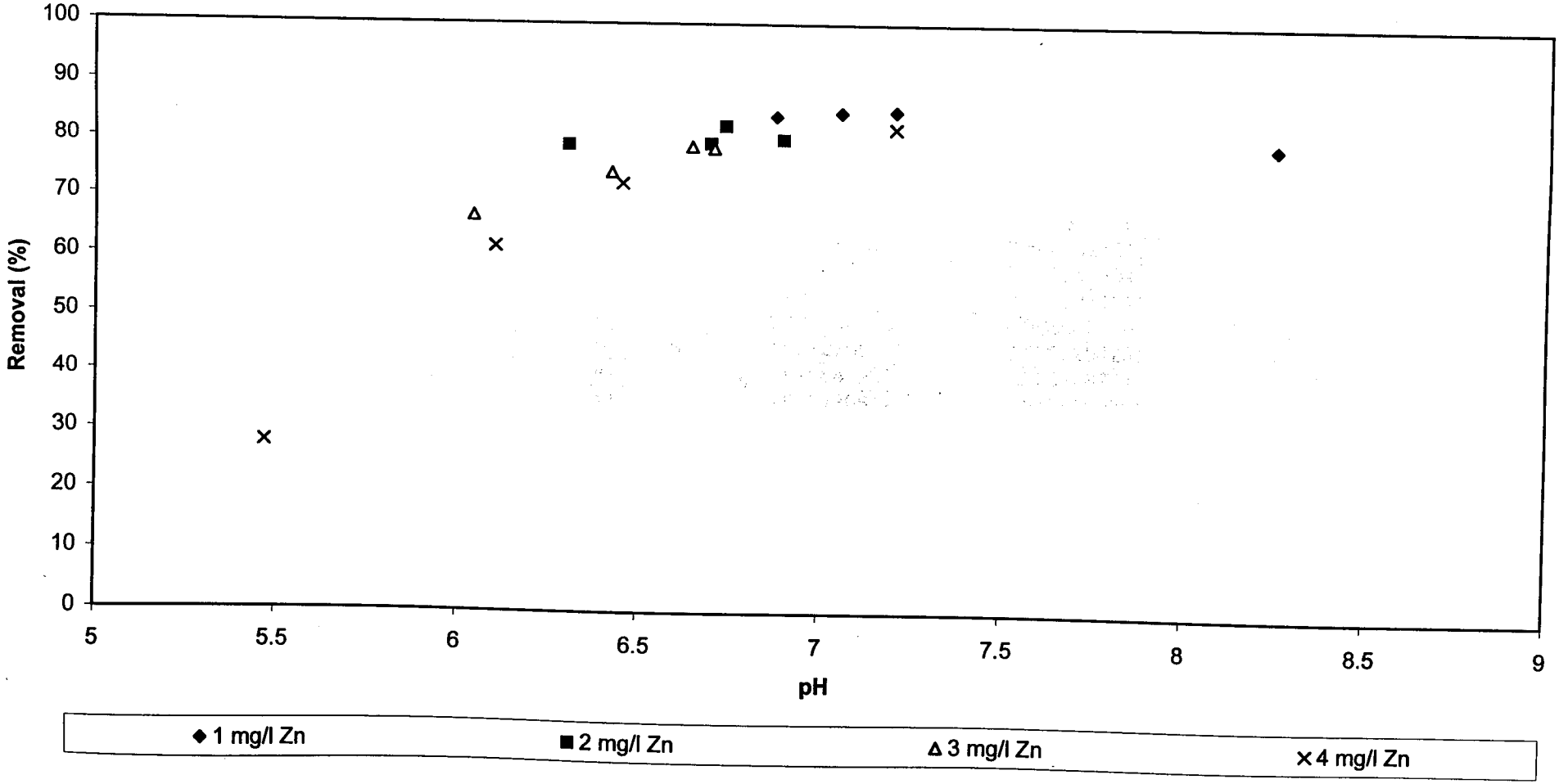


Table C.17 *Zn adsorption in final effluent*

Date carried out: 22-Aug-00

Date analysed: 31-Aug-00

Initial Total Zn (mg/l) 0.04

Actual Sample	TSS (mg/l)	pH	Zn Added (mg/l)	Residual Soluble Zn (mg/l)	Total adsorbed (mg/l)	Adsorbed (mg/kg)	Total metal (mg/l)
A-1-1	32	6.54	1	1.006081941	0.033918059	1177.710377	1.04
A-1-2	32	7	1	0.859718439	0.180281561	6259.776438	1.04
A-1-3	32	7.05	1	0.927406514	0.112593486	3909.496052	1.04
A-1-4	32	8.4	1	0.149001013	0.890998987	30937.46481	1.04
A-2-1	32	6	2	2.03311069	0.00688931	239.2121379	2.04
A-2-2	32	6.2	2	0.526438529	1.513561471	52554.21775	2.04
A-2-3	32	6.32	2	1.844495045	0.195504955	6788.366507	2.04
A-2-4	32	6.5	2	1.743901301	0.296098699	10281.20484	2.04
A-3-1	32	5.5	3	2.784413781	0.255586219	8874.521491	3.04
A-3-2	32	6.05	3	2.491247879	0.548752121	19053.89308	3.04
A-3-3	32	6.5	3	2.484058596	0.555941404	19303.52098	3.04
A-3-4	32	6.46	3	2.469278819	0.570721181	19816.70769	3.04
A-4-1	32	3.74	4	4.136560166	-0.096560166	-3352.783552	4.04
A-4-2	32	5.9	4	3.933270571	0.106729429	3705.88296	4.04
A-4-3	32	5.94	4	3.75841209	0.28158791	9777.357974	4.04
A-4-4	32	6.22	4	3.692130612	0.347869388	12078.79819	4.04
B-1-1	31	8.05	1	0.265554993	0.774445007	27757.88556	1.04
B-1-2	31	6.87	1	0.943450294	0.096549706	3460.562926	1.04
B-1-3	31	8.23	1	0.440768592	0.599231408	21477.82825	1.04
B-1-4	31	6.6	1	0.966957349	0.073042651	2618.016162	1.04
B-2-1	31	5.9	2	1.900216587	0.139783413	5010.158173	2.04
B-2-2	31	6.29	2	1.801878326	0.238121674	8534.827032	2.04
B-2-3	31	6.28	2	1.745272467	0.294727533	10563.71088	2.04
B-2-4	31	6.05	2	1.803712076	0.236287924	8469.101203	2.04
B-3-1	31	3.15	3	3.157227848	-0.117227848	-4201.714967	3.04
B-3-2	31	5.73	3	2.816804978	0.223195022	7999.821565	3.04
B-3-3	31	6.3	3	2.564424513	0.475575487	17045.71639	3.04
B-3-4	31	6.44	3	2.652149201	0.387850799	13901.46232	3.04
B-4-1	31	3.35	4	4.147102998	-0.107102998	-3838.81715	4.04
B-4-2	31	4.5	4	3.924540006	0.115459994	4138.351037	4.04
B-4-3	31	5.11	4	3.961954871	0.078045129	2797.316454	4.04
B-4-4	31	5.74	4	3.615073831	0.424926169	15230.32863	4.04

Figure C.78: ***Zn adsorption in Final Effluent Solids Concentration (31 mg/l)***

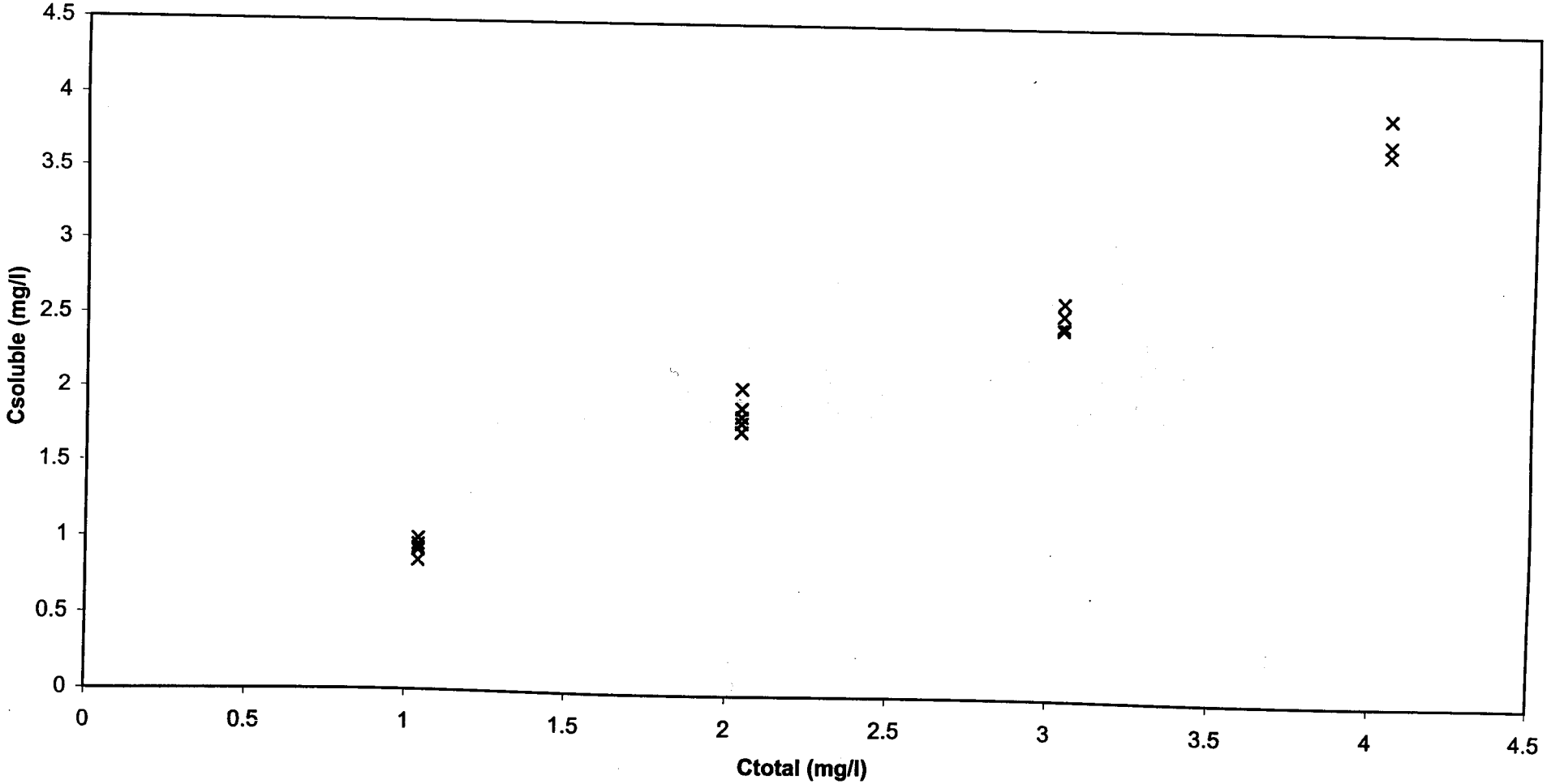


Figure C.79: ***Zn adsorption in Final Effluent Solids Concentration (31 mg/l)***

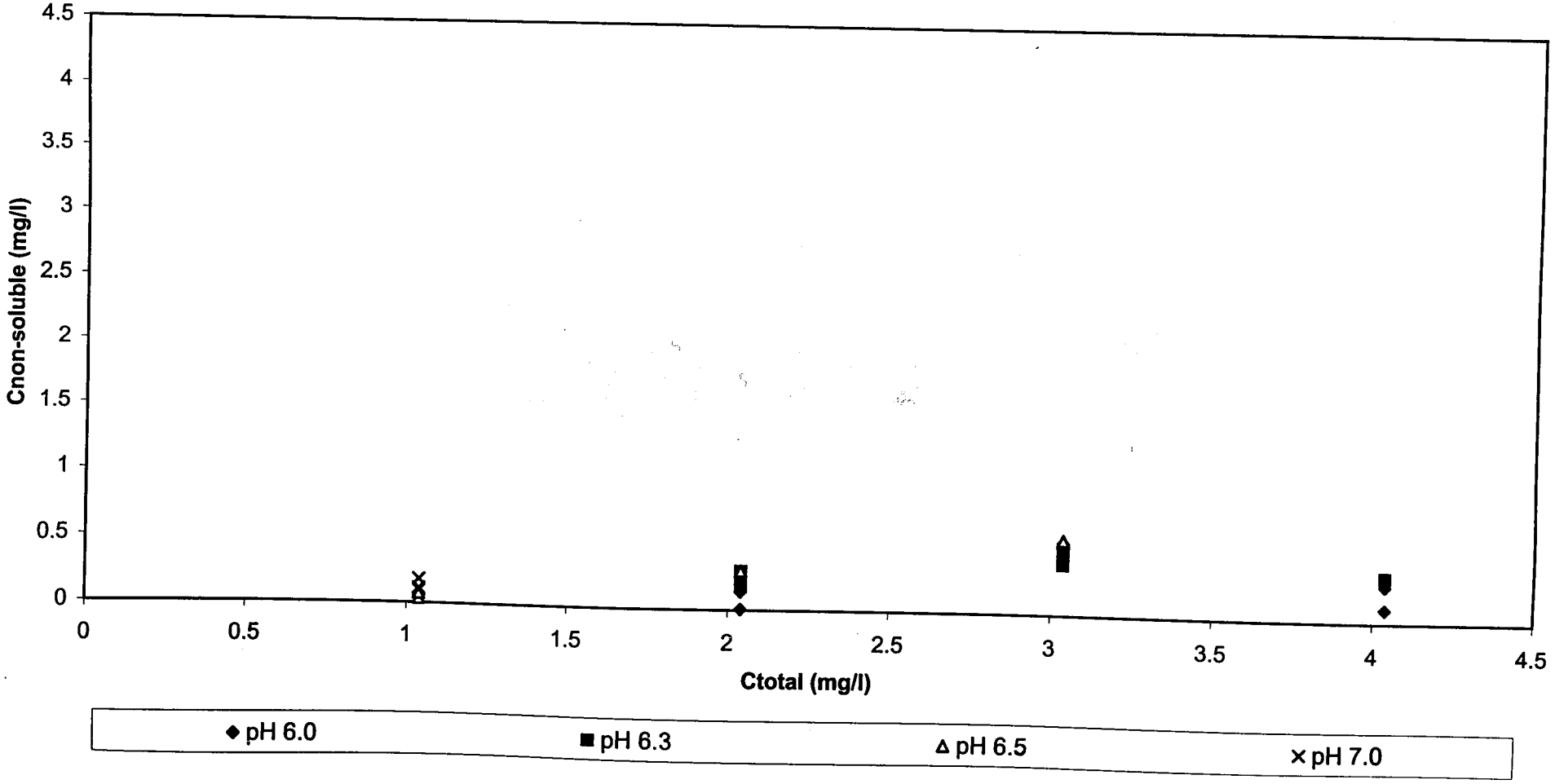


Figure C.80: ***Zn adsorption in Final Effluent Solids Concentration (31 mg/l)***

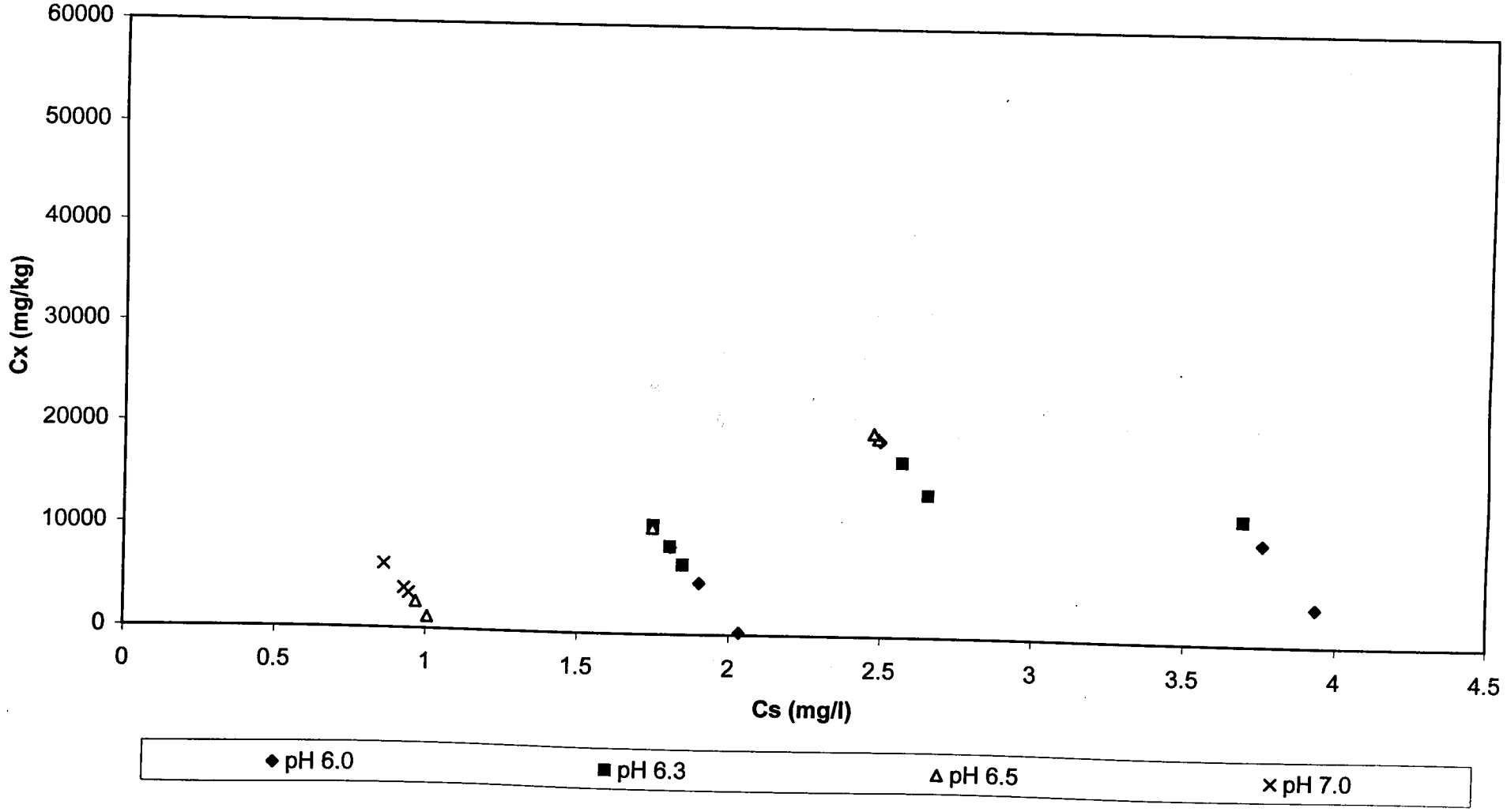


Figure C.81: ***Zn adsorption in Final Effluent Solids Concentration (31 mg/l)***

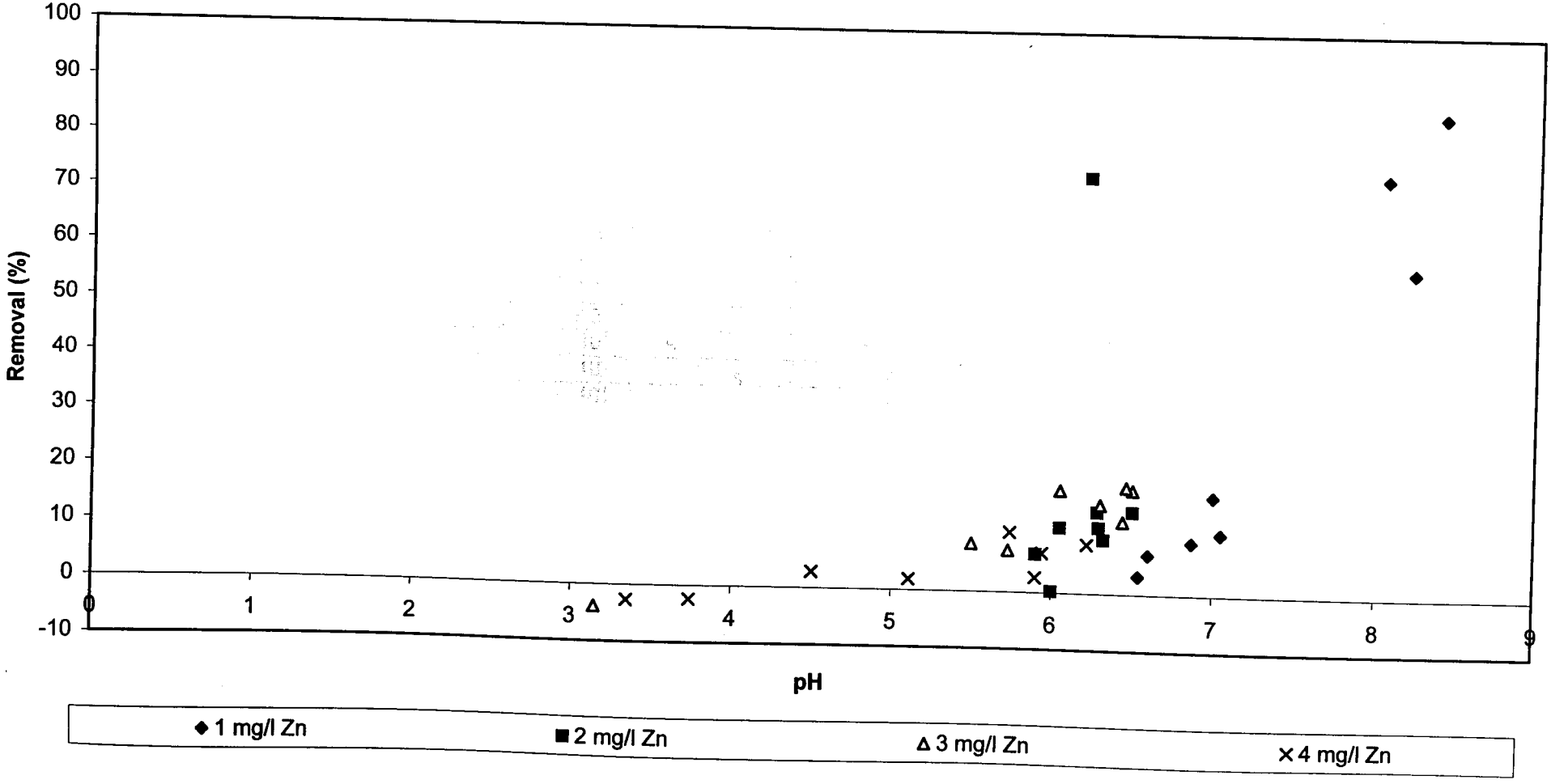


Table C.18 *Competition Adsorption Experiments Raw Sewage*

Date Carried out 29-Aug-00

Date analysed: 07-Sep-00

Initial Total Cu (mg/l) 0.1915

Initial Total Zn (mg/l) 0.1565

Actual Sample	TSS (mg/l)	pH	Cu Added (mg/l)	Residual Soluble Cu (mg/l)	Adsorbed Cu (mg/l)	Adsorbed Cu (mg/kg)	Total Cu (mg/l)
A-1-1	474	6.4	2.5	1.89	0.8015	1878.809189	2.6915
A-1-2	474	6.95	2.5	2.032	0.6595	1545.944679	2.6915
A-1-3	474	7.21	2.5	1.869	0.8225	1928.035631	2.6915
A-1-4	474	7.9	2.5	2.134	0.5575	1306.84482	2.6915
A-2-1	474	6.75	5	3.979	1.2125	2842.240975	5.1915
A-2-2	474	6.71	5	4.055	1.1365	2664.088139	5.1915
A-2-3	474	7.22	5	4.298	0.8935	2094.467886	5.1915
A-2-4	474	8.02	5	4.332	0.8595	2014.767932	5.1915
A-3-1	474	6.67	7.5	6.482	1.2095	2835.208626	7.6915
A-3-2	474	6.98	7.5	6.525	1.1665	2734.411627	7.6915
A-3-3	474	7.4	7.5	6.371	1.3205	3095.405532	7.6915
A-3-4	474	8.24	7.5	6.573	1.1185	2621.894046	7.6915
A-4-1	474	6.42	10	8.132	2.0595	4827.707454	10.1915
A-4-2	474	6.71	10	8.317	1.8745	4394.045945	10.1915
A-4-3	474	7.05	10	8.177	2.0145	4722.222222	10.1915
A-4-4	474	7.66	10	8.483	1.7085	4004.922644	10.1915
B-1-1	322	6.98	2.5	2.108	0.5835	2013.457557	2.6915
B-1-2	322	7.53	2.5	2.135	0.5565	1920.289855	2.6915
B-1-3	322	8.05	2.5	2.139	0.5525	1906.487233	2.6915
B-1-4	322	8.82	2.5	2.155	0.5365	1851.276743	2.6915
B-2-1	322	6.82	5	4.577	0.6145	2120.427881	5.1915
B-2-2	322	7.32	5	4.596	0.5955	2054.865424	5.1915
B-2-3	322	8.07	5	4.534	0.6575	2268.806073	5.1915
B-2-4	322	8.42	5	4.662	0.5295	1827.122153	5.1915
B-3-1	322	6.61	7.5	6.625	1.0665	3680.124224	7.6915
B-3-2	322	7.24	7.5	6.705	0.9865	3404.071774	7.6915
B-3-3	322	8.28	7.5	6.768	0.9235	3186.680469	7.6915
B-3-4	322	8.93	7.5	6.764	0.9275	3200.483092	7.6915
B-4-1	322	6.52	10	8.705	1.4865	5129.399586	10.1915

Cu and Zn competitive adsorption in raw sewage

Actual Sample	TSS (mg/l)	pH	Cu Added (mg/l)	Residual Soluble Cu (mg/l)	Adsorbed Cu (mg/l)	Adsorbed Cu (mg/kg)	Total Cu (mg/l)
B-4-2	322	7	10	8.552	1.6395	5657.349896	10.1915
B-4-3	322	7.72	10	8.763	1.4285	4929.26156	10.1915
B-4-4	322	8.65	10	9.045	1.1465	3956.176674	10.1915
C-1-1	668	7.22	2.5	1.947	0.7445	1238.35662	2.6915
C-1-2	668	7.64	2.5	2.016	0.6755	1123.586161	2.6915
C-1-3	668	8.06	2.5	1.994	0.6975	1160.179641	2.6915
C-1-4	668	8.82	2.5	1.987	0.7045	1171.823021	2.6915
C-2-1	668	6.97	5	4.35	0.8415	1399.700599	5.1915
C-2-2	668	7.2	5	4.402	0.7895	1313.206919	5.1915
C-2-3	668	8.17	5	4.534	0.6575	1093.646041	5.1915
C-2-4	668	8.83	5	4.348	0.8435	1403.027279	5.1915
C-3-1	668	6.8	7.5	6.226	1.4655	2437.62475	7.6915
C-3-2	668	7.27	7.5	6.23	1.4615	2430.971391	7.6915
C-3-3	668	8.23	7.5	6.651	1.0405	1730.705256	7.6915
C-3-4	668	8.73	7.5	6.635	1.0565	1757.318696	7.6915
C-4-1	668	6.48	10	7.769	2.4225	4029.441118	10.1915
C-4-2	668	7.05	10	8.214	1.9775	3289.254824	10.1915
C-4-3	668	7.49	10	8.117	2.0745	3450.598802	10.1915
C-4-4	668	8.65	10	8.682	1.5095	2510.81171	10.1915

Cu and Zn competitive adsorption in raw sewage

Zn Added (mg/l)	Residual Soluble Zn (mg/l)	Adsorbed Zn (mg/l)	Adsorbed Zn (mg/kg)	Total Zn (mg/l)
1	0.475	0.6815	1597.515237	1.1565
1	0.437	0.7195	1686.591655	1.1565
1	0.285	0.8715	2042.897328	1.1565
1	0.277	0.8795	2061.650258	1.1565
2	0.949	1.2075	2830.520394	2.1565
2	1.018	1.1385	2668.776371	2.1565
2	0.855	1.3015	3050.867323	2.1565
2	0.358	1.7985	4215.893108	2.1565
3	2.12	1.0365	2429.676512	3.1565
3	1.768	1.3885	3254.805438	3.1565
3	0.875	2.2815	5348.101266	3.1565
3	0.243	2.9135	6829.582747	3.1565
4	2.839	1.3175	3088.373183	4.1565
4	2.554	1.6025	3756.44632	4.1565
4	1.575	2.5815	6051.336146	4.1565
4	0.492	3.6645	8590.014065	4.1565
1	0.444	0.7125	2458.592133	1.1565
1	0.369	0.7875	2717.391304	1.1565
1	0.289	0.8675	2993.443754	1.1565
1	0.182	0.9745	3362.663906	1.1565
2	1.332	0.8245	2845.065562	2.1565
2	0.932	1.2245	4225.327812	2.1565
2	0.395	1.7615	6078.329883	2.1565
2	0.337	1.8195	6278.467909	2.1565
3	2.187	0.9695	3345.410628	3.1565
3	1.305	1.8515	6388.888889	3.1565
3	0.332	2.8245	9746.376812	3.1565
3	0.191	2.9655	10232.91925	3.1565
4	3.064	1.0725	3700.828157	4.1565

Cu and Zn competitive adsorption in raw sewage

Zn Added (mg/l)	Residual Soluble Zn (mg/l)	Adsorbed Zn (mg/l)	Adsorbed Zn (mg/kg)	Total Zn (mg/l)
4	2.045	2.1115	7286.059351	4.1565
4	0.707	3.4495	11903.03658	4.1565
4	0.241	3.9155	13511.0421	4.1565
1	0.311	0.8455	1406.353959	1.1565
1	0.272	0.8845	1471.224218	1.1565
1	0.246	0.9105	1514.471058	1.1565
1	0.166	0.9905	1647.538257	1.1565
2	1.139	1.0175	1692.448436	2.1565
2	0.986	1.1705	1946.939454	2.1565
2	0.42	1.7365	2888.389887	2.1565
2	0.296	1.8605	3094.644045	2.1565
3	1.582	1.5745	2618.928809	3.1565
3	1.001	2.1555	3585.329341	3.1565
3	0.335	2.8215	4693.113772	3.1565
3	0.25	2.9065	4834.497671	3.1565
4	2.223	1.9335	3216.067864	4.1565
4	1.577	2.5795	4290.585496	4.1565
4	0.85	3.3065	5499.833666	4.1565
4	0.272	3.8845	6461.244178	4.1565

Cu and Zn competitive adsorption in raw sewage

Figure C.82: ***Cu adsorption in Raw Sewage in Competition Experiment Solids Concentration A (474 mg/l)***

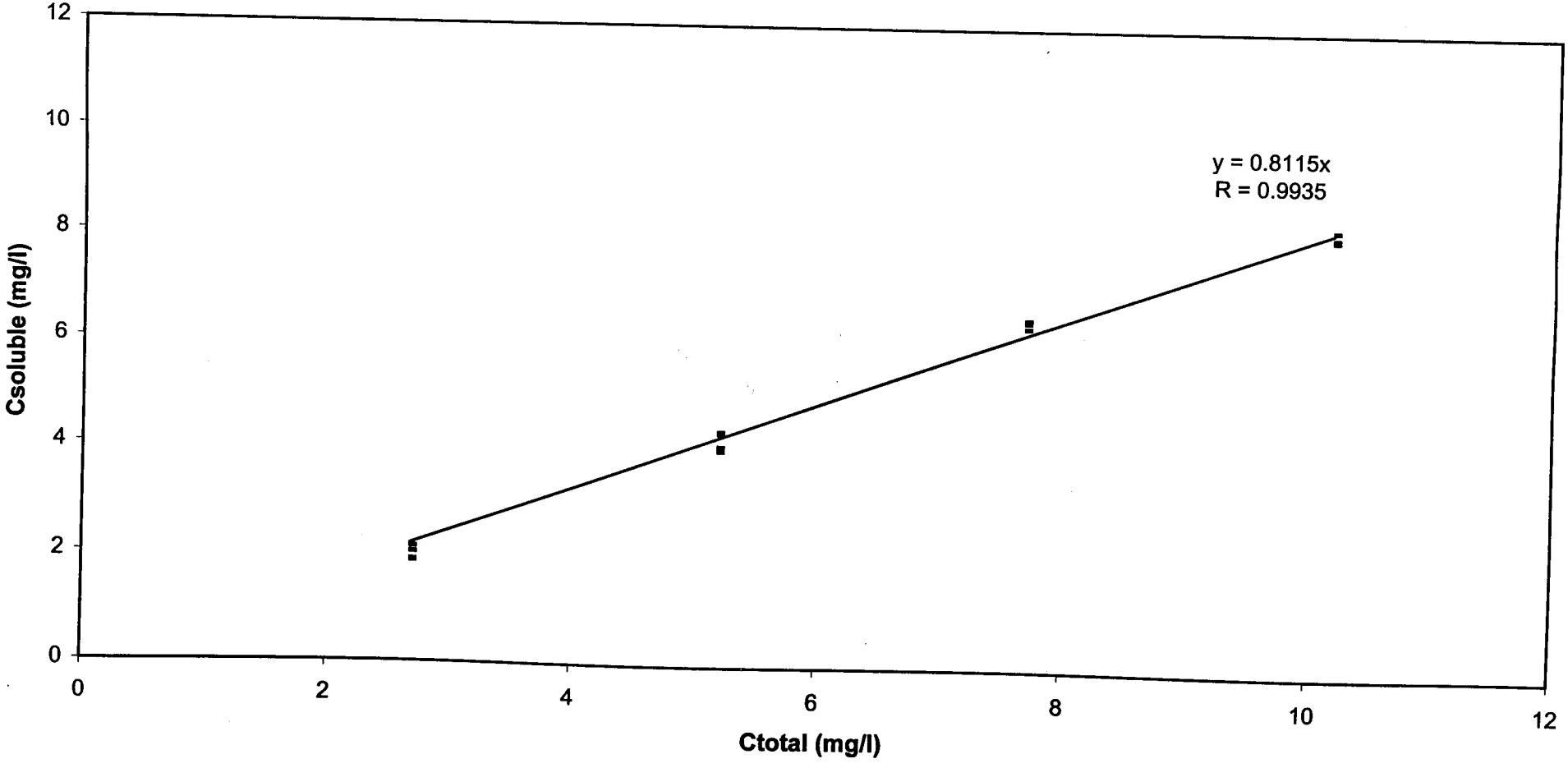


Figure C.83: ***Cu adsorption in Raw Sewage in Competition Experiment Solids Concentration A (474 mg/l)***

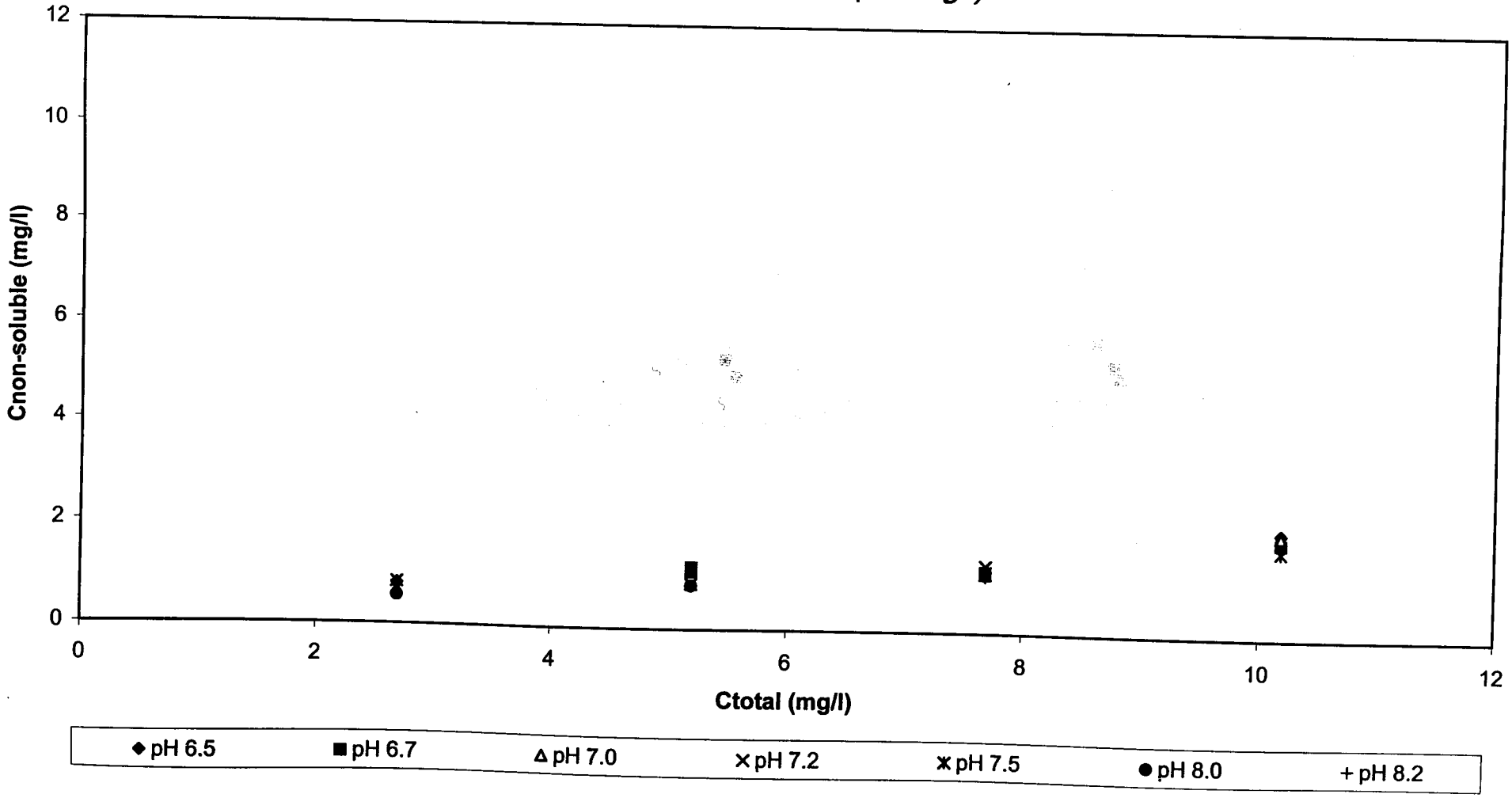


Figure C.84: ***Cu adsorption in Raw Sewage in Competition Experiment Solids Concentration A (474 mg/l)***

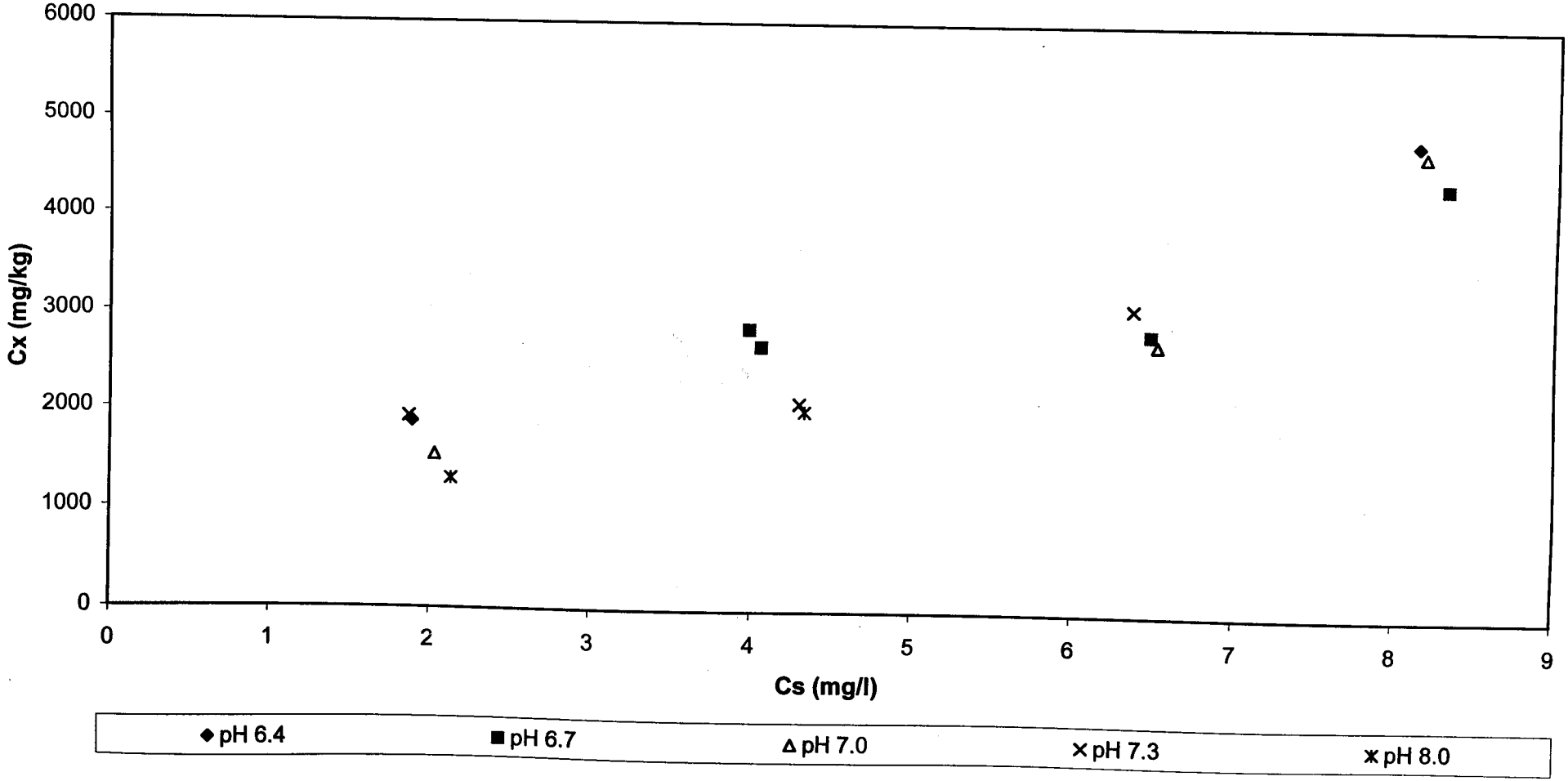


Figure C.85: ***Cu adsorption in Raw Sewage in Competition Experiment Solids Concentration A (474 mg/l)***

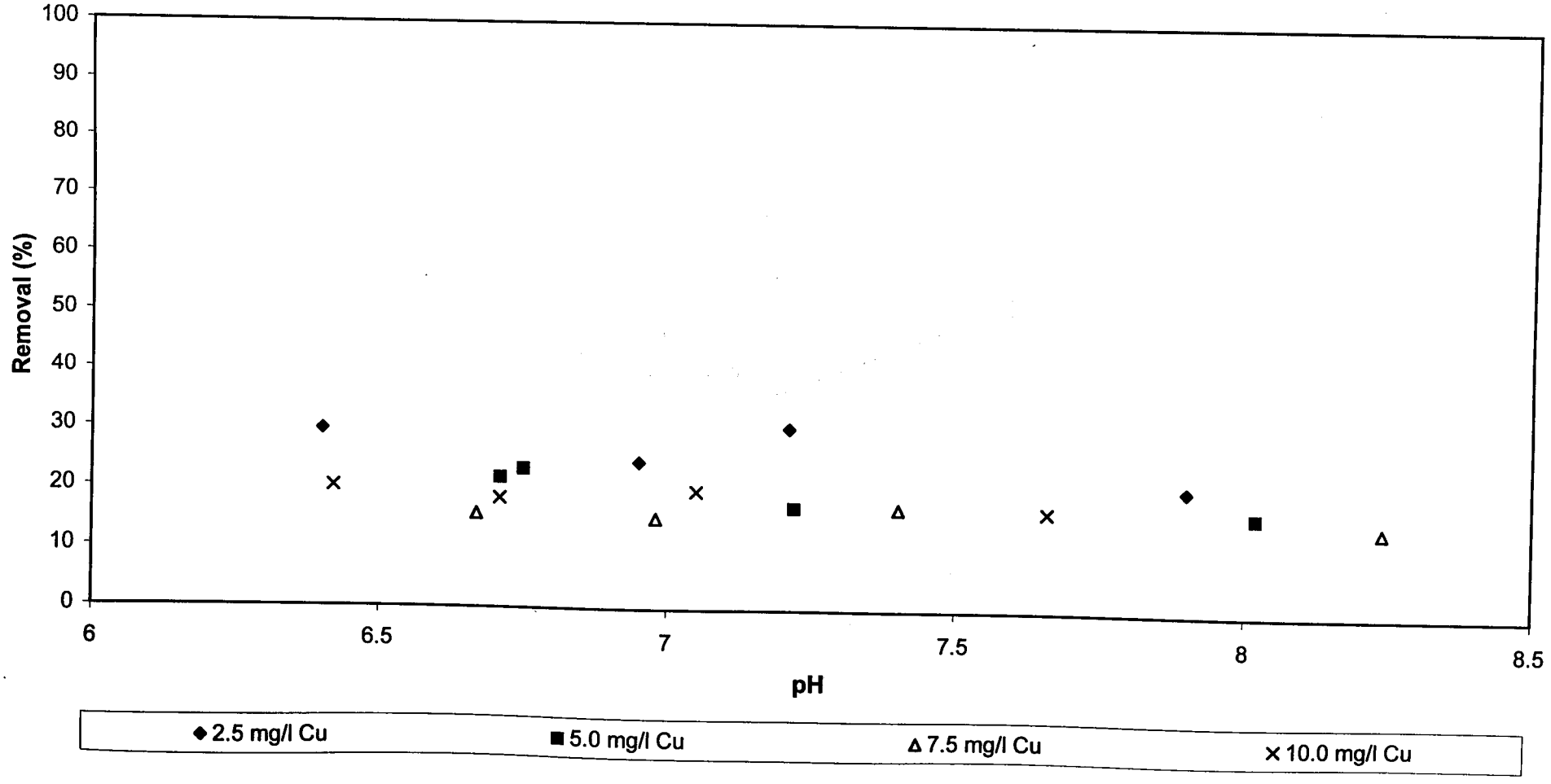


Figure C.86: ***Cu adsorption in Raw Sewage in Competition Experiment Solids Concentration B (322 mg/l)***

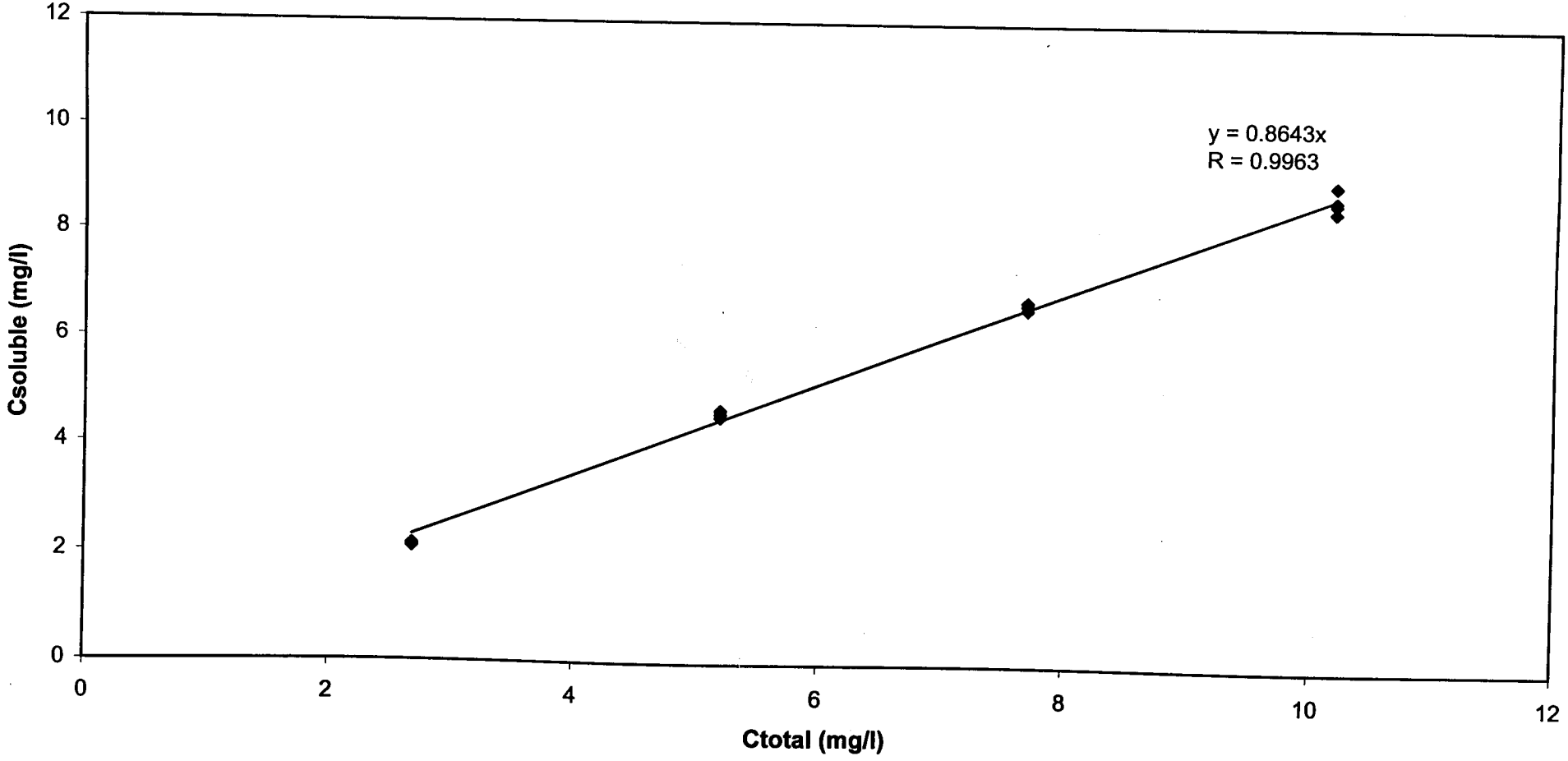


Figure C.87: ***Cu adsorption in Raw Sewage in Competition Experiment Solids Concentration B (322 mg/l)***

