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Anodic oxidation of phenol for waste water treatment

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The electrochemical oxidation of phenol for waste water treatment was studied at a platinum anode. Analysis of reaction intermediates and a carbon balance has shown that the reaction occurs by two parallel pathways; chemical oxidation with electrogenerated hydroxyl radicals and direct combustion of adsorbed phenol or/and its aromatic intermediates to CO_2.

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1. Introduction

Many industries are characteristic sources of phenolic pollutants, including oil refineries, coke plants, chemical and plastic plants. Present Swiss guidelines limit phenol concentration to $0.05\,mg\,dm^{-3}$ and lower concentration limits are in discussion. Phenols here refer to aromatic derivatives that contain one or more hydroxyl groups.

Many treatment technologies are in use or have been proposed, for phenol recovery or destruction. These include activated carbon adsorption [1] and solvent extraction [2] for recovery and biological [3] chemical [4] and electrochemical oxidation [5, 6, 7] for phenol destruction. Several applications of chemical oxidation of phenol have been reported. Oxidants employed include hydrogen peroxide (in the presence of Fe^{2+}), ozone and chlorine. The more costly oxidants are of interest where concentrations are too high or too variable for treatment by biological processes.

The electrochemical oxidation of phenol has been suited for synthesis of hydroquinone or benzoquinone [8] and has been reported as a means of waste water treatment. Smith de Sucre and Watkinson [5] reported that for waste water treatment, phenol could be readily oxidized at a lead dioxide anode but complete total organic carbon (TOC) removal was more difficult. Similar results have been obtained by Sharifian and Kirk [6]. In the present investigation the aim was to examine the anodic oxidation of phenol at a platinum anode to find the most favourable conditions of oxidation and to elucidate the mechanism of the reaction.

2. Experimental details

2.1. *Determination of the current efficiency*

Two methods have been used for the determination of the current efficiency during the electrochemical oxidation of phenol; The oxygen flow rate method and the COD (chemical oxygen demand) method.

In the oxygen flow rate method the oxygen flow rate was measured during electrolysis and the instantaneous current efficiency (ICE) for oxidation of phenol at given experimental conditions was calculated using the relation

$$\mathrm{ICE} = \frac{\dot{V}_0 - (\dot{V}_t)_{\mathrm{org}}}{\dot{V}_0}$$

where $\dot{V}_0$ is the oxygen flow rate in the absence of phenol in the electrolyte and $(\dot{V}_t)_{\mathrm{org}}$ is the oxygen flow rate at a given time t in the presence of phenol. Both are measured in $cm^3\,min^{-1}$.

In the COD method the chemical oxygen demand was measured (COD, Hach Dr/2000) during electrolysis and the ICE was calculated using the relation

$$\mathrm{ICE} = \frac{[(\mathrm{COD})_t - (\mathrm{COD})_{t+\Delta t}]}{8I\Delta t} F \cdot V$$

where $(\mathrm{COD})_t$ and $(\mathrm{COD})_{t+\Delta t}$ are the chemical oxygen demands at times t and $t + \Delta t$ (in $g\,O_2\,dm^{-3}$), respectively, and I is the current (A), F is the Faraday constant ($96\,487\,C\,mol^{-1}$), and V is the volume of electrolyte (dm^3).

The choice of the method of measuring ICE depends on the solubility of the electrolysis product. Thus the COD method is used only if the electrolysis products are soluble in the electrolyte (absence of film at the electrode) contrary to the oxygen flow rate method where the electrolysis product may be soluble or insoluble. Measurements of ICE by both techniques gives information about the formation of polymeric products at the anode surface.

The ICE decreases with time during electrolysis to finally reach a value of about zero (Fig. 1). From the ICE/t curve an average value can be calculated and defined as the *electrochemical oxidation index* (EOI) [7]

$$\mathrm{EOI} = \frac{\int_0^t \mathrm{ICE}\,\mathrm{d}t}{\tau}$$

where τ is the time of electrolysis at which ICE is almost zero. EOI expresses the average current efficiency and is a measure of the facility of the electrochemical oxidation of phenol (or other organic compounds) at given experimental conditions.

