# *In situ* paired electrooxidative degradation of formaldehyde with electrogenerated hydrogen peroxide and hypochlorite ion

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Formaldehyde was degraded with hydrogen peroxide and hypochlorite ion electrogenerated by paired electrolysis of dissolved oxygen and chloride ion in aqueous solution. Degradation of formaldehyde in the cathodic compartment was significantly affected by the ratio of electrolyte volume to cathodic surface area, oxygen sparging rate and stirring rate. The model calculations correlated sufficiently well with the experimental results. The average current efficiency and degradation fraction of the *in situ* paired electrooxidative degradation of formaldehyde were experimentally found to be 62.0% and 93.2%, respectively.

Keywords: *paired electrolysis*, *oxidative degradation*, *formaldehyde*, *hydrogen peroxide*, *hypochlorite*

## List of symbols

| | | | |
|---|---|---|---|
| $A$ | surface area of anode $(cm^2)$ | $V$ | volume of solution (ml) |
| $F$ | Faraday's constant (C) | | |
| $i$ | current density $(A\,cm^{-2})$ | | *Greek symbols* |
| $k$ | rate constant | $\alpha$ | charge-transfer coefficient |
| $K$ | equilibrium constant | $\eta$ | overpotential (V) |
| $k^0$ | electrochemical rate constant at $\eta = 0$ | | |
| $r$ | reaction rate $(mol\,min^{-1})$ | | *Subscripts* |
| $t$ | time | a | anode |
| $T$ | temperature | c | cathode |
| | | h | homogeneous |
| | | 0 | initial state |

## 1. Introduction

Normal microorganisms are destroyed by the action of high concentrations of formaldehyde in biological wastewater treatment units [1]. Hence, reducing the concentration of formaldehyde by pretreatment prior to biological treatment is necessary. Hydrogen peroxide and hypochlorite ion are good oxidants for the pretreatment of formaldehyde [2–4]. The concentration of formaldehyde can be reduced from 1000 to 2 ppm using *in situ* electrogenerated hydrogen peroxide [2]. The limiting current density of the cathodic reduction of oxygen to hydrogen peroxide is increased by 50% when an anodized graphite was used as cathode [5]. Using anodized graphite as cathode, the kinetics of the cathodic reduction of oxygen dissolved in the aqueous phase and the oxidation of formaldehyde with the generated hydrogen peroxide have been previously discussed [6]. The current efficiency of the oxidative degradation of formaldehyde using the electrogenerated hypochlorite ion was

69.8% when the initial concentration of formaldehyde was 3000 ppm and 1500 C was charged into the reaction system [3]. The kinetics of the anodic oxidation of chloride ion on SPR $(SnO_2–PdO–RuO_2–TiO_2/Ti)$ was investigated and it was found that the reaction was first order with respect to chloride ion [7]. The mechanisms and kinetics of the oxidation of formaldehyde by hypochlorite ion were also investigated [7]. Thus it would be of interest to study the degradation of formaldehyde by hydrogen peroxide and hypochlorite ion generated simultaneously by a cathodic reduction of dissolved oxygen and an anodic oxidation of chloride ion, respectively.

A comparison of the ordinary electrolysis system containing a single working electrode has revealed that the current efficiency increased and the power consumption decreased for paired electrolysis [8]. Paired electrolysis of organic compounds has received growing attention in recent years [9–18]. Paired electrolysis is especially useful when the anodic and cathodic reactions produce oxidants, that can degrade organic substances in wastewaters. Paired electrogenerated hydrogen peroxide and hypochlorite have

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been used to degrade phenol in aqueous solution [19]. The removal of phenol increased significantly when paired electrooxidative phenol degradation was used as compared to a single working electrode system [19].

In this work the paired electrooxidative degradation of formaldehyde using cathodically electrogenerated hydrogen peroxide and anodically generated hypochlorite ion were investigated. Additionally, effects of oxygen sparging rate, stirring rate and the ratio of solution volume and cathodic area on the current efficiency of formaldehyde degradation with electrogenerated hydrogen peroxide is discussed. A comparison of experimental results with model calculations is also presented.

## 2. Experimental details

Electrolysis was carried out in a divided cell where anodic and cathodic chambers were separated by a sintered glass frit (Pyrex 4G). A prepared SPR ($SnO_2$–$PdO$–$RuO_2$–$TiO_2$/Ti) [3] served as anode and anodized graphite as cathode [5]. The solutions in the anodic and cathodic compartments (250 and 120 ml, respectively) were stirred with two magnetic bars. D.c. power was supplied using a potentiostat/galvanostat (Nichia G1005E), and the amount of electricity passed was measured by a coulometer (Nichia N-CR 760). Oxygen was introduced into the cathodic chamber through a glass gas dispenser.

At the beginning of a run, the anolyte and catholyte was introduced into the anodic and cathodic chambers, respectively, and the stirrers were switched on. Oxygen was sparged into the cathodic chamber at a desired flow rate for a few minutes until the catholyte was oxygen saturated. The electrolysis was then carried out at constant current until a preset amount of electricity had been passed. During the run, the catholyte and anolyte were periodically sampled. The concentration of formaldehyde was analysed by measuring the light adsorption of chromotropic acid-formaldehyde coloured complex at 575 nm [2, 20].

