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Paired electrooxidative degradation of phenol with *in situ* electrogenerated hydrogen peroxide and hypochlorite

J.-S. DO*, W.-C. YEH

Department of Chemical Engineering, Tunghai University, Taichung, Taiwan 40704, Republic of China

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The oxidants, hydrogen peroxide and hypochlorite, were generated by the cathodic reduction of oxygen and anodic oxidation of chloride ion in a paired electrolysis process and used for phenol degradation. The degradation of phenol with electrogenerated hydrogen peroxide was slightly affected by pH and ferrous ion concentration. The oxidative degradation of phenol with paired electrogenerated hydrogen peroxide and hypochlorite was significantly affected by phenol concentration. In comparison with the cathodic and anodic degradation of phenol, the removal of phenol increased by 56.1% and 178.1%, respectively, in the case of paired electrooxidative phenol degradation. The COD decreased from 3222 and 3222 ppm to 2253 and 2746 ppm in the anodic and cathodic compartments when the charge passed increased from 0 to 2500 C.

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1. Introduction

A toxic organic effluent which cannot be easily degraded using microorganisms must be treated by chemical oxidation. The activity of oxidants can be reduced and transportation hazards can be prevented when the oxidants, such as hydrogen peroxide and hypochlorite ion, are generated *in situ*. Kalu and White reported that polyhalogenated aromatic hydrocarbons can be degraded with electrochemically generated superoxide ions [1]. Organic compounds and chlorinated organics were destroyed by electrogenerated barium peroxide [2] and cobalt (III)-mediated electrochemical oxidation [3], respectively. Hydrogen peroxide and hypochlorite ion have been found to be suitable for the chemical oxidation of toxic organic compounds in waste water treatment [4–7]. The degradation of CN^- with electrogenerated hypochlorite ion was investigated by Woolley [8]. Formaldehyde in aqueous effluent was effectively degraded from 1000 ppm to 2 ppm with electrogenerated hydrogen peroxide [5]. The degree of degradation of formaldehyde was 90% when *in situ* electrogenerated hypochlorite ions were used [7].

The main sources of phenolic waste are in glass fibre insulation manufacture and petroleum refineries [9]. Phenols can be effectively destroyed by hydrogen peroxide when ferric and ferrous irons are used as catalysts [9]. Phenol was oxidatively degraded to oxalic acid and carbon dioxide with electrogenerated hydrogen peroxide at pH 3 [10, 11] and also electrogenerated hypochlorite ion in the presence of Ni(II) [12].

The current efficiency can theoretically be increased from 100% to 200% when an electrolysis system with only one working electrode, an anode or a cathode, is replaced by paired electrolysis. The paired electrolysis method has been used for the synthesis of organic compounds [13–22]. Using paired electrolysis in waste water treatment, the degradation time may be reduced and the total current efficiency increased [23]. Using paired electrogenerated hydrogen peroxide and hypochlorite as oxidants, the degree of degradation was 124% for concentrations of formaldehyde in the cathodic and anodic chambers of 1500 ppm and 3000 ppm, respectively [24].

The *in situ* oxidative degradation of phenol with paired electrogenerated hydrogen peroxide and hypochlorite ion in a divided cell was carried out in this work. The effect of pH and Fe^{2+} concentration on the oxidative degradation of phenol in the cathodic chamber and the effect of phenol concentration on paired electrooxidative degradation were also explored.

2. Experimental details

Paired electrooxidative degradation of phenol with electrogenerated hydrogen peroxide and hypochlorite ion was carried out in an undivided cell in which the anodic and cathodic chambers were separated by a sintered glass frit (Pyrex 4G). A prepared SPR (SnO_2–PdO–RuO_2–TiO_2/Ti) [6], anodically treated graphite [25] and two Ag/AgCl/3 M NaCl reference electrodes were used as anode, cathode and reference, respectively. D.c. power was supplied by means of a potentiostat/galvanostat (Nichia G1005E), and the amount of electricity passed was measured by a coulometer (Nichia N-CR 760). Oxygen was introduced to the cathodic chamber through a glass disperser.