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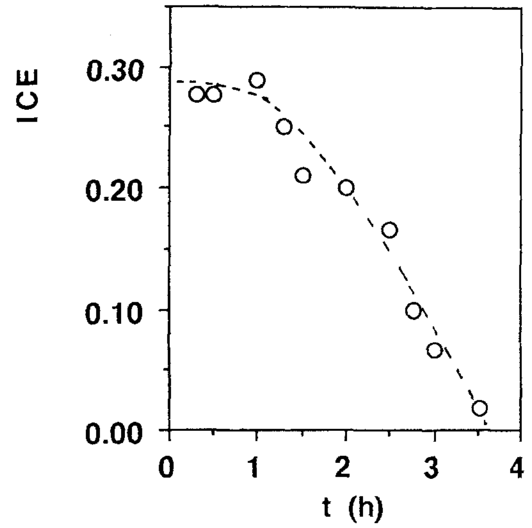

Fig. 1. Evolution of the ICE (from the oxygen flow rate method) during the electrochemical oxidation of phenol. $i = 57\,\mathrm{mA\,cm^{-2}}$, $T = 70°\mathrm{C}$, pH 12.5 (constant). Initial phenol concentration: $23\,\mathrm{mmol\,dm^{-3}}$.

The *electrochemical oxygen demand* (EOD) was calculated using the relation

$$\mathrm{EOD} = \frac{8\,(\mathrm{EOI} \times I\tau)}{F\,[\mathrm{PhOH}]}$$

where [PhOH] is the amount of phenol in the electrolyte (g) and EOD is expressed in $\mathrm{g\,O_2}$ (g phenol)$^{-1}$.

From the EOD value the degree of oxidation $\chi(\%)$ (at given experimental conditions) can be obtained using the relation

$$\chi = \frac{\mathrm{EOD}}{(\mathrm{COD})_0} \times 100$$

where $(\mathrm{COD})_0$ is the initial COD value expressed in $\mathrm{g\,O_2}$ (g phenol)$^{-1}$.

2.2. *Electrochemical cell*

A two compartment cell of $150\,\mathrm{cm^3}$ capacity was used; the anode was a platinum cylinder of $35\,\mathrm{cm^2}$ surface area and the cathode was a platinum spiral ($4\,\mathrm{cm^2}$) enclosed in a $10\,\mathrm{cm^3}$ porous porcelain pot; stirring was provided by a magnetic bar.

The pH of the anolyte was maintained constant (pH 12.5 or 3) during electrolysis by continuous introduction of a solution of NaOH or H_2SO_4 to the anolyte ($150\,\mathrm{g\,dm^{-3}}$ Na_2SO_4) containing phenol.

The oxygen formed in the anolyte during electrolysis in the presence and in the absence of phenol was measured using a gas burette and analysed by gas chromatography.

2.3. *Analysis*

The progress of the electrochemical oxidation of phenol was monitored by measuring the total organic carbon (TOC, XERTEX Dohrman) and the chemical oxidation demand (COD, Hach DR/2000). The disappearance of phenol and the appearance of its oxidation products were monitored by HPLC (Shimazu 8 A).

3. Results and discussion

3.1. *Film formation at the anode*

During the anodic oxidation of phenol a yellow brown polymeric product, which was insoluble in acetone were formed at the surface of the platinum anode. The formation of this anodic film depended strongly on the experimental conditions used, thus alkaline media (pH > 9), low current density ($< 30\,\mathrm{mA\,cm^{-2}}$), high temperature ($\geqslant 50°\mathrm{C}$) and high phenol concentration ($50\,\mathrm{mmol\,dm^{-3}}$) favoured film formation.

Polarization measurements obtained in alkaline and neutral media (Fig. 2) showed that the film has good electrical conductivity. The subject of the polymer formation has been studied in a number of investigations [9, 10] and a reaction mechanism via phenate anions with the formation of a polyoxyphenylene film is proposed.

