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In situ degradation of formaldehyde with electrogenerated hypochlorite ion

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The oxidant ClO^- was generated on an SPR (SnO_2–PdO–RuO_2–TiO_2) anode and used to degrade formaldehyde in aqueous solution. The current efficiency of the production of hypochlorite ion was significantly affected by the concentration of chloride ion, pH and stirring rate. The effect of current density and temperature on the current efficiency for electrogeneration of hypochlorite ion was slight. The maximum anodic current efficiency was 99.3% when 100 C was charged. Increasing the concentration of chloride ion, pH, temperature, stirring rate and the concentration of formaldehyde in the solution and decreasing the current density and charge passed resulted in increased current efficiency of degradation of formaldehye with electrogenerated hypochlorite ion.

1. Introduction

Hypochlorite ion is a good oxidant for treatment of waste waters containing organic compounds [1]. Formaldehyde is a toxic compound which must be degraded before industrial waste waters can be discharged or treated in a biological clarification plant. Hypochlorite ion is a suitable oxidant for pretreatment of waste waters containing formaldehyde and toxic substances. However, the quantity of hypochlorite ion added to a treatment unit is not easily controllable. Hypochlorite ion is lost by decomposition when the quantity added is excessive. Whenever the addition of hypochlorite ion is insufficient, the oxidative degradation of formaldehyde is incomplete. The degradation of formaldehyde with electrogenerated hypochlorite ion *in situ* has the advantages that the transportation of dangerous oxidant is unnecessary, and that the quantity of hypochlorite added to the treatment unit can be controlled. Using hypochlorite ion electrogenerated at the anode, the indirect anodic oxidation of organic substances, such as benzyl alcohol, in a two-phase system has been reported [2–4].

The anodic oxidation of chloride ion on DSA® type anodes has been extensively investigated [5–15]. Most of the investigations have described the mechanisms and kinetics of the anodic oxidation of chloride ion [5–7, 9, 11, 12, 14]. Using DSA® anodes, the current efficiency for producing hypochlorite (as chlorine) is approximately 40% when the available chlorine is $10\,g\,dm^{-3}$ [10]. The chlorine current efficiency decreased when the concentration of NaOH in the catholyte increased from 0.86 to 3.16 M and ruthenium oxide–titanium was used as anode [13]. The current efficiency of chlorine evolution from dilute brines (0.5–0.1 M) was studied on RuO_2 and IrO_2 and is generally much greater than on graphite electrodes [8]. Increasing the concentration of chloride ion and decreasing the current density and concentration of chlorate resulted in an increase in hypochlorite current efficiency at a commercial RuO_2/TiO_2 electrode [15].

The treatment of wastewaters with electrogenerated hypochlorite *in situ* has been investigated previously [16–18]. Cyanide ion was oxidized to CO_3^{2-} with electrogenerated hypochlorite ion [19]. Complete decomposition of phenol with Ni_2O_3 formed from oxidized Ni^{2+} with electrogenerated hypochlorite ion occurred in a half hour electrolysis [20]. Formaldehyde in aqueous solution can be degraded from 1000 to 2 ppm with hydrogen peroxide electrogenerated *in situ* [21], but this degradation with hypochlorite ion electrogenerated *in situ* has not been previously investigated. Understanding of the factors affecting the degradation of formaldehyde with electrogenerated hypochlorite ion is of interest.

The oxidant hypochlorite ion is generated by anodic oxidation of chloride ion at an SPR (SnO_2–PdO–RuO_2–TiO_2) anode and reacts to degrade formaldehyde in solution. Factors affecting the current efficiency of the anodic oxidation of chloride ion to hypochlorite and the degradation of formaldehyde are reported in this paper.

2. Experimental details

2.1. *Preparation of SPR (SnO_2–PdO–RuO_2–TiO_2/Ti) anode*

An SPR electrode was prepared by thermal decomposition [22]. A titanium sheet was polished with fine emery paper and washed with distilled water in an ultrasonic cleaner. The impurities, oxides and

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surface grease were removed by dipping for 30 s in an aqueous solution consisting of 10 ml of 46% hydrofluoric acid, 30 ml of 65% nitric acid and 60 ml of distilled water. The titanium sheet was then washed with distilled water several times.

The coating was obtained by painting a titanium sheet pretreated as above with an aqueous solution prepared by mixing $RuCl_3$ solution (0.72 M, 4.8 ml), $TiCl_4$ solution (1.16 M, 4.3 ml), $SnCl_2$ solution (1.59 M, 3.2 ml) and saturated $PdCl_2$ solution (3.0 ml). After the coated Ti sheet was dried in air at 150 °C for 12 h, the painting and drying procedure was repeated. Then the coated and dried sheet was painted with the above aqueous solution and fired at 350 °C for 1 h; this process was repeated. Thereafter, the coated sheet was again painted with the above aqueous solution and fired at 500 °C for 2 h; the latter process was repeated. The thickness of coating obtained in this procedure was in the range 0.02–0.04 mm.