Oxygen was sparged into the cathodic chamber for a few minutes to saturate the catholyte. Electrolysis was carried out at constant current until a preset amount of electricity had been passed. During the run, the catholyte and anolyte were periodically

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* Author to whom correspondence should be addressed.

sampled. The concentration of phenol in the aqueous solution was analysed by GC (Shimadzu GC-14A).

3. Results and discussion

3.1. *Oxidative degradation of phenol with catholyte dissolved oxygen*

The concentration of phenol decreased from 1544 ppm to 1532 ppm when the oxygen sparging time increased from 0 to 115 min for a sparging rate of 13 ml s^{-1}, as shown in Fig.1 giving a degradation fraction of 0.7%. The intermediates of the phenol degradation were found to be hydroquinone, catechol, *p*-quinone, muconic acid, maleic acid and oxalic acid [10, 11]. The final products were CO_2 and water. For comparison, the degradation fraction of formaldehyde by oxygen saturated aqueous solution was 7.2% [5]. Thus the degradation of phenol with aqueous dissolved oxygen was insignificant.

3.2. *Effect of pH on cathodic oxidative phenol degradation*

In the cathodic chamber, oxygen was reduced to hydrogen peroxide [5]:

$$O_2(g) \rightleftharpoons O_2(aq) \qquad (1)$$

$$O_2(aq) \rightleftharpoons O_2(s) \qquad (2)$$

$$O_2(s) + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^- \qquad (3)$$

where ‘s’ indicates the electrode surface.

As discussed above, the degradation of phenol with dissolved oxygen was small and the main reaction pathway was by oxidation with electrogenerated hydrogen peroxide. The degradation fraction of phenol increased slightly from 27.2% to 30.1% when the pH increased from 3 to 13 and the charge passed was 800 C as illustrated in Fig 2. Thus the effect of pH on the phenol degradation was small. Current efficiencies for the cathodic reduction of oxygen to hydrogen peroxide in acidic and basic solutions are greater than that in neutral solution [5]. This suggests that the cathodic reduction of dissolved oxygen was not the rate determining step (r.d.s.) in phenol degradation. The r.d.s. is the mass transfer of oxygen from the aqueous phase to the cathodic surface or the oxidation of phenol with electrogenerated hydrogen peroxide in the bulk solution.

3.3. *Effect of ferrous ion concentration on the cathodic oxidative degradation of phenol*

In the oxidative degradation of organic compounds with hydrogen peroxide, an intermediate free radical (OH·) is formed in the presence of ferrous ion [10]

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH\cdot \qquad (4)$$

Organic compounds in waste water react with the free radical, Fe^{3+} and Fe^{2+} as follows

$$RH + OH\cdot \longrightarrow R_1\cdot + H_2O \qquad (5)$$

$$RH + OH\cdot \longrightarrow R_2\cdot + H_2O \qquad (6)$$

$$R_1\cdot + Fe^{3+} \longrightarrow R_1^+ + Fe^{2+} \qquad (7)$$

$$R_2\cdot + Fe^{2+} \longrightarrow R_2^- + Fe^{3+} \qquad (8)$$

Free radicals (OH·) can also be consumed by ferrous ions [10] and the inert surface [26–28]