## 3. Theoretical analysis

The reactions of the paired electrooxidative degradation of formaldehyde with electrogenerated hydrogen peroxide and hypochlorite ion are described in Fig. 1. Hypochlorite ion is produced by the oxidation of chloride ion in the anolyte and oxidized with formaldehyde to chloride ion. Hypochlorite ion/ chloride ion act as mediators. In the catholyte, hydrogen peroxide is formed by the cathodic reduction of oxygen dissolved in the aqueous phase. Formaldehyde in the anolyte and catholyte is oxidized to formic acid with electrogenerated hypochlorite ion and hydrogen peroxide.

The equations for the anodic oxidation of chloride ion to chlorine on an SPR anode and the hydrolysis of chlorine to hypochlorite ion can be represented by the following equations [7, 21]
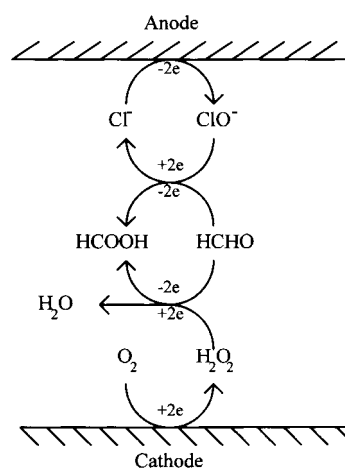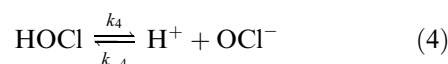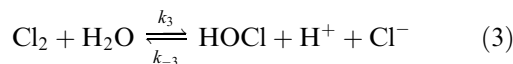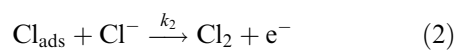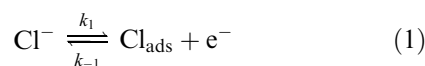


Fig. 1. Scheme of the paired electrooxidative degradation of formaldehyde with electrogenerated hydrogen peroxide and hypochlorite ion.

$$Cl^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cl_{ads} + e^- \tag{1}$$

$$Cl_{ads} + Cl^- \overset{k_2}{\longrightarrow} Cl_2 + e^- \tag{2}$$

$$Cl_2 + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} HOCl + H^+ + Cl^- \tag{3}$$

$$HOCl \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} H^+ + OCl^- \tag{4}$$

Although it is thermodynamically possible to directly electrooxidize formaldehyde to formic acid and carbon dioxide on SPR, the electrocatalytic activity found in previous work [4] is poor. The poor electroactivity is proved by experimental results that the current efficiency for oxidizing formaldehyde to formic acid direct on the anode (SPR) in the absence of chloride ion is very low (8.0%) [4]. Therefore, formaldehyde considered here is oxidized with electrogenerated hypochlorite ion in the anodic compartment according to the following equation [7]

$$2CH_2O + ClO^- + 2OH^- \overset{k_5}{\longrightarrow} 2HCOO^- + Cl^- \\ + H_2 + H_2O \tag{5}$$
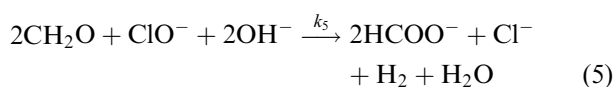
The production of hydrogen in Equation 5 has been qualitatively determined by gas chromatography (Porapak Q (80/100 mesh) packed column).

The equations of cathodic reduction to produce hydrogen peroxide were studied previously [6]:

$$(O_2)_{aq} + H_2O + 2e^- \overset{k_6}{\longrightarrow} HO_2^- + OH^- \tag{6}$$
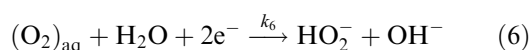
The contribution due to the degradation of formaldehyde by oxygen dissolved in the aqueous solution is negligible [2]. Formaldehyde is mainly oxidized by hydrogen peroxide electrogenerated in the cathodic chamber. The oxidation of formaldehyde with electrogenerated hydrogen peroxide in the alkaline solution [6, 22, 23] may be expressed as

$$2CH_2O + HO_2^- + OH^- \overset{k_7}{\longrightarrow} 2HCO_2^- + H_2O + H_2 \tag{7}$$
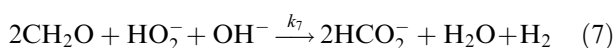
## 3.1. Mass balance in the anodic chamber

The anodic oxidation of chloride ion on SPR is found to be first order with respect to the concentration of chloride ion and the current density is obtained as [7]

$$i_a = 2Fk_2^0 e^{\alpha F\eta/RT}[\text{Cl}^-]_a \qquad (8)$$

where $k_2^0$ is the rate constant of Equation 2 at $\eta = 0$, $\eta$ is the overpotential, $F$ is Faraday's constant and $\alpha$ is the charge transfer coefficient. The reaction orders of the oxidation of formaldehyde with hypochlorite ion are 2 and 1 with respect to formaldehyde and hypochlorite ion, respectively, and the rate equation is expressed as [7]

$$r_{ha} = k_5[\text{CH}_2\text{O}]_a^2[\text{ClO}^-]_a \qquad (9)$$

where $k_5$ has been evaluated as $1.27 \times 10^8$ $\exp(-37\,900/RT)$ $\text{M}^{-2}$ $\text{min}^{-1}$ [7].

