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Removal of formaldehyde from aqueous solutions via oxygen reduction using a reticulated vitreous carbon cathode cell

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The removal of formaldehyde from waste streams to <0.3 ppm has been demonstrated using a cell with a reticulated vitreous carbon cathode; the formaldehyde is oxidized by hydrogen peroxide, formed at the cathode by reduction of oxygen. In most electrolytes studied (e.g. NaOH, NaCl and Na_2SO_4), the formaldehyde is oxidised only to formic acid. On the other hand, the addition of a low concentration of an iron salt (i.e. 0.5 mM), catalyses the complete oxidation to carbon dioxide. The removal of formaldehyde can be achieved in media of low ionic strength (<10 mM) although the use of iron salts necessitates the adjustment of pH to 3 to maintain the catalyst in solution.

1. Introduction

Formaldehyde has many, diverse uses in the chemical industry and is also used as a disinfectant in hospitals; production of formaldehyde in the US alone exceeds six million tons per year [1]. Unfortunately, formaldehyde can cause damage in the aquatic environment at levels <1 ppm [2] and in air, its threshold-limit value (TLV) is 5 mg m^{-3} [3]. Hence, there is a clear requirement for efficient technology to remove formaldehyde from effluents.

One electrolytic approach envisages the anodic oxidation of the formaldehyde. While there is an extensive literature on this and similar reactions [4, 5], they require the use of precious metal catalysts and are not satisfactory reactions; the surface of the electrocatalysts are quickly poisoned by adsorbed intermediates and almost complete loss of activity is observed. A recent paper [6] has proposed an alternative electrochemical approach, an electrolytic version of the widely used [7] hydrogen peroxide destruction of formaldehyde. The hydrogen peroxide is produced by reduction of oxygen at a carbon cathode. While the chemistry appeared to work well, a small laboratory cell, unsuited to scale up for effluent treatment, was employed. Therefore, we initiated a study of this chemistry in a flow cell with a three-dimensional electrode manufactured from reticulated vitreous carbon. The theory and applications of three dimensional electrodes including those based on reticulated vitreous carbon have recently been reviewed [8]. Certainly, such electrodes, usually of a carbon, have previously been used for the reduction of air and/or oxygen to hydrogen peroxide [9–13] and, indeed, such technology forms the basis of an industrial process for the manufacture on site of hydrogen peroxide for the pulp and paper industry [14, 15].

Oxygen reduction occurs either in a single $4e^-$ step

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \quad (1)$$

or, in two discrete steps

$$O_2 + H_2O + 2e^- \longrightarrow HO_2^- + OH^- \quad (2)$$

$$HO_2^- + H_2O + 2e^- \longrightarrow 3OH^- \quad (3)$$

where hydrogen peroxide may be a stable product over a range of potential. The product (hydrogen peroxide or water), as well as the mechanism and kinetics of this reaction, depend strongly on the choice of cathode material and even on the form of carbon used [16–18]. With vitreous carbon as the cathode in aqueous sodium hydroxide, there have been several previous studies [19–25]; some workers, on seeing two reduction waves, assumed that the reduction occurred in two $2e^-$ steps to hydrogen peroxide and water but there is convincing evidence [24, 25] from RRDE experiments that, in fact, both the processes lead to hydrogen peroxide and hydrogen peroxide reduction does not occur positive to hydrogen evolution. These conclusions were partially confirmed in the earlier experiments with three dimensional electrodes [11, 13]. Oloman *et al.* [11] using a trickle-bed of graphite particles report significant current yields of hydrogen peroxide over a range of current densities. Davison and coworkers [13] using cathodes consisting of a bed of graphite chips as well as reticulated vitreous carbon also report hydrogen peroxide formation over a broad potential range but find that the current efficiency drops off at more negative potentials.

2. Experimental details

The cell [26] is sketched in Fig. 1. It was fabricated from four blocks of polypropylene, each 280 mm × 100 mm × 12 mm thick. The steel plate

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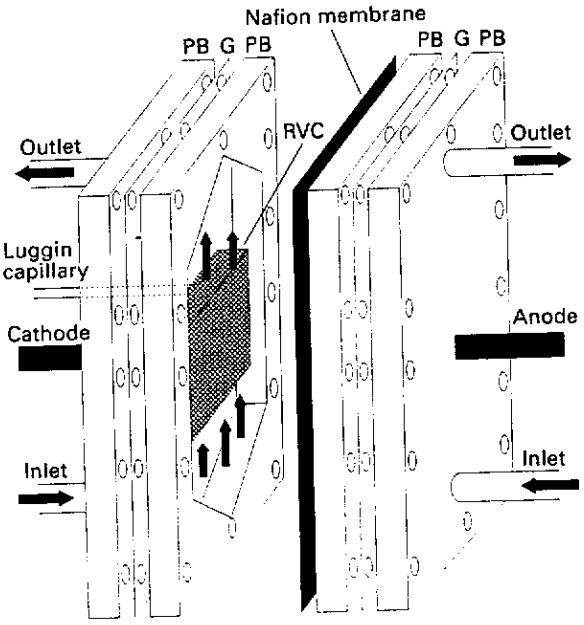