3.2. *Influence of electrolysis conditions on EOI and EOD*

The anodic oxidation of phenol was effected under different conditions and both EOI and EOD were determined using the oxygen flow rate method. (This method was chosen as in some experiments insoluble products were formed.) EOI and EOD values were practically independent of current density and temperature (Fig. 3 and Fig. 4) but depend on pH (Table 1) and phenol concentration (Fig. 5).

This process is certainly not limited by mass transfer at the anode (EOI independent of i) and the oxidation occurs by electrophilic attack of $OH^{\cdot}$ (formed by anodic oxidation of H_2O) on the aromatic nucleus; this explains the increase of EOI with pH (phenate ion is more reactive than phenol toward electrophilic attack).

The influence of phenol concentration on EOI and EOD was much more complex (Fig. 5), at low phenol concentrations ($< 20\,\mathrm{mmol\,dm^{-3}}$) EOI and EOD varied linearly with phenol concentration, contrary to high phenol concentration where EOI increased only slowly and EOD decreased with phenol concentration. This complex behaviour is due to the fact that at high phenol concentrations a thick polyoxyphenolene film

Table 1. Influence of pH on EOI and EOD values for $i = 57\,mA\,cm^{-2}$ and initial phenol concentration of $10\,mmol\,dm^{-3}$

pH	*T* (°C)	*EOI*	*EOD*
1.3–2.0	70	0.078	0.99
12–13	70	0.143	1.41
1.5–1.7	15	0.048	0.76
12–13	15	0.121	1.20

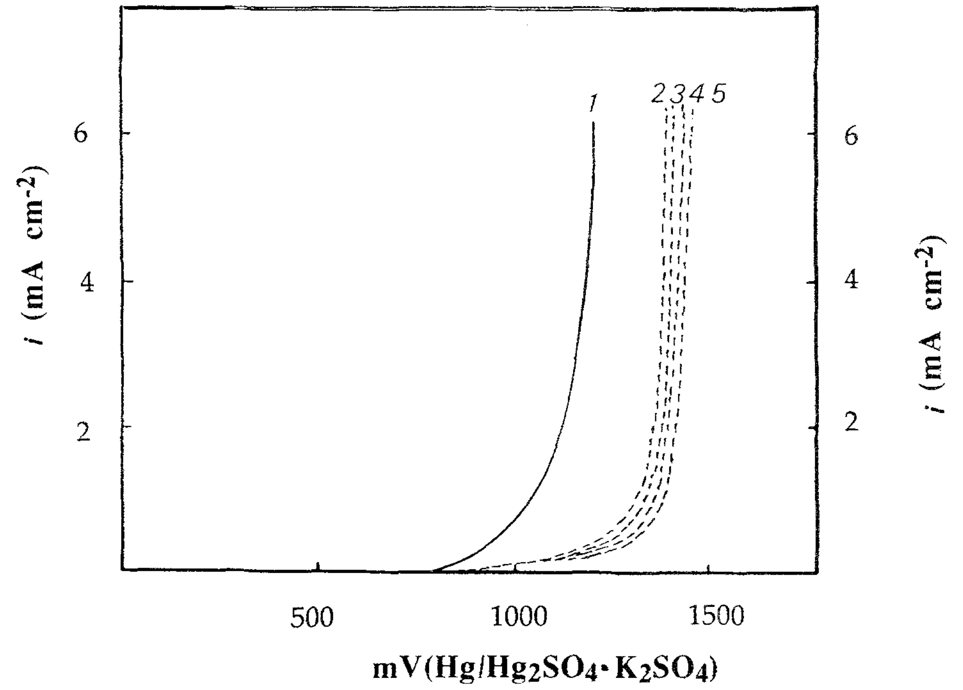

Fig. 2. Steady state polarization curves at rotating platinum electrode (T = 25°C, pH 7) (1): 50 g dm^{-3} Na_2SO_4; (2), (3), (4) and (5): 50 g dm^{-3} Na_2SO_4 + 1, 2, 4, 10 mmol dm^{-3} phenol.

is formed at the anode which modifies its electrochemical properties. Further work has to be done in this field.