As shown in Fig. 1 and Equations 1 to 5, the concentration of chloride ion in the anolyte is consumed due to the anodic oxidation of chloride ion on the anodic surface. The generation rate of chloride ion by oxidation of formaldehyde with hypochlorite ion in the bulk of anolyte is expressed in Equation 9. Disregarding the mass transfer from anodic chamber to cathodic chamber, the mass balance of chloride ion in the anodic chamber consequently becomes

$$d[\text{Cl}^-]_a/dt = -(i_a A_a/2FV_a) + 0.5\,k_5[\text{CH}_2\text{O}]_a^2[\text{ClO}^-]_a \qquad (10)$$

where $A_a$ and $V_a$ are the anodic surface area and the volume of anolyte, respectively. According to Equations 3 and 4, the concentration of hypochlorite ion in the anolyte at pH 13 can be expressed as [7]

$$[\text{ClO}^-]_a = [\text{Cl}^-]_{a0} - [\text{Cl}^-]_a \qquad (11)$$

where $[\text{Cl}^-]_{a0}$ is the initial concentration of chloride ion in the anodic chamber. Substituting from Equation 11 into Equation 10, the decreasing rate in concentration of hypochlorite ion is expressed as

$$d[\text{ClO}^-]_a/dt = (i_a A_a/2FV_a) - 0.5\,k_5[\text{CH}_2\text{O}]_a^2[\text{ClO}^-]_a \qquad (12)$$

The concentration of formaldehyde in the anodic chamber is

$$d[\text{CH}_2\text{O}]_a/dt = -k_5[\text{CH}_2\text{O}]_a^2[\text{ClO}^-]_a \qquad (13)$$

When the electrolysis is controlled potentiostatically, the concentrations of chloride ion, hypochlorite ion and formaldehyde in the anodic chamber can be evaluated by Equations 8, 10, 11 and 13. The concentrations of chloride ion, hypochlorite ion and formaldehyde can be theoretically calculated by substituting the current density into Equation 10 and solving Equations 10, 11 and 13 simultaneously under constant current conditions.

## 3.2. Mass balance in the cathodic chamber

The reaction order of the cathodic reduction of oxygen dissolved in the catholyte is unity with respect to the concentration of oxygen in the aqueous solution and the current density of the cathodic reduction of oxygen to hydrogen peroxide is derived as [6]

$$i_c = 2Fk_6^0 e^{-F\eta/RT}[(\text{O}_2)_{aq}]_c \qquad (14)$$

where $k_6^0$ and $[(\text{O}_2)_{aq}]_c$ are the rate constant of the cathodic reduction of oxygen at $\eta = 0$ and the concentration of oxygen dissolved in the aqueous phase, respectively. The reaction orders of oxidation of formaldehyde with hydrogen peroxide are 2 and 1 with respect to formaldehyde and hydrogen peroxide, respectively, and the reaction rate is expressed as [6]

$$r_{hc} = k_7[\text{CH}_2\text{O}]_c^2[\text{HO}_2^-]_c \qquad (15)$$

where $k_7$, obtained in previous work [6], is $5.47 \times 10^8 \exp(-36\,000/RT)$ $\text{M}^{-2}$ $\text{min}^{-1}$.

The generation rate of hydrogen peroxide from the cathodic surface is expressed in Equation 14. The oxidation of formaldehyde results in consumption of hydrogen peroxide as indicated in Equation 15. Therefore, the mass balance of hydrogen peroxide in the catholyte is

$$d[\text{HO}_2^-]_c/dt = (i_c A_c/2FV_c) - 0.5\,k_7[\text{CH}_2\text{O}]_c^2[\text{HO}_2^-]_c \qquad (16)$$

where $A_c$ and $V_c$ are the cathodic surface area and the volume of catholyte, respectively. The decreasing rate of concentration of formaldehyde in the cathodic chamber is expressed as

$$d[\text{CH}_2\text{O}]_c/dt = -k_7[\text{CH}_2\text{O}]_c^2[\text{HO}_2^-]_c \qquad (17)$$

The concentrations of formaldehyde and hydrogen peroxide are evaluated by solving Equations 14, 16 and 17 simultaneously when the cathodic reduction of oxygen dissolved in the aqueous solution is operated potentiostatically. For constant current, substituting the current density into Equation 16, the concentrations of formaldehyde and hydrogen peroxide in the catholyte are obtained by solving Equations 16 and 17 simultaneously.

## 4. Results and discussion

### 4.1. Oxidative degradation of formaldehyde with hydrogen peroxide electrogenerated in the cathodic chamber

*4.1.1. Effect of $V/A$.* The concentration of formaldehyde decreased from 1000 to 150 ppm when the value of $V/A$, charge passed and current density were 0.76 cm, 1.25 F mol$^{-1}$ of CH$_2$O and 0.75 mA cm$^{-2}$ as shown in Fig. 2. According to Equations 16 and 17, the model calculations of the oxidative degradation of formaldehyde with hydrogen peroxide electrogenerated in the cathodic chamber correlated well with the experimental results when $V/A$ was equal to 0.76 cm (Fig. 2). When the volume of catholyte and the cathodic surface area were 125 ml and 50.4 cm$^2$, respectively, (i.e. $V/A = 2.48$ cm), the concentration of formaldehyde decreased from 1000 to 3 ppm at