Fig. 1. The construction of the flow cell: (PB) polymer block, (G) gasket, (RVC) reticulated vitreous carbon cathode.

cathode current collector (50 mm × 50 mm) was sunk into one of the outer blocks. The inner polymer blocks were machined to form the electrolyte channels. Each had extended entry and exit lengths while the reticulated vitreous carbon cathodes (50 mm× 50 mm × 12 mm thick) fitted tightly into the centre of the catholyte channel and electrical contact with the current collector was made with conducting carbon cement (Leit-C from Agar Aids). The reticulated vitreous carbon (10, 30, 60 and 100 pores per inch) was supplied by the Electrosynthesis Co. The anode was a platinum gauze (50 mm × 50 mm) placed in the anolyte stream so that it faced the reticulated vitreous carbon cathode and electrical connection was made via a contact through the second outer polymer block. The Luggin capillary was a small plastic tube inserted through a 3 mm hole drilled through the steel current collector; the tip of the tube was positioned ~2 mm into the reticulated

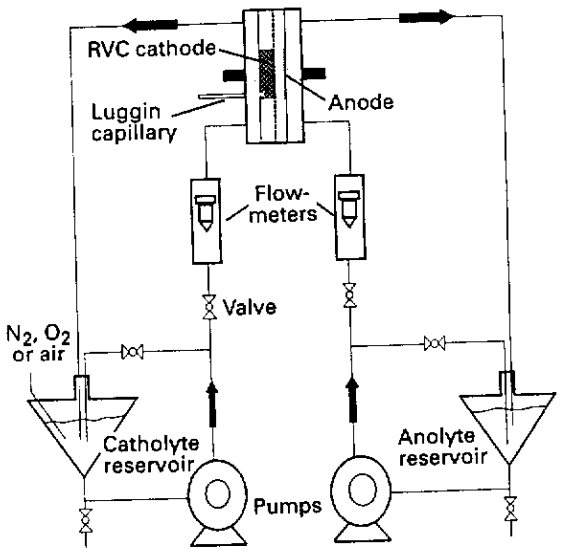

Fig. 2. The design of the electrolyte flow circuits.

vitreous carbon structure. The reference electrode was a Radiometer type K401 saturated calomel electrode. The separator was a Nafion® 417 cation permeable membrane and the gaskets were cut from sheets of 1 mm silicone rubber. Electrolyte streams entered and left the cell through 0.5 inch 'Fast and Tite' fittings. The hydraulic circuit is shown in Fig. 2. Typically, experiments were carried out with 2.5 dm^3 of catholyte and a similar volume of anolyte and the solutions were continuously recycled through the cell. The pumps were obtained from Totton Pumps, model EMP 40/4 and flow velocities were measured with KDG 18XE flowmeters. These were calibrated and gave flow rates in the range 0 to 8 $dm^3\ min^{-1}$ or linear flow velocities for 0 to 0.22 $m\ s^{-1}$ through the cathode. The catholyte reservoir was fitted with a sparger and a fast stream of nitrogen, air or oxygen was passed throughout each electrolysis. With the exception of the reservoirs, flow meters and the cell, the electrolyte circuit was constructed from PVC pipework, GF 0.5 inch valves and Gielle three-way connectors. Experiments were carried out at 298 ± 3 K except where otherwise stated.

In the experiments, a Hitek model DT2101 potentiostat and model PPR1 function generator were used. Responses were recorded on a Gould 60000 series X-Y recorder.

The electrolytes (NaOH, NaCl and Na_2SO_4) as well as potassium ferricyanide and copper sulfate were BDH Analar grade. $FeCl_2.4H_2O$ was reagent grade supplied by Aldrich. Formaldehyde solutions were prepared by dilution of 37–41% solution supplied by BDH. All solutions were prepared with water from a Milli-Ro 15/Milli-Q purification system.