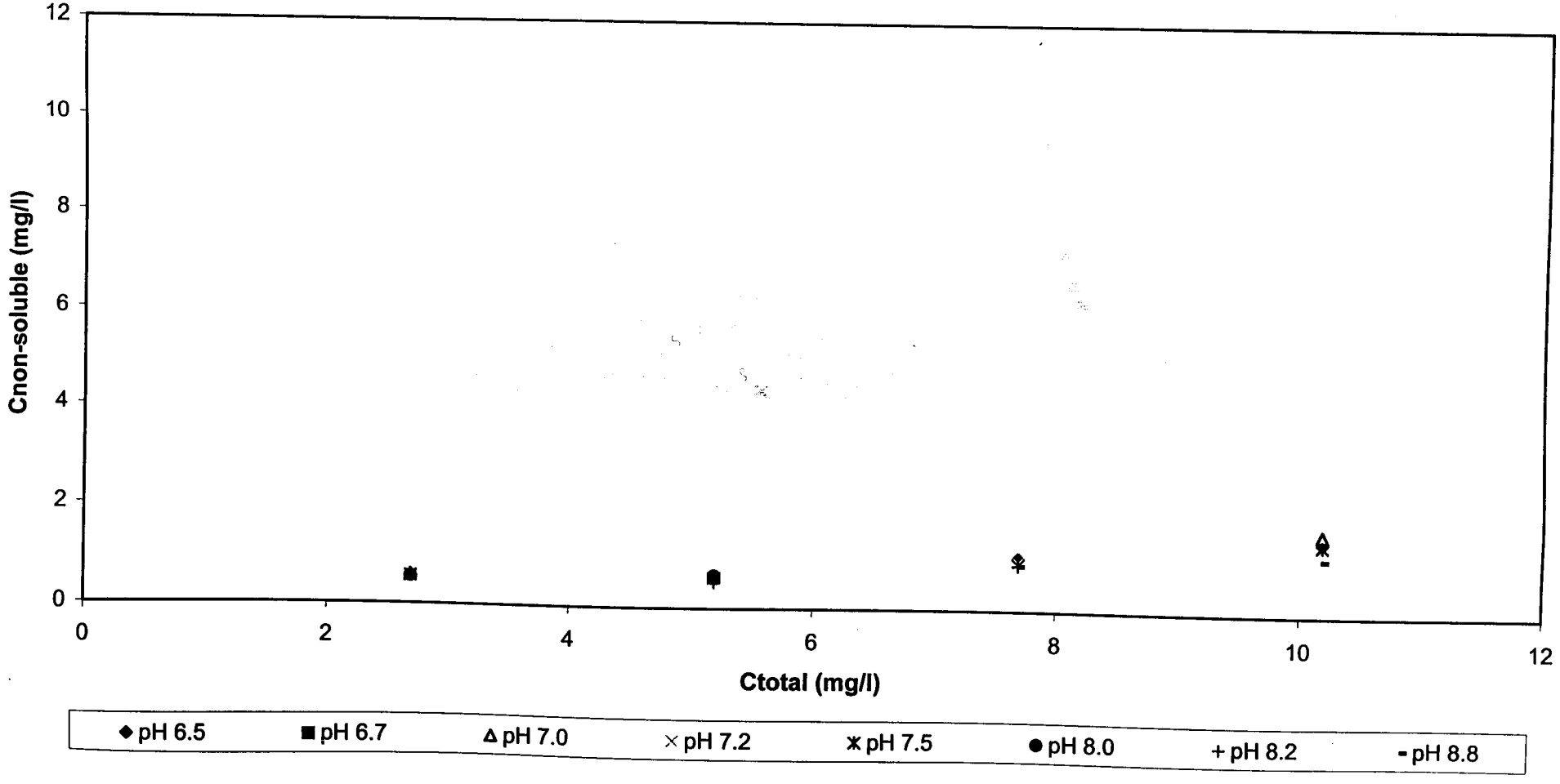


Figure C.88: ***Cu adsorption in Raw Sewage in Competition Experiment Solids Concentration B (322 mg/l)***

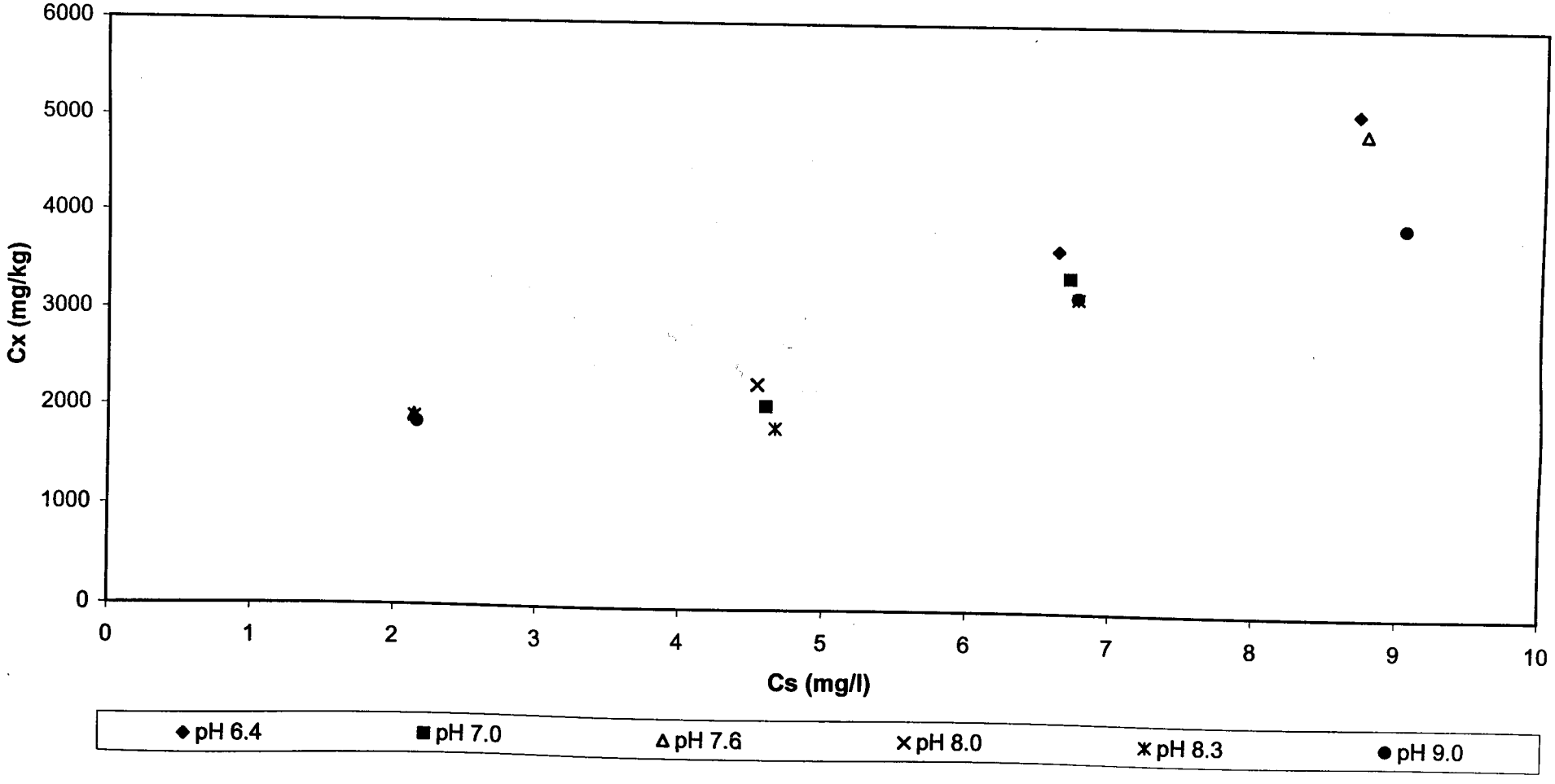


Figure C.89: ***Cu adsorption in Raw Sewage in Competition Experiment Solids Concentration B (322 mg/l)***

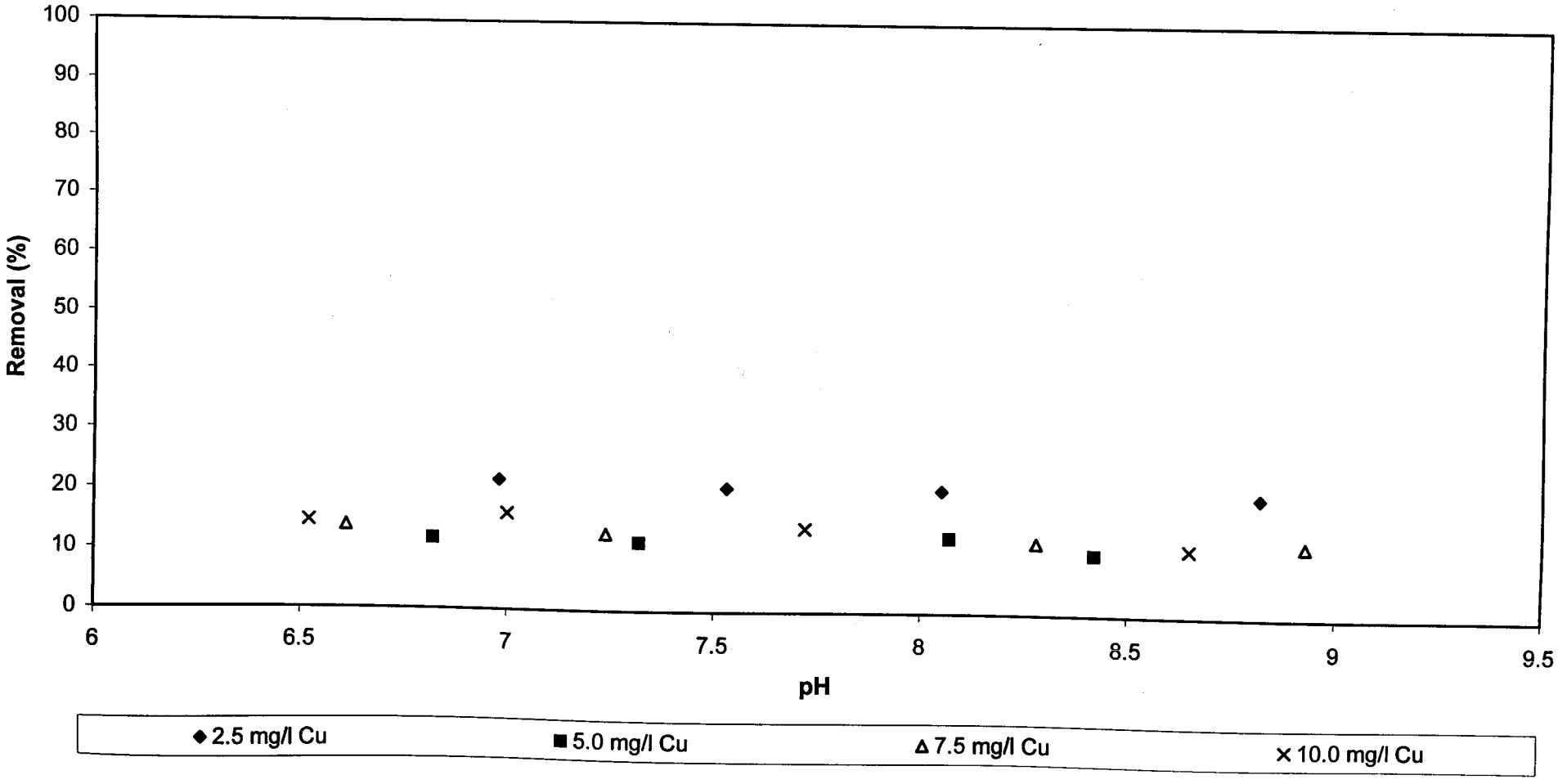


Figure C.90: ***Cu adsorption in Raw Sewage in Competition Experiment Solids Concentration C (668 mg/l)***

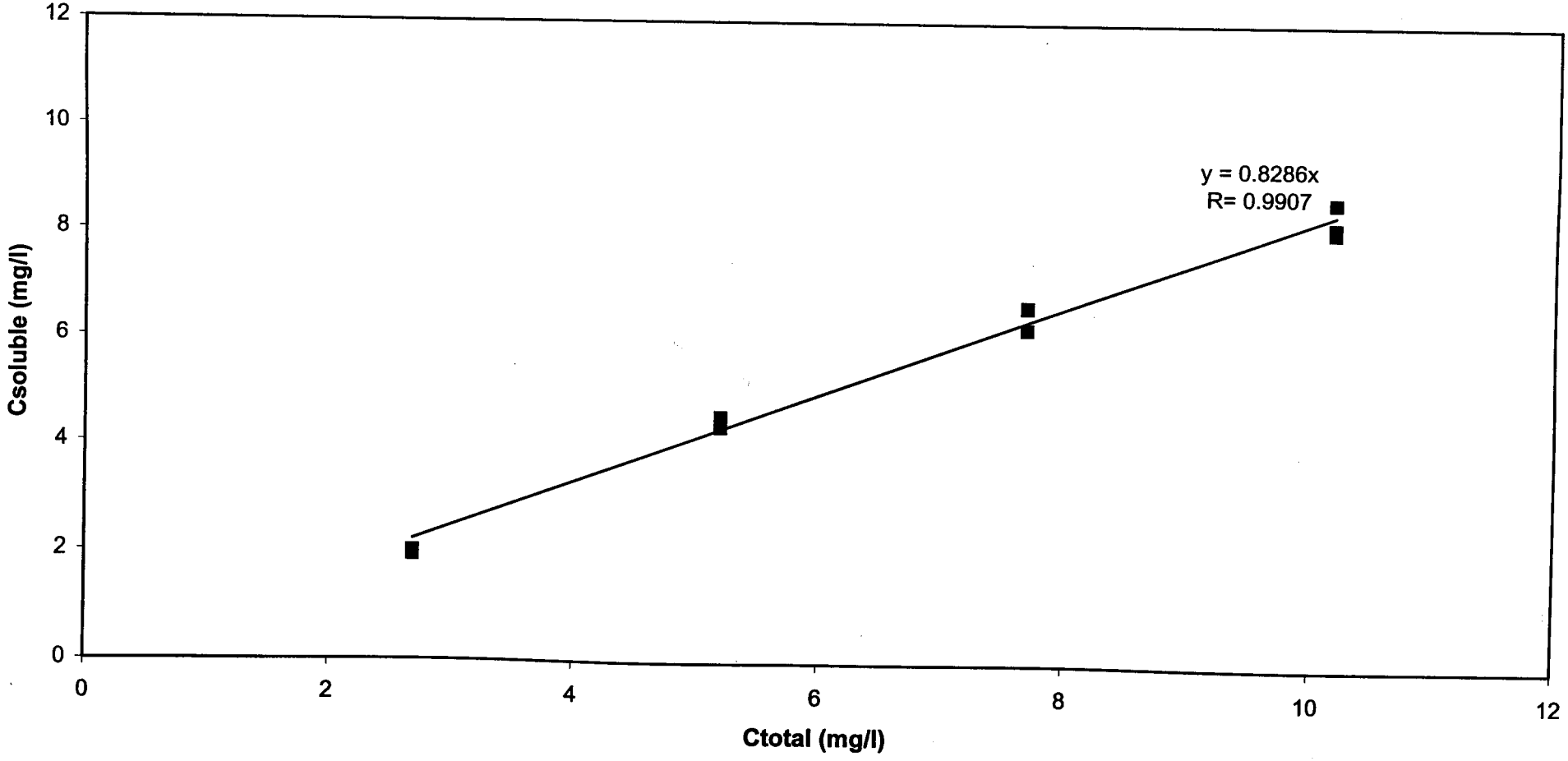


Figure C.91: ***Cu adsorption in Raw Sewage in Competition Experiment Solids Concentration C (668 mg/l)***

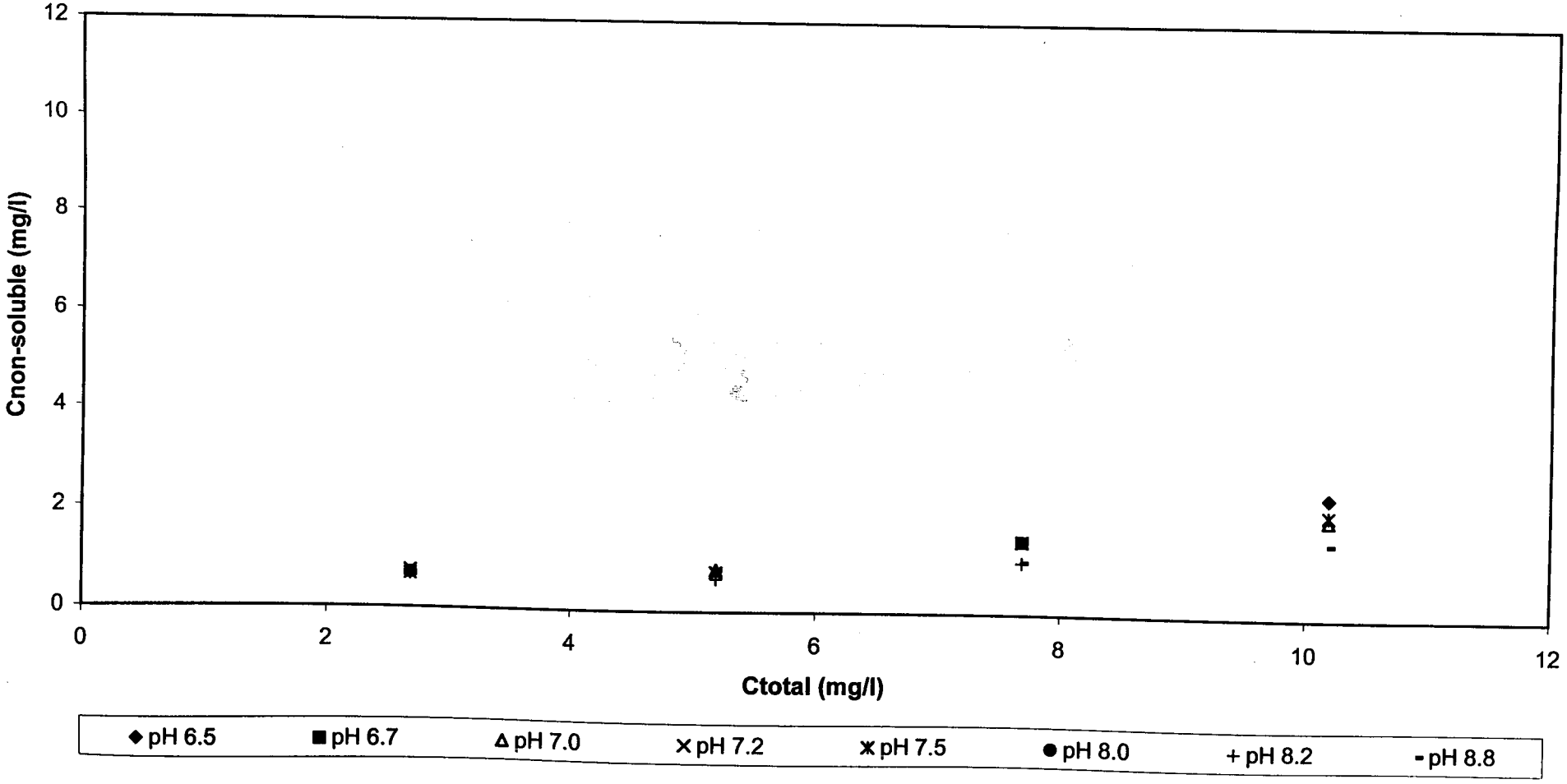


Figure C.92: ***Cu adsorption in Raw Sewage in Competition Experiment Solids Concentration C (668 mg/l)***

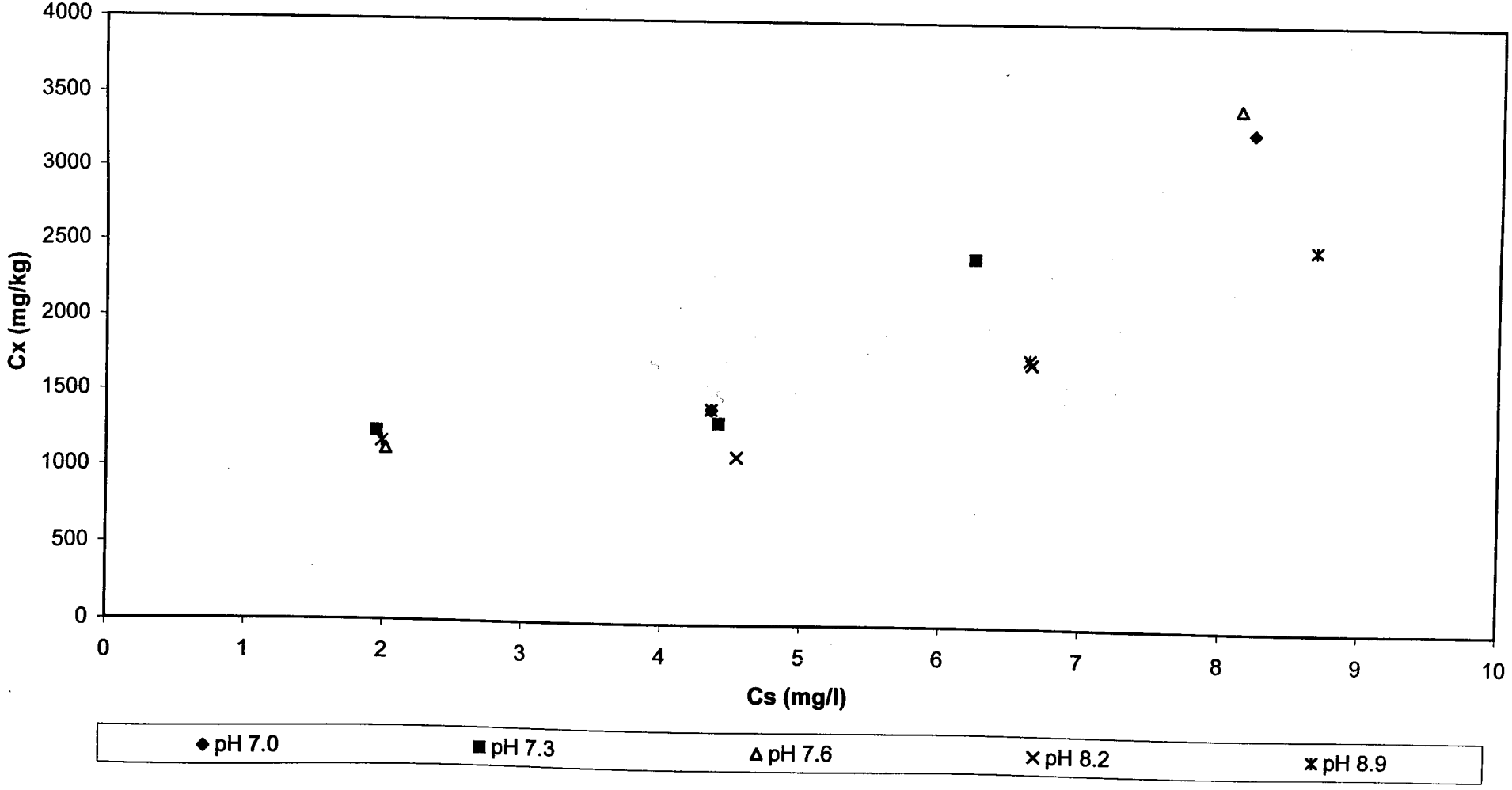


Figure C.93: ***Cu adsorption in Raw Sewage in Competition Experiment Solids Concentration C (668 mg/l)***

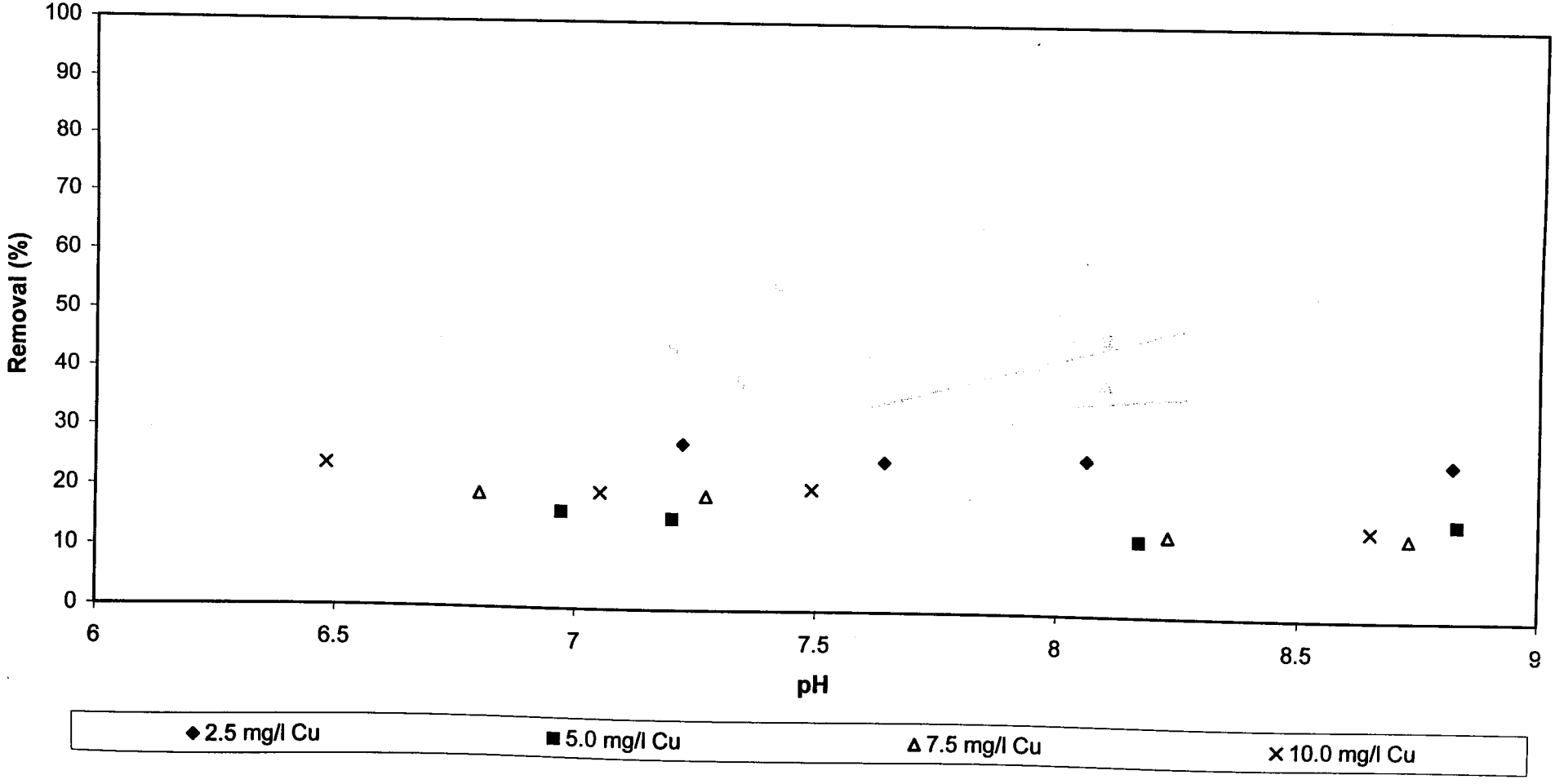


Figure C.94: ***Zn adsorption in Raw Sewage in Competition Experiment Solids Concentration A (474 mg/l)***

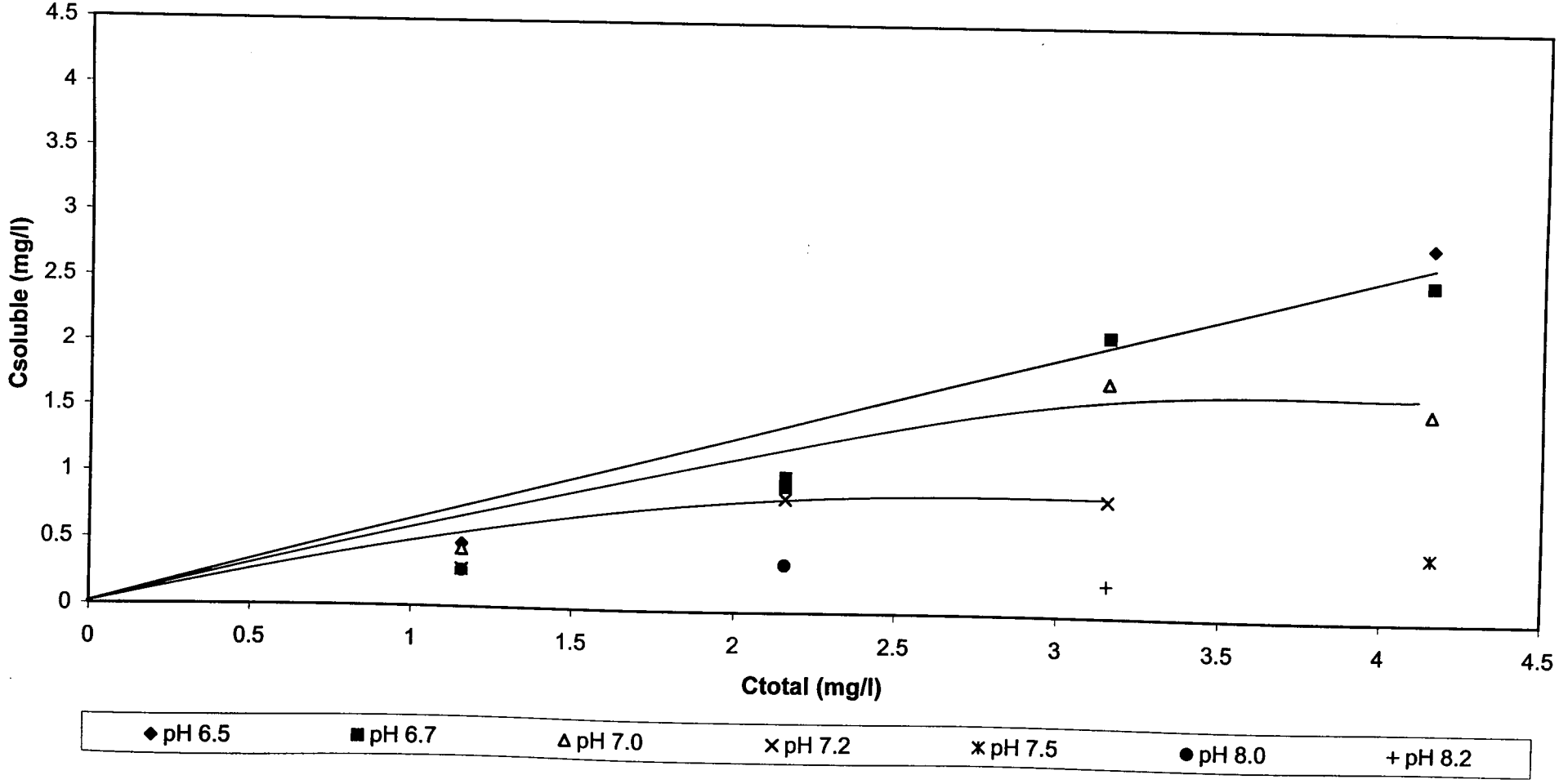


Figure C.95: ***Zn adsorption in Raw Sewage in Competition Experiment Solids Concentration A (474 mg/l)***

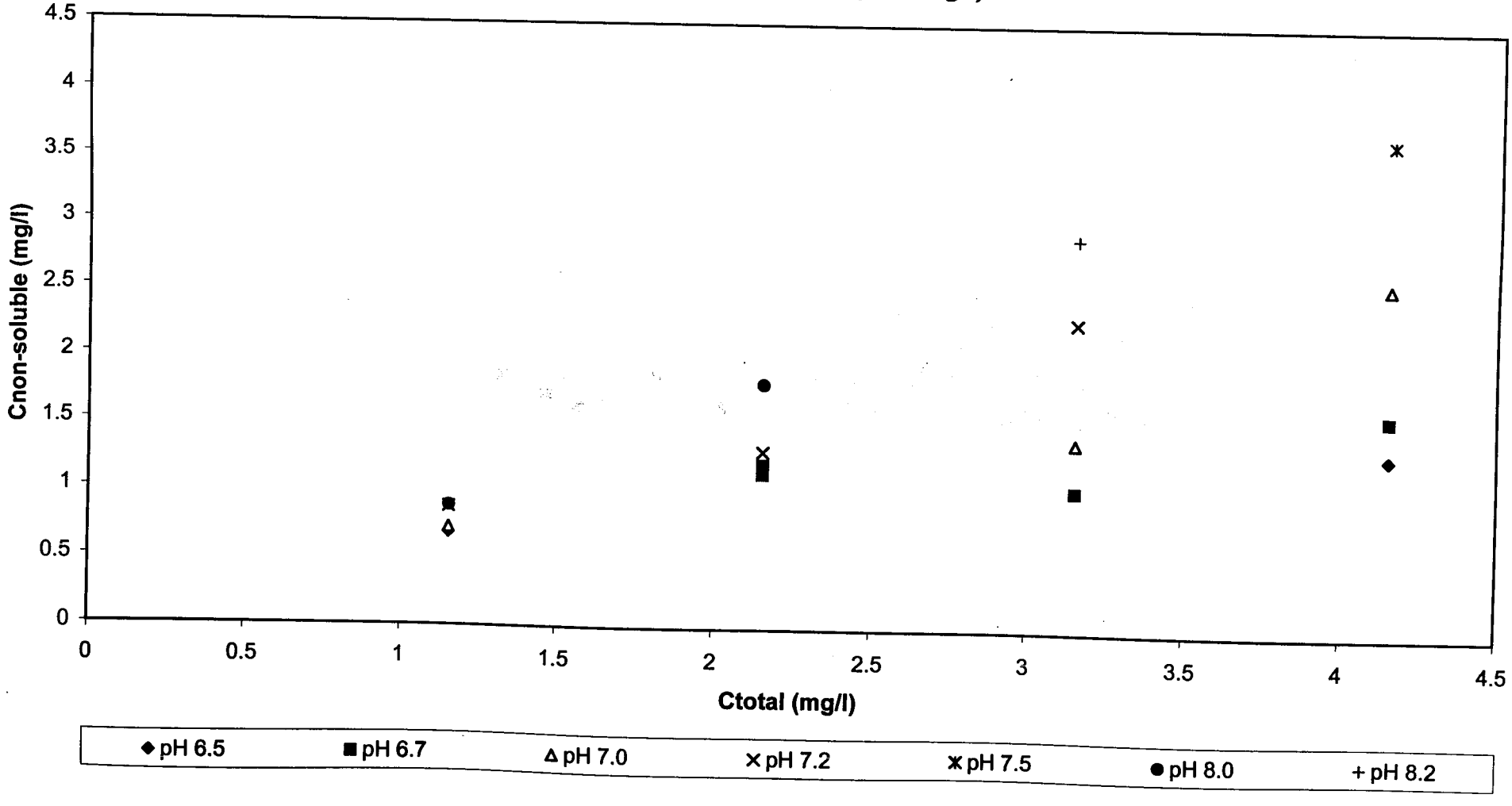


Figure C.96: ***Zn adsorption in Raw Sewage in Competition Experiment Solids Concentration A (474 mg/l)***

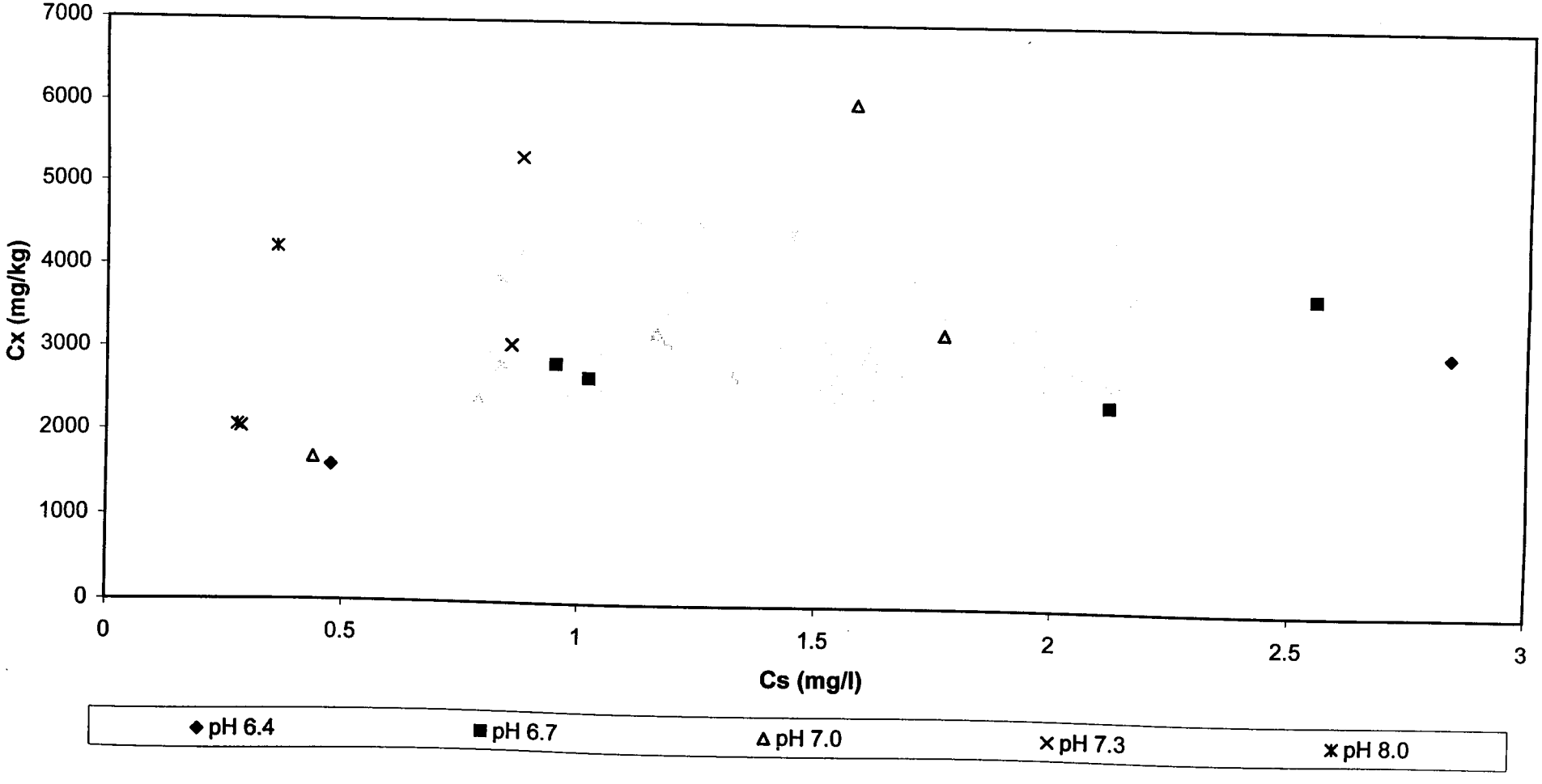


Figure C.97: ***Zn adsorption in Raw Sewage in Competition Experiment Solids Concentration A (474 mg/l)***

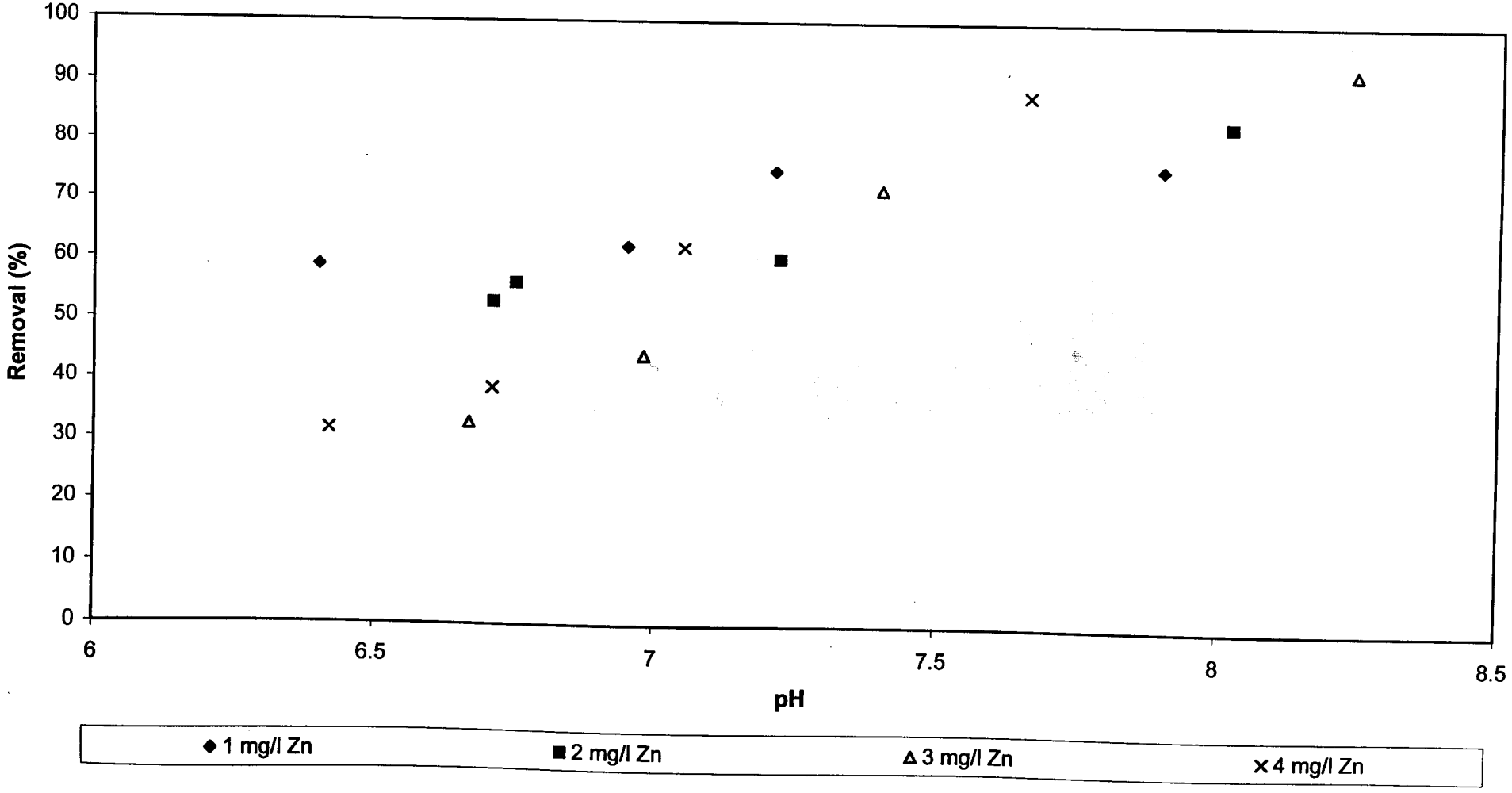


Figure C.98: ***Zn adsorption in Raw Sewage in Competition Experiment Solids Concentration B (322 mg/l)***

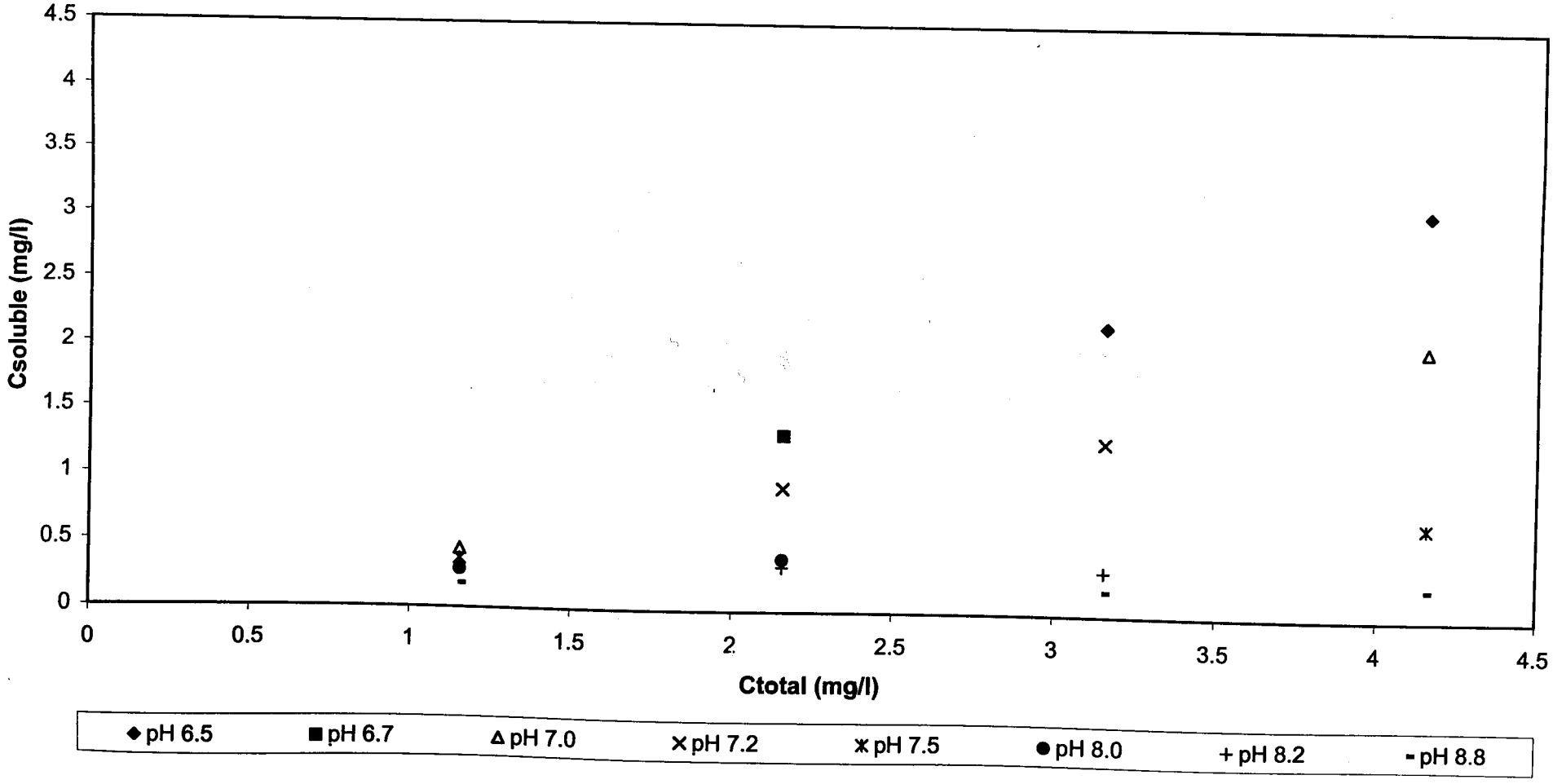


Figure C.99: ***Zn adsorption in Raw Sewage in Competition Experiment Solids Concentration B (322 mg/l)***