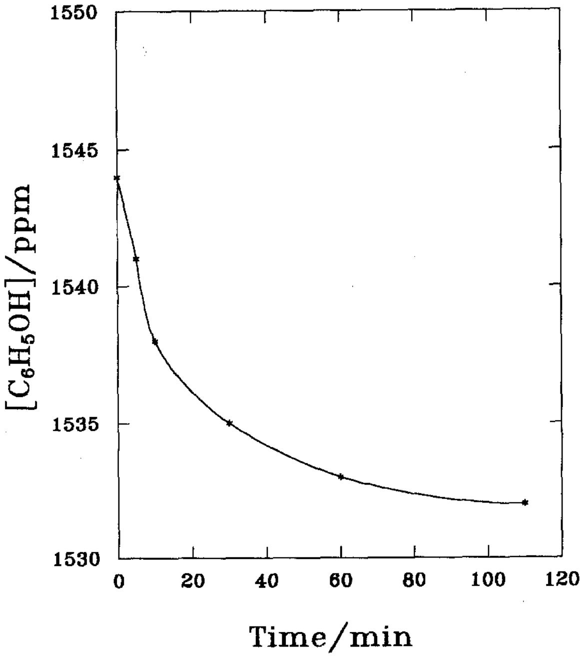

Fig. 1. Effect of time on the oxidative degradation of phenol with dissolved oxygen. Conditions: $[C_6H_5OH]$ = 1544 ppm, T = 45 °C, O_2 sparging rate = 13 ml s^{-1}, pH 13, V = 250 ml, stirring rate = 600 rpm.

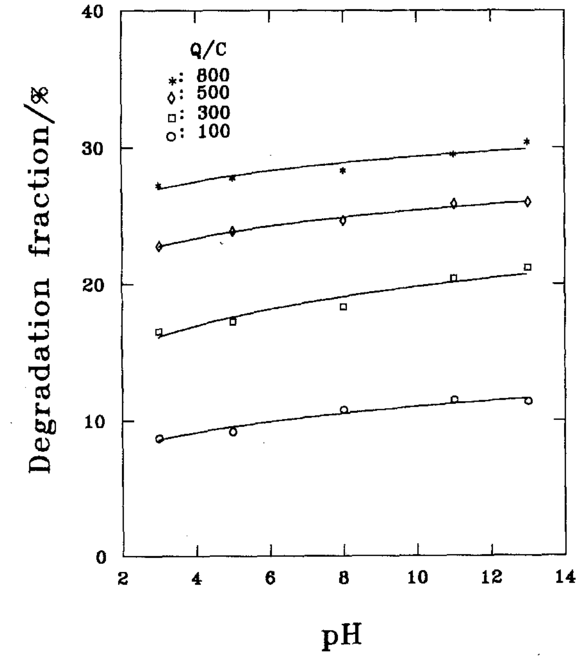

Fig. 2. Effect of pH on the degradation fraction of phenol in the cathodic chamber. Conditions: $[C_6H_5OH]$ = 1050 ppm, T = 45 °C, O_2 sparging rate = 13 ml s^{-1}, current density = 0.75 mA cm^{-2}, cathodic area = 330 cm^2, V_c = 250 ml, stirring rate = 600 rpm. Charge passed, Q: (○) 100, (□) 300, (◇) 500 and (∗) 800 C.

$$\mathrm{Fe}^{2+} + \mathrm{OH}\cdot \longrightarrow \mathrm{Fe}^{3+} + \mathrm{OH}^- \quad (9)$$

$$\mathrm{OH}\cdot + \mathrm{S} \longrightarrow \text{inactive} \quad (10)$$

where S is the inert surface. Therefore, in free radical reactions, the reaction rate is significantly affected by the inert surface [26–28]. The degradation fraction of phenol increased slightly when the concentration of ferrous ion increased from 0 mM to 0.29 mM (Fig. 3). The cathodic surface area was 330 cm^2 and the ratio of surface area to catholyte volume was 1.32 cm^{-1}. The insignificant effect of ferrous ion concentration on the degradation of phenol with electrogenerated hydrogen peroxide may be due to the large inert surface area in the cathodic chamber. Most of the free radicals generated in the catholyte are destroyed at the cathodic surface Equation 10.