Hydrogen peroxide yields were determined by titration with potassium permanganate and frequently checked using an iodometric titration [27]. The absolute concentration of the supplied formaldehyde solution was determined following dilution by a factor of ten using a procedure based on reaction with sodium sulfite [28]. During electrolyses, the concentration of formaldehyde was monitored using a colorimetric method based on reaction with chromotropic acid [29]. Typically, 1 cm^3 of the electrolyte was mixed with 5 cm^3 of a stock solution of chromotropic acid [29] and the solution was stood in a bath of boiling water for 30 min. A purple colour developed and the absorbance of the solution was measured at 573 nm in a Phillips u.v./vis. spectrometer, model PU8730. The absorbance was compared with those on calibration plots of 0–5 ppm and 0–20 ppm formaldehyde. These were linear passing through the origin with points as low as 0.3 ppm. With the electrolysis solutions, however, there was an interference (probably free H_2O_2) which sometimes prevented precise quantitative determinations <1 ppm. When electrolyses employed more concentrated solutions, anolytes were diluted to the 0–20 ppm range. Total organic carbon (TOC) was determined by Southern Science Ltd using a procedure based on photocatalytic oxidation.

3. Results and discussion

3.1. *Reduction of oxygen on reticulated vitreous carbon in 1 M NaOH*

Current vs potential curves recorded at several linear flow velocities for an air equilibrated 1 M sodium hydroxide solution at a 60 ppi reticulated vitreous carbon cathode are shown in Fig. 3; also shown is the response at one flow rate when the oxygen is removed with a fast stream of nitrogen. It can be seen that, in the presence of oxygen, two reduction waves are observed at $E_{1/2} = -460$ mV and -970 mV vs SCE. Hence, oxygen reduction appears to occur in two steps. The two waves are, however, not of equal height. Moreover, the limiting current for the first wave is little influenced by solution velocity and hence the electrode reaction associated with the wave appears to be kinetically controlled. In contrast, the current in the second limiting current plateau region varies markedly with linear velocity and the electrode reaction appears to be at least partially mass transport controlled.

Controlled potential electrolyses were carried out on air equilibrated 1 M NaOH solutions at a series of potentials and the results are summarized in Table 1. In all cases, the concentration of hydrogen peroxide in the catholyte increased linearly with time and, although it was not the objective of this work to prepare high concentrations, it was possible to build up the hydrogen peroxide concentration to >10 mM. As expected, the steady state current through the cell increased as the cathode potential was made more negative but the current yield of hydrogen peroxide was found to decay steadily; at -600 mV, the current efficiency was >90% but it dropped to 57% by -1400 mV and to very low values once significant hydrogen evolution had commenced. Even so, it can be seen that significant amounts of hydrogen peroxide were formed in the plateau region of the second wave. These data are similar, but not identical, to those of Oloman *et al.* [11] and Davison *et al.* [13] using three dimensional cathodes and also the RRDE studies using vitreous carbon disc electrodes [24, 25]. It has been proposed [25] that multiple waves for oxygen reduction on carbon arise from different surface sites and this would certainly explain the sensitivity of the data to the type of

Table 1. Controlled potential electrolyses carried out for air saturated 1 M NaOH at a reticulated vitreous carbon cathode (60 ppi)

E /mV vs SCE	*I* /mA	*Current efficiency* /%	*Final* $[H_2O_2]$ /mM
−600	95	94	6
−900	254	80	8
−1200	270	66	9
−1400	320	57	10
−1700	923	2	0.6

* *Conditions*: electrolyte linear flow velocity: 0.19 m s^{-1}; temperature 25 ± 3° C.