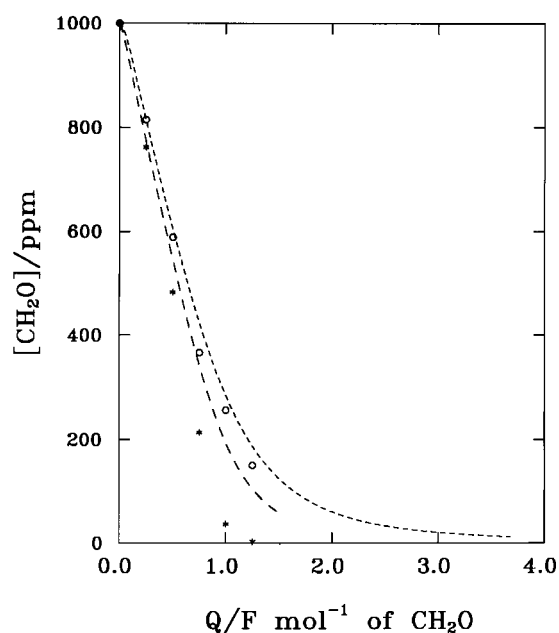Fig. 2. Effect of charge passed on the residual concentration of formaldehyde in the cathodic chamber. $[CH_2O] = 1000$ ppm, pH 13, temperature $= 45\,°C$, $O_2$ sparging rate $= 13$ ml s$^{-1}$, $i = 0.75$ mA cm$^{-2}$, $A_c = 330$ cm$^2$, $V_c = 250$ ml, stirring rate $= 600$ rpm. (Note: data of $V/A = 2.48$ were obtained from the experimental results of [6].) $(V/A)$/cm: 2.48 (----: model calculations, $*$: experimental data); 0.76 (— — —: model calculations, $*$: experimental data).

1.25 F mol$^{-1}$ of $CH_2O$ and 0.75 mA cm$^{-2}$ [6] (Fig. 2). The experimental results indicated that the residual concentration of formaldehyde decreased when the value of $V/A$ increased. Furthermore the deviation between the experimental data and the theoretical analysis was found to increase when the value of $V/A$ increased. According to the reaction conditions in the previous [6] and present work, the time for charging 1.25 F mol$^{-1}$ $CH_2O$ into the reaction systems were 67.7 and 221.6 min when the values of $V/A$ were 0.76 and 2.48, respectively. Since formaldehyde would be degraded by the oxygen dissolved in the aqueous solution [2], the amount of formaldehyde degraded by dissolved oxygen increased and the deviation of experimental and theoretical results increased when the value of $V/A$ increased.

The percentage degradation fraction of formaldehyde is defined as

$$\text{degradation fraction} = \frac{([CH_2O]_0 - [CH_2O])}{[CH_2O]_0} \times 100\%$$

(18)

where $[CH_2O]_0$ is the initial concentration of formaldehyde. The degradation fraction of formaldehyde based on theoretical calculations increased with increase in $V/A$ at equal charge passed (Fig. 3). An increase in $V/A$ from 0.38 to 2.48 cm caused the formaldehyde degradation fraction to increase from 89.8 to 97.6%, when the charge passed was 2.0 F mol$^{-1}$ of $CH_2O$ (Fig. 3).

As indicated in Equations 6 and 7, hydrogen peroxide generated on the cathodic surface transfers to the bulk catholyte solution where it reacts with formaldehyde. The concentration of hydrogen per-
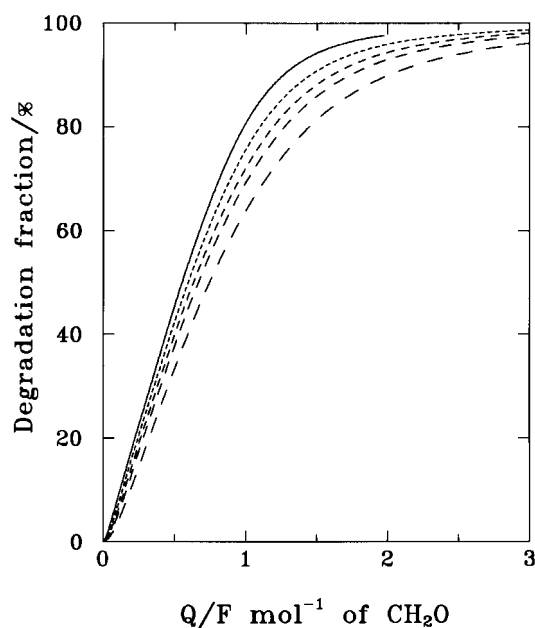


Fig. 3. Effect of charge passed on formaldehyde degradation in the cathodic chamber. $[CH_2O] = 1000$ ppm, pH 13, temperature $= 45\,°C$, $O_2$ sparging rate $= 13$ ml s$^{-1}$, $i = 0.75$ mA cm$^{-2}$, $V_c = 125$ ml, stirring rate $= 600$ rpm. $(V/A)$/cm: (——) 2.48; (----) 1.24; (- - - -) 0.83; (— — —) 0.62; (—— ——) 0.38.

oxide increased due to the cathodic reduction of dissolved oxygen and this hydrogen peroxide was consumed in the oxidative degradation of formaldehyde in the bulk phase (Equation 16). At the inception of a run, the low concentration of hydrogen peroxide in the solution resulted in a slow oxidation rate of formaldehyde by hydrogen peroxide. On the other hand, the rate of electrogeneration of hydrogen peroxide on the cathodic surface was maintained constant due to the application of constant current. This lead to an accumulation of hydrogen peroxide in the catholyte and most of the current being used in the generation of hydrogen peroxide (Equation 6). Hence, the current efficiency for accumulation of hydrogen peroxide was greater than that of oxidative formaldehyde degradation by electrogenerated hydrogen peroxide in the initial stages as illustrated in Figs 4 and 5. The percentage current efficiency for accumulation of hydrogen peroxide was defined as

current efficiency for accumulating $H_2O_2$

$$= \frac{\text{charge used in accumulating } H_2O_2}{\text{total charge}} \times 100\% \quad (19)$$