3.3. *Analysis of reaction products*

The pH of electrolysis strongly influences the nature of intermediates formed; thus in electrolysis in alkaline media hydroquinone and 1-4 benzoquinone are not detected (benzoquinone itself is unstable in alkaline solution) and the conditions of film formation at the anode are favourable. The situation is quite different for electrolysis in acidic media where hydroquinone and benzoquinone are the principle oxidation intermediates and the formation of the anodic films is inhibited. It must also be noted that, in acid media, the carbon dioxide formed during the oxidation of phenol (or its intermediate product) escapes from the electrolyte; contrary to alkaline media where it reacts with alkali forming CO_3^{2-} or/and HCO_3^-.

In Fig. 6 the evolution of phenol and its oxidation products during electrolysis are given. The carbon-dioxide concentration is not a true concentration but is the number of moles of formed carbon dioxide and reported as mmole of CO_2 per litre of anolyte.

The concentration of the other non identified intermediates (curve 7 in Fig. 6d) has been calculated from the relation

$$\begin{bmatrix}\text{Non identified}\\ \text{intermediates}\end{bmatrix} = \begin{bmatrix}\text{Initial}\\ \text{Phenol}\end{bmatrix} - \begin{bmatrix}\text{Mass balance}\\ \text{identified intermediates}\end{bmatrix}$$

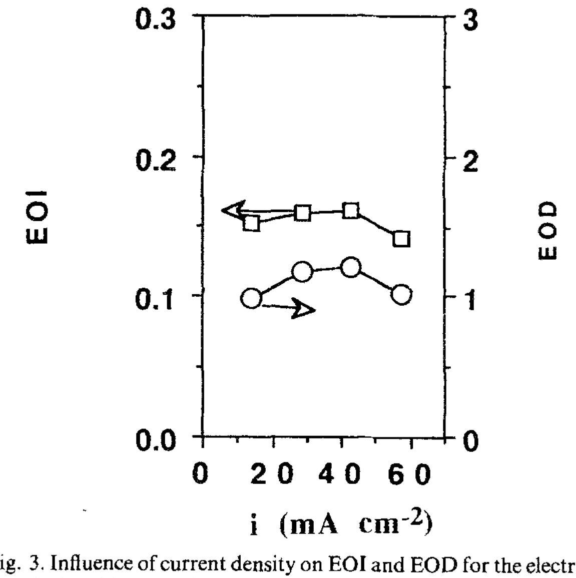

Fig. 3. Influence of current density on EOI and EOD for the electrochemical oxidation of phenol. Conditions as for Fig. 1. Initial phenol concentration: 10 mmol dm^{-3}.

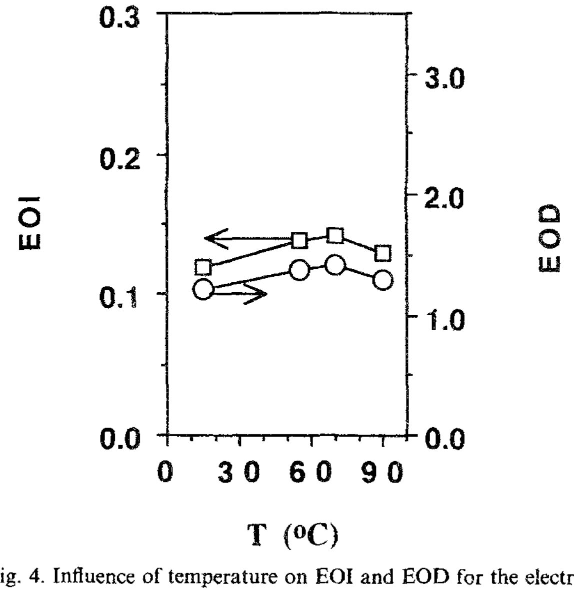

Fig. 4. Influence of temperature on EOI and EOD for the electrochemical oxidation of phenol. Conditions as for Fig. 1. Initial phenol concentration: 10 mmol dm^{-3}.