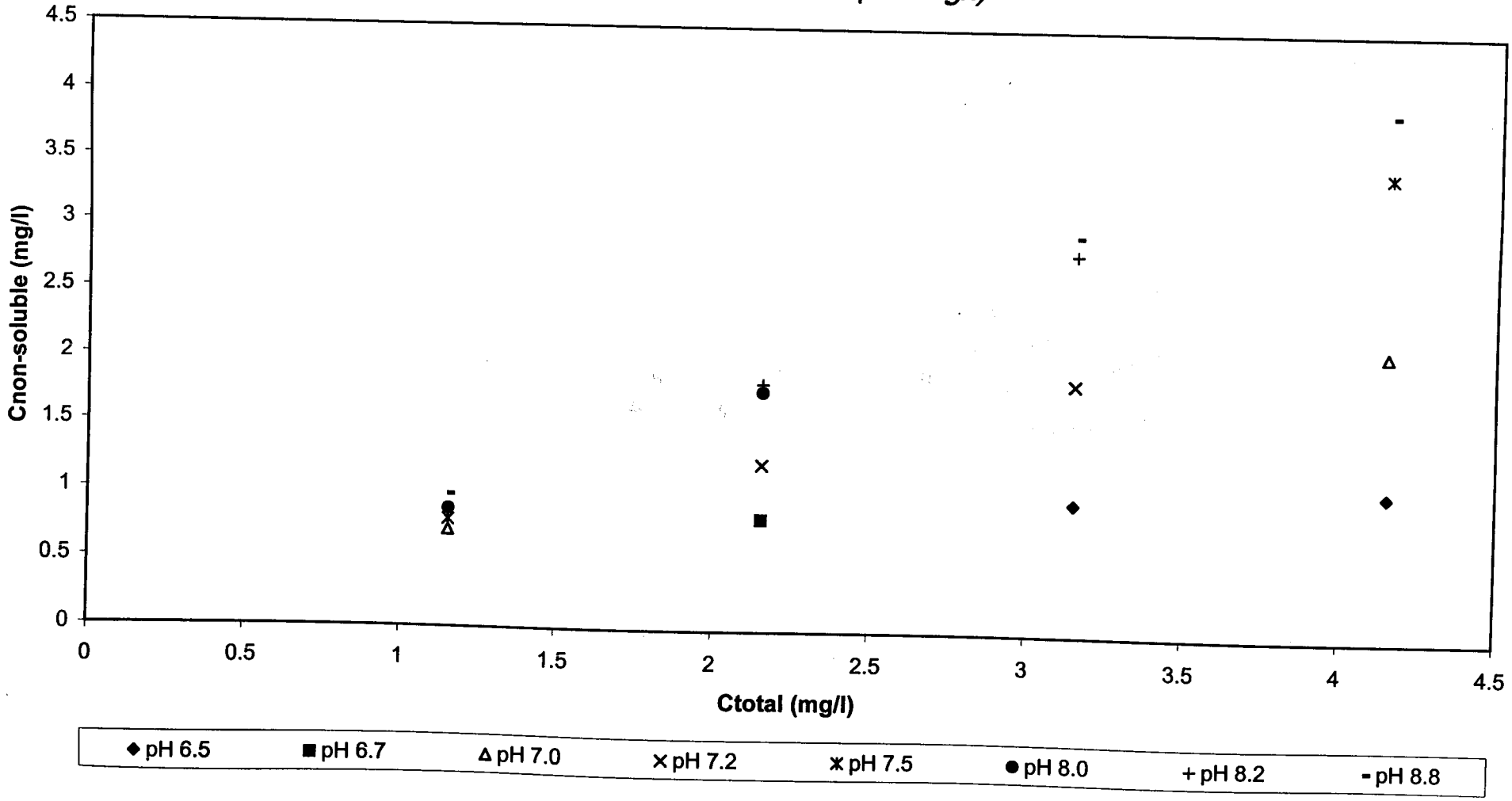


Figure C.100: ***Zn adsorption in Raw Sewage in Competition Experiment Solids Concentration B (322 mg/l)***

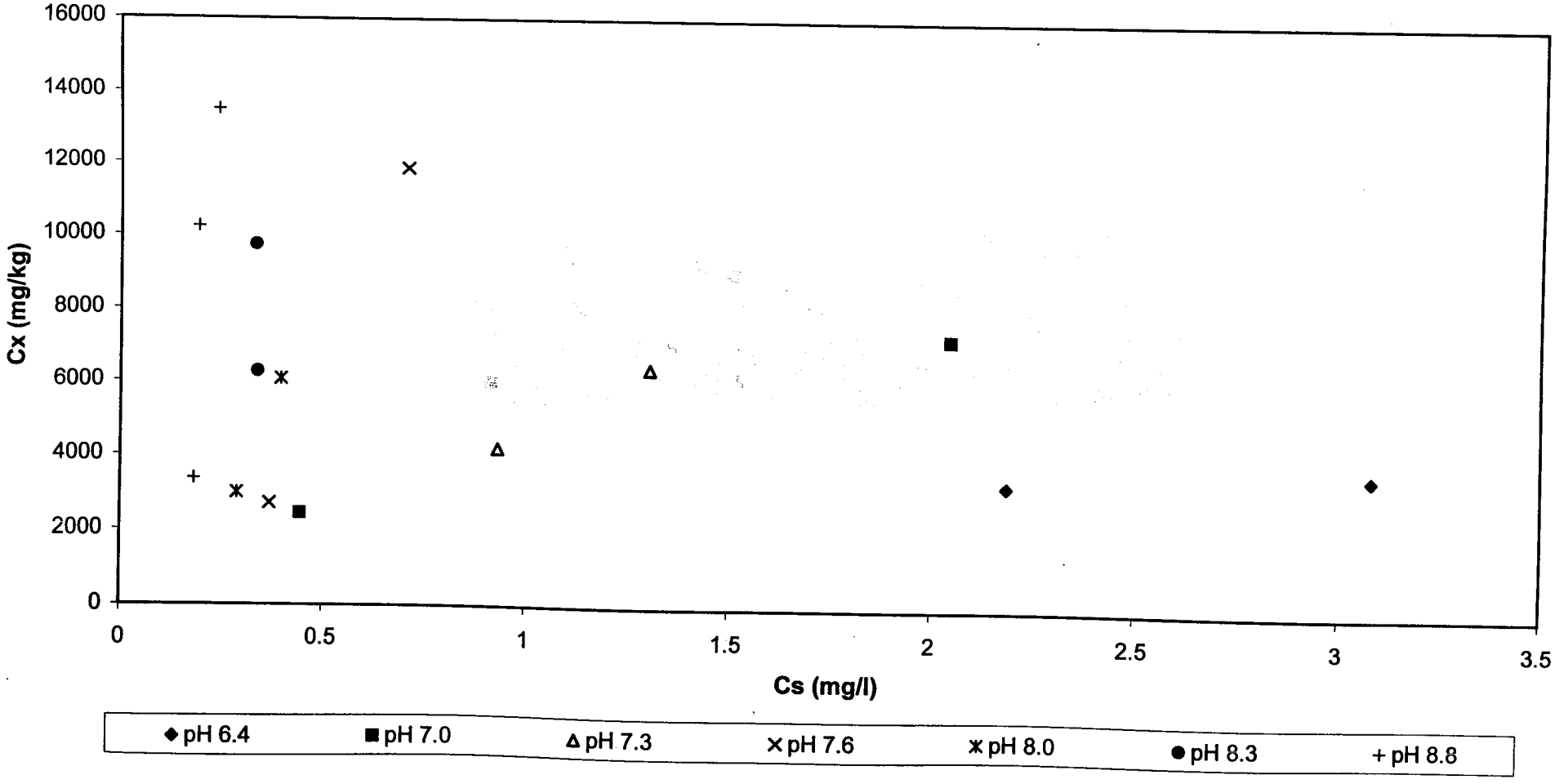


Figure C.101: ***Zn adsorption in Raw Sewage in Competition Experiment Solids Concentration B (322 mg/l)***

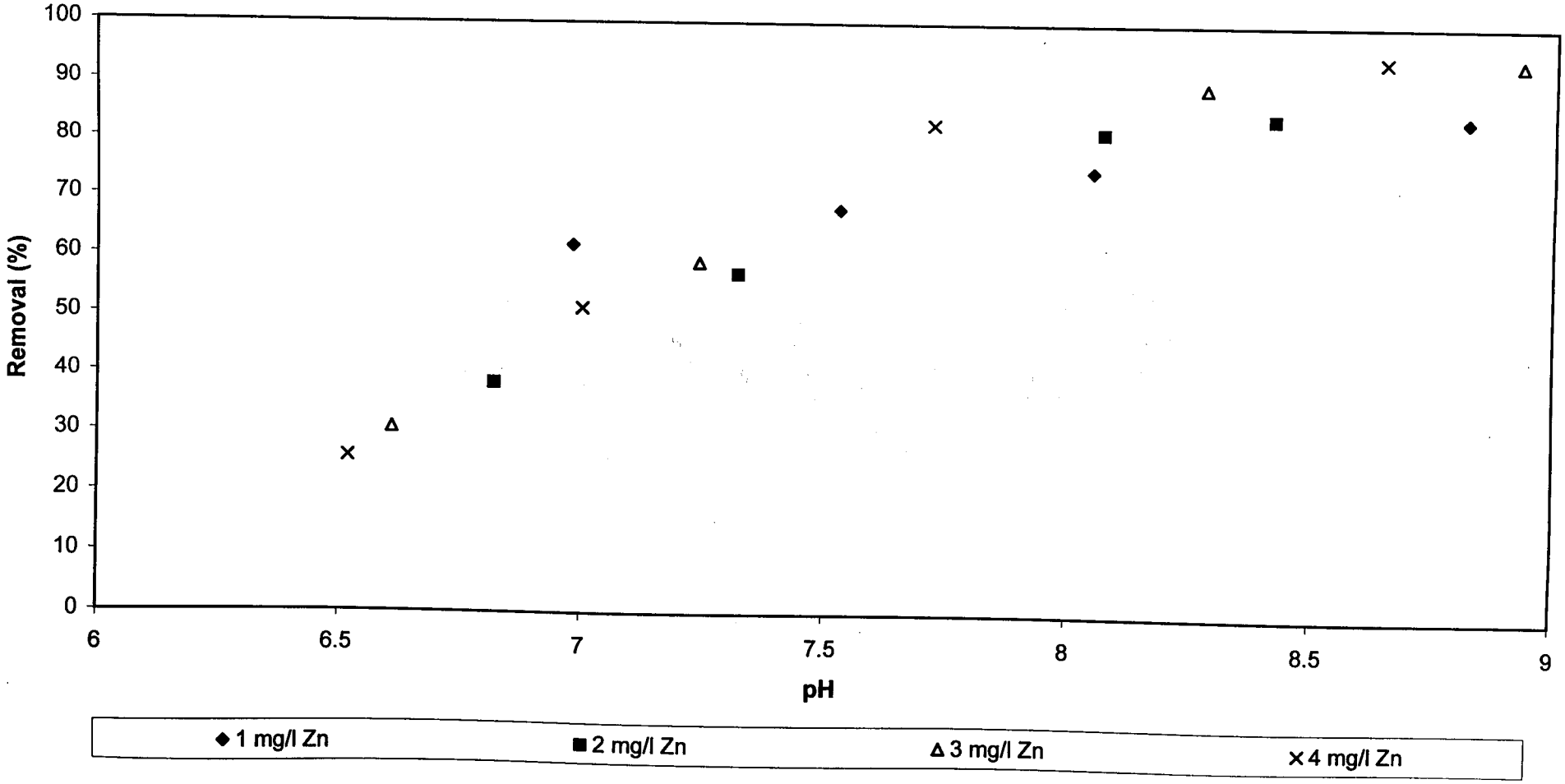


Figure C.102: ***Zn adsorption in Raw Sewage in Competition Experiment Solids Concentration C (668 mg/l)***

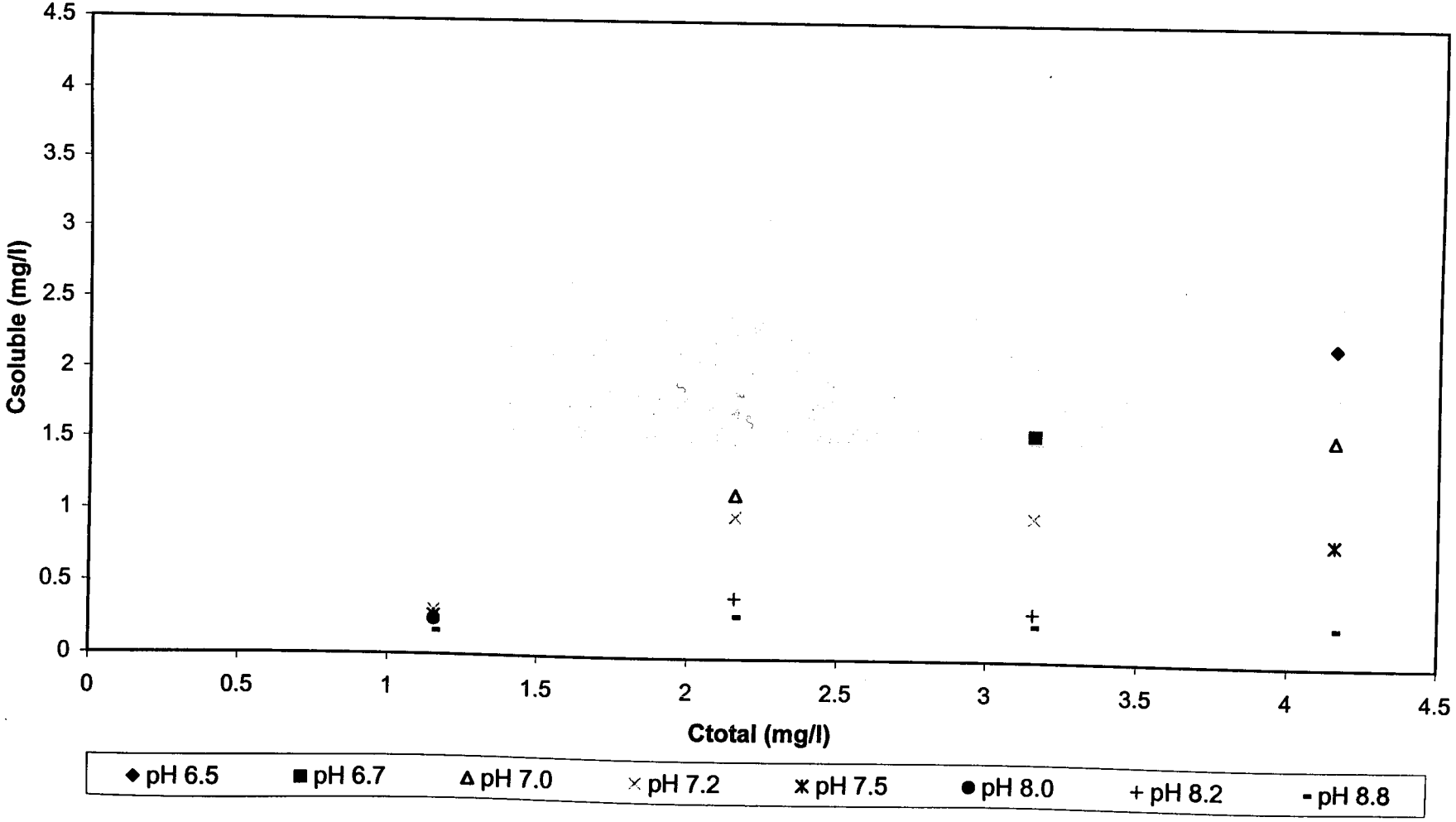


Figure C.103: ***Zn adsorption in Raw Sewage in Competition Experiment Solids Concentration C (668 mg/l)***

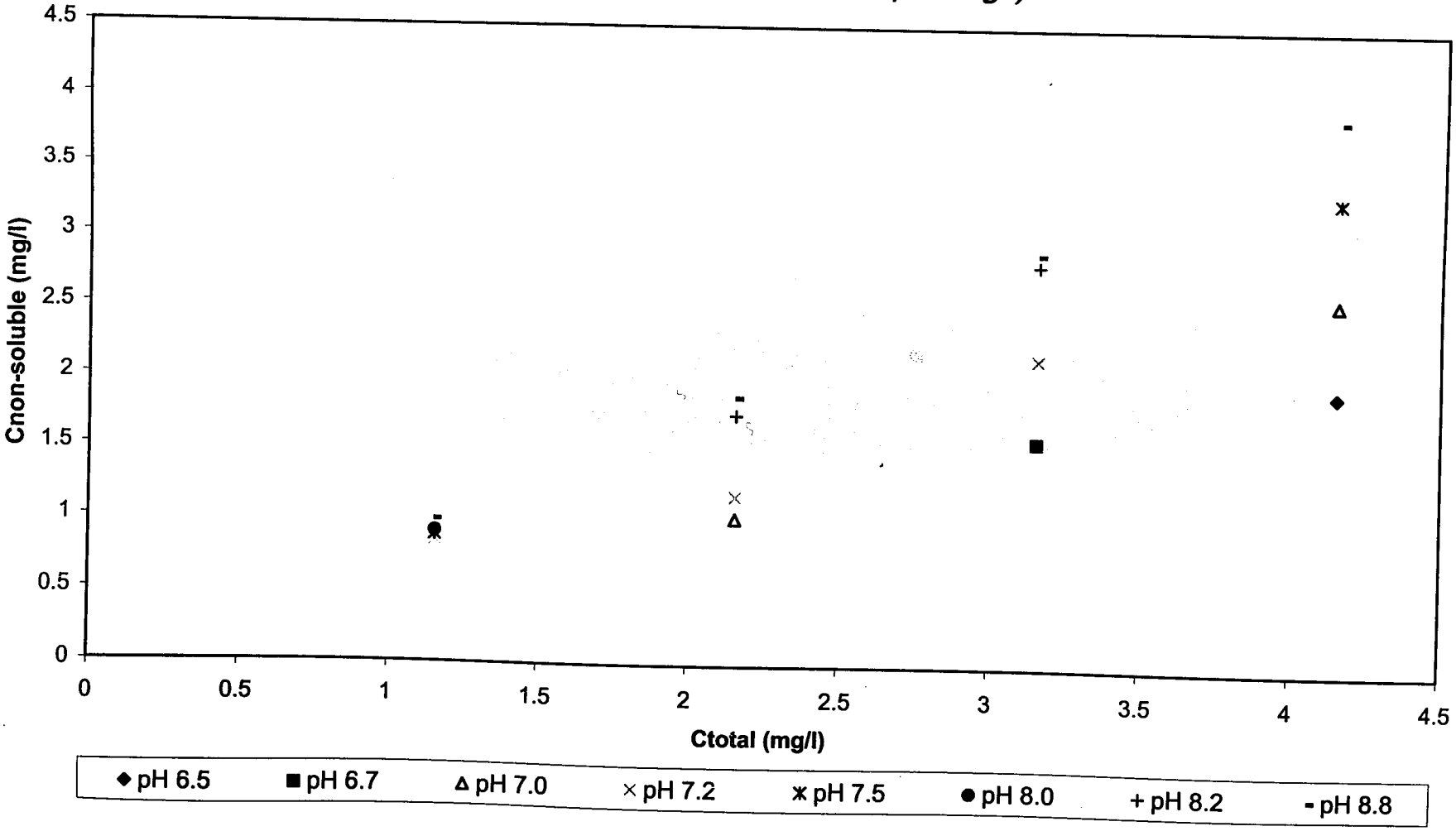


Figure C.104: ***Zn adsorption in Raw Sewage in Competition Experiment Solids Concentration C (668 mg/l)***

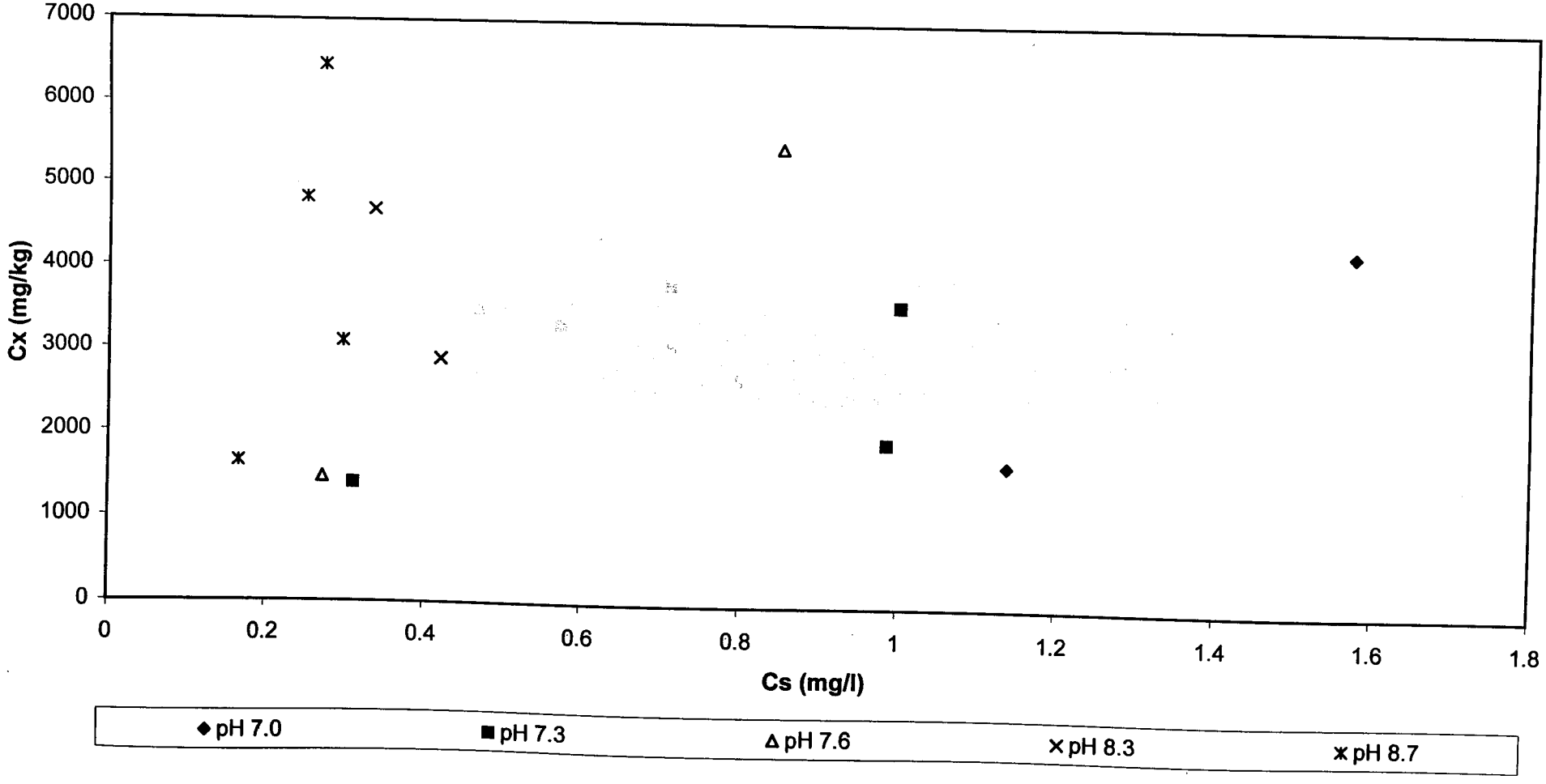


Figure C.105: ***Zn adsorption in Raw Sewage in Competition Experiment Solids Concentration C (668 mg/l)***

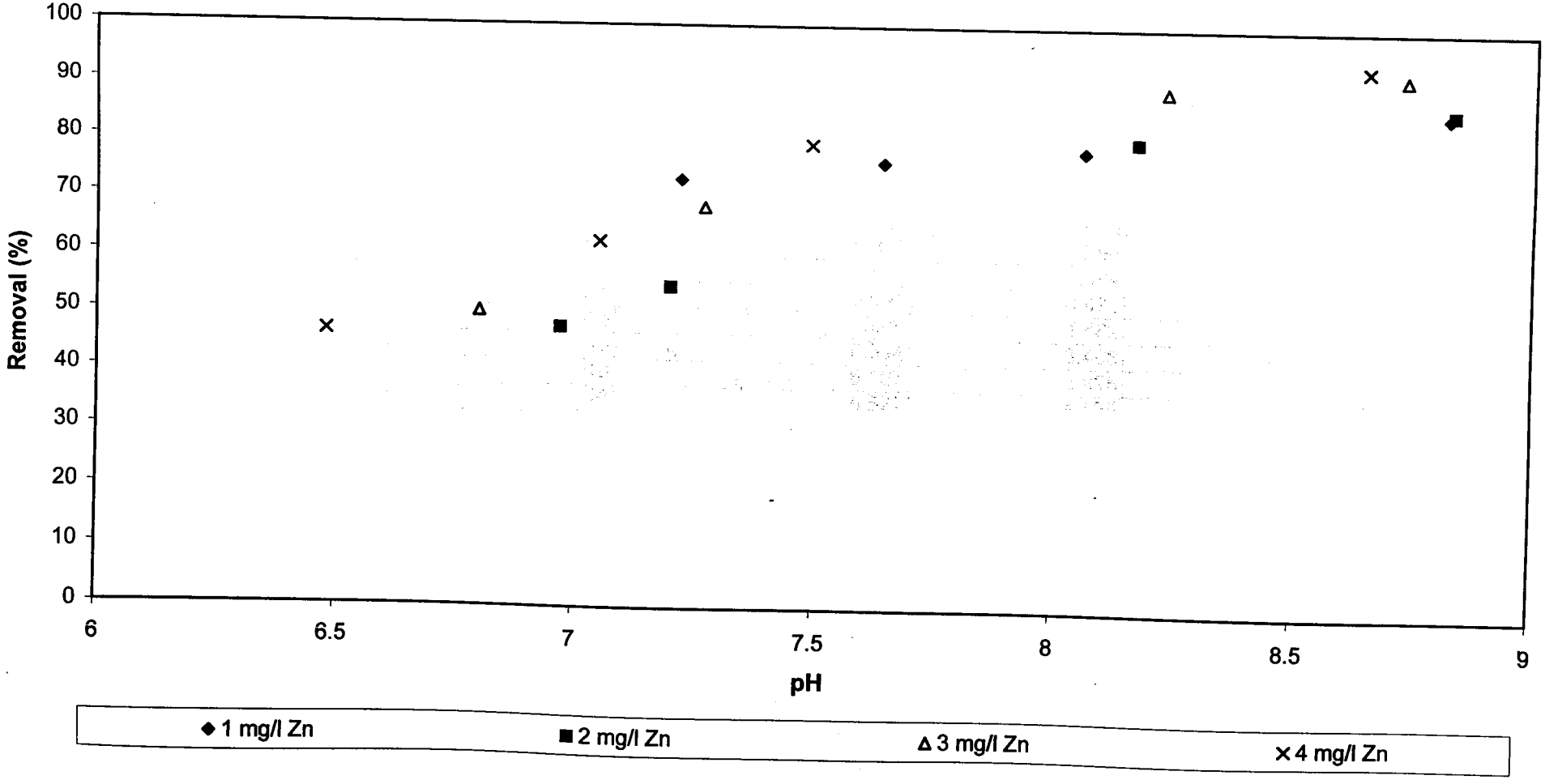


Table C.19 *Competition Adsorption Experiments Primary Effluent*

Date Carried out 30-Aug-00

Date analysed: 08-Sep-00

Initial Total Cu (mg/l) 0.062

Initial Total Zn (mg/l) 0.0509

Actual Sample	TSS (mg/l)	pH	Cu Added (mg/l)	Residual Soluble Cu (mg/l)	Adsorbed Cu (mg/l)	Adsorbed Cu (mg/kg)	Total Cu (mg/l)
A-1-1	94	6.63	2.5	1.969	0.593	7009.456265	2.562
A-1-2	94	6.99	2.5	1.91	0.652	7706.855792	2.562
A-1-3	94	7.55	2.5	1.853	0.709	8380.614657	2.562
A-1-4	94	8.41	2.5	1.85	0.712	8416.07565	2.562
A-2-1	94	6.4	5	3.759	1.303	15401.89125	5.062
A-2-2	94	6.77	5	3.363	1.699	20082.74232	5.062
A-2-3	94	6.75	5	3.485	1.577	18640.66194	5.062
A-2-4	94	7.12	5	3.06	2.002	23664.3026	5.062
A-3-1	94	5.95	7.5	5.622	1.94	22931.44208	7.562
A-3-2	94	6.55	7.5	4.578	2.984	35271.86761	7.562
A-3-3	94	7.12	7.5	3.091	4.471	52848.69976	7.562
A-3-4	94	7.12	7.5	3.08	4.482	52978.7234	7.562
A-4-1	94	6.09	10	6.594	3.468	40992.9078	10.062
A-4-2	94	6.25	10	6.167	3.895	46040.18913	10.062
A-4-3	94	6.38	10	5.527	4.535	53605.20095	10.062
A-4-4	94	6.74	10	3.801	6.261	74007.0922	10.062
B-1-1	86	6.4	2.5	1.913	0.649	8385.01292	2.562
B-1-2	86	6.94	2.5	1.876	0.686	8863.049096	2.562
B-1-3	86	7.89	2.5	1.655	0.907	11718.34625	2.562
B-1-4	86	8.59	2.5	1.655	0.907	11718.34625	2.562
B-2-1	86	6.28	5	3.929	1.133	14638.24289	5.062
B-2-2	86	6.56	5	3.505	1.557	20116.27907	5.062
B-2-3	86	6.6	5	3.499	1.563	20193.79845	5.062
B-2-4	86	6.55	5	3.188	1.874	24211.8863	5.062
B-3-1	86	5.44	7.5	6.084	1.478	19095.60724	7.562
B-3-2	86	6.12	7.5	5.794	1.768	22842.37726	7.562
B-3-3	86	6.61	7.5	3.722	3.84	49612.4031	7.562
B-3-4	86	7.55	7.5	2.211	5.351	69134.36693	7.562
B-4-1	86	5.55	10	8.462	1.6	20671.83463	10.062

Cu and Zn competitive adsorption in primary effluent

Actual Sample	TSS (mg/l)	pH	Cu Added (mg/l)	Residual Soluble Cu (mg/l)	Adsorbed Cu (mg/l)	Adsorbed Cu (mg/kg)	Total Cu (mg/l)
B-4-2	86	6.15	10	6.935	3.127	40400.5168	10.062
B-4-3	86	6.36	10	5.174	4.888	63152.45478	10.062
B-4-4	86	6.52	10	4.02	6.042	78062.0155	10.062
C-1-1	125	6.87	2.5	1.919	0.643	5715.555556	2.562
C-1-2	125	7.29	2.5	1.91	0.652	5795.555556	2.562
C-1-3	125	8.4	2.5	1.881	0.681	6053.333333	2.562
C-1-4	125	8.58	2.5	1.87	0.692	6151.111111	2.562
C-2-1	125	6.48	5	3.47	1.592	14151.11111	5.062
C-2-2	125	6.76	5	3.339	1.723	15315.55556	5.062
C-2-3	125	6.91	5	3.246	1.816	16142.22222	5.062
C-2-4	125	7.26	5	2.803	2.259	20080	5.062
C-3-1	125	6.25	7.5	5.336	2.226	19786.66667	7.562
C-3-2	125	6.51	7.5	4.637	2.925	26000	7.562
C-3-3	125	6.89	7.5	3.425	4.137	36773.33333	7.562
C-3-4	125	7.85	7.5	3.011	4.551	40453.33333	7.562
C-4-1	125	6.15	10	7.139	2.923	25982.22222	10.062
C-4-2	125	6.43	10	5.519	4.543	40382.22222	10.062
C-4-3	125	6.69	10	4.252	5.81	51644.44444	10.062
C-4-4	125	6.92	10	3.687	6.375	56666.66667	10.062

Cu and Zn competitive adsorption in primary effluent

Zn Added (mg/l)	Residual Soluble Zn (mg/l)	Adsorbed Zn (mg/l)	Adsorbed Zn (mg/kg)	Total Zn (mg/l)
1	0.897	0.1539	1819.148936	1.0509
1	0.809	0.2419	2859.338061	1.0509
1	0.26	0.7909	9348.699764	1.0509
1	0.085	0.9659	11417.25768	1.0509
2	1.86	0.1909	2256.501182	2.0509
2	1.622	0.4289	5069.739953	2.0509
2	1.694	0.3569	4218.676123	2.0509
2	1.264	0.7869	9301.41844	2.0509
3	2.718	0.3329	3934.98818	3.0509
3	2.384	0.6669	7882.978723	3.0509
3	0.995	2.0559	24301.41844	3.0509
3	1.04	2.0109	23769.50355	3.0509
4	3.472	0.5789	6842.789598	4.0509
4	3.34	0.7109	8403.073286	4.0509
4	3.167	0.8839	10447.99054	4.0509
4	2.146	1.9049	22516.54846	4.0509
1	0.977	0.0739	954.7803618	1.0509
1	0.879	0.1719	2220.930233	1.0509
1	0.268	0.7829	10114.98708	1.0509
1	0.105	0.9459	12220.93023	1.0509
2	1.923	0.1279	1652.45478	2.0509
2	1.778	0.2729	3525.839793	2.0509
2	1.745	0.3059	3952.196382	2.0509
2	1.647	0.4039	5218.346253	2.0509
3	2.743	0.3079	3978.036176	3.0509
3	2.77	0.2809	3629.198966	3.0509
3	2.278	0.7729	9985.788114	3.0509
3	0.456	2.5949	33525.83979	3.0509
4	3.618	0.4329	5593.023256	4.0509

Cu and Zn competitive adsorption in primary effluent

Zn Added (mg/l)	Residual Soluble Zn (mg/l)	Adsorbed Zn (mg/l)	Adsorbed Zn (mg/kg)	Total Zn (mg/l)
4	3.529	0.5219	6742.894057	4.0509
4	3.224	0.8269	10683.46253	4.0509
4	2.843	1.2079	15605.94315	4.0509
1	0.832	0.2189	1945.777778	1.0509
1	0.638	0.4129	3670.222222	1.0509
1	0.139	0.9119	8105.777778	1.0509
1	0.075	0.9759	8674.666667	1.0509
2	1.655	0.3959	3519.111111	2.0509
2	1.547	0.5039	4479.111111	2.0509
2	1.417	0.6339	5634.666667	2.0509
2	0.777	1.2739	11323.55556	2.0509
3	2.619	0.4319	3839.111111	3.0509
3	2.392	0.6589	5856.888889	3.0509
3	1.417	1.6339	14523.55556	3.0509
3	0.218	2.8329	25181.33333	3.0509
4	3.49	0.5609	4985.777778	4.0509
4	3.078	0.9729	8648	4.0509
4	2.429	1.6219	14416.88889	4.0509
4	1.768	2.2829	20292.44444	4.0509

Cu and Zn competitive adsorption in primary effluent

Figure C.106: ***Cu adsorption in Primary Effluent in Competition Experiment Solids Concentration A (94 mg/l)***

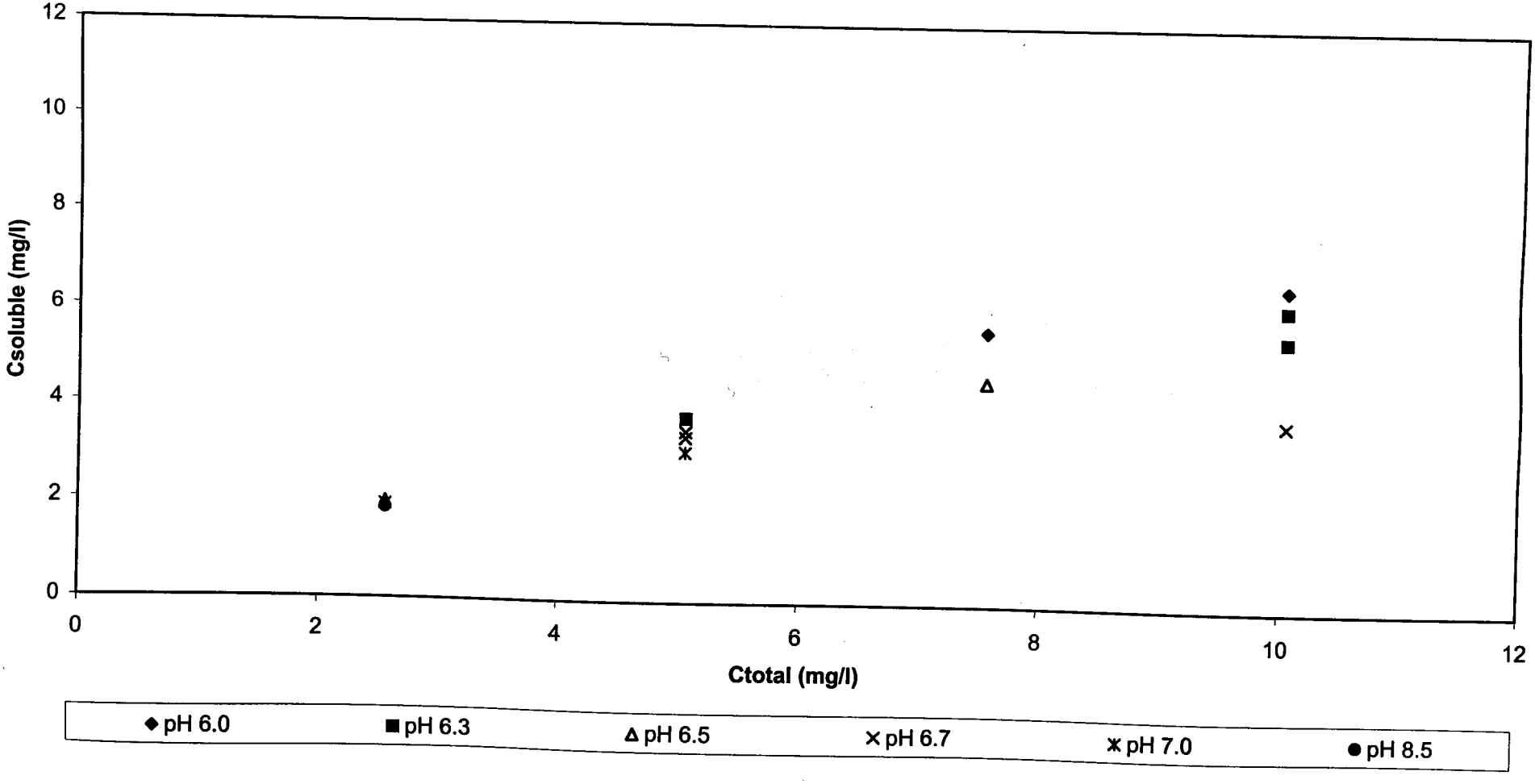


Figure C.107: ***Cu adsorption in Primary Effluent in Competition Experiment Solids Concentration A (94 mg/l)***

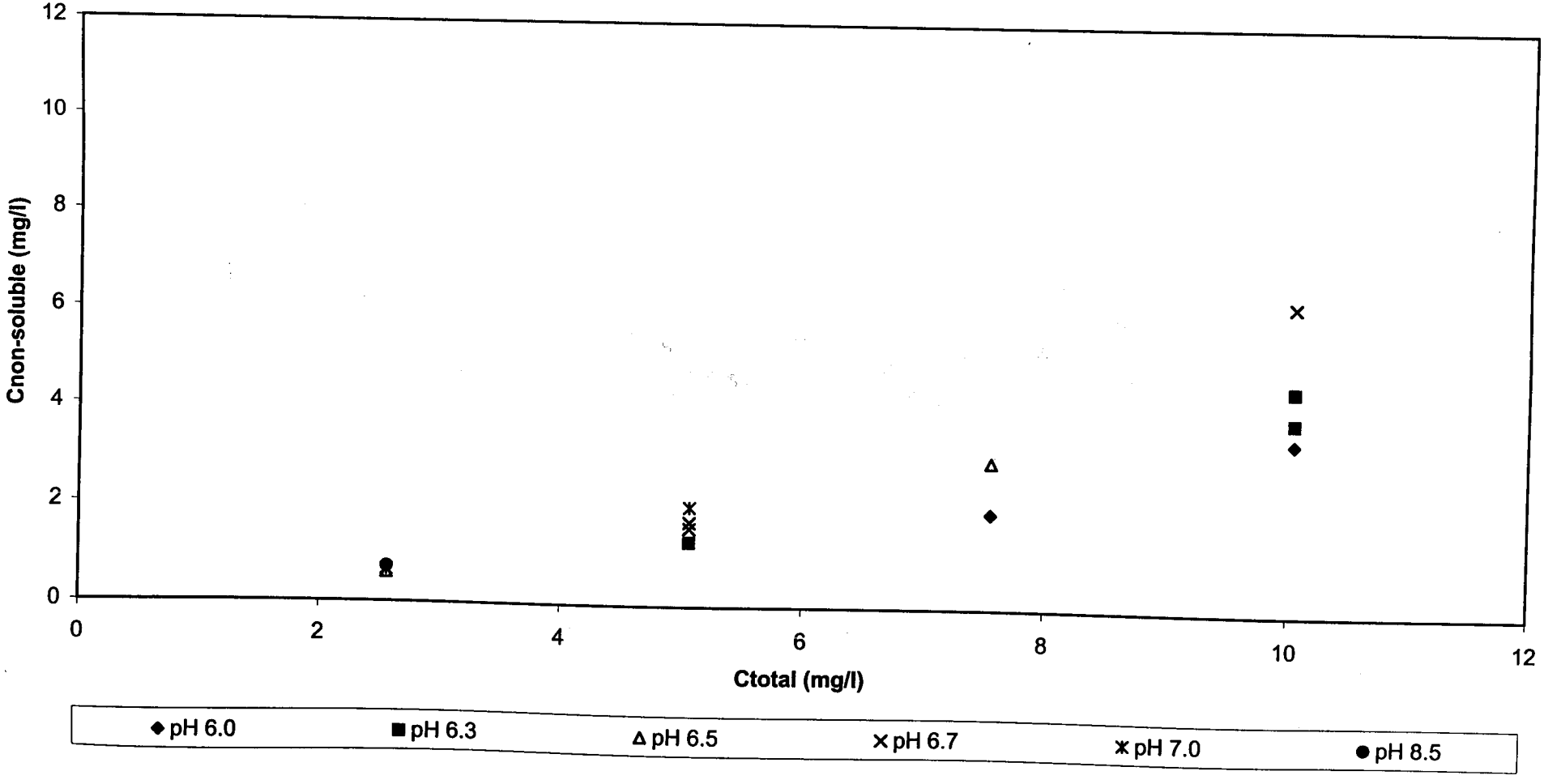


Figure C.108: ***Cu adsorption in Primary Effluent in Competition Experiment Solids Concentration A (94 mg/l)***

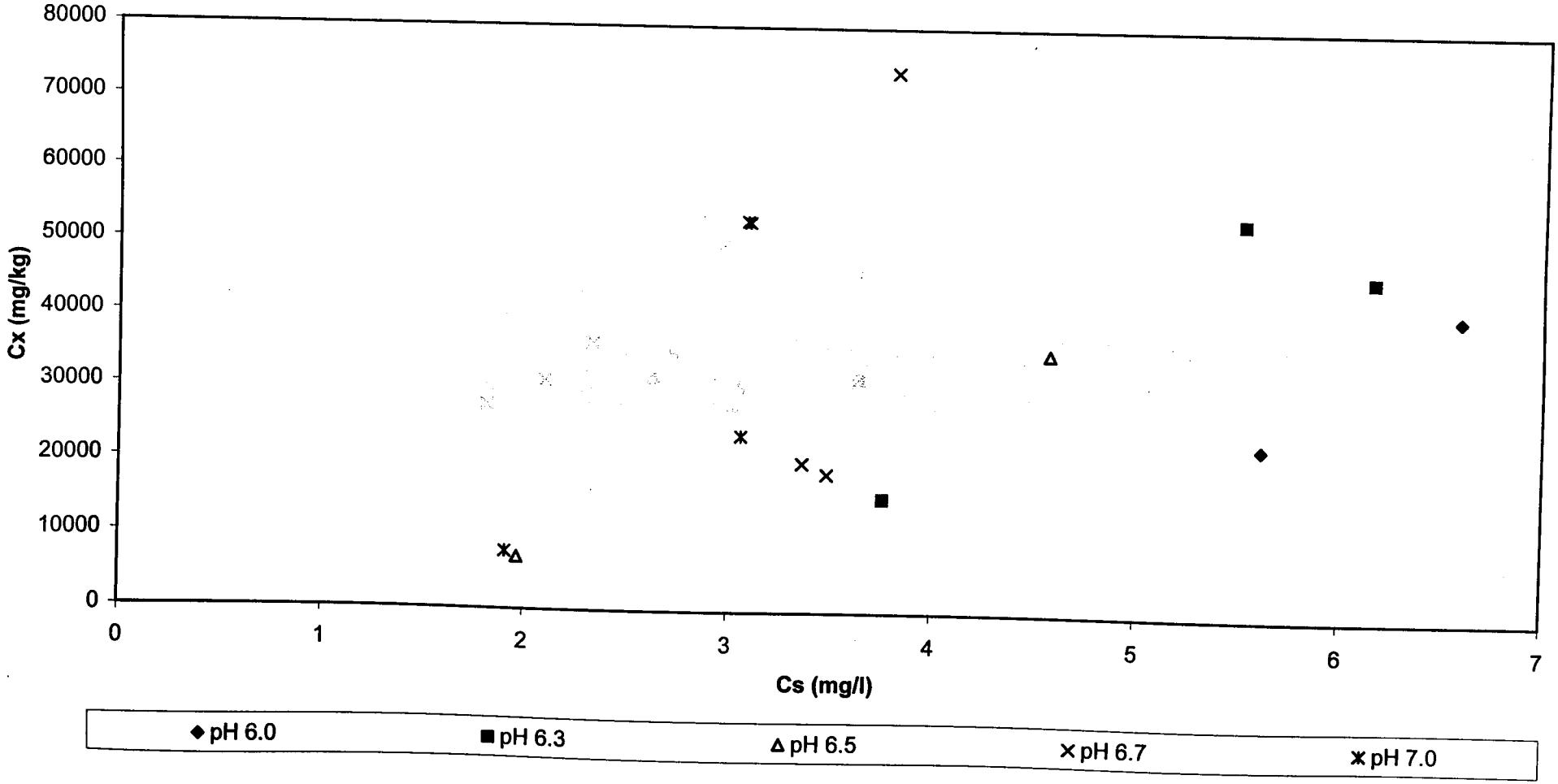


Figure C.109: ***Cu adsorption in Primary Effluent in Competition Experiment Solids Concentration A (94 mg/l)***

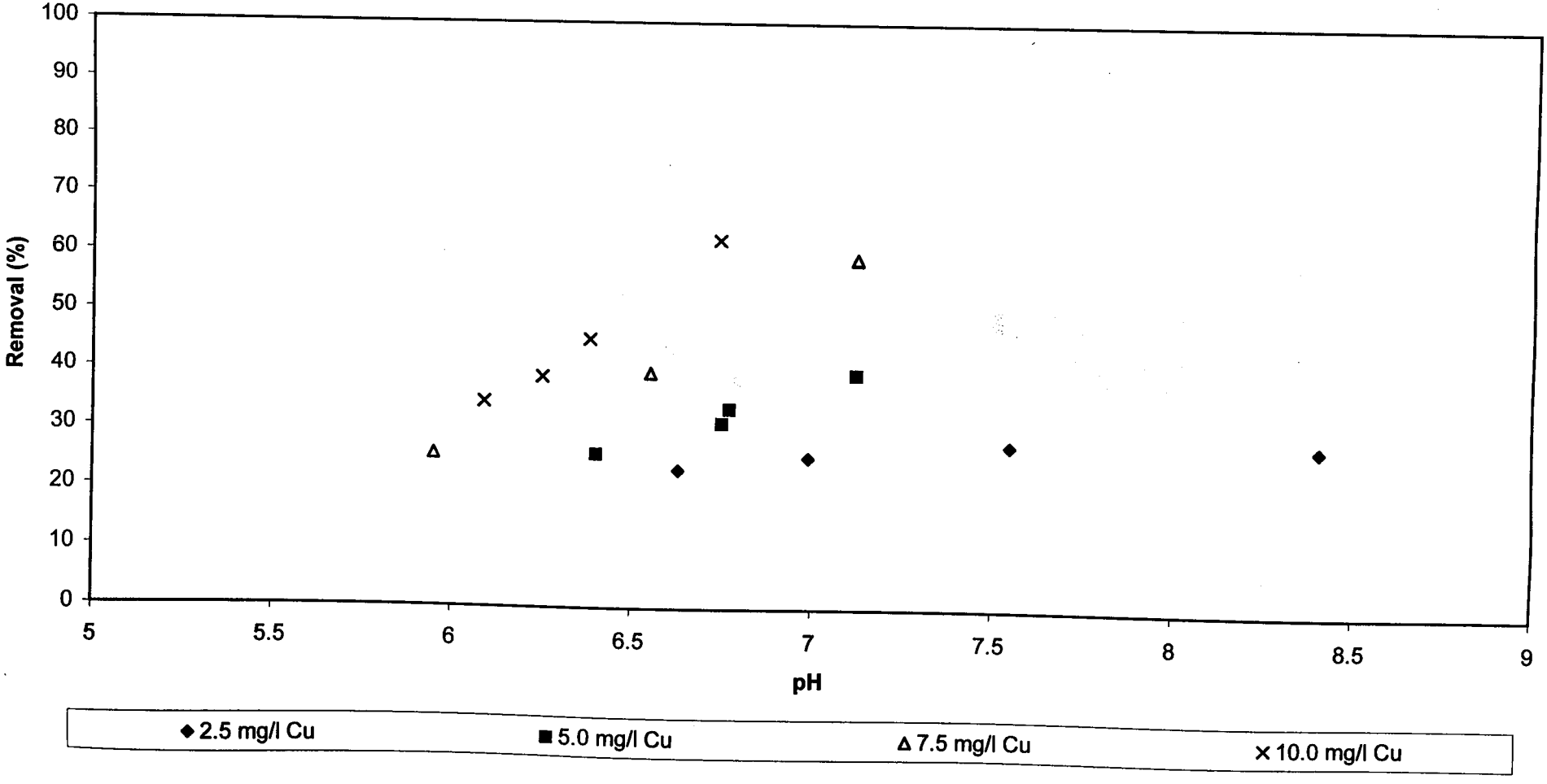


Figure C.110: ***Cu adsorption in Primary Effluent in Competition Experiment Solids Concentration B (86 mg/l)***