3.4. *Effect of phenol concentration*

The degradation of phenol in the cathodic chamber decreased from 58.8% to 26.9% and the amount of phenol removed increased from 0.69 to 1.87 mmol when the phenol concentration increased from 440 to 2600 ppm and the charge passed was 1500 C (Figs 4 and 5). In the anodic chamber, chloride ion was oxidized to hypochlorite ion [6, 7]

$$2\mathrm{Cl}^- \rightleftharpoons \mathrm{Cl}_2 + 2\mathrm{e}^- \quad (11)$$

$$\mathrm{Cl}_2 + \mathrm{H}_2\mathrm{O} \rightleftharpoons \mathrm{HOCl} + \mathrm{H}^+ + \mathrm{Cl}^- \quad (12)$$

$$\mathrm{HOCl} \rightleftharpoons \mathrm{H}^+ + \mathrm{Cl}^- \quad (13)$$

Phenol was degraded with the electrogenerated hypochlorite ion. Raising the concentration of phenol from 440 to 2600 ppm resulted in a decrease in degradation from 67.2% to 31.6% and an increase in the amount of phenol removed from 0.38 to 1.05 mmol in the anodic chamber when 1500 C was charged (Figs 6 and 7). This indicates that both the degradation fraction and the amount of phenol removed increased in both the cathodic and anodic chambers as the charge passed increased.

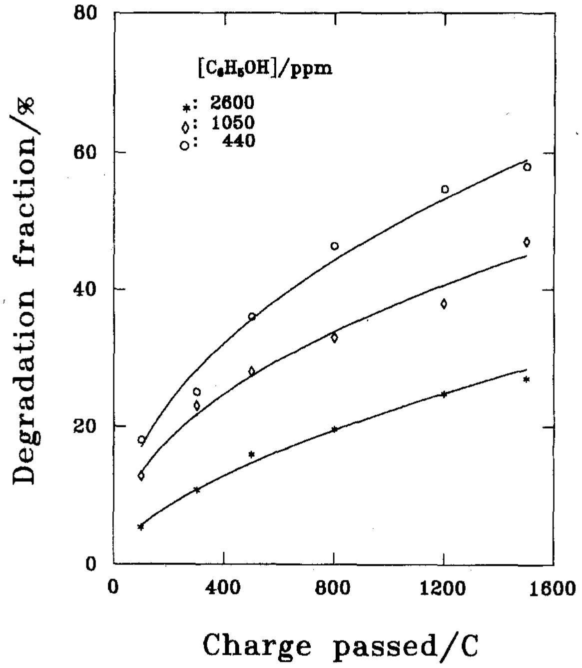

Fig. 4. Effect of charge passed on the degradation of phenol in the cathodic chamber. Conditions: $T = 45\,^\circ\mathrm{C}$, O_2 sparging rate = 13 ml s^{-1}, current density = 0.75 mA cm^{-2}, cathode area = 330 cm^2, $V_c = 250$ ml, stirring rate = 600 rpm, pH 13. [$\mathrm{C}_6\mathrm{H}_5\mathrm{OH}$]: (o) 440, (◊) 1050 and (*) 2600 ppm.