2.2. *In situ degradation of formaldehyde with electrogenerated hypochlorite ion*

An H-type two-compartment glass cell was used for the *in situ* degradation of formaldehyde with electrogenerated hypochlorite ion. The working electrode was the prepared SPR plate and the counter electrode was a platinum wire. The solution in the anodic compartment (120 ml) was stirred with a magnetic bar and separated by a sintered glass frit (Pyrex 4G) from the cathodic compartment. D.c. power was supplied with a potentiostat/galvanostat (Nichia G1005E), and the amount of charge passed was measured with a coulometer (Nichia N-CR 760).

The concentration of formaldehyde was analysed by measuring the light adsorption of chromotropic acid-formaldehyde coloured complex at 575 nm [21, 23]. The concentration of formic acid, which was the primary product of the degradation of formaldehyde with electrogenerated hypochlorite, was determined as follows: the sample was oxidized by $KMnO_4$. The residual concentration of $KMnO_4$ was determined by iodometric titration. The calculation of formic acid was described previously [21].

3. Results and discussion

3.1. *Anodic oxidation of chloride ion to hypochlorite*

The current efficiency of the anodic oxidation of chloride ion to hypochlorite was calculated as follows:

$$\text{Current efficiency of hypochlorite production} = \frac{2F[\mathrm{ClO^-}]V}{It} \times 100\% \qquad (1)$$

where V is the volume of solution (l), F is the Faraday constant (96 485 C mol^{-1}), I is the current applied (A), and t is the electrolysis time (s).

3.1.1. Effect of concentration of chloride ion. The main side reaction on the anode was evolution of oxygen when hypochlorite ion was produced from anodically oxidized chloride ion in the aqueous solution. Increasing the concentration of chloride ion resulted in a decrease in oxygen evolution and an increase in current efficiency for the generation of hypochlorite ion. The current efficiency increased from 78.0 to 98.0% when the concentration of chloride ion was increased from 0.1 to 1.0 M as shown in Fig. 1. On further increase of the concentration of chloride ion to 3.0 M the current efficiency changed slightly. Similar results were obtained at a RuO_2/TiO_2 anode [15].

3.1.2. Effect of temperature. With increase in the reaction temperature from 15 to 35 °C the current efficiency increased from 95.7 to 99.4% (Fig. 2). The current efficiency decreased slightly when the temperature was increased to 45 °C. Increasing the reaction temperature resulted in an increased rate of anodic oxidation of chloride ion, but the hypochlorite ion generated at the anode decomposed in the aqueous solution as follows [24]

$$2\mathrm{OCl^-} \rightleftharpoons \mathrm{O_2} + 2\mathrm{Cl^-} \qquad (2)$$

When the reaction temperature was increased the rate of decomposition increased. Maximum current efficiency for the generation of hypochlorite ion occurred at 35 °C.

3.1.3. Effect of pH. Increasing the pH from 3.0 to 7.0 resulted in a current efficiency increase from 78.0 to 96.0% (Fig. 3). Further increase of pH affected the current efficiency only slightly. Chlorine was generated from Cl^- at the anode surface and diffused

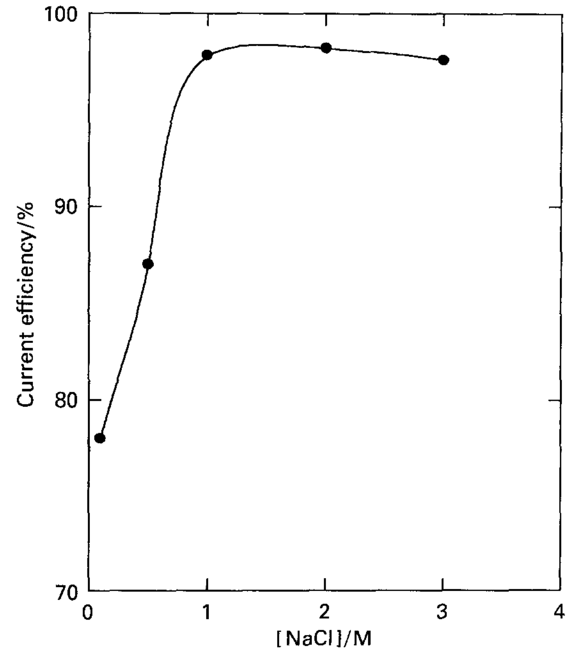

Fig. 1. Effect of the concentration of chloride ion on the current efficiency for producing hypochlorite ion. Temp: 25 °C; stirring rate: 600 rpm; pH 13; anode: 3 cm^2 SPR; current density: 100 mA cm^{-2}, volume of anolyte: 120 ml, charge passed: 100 C.