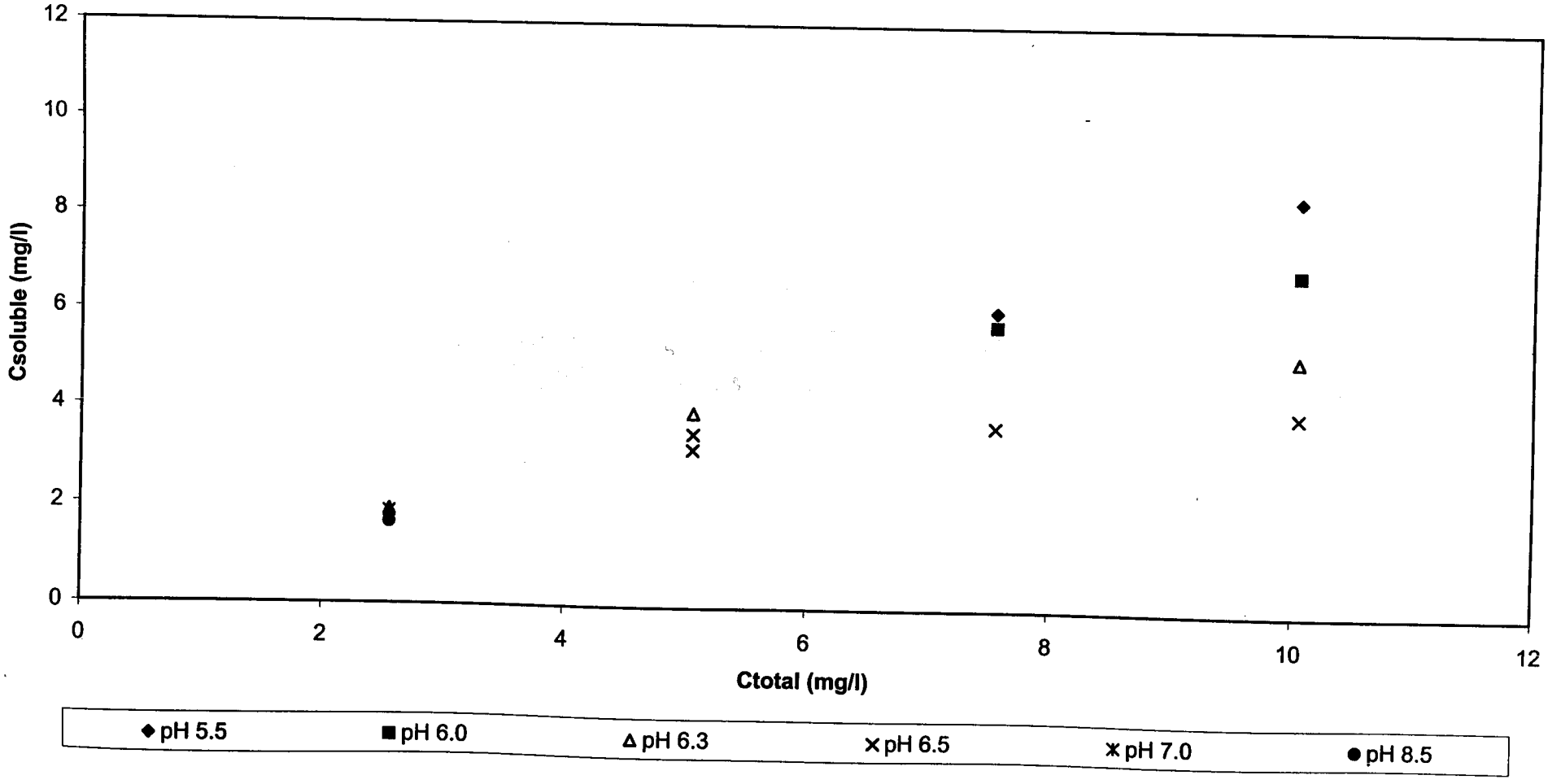


Figure C.111: ***Cu adsorption in Primary Effluent in Competition Experiment Solids Concentration B (86 mg/l)***

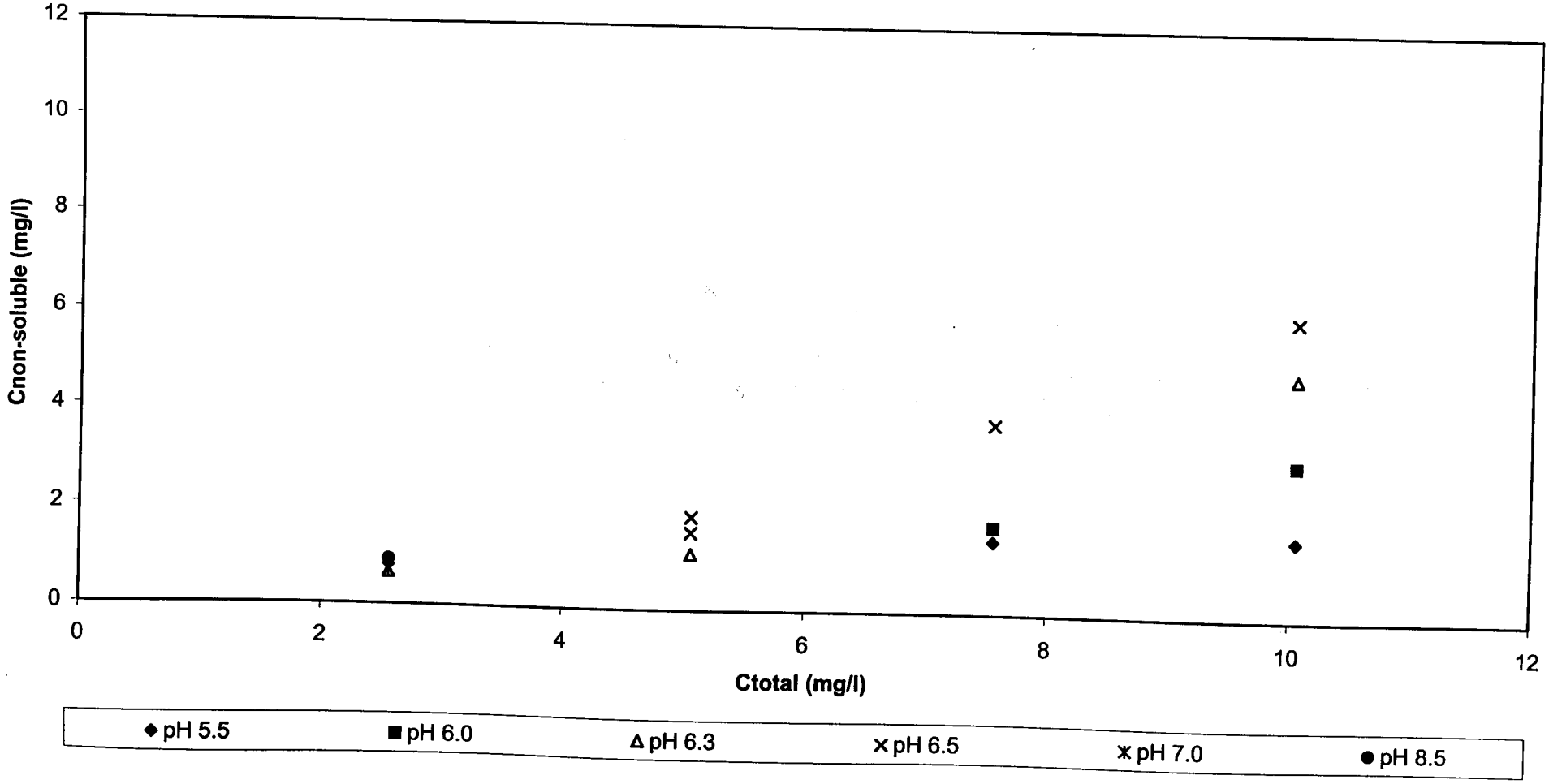


Figure C.112: ***Cd adsorption in Primary Effluent in Competition Experiment Solids Concentration B (86 mg/l)***

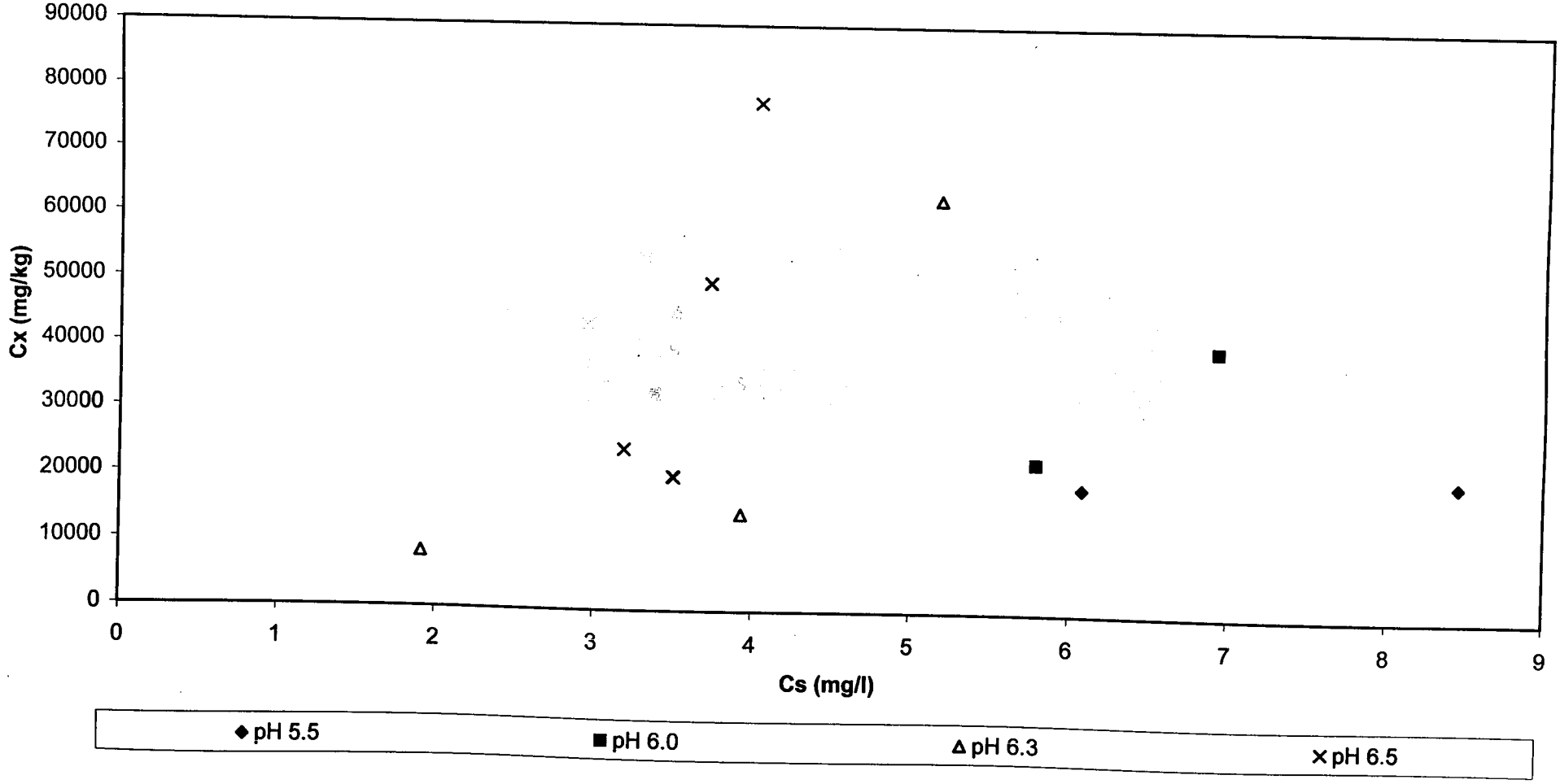


Figure C.113: ***Cu adsorption in Primary Effluent in Competition Experiment Solids Concentration B (86 mg/l)***

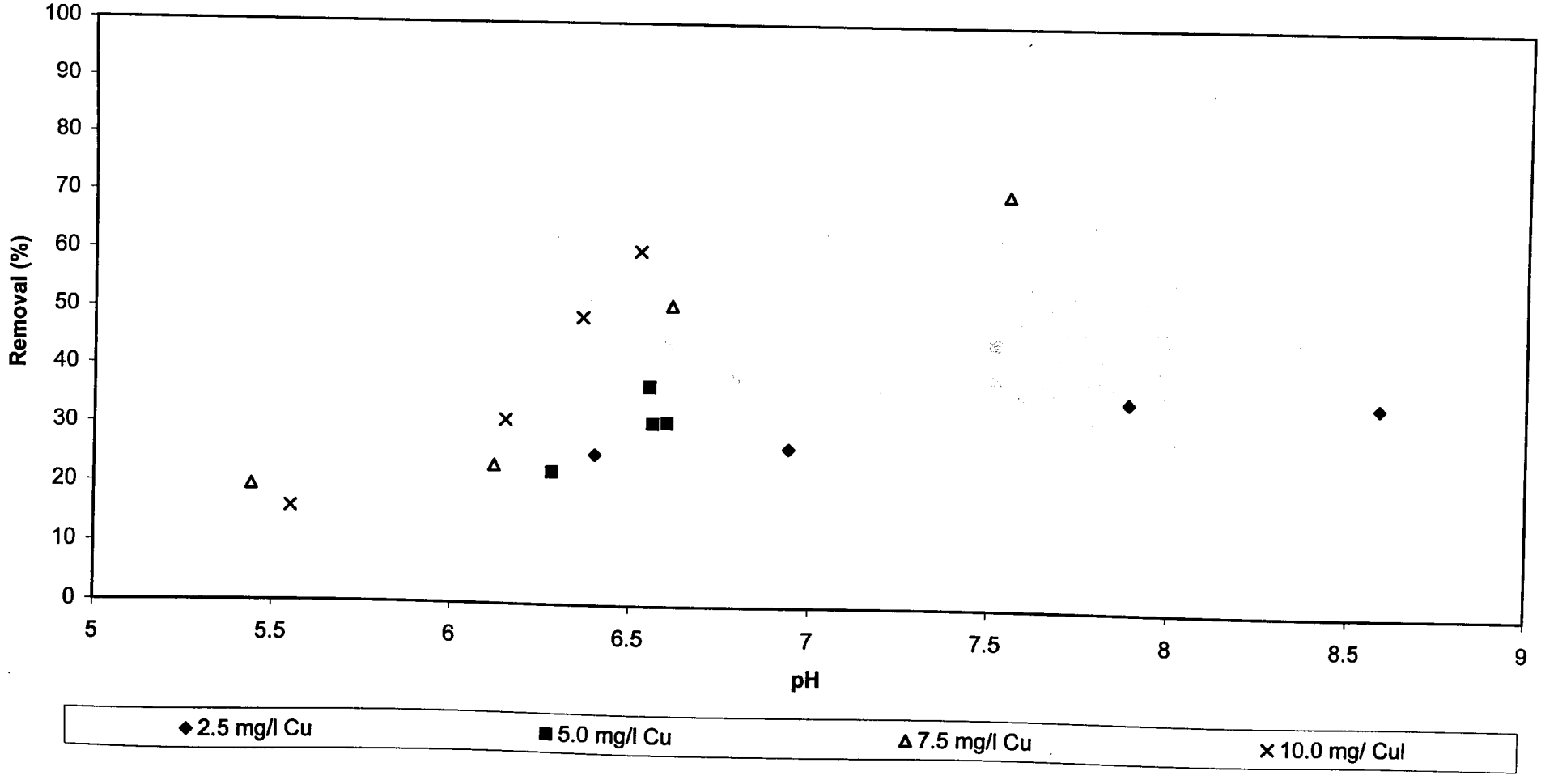


Figure C.114: ***Cu adsorption in Primary Effluent in Competition Experiment Solids Concentration C (125 mg/l)***

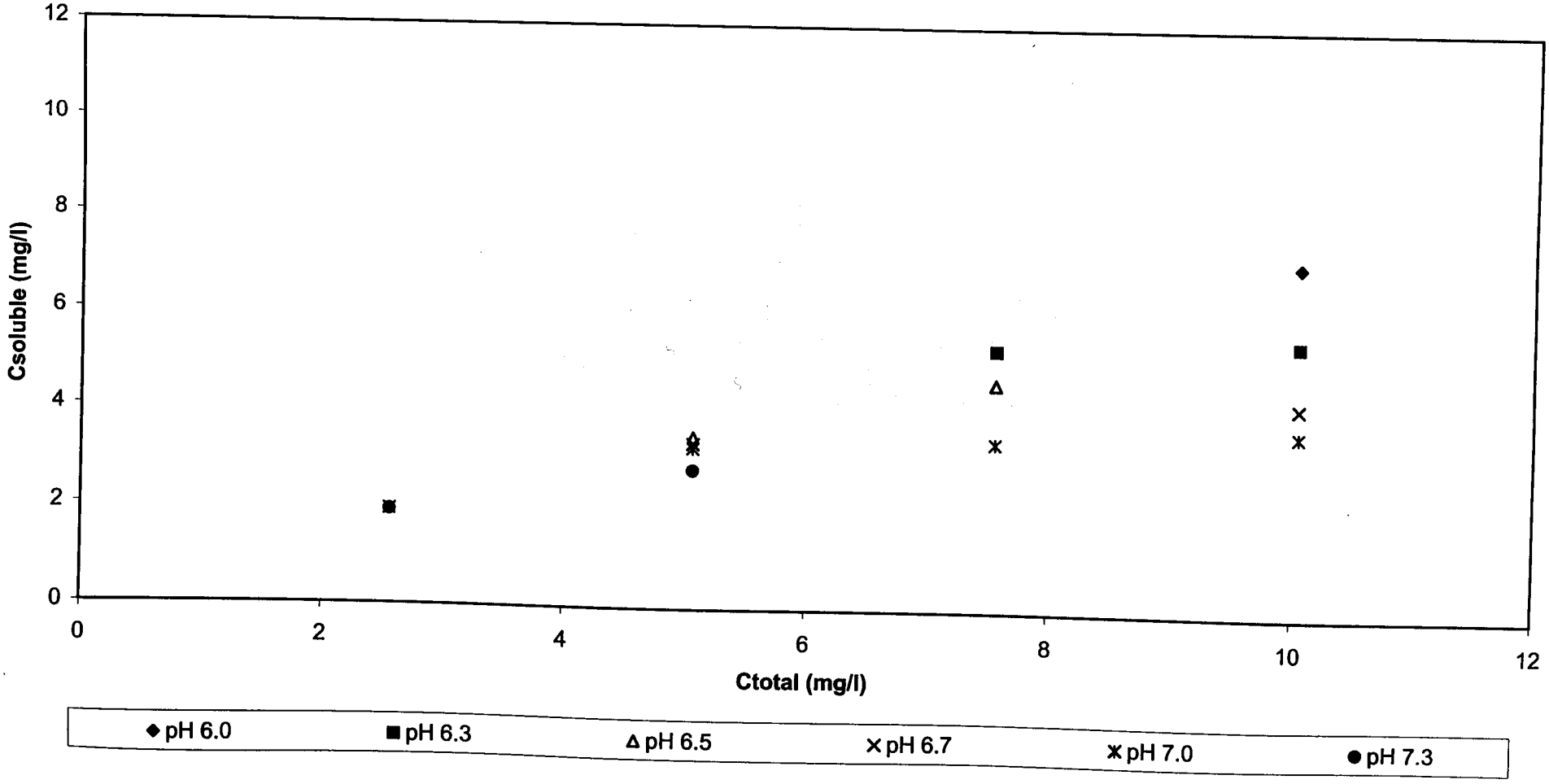


Figure C.115: ***Cu adsorption in Primary Effluent in Competition Experiment Solids Concentration C (125 mg/l)***

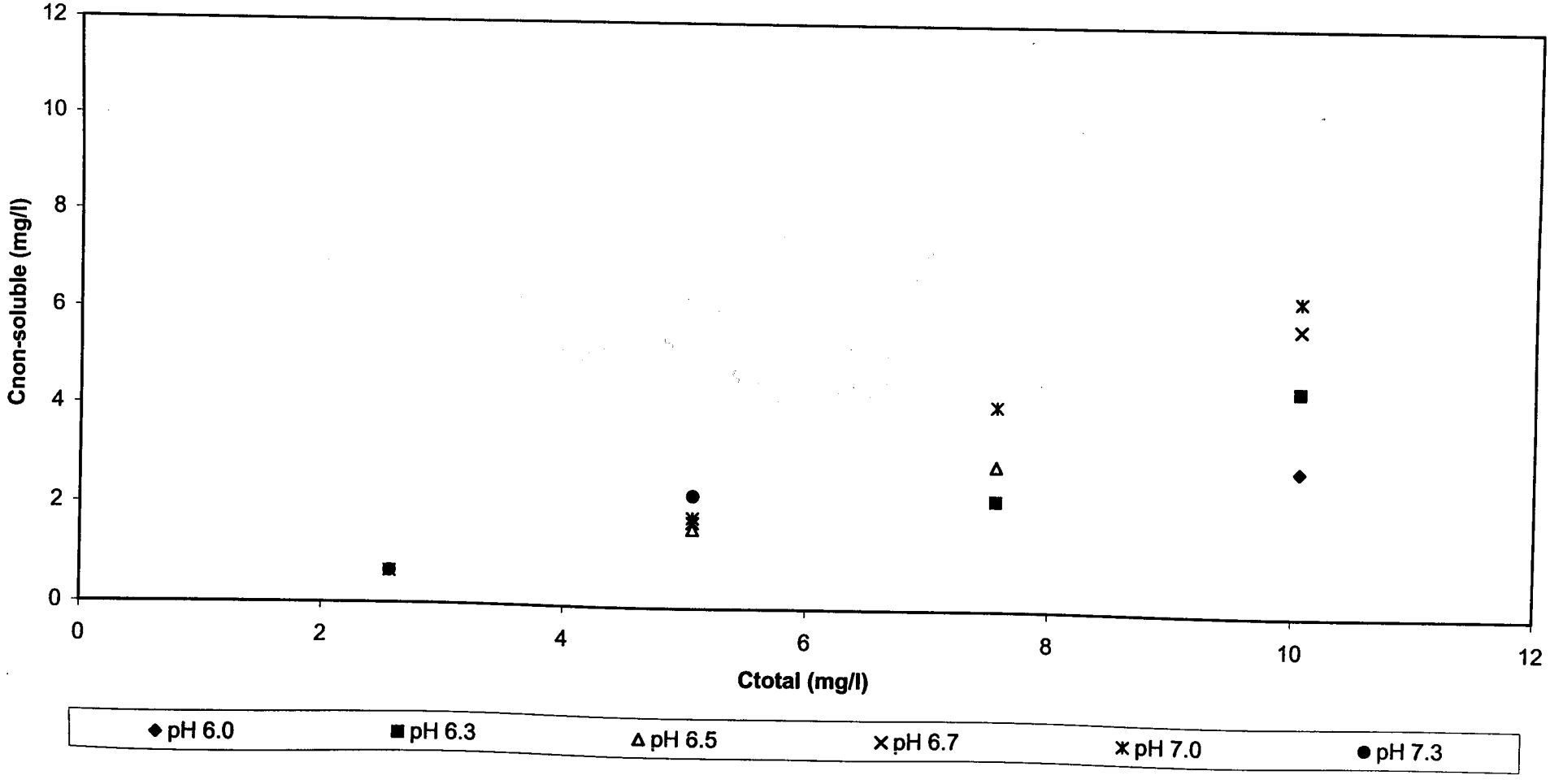


Figure C.116: ***Cu adsorption in Primary Effluent in Competition Experiment Solids Concentration C (125 mg/l)***

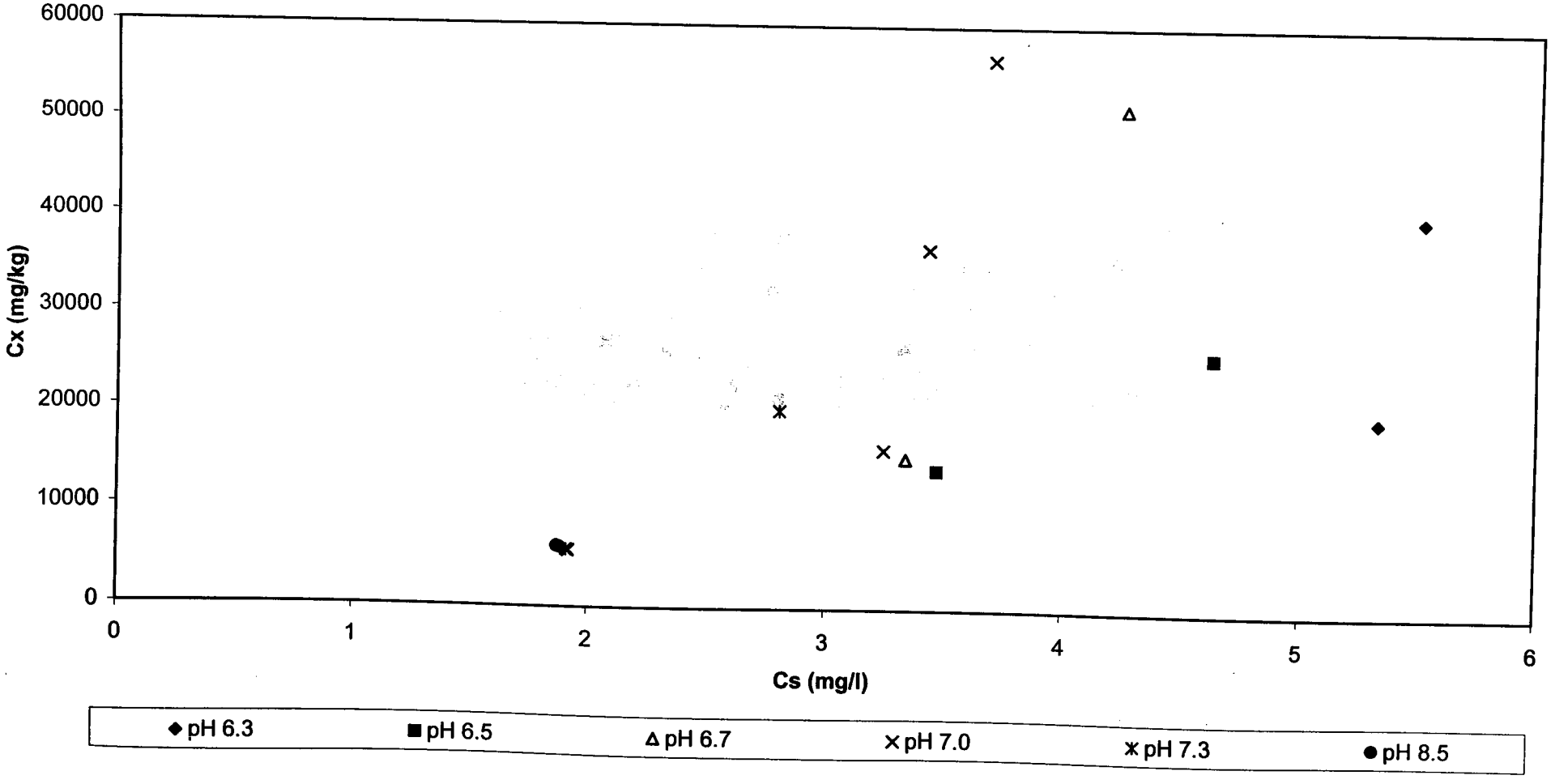


Figure C.117: ***Cu adsorption in Primary Effluent in Competition Experiment Solids Concentration C (125 mg/l)***

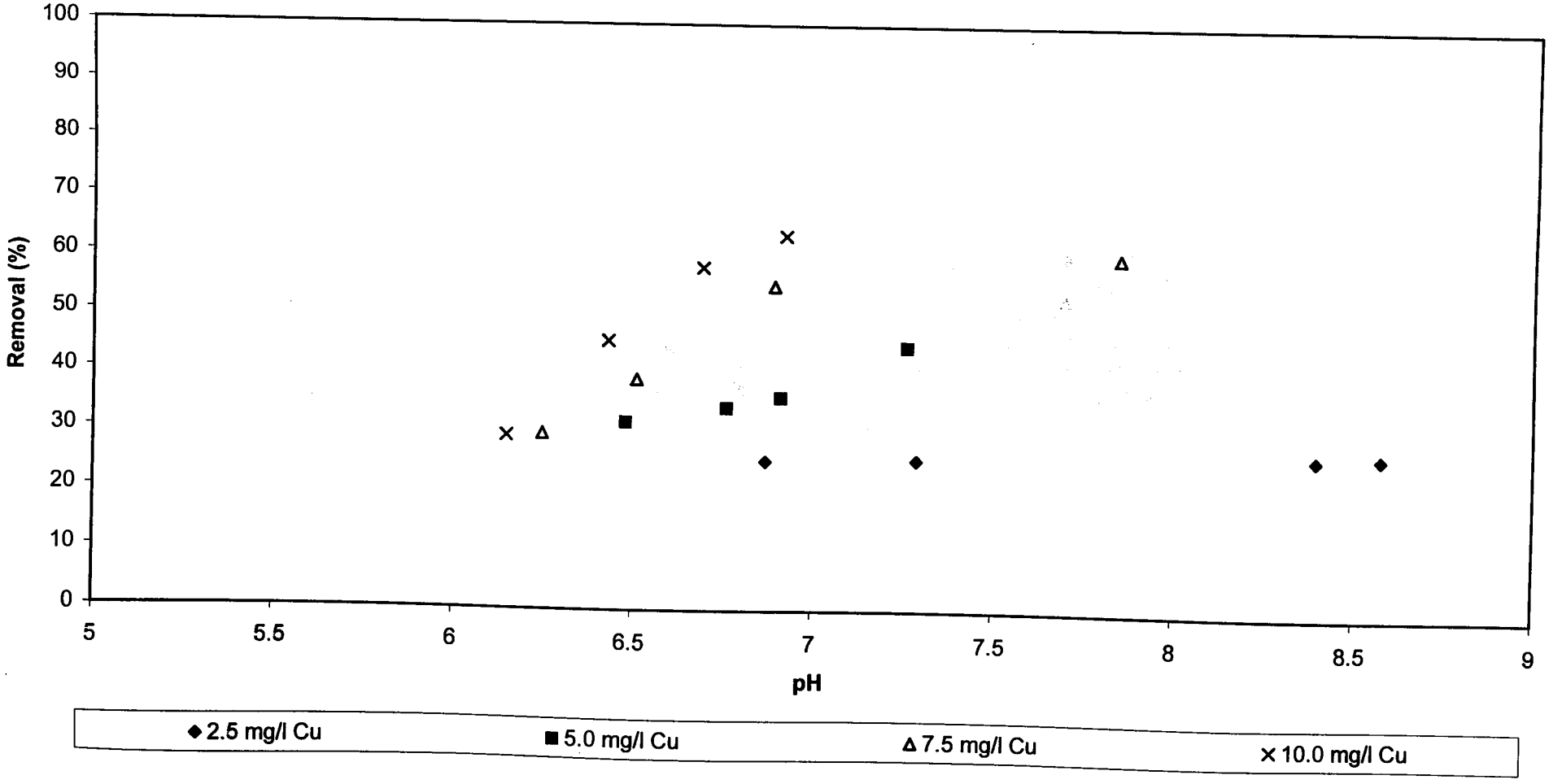


Figure C.118: ***Zn adsorption in Primary Effluent in Competition Experiment Solids Concentration A (94 mg/l)***

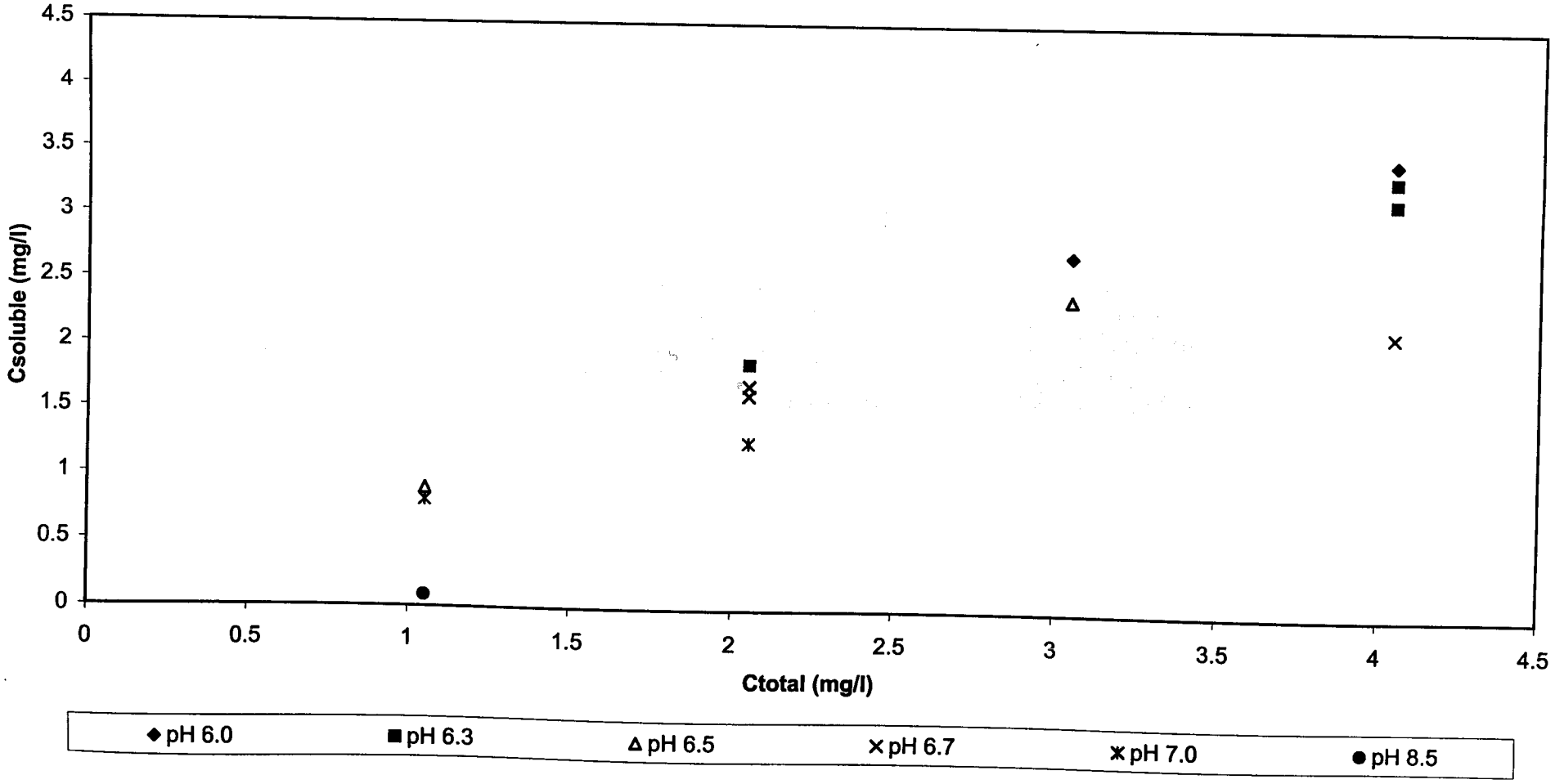


Figure C.119: ***Zn adsorption in Primary Effluent in Competition Experiment Solids Concentration A (94 mg/l)***

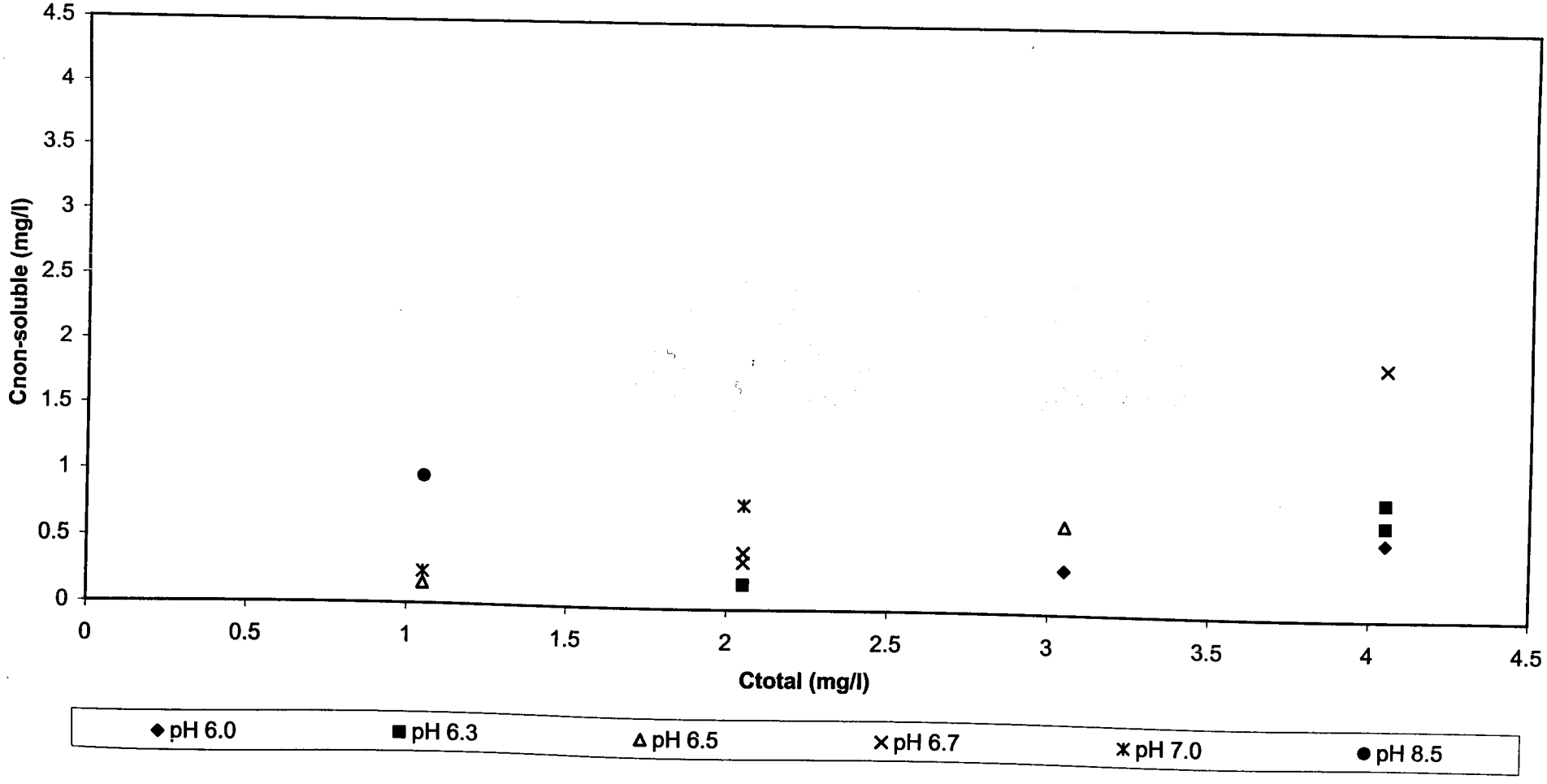


Figure C.120: ***Zn adsorption in Primary Effluent in Competition Experiment Solids Concentration A (94 mg/l)***

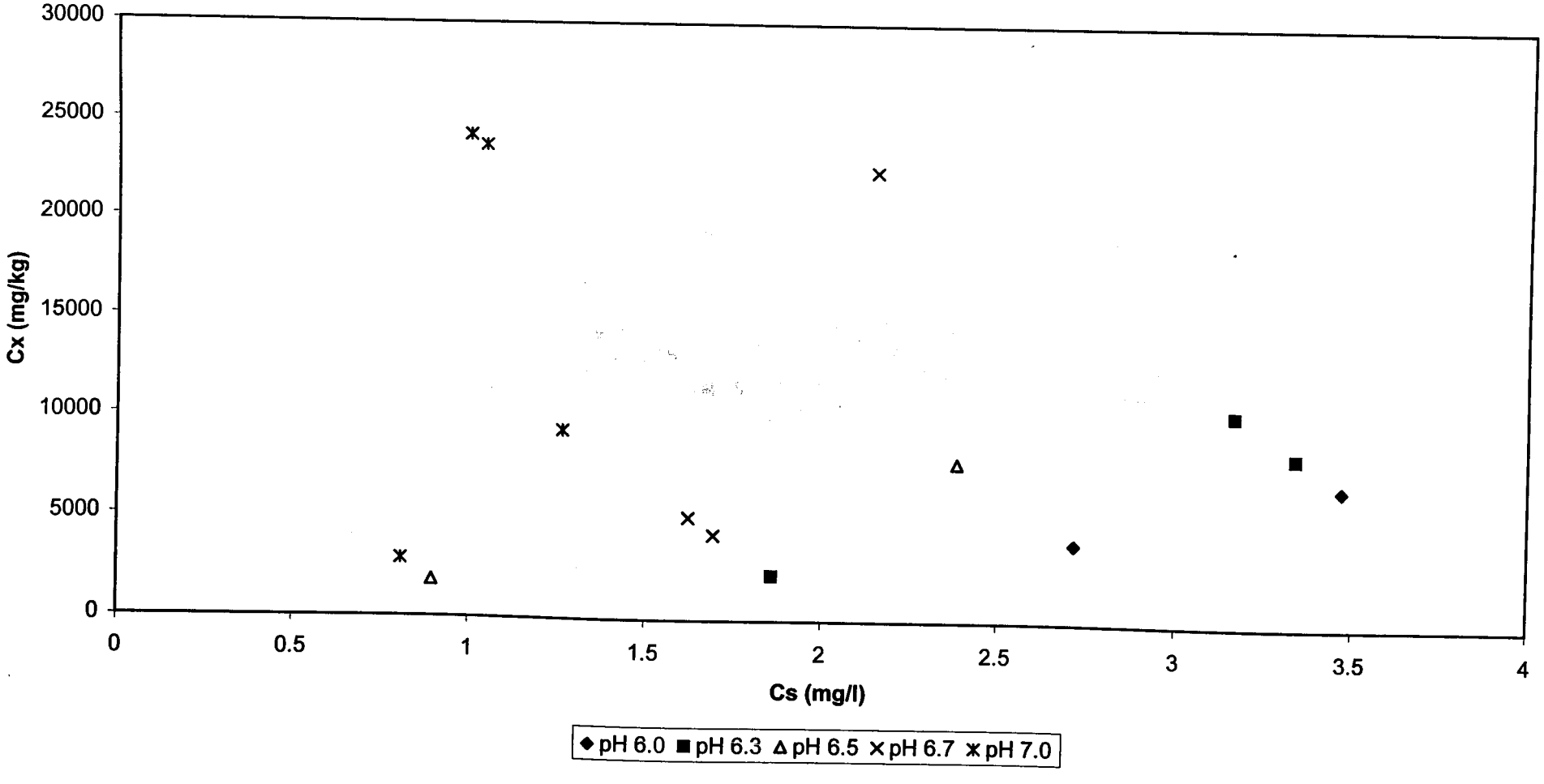


Figure C.121: ***Zn adsorption in Primary Effluent in Competition Experiment Solids Concentration A (94 mg/l)***

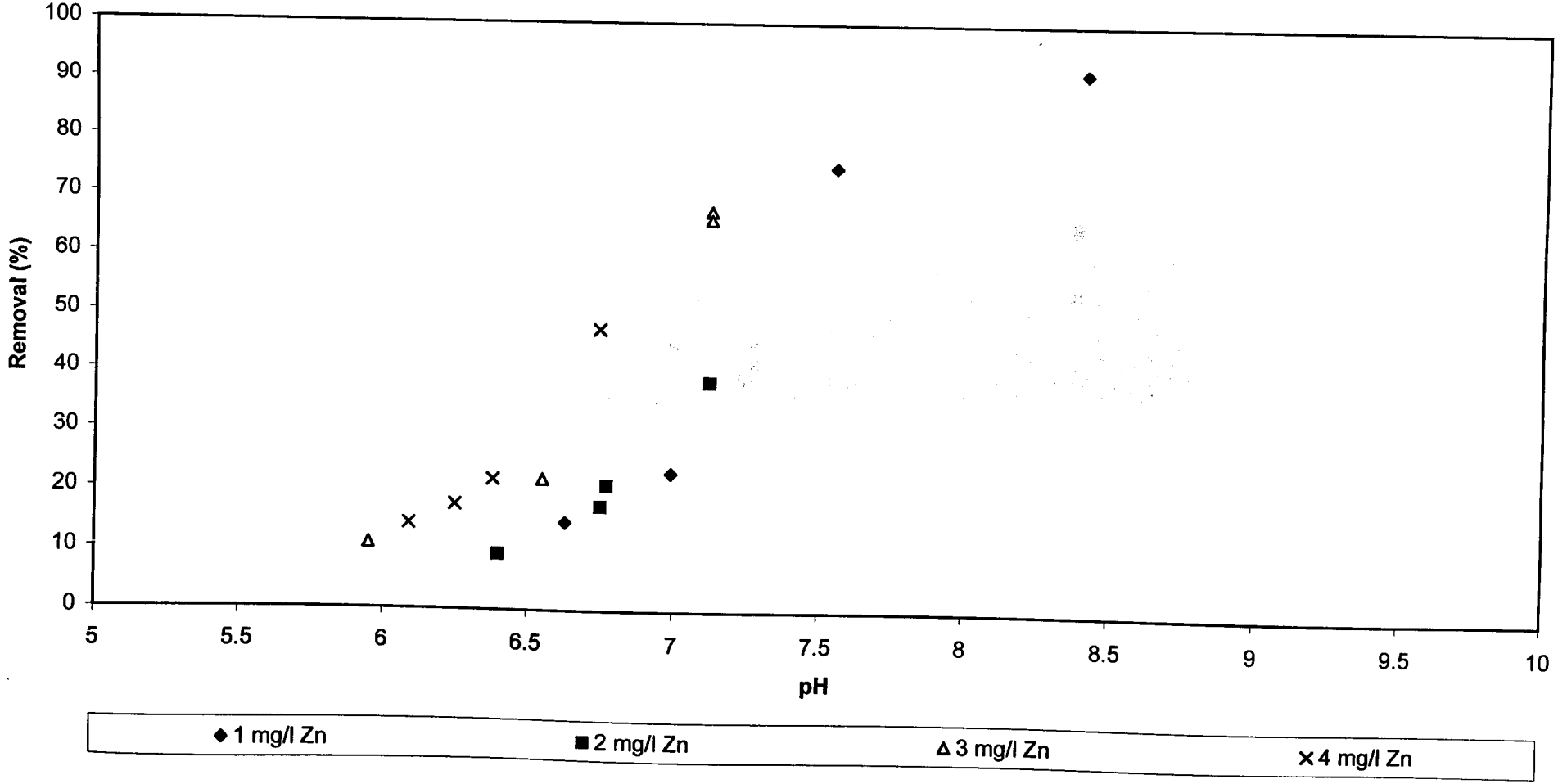


Figure C.122: ***Zn adsorption in Primary Effluent in Competition Experiment Solids Concentration B (86 mg/l)***