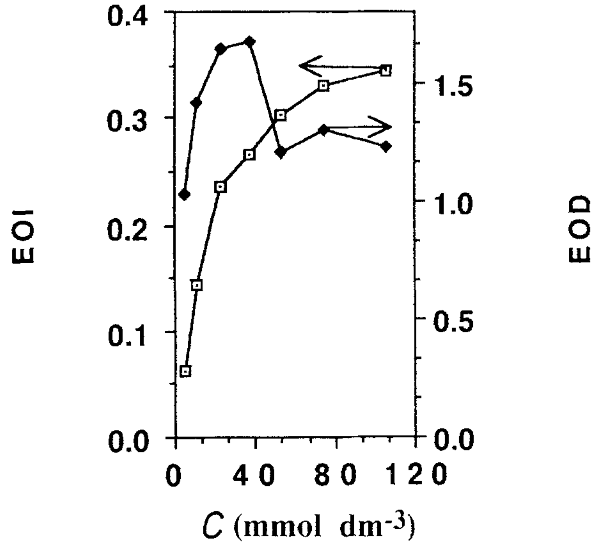

Fig. 5. Influence of the initial phenol concentration on the EOI and EOD values. Conditions as for Fig. 1.

The mass balance of the identified reaction intermediates (or product) has been calculated using the relation

$$\begin{pmatrix}\text{Phenol}\\ \text{hydroquinone}\\ \text{catecol}\\ \text{benzoquinone}\end{pmatrix} + \begin{pmatrix}\text{Maleic}\\ \text{Fumaric}\end{pmatrix} + \frac{1}{3}\,(\text{oxalic}) + \frac{1}{6}\left[(CO_2) - 2\begin{pmatrix}\text{Maleic}\\ \text{Fumaric}\end{pmatrix}\right]$$

In Fig. 7 the evolution of ICE during the electrochemical oxidation of phenol is given. Both the oxygen flow rate method and the COD method were used (see experimental part). The fact that both methods give the same result demonstrates the absence of polymeric film at the anode.

In Figs 6 and 7 three regions can be defined:

Region I (For Electrolysis time $t \leqslant 1.5$ h)
In this region the ICE is relatively high and the principal reaction is oxidation of phenol, giving a series of intermediate product.

Region II (1.5 h $< t < 7$ h)
The ICE decreases rapidly in this region and oxida-