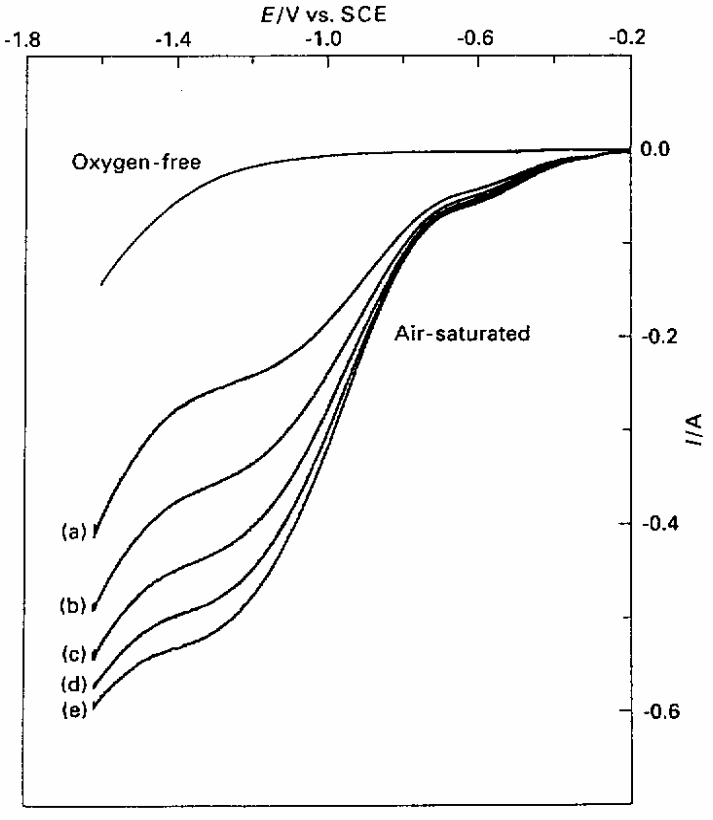

Fig. 3. Current/potential curves for the reduction of oxygen at a 60 ppi reticulated vitreous carbon cathode in the flow cell. Electrolyte: air saturated 1 M NaOH. Catholyte flow rate: (a) 0.016, (b) 0.045, (c) 0.09, (d) 0.13 and (e) 0.17 m s^{-1}. The figure also shows the curve for the solution deoxygenated with nitrogen; flow rate 0.09 m s^{-1}.

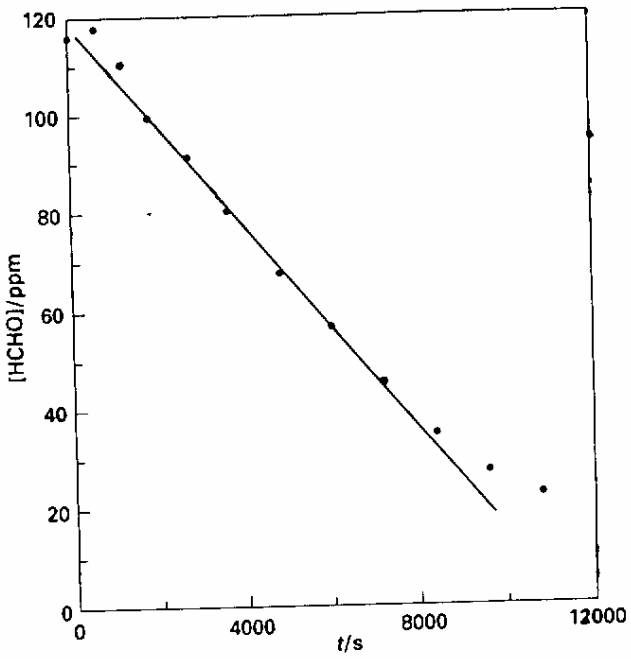

Fig. 4. Formaldehyde concentration as a function of time during the electrolysis of oxygen-saturated 1 M NaOH at a 60 ppi reticulated vitreous carbon cathode. Catholyte flow rate 0.20 m s^{-1}. Potential −0.60 V vs SCE. Initial formaldehyde concentration: 116 ppm. Temperature: 25 ± 3° C.

carbon employed. With the reticulated vitreous carbon used in these experiments, the first wave appears to lead only to hydrogen peroxide while the second results from a mixture of $2e^-$ and $4e^-$ reduction.

Further experiments were carried out with oxygen saturated 1 M sodium hydroxide. The current/potential curves were then less reproducible and at more negative potentials the currents were not proportional to the oxygen concentration; this suggests problems from a potential distribution within the cathode at higher currents. At −600 mV, however, the current increased fivefold compared to the air equilibrated solution and the current efficiency remained above 90%. The 'membrane' current density reached ~15 mA cm^{-2} at −600 mV with oxygen saturated solutions. This current density leads to a sufficient flux of hydrogen peroxide from the cathode surface for the removal of low concentrations of formaldehyde, provided the reaction between hydrogen peroxide and formaldehyde is fast. These, therefore, were the conditions employed for the study of formaldehyde removal, although it is recognized that the rate of removal would be higher using a more negative potential, perhaps at the expense of a lower current efficiency.

It should also be noted that the current against potential curves for oxygen reduction are not influenced by the presence of formaldehyde.