With increased concentration of phenol, the

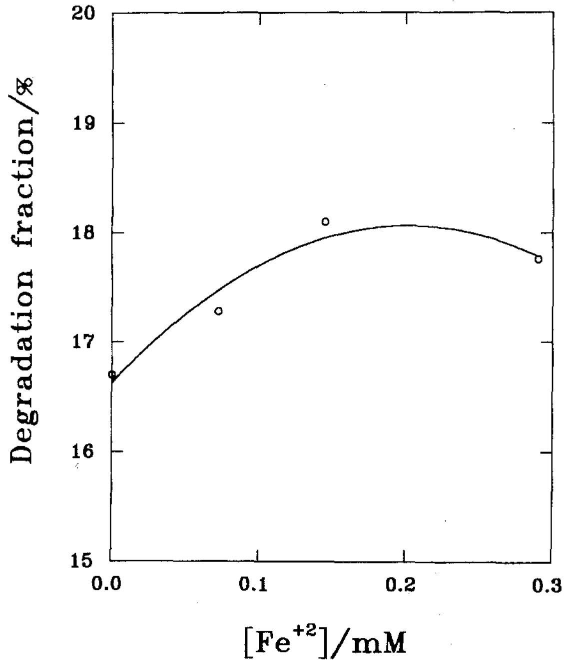

Fig. 3. Effect of ferrous ion concentration on the degradation fraction of phenol in the cathodic chamber. Conditions: [$\mathrm{C}_6\mathrm{H}_5\mathrm{OH}$] = 1050 ppm, $T = 45\,^\circ\mathrm{C}$, O_2 sparging rate = 13 ml s^{-1}, current density = 0.75 mA cm^{-2}, cathode area = 330 cm^2, V_c = 250 ml, stirring rate = 600 rpm, pH 3.

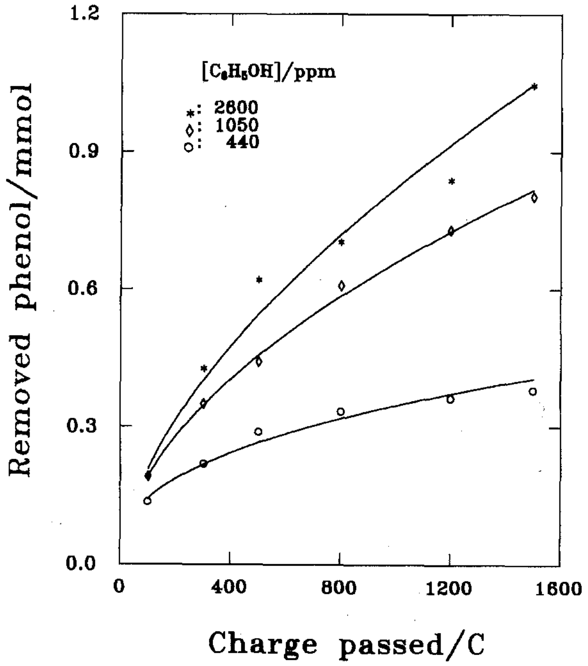

Fig. 5. Effect of charge passed on the amount of removal phenol in the cathodic chamber. Conditions: $T = 45\,^\circ\mathrm{C}$, O_2 sparging rate = 13 ml s^{-1}, current density = 0.75 mA cm^{-2}, cathode area = 330 cm^2, V_c = 250 ml, stirring rate = 600 rpm, pH 13, [$\mathrm{C}_6\mathrm{H}_5\mathrm{OH}$]: (o) 440, (◊) 1050 and (*) 2600 ppm.

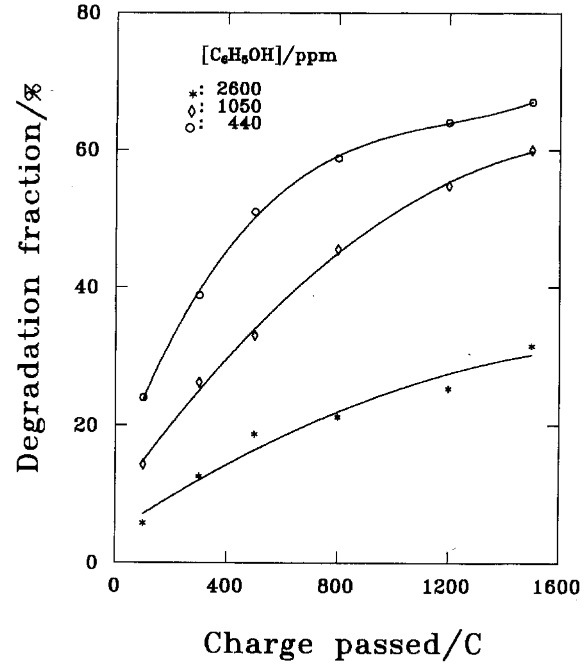

Fig. 6. Effect of charge passed on the degradation of phenol in the anodic chamber. Conditions: $T = 45\,°C$, [NaCl] = 1.0 M, current density = 41 mA cm^{-2}, area of anode = 6 cm^2, V_a = 120 ml, stirring rate = 600 rpm, pH 13. [C$_6$H$_5$OH]: (○) 440, (◇) 1050 and (*) 2600 ppm.