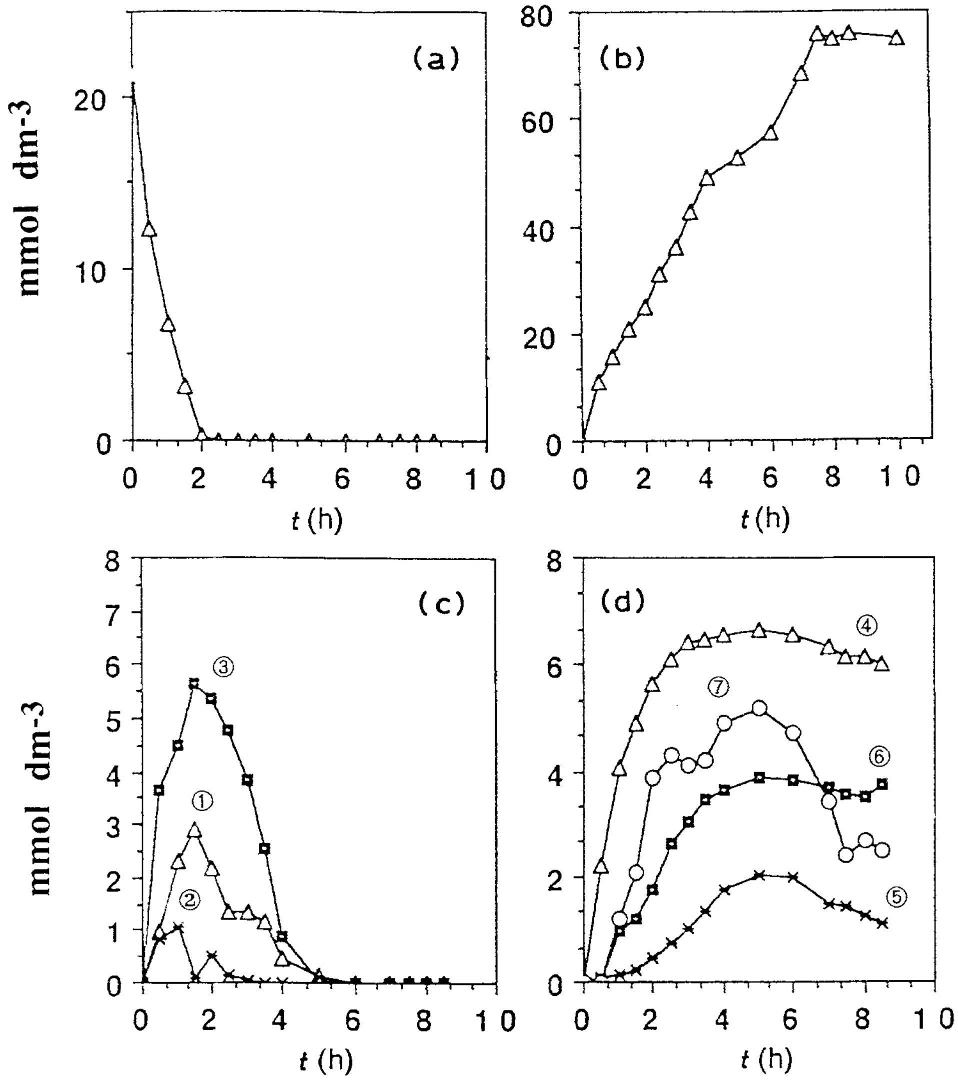

Fig. 6. Electrochemical oxidation of phenol (Conditions as for Fig. 7). (a) Evolution of phenol during electrolysis, (b) evolution of CO_2, (c) and (d) evolution of reaction products. Key: (1) Hydroquinone, (2) catecol, (3) benzoquinone, (4) maleic acid, (5) fumaric acid, (6) oxalic acid, (7) other intermediates (Δ).

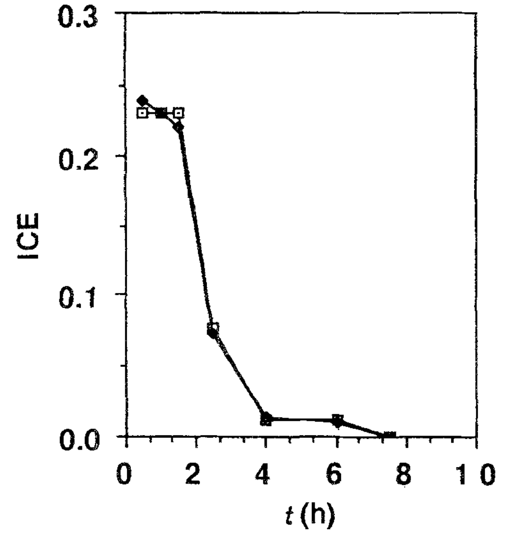

Fig. 7. Evolution of ICE during the electrochemical oxidation of phenol. (□) COD method and (◆) O_2 flow rate method. i = 50 mA cm^{-2}, T = 70°C, pH 3. Initial phenol concentration: 21 mmol dm^{-3}.

tion of intermediate product formed in region I is the main reaction.

Region III ($t > 7$ h)

The composition of the anolyte remains unchanged in this region and the ICE is almost zero; oxygen evolution due to water electrolysis is the only reaction occurring in this region.

The evolution of CO_2 production during electrolysis (Fig. 6b) gives interesting information concerning the mechanism of the electrochemical oxidation. Thus CO_2 is found in the initial stages of phenol oxidation and the amount of CO_2 produced in region I is much higher than that calculated from the amount of maleic acid formed. This acid, together with oxalic, fumaric and other intermediates, is only very slowly oxidized to CO_2 (Regions III). This shows clearly that CO_2 is formed by direct oxidation to CO_2 (electrochemical cold combustion) of phenol or/and its aromatic intermediates (hydroquinone, catecol, benzoquinone).