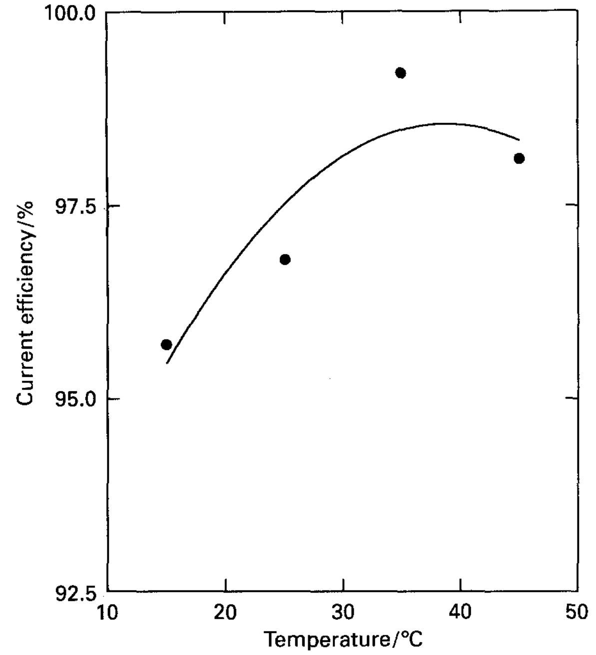

Fig. 2. Effect of the temperature on the current efficiency for producing hypochlorite ion. [NaCl] = 1.0 M; stirring rate: 600 rpm; pH 13; anode: 3 cm^2 SPR; current density: 100 mA cm^{-2}; volume of anolyte: 120 ml; charge passed: 100 C.

to the bulk solution where chlorine was hydrolysed to hypochlorite [2, 3, 25–27]

$$2Cl^- \rightleftharpoons Cl_2 + 2e^- \quad (3)$$

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \quad (4)$$

$$HOCl \rightleftharpoons H^+ + OCl^- \quad (5)$$

As indicated by Equations 4 and 5, the hydrolysis of chlorine in the bulk phase is inhibited in acidic conditions. Therefore, current efficiency decreased with decrease in pH.

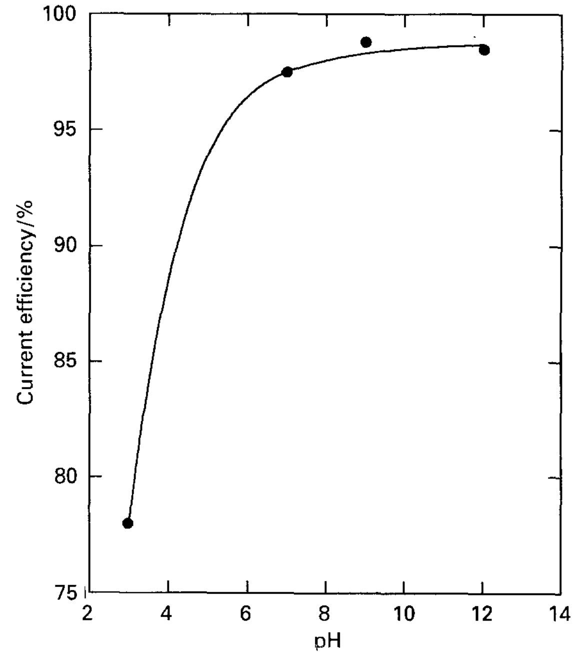

Fig. 3. Effect of the pH on the current efficiency for producing hypochlorite ion. Temp: 25 °C; stirring rate: 600 rpm, [NaCl] = 1.0 M; anode: 3 cm^2 SPR; current density: 100 mA cm^{-2}; volume of anolyte: 120 ml; charge passed: 100 C.

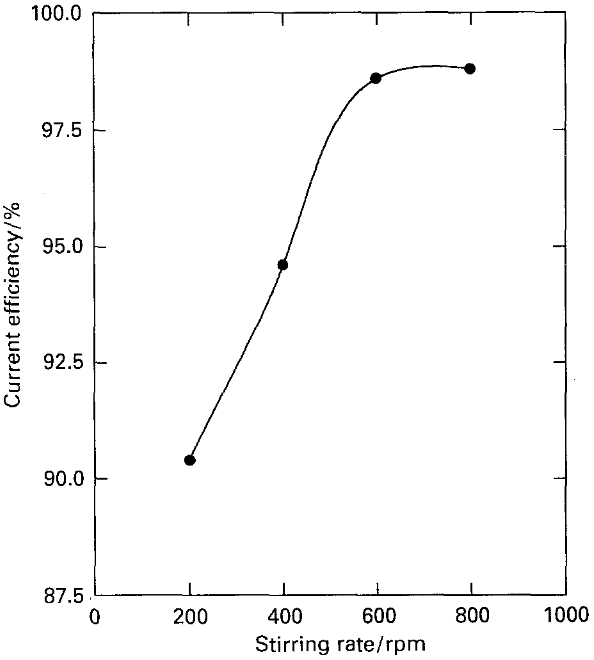

Fig. 4. Effect of the stirring rate on the current efficiency for producing hypochlorite ion. Temp: 25 °C; [NaCl] = 1.0 M; pH 13; anode: 3 cm^2 SPR; current density: 100 mA cm^{-2}; volume of anolyte: 120 ml; charge passed: 100 C.