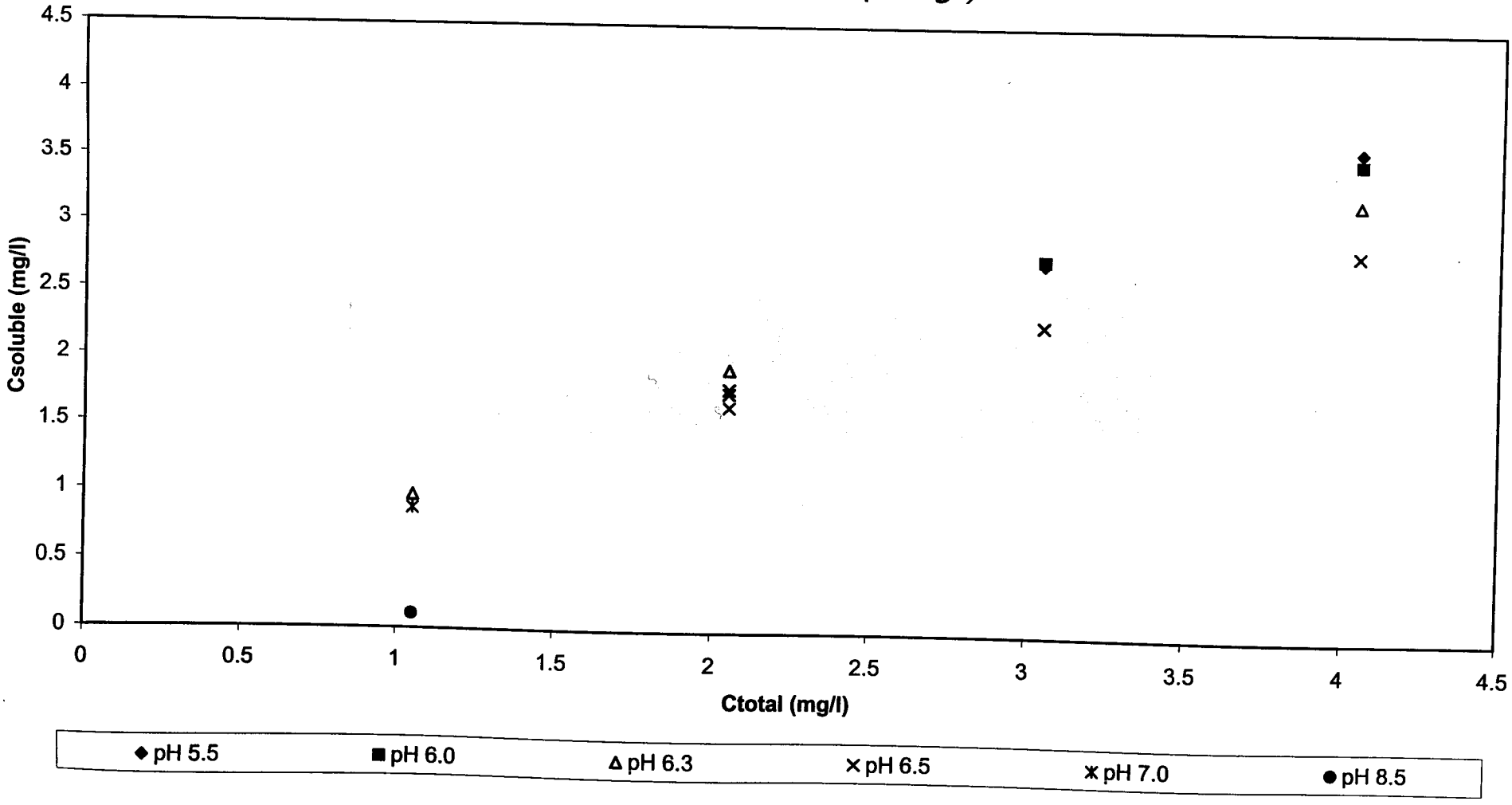


Figure C.123: ***Zn adsorption in Primary Effluent in Competition Experiment Solids Concentration B (86 mg/l)***

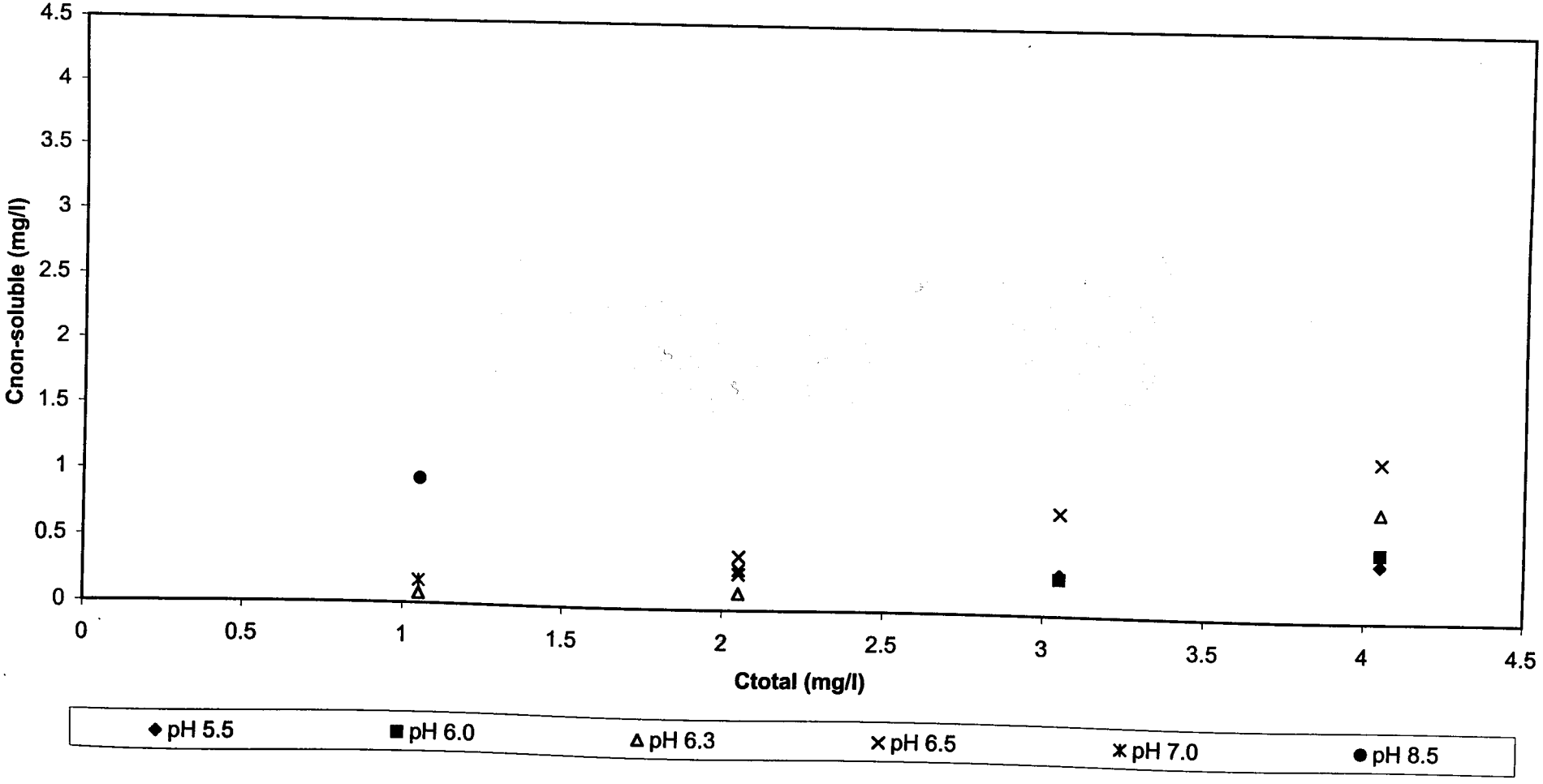


Figure C.124: ***Zn adsorption in Primary Effluent in Competition Experiment Solids Concentration B (86 mg/l)***

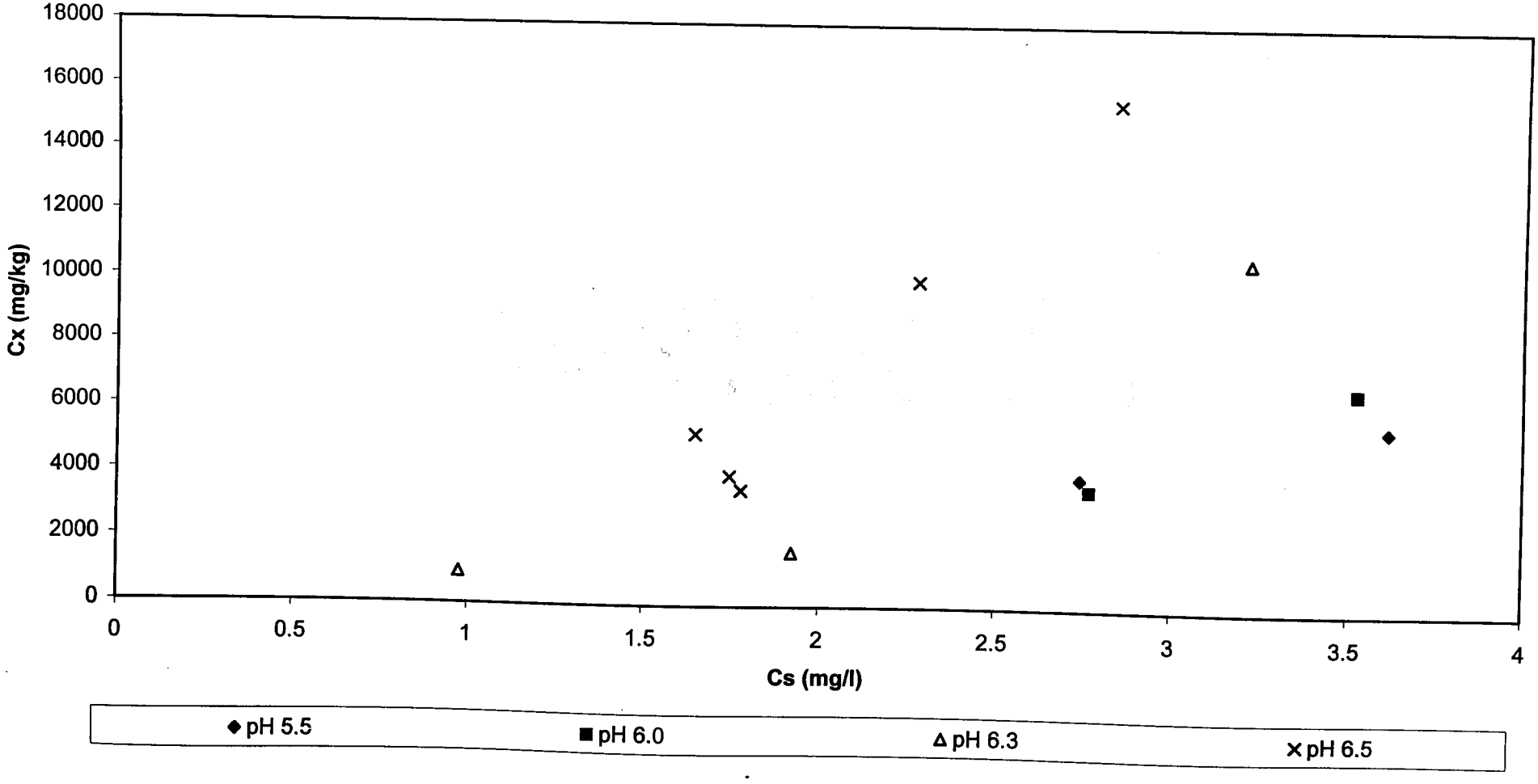


Figure C.125: ***Zn adsorption in Primary Effluent in Competition Experiment Solids Concentration B (86 mg/l)***

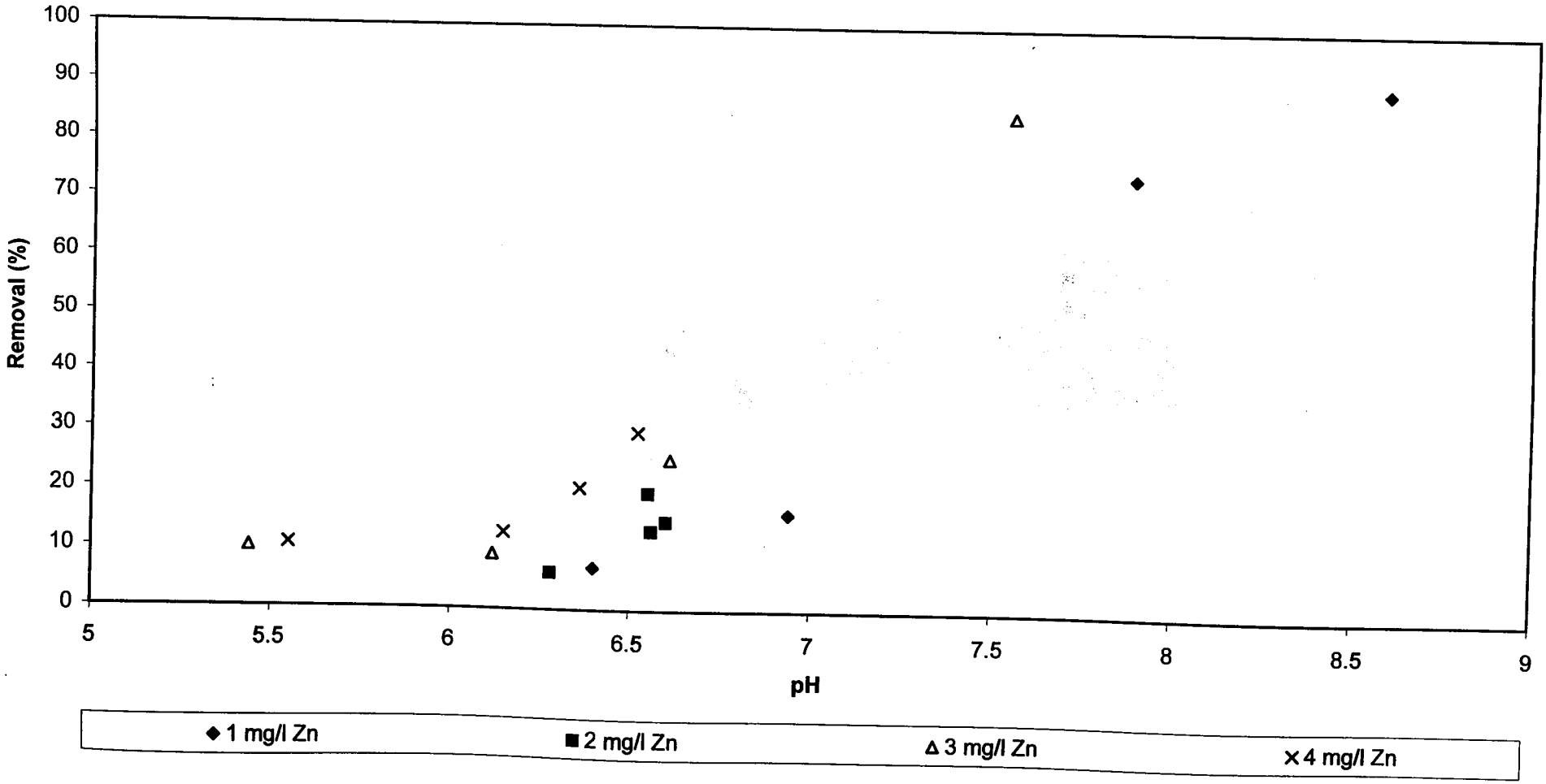


Figure C.126: ***Zn adsorption in Primary Effluent in Competition Experiment Solids Concentration C (125 mg/l)***

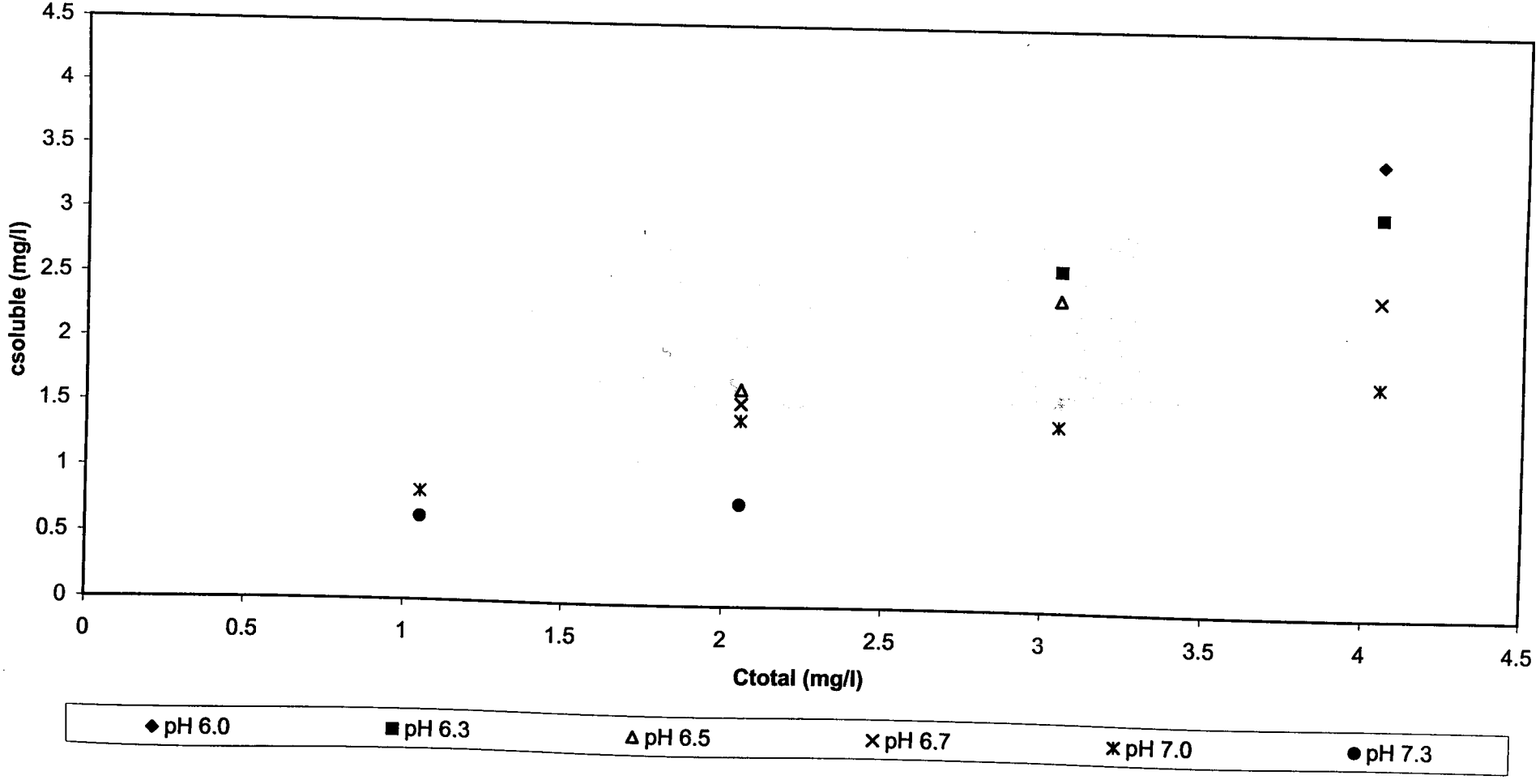


Figure C.127: ***Zn adsorption in Primary Effluent in Competition Experiment Solids Concentration C (125 mg/l)***

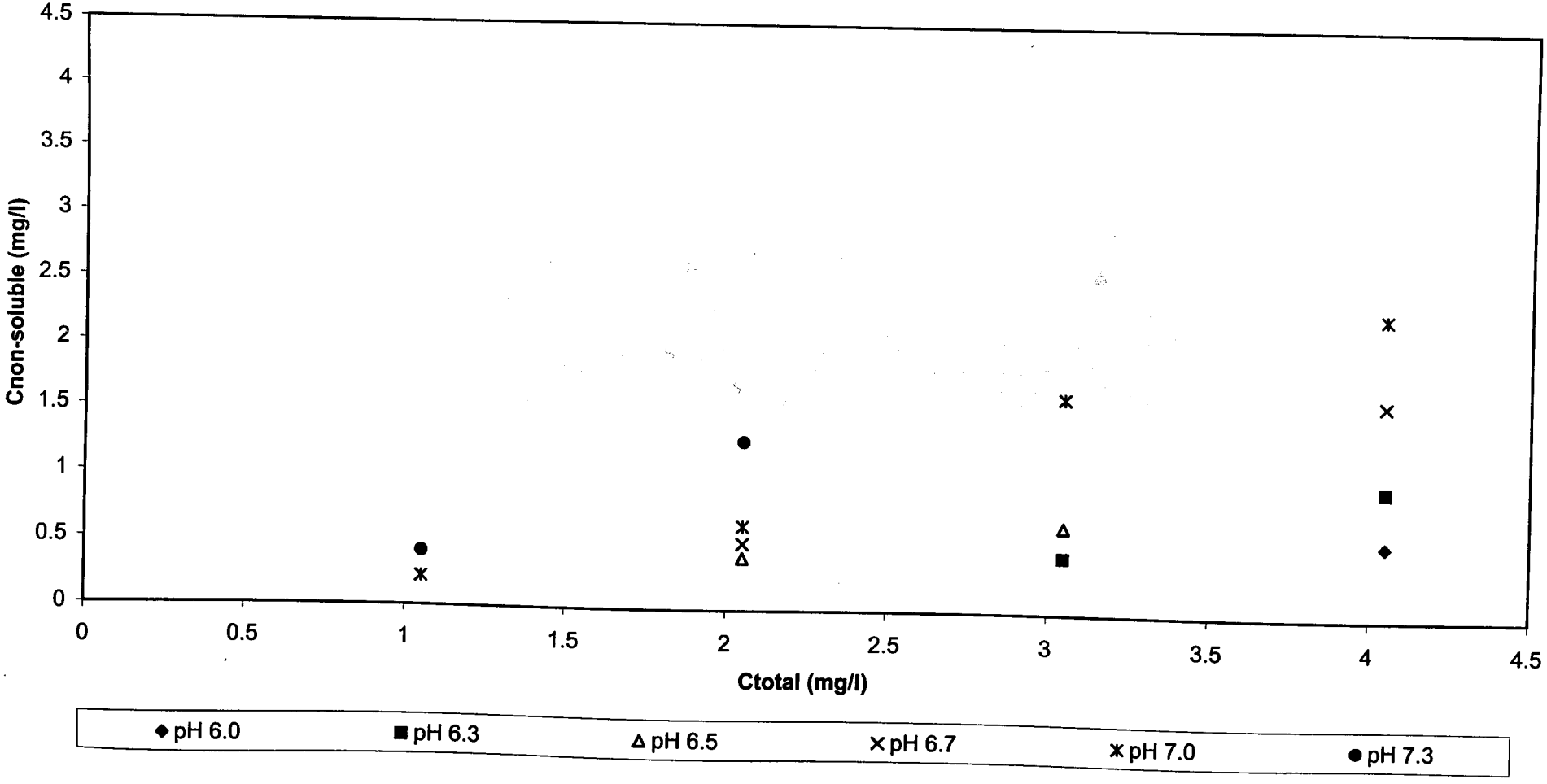


Figure C.128: ***Zn adsorption in Primary Effluent in Competition Experiment Solids Concentration C (125 mg/l)***

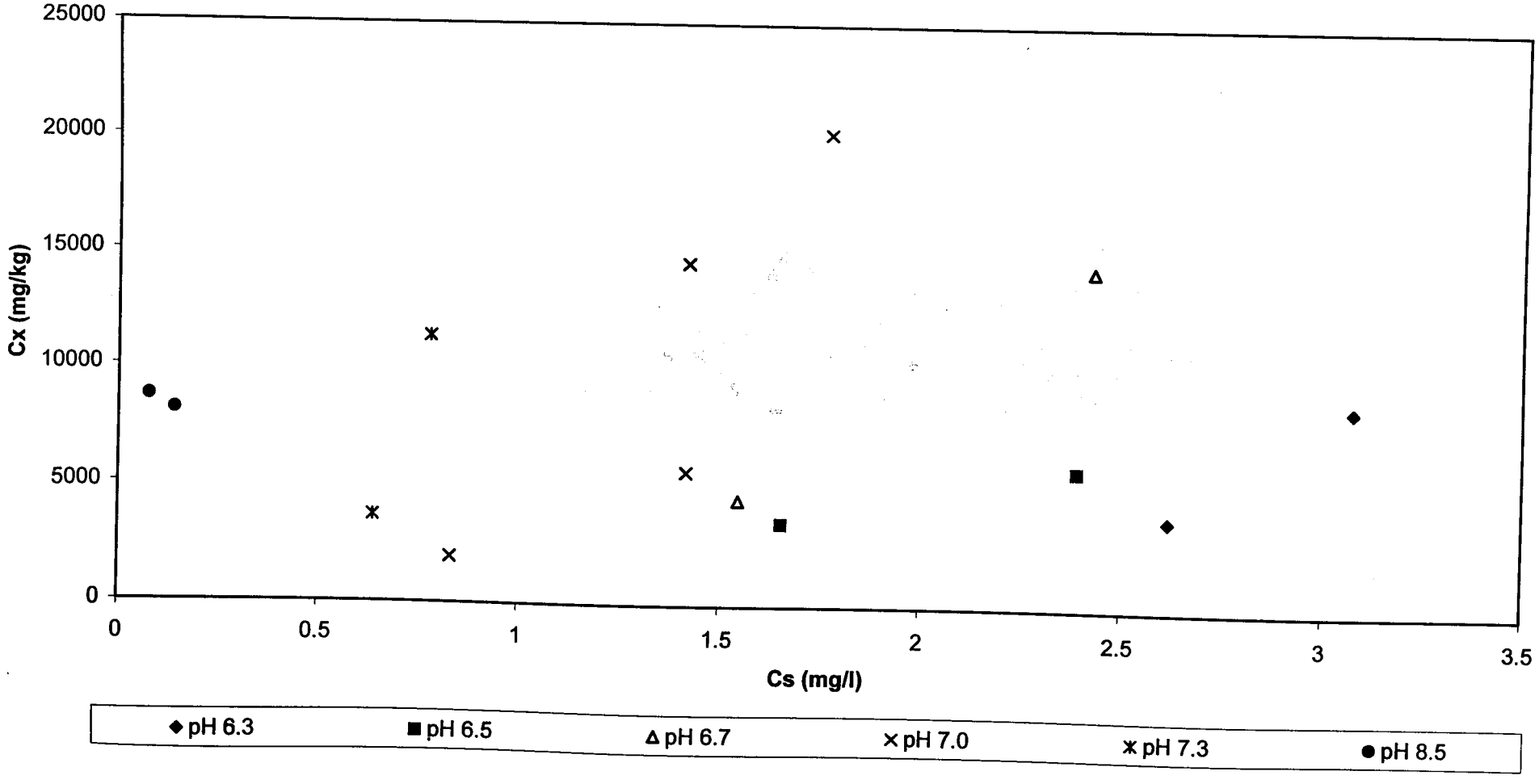


Figure C.129: ***Zn adsorption in Primary Effluent in Competition Experiment Solids Concentration C (125 mg/l)***

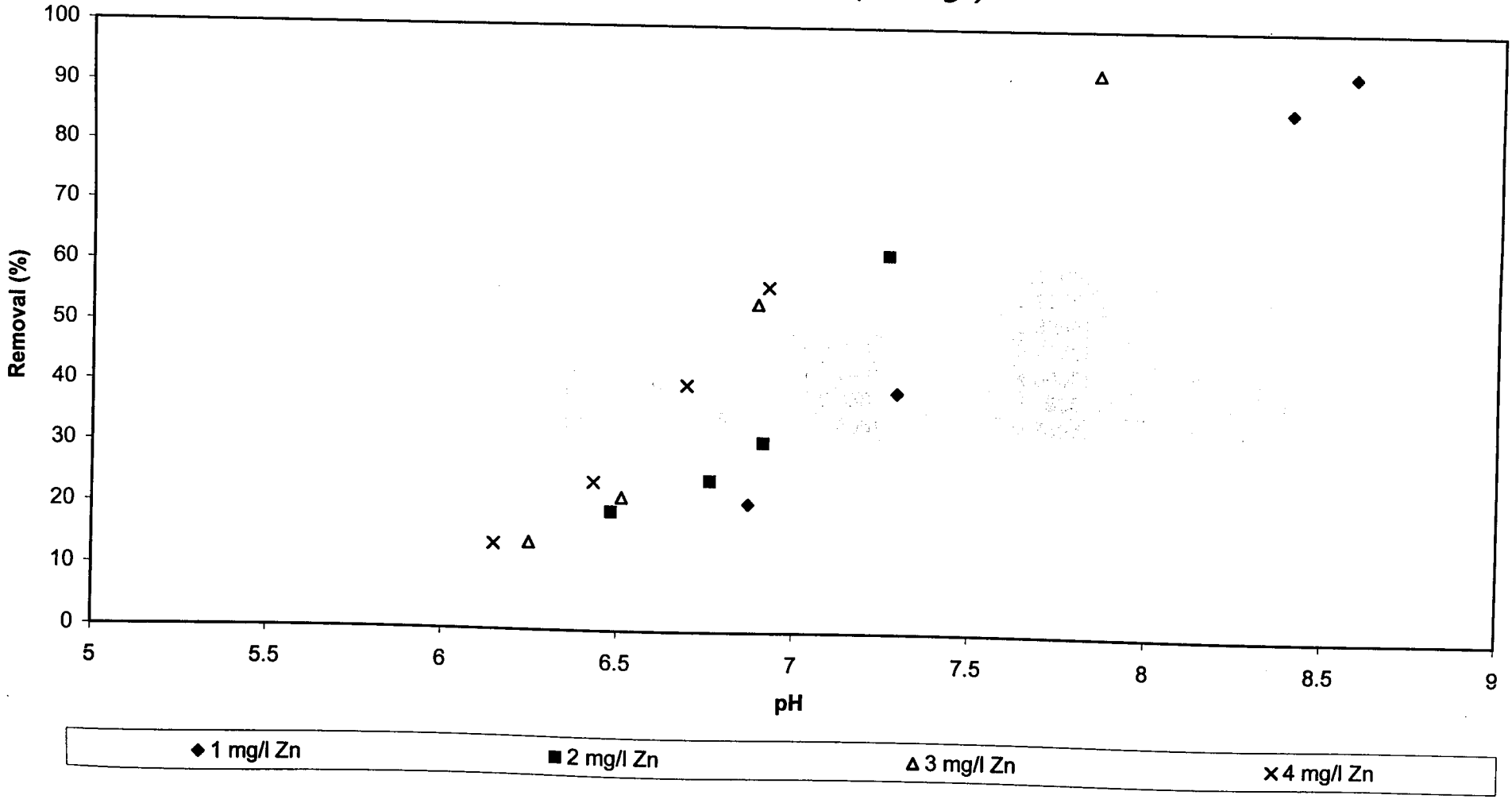


Table C.20 *Competition Adsorption Experiments Mixed Liquor*

Date Carried out 31-Aug-00

Date analysed: 11-Sep-00

Initial Total Cu (mg/l) 0.5515

Initial Total Zn (mg/l) 0.3621

Actual Sample	TSS (mg/l)	pH	Cu Added (mg/l)	Residual Soluble Cu (mg/l)	Adsorbed Cu (mg/l)	Adsorbed Cu (mg/kg)	Total Cu (mg/l)
A-1-1	1800	6.77	2.5	1.566	1.4855	916.9753086	3.0515
A-1-2	1800	6.72	2.5	1.535	1.5165	936.1111111	3.0515
A-1-3	1800	6.85	2.5	1.67	1.3815	852.7777778	3.0515
A-1-4	1800	7.18	2.5	1.574	1.4775	912.037037	3.0515
A-2-1	1800	6.41	5	3.206	2.3455	1447.839506	5.5515
A-2-2	1800	6.85	5	3.316	2.2355	1379.938272	5.5515
A-2-3	1800	6.96	5	3.453	2.0985	1295.37037	5.5515
A-2-4	1800	7.2	5	3.378	2.1735	1341.666667	5.5515
A-3-1	1800	6.44	7.5	4.941	3.1105	1920.061728	8.0515
A-3-2	1800	6.8	7.5	5.074	2.9775	1837.962963	8.0515
A-3-3	1800	6.71	7.5	5.222	2.8295	1746.604938	8.0515
A-3-4	1800	7.1	7.5	5.274	2.7775	1714.506173	8.0515
A-4-1	1800	6.05	10	6.248	4.3035	2656.481481	10.5515
A-4-2	1800	6.4	10	6.658	3.8935	2403.395062	10.5515
A-4-3	1800	6.66	10	6.806	3.7455	2312.037037	10.5515
A-4-4	1800	6.82	10	6.934	3.6175	2233.024691	10.5515
B-1-1	1058	6.83	2.5	1.691	1.3605	1428.796471	3.0515
B-1-2	1058	7.2	2.5	1.782	1.2695	1333.228313	3.0515
B-1-3	1058	7.35	2.5	1.868	1.1835	1242.911153	3.0515
B-1-4	1058	8.15	2.5	1.929	1.1225	1178.848981	3.0515
B-2-1	1058	6.47	5	3.346	2.2055	2316.215081	5.5515
B-2-2	1058	6.74	5	3.364	2.1875	2297.311489	5.5515
B-2-3	1058	7.1	5	3.701	1.8505	1943.394245	5.5515
B-2-4	1058	7.25	5	3.762	1.7895	1879.332073	5.5515
B-3-1	1058	6.51	7.5	5.385	2.6665	2800.357068	8.0515
B-3-2	1058	6.84	7.5	5.746	2.3055	2421.235035	8.0515
B-3-3	1058	7.19	7.5	5.687	2.3645	2483.196807	8.0515
B-3-4	1058	7.2	7.5	5.779	2.2725	2386.57845	8.0515
B-4-1	1058	6.27	10	7.114	3.4375	3610.060912	10.5515

Cu and Zn competitive adsorption in mixed liquor

Actual Sample	TSS (mg/l)	pH	Cu Added (mg/l)	Residual Soluble Cu (mg/l)	Adsorbed Cu (mg/l)	Adsorbed Cu (mg/kg)	Total Cu (mg/l)
B-4-2	1058	6.67	10	7.151	3.4005	3571.203529	10.5515
B-4-3	1058	6.67	10	7.265	3.2865	3451.480781	10.5515
B-4-4	1058	6.8	10	7.396	3.1555	3313.904642	10.5515
C-1-1	2500	6.61	2.5	1.385	1.6665	740.6666667	3.0515
C-1-2	2500	7	2.5	1.441	1.6105	715.7777778	3.0515
C-1-3	2500	7.26	2.5	1.417	1.6345	726.4444444	3.0515
C-1-4	2500	7.3	2.5	1.492	1.5595	693.1111111	3.0515
C-2-1	2500	6.43	5	2.776	2.7755	1233.555556	5.5515
C-2-2	2500	6.68	5	2.781	2.7705	1231.333333	5.5515
C-2-3	2500	6.83	5	2.917	2.6345	1170.888889	5.5515
C-2-4	2500	7	5	3.07	2.4815	1102.888889	5.5515
C-3-1	2500	6.48	7.5	4.52	3.5315	1569.555556	8.0515
C-3-2	2500	6.71	7.5	4.619	3.4325	1525.555556	8.0515
C-3-3	2500	6.99	7.5	4.734	3.3175	1474.444444	8.0515
C-3-4	2500	7.26	7.5	4.952	3.0995	1377.555556	8.0515
C-4-1	2500	6.23	10	5.815	4.7365	2105.111111	10.5515
C-4-2	2500	6.46	10	5.916	4.6355	2060.222222	10.5515
C-4-3	2500	6.66	10	6.292	4.2595	1893.111111	10.5515
C-4-4	2500	6.8	10	6.303	4.2485	1888.222222	10.5515

Cu and Zn competitive adsorption in mixed liquor

Zn Added (mg/l)	Residual Soluble Zn (mg/l)	Adsorbed Zn (mg/l)	Adsorbed Zn (mg/kg)	Total Zn (mg/l)
1	0.256	1.1061	682.7777778	1.3621
1	0.242	1.1201	691.4197531	1.3621
1	0.284	1.0781	665.4938272	1.3621
1	0.191	1.1711	722.9012346	1.3621
2	0.712	1.6501	1018.580247	2.3621
2	0.419	1.9431	1199.444444	2.3621
2	0.51	1.8521	1143.271605	2.3621
2	0.357	2.0051	1237.716049	2.3621
3	0.936	2.4261	1497.592593	3.3621
3	0.788	2.5741	1588.950617	3.3621
3	0.831	2.5311	1562.407407	3.3621
3	0.617	2.7451	1694.506173	3.3621
4	1.667	2.6951	1663.641975	4.3621
4	1.307	3.0551	1885.864198	4.3621
4	1.183	3.1791	1962.407407	4.3621
4	0.996	3.3661	2077.839506	4.3621
1	0.304	1.0581	1111.216131	1.3621
1	0.274	1.0881	1142.722117	1.3621
1	0.263	1.0991	1154.274312	1.3621
1	0.213	1.1491	1206.784289	1.3621
2	0.915	1.4471	1519.743751	2.3621
2	0.57	1.7921	1882.062592	2.3621
2	0.579	1.7831	1872.610796	2.3621
2	0.521	1.8411	1933.522369	2.3621
3	1.364	1.9981	2098.403697	3.3621
3	1.161	2.2011	2311.594203	3.3621
3	0.699	2.6631	2796.786389	3.3621
3	0.708	2.6541	2787.334594	3.3621
4	2.182	2.1801	2289.540013	4.3621

Cu and Zn competitive adsorption in mixed liquor

Zn Added (mg/l)	Residual Soluble Zn (mg/l)	Adsorbed Zn (mg/l)	Adsorbed Zn (mg/kg)	Total Zn (mg/l)
4	1.659	2.7031	2838.794371	4.3621
4	1.757	2.6051	2735.874816	4.3621
4	1.528	2.8341	2976.37051	4.3621
1	0.194	1.1681	519.1555556	1.3621
1	0.189	1.1731	521.3777778	1.3621
1	0.184	1.1781	523.6	1.3621
1	0.168	1.1941	530.7111111	1.3621
2	0.452	1.9101	848.9333333	2.3621
2	0.415	1.9471	865.3777778	2.3621
2	0.391	1.9711	876.0444444	2.3621
2	0.426	1.9361	860.4888889	2.3621
3	0.701	2.6611	1182.711111	3.3621
3	0.692	2.6701	1186.711111	3.3621
3	0.618	2.7441	1219.6	3.3621
3	0.561	2.8011	1244.933333	3.3621
4	1.178	3.1841	1415.155556	4.3621
4	1.012	3.3501	1488.933333	4.3621
4	0.887	3.4751	1544.488889	4.3621
4	0.855	3.5071	1558.711111	4.3621

Cu and Zn competitive adsorption in mixed liquor

Figure C.130: ***Cu adsorption in Mixed Liquor in Competition Experiment Solids Concentration A (1800 mg/l)***

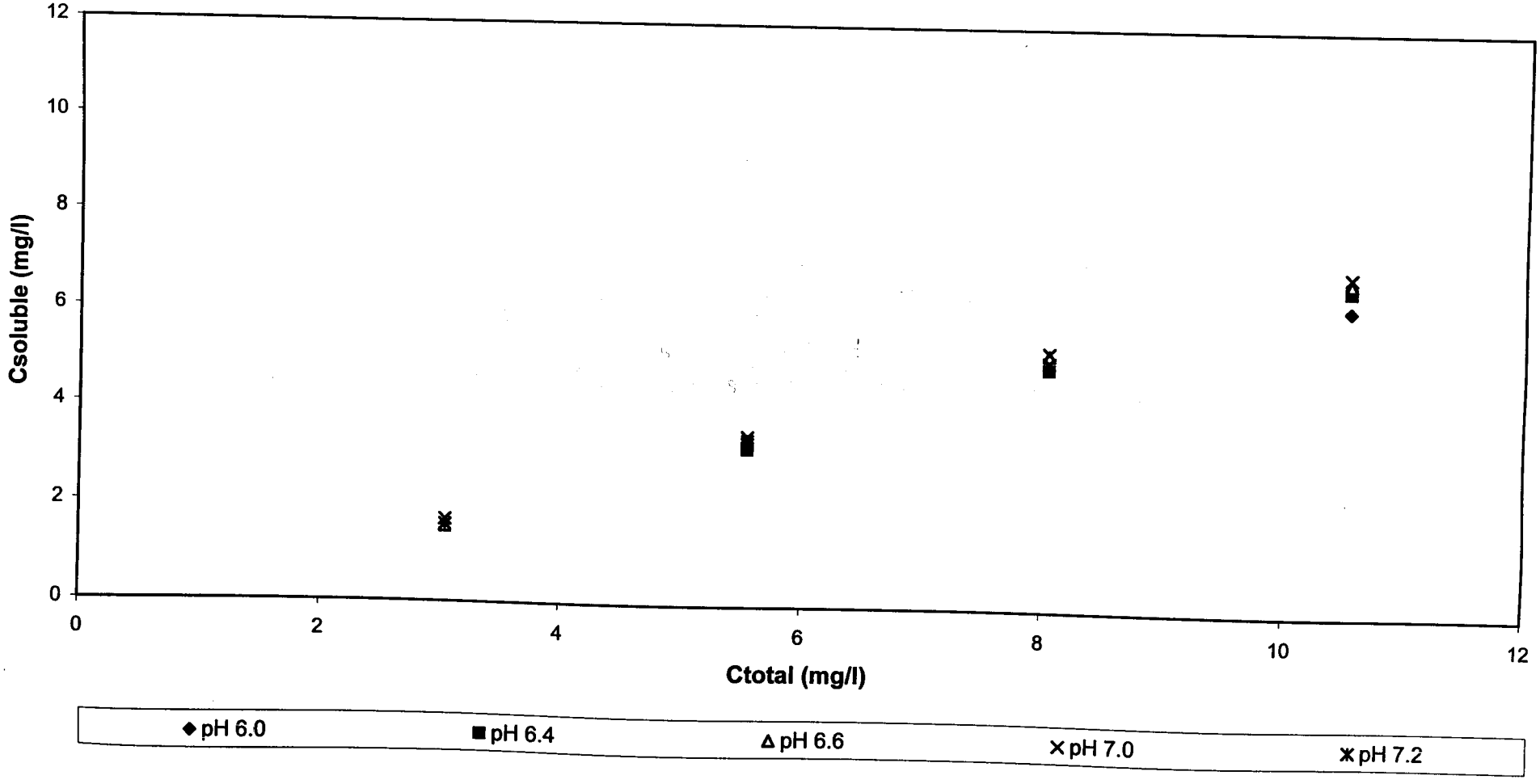


Figure C.131: ***Cu adsorption in Mixed Liquor in Competition Experiment Solids Concentration A (1800 mg/l)***

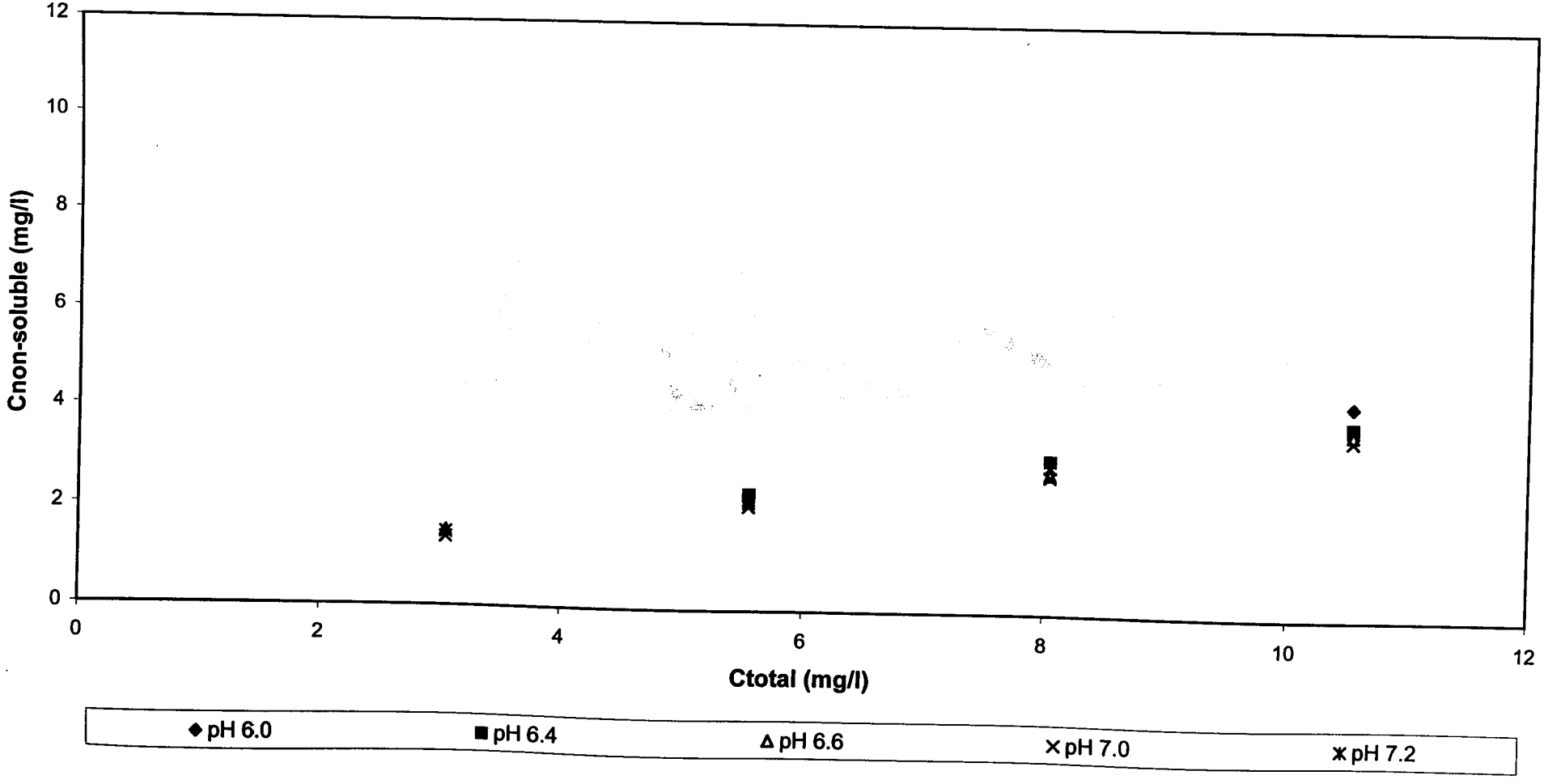


Figure C.132: ***Ca adsorption in Mixed Liquor in Competition Experiment Solids Concentration A (1800 mg/l)***

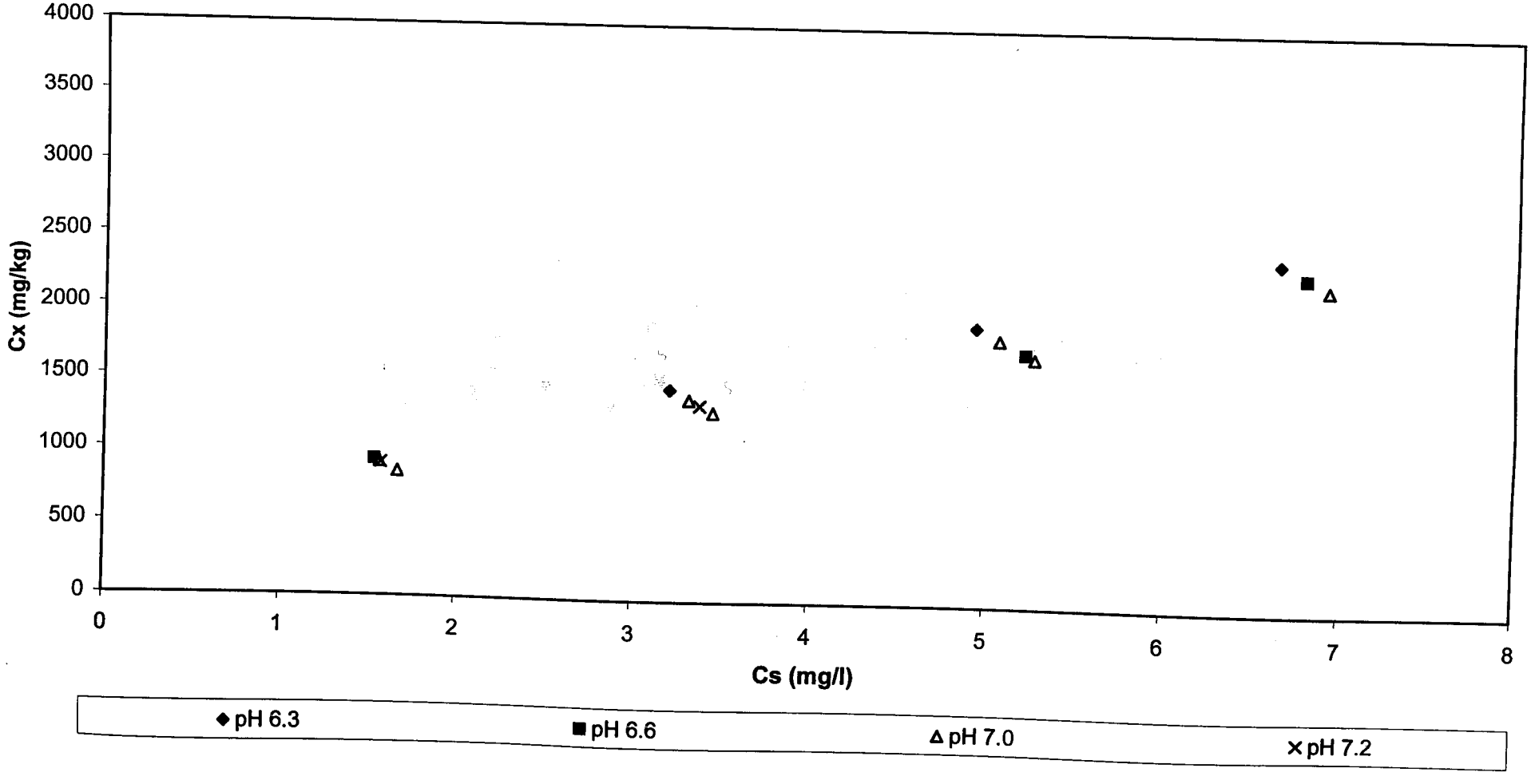


Figure C.133: ***Cu adsorption in Mixed Liquor in Competition Experiment Solids Concentration A (1800 mg/l)***