When the reaction time increased, the increase in concentration of hydrogen peroxide in the bulk solution caused an increase in the rate of oxidative degradation of formaldehyde (Equation 7). At this stage, most of the charge passed was used to degrade formaldehyde and the current efficiency of the oxidative degradation of formaldehyde increased. Hence, the current efficiency for accumulation of hydrogen peroxide decreased (Figs 4 and 5). A further increase in the reaction time caused the current efficiency of formaldehyde degradation to decrease due to a decrease in the formaldehyde concentration
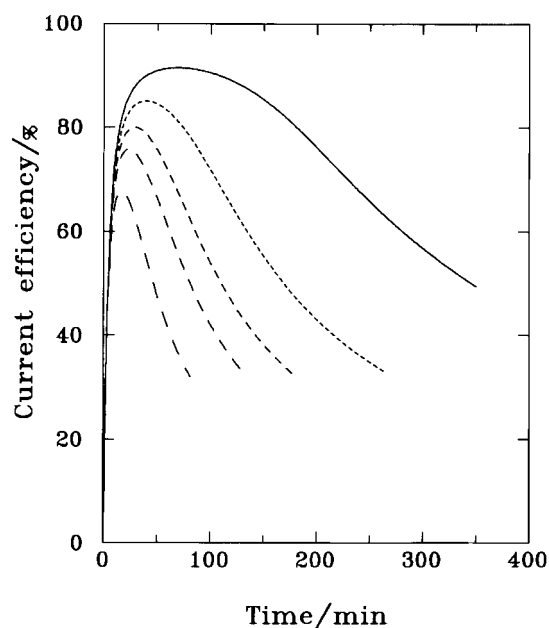
Fig. 4. Effect of electrolysis time on the current efficiency of formaldehyde degradation in the cathodic chamber. $[CH_2O] = 1000$ ppm, pH 13, temperature $= 45\,°C$, $O_2$ sparging rate $= 13\,ml\,s^{-1}$, $i = 0.75\,mA\,cm^{-2}$, $V_c = 125\,ml$, stirring rate $= 600\,rpm$. $(V/A)/cm$: (———) 2.48; (----) 1.24; (- - - -) 0.83; (– – –) 0.62; (— —) 0.38.

At constant current density for the cathodic oxygen reduction, a decrease in $V/A$ resulted in an increase in the hydrogen peroxide generation rate per unit volume of catholyte. When the reaction system was at pseudo-steady state, increasing the hydrogen peroxide generation rate per unit volume of catholyte resulted in an increase in the rate of oxidative formaldehyde degradation with electrogenerated hydrogen peroxide. This increase in the formaldehyde oxidation rate was caused by the increase in hydrogen peroxide concentration at a lower values of $V/A$. This resulted in a decrease in the current efficiency for oxidative formaldehyde degradation (Fig. 4) and an increase in the current efficiency for hydrogen peroxide accumulation (Fig. 5) when the value of $V/A$ decreased.

The maximum current efficiency oxidative formaldehyde degradation decreased from 91.4 to 67.8% when $V/A$ decreased from 2.48 to 0.38 cm (Fig. 4). Based on these observations, it was apparent that decreasing $V/A$ resulted in an increase in the rate of hydrogen peroxide generation per unit volume of catholyte. Therefore, the oxidative formaldehyde degradation rate with electrogenerated hydrogen peroxide increased and the electrolysis time decreased as $V/A$ decreased. As shown in Fig. 4, the electrolysis time for reaching the maximum current efficiency decreased from 70 to 17 min when $V/A$ decreased from 2.48 to 0.38 cm. Similar results are also indicated in Fig. 6. This is despite the fact that the formaldehyde degradation fraction and the current efficiency of oxidative formaldehyde degradation increased when $V/A$ increased (Figs 3 and 4). The electrolysis time for a constant formaldehyde degra-

in the bulk solution (Fig. 4). As shown in Fig. 5, the current efficiency for the accumulation of hydrogen peroxide was found to increase, again as the concentration of hydrogen peroxide in the catholyte increased. Therefore, the maximum current efficiency for the formaldehyde degradation and the minimum current efficiency for the hydrogen peroxide production were found in Figs 4 and 5, respectively.
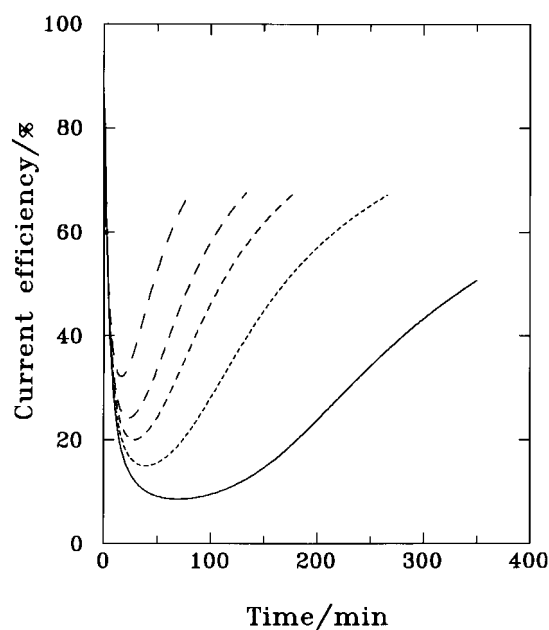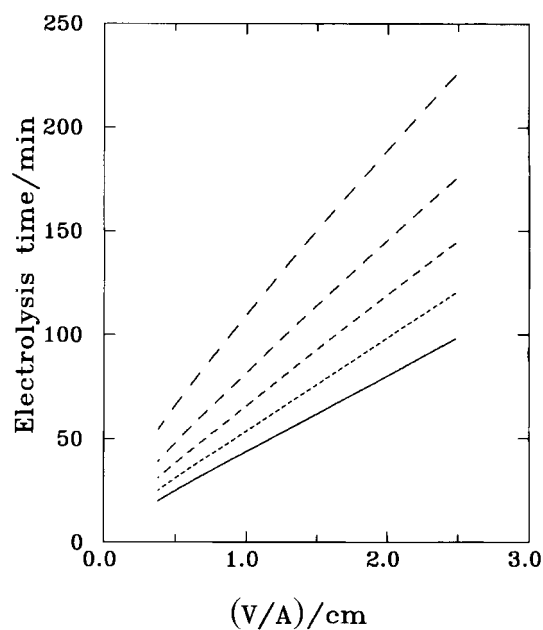