3.1.4. Effect of stirring rate. Increasing the stirring rate initially resulted in an increased rate of anodic oxidation of chloride when the reaction was controlled by the mass transfer of Cl^- from the bulk solution to the anode. On further increase of the stirring rate the anodic oxidation of chloride ion shifted from mass transfer control to kinetic control, where the rate of anodic oxidation of chloride ion was unaffected by stirring. As shown in Fig. 4, the current efficiency to produce hypochlorite ion increased from 90.4 to 98.5% with increase of stirring rate from 200 to 600 rpm. The current efficiency remained constant and the reaction system was controlled by the kinetics of the anodic oxidation of chloride ion when the stirring rate exceeded 600 rpm.

3.1.5. Effect of current density. Increased current density resulted in increased side reaction (oxygen evolution) at the anode and decreased the hypochlorite current efficiency. The current efficiency decreased slightly from 99.3 to 97.1% when the current density increased from 5 to 100 mA cm^{-2} as shown in Fig. 5. The good current efficiency is attributable to the excellent electrocatalytic activity for hypochlorite of the SPR anode and the inhibition of oxygen evolution by the PdO component [22, 28]. The results reveal that a wide current density may be used for the anodic oxidation of chloride ion on SPR. Using RuO_2/TiO_2 as anode, the current efficiency for producing hypochlorite significantly decreased from 90 to 60% when the NaCl concentration was 0.1 M and the current density increased from 100 to 500 mA cm^{-2} [15].

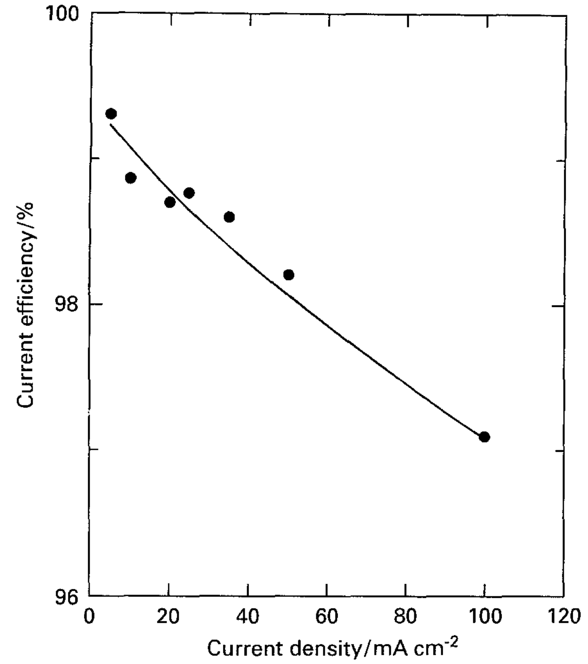

Fig. 5. Effect of the current density on the current efficiency for producing hypochlorite ion. Temp: 25 °C; stirring rate: 600 rpm; pH 13; anode: 3 cm^2 SPR; [NaCl] = 1.0 M; volume of anolyte: 120 ml, charge passed: 100 C.

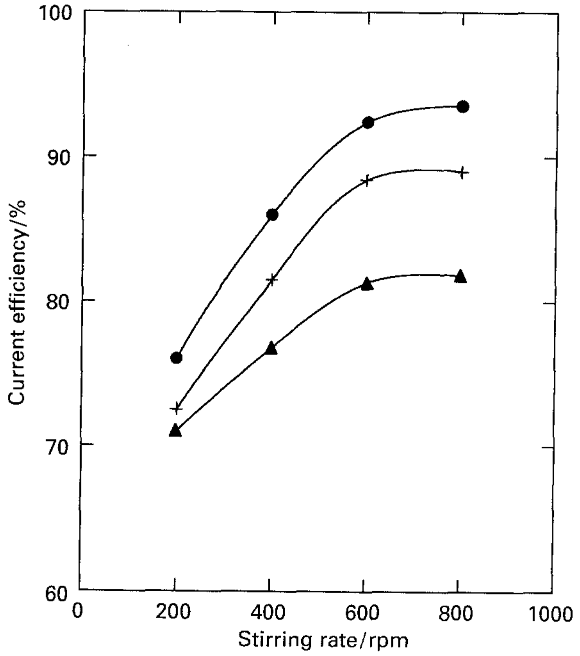

Fig. 6. Effect of the stirring rate on the current efficiency of the anodic degradation of formaldehyde. Temp: 45 °C; [NaCl]: 1.0 M; pH 13; anode: 3 cm^2 SPR; current density: 75 mA cm^{-2}; volume of anolyte: 120 ml; [HCHO] = 3000 ppm. Charge passed: (●) 0.086, (+) 0.259 and (▲) 0.518 F mol^{-1} of HCHO.