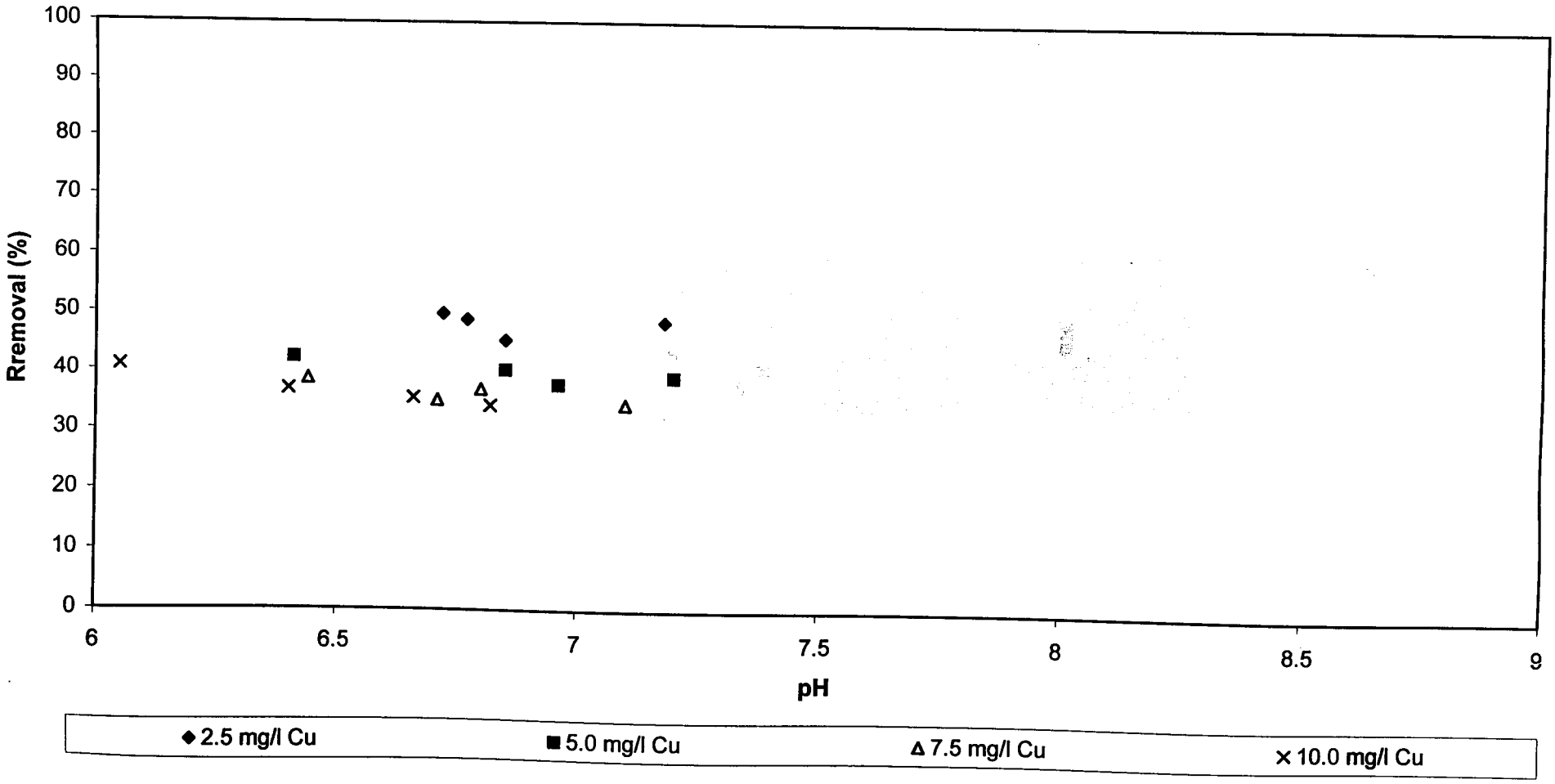


Figure C.134: ***Cu adsorption in Mixed Liquor in Competition Experiment Solids Concentration B (1058 mg/l)***

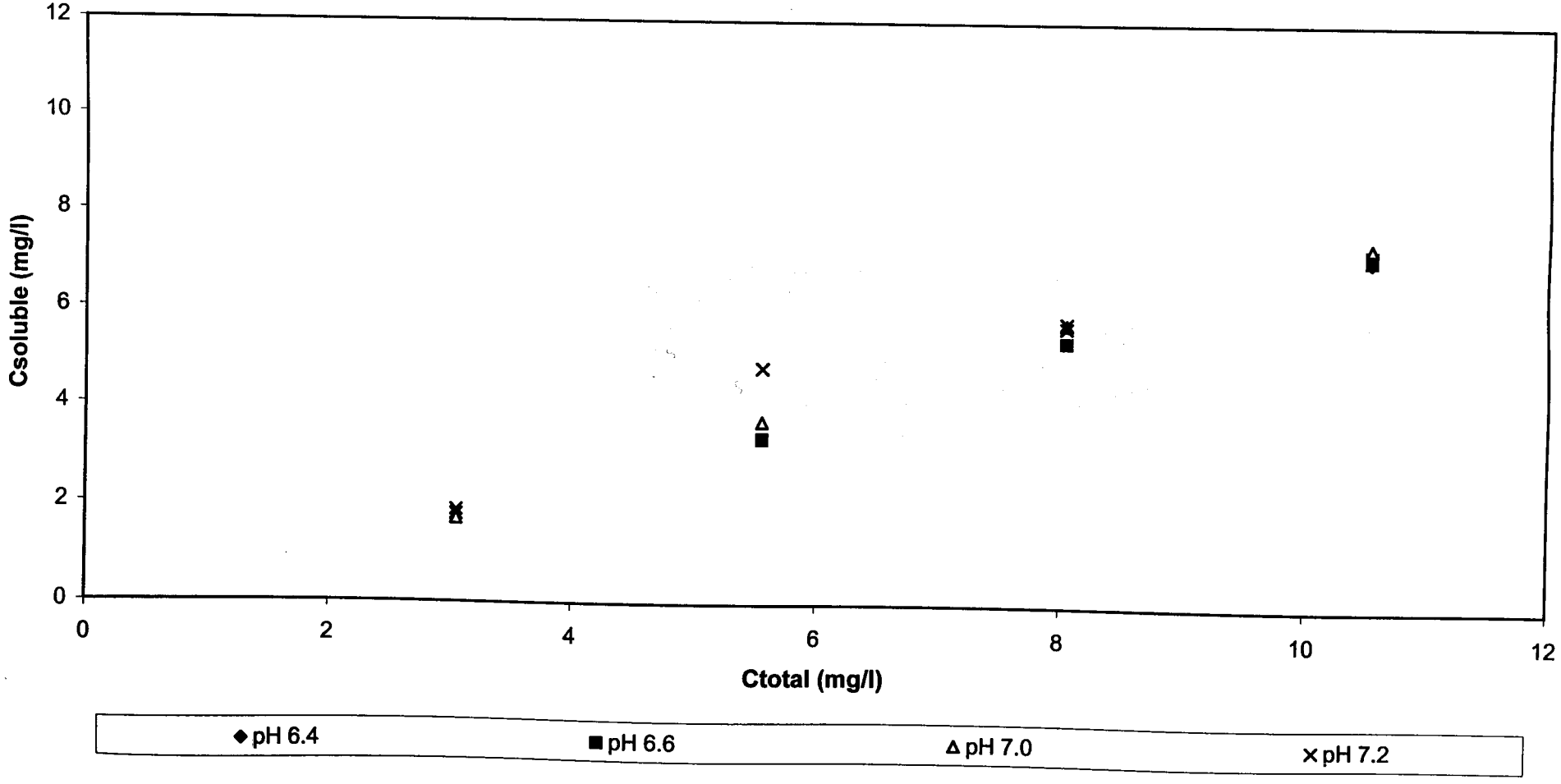


Figure C.135: ***Cu adsorption in Mixed Liquor in Competition Experiment Solids Concentration B (1058 mg/l)***

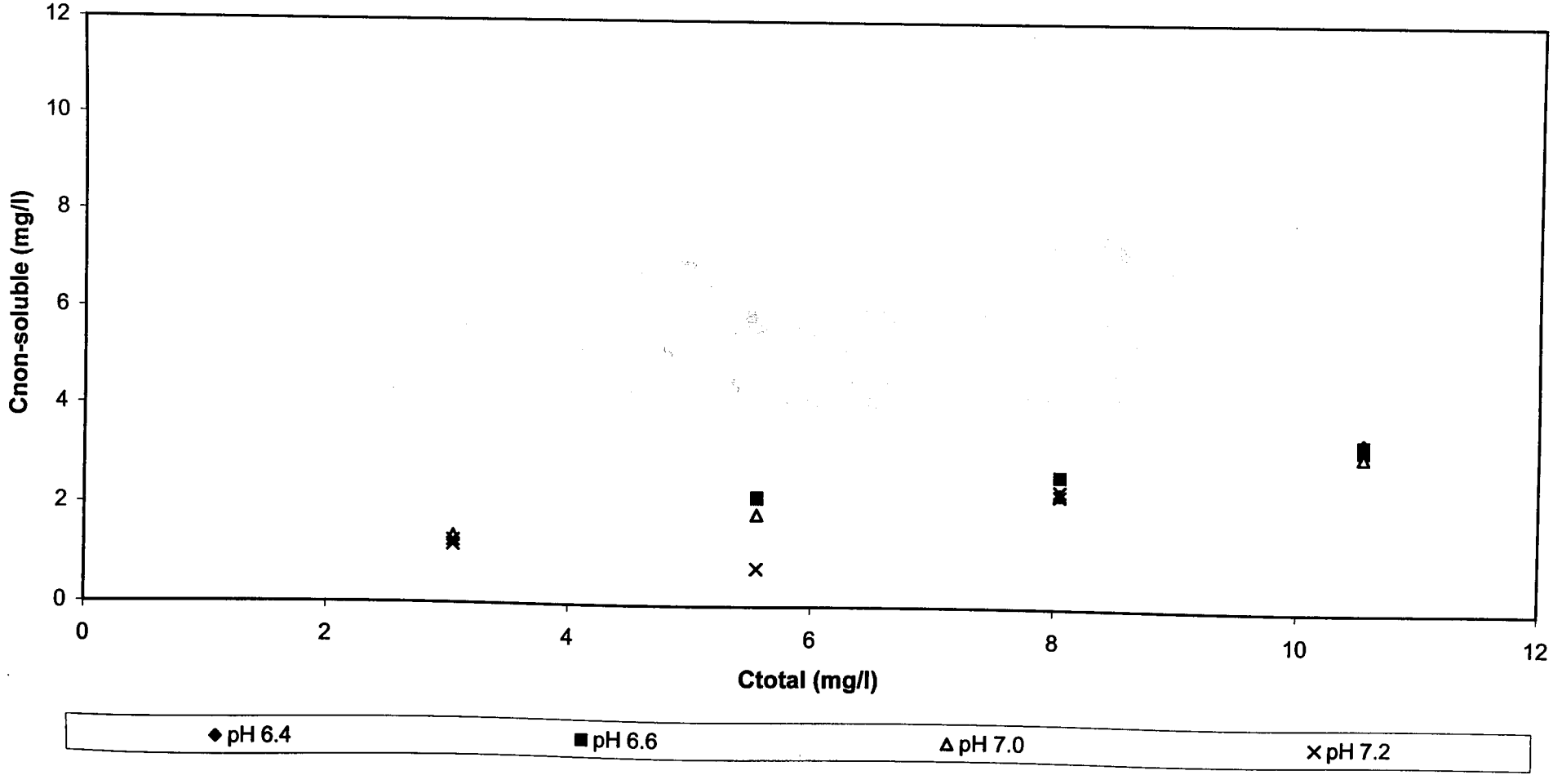


Figure C.136: ***Cu adsorption in Mixed Liquor in Competition Experiment Solids Concentration B (1058 mg/l)***

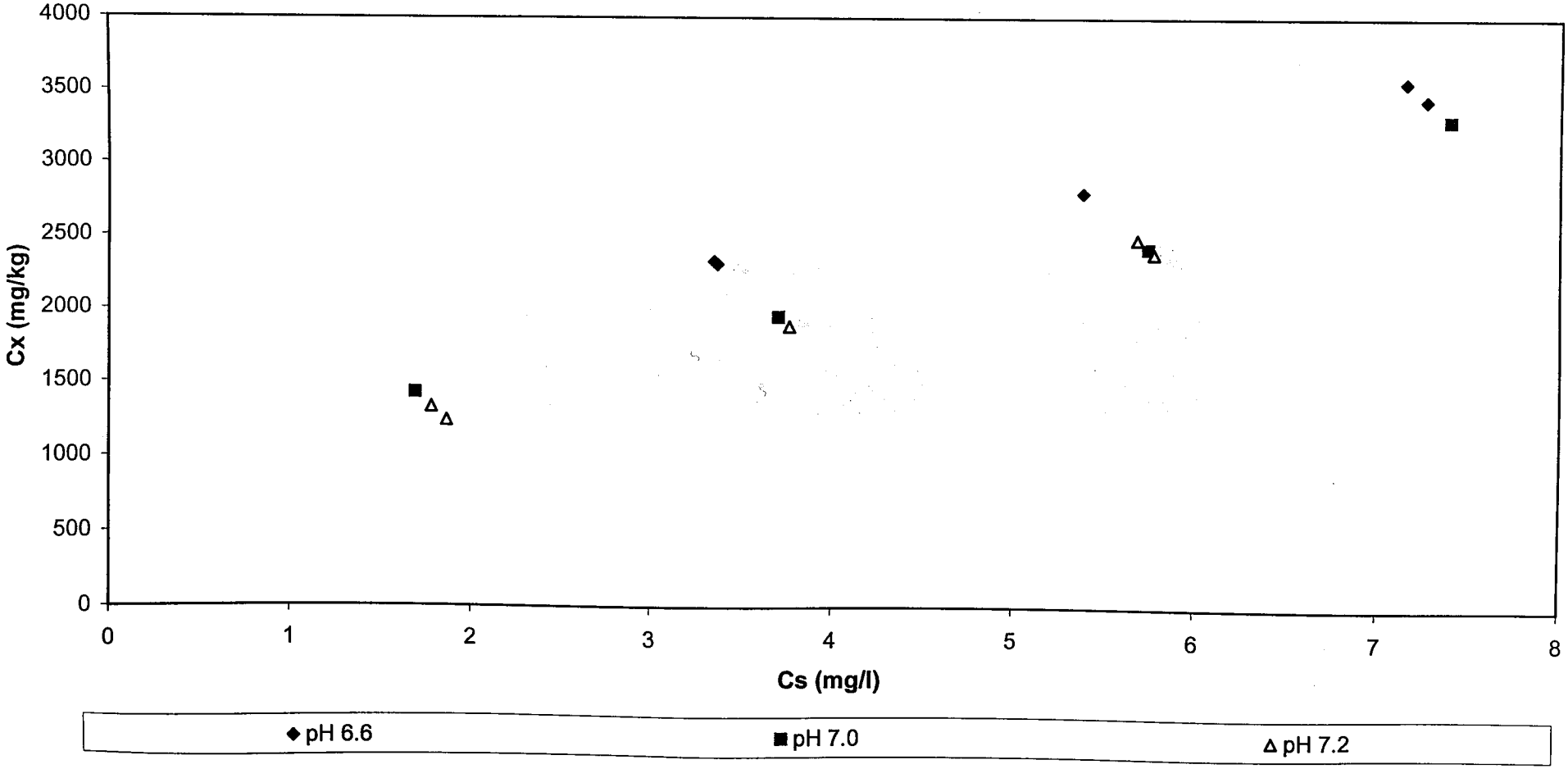


Figure C.136: ***Cu adsorption in Mixed Liquor in Competition Experiment Solids Concentration B (1058 mg/l)***

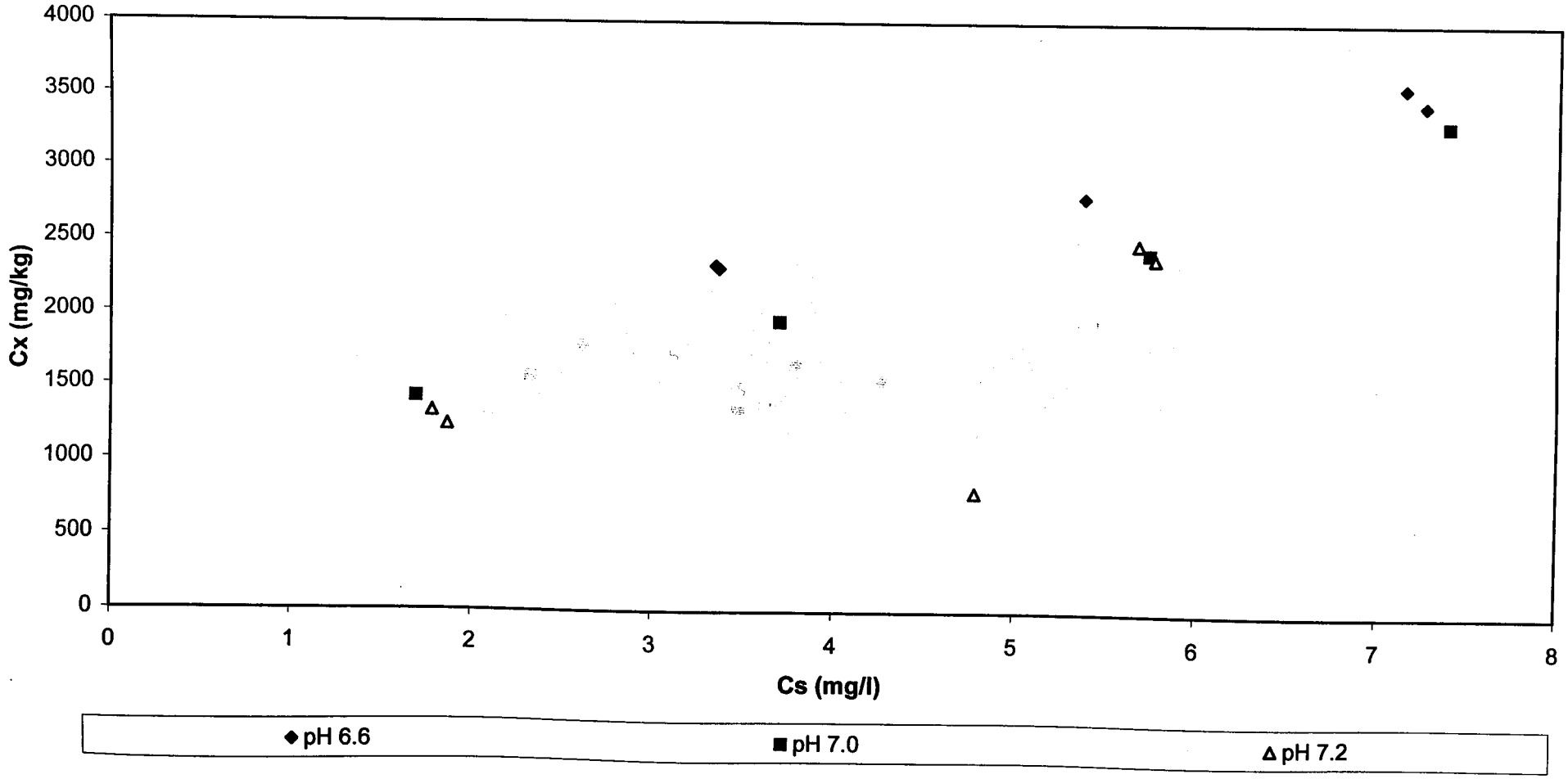


Figure C.137: ***Cu adsorption in Mixed Liquor in Competition Experiment Solids Concentration B (1058 mg/l)***

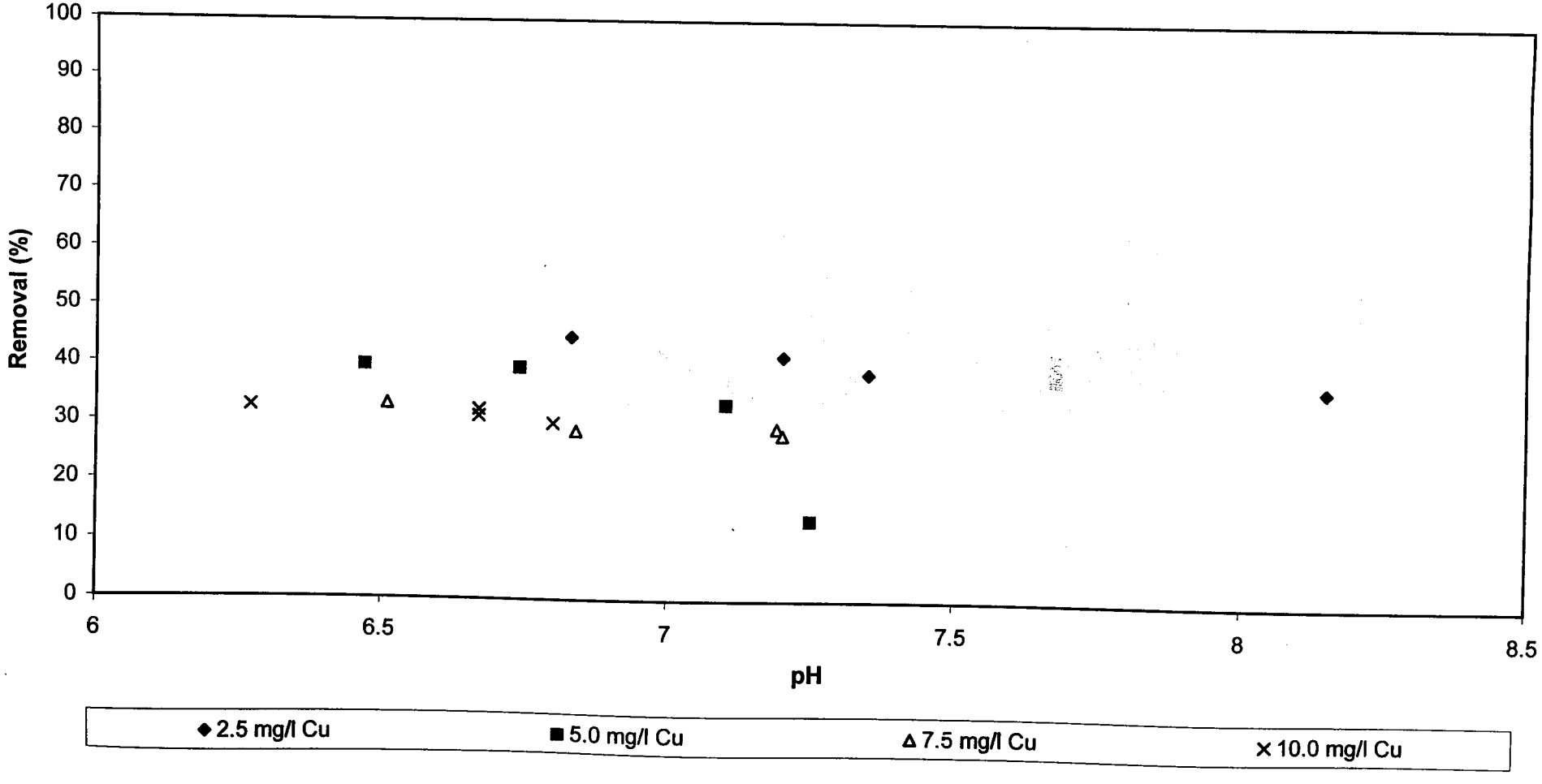


Figure C.138: ***Cu adsorption in Mixed Liquor in Competition Experiment Solids Concentration C (2500 mg/l)***

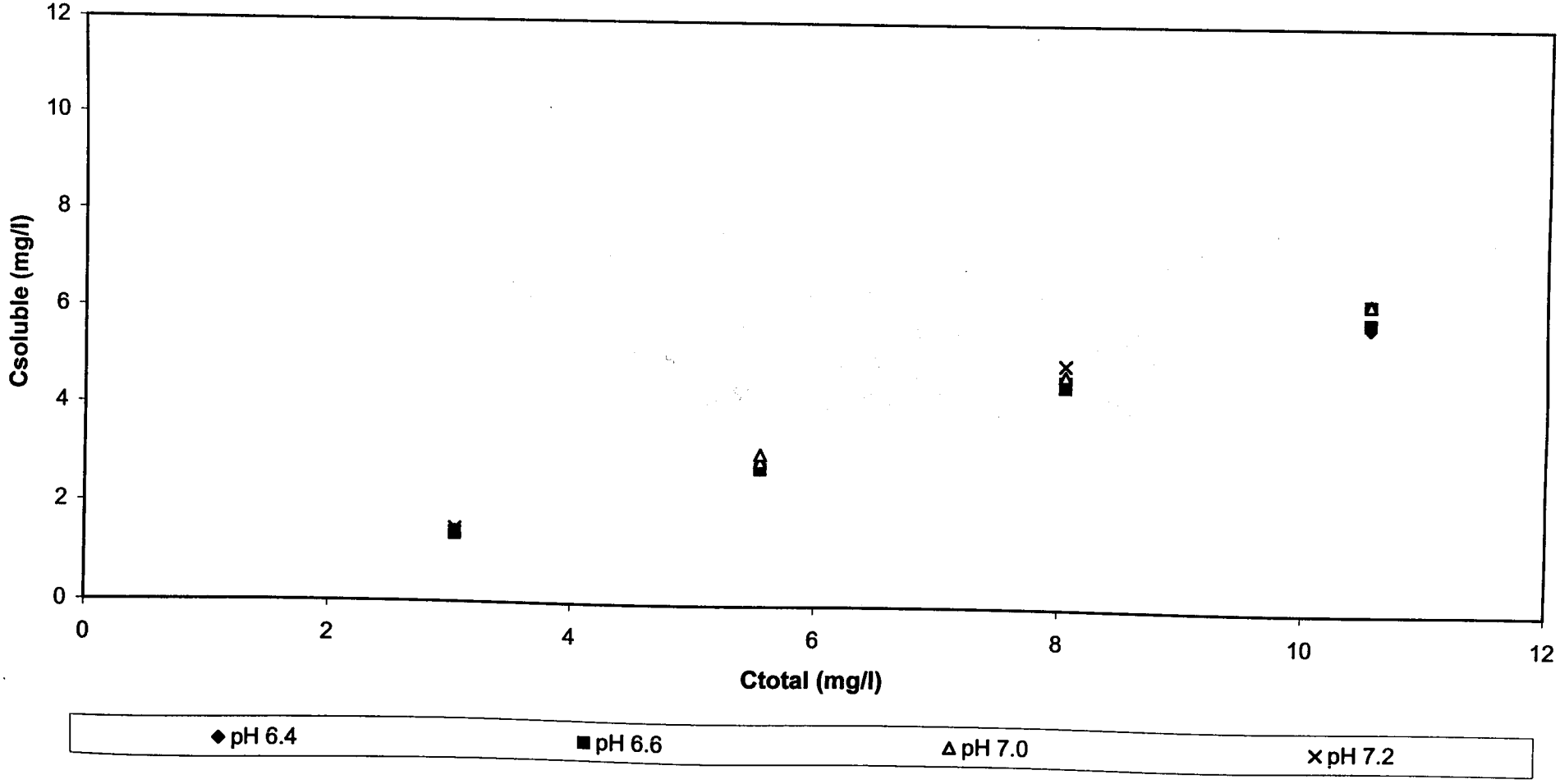


Figure C.139: ***Cu adsorption in Mixed Liquor in Competition Experiment Solids Concentration C (2500 mg/l)***

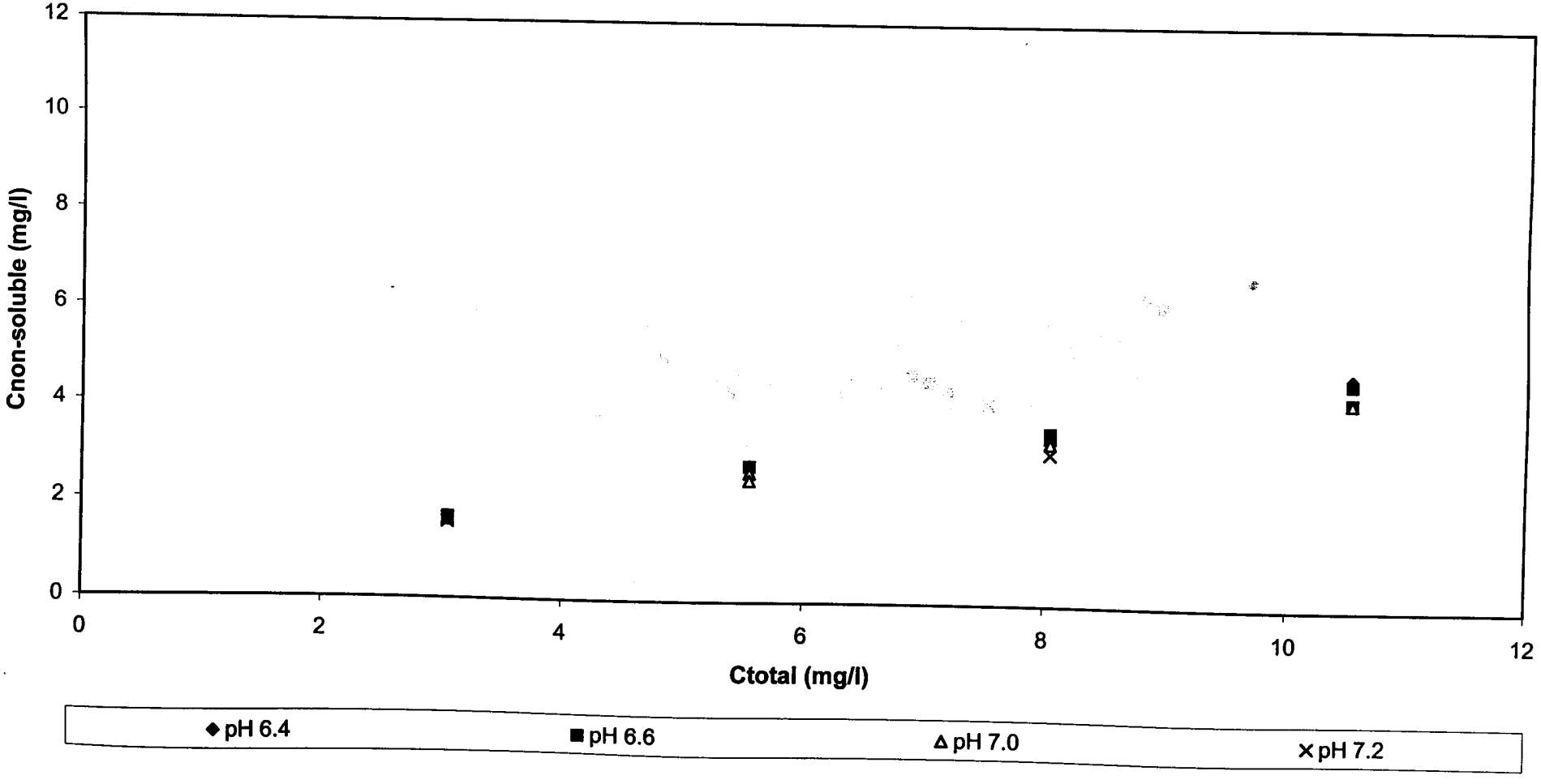


Figure C.140: ***Cu adsorption in Mixed Liquor in Competition Experiment Solids Concentration C (2500 mg/l)***

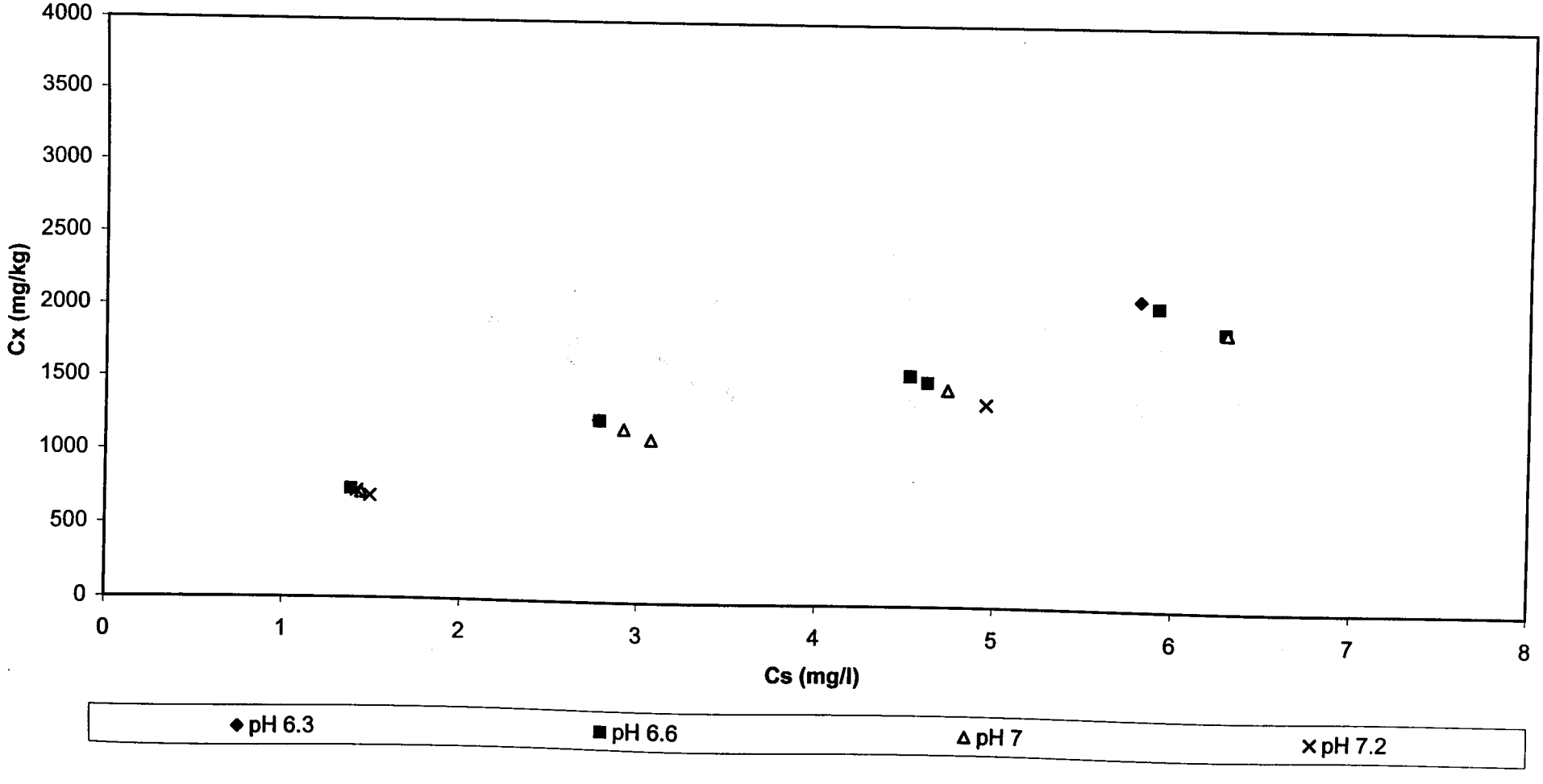


Figure C.141: ***Cu adsorption in Mixed Liquor in Competition Experiment Solids Concentration C (2500 mg/l)***

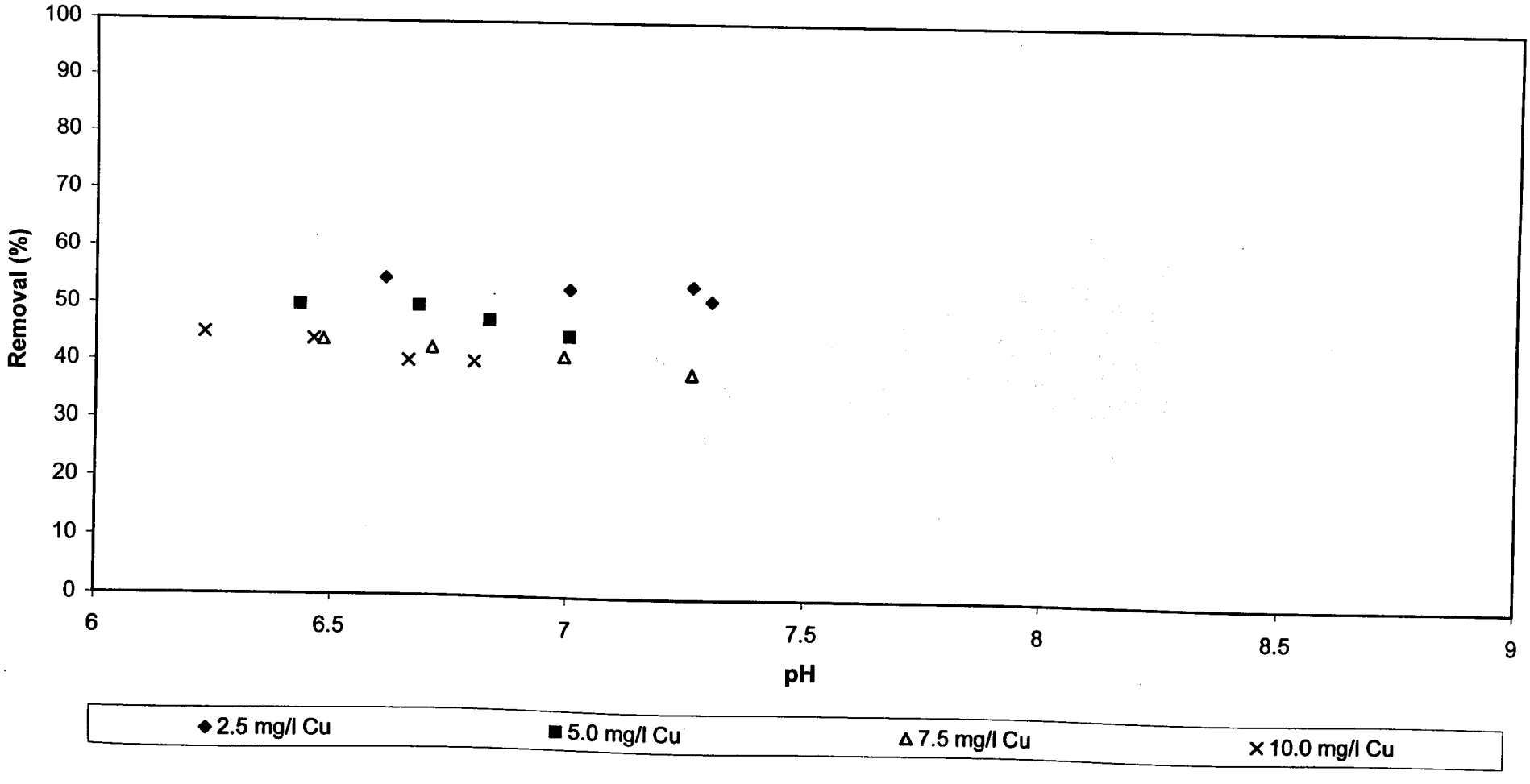


Figure C.142: ***Zn adsorption in Mixed Liquor in Competition Experiment Solids Concentration A (1800 mg/l)***

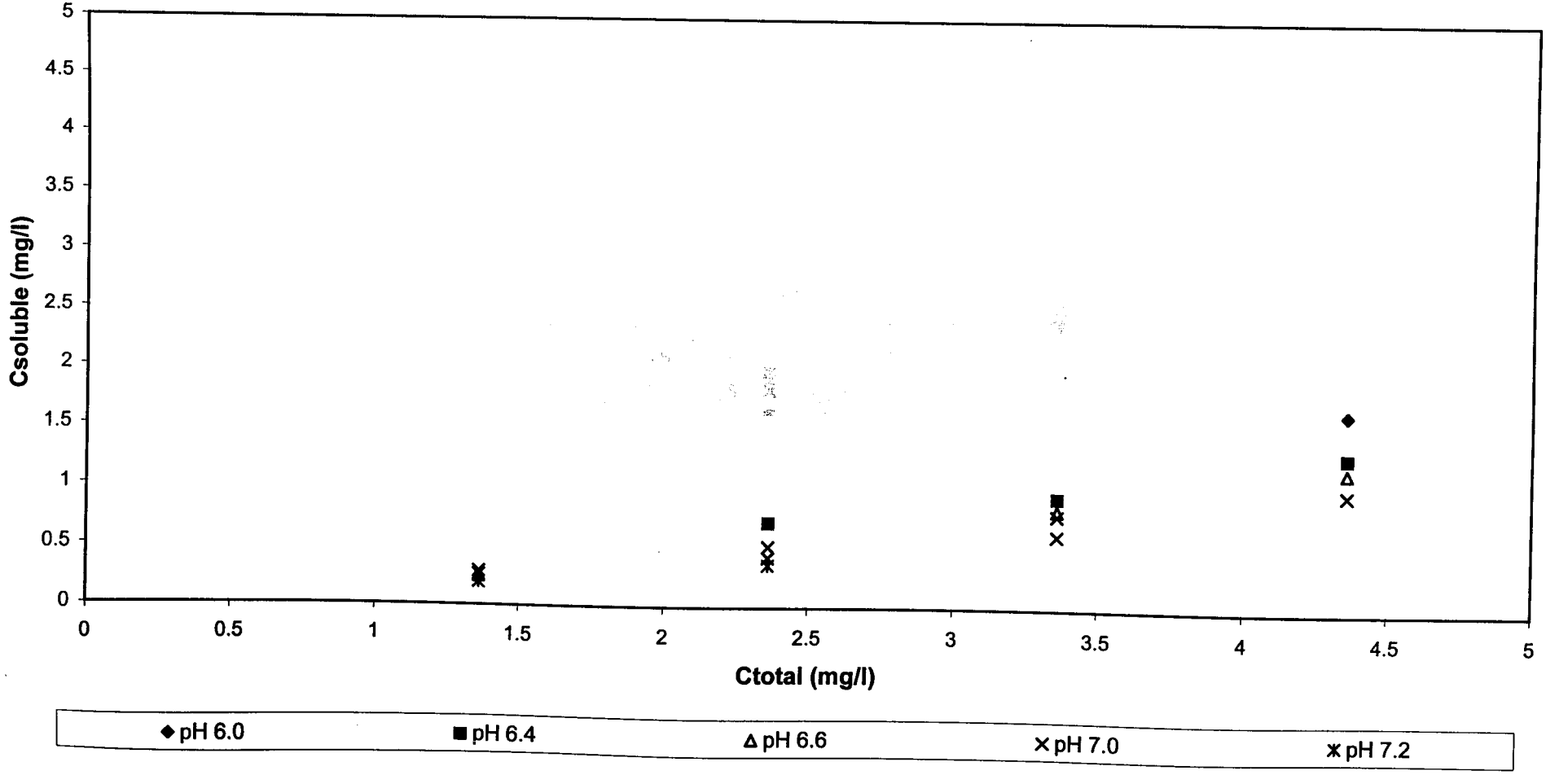


Figure C.143: ***Zn adsorption in Mixed Liquor in Competition Experiment Solids Concentration A (1800 mg/l)***

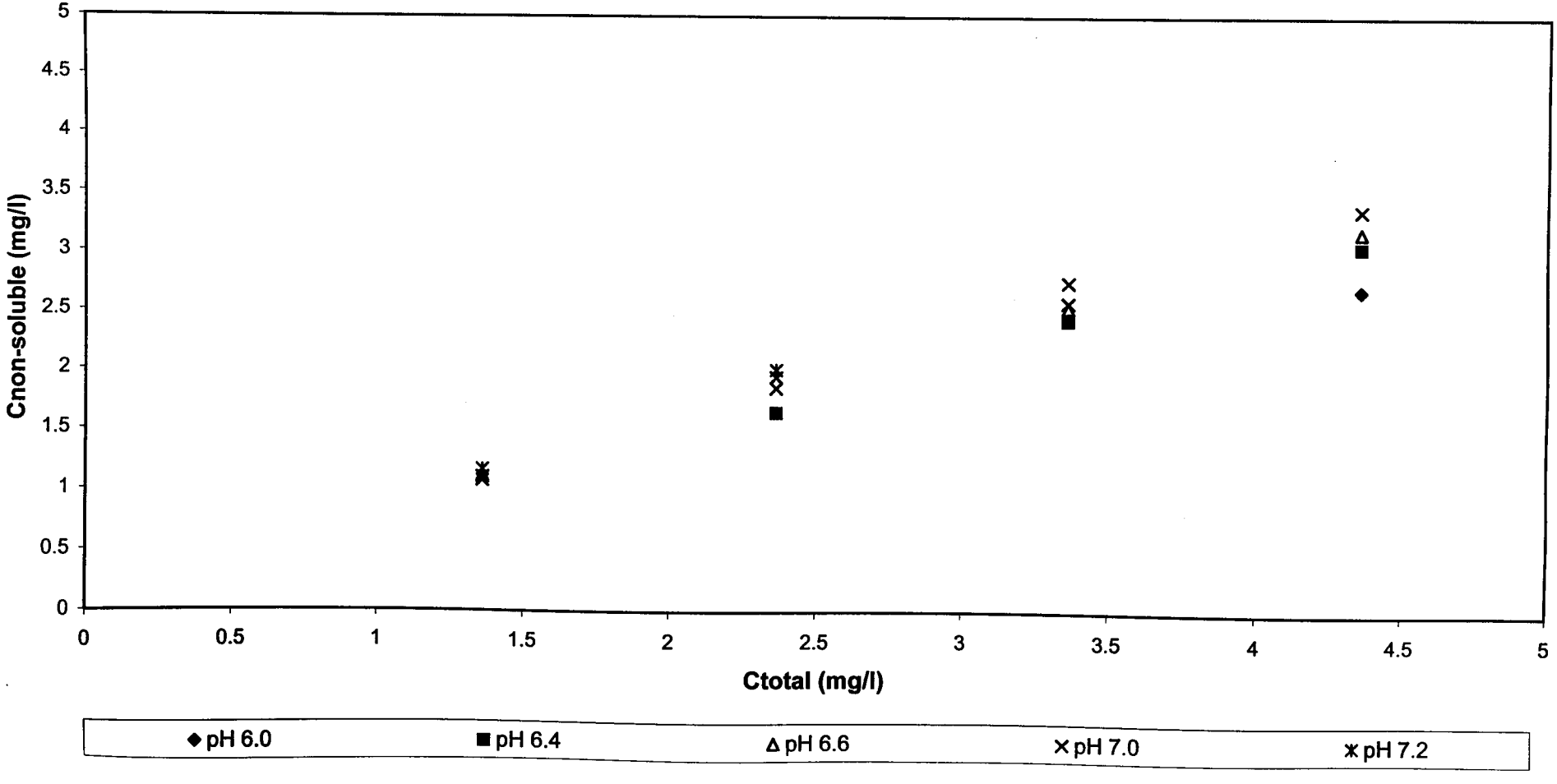


Figure C.144: ***Zn adsorption in Mixed Liquor in Competition Experiment Solids Concentration A (1800 mg/l)***