oxidants (hydrogen peroxide and hypochlorite) electrogenerated were effectively used to degrade phenol. The amount of phenol removed in the cathodic chamber was greater than that in the anodic chamber as illustrated in Figs 5 and 7. The current efficiency of phenol degradation with electrogenerated hydrogen peroxide was higher than that with electrogenerated hypochlorite ion. On the other hand, the degradation fraction of phenol in the cathodic chamber was smaller than that in the anodic chamber (Figs 4 and 6). The smaller degradation in the cathodic chamber was due to the larger electrolyte volume.

The amount of phenol removed by paired electro-oxidative degradation increased from 1.07 to 2.92 mmol when the concentration of phenol was increased from 440 to 2600 ppm and the charge passed was 1500 C (Fig. 8). In comparison with the results of one working electrode systems (cathodic and anodic chambers), the amount of phenol removed with the paired degradation method increased by 56.1% and 178.1%, respectively, when the phenol concentration was 2600 ppm.

3.5. *Effect of temperature*

Increase in temperature caused an increase in the oxidation rate and an increase in the phenol degradation fraction in both the cathodic and anodic chambers. On the other hand, the degradation fraction decreased with increase in the oxidant self-decomposition rate as the solution temperature increased [5]. Therefore, an optimal electrolysis temperature may be identified. As illustrated in Fig. 9, the degradation fraction in the cathodic and anodic chambers increased from 22.4% and 32.1% to 27.0% and 36.0%, respectively, when the temperature was increased from 15 to 35 °C. With further increase in temperature to 45 °C, the degradation fraction decreased to 25.3% and 35.3%, respectively. The decrease is probably due to oxidant self-decomposition. The optimal degradation temperature was

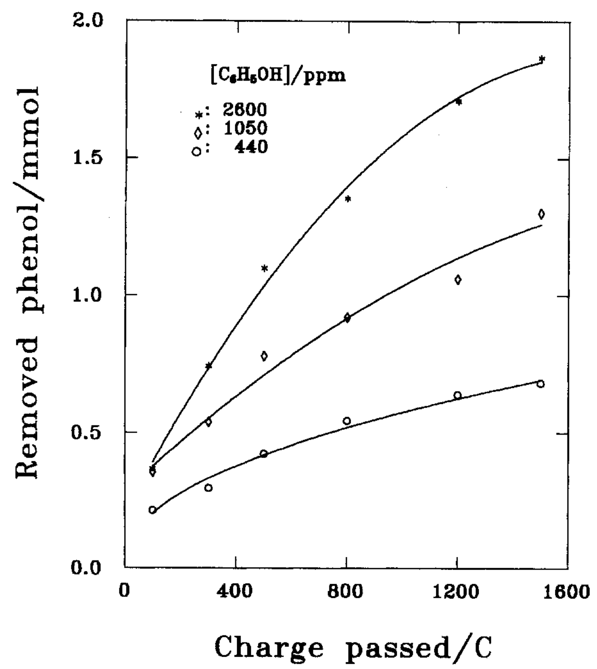

Fig. 7. Effect of charge passed on the amount of removal phenol in the anodic chamber. Conditions: $T = 45\,°C$, [NaCl] = 1.0 M, current density = 41 mA cm^{-2}, anode area = 6 cm^2, V_a = 120 ml, stirring rate = 600 rpm, pH 13. [C$_6$H$_5$OH]: (○) 440, (◇) 1050 and (*) 2600 ppm.