3.2. *In situ oxidative degradation of formaldehyde with electrogenerated hypochlorite ion*

The main product of formaldehyde degradation was formic acid, as illustrated in Table 1. The selectivity of formic acid lay in the range 0.94 to 0.98 when the initial concentration of formaldehyde was changed from 500 to 3000 ppm. The other product of formaldehyde degradation was carbon dioxide. The results indicated that the oxidation of formic acid to carbon dioxide with electrogenerated hypochlorite was insignificant.

3.2.1. Effect of stirring rate. When hypochlorite ion is obtained by the hydrolysis of chlorine (Equations 4 and 5), formaldehyde may be oxidized by hypochlorite ion in the bulk solution [22]

$$2HCHO + OCl^- + 2OH^- \rightleftharpoons 2HCOO^- + Cl^- + H_2 + H_2O \qquad (6)$$

According to Equation 6, one mole of electrogenerated hypochlorite can react with two moles of formaldehyde to formic acid. Therefore, the current efficiency of formaldehyde degradation is calculated as follows:

$$\eta = \frac{F([HCHO]_i - [HCHO]_f)V}{1000 M_{HCHO} It} \times 100\% \qquad (7)$$

where $[HCHO]_i$ and $[HCHO]_f$ are the initial and final concentrations of formaldehyde (ppm), and M_{HCHO} is the molecular weight of formaldehyde.

Table 1. Selectivity of formic acid

[HCHO]$_i$ /ppm	*[HCHO]$_f$ /ppm*	*[HCOOH] /ppm*	*Selectivity of HCOOH**
500	52	674	0.98
1000	364	914	0.94
3000	1720	1894	0.97

$$* \text{ Selectivity of HCOOH} = \frac{[HCOOH] \times M_{HCHO}}{M_{HCOOH}([HCHO]_i - [HCHO]_f)}$$

where M_{HCHO} and M_{HCOOH} are the molecular weight of formaldehyde and formic acid, respectively.

Temp: 25 °C; stirring rate: 600 rpm; pH 13; anode: 3 cm^2 SPR; [NaCl]: 1.0 M; volume of anolyte: 120 ml; charge passed: 600 C.

As indicated in Fig. 6, the degradation of formaldehyde with hypochlorite ion was limited by mass transfer of chloride from the bulk phase to the anodic surface when the stirring rate was less than 400 rpm. The reaction is controlled by the kinetics of the anodic oxidation of chloride ion and the oxidation of formaldehyde with hypochlorite ion in the bulk solution when the stirring rate exceeded 600 rpm.

3.2.2. Effect of concentration of chloride ion. The current efficiency of direct anodic degradation of formaldehyde was 8.0% in the absence of chloride ion from aqueous solution (Fig. 7). When the concentration of chloride ion was 0.1 M, the current efficiency increased to 51.0%. The results indicate that formaldehyde is mainly degraded by hypochlorite electrogenerated at the anode as illustrated in Equations 3 to 6. The contribution of direct anodic degradation is insignificant.

Increasing the concentration of chloride ion from 0.1 to 1.0 M the current efficiency increased from 51.0 to 82.0% (Fig. 7). As shown in Fig. 1, the effect of chloride ion concentration on the generation of hypochlorite ion at the anode was insignificant when the concentration of chloride ion exceeded 1.0 M. The current efficiency for formaldehyde degradation