3.4. *Comparison of electrochemical with chemical oxidation*

For better understanding the mechanism of electrochemical oxidation of phenol a comparative study was undertaken between electrochemical and chemical oxidation of phenol with H_2O_2 (in presence of Fe^{2+} catalyst).

Oxidation with H_2O_2 in presence of Fe^{2+} catalyst (Fenton's reagent) is well known to occur by electrophilic attack of hydroxyl radicals on the organic compound [4, 11]

$$\begin{array}{lcl} Fe^{2+} + H_2O_2 & \longrightarrow & Fe^{3+} + OH^- + OH^{\cdot} \\ \phi\text{-H} + Fe^{3+} + OH^{\cdot} & \longrightarrow & \phi\text{-OH} + Fe^{2+} + H^+ \\ \hline \phi\text{-H} + H_2O_2 & \xrightarrow{Fe^{2+}/Fe^{3+}} & \phi\text{-OH} + H_2O \end{array}$$

The oxidation of phenol with Fenton's reagent has been studied by Dore [4, 11] who analyzed the oxidation products. Comparison of reaction products formed by electrochemical oxidation and with Fenton's reagent shows that the reaction products are almost the same for the chemical and electrochemical reaction. Thus both reactions probably occur by the same mechanism, i.e. electrophilic attack of hydroxyl radical on the phenol or its oxidation product. The evolution of TOC with the excess of H_2O_2 used for the oxidation of phenol initially shows a rapid decrease then stabilizes to a value corresponding to ≃30% TOC removal (Fig. 8b). This value may be compared with the 60% removal by electrochemical oxidation. (Fig. 8a) This higher removal using electrochemical oxidation is probably due to the direct oxidation of phenol or/and its intermediate at the anode.

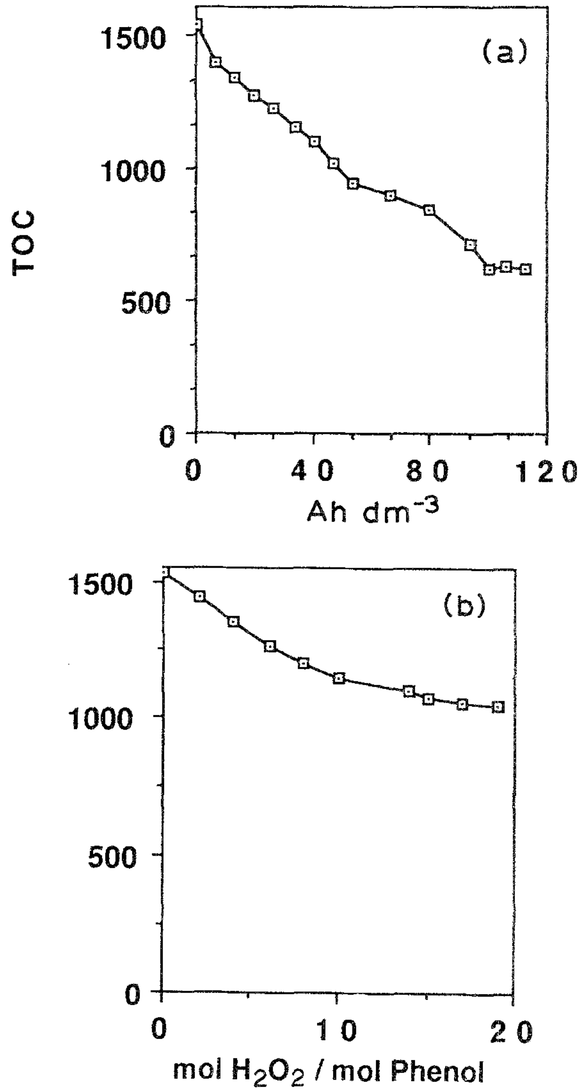

Fig. 8. Evolution of TOC during (a) the electrochemical oxidation of phenol, and (b) the chemical oxidation with H_2O_2/Fe^{2+}. Conditions as for Fig. 7.