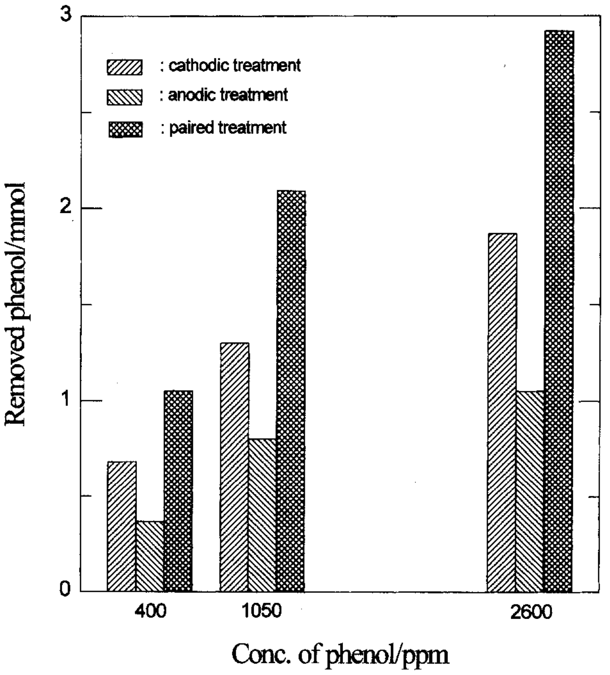

Fig. 8. Effect of phenol concentration on the removal phenol. Conditions: $T = 45\,°C$, [NaCl] = 1.0 M, $i_a = 41$ mA cm^{-2}, $i_c = 0.75$ mA cm^{-2}, anode area = 6 cm^2, cathode area = 330 cm^2, oxygen sparging rate = 13 ml s^{-1}, V_a = 120 ml, V_c = 250 ml, charge passed = 1500 C, stirring rate = 600 rpm, pH 13.

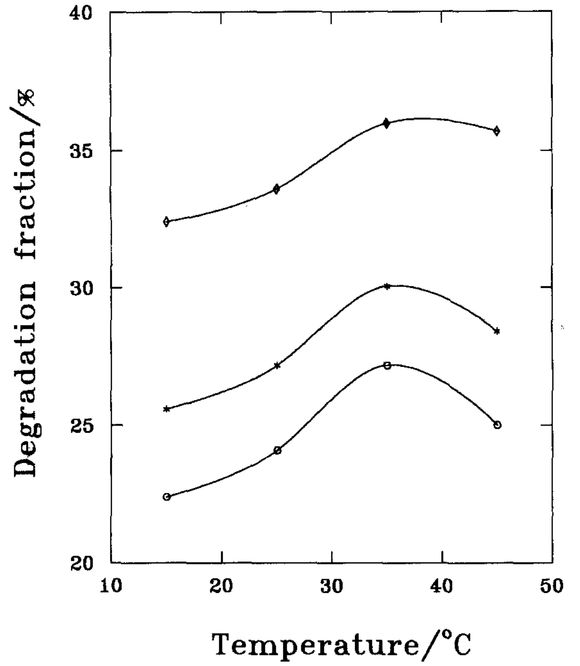

Fig. 9. Effect of temperature on the degradation fraction of phenol. Conditions: $[C_6H_5OH] = 1500$ ppm, $T = 45$ °C, [NaCl] = 1.0 M, $i_a = 41$ mA cm^{-2}, $i_c = 0.75$ mA cm^{-2}, anode area = 6 cm^2, area of cathode = 330 cm^2, oxygen sparging rate = 13 ml s^{-1}, $V_a = 120$ ml, $V_c = 250$ ml, charge passed = 800 C, stirring rate = 600 rpm, pH 13. Key: (○) cathodic treatment; (◇) anodic treatment; (∗) paired treatment.