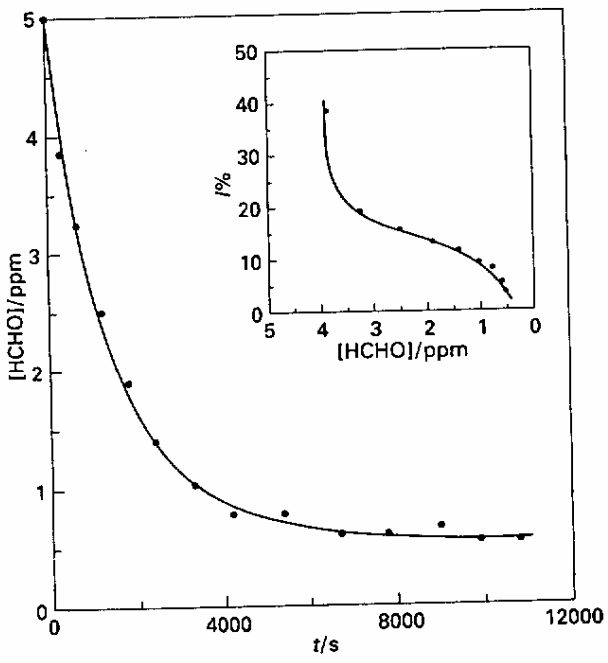

Fig. 5. Formaldehyde concentration as a function of time during the electrolysis of oxygen-saturated 1 M NaOH at a 60 ppi reticulated vitreous carbon cathode. Catholyte flow rate 0.20 m s^{-1}. Potential −0.60V vs SCE. Initial formaldehyde concentration 5 ppm. Temperature 25 ± 3° C. The inset shows the variation of current efficiency with formaldehyde concentration.

3.2. *Removal of formaldehyde from 1 M NaOH*

The removal of formaldehyde was first investigated from 1 M NaOH solutions where the initial concentration of formaldehyde varied between 5 and 150 ppm. The solutions were saturated with oxygen and the electrolyses were carried out at −600 mV vs SCE, initially at room temperature using a cell with a 60 ppi reticulated vitreous carbon cathode. Figures 4 and 5 report the decrease in formaldehyde concentration with time for electrolyses where the initial concentrations are 116 ppm and 5 ppm, respectively. It can be seen that the decay curves have different shapes. With the higher initial concentration, the formaldehyde concentration decayed linearly, at least through the first 6000 s of the electrolysis. Extrapolation of this linear decay shows that 90% depletion would require approximately 10 000 s (in practice, it would probably take longer). In addition, the current efficiency at the end of the electrolysis was 75%, assuming that the product was formic acid (see below), showing that most of the hydrogen peroxide generated was consumed in the removal of formaldehyde. In contrast, with the lower initial formaldehyde concentration, a 90% removal was achieved much more rapidly (*ca.* 2700 s) and the concentration was readily decreased to <0.6 ppm, close to the lowest detection limit for the analytical procedure; the decay appears to be exponential. On the other hand, the current efficiency, shown as an inset in Fig. 5, was low (10–20% during most of the electrolysis). Analysis of the solution showed that hydrogen peroxide did not accumulate in the catholyte until the final stages of the electrolysis; hydrogen peroxide is, however, stable in 1 M NaOH during the timescale of this electrolysis (Section 3.1) and some other competing reactions must therefore occur in order to account for the low current efficiency. Presumably, the catalytic decomposition of hydrogen peroxide is accelerated

*Table 2. Electrolysis for the removal of formaldehyde at −0.6 V vs SCE. Reticulated vitreous carbon cathode of the grade shown. Catholyte: 1 M NaOH saturated with oxygen**

Grade RVC /ppi	$[HCHO]_{t=0}$ /ppm	*For 75% removal of HCHO* *time*/s	*Current eff.*†/%	$[HCHO]_{final}$‡ /ppm	*Other conditions*
100	18	2700	22	<1.5	
	6	2400	5	<1	
60	116	9600	74	<4	
	11	3600	18	<2	
	5	2500	11	<0.6	
	19	2700	23	<0.3	40° C
	6	1000	9	<0.4	40° C
	17	3600	23	<0.8	undivided cell
10	17	3600	23	<1	

* *Conditions*: temperature 25 ± 3° C; catholyte linear flow velocity 0.19 m s^{-1}.
† Assumes 2e$^-$ oxidation.
‡ These are the formaldehyde concentrations when the electrolyses were terminated.

by a species in solution (associated with HCHO or its oxidation products), possibly present only as a minor constituent.

These differences in the decay curves with initial formaldehyde concentration may be understood in terms of the relative concentrations of hydrogen peroxide and formaldehyde within the reaction layer at the cathode surface. The limiting cases will be as follows.