3.5. *Mechanism of electrochemical oxidation of phenol for waste water treatment*

The mechanism of electrochemical oxidation of phenol has been studied by various workers as a means of producing hydroquinone and benzoquinone [8]. However, the reaction sequence transforming a dilute solution of phenol to maleic acid, oxalic acid

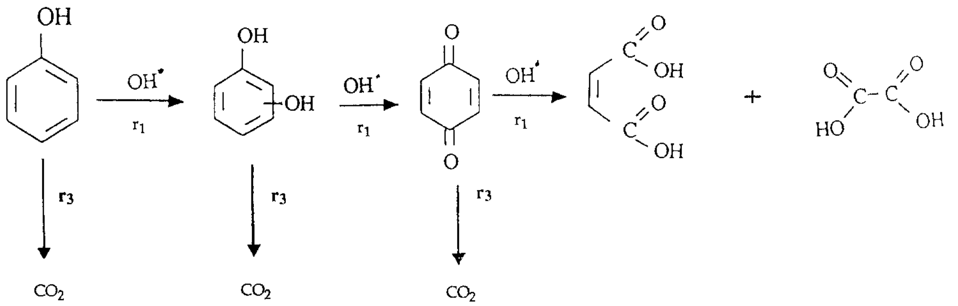

Fig. 9. Reaction sequence of the electrochemical oxidation of phenol. (r_1) Chemical reaction of adsorbed hydroxyl radicals with the organic molecule, and (r_3) electrochemical oxidation to CO_2 of adsorbed organic molecules.

and finally carbon dioxide is not well understood [6]. The experimental results obtained in this paper have shown that the reaction products obtained by electrochemical oxidation of a dilute solution of phenol are very similar to those obtained by chemical oxidation with Fenton's reagent ($H_2O_2 + Fe^{2+}$), which is known to generate hydroxyl radicals in solution having a high oxidation potential [4]. The main difference obtained between the electrochemical oxidation and chemical oxidation with Fenton's reagent is that the TOC (total organic carbon) removal is much higher in the electrochemical oxidation than in the chemical oxidation using Fenton's reagent. This high TOC removal obtained with the electrochemical method cannot be attributed to the oxidation of maleic, oxalic or fumaric acid (consecutive reaction sequence) as these acids are only very slowly further oxidized at a platinum anode (Fig. 6).

To explain these unexpected results we propose the reaction sequence given in Fig. 9 for the electrochemical oxidation of phenol.

In the first stage hydroxyl radicals are produced by electrochemical oxidation of water

$$2H_2O \longrightarrow 2OH^{\cdot} + 2H^+ + 2e^-$$

The hydroxyl radicals are adsorbed at the electrode surface and react with the organic molecule (phenol or its oxidation product) (Equation 1) or can subsequently react giving O_2 (Equation 2).

$$\text{Org} + OH^{\cdot}_{\text{ads}} \xrightarrow{r_1} \text{product} \qquad (1)$$

$$2OH^{\cdot}_{\text{ads}} \xrightarrow{r_2} H_2O + 1/2O_2 \qquad (2)$$

At the same time organics are adsorbed at the electrode surface and oxidation to carbon dioxide occurs (electrochemical cold combustion), (Equation 3).

$$(\text{Org})_{\text{ads}} \xrightarrow{r_3} CO_2 + H_2O \qquad (3)$$

The value of the relative rates r_1, r_2 and r_3 depends strongly on the type of anode material used. In a following paper [12] we demonstrate that using a doped SnO_2 anode the rate of the electrochemical cold combustion (r_3) can be significantly increased.

Conclusion

A simple method is presented which allows to estimate the average current efficiency (EOI) and the degree of oxidation of phenol for waste water treatment. Using this method we have found that at platinum anode EOI values were practically independent of current density and temperature but depend on pH and phenol concentration. Analysis of reaction intermediates has shown that the reaction occurs by two parallel pathways: chemical oxidation with electrogenerated $OH^{\cdot}$ and direct combustion of adsorbed phenol or/and its aromatic intermediates to CO_2.

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