Fig. 5. Effect of electrolysis time on current efficiency for hydrogen peroxide accumulating in the cathodic chamber. $[CH_2O] = 1000$ ppm, pH 13, temperature $= 45\,°C$, $O_2$ sparging rate $= 13\,ml\,s^{-1}$, $i = 0.75\,mA\,cm^{-2}$, $V_c = 125\,ml$, stirring rate $= 600\,rpm$. $(V/A)/cm$: (———) 2.48; (----) 1.24; (- - - -) 0.83; (– – –) 0.62; (— —) 0.38.



Fig. 6. Effect of $V/A$ on the electrolysis time for various fractions formaldehyde degradation in the cathodic chamber. $[CH_2O] = 1000$ ppm, pH 13, temperature $= 45\,°C$, $O_2$ sparging rate $= 13\,ml\,s^{-1}$, $i = 0.75\,mA\,cm^{-2}$, $V_c = 125\,ml$, stirring rate $= 600\,rpm$. Degradation fraction/%: (———) 50; (----) 60; (- - - -) 70; (– – –) 80; (— —) 90.

dation fraction increased with $V/A$. As illustrated in Fig. 6, the electrolysis time increased from 54.5 to 225 min when $V/A$ increased from 0.38 to 2.48 cm at a fixed degradation fraction of 90%. Increasing the electrolysis time resulted in an increase in wastewater treatment time.

*4.1.2. Effect of oxygen sparging rate.* In the cathodic reduction of dissolved oxygen, oxygen is transferred from the gaseous phase to the aqueous phase, and the dissolved oxygen is transferred from the bulk aqueous solution to the cathodic surface. The oxygen adsorbed on active cathodic sites is reduced to hydrogen peroxide. Hence, the mass transfer rate of oxygen from the gaseous to the aqueous phase is enhanced and the current efficiency increased when the oxygen sparging rate is increased. Increasing the oxygen sparging rate from 2 to 13 ml s$^{-1}$ resulted in an increase in the current efficiency for the oxidative formaldehyde degradation from 41 to 82% at a fixed $V/A$ value of 0.76 cm (Fig. 7). The current efficiency remained constant when the oxygen sparging rate was greater than 13 ml s$^{-1}$. Experimental results indicated that the rate-determining step was the mass transfer of oxygen from the gaseous phase to the aqueous solution, when the oxygen sparging rate was less than 13 ml s$^{-1}$. At oxygen sparging rates greater than 13 ml s$^{-1}$, the rate-determining step was the cathodic reduction of oxygen or the mass transfer of dissolved oxygen from bulk phase to the cathodic surface.

As indicated in our previous work [2], the current efficiency for the oxidative degradation of formaldehyde with electrogenerated hydrogen peroxide remained constant when the oxygen sparging rate was greater than 3 ml s$^{-1}$ and $V/A$ was 2.48. The different results of this work and [2] are due to the varying

$V/A$. According to above discussion, the rate of cathodic reduction of dissolved oxygen would be expected to increase with decrease in $V/A$ and at constant current density. Thus the mass transfer of oxygen from gaseous to aqueous phase (oxygen sparging rate) must be increased to overcome an increase in the oxygen reduction rate when the value of $V/A$ decreases.

*4.1.3. Effect of stirring rate.* Increasing the stirring rate was found to increase the dissolved oxygen and hydrogen peroxide mass transfer rates between the aqueous phase and the cathodic surface. Hence, the current efficiency for oxidative formaldehyde degradation increased with increase in stirring rate. The current efficiency of oxidative degradation of formaldehyde increased from 57 to 82% when the stirring rate increased from 0 to 600 rpm and the charge passed and oxygen sparging rate were 0.60 F mol$^{-1}$ of $CH_2O$ and 13 ml s$^{-1}$, as illustrated in Fig. 8. A further increase in the stirring rate, to 800 rpm, slightly altered the current efficiency. Figure 8 shows that the rate-determining step was the mass transfer of dissolved oxygen from bulk phase to cathodic surface when the stirring rate was less than 600 rpm. When the stirring rate was faster than 600 rpm, the reaction was controlled by cathodic oxygen reduction.