(a) When [HCHO] ≫ [H_2O_2] within the reaction layer at the cathode surface, a situation which must arise when [HCHO] ≫ [O_2] and there is no accumulation of hydrogen peroxide in the bulk, the maximum rate of removal of the formaldehyde will be limited by the rate of generation of hydrogen peroxide. The reaction kinetics will be equivalent to the removal of formaldehyde at a constant current, much below the mass transport limited current for the oxidation/reduction of the formaldehyde in solution. The formaldehyde concentration should drop linearly with time (or charge). Moreover, the rate of formaldehyde removal will be much slower than if it occurred by a reaction limited by mass transport of formaldehyde to the surface.

(b) On the other hand, when [HCHO] ≪ [H_2O_2] within the reaction layer, and if the reaction between formaldehyde and hydrogen peroxide is fast, the oxidation of formaldehyde will be mass transport controlled with respect to formaldehyde and its concentration will decay according to the equation

$$[HCHO] = [HCHO]_{t=0} \exp\left(\frac{-k_m A_e V_e t}{V}\right) \quad (4)$$

where k_m is the mass transfer coefficient, A_e the specific electrode area, V_e the volume of the cathode and V is the volume of the catholyte. Equation 4 is only appropriate if the potential distribution within the three dimensional cathode is sufficiently uniform that all the surface operates in the limiting current region. In fact, with the cell and flow circuit employed here, it has been confirmed [26] that Equation 4 is followed when a simple mass transport controlled reaction, the reduction of Cu^{2+} in acid sulfate, is carried out (the reactant concentrations and electrolyte conductivities were also similar to those used in the present study). Moreover, 90% depletion of Cu^{2+} was achieved in approximately 1200 s with an electrolyte flow velocity rate of 0.19 m s^{-1}. The depletion of formaldehyde was not this rapid even with an initial concentration of 5 ppm, so the reaction is still not fully mass transport controlled with respect to formaldehyde. There is, in addition, the possibility that the excess hydrogen peroxide leaving the electrode will react with formaldehyde in the reservoir. Then, the removal of the formaldehyde will occur even more rapidly.

The solutions were maintained saturated with oxygen by passing a stream of the gas at atmospheric pressure through the 1 M NaOH in the reservoir and hence its concentration was 0.7 mM. 100 ppm formaldehyde is ~3.3 mM. Case (a) should therefore certainly be observed when the [HCHO] > 50 ppm. If the reduction of oxygen to hydrogen peroxide were limited by the mass transport of oxygen to the electrode, case (b) would be observed when [HCHO] < 10 ppm. In fact, it was concluded above that the rate of reduction of oxygen at −600 mV was well below mass transport control (the current at −600 mV is 10–20% of the plateau current in Fig. 3). Therefore, the limiting case (b) may not be seen until [HCHO] < 1 ppm. This range of formaldehyde concentrations could not be studied effectively because the analytical procedure was not sufficiently sensitive. With 5 ppm formaldehyde, however, the depletion rate would be expected to approach that predicted by Equation 4 as was observed.

Table 2 reports data from formaldehyde depletion experiments carried out over a wider range of conditions. When $[HCHO]_{t=0}$ < 20 ppm, the electrolyses were always continued until the level of formaldehyde fell to less than 2 ppm. Indeed, there was no problem in taking the formaldehyde to below the detection limit of the analytical method (0.3–1 ppm)

Table 3. Electrolysis for the removal of formaldehyde at −0.6 V vs SCE in different aqueous electrolytes saturated with oxygen. Reticulated vitreous carbon cathode, 60 ppi*

Electrolyte	$[HCHO]_{t=0}$ /ppm	*For 75% removal* time/s	*Current eff./%*	$[HCHO]_{final}$§ /ppm
10 mM NaOH	18	6000	23†	<1
0.5 M Na_2SO_4	18	4800	20†	<0.3
10 mM NaCl	17	3600	17†	<0.8
	6	2000	8†	<0.2
	3	2700	5†	<0.4
10 mM NaCl + 0.5 mM $FeCl_2$	12	Little formaldehyde removal, ferrous hydroxide/oxide on cathode		
10 mM HCl + 0.5 mM $FeCl_2$	13	3500	6‡	<0.3
10 mM NaCl + 0.5 mM $FeCl_2$, pH 3	12	3000	8‡	<0.4
0.5 mM $FeCl_2$, pH 3**	12	2000	24‡	<0.3
0.5 mM $FeCl_2$, pH 3§§	11	2900	10‡	<0.3

* *Conditions*: temperature 25 ± 3° C; catholyte linear flow velocity 0.19 m s^{-1}.
† Assumes $2e^-$ oxidation.
‡ Assumes $4e^-$ oxidation.
§ These are the formaldehyde concentrations when the electrolyses were terminated.
** pH adjusted to 3 throughout the electrolysis
§§ 0.1 M H_2SO_4 as the electrolyte in the anode compartment.