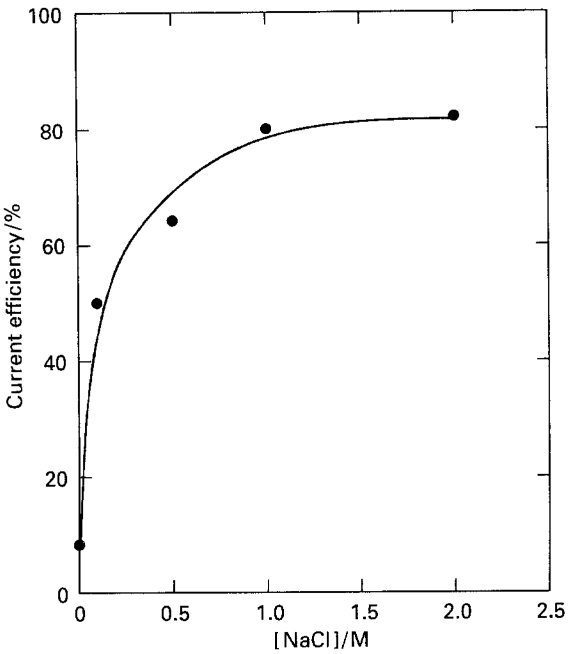

Fig. 7. Effect of the concentration of chloride ion on the current efficiency of the anodic degradation of formaldehyde. Temp: 25 °C; stirring rate: 600 rpm; pH 13; anode: 3 cm^2 SPR; current density: 75 mA cm^{-2}; volume of anolyte: 120 ml; [HCHO] = 3000 ppm; charge passed: 0.6 F mol^{-1} of HCHO.

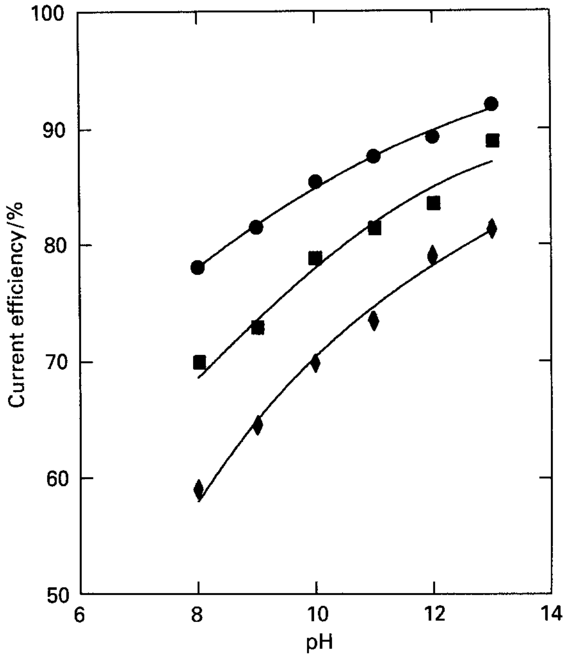

Fig. 8. Effect of the pH on the current efficiency of the anodic degradation of formaldehyde. Temp: 25 °C; [NaCl] = 1.0 M; stirring rate: 600 rpm; anode: 3 cm^2 SPR; current density: 75 mA cm^{-2}; volume of anolyte: 120 ml; [HCHO] = 3000 ppm. Charge passed: (●) 0.086, (■) 0.259 and (◆) 0.518 F mol^{-1} of HCHO.

correlated well with the results of Fig. 1. When the concentration of chloride ion increased from 1.0 to 2.0 M, the current efficiency changed slightly (Fig. 7).

3.2.3. Effect of pH. As indicated in Equations 4 and 5, the efficiency of hydrolysis of chlorine increases when the concentration of OH^- increases. The maximum current efficiency of hypochlorite ion generation by the anodic oxidation of chloride ion was found when the pH exceeded 8.0 (Fig. 3). The pH was thus maintained at values greater than 8.0. The current efficiency increased from 76.0 to 92.0% when the pH increased from 8.0 to 13.0 and the charge passed was 0.086 F mol^{-1} of formaldehyde (Fig. 8). According to Equation 6 the degradation of formaldehyde with electrogenerated hypochlorite ion was promoted when the concentration of hydroxyl ion increased. Hence the current efficiency increased with pH.

3.2.4. Effect of temperature. Increase in temperature causes the rates of electrogeneration of hypochlorite (Equation 3), the degradation of formaldehyde with electrogenerated hypochlorite (Equation 6), and the self-decomposition of hypochlorite to increase (Equation 2). Increase in the rates of generation of hypochlorite and of degradation of formaldehyde caused an increase in the current efficiency of anodic oxidative degradation of formaldehyde, but the current efficiency decreased when the rate of self-decomposition of hypochlorite ion increased. As shown in Fig. 9, the current efficiency for the degradation of formaldehyde increased from 86.0 to 91.9% when the temperature increased from 15 to 25 °C and the charge passed was 0.086 F mol^{-1} of formaldehyde. With further increase in temperature to 45 °C the current efficiency increased slightly to 93.0%.