### 4.2. In situ *oxidative degradation of formaldehyde with paired electrogenerated hydrogen peroxide and hypochlorite ion*

An increase in the concentration of formaldehyde in the anolyte, as well as the catholyte, resulted in an increase in the current efficiency of formaldehyde
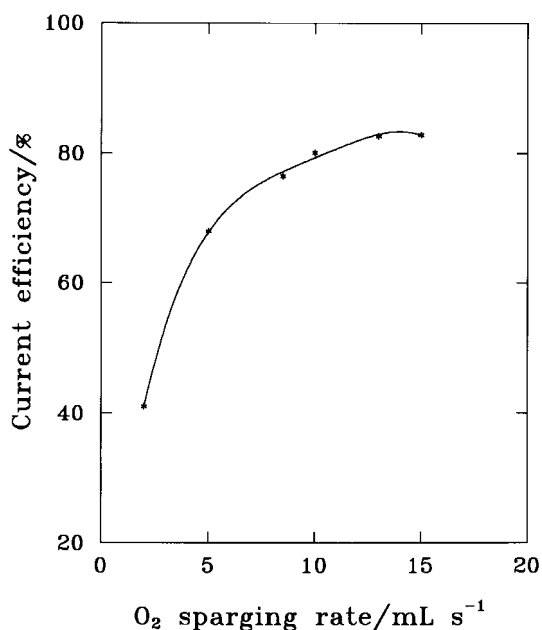


Fig. 7. Effect of oxygen sparging rate on the current efficiency for formaldehyde degradation in the cathodic chamber. [$CH_2O$] = 1000 ppm, pH 13, temperature = 45 °C, $A_c$ = 330 cm$^2$, $i$ = 0.75 mA cm$^{-2}$, $V_c$ = 250 ml, stirring rate = 600 rpm.
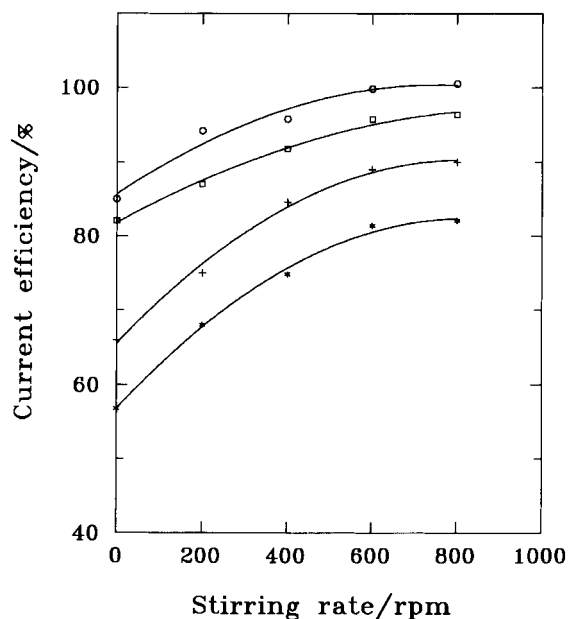


Fig. 8. Effect of stirring rate on the current efficiency of formaldehyde degradation in the cathodic chamber. [$CH_2O$] = 1000 ppm, pH 13, temperature = 45 °C, $A_c$ = 330 cm$^2$, $i$ = 0.75 mA cm$^{-2}$, $V_c$ = 250 ml, $O_2$ sparging rate = 13 ml s$^{-1}$. $Q$/F mol$^{-1}$ of $CH_2O$: (○) 0.12; (□) 0.31; (+) 0.62; (*) 0.87.

*Table 1. Effect of charge passed on the current efficiency of paired oxidative degradation of formaldehyde*

Cathodic chamber: pH 13, temperature $= 45\,^\circ$C, $A_c = 330\,cm^2$, $i = 0.75\,mA\,cm^{-2}$, $V_c = 250\,ml$, stirring rate 600 rpm.
Anodic chamber: pH 13, temperature $= 45\,^\circ$C, $A_a = 6.0\,cm^2$, $i = 41\,mA\,cm^{-2}$, $V_a = 120\,ml$, stirring rate 600 rpm, [NaCl] $= 1.0\,$M.

| $Q/C$ | Average current efficiency/% | | | | | |
|-------|------------------|--------|--------|------------------|--------|--------|
| | Model calculations | | | Experimental data | | |
| | case 1 | case 2 | case 3 | case 1 | case 2 | case 3 |
| 800 | 51.0 | 66.5 | 85.5 | 52.5 | 67.0 | 84.5 |
| 1500 | 36.0 | 47.5 | 69.0 | 40.5 | 47.0 | 72.5 |
| 1800 | 31.0 | 40.5 | 61.0 | 37.0 | 41.0 | 62.0 |

Case 1: $[HCHO]_a + [HCHO]_c = 1000\,ppm + 1000\,ppm$.
Case 2: $[HCHO]_a + [HCHO]_c = 2000\,ppm + 1000\,ppm$.
Case 3: $[HCHO]_a + [HCHO]_c = 3000\,ppm + 1500\,ppm$.

degradation by paired electrogenerated hydrogen peroxide and hypochlorite ion (Table 1). The average current efficiency increased from 52.5 to 84.5% with increase in formaldehyde concentration in the cathodic and anodic chambers, from 1000 ppm to 1500 and 3000 ppm, respectively, at a charge passed of 800 C. The average current efficiency is defined as the average of the current efficiencies in the anodic and cathodic chambers. The average current efficiency of paired oxidative degradation of formaldehyde decreased from 84.5 to 62.0% with increase in charge passed from 800 to 1800 C at an initial concentration of 3000 and 1500 ppm of formaldehyde in the anolyte and catholyte, respectively (Table 1). The average current efficiency for the paired oxidative formalde-

hyde degradation obtained by the model calculations shown in Table 1 correlated well with the experimental results.