which varied slightly due to an interference, thought to be due to unreacted hydrogen peroxide. Similar formaldehyde levels were also possible with higher initial concentrations but the electrolysis time became long. The expected trend in depletion rate with grade of reticulated vitreous carbon was observed; the removal of formaldehyde was fastest with 100 ppi material. Two further experiments demonstrated that the rate of depletion was higher at 40° C than at room temperature; the removal was again most rapid when the initial concentration was low but even with $[HCHO]_{t=0} = 6$ ppm and 40° C, the electrolysis was still not fully mass transport controlled with respect to formaldehyde. Electrolysis in an undivided cell gave comparable performance to that in the membrane cell used in other experiments. In all electrolyses with 1 M NaOH as the electrolyte the cell voltage was low, in the range 1.5–3 V.

Total organic carbon (TOC) was determined during an electrolysis where $[HCHO]_{t=0}$ was 25 ppm. Although the formaldehyde concentration dropped to <1 ppm, there was only a minimal change in TOC, from 10 mg dm^{-3} to 9.3 mg dm^{-3}. This is a clear indication that, in these conditions, the formaldehyde is oxidised to formic acid and almost no further oxidation to carbon dioxide takes place.

3.3. *Removal of formaldehyde from other aqueous media*

If the treatment of a formaldehyde containing effluent required the addition of a high concentration of sodium hydroxide, the procedure would clearly not be attractive. Hence, the electrolyses were also carried out in several other media. Three other electrolytes were chosen and using an initial concentration of formaldehyde of about 18 ppm, an experiment in each electrolyte was carried out. The data are reported in Table 3. It can be seen that the removal of formaldehyde was possible from both dilute alkali and neutral solution without any marked decline in performance. Indeed, the current efficiencies were very similar and the formaldehyde concentration could always be decreased below 1 ppm. There were, however, differences in the rate of the electrolyses and the times for 75% removal was shortest in 10 mM NaCl. These electrolyses were again carried out at −600 mV vs SCE. In the neutral solutions, it was not possible to record current/potential curves with well formed waves, probably because of a poor potential distribution within the electrode with the higher electrolyte resistance, but at −600 mV oxygen reduction gave a similar current to the experiments with 1 M NaOH. Table 3 also reports data for electrolyses in 10 mM NaCl with lower initial formaldehyde concentrations. As in base, the current efficiency decreased with lower $[HCHO]_{t=0}$. On the other hand, the time for the 75% removal of the formaldehyde was again decreased. In the electrolysis with $[HCHO]_{t=0} = 3$ ppm, the decay was initially very rapid but the very poor current inefficiency as the formaldehyde was depleted eventually slowed further removal. As expected, the cell voltage was always higher with a low electrolyte concentration and was generally in the range 10–30 V (when the anolyte was the same as the catholyte).

3.4. *Removal of formaldehyde in media containing an iron salt*

A recent paper [7] reported that the oxidation of formic acid by hydrogen peroxide is catalysed by several iron salts. Hence, the treatment of formaldehyde with hydrogen peroxide in the presence of iron salts led to the complete oxidation of formaldehyde to carbon dioxide. This would obviously be attractive for effluent treatment. Therefore, it seemed interesting to investigate the electrolytic removal with iron salts in the medium.

In the first experiment, the electrolyte was 10 mM

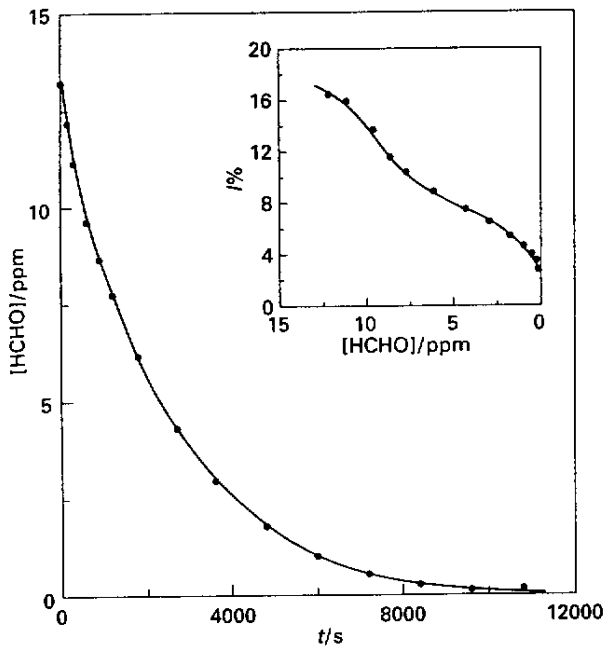

Fig. 6. Formaldehyde concentration as a function of time during the electrolysis of oxygen-saturated 10 mM HCl + 0.5 mM $FeCl_2$ at a 60 ppi reticulated vitreous carbon cathode. Catholyte flow rate 0.20 m s^{-1}. Potential −0.60 V vs SCE. Temperature 25 ± 3° C. Initial formaldehyde concentration 13 ppm. The inset shows the variation of current efficiency with formaldehyde concentration.