3.2.5. Effect of charge passed. When the charge passed increased from 0.086 to 0.691 F mol^{-1} of formaldehyde and the initial concentration of formaldehyde was 3000 ppm, the current efficiency

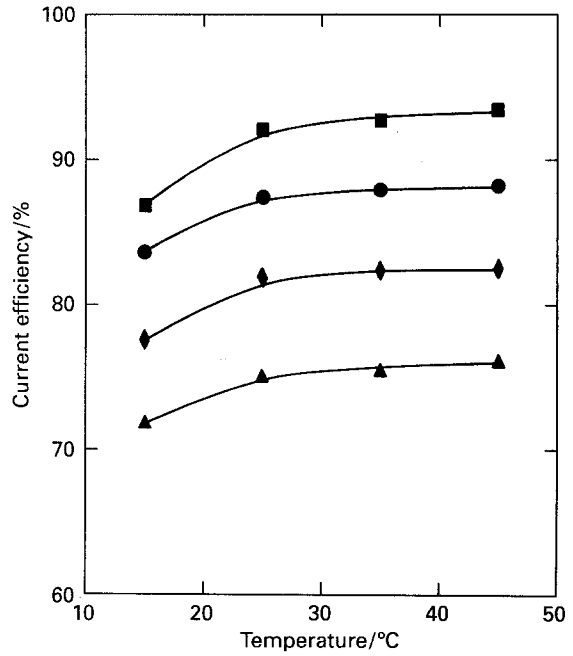

Fig. 9. Effect of the temperature on the current efficiency of the anodic degradation of formaldehyde. [NaCl] = 1.0 M; pH 13; stirring rate: 600 rpm; anode: 3 cm^2 SPR; current density: 75 mA cm^{-2}; volume of anolyte: 120 ml; [HCHO] = 3000 ppm. Charge passed: (■) 0.086, (●) 0.259, (◆) 0.518 and (▲) 0.688 F mol^{-1} of HCHO.

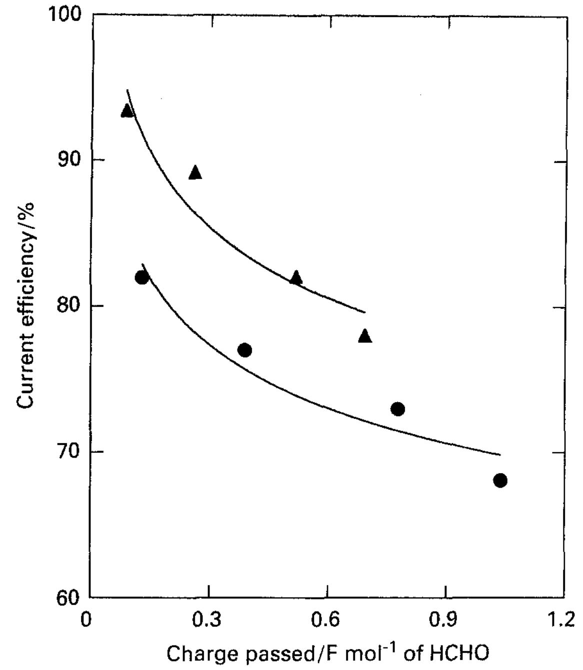

Fig. 10. Effect of the charge passed on the current efficiency of the anodic degradation of formaldehyde. Temp: 45 °C; [NaCl] = 1.0 M, pH 13; stirring rate: 600 rpm; anode: 3 cm^2 SPR; current density: 75 mA cm^{-2}; volume of anolyte: 120 ml. [HCHO]: (▲) 3000 and (●) 2000 ppm.

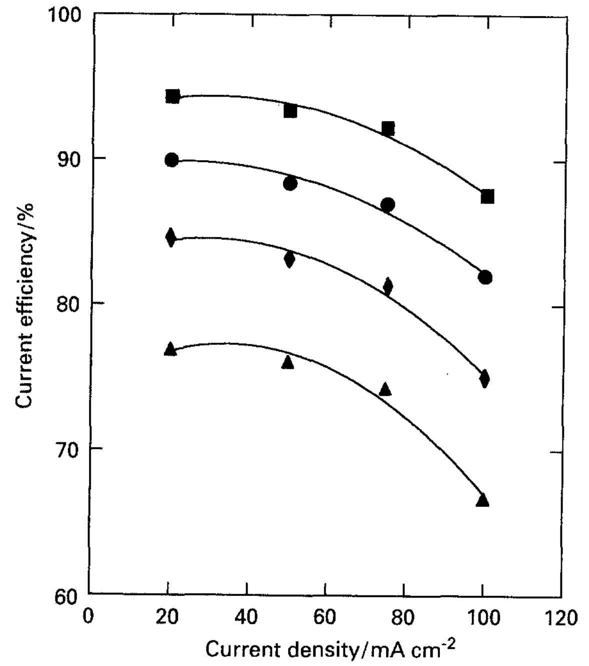

Fig. 11. Effect of the current density on the current efficiency of the anodic degradation of formaldehyde. Temp: 45 °C; [NaCl] = 1.0 M; pH 13; stirring rate: 600 rpm; anode: 3 cm^2 SPR; volume of anolyte: 120 ml; [HCHO] = 3000 ppm. Charge passed: (■) 0.086, (●) 0.259, (◆) 0.518 and (▲) 0.688 F mol^{-1} of HCHO.

decreased from 94.0 to 81.0% (Fig. 10). In the initial period of a run, the hypochlorite ion electrogenerated on the anode was readily consumed due to the high concentration of formaldehyde in the solution. Therefore, a greater current efficiency for formaldehyde degradation was found. Increasing the charge passed caused the concentration of formaldehyde to decrease and the charge used to accumulate hypochlorite ion in the aqueous solution increased. Hence the current efficiency decreased.