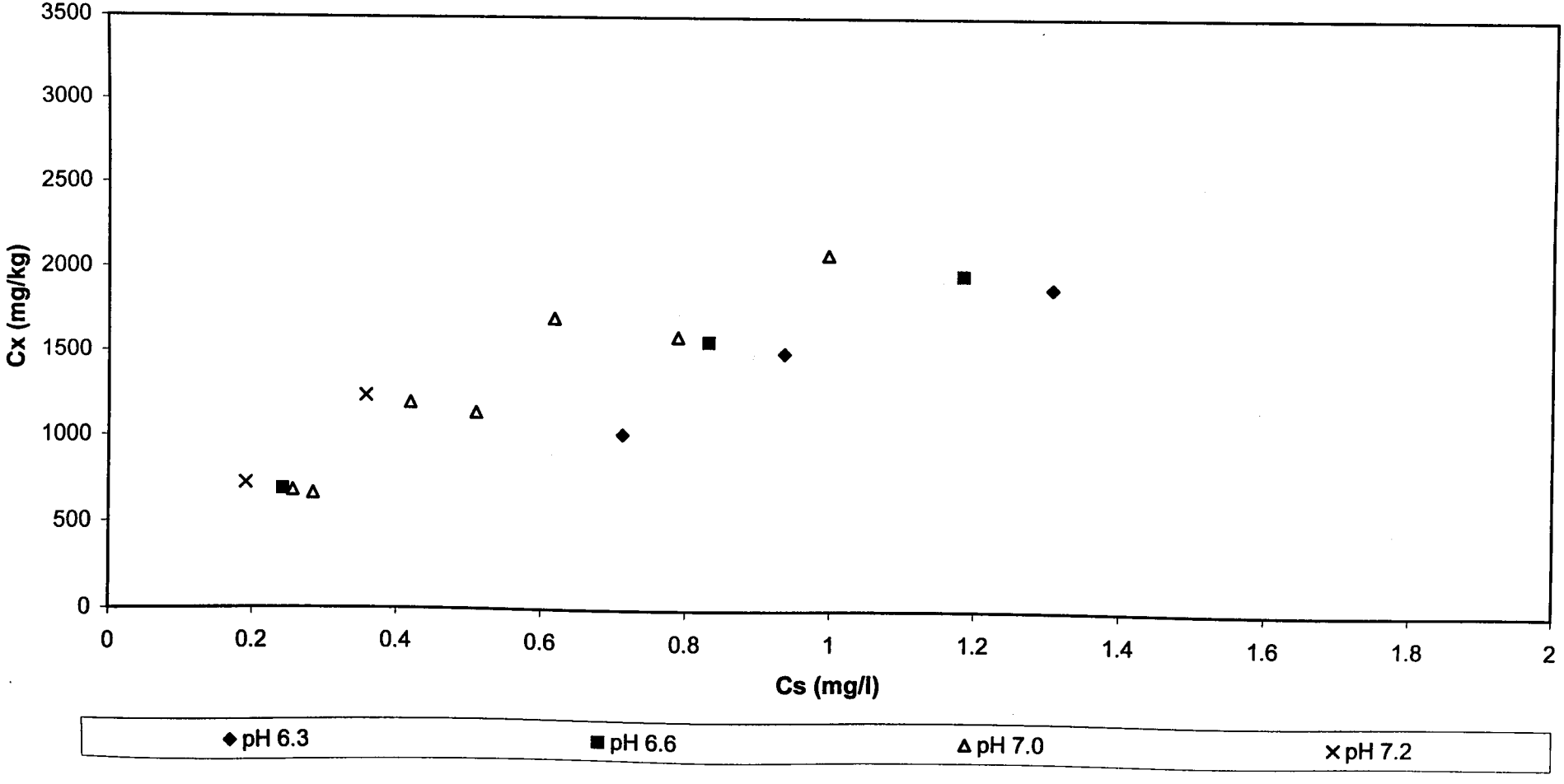


Figure C.145: ***Zn adsorption in Mixed Liquor in Competition Experiment Solids Concentration A (1800 mg/l)***

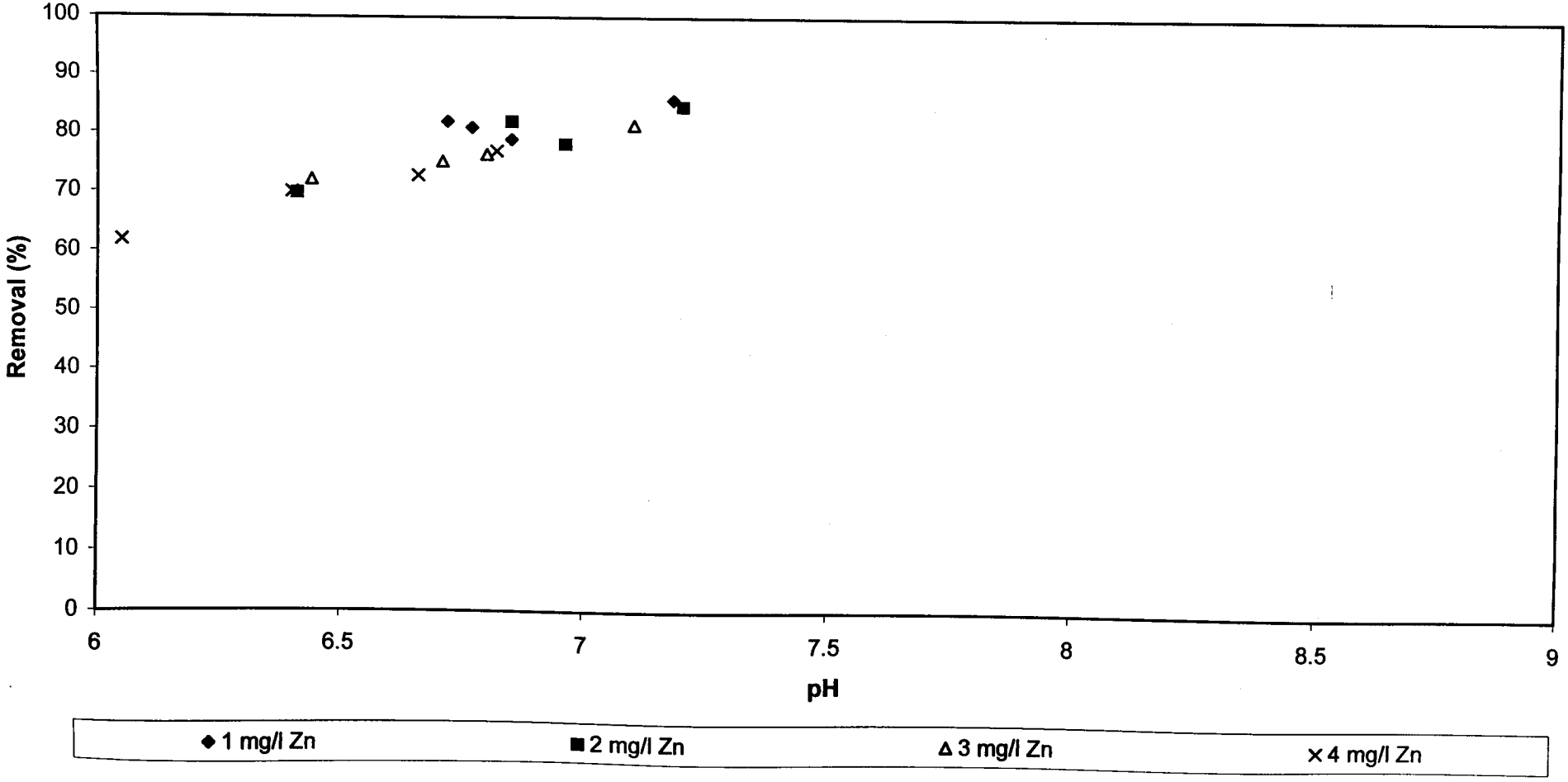


Figure C.146: ***Zn adsorption in Mixed Liquor in Competition Experiment Solids Concentration B (1058 mg/l)***

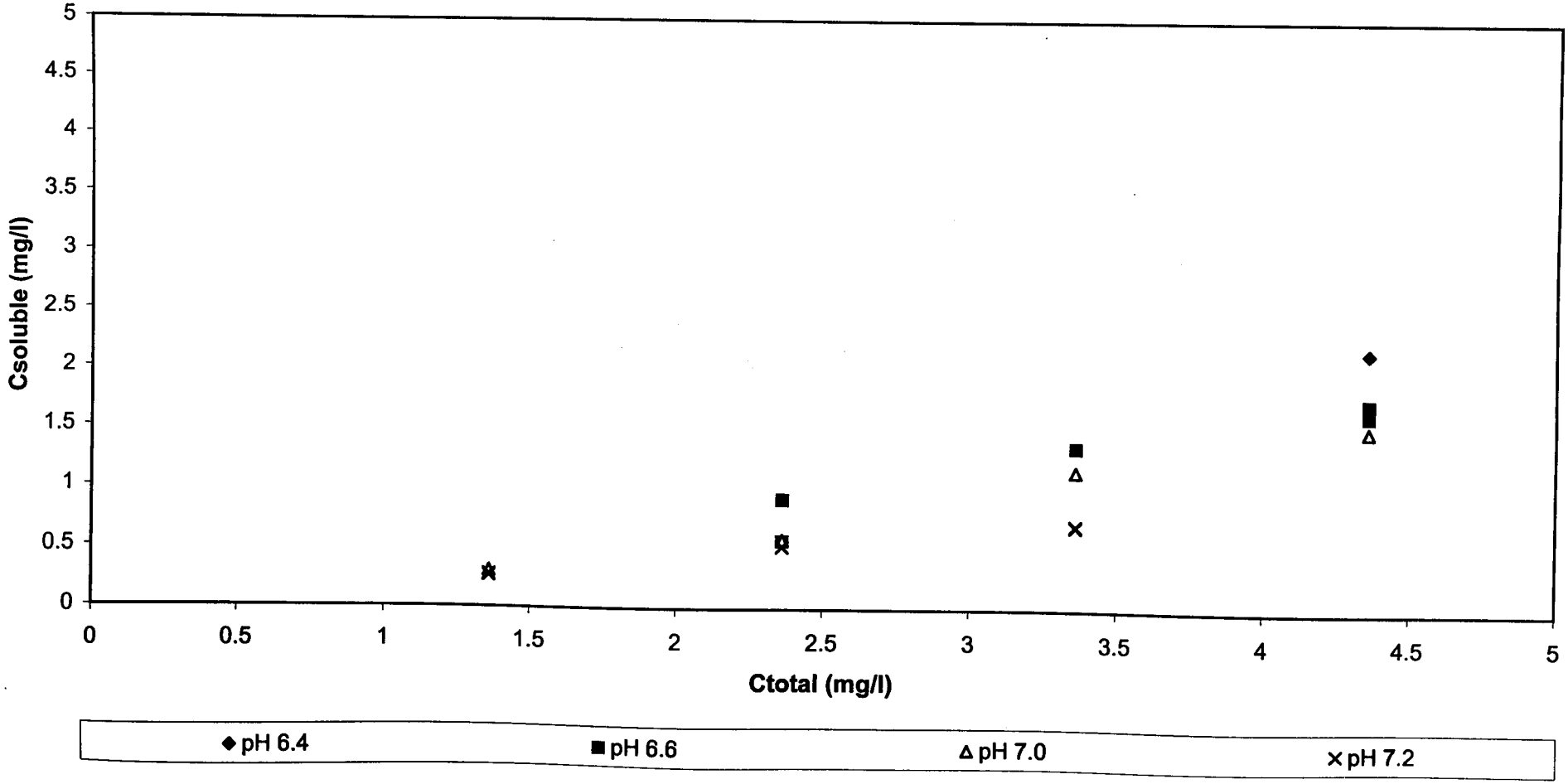


Figure C.147: ***Zn adsorption in Mixed Liquor in Competition Experiment Solids Concentration B (1058 mg/l)***

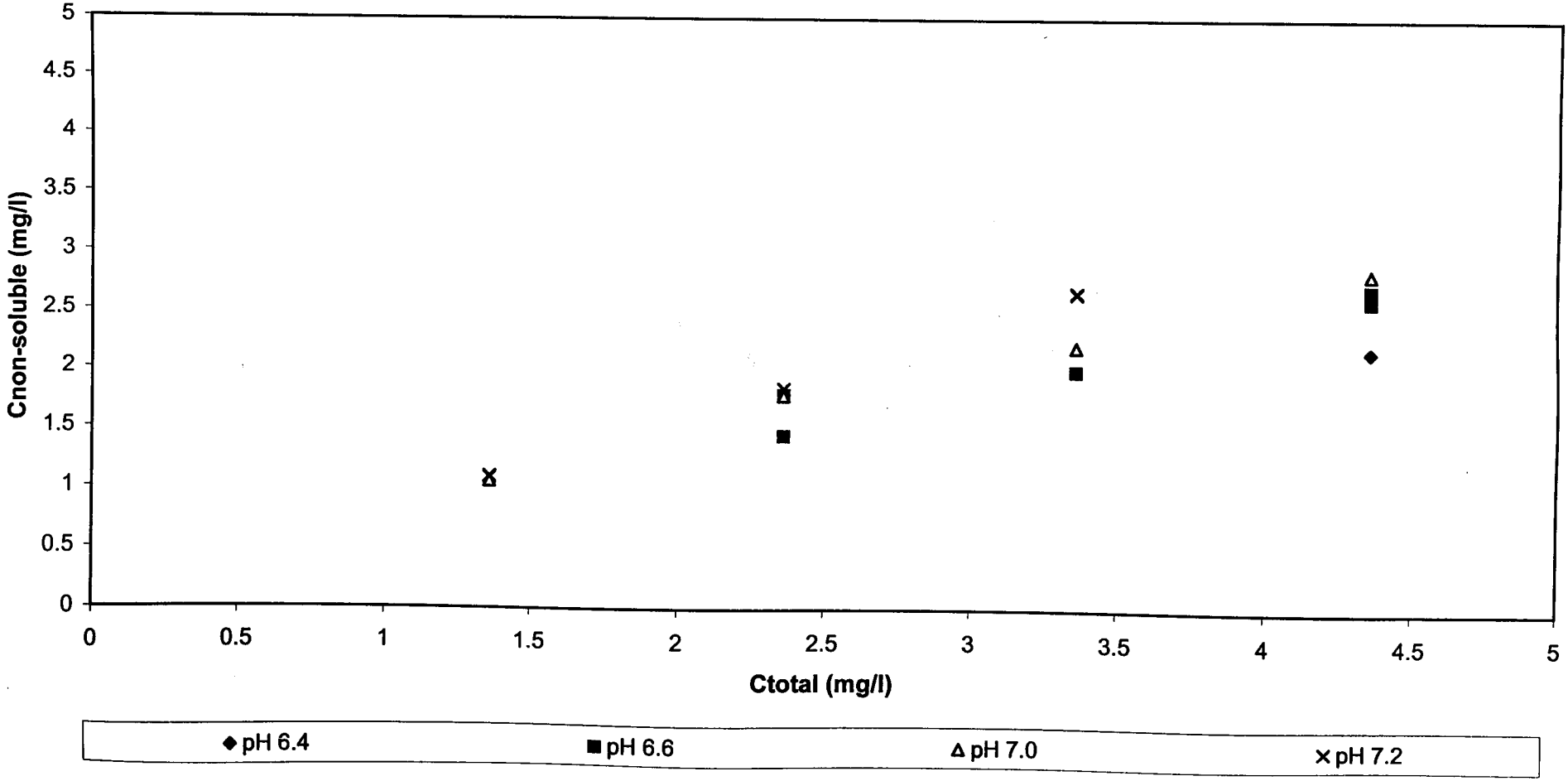


Figure C.148: ***Zn adsorption in Mixed Liquor in Competition Experiment Solids Concentration B (1058 mg/l)***

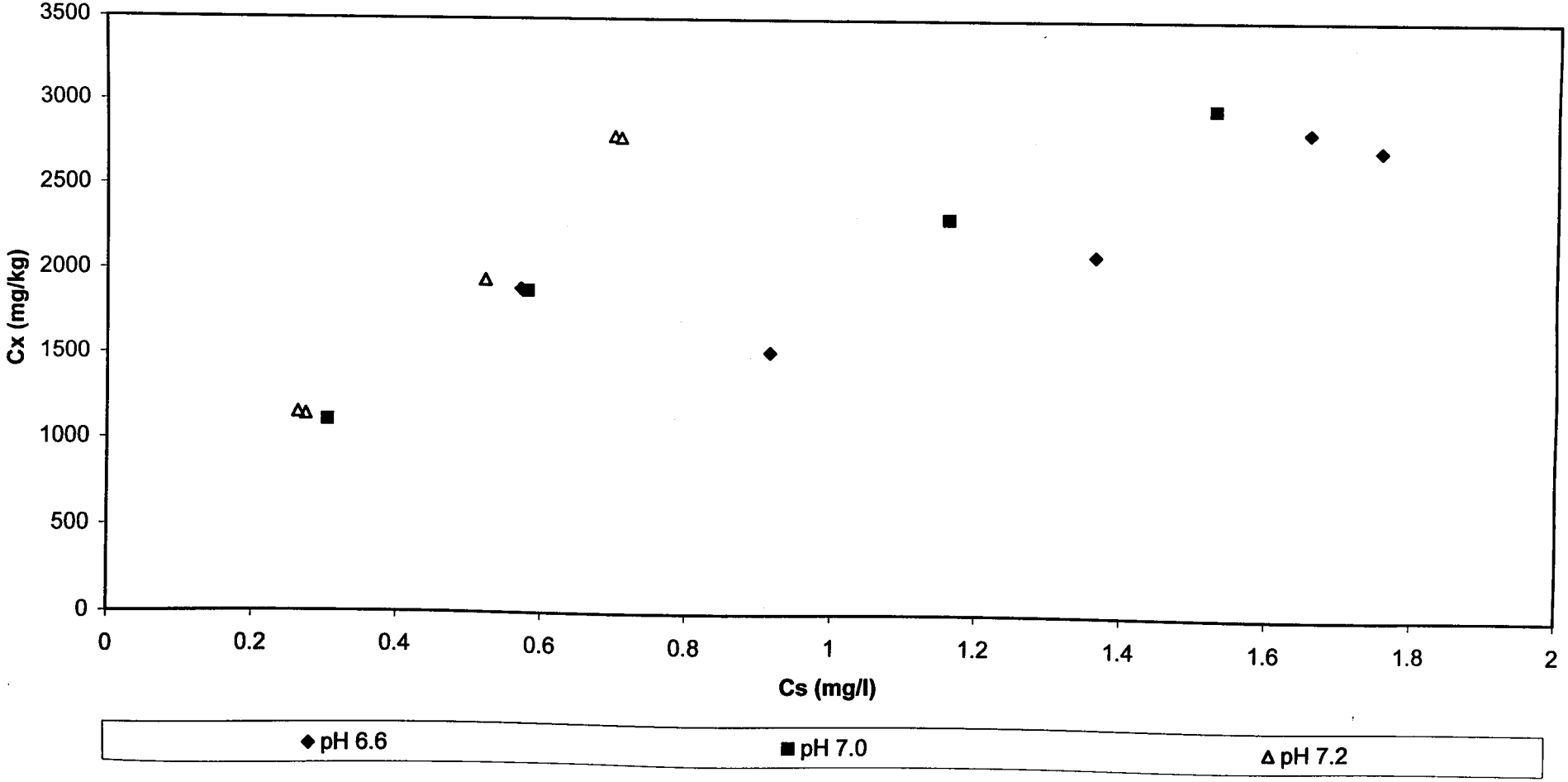


Figure C.149: ***Cu adsorption in Mixed Liquor in Competition Experiment Solids Concentration B (1058 mg/l)***

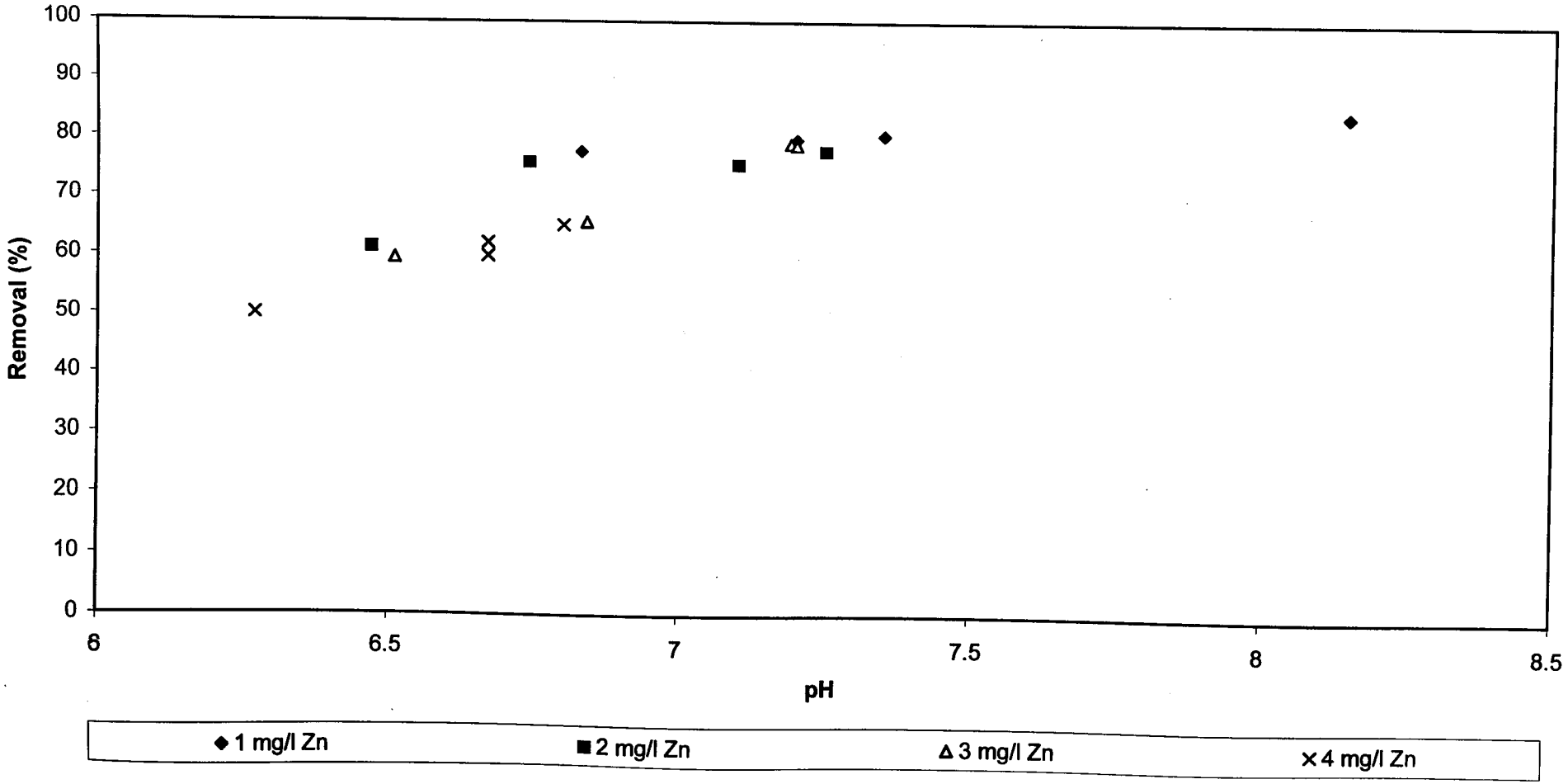


Figure C.150: ***Zn adsorption in Mixed Liquor in Competition Experiment Solids Concentration C (2500 mg/l)***

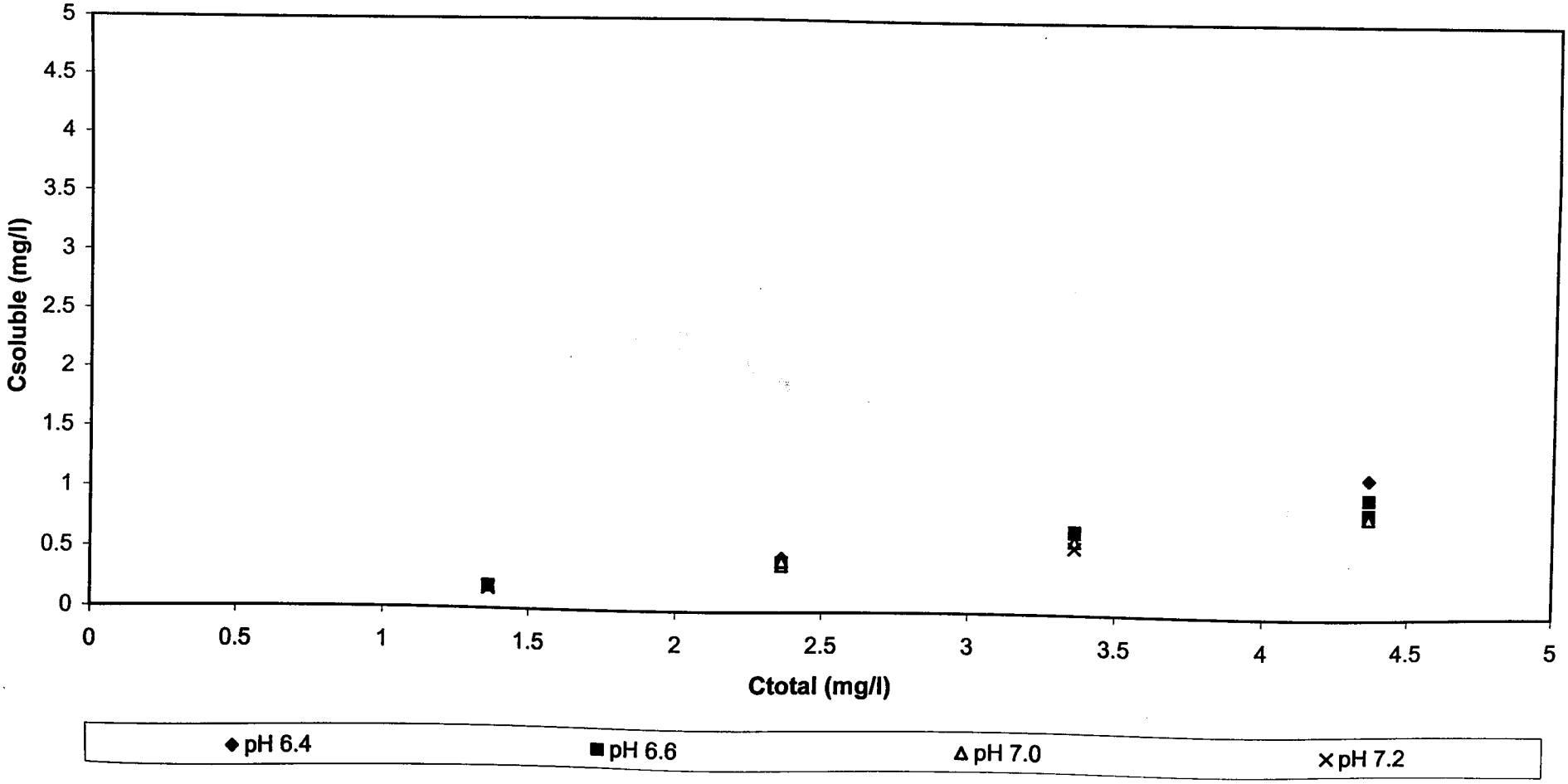


Figure C.151: ***Zn adsorption in Mixed Liquor in Competition Experiment Solids Concentration C (2500 mg/l))***

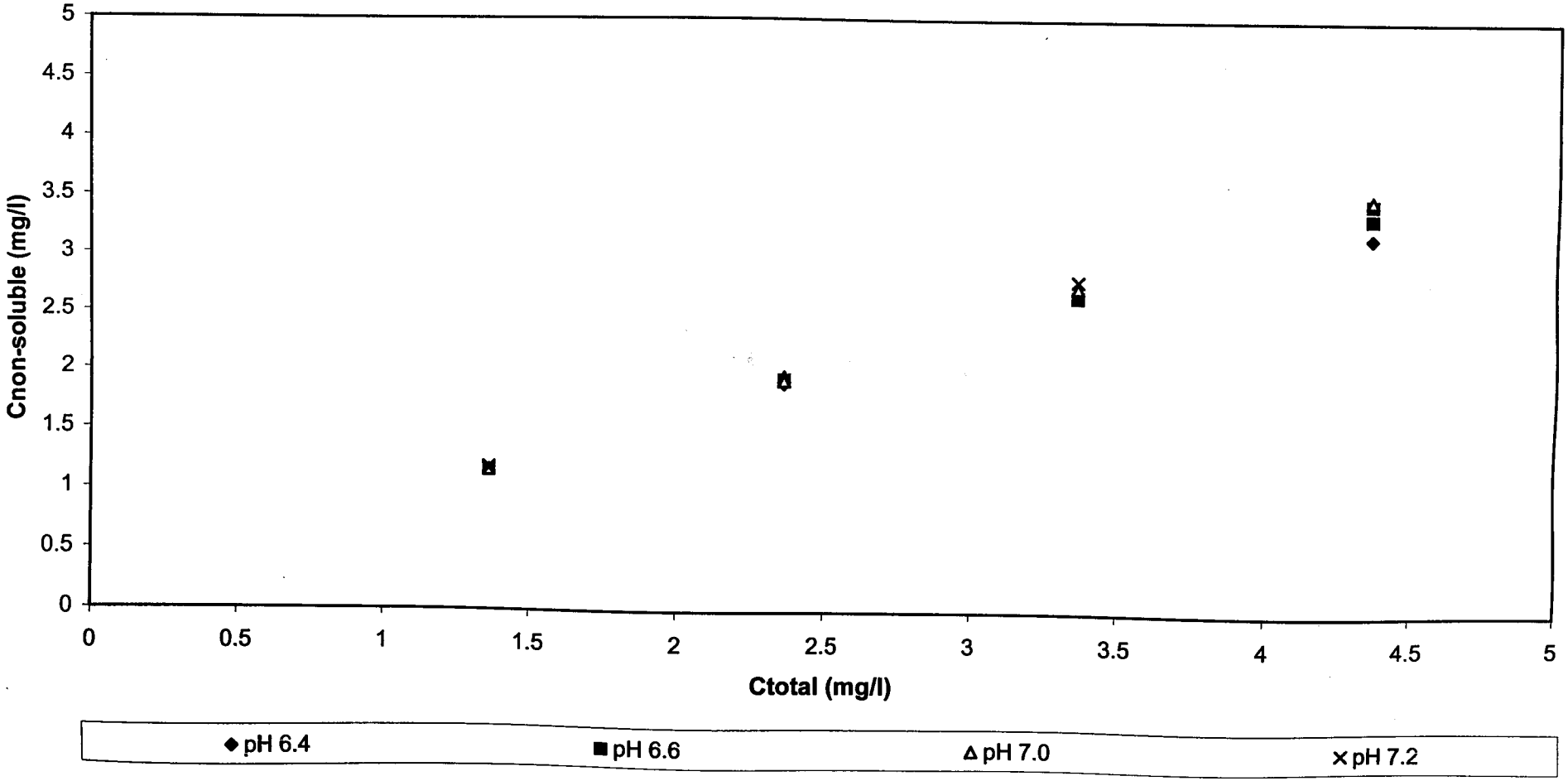


Figure C.152: ***Zn adsorption in Mixed Liquor in Competition Experiment Solids Concentration C (2500 mg/l)***

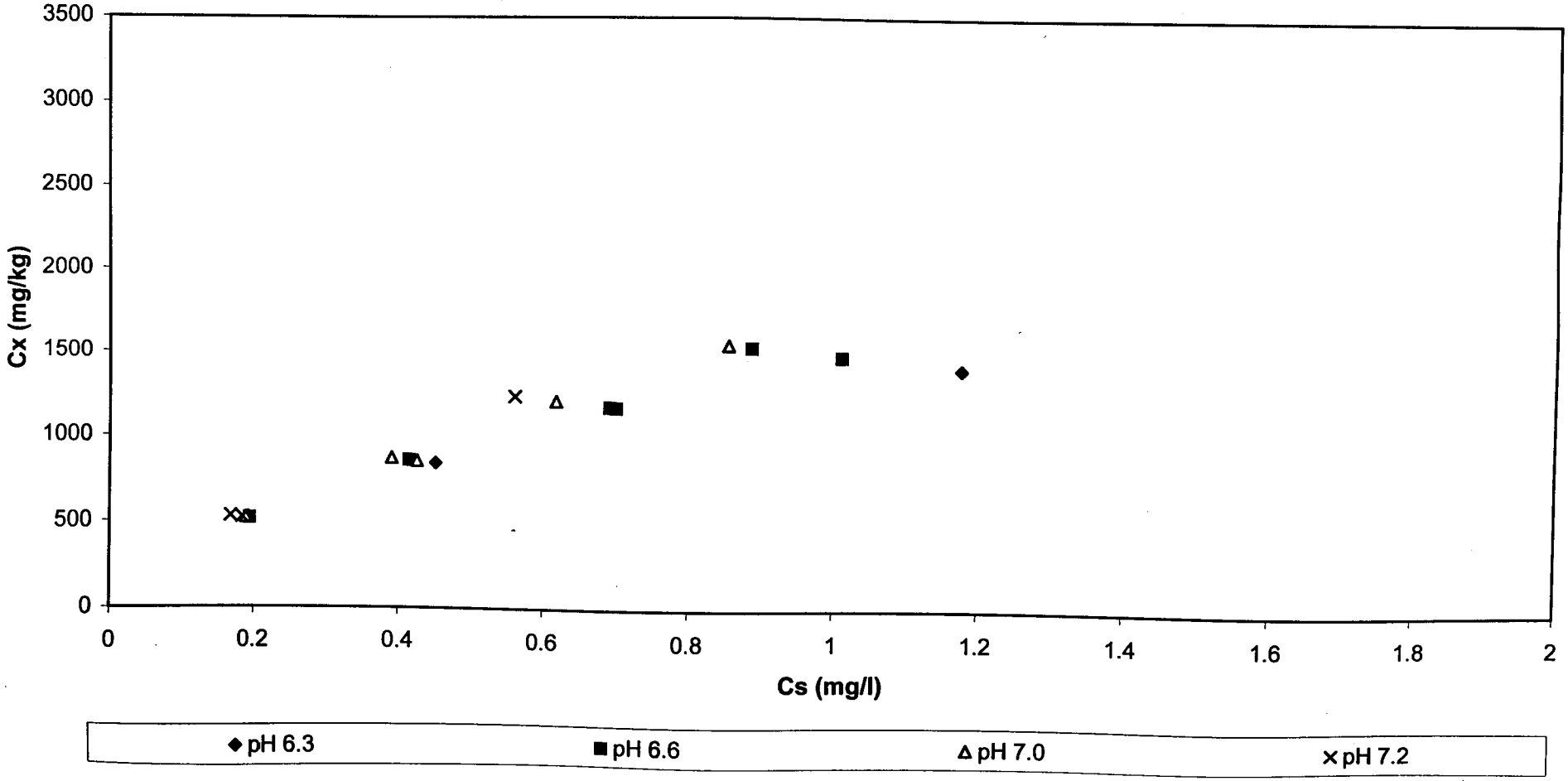


Figure C.153: ***Zn adsorption in Mixed Liquor in Competition Experiment Solids Concentration C (2500 mg/l)***

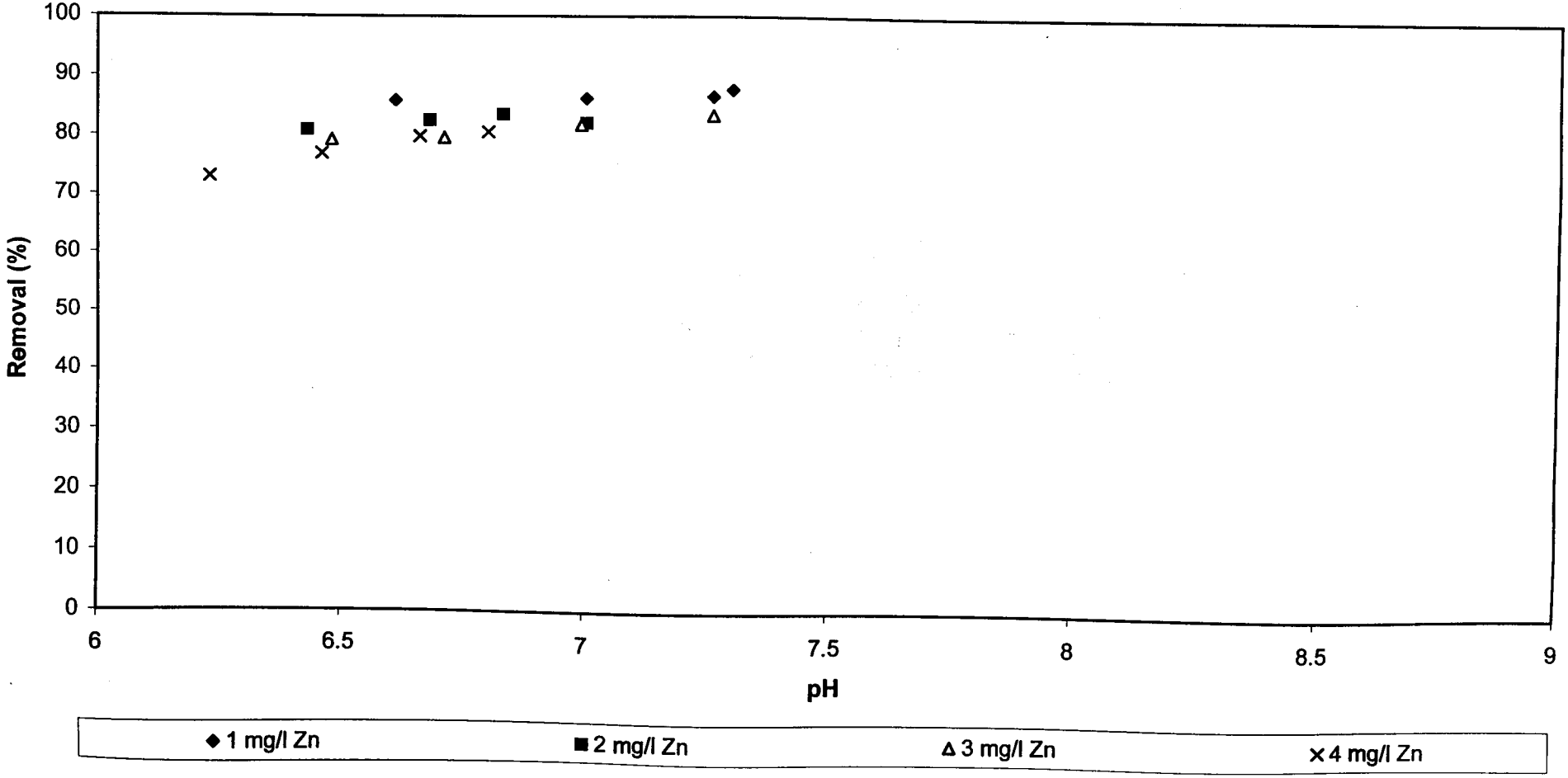


Table C.21 *Competition Adsorption Experiments Final Effluent*

Date Carried out 01-Sep-00

Date analysed: 12-Sep-00

Initial Total Cu (mg/l) 0.0355

Initial Total Zn (mg/l) 0.03915

Actual Sample	TSS (mg/l)	pH	Cu Added (mg/l)	Residual Soluble Cu (mg/l)	Adsorbed Cu (mg/l)	Adsorbed Cu (mg/kg)	Total Cu (mg/l)
A-1-1	32	6.24	2.5	2.2	0.3355	11649.30556	2.5355
A-1-2	32	6.7	2.5	1.525	1.0105	35086.80556	2.5355
A-1-3	32	6.95	2.5	1.172	1.3635	47343.75	2.5355
A-1-4	32	7.15	2.5	0.871	1.6645	57795.13889	2.5355
A-2-1	32	6.27	5	3.511	1.5245	52934.02778	5.0355
A-2-2	32	6.58	5	2.549	2.4865	86336.80556	5.0355
A-2-3	32	6.52	5	2.663	2.3725	82378.47222	5.0355
A-2-4	32	6.95	5	1.522	3.5135	121996.5278	5.0355
A-3-1	32	6.26	7.5	4.66	2.8755	99843.75	7.5355
A-3-2	32	6.73	7.5	1.776	5.7595	199982.6389	7.5355
A-3-3	32	6.93	7.5	1.54	5.9955	208177.0833	7.5355
A-3-4	32	7.14	7.5	1.13	6.4055	222413.1944	7.5355
A-4-1	32	6.03	10	7.288	2.7475	95399.30556	10.0355
A-4-2	32	6.09	10	6.615	3.4205	118767.3611	10.0355
A-4-3	32	6.2	10	5.862	4.1735	144913.1944	10.0355
A-4-4	32	6.63	10	2.467	7.5685	262795.1389	10.0355
B-1-1	31	2.8	2.5	2.458	0.0775	2777.777778	2.5355
B-1-2	31	6.43	2.5	2.085	0.4505	16146.95341	2.5355
B-1-3	31	7.08	2.5	1.005	1.5305	54856.63082	2.5355
B-1-4	31	7.24	2.5	0.884	1.6515	59193.54839	2.5355
B-2-1	31	6.3	5	3.761	1.2745	45681.00358	5.0355
B-2-2	31	6.38	5	2.674	2.3615	84641.57706	5.0355
B-2-3	31	6.67	5	1.957	3.0785	110340.5018	5.0355
B-2-4	31	6.84	5	1.6	3.4355	123136.2007	5.0355
B-3-1	31	5.82	7.5	6.864	0.6715	24068.10036	7.5355
B-3-2	31	6.61	7.5	2.252	5.2835	189372.7599	7.5355
B-3-3	31	6.85	7.5	1.446	6.0895	218261.6487	7.5355
B-3-4	31	6.87	7.5	1.597	5.9385	212849.4624	7.5355
B-4-1	31	5.7	10	9.047	0.9885	35430.10753	10.0355

Cu and Zn competitive adsorption in final effluent

Actual Sample	TSS (mg/l)	pH	Cu Added (mg/l)	Residual Soluble Cu (mg/l)	Adsorbed Cu (mg/l)	Adsorbed Cu (mg/kg)	Total Cu (mg/l)
B-4-2	31	6.08	10	7.441	2.5945	92992.83154	10.0355
B-4-3	31	6.14	10	6.59	3.4455	123494.6237	10.0355
B-4-4	31	6.33	10	4.126	5.9095	211810.0358	10.0355

Cu and Zn competitive adsorption in final effluent

Zn Added (mg/l)	Residual Soluble Zn (mg/l)	Adsorbed Zn (mg/l)	Adsorbed Zn (mg/kg)	Total Zn (mg/l)
1	1.028	0.01115	387.1527778	1.03915
1	0.802	0.23715	8234.375	1.03915
1	0.61	0.42915	14901.04167	1.03915
1	0.313	0.72615	25213.54167	1.03915
2	1.765	0.27415	9519.097222	2.03915
2	1.57	0.46915	16289.93056	2.03915
2	1.566	0.47315	16428.81944	2.03915
2	1.094	0.94515	32817.70833	2.03915
3	2.554	0.48515	16845.48611	3.03915
3	1.664	1.37515	47748.26389	3.03915
3	1.484	1.55515	53998.26389	3.03915
3	0.836	2.20315	76498.26389	3.03915
4	3.364	0.67515	23442.70833	4.03915
4	3.388	0.65115	22609.375	4.03915
4	3.212	0.82715	28720.48611	4.03915
4	2.311	1.72815	60005.20833	4.03915
1	0.971	0.06815	2442.65233	1.03915
1	0.934	0.10515	3768.817204	1.03915
1	0.587	0.45215	16206.09319	1.03915
1	0.444	0.59515	21331.54122	1.03915
2	1.776	0.26315	9431.899642	2.03915
2	1.611	0.42815	15345.87814	2.03915
2	1.423	0.61615	22084.22939	2.03915
2	1.189	0.85015	30471.32616	2.03915
3	2.723	0.31615	11331.54122	3.03915
3	1.797	1.24215	44521.50538	3.03915
3	1.407	1.63215	58500	3.03915
3	1.452	1.58715	56887.09677	3.03915
4	3.615	0.42415	15202.50896	4.03915

Cu and Zn competitive adsorption in final effluent

Zn Added (mg/l)	Residual Soluble Zn (mg/l)	Adsorbed Zn (mg/l)	Adsorbed Zn (mg/kg)	Total Zn (mg/l)
4	3.448	0.59115	21188.17204	4.03915
4	3.34	0.69915	25059.13978	4.03915
4	3.021	1.01815	36492.83154	4.03915

Cu and Zn competitive adsorption in final effluent

Figure C.154: ***Cu adsorption in Final Effluent in Competition Experiment Solids Concentration (31 mg/l)***

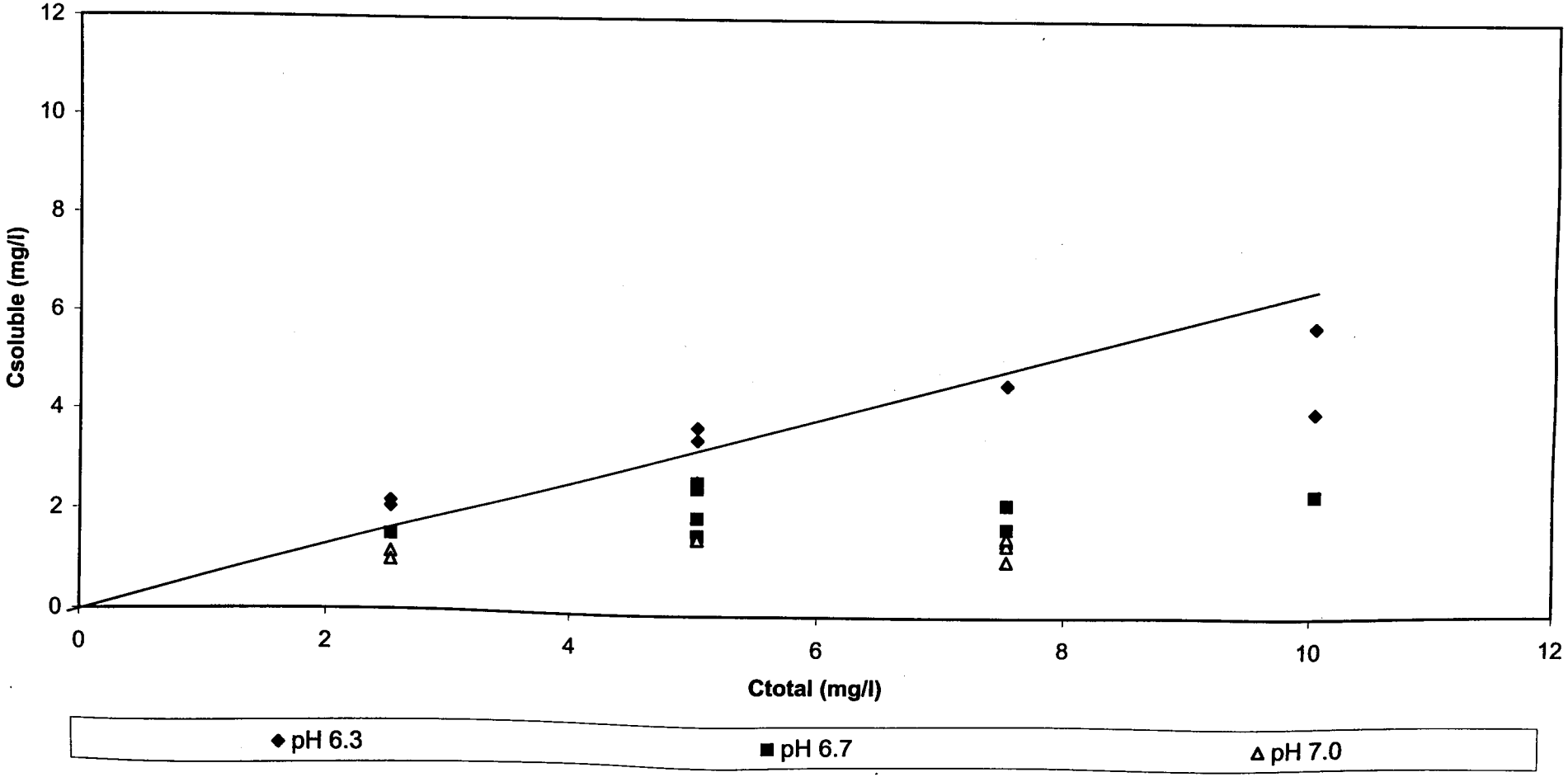


Figure C.155: ***Cu adsorption in Final Effluent in Competition Experiment Solids Concentration (31 mg/l)***