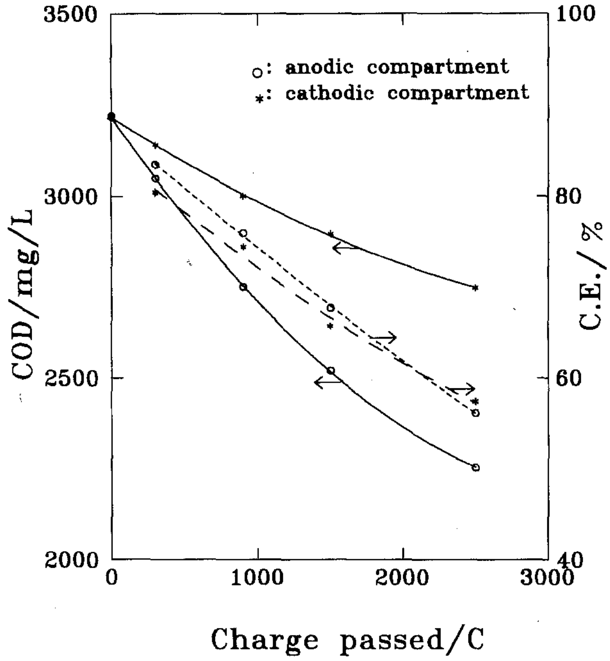

Fig. 10. Effect of charge passed on *COD* and current efficiency of the degradation of phenol. Conditions: $T = 45$ °C, [NaCl] = 1.0 M, $i_a = 41$ mA cm^{-2}, $i_c = 0.75$ mA cm^{-2}, anode area = 6 cm^2, cathode area = 330 cm^2, oxygen sparging rate = 13 ml s^{-1}, $V_a = 120$ ml, $V_c = 250$ ml, stirring rate = 600 rpm, pH 13. Compartment: (∗) cathodic; (○) anodic.

experimentally obtained as 35 °C and the degradation fraction by paired electrooxidative degradation was 30.1% (Fig. 9).

3.6. *Effect of charge passed on chemical oxygen demand and current efficiency*

Increasing the charge passed from 0 to 2500 C resulted in a decrease in chemical oxygen demand (*COD*) in the anodic and cathodic compartments from 3222 and 3222 to 2253 and 2746 ppm, respectively (Fig. 10). The current efficiency, η, for phenol degradation was calculated as

$$\eta = \frac{[(COD)_i - (COD)_f] \times 96485 \times V_s}{8000Q} \times 100\% \quad (14)$$

where $(COD)_i$ and $(COD)_f$ are the initial and final values in ppm, V_s is the volume of solution (l), and Q is the charge passed. The current efficiency decreased from 83.5 and 80.4% to 56.1 and 57.4%, respectively when the charge passed was increased from 300 to 2500 C (Fig.10).This shows that the difference in the current efficiencies in the two compartments was insignificant. On the other hand, the amount of phenol removed in the cathodic compartment was greater than that in the anodic compartment, as shown in Fig. 8. This shows that the carbon in the phenol molecule may be oxidized to a higher valence state in the anodic compartment compared to the cathodic compartment. Because the volume of anodic solution was less than that of cathodic solution, the decrease in *COD* in the anodic compartment was faster than that in the cathodic compartment.

4. Conclusions

The oxidative degradation of phenol with electrogenerated hydrogen peroxide in the cathodic chamber was slightly affected by pH, ferrous ion concentration and temperature. The degradation of phenol with catholyte dissolved oxygen was insignificant. With increase in the phenol concentration the degradation fraction of phenol with paired electrogenerated hydrogen peroxide and hypochlorite decreased and the amount of phenol removal increased. The optimal temperature for the paired electrooxidative degradation of phenol was 35 °C. Compared with oxidative degradation of phenol in the cathodic and anodic chambers, the amount of removal phenol by the paired electrooxidative degradation of phenol increased by 56.1% and 178.1%, respectively. The *COD* of the anolyte and catholyte decreased from 3222 to 3222 ppm to 2253 and 2746 ppm when the charge passed increased from 0 to 2500 C. Similar current efficiencies for anodic and cathodic oxidative degradation were obtained.

Acknowledgements

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