3.2.6. Effect of current density. The current efficiency of anodic formaldehyde degradation decreased from 94.0 to 87.0% when the current density increased from 20 to 100 mA cm^{-2} and the charge passed was 0.086 F mol^{-1} of formaldehyde (Fig. 11). As indicated in Fig. 5, the effect of current density on the anodic oxidation of chloride ion on the SPR anode was small when the current density increased from 5 to 100 mA cm^{-2}. According to Equations 3 to 6, a pseudo-steady state was achieved when the rate of generation of hypochlorite ion on the anode (Equations 3 to 5) was equal to the rate of oxidation of formaldehyde with hypochlorite ion (Equation 6). Increasing the current density resulted in an increase in the rate of hypochlorite ion generation and formaldehyde oxidation by hypochlorite ion. Therefore, the pseudo-steady state concentration of hypochlorite ion increased with current density. Increase in the pseudo-steady state concentration of hypochlorite ion caused an increase in that part of the current used to accumulate hypochlorite ion in the aqueous phase. The current efficiency for the oxidative degradation of formaldehyde thus decreased with increase in current density.

3.2.7. Effect of concentration of formaldehyde. Increased concentration of formaldehyde caused an increased rate of oxidative formaldehyde degradation (Equation 6). The concentration of hypochlorite ion and the rate of self-decomposition of hypochlorite ion (Equation 2) therefore decreased and the current efficiency increased with increase in formaldehyde. As illustrated in Fig. 12, the current efficiency increased from 42.8 to 92.0% when the

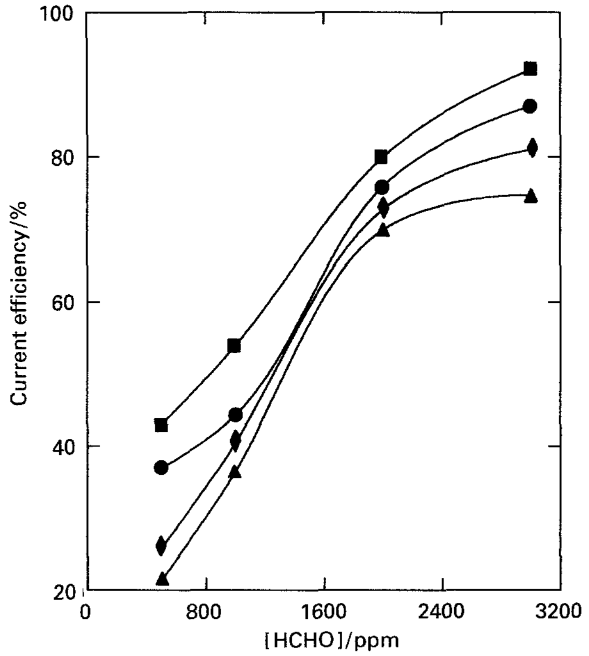

Fig. 12. Effect of the concentration of formaldehyde on the current efficiency of the anodic degradation of formaldehyde. Temp: 45 °C; [NaCl] = 1.0 M; pH 13; stirring rate: 600 rpm; anode: 3 cm^2 SPR; volume of anolyte: 120 ml; current density: 75 mA cm^{-2}. Charge passed: (■) 0.086, (●) 0.259, (◆) 0.518 and (▲) 0.688 F mol^{-1} of HCHO.

concentration of formaldehyde increased from 500 to 3000 ppm and the charge passed was 0.086 F mol^{-1} of formaldehyde.

4. Conclusions

The maximum current efficiency to generate hypochlorite ion was 99.3%. The current efficiency of the anodic oxidation of chloride ion increased when the concentration of chloride ion, pH and stirring rate increased. The effect of temperature and current density on the anodic oxidation of chloride ion was slight. The current efficiency for hypochlorite ion production was in the range 99.3–97.1% when the current density was controlled in the region 5–100 mA cm^{-2}. The results showed that the selectivity of anodic oxidation of chloride ion to hypochlorite ion was high and oxygen evolution was effectively inhibited at an SPR anode. The results also indicated that the current efficiency for formaldehyde degradation with electrogenerated hypochlorite ion *in situ* was significantly affected by the stirring rate, concentration of chloride ion, pH, charge passed, current density and formaldehyde concentration. The effect of temperature on formaldehyde degradation was insignificant. The system was controlled by the mass transfer when the stirring rate was less than 400 rpm and by surface kinetics at 500 rpm or greater.

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