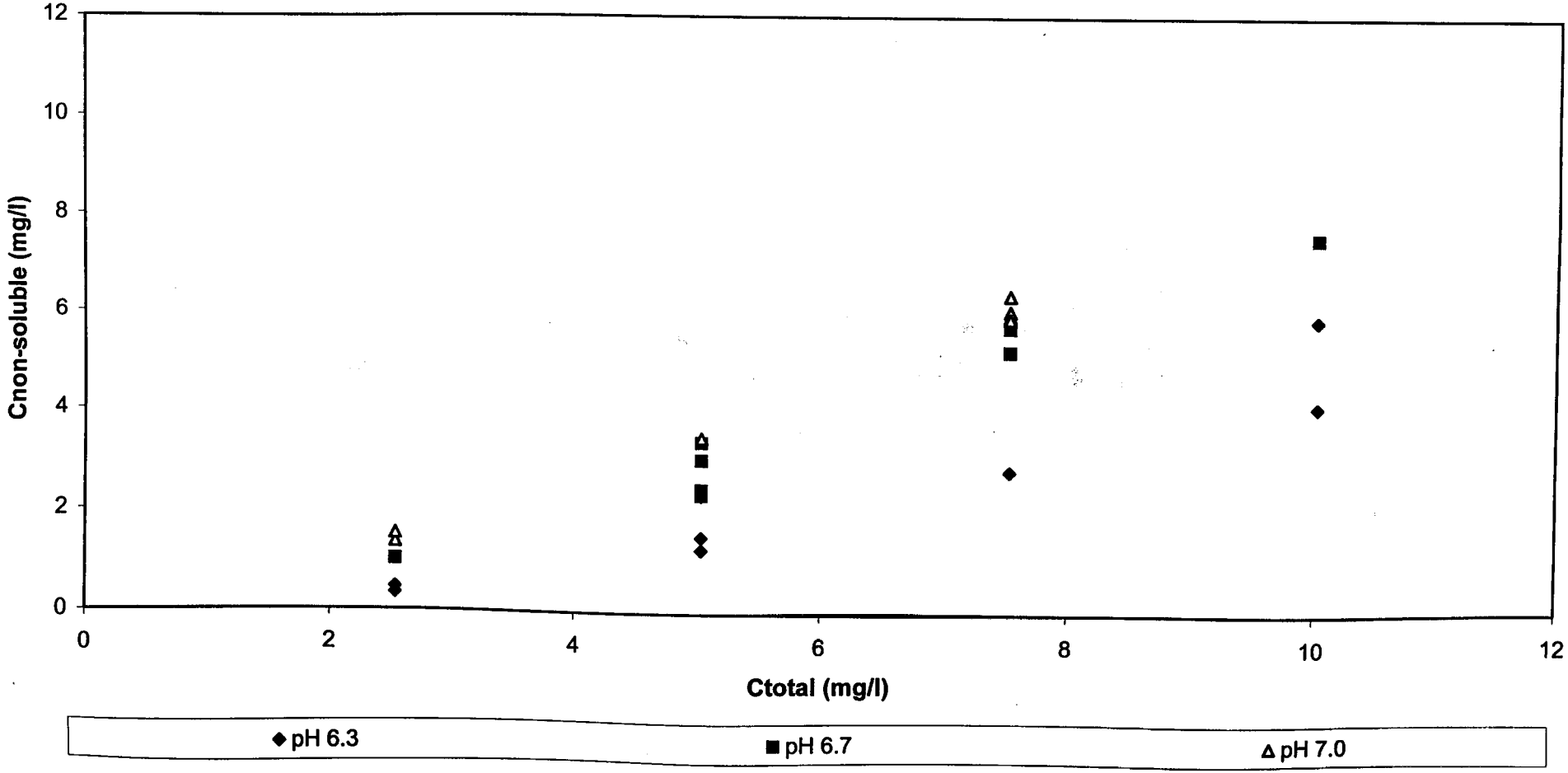


Figure C.156: ***Cu adsorption in Final Effluent in Competition Experiment Solids Concentration (31 mg/l)***

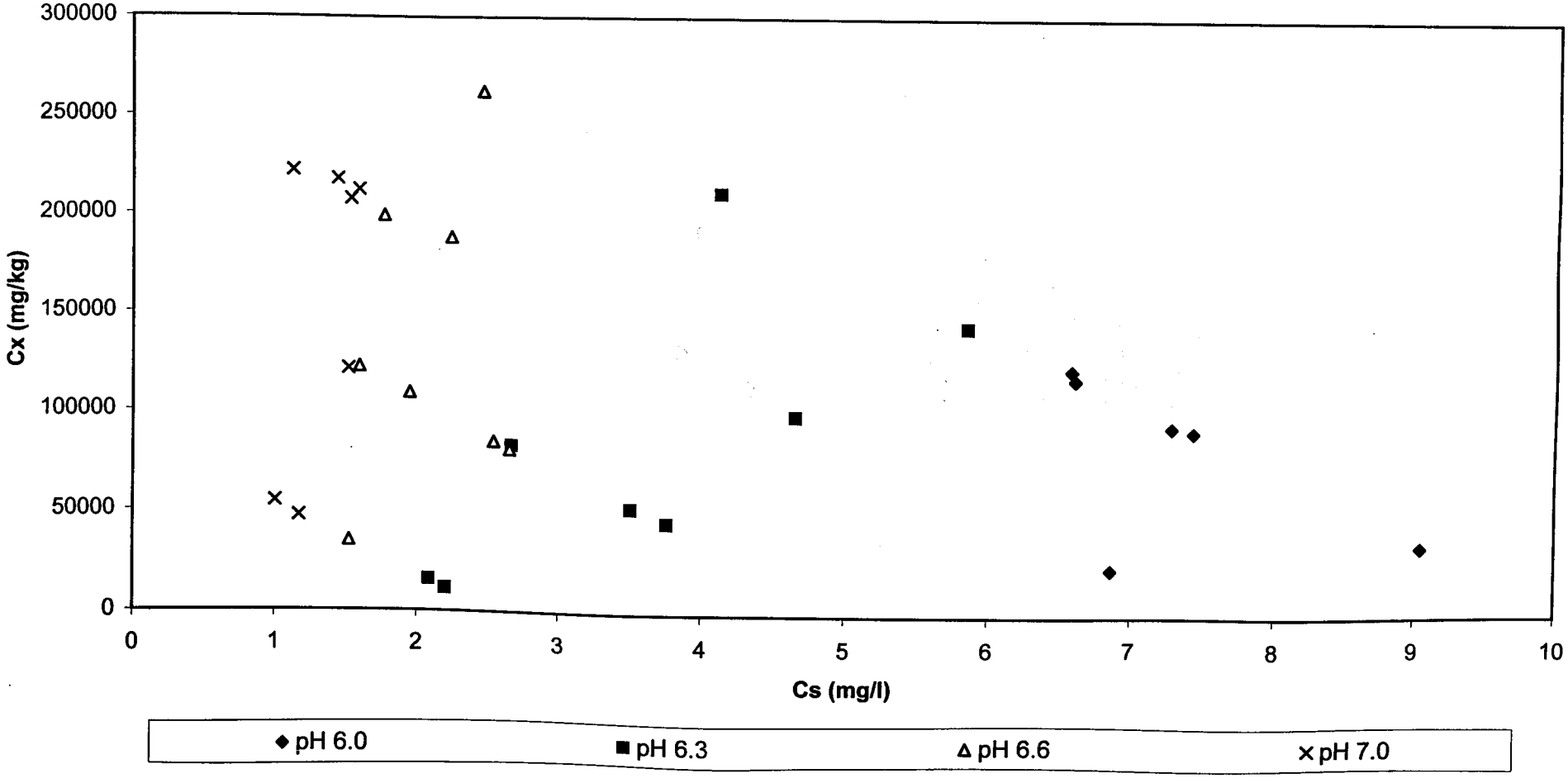


Figure C.157: ***Cu adsorption in Final Effluent in Competition Experiment Solids Concentration (31 mg/l)***

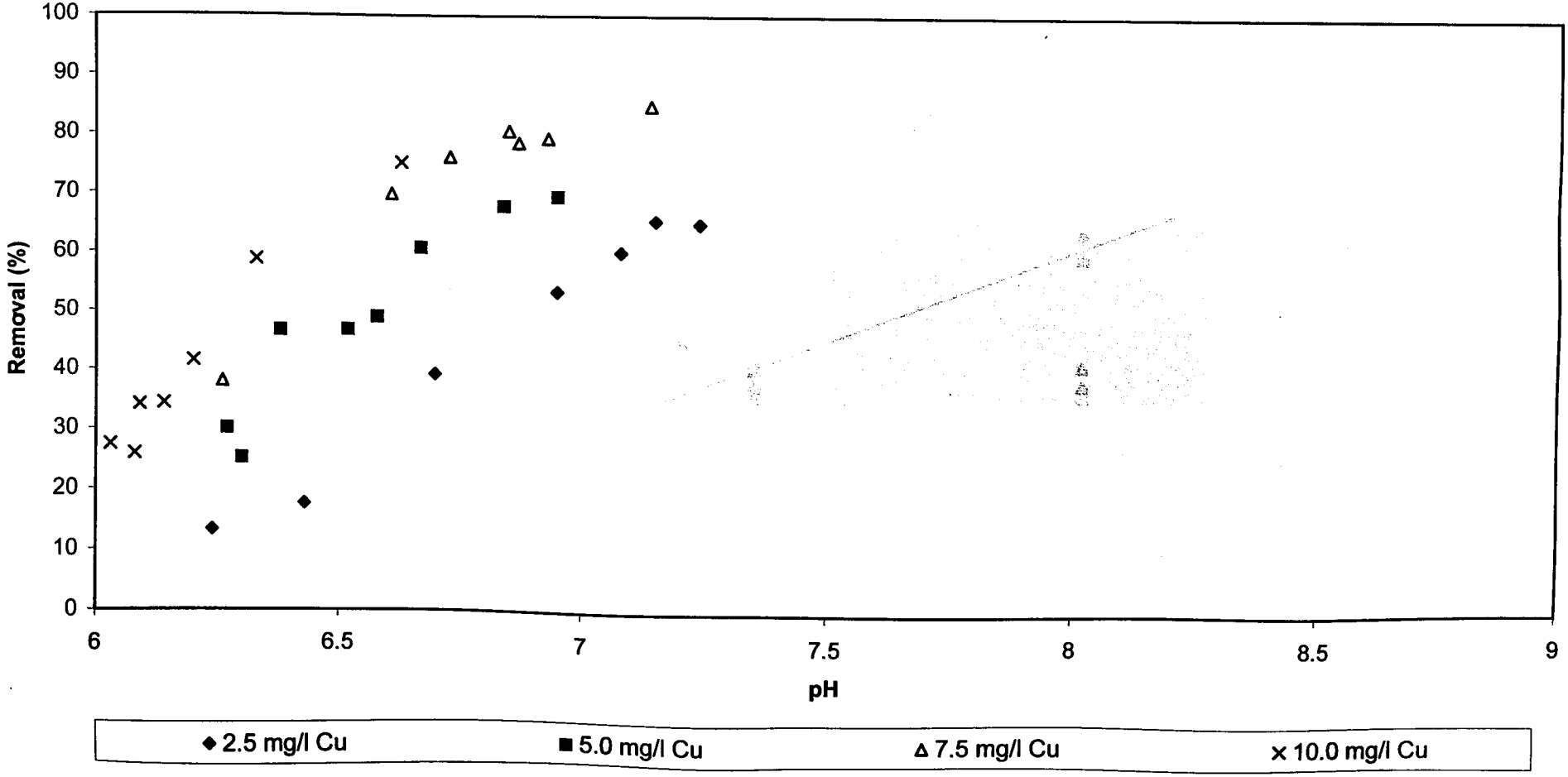


Figure C.158: ***Zn adsorption in Final Effluent in Competition Experiment Solids Concentration (31 mg/l)***

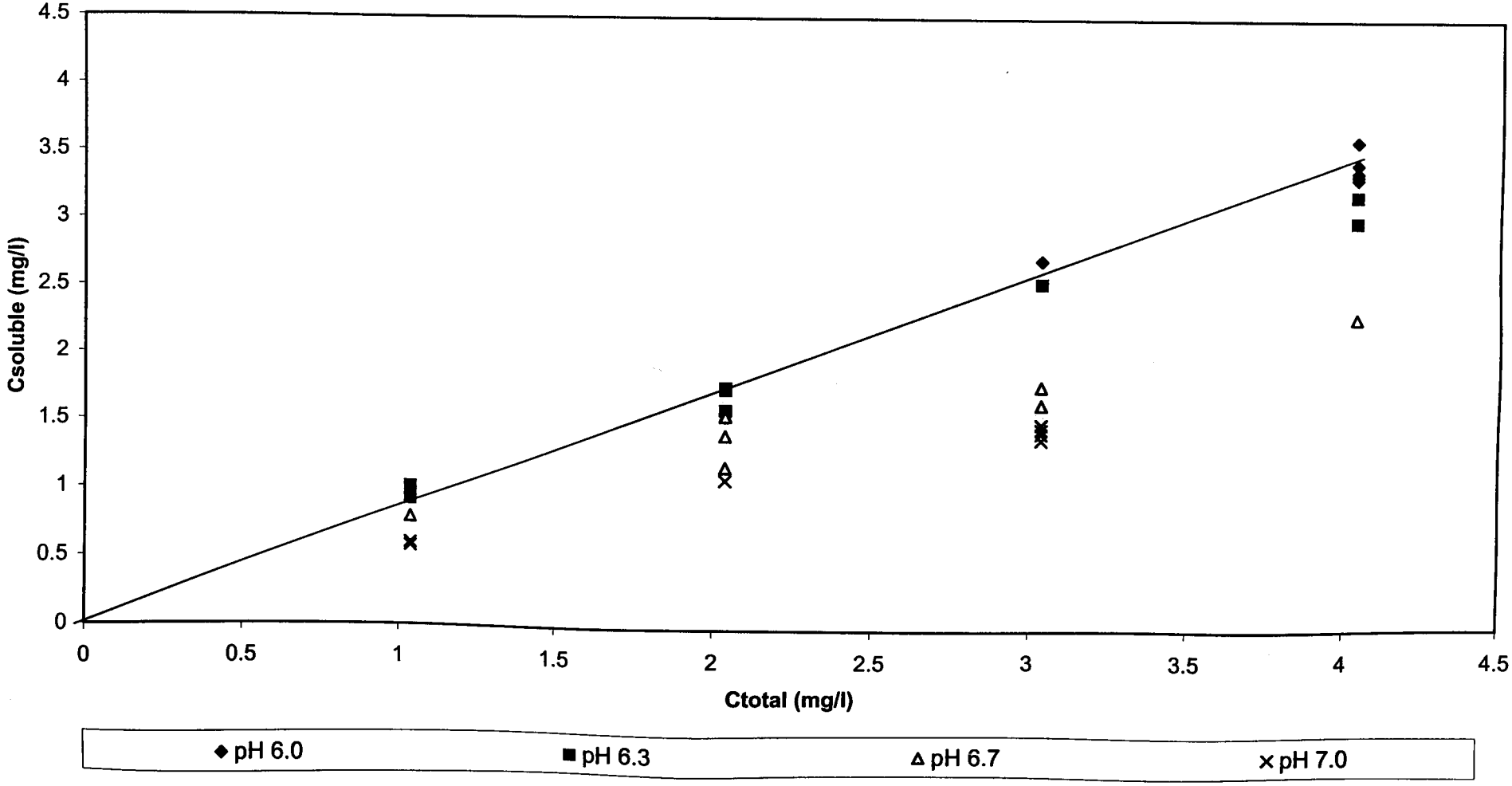


Figure C.159: ***Zn adsorption in Final Effluent in Competition Experiment Solids Concentration (31 mg/l)***

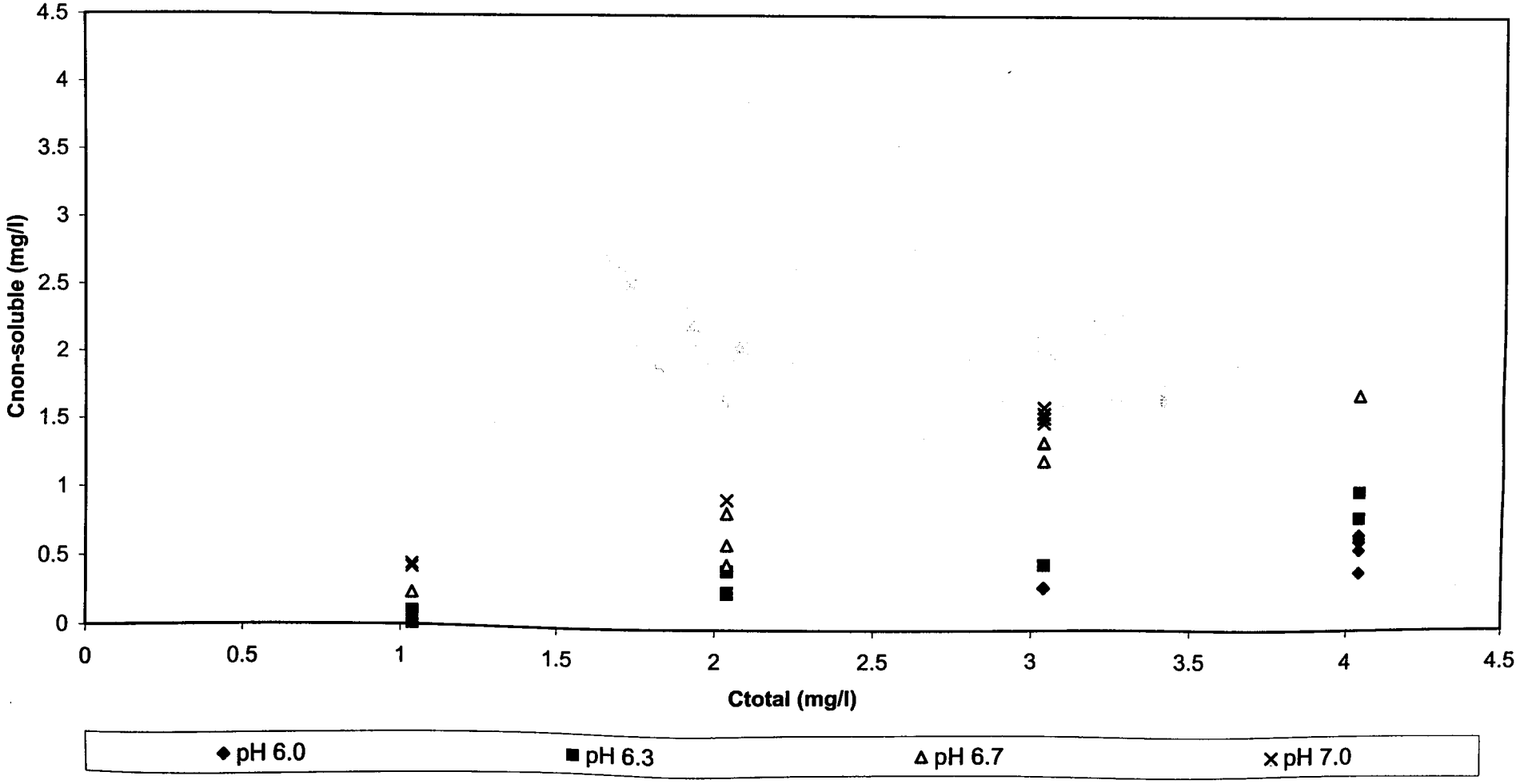


Figure C.160: ***Zn adsorption in Final Effluent in Competition Experiment Solids Concentration (31 mg/l)***

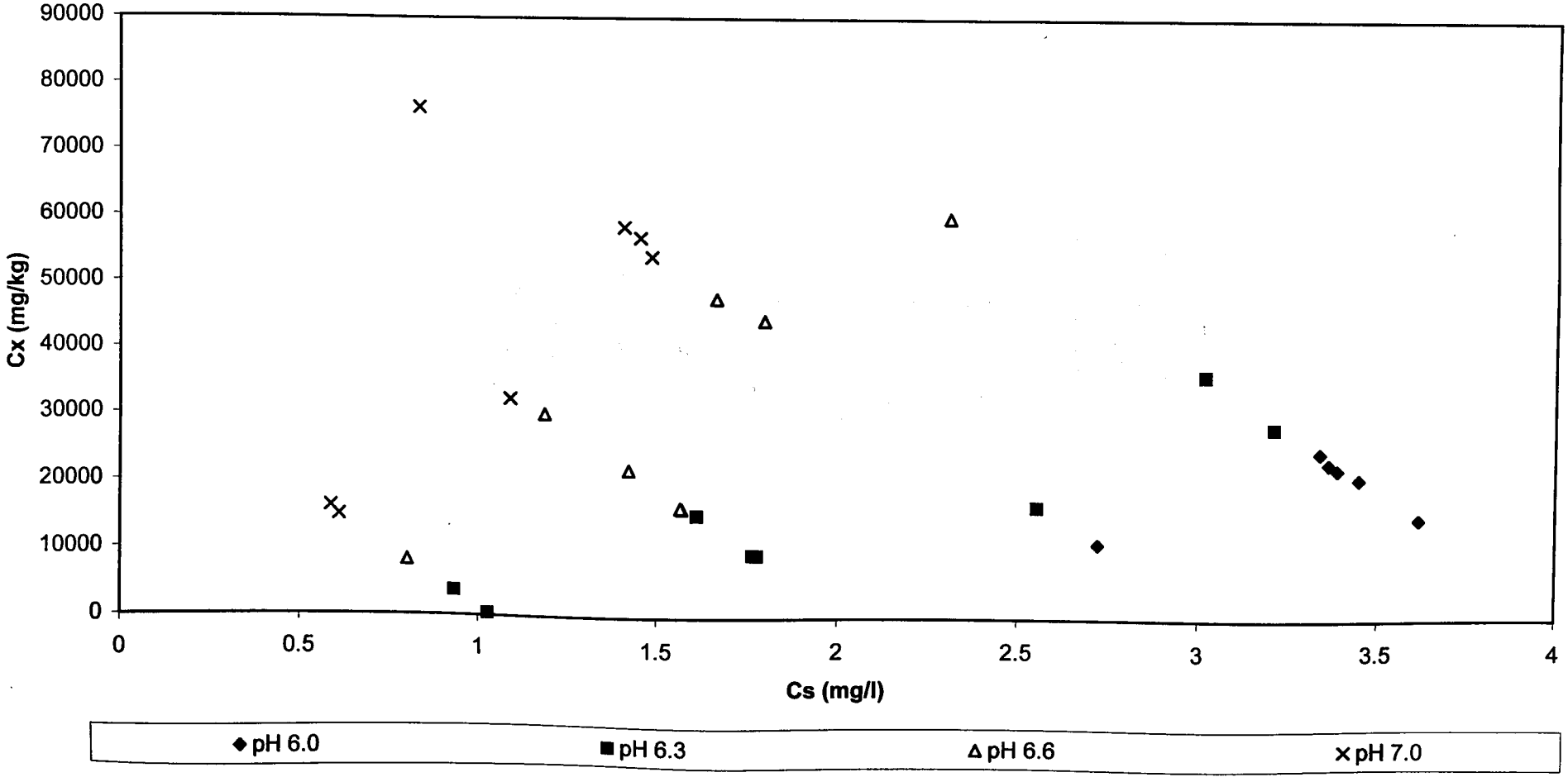


Figure C.161: ***Zn adsorption in Final Effluent in Competition Experiment Solids Concentration (31 mg/l)***

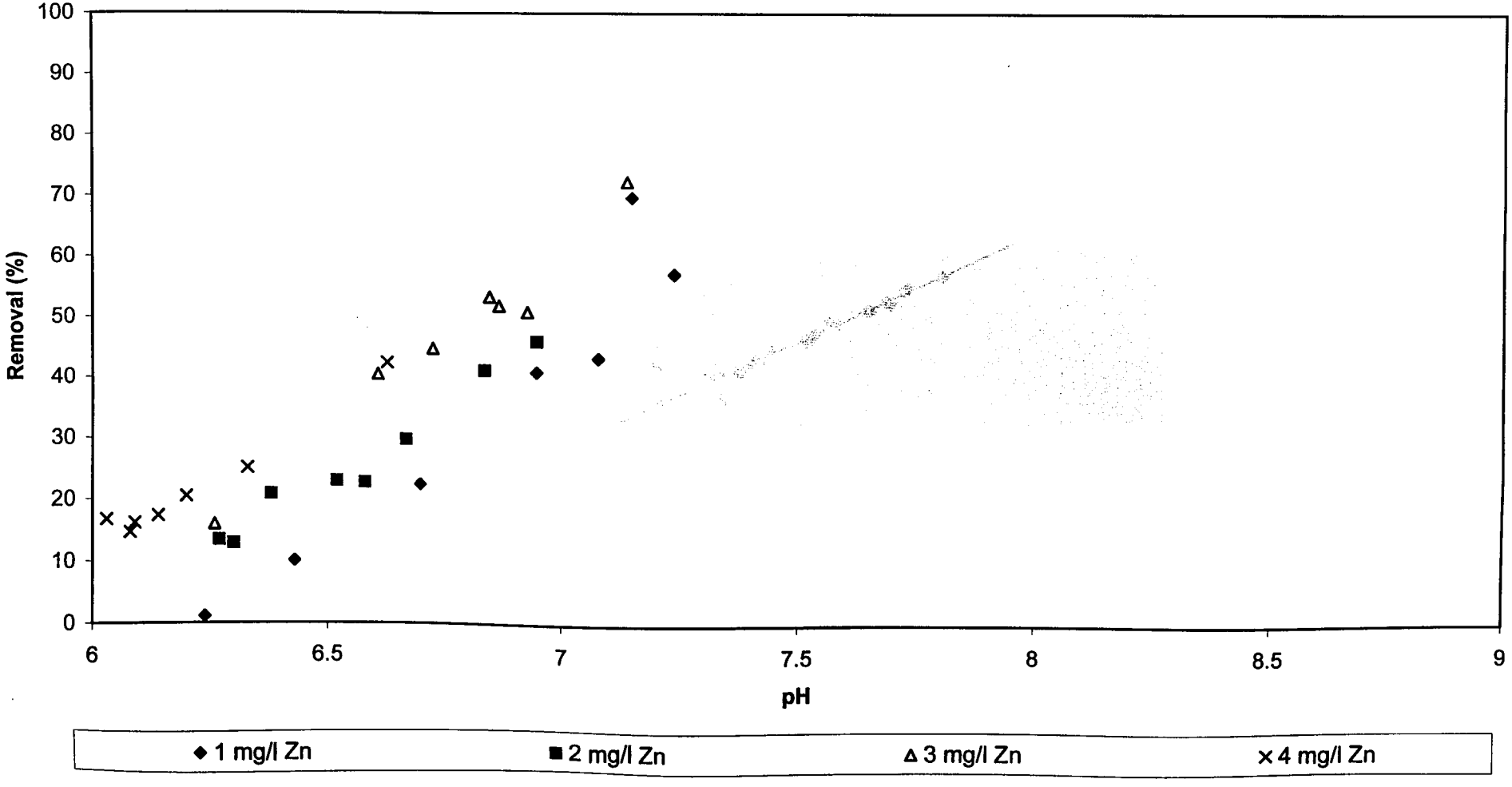
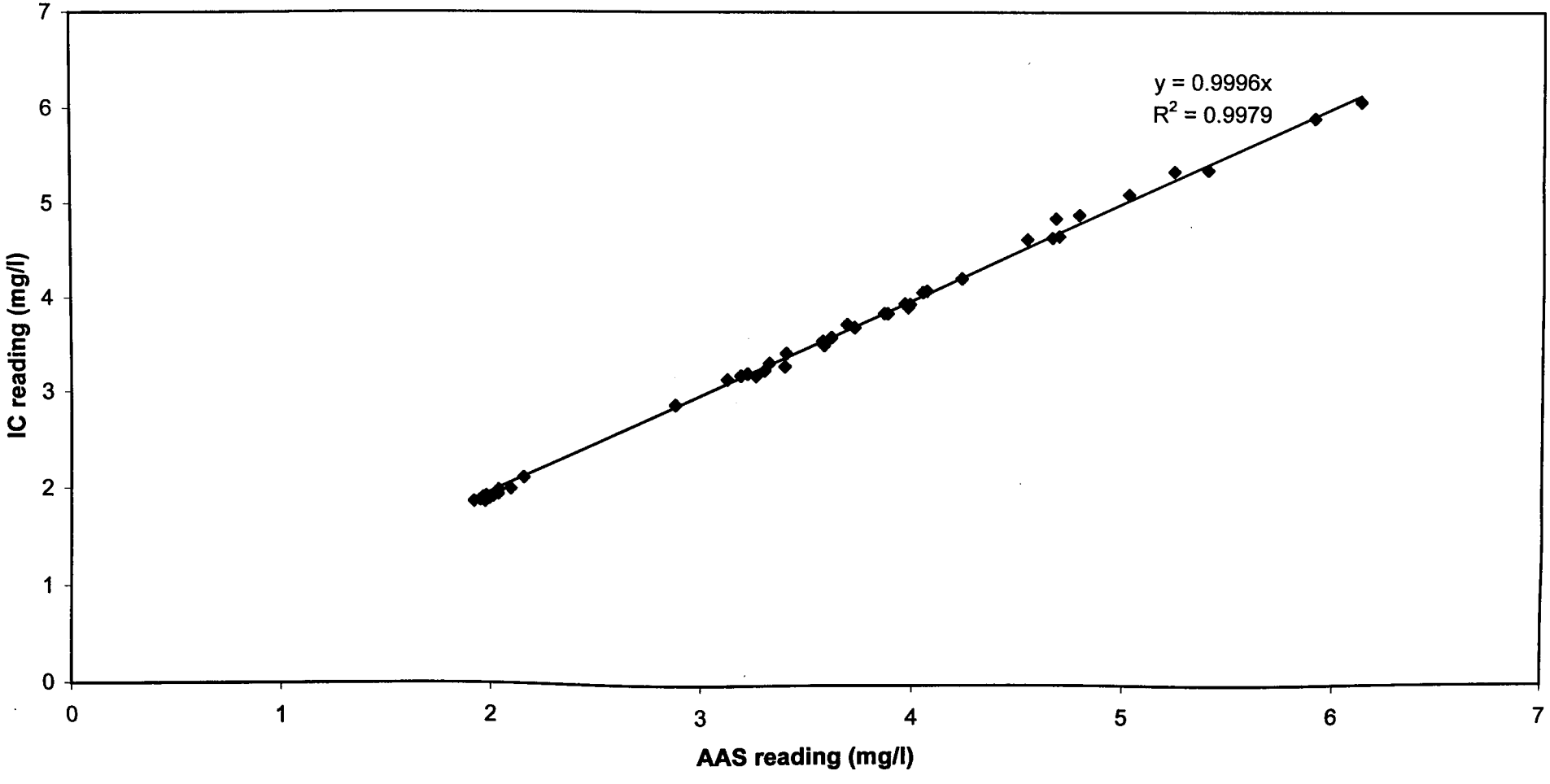


Figure C.162: ***Comparison between IC analysis and AAS analysis***



APPENDIX D

RESULTS OF FIELD STUDIES

Table D.1 *Variations in Zn concentrations over the two week period*
Field Study: Millbrook WWTP
Date: 9 August-20 August 1999

Sample	09/08/99	10/08/99	11/08/99	12/08/99	13/08/99	16/08/99	17/08/99	18/98/99	19/08/99	20/08/99	Average
Crude sewage + RSL	0.6819	0.23195	0.2861	0.18745	0.22995	0.2296	0.2106	0.242			0.28744
Crude sewage + RSL (screened)	0.3592	0.2323	0.18785	0.21305	0.22485	0.2031	0.3554	0.51135	0.18175	0.28825	0.27571
Influent into primary tank (old works)	0.4422	0.20285	0.22435	0.1341	0.22895	0.2163	0.1872	0.27035	0.2244	0.1989	0.23296
Primary effluent (old works)	0.256	0.20355	0.2276	0.15705	0.2149	0.22005	0.21585	0.2371	0.39345	0.14595	0.22715
Influent into aeration tanks (old works)	0.32935	0.2267	0.43095	0.14715	0.2333	0.16895	0.2598	0.2453	0.18725	0.6657	0.28945
Mixed liquor (old works)	0.3298	0.22985	0.35035	0.16495	0.2374	0.1781	0.1705	0.27245	0.1787	0.20675	0.23189
Final effluent (old works)	0.22175	0.2172	0.2045	0.19235	0.25565	0.20985	0.23635	0.2744	0.1758	0.25	0.22379
Influent into primary tank (new works)	0.21885	0.3021	0.3517	0.14705	0.2086	0.1976	0.18495	0.25055	0.13515	0.15185	0.21484
Primary effluent (new works)	0.3008	0.39	0.37915	0.2571	0.29	0.16015	0.1607	0.2367	0.16075	0.16745	0.25028
Influent into aeration tanks (new works)	0.3173	0.21925	0.2282	0.1723	0.21125	0.1742	0.18395	0.2133	0.1536	0.19985	0.20732
Mixed liquor (new works)	0.35645	0.24195	0.35165	0.2151	0.29095	0.17415	0.32295	0.23515	0.16905	0.20645	0.25639
Final effluent (new works)	0.3276	0.34165	0.1934	0.35835	0.221	0.38645	0.31135	0.2716	0.30645	0.2059	0.29238
Return Activated Sludge (old works)	0.1963	0.31505	0.26405	0.22785	0.25065	0.25415	0.2009	0.23925	0.2527	0.205	0.24059
Return Activated Sludge (new works)	0.22185	0.28665	0.43225	0.24155	0.2818	0.2212	0.2493	0.27935	0.29225	0.1983	0.27045
Thickener supernatant	0.3138	0.2569	0.2823	0.14455	0.3395	0.22655	0.2691	0.3948		0.1944	0.2691
Centrifuge supernatant	0.71825	0.21	0.28045	0.1375	0.25385	0.1917	0.52795	0.5072	0.3466	0.2236	0.33971
SBR influent	0.44035	0.2285		0.2359	0.3477	0.2929		0.3374	0.26685	0.19525	0.29311
SBR supernatant	0.3431	0.15835			0.3228	0.3308		0.2421	0.23115	0.6421	0.32434
Primary sludge	0.3114	0.3146	0.31245	0.20175	0.49945	0.4095	1.2153	0.86105	0.7872	1.1306	0.60433
Slowhill Sludge	68.19			91.94	114.05	97.73	47.4	88.68	57.44		80.7757
Inlet to thickeners	1.06925										1.06925

All values are in mg/l

Table D.2 Raw Sewage Samples
Field Study: Portswood WWTP
Date: 31/7/00-3/8/00

Sample Time	TSS (mg/l)	Cs Cu (mg/l)	Ct Cu (mg/l)	Ct Cu (mg/kg)	Cx Cu (mg/kg)	Cs Zn (mg/l)	Ct Zn (mg/l)	Ct Zn (mg/kg)	Cx Zn (mg/kg)
31/7/00 8:30	476	0.027	2.08	281.8428184	278.1842818	0.0796	7.18	972.899729	962.1138211
31/7/00 9:30	480	0.006	1.92	301.4128728	300.4709576	0.0354	6.976	1095.133438	1089.576138
31/7/00 10:30	454	0.013	1.8	280.8112324	278.7831513	0.077	10.764	1679.25117	1667.23869
31/7/00 11:30	388	0.003	1	240.9638554	240.2409639	0.0632	7.176	1729.156627	1713.927711
31/7/00 12:30	366	0.007	1.52	304	302.6	0.0654	9.596	1919.2	1906.12
31/7/00 13:30	346	0.008	1.36	293.1034483	291.3793103	0.1005	3.3	711.2068966	689.5474138
31/7/00 14:30	560	0.009	2.64	331.2421581	330.1129235	0.2188	14.032	1760.602258	1733.14931
31/7/00 15:30	318	0.007	1.4	309.7345133	308.1858407	0.1214	3.356	742.4778761	715.619469
31/7/00 16:30	244	0.013				0.061			
1/8/00 8:30	490	0.007	0.121	246.9387755	232.6530612	0.0565	0.1913	390.4081633	275.1020408
1/8/00 9:30	426	0.02	0.154	361.5023474	314.5539906	0.0668	0.1969	462.2065728	305.399061
1/8/00 10:30	408	0.017	0.15	367.6470588	325.9803922	0.1427	0.1802	441.6666667	91.91176471
1/8/00 11:30	518	0.035	0.117	225.8687259	158.3011583	0.102	0.1592	307.3359073	110.4247104
1/8/00 12:30	252	0.013	0.131	519.8412698	468.2539683	0.0693	0.1536	609.5238095	334.5238095
1/8/00 13:30	484	0.025	0.101	208.677686	157.0247934	0.0774	0.1973	407.6446281	247.7272727
1/8/00 14:30	344	0.004	0.136	395.3488372	383.7209302	0.0709	0.1735	504.3604651	298.255814
1/8/00 15:30	360	0.021	0.135	375	316.6666667	0.0692	0.1721	478.0555556	285.8333333
1/8/00 16:30	192	0.089	0.121	630.2083333	166.6666667	0.0545	0.1598	832.2916667	548.4375
2/8/00 8:30	598	0.01	0.129	215.7190635	198.9966555	0.0562	0.2062	344.8160535	250.8361204
2/8/00 9:30	438	0.034	0.145	331.0502283	253.4246575	0.0497	0.164	374.4292237	260.9589041
2/8/00 10:30	416	0.018	0.141	338.9423077	295.6730769	0.1038	0.149	358.1730769	108.6538462
2/8/00 11:30	380	0.01	0.112	294.7368421	268.4210526	0.0972	0.236	621.0526316	365.2631579
2/8/00 12:30	376	0.034	0.138	367.0212766	276.5957447	0.0968	0.1622	431.3829787	173.9361702
2/8/00 13:30	350	0.025	0.095	271.4285714	200	0.065	0.1124	321.1428571	135.4285714
2/8/00 14:30	322	0.013	0.132	409.9378882	369.5652174	0.1058	0.1633	507.1428571	178.5714286
2/8/00 15:30	300	0.002	0.124	413.3333333	406.6666667	0.1137	0.1296	432	53
2/8/00 16:30	122	0.001	0.061	500	491.8032787	0.0768	0.0746	611.4754098	-18.03278689
3/8/00 8:30	348	0.002	0.136	390.8045977	385.0574713	0.0646	0.1946	559.1954023	373.5632184
3/8/00 9:30	376	0.01	0.139	369.6808511	343.0851064	0.1029	0.1881	500.2659574	226.5957447
3/8/00 10:30	882	0.006	0.182	206.3492063	199.5464853	0.0831	0.2549	289.0022676	194.7845805
3/8/00 11:30	774	0.001	0.172	222.2222222	220.9302326	0.0545	0.2686	347.0284238	276.6149871
3/8/00 12:30	690	0.002	0.094	136.2318841	133.3333333	0.0528	0.1572	227.826087	151.3043478

Table D.3 Primary Effluent Samples
Field Study: Portswood WWTP
Date: 31/7/00-3/8/00

D&T	TSS (mg/l)	Cs Cu (mg/l)	Ct Cu (mg/l)	Ct Cu (mg/kg)	Cx Cu (mg/kg)	Cs Zn (mg/l)	Ct Zn (mg/l)	Ct Zn (mg/kg)	Cx Zn (mg/kg)
31/7/00 11:30	146	0.029	0.065	445.2054795	246.5753425	0.0703	0.0904	619.1780822	137.6712329
31/7/00 12:30	150	0.081	0.063	420	-120	0.0772	0.0871	580.6666667	66
31/7/00 13:30	126	0	0.051	404.7619048	404.7619048	0.0474	0.0782	620.6349206	244.4444444
31/7/00 14:30	132	0.008	0.047	356.0606061	295.4545455	0.0639	0.0659	499.2424242	15.15151515
31/7/00 15:30	138	0.01	0.053	384.057971	311.5942029	0.1722	0.0819	593.4782609	-654.3478261
31/7/00 16:30	134	0.015	0.056	417.9104478	305.9701493	0.2047	0.1147	855.9701493	-671.641791
31/7/00 17:30	118	0.01	0.064	542.3728814	457.6271186	0.0405	0.0825	699.1525424	355.9322034
31/7/00 18:30	122	0.01	0.06	491.8032787	409.8360656	0.0707	0.0906	742.6229508	163.1147541
31/7/00 19:30	136	0.004	0.066	485.2941176	455.8823529	0.0544	0.0885	650.7352941	250.7352941
1/8/00 11:30	114	0.018	0.072	631.5789474	473.6842105	0.0615	0.0911	799.122807	259.6491228
1/8/00 12:30	144	0.026	0.068	472.2222222	291.6666667	0.058	0.0915	635.4166667	232.6388889
1/8/00 13:30	122	0.001	0.06	491.8032787	483.6065574	0.0838	0.0878	719.6721311	32.78688525
1/8/00 14:30	108	0.018	0.055	509.2592593	342.5925926	0.0422	0.0662	612.962963	222.2222222
1/8/00 15:30	94	0.005	0.047	500	446.8085106	0.0417	0.0676	719.1489362	275.5319149
1/8/00 16:30	112	0.008	0.063	562.5	491.0714286	0.0586	0.0848	757.1428571	233.9285714
1/8/00 17:30	106	0.004	0.052	490.5660377	452.8301887	0.048	0.071	669.8113208	216.9811321
1/8/00 18:30	128	0.015	0.062	484.375	367.1875	0.0471	0.0766	598.4375	230.46875
1/8/00 19:30	146	0.034	0.065	445.2054795	212.3287671	0.0538	0.0914	626.0273973	257.5342466
2/8/00 11:30	138	0.016	0.073	528.9855072	413.0434783	0.0762	0.087	630.4347826	78.26086957
2/8/00 12:30	130	0.006	0.07	538.4615385	492.3076923	0.1052	0.1104	849.2307692	40
2/8/00 13:30	124	0.014	0.066	532.2580645	419.3548387	0.0756	0.0821	662.0967742	52.41935484
2/8/00 14:30	116	0.009	0.06	517.2413793	439.6551724	0.1123	0.0793	683.6206897	-284.4827586
2/8/00 15:30	116	0.02	0.057	491.3793103	318.9655172	0.0867	0.0733	631.8965517	-115.5172414
2/8/00 16:30	112	0.015	0.052	464.2857143	330.3571429	0.0606	0.0857	765.1785714	224.1071429
2/8/00 17:30	122	0.014	0.056	459.0163934	344.2622951	0.0652	0.0645	528.6885246	-5.737704918
2/8/00 18:30	134	0.014	0.063	470.1492537	365.6716418	0.0557	0.0809	603.7313433	188.0597015
2/8/00 19:30	242	0.009	0.094	388.4297521	351.2396694	0.0685	0.1686	696.6942149	413.6363636
3/8/00 11:30	86	0	0.045	523.255814	523.255814	0.0566	0.0556	646.5116279	-11.62790698
3/8/00 12:30	70	0.011	0.042	600	442.8571429	0.0784	0.0482	688.5714286	-431.4285714

Table D.4 Mixed Liquor Samples
Field Study: Portswood WWTP
Date: 31/7/00-3/8/00

D&T	TSS (mg/l)	Cs Cu (mg/l)	Ct Cu (mg/l)	Ct Cu (mg/kg)	Cx Cu (mg/kg)	Cs Zn (mg/l)	Ct Zn (mg/l)	Ct Zn (mg/kg)	Cx Zn (mg/kg)
31/7/00 14:30	1740	0.009	7.64	370.1550388	369.7189922	0.1389	9.072	439.5348837	432.8052326
31/7/00 15:30	1550	0.002	7.36	350.1427212	350.0475737	0.1696	9.296	442.2454805	434.1769743
31/7/00 16:30	1750	0.012	7.64	372.1383341	371.5538237	0.1073	9.624	468.7773989	463.5509011
31/7/00 17:30	2040	0.01	7.64	367.1311869	366.6506487	0.1398	9.228	443.4406535	436.7227295
31/7/00 18:30	1860	0.009	7.44	362.3964929	361.9581101	0.0961	8.984	437.6035071	432.9225524
31/7/00 19:30	1760	0.005	7.6	373.8317757	373.5858337	0.0601	9.044	444.8598131	441.9035908
31/7/00 20:30	1690	0.007	8.4	399.2395437	398.9068441	0.0443	9.692	460.6463878	458.5408745
1/8/00 14:30	1750	0.01	7.16	348.9278752	348.4405458	0.0979	8.056	392.5925926	387.8216374
1/8/00 15:30	1710	0.031	4.32	205.3231939	203.8498099	0.3175	4.516	214.6387833	199.5484791
1/8/00 16:30	1860	0.037	5.56	275.7936508	273.9583333	0.1219	8.456	419.4444444	413.3978175
1/8/00 17:30	1860	0.003	4.96	240.0774443	239.9322362	0.0857	8.036	388.964182	384.8160697
1/8/00 18:30	1680	0.021	4.76	222.2222222	221.2418301	0.0747	7.72	360.410831	356.923436
1/8/00 19:30	1580	0.015	4.24	207.1323889	206.3996092	0.0757	6.58	321.4460186	317.7479238
1/8/00 20:30	1610	0.006	5.16	255.952381	255.6547619	0.0516	8.528	423.015873	420.4563492
2/8/00 14:30	1470	0.005	7.88	385.518591	385.2739726	0.079	7.708	377.1037182	373.2387476
2/8/00 15:30	1310	0.014	7.48	361.003861	360.3281853	0.1083	8.052	388.6100386	383.3832046
2/8/00 16:30	1580	0.026	8.12	393.7924345	392.5315228	0.0694	7.768	376.7216295	373.3559651
2/8/00 17:30	1650	0.012	8.04	377.1106942	376.5478424	0.1341	9.204	431.7073171	425.4174484
2/8/00 18:30	1660	0.017	8.28	406.6797642	405.8447937	0.06	8.984	441.2573674	438.3104126
2/8/00 19:30	1530	0.005	7.6	377.1712159	376.9230769	0.1018	9.232	458.1637717	453.1116625
2/8/00 20:30	1320	0.016	8.84	413.2772324	412.5292193	0.0854	9.948	465.0771388	461.084619

APPENDIX E

MODEL CONFIRMATION

Table E.1 *Sensitivity Check for Zn Calculations*

Inputs

Coefficient	Value 1	Value 2	Value 3
Kp1	0.0015	0.00075	0.003
Sol1	0.41438	0.41438	0.41438
Ka1	5000	2500	10000
Kp2	0.0018	0.0009	0.0036
Sol2	0.54486	0.54486	0.54486
Ka2	4000	2000	8000
Kp3	0.0025	0.00125	0.005
Sol3	0.0659	0.0659	0.0659
Ka3	1700	850	3400
Kp4	0.0045	0.00225	0.009
Sol4	0.0659	0.0659	0.0659
Ka4	4000	2000	8000

Outputs *after 10 interations*

Parameter	Using Value 1	Using Value 2	Using value 3	
minn	1.18	1.07	1.16	**Total Metal**
mpe	0.49	0.5	0.45	
mml	1.9	1.2	1.77	
mfe	0.07	0.07	0.07	
				Solids Bound Metal
mxinn	812.92	473.5	1122.08	
mxpe	162.6	94.71	224.45	
mxml	1174.76	573.23	1280.86	
mxfe	17.62	8.6	19.21	
				Soluble Metal
msinn	0.41	0.41	0.41438	
mspe	0.41	0.41	0.41	
msml	0.07	0.07	0.07	
msfe	0.07	0.07	0.07	
mpinn	0.26	0.37	0.05	**Precipitated Metal**
mppe	0.05	0.07	0.01	
mpml	0.49	0.48	0.24	
mpfe	0.01	0.01	0.0036	
mps	1411.15	1183.03	1445.51	**Sludge**
mses	1650.15	850	1533.21	
mws	1650.15	850	1533.21	
mrs	1650.15	850	1533.21	

Table E.2 *Sensitivity Check for Cu Calculations*

Inputs

Coefficient	Value 1	Value 2	Value 3
Kp1	0.0005	0.00025	0.001
Sol1	2.65488	2.65488	2.65488
Ka1	4000	2000	8000
Kp2	0.008	0.004	0.016
Sol2	1.475	1.475	1.475
Ka2	5000	2500	10000
Kp3	0.0008	0.0004	0.0016
Sol3	2.0073816	2.0073816	2.0073816
Ka3	3000	1500	6000
Kp4	0.014	0.0007	0.0028
Sol4	2.3439	2.3439	2.3439
Ka4	10000	5000	20000

Outputs *after 10 interations*

Parameter	Using Value 1	Using Value 2	Using value 3	
minn	1.06	1.04	1.1	**Total Metal**
mpe	0.86	0.93	0.74	
mml	1.36	1.22	1.51	
mfe	0.7732	0.8794	0.598	
mxinn	343.99	186.27	589.97	**Solids Bound Metal**
mxpe	68.94	37.33	118.23	
mxml	518.52	294.89	801.37	
mxfe	7.78	4.425	12.03	
msinn	0.85	0.92	0.73	**Soluble Metal**
mspe	0.85	0.92	0.73	
msml	0.77	0.88	0.6	
msfe	0.773022	0.8793	0.597	

mpinn	0	0	0	**Precipitated Metal**
mppe	0	0	0	
mpml	0	0	0	
mpfe	0	0	0	

mps	455.48	269.69	744.69	**Sludge**
mses	783.97	592.4	1012.5	
mws	783.97	592.4	1012.5	
mrs	783.97	592.4	1012.5	