As indicated in Fig. 9, the residual formaldehyde decreased from 24.5 to 1.67 mmol when the charge passed was 1800 C and the initial concentration of formaldehyde in the anodic and cathodic chambers were 3000 and 1500 ppm, respectively. The formaldehyde degradation fraction increased from 0 to 93.2% with increase in charge passed from 0 to 1800 C (Fig. 10). The degradation fraction increased sharply with increase in charge passed from 0 to 1000 C. When the charge passed exceeded 1500 C, the increase in degradation fraction slowed due to the decrease in formaldehyde in the solution. The con-
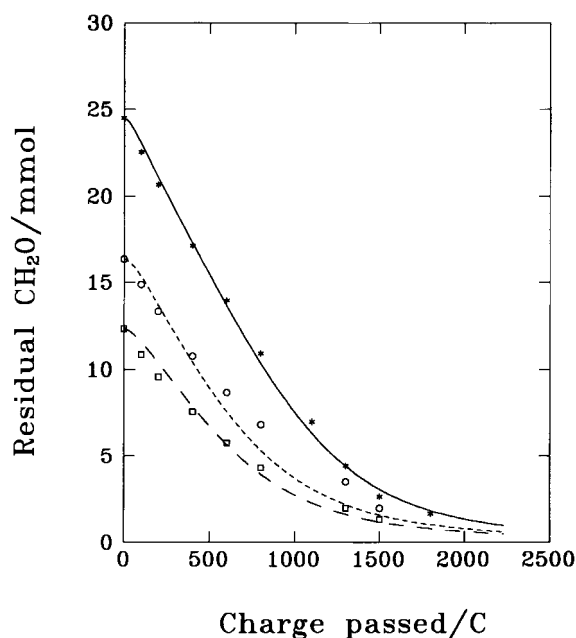


Fig. 9. Effect of charge passed on the residual formaldehyde in the paired electrooxidative degradation of formaldehyde. Cathodic chamber: pH 13, temperature $= 45\,^\circ$C, $A_c = 330\,cm^2$, $i = 0.75$ mA cm$^{-2}$, $V_c = 250\,ml$, stirring rate $= 600$ rpm. Anodic chamber: pH 13, temperature $= 45\,^\circ$C, $A_a = 6.0\,cm^2$, $i = 41\,mA\,cm^{-2}$, $V_a = 120\,ml$, stirring rate $= 600$ rpm, [NaCl] $= 1.0$ M. $[CH_2O]_a + [CH_2O]_c$/ppm: $3000 + 1500$ (——: model calculation; $*$: experimental data); $2000 + 1000$ (----: model calculation; $\bigcirc$: experimental data); $1000 + 1000$ (- - - -: model calculation; $\square$: experimental data).
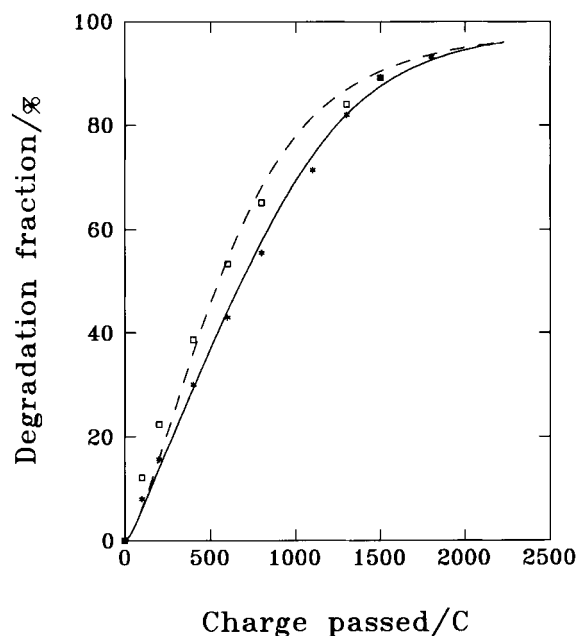


Fig. 10. Effect of charge passed on the degradation fraction in the paired electrooxidative degradation of formaldehyde. Cathodic chamber: pH 13, temperature $= 45\,^\circ$C, $A_c = 330\,cm^2$, $i = 0.75\,mA\,cm^{-2}$, $V_c = 250\,ml$, stirring rate $= 600$ rpm. Anodic chamber: pH 13, temperature $= 45\,^\circ$C, $A_a = 6.0\,cm^2$, $i = 41\,mA\,cm^{-2}$, $V_a = 120\,ml$, stirring rate $= 600$ rpm, [NaCl] $= 1.0$ M. $[CH_2O]_a + [CH_2O]_c$/ppm: $3000 + 1500$ (——: model calculation; $*$: experimental data); $1000 + 1000$ (- - - -: model calculation; $\square$: experimental data).

sistency of model calculations with the experimental results indicates the reliability of the theoretical model.

## 5. Conclusions

The model calculations for oxidative formaldehyde degradation with paired electrogenerated hydrogen peroxide and hypochlorite ion correlate well with experimental results. Both the model calculations and the experimental results indicate that the current efficiency and degradation fraction of formaldehyde increase with increase in $V/A$. The rate-determining step for the oxidative degradation of formaldehyde in the cathodic chamber is the mass transfer of oxygen from gaseous to aqueous phase at oxygen sparging rates lower than $13$ ml s$^{-1}$. When the stirring rate and oxygen sparging rate are greater than 600 rpm and $13$ ml s$^{-1}$, respectively, the rate-determining step is cathodic oxygen reduction in the cathodic chamber. The average current efficiency and degradation fraction of formaldehyde are obtained as 62.0 and 93.2% when the concentrations of formaldehyde in the anolyte and catholyte are 3000 and 1500 ppm, respectively, and the charge passed is 1800 C.

## Acknowledgement

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