NaCl + 0.5 mM $FeCl_2$ and the initial concentration of formaldehyde was 12 ppm. The electrolysis was carried at −600 mV vs. SCE but the depletion of formaldehyde was extremely slow (~20% over 10 000 s). It was, however, noted that a yellow green deposit was formed on the reticulated vitreous carbon cathode. This was presumably a ferrous hydroxide/oxide resulting from the combination of ferrous ion with hydroxide generated from reduction of water at the cathode.

Hence, further electrolyses were carried out with slightly acidic solutions. The results for an electrolysis where the catholyte was 10 mM HCl + 0.5 mM $FeCl_2$ are shown in Fig. 6 and data taken during the experiment are summarised in Table 3. It can be seen that the formaldehyde concentration drops smoothly from 13 ppm down to <0.3 ppm and the electrolysis is 75% complete in 3500 s. This electrolysis time was again longer than would be the case if the reaction were mass transport limited with respect to formaldehyde. Indeed, if the rate of generation of hydrogen peroxide controls the rate of depletion, the depletion in the presence of an iron salt will take longer since the oxidation of formaldehyde is expected to involve more electrons (the oxidation of formaldehyde involves $4e^-$ if the product is carbon dioxide and $2e^-$ to formic acid) and hence more hydrogen peroxide. The total organic carbon analysis confirmed that complete oxidation was occurring; during this electrolysis the TOC drops from 6.8 to 1.3 mg dm^{-3}.

The removal of formaldehyde also occurred smoothly from a solution containing 10 mM NaCl + 0.5 mM $FeCl_2$ at pH 3 and another solution containing only 0.5 mM $FeCl_2$ at pH 3 (see Table 3) although in the former electrolysis it was necessary to add acid slowly to keep the pH down at 3. Indeed, electrolysis in the absence of NaCl appeared to proceed better in other ways; the rate of removal was higher and the current efficiency higher. With the low concentration of electrolytes (and the same electrolyte in the anolyte), the cell voltage was markedly higher, about 30 V, than with 1 M electrolytes. This is to be expected. Furthermore, the cell voltage was readily decreased by using 0.1 M H_2SO_4 as the electrolyte in the anode compartment and in an experiment performed in this way, the cell voltage decreased to ~5 V.

4. Conclusion

It has been shown that formaldehyde may be removed from waste waters in a process where the oxidant is hydrogen peroxide produced by the cathodic reduction of oxygen. In sodium hydroxide, sodium chloride and sodium sulfate, the product is formic acid but in slightly acidic solutions containing an iron salt as catalyst, complete oxidation to carbon dioxide occurs. In all media studied, the formaldehyde concentration could be decreased to <1 ppm and generally to the lowest detection limit for the analysis.

The application of a flow cell with a reticulated vitreous carbon cathode allows the removal to be achieved at a reasonable rate but the rate is never as high as is to be expected if the removal were limited by mass transport of formaldehyde to the electrode surface. In fact, the rate of removal of formaldehyde is always limited by the rate of formation of hydrogen peroxide, hence by the supply of oxygen to the cathode and the complex kinetics of oxygen reduction to hydrogen peroxide at the carbon surface. There is, however, little doubt that the rate would be enhanced by increasing further the oxygen concentration, for example, by working at high pressure, about 5–10 atmospheres, or using a trickle-bed cell.

It is particularly advantageous that, although the use of a low electrolyte concentration must degrade the behaviour of a three dimensional electrode, the depletion of formaldehyde at the concentrations investigated is possible from such solutions and, indeed, without much loss in cell performance. Indeed, it is likely that many effluents could be treated with only their residual electrolyte and the addition of a trace of iron salt if the desired product was carbon dioxide; transport through the membrane could also be used to supply the proton necessary to maintain the iron in solution. If no electrolyte is present in the solution to be treated, a very small addition of an innocuous and cheap electrolyte such as NaCl (+ $FeCl_2$) would suffice.

Acknowledgement

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