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Anodic oxidation of phenol in the presence of NaCl for wastewater treatment

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The electrochemical oxidation of phenol in the presence of NaCl for wastewater treatment was studied at Ti/SnO_2 and Ti/IrO_2 anodes. The experimental results have shown that the presence of NaCl catalyses the anodic oxidation of phenol only at Ti/IrO_2 anodes due to the participation of electrogenerated ClO^- in the oxidation. Analysis of the oxidation products has shown that initially organochlorinated compounds are formed in the electrolyte which are further oxidized to volatile organics ($CHCl_3$).

1. Introduction

Besides inorganic materials (heavy metals, acids, bases and salts), industrial wastewaters also contain organic pollutants which have to be treated before the water can be discharged. There are several methods of treating industrial wastewater containing organic pollutants including incineration, adsorption, biological treatment and chemical or electrochemical oxidation. The choice of treatment depends on economics as well as ease of control, reliability and treatment efficiency [1].

The electrochemical method for wastewater treatment has attracted a great deal of attention recently [2–6], mainly because of the ease of control and the increased efficiencies provided by the use of compact bipolar electrochemical reactors and by the large surface area of three dimensional electrodes.

In previous work, the electrochemical oxidation of phenol for wastewater treatment was studied at Pt and DSA® anodes. Analysis of reaction intermediates and measurement of current efficiency have shown that traditional anodes (Pt, Ti/IrO_2, Ti/RuO_2, Ti/PbO_2) give relatively low current efficiencies in contrast to the Ti/SnO_2 anode, which not only gives high current efficiency, but allows quasi complete total organic carbon (TOC) elimination [7–9]. The electrochemical oxidation was compared with the chemical oxidation using H_2O_2 [10] and a mechanism for the electrochemical oxidation was proposed [11].

In the present investigation the aim was to examine the influence of NaCl (which is usually present in wastewater) on the anodic oxidation of phenol in alkaline solution for wastewater treatment.

Anodic oxidation of organics in the presence of NaCl has been studied previously [12] and it has been reported that the major problem in this process was that some of the organics become chlorinated. This can potentially increase the toxicity and the environmental hazard associated with the wastewater.

2. Chemistry of the process

The main reactions occurring during the anodic oxidation of phenol in alkaline electrolyte and in the presence of NaCl are:

Anode:
Direct oxidation of phenol (Ph) or/and its oxidation intermediate (O_x)

$$\mathrm{Ph} \xrightarrow{-z_e} \mathrm{O}_x \xrightarrow{-z'_e} \text{final product} \tag{1}$$

Hypochlorite formation

$$\mathrm{Cl^-} + 2\mathrm{OH^-} \longrightarrow \mathrm{OCl^-} + \mathrm{H_2O} + 2\mathrm{e^-} \tag{2}$$

Chlorate formation

$$6\mathrm{ClO^-} + 3\mathrm{H_2O} \longrightarrow 2\mathrm{ClO_3^-} + 4\mathrm{Cl^-} + 6\mathrm{H^+} + \tfrac{3}{2}\mathrm{O_2} + 6\mathrm{e^-} \tag{3}$$

Oxygen evolution

$$4\mathrm{OH^-} \longrightarrow 2\mathrm{H_2O} + \mathrm{O_2} + 4\mathrm{e^-} \tag{4}$$

Cathode:
Hydrogen evolution

$$2\mathrm{H_2O} + 2\mathrm{e^-} \longrightarrow \mathrm{H_2} + 2\mathrm{OH^-} \tag{5}$$

Solution and/or near the anode surface
Indirect oxidation of phenol or/and its oxidation intermediate with hypochlorite.

$$\mathrm{Ph} \xrightarrow{\mathrm{ClO^-}} \mathrm{O}_x \xrightarrow{\mathrm{ClO^-}} \text{final product} \tag{6}$$

where Reactions 3 and 4 are the loss reactions.

The rate equation for Reaction 6 is given by

$$\frac{\mathrm{d[ClO^-]}}{\mathrm{d}t} = -k_i[\mathrm{Org}]_i[\mathrm{ClO^-}] + \frac{I}{2FV} \tag{7}$$

where I is the electrolysis current, V the reaction volume, F the Faraday constant, $[\mathrm{Org}]_i$ the

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concentration of a given organic compound during electrolysis (phenol or other oxidation intermediates (benzoquinone, maleic acid ...)) and k_i the second order reaction rate constant between hypochlorite and a given organic compound during electrolysis.

During electrolysis, the composition and the concentration of organics changes (both k_i and $[\mathrm{Org}]_i$ are time dependent). Let us consider the following two main cases or conditions:

Case (*a*): when $k_i[\mathrm{Org}]_i[\mathrm{ClO}^-] \gg I/2FV$ for $0 < Q < Q^*$

The term Q^* is the electrical charge at which the concentration of the more reactive organics is very low. For any $Q > Q^*$ the concentration of hypochlorite in the electrolyte increases with time.

Case (*b*): when $k_i[\mathrm{Org}]_i[\mathrm{ClO}^-] \approx I/2FV$ for $Q^* < Q < Q^{**}$

where the term Q^{**} is the electrochemical charge at which there is no consumption of ClO^- as a function of time. After the electrical charge Q^{**} has been passed, the concentration of ClO^- increases linearly with time.

In case (a), the reaction between organics and ClO^- occurs in a reaction volume (V_R) near the anode surface given by the relation:

$$V_\mathrm{R} = S_\mathrm{a}\delta_\mathrm{r} = A_\mathrm{SP}V\delta_\mathrm{r} \tag{8}$$

where S_a is the anodic surface area, δ_r the reaction layer thickness, A_SP the specific electrode area (anode surface/electrolyte volume) and V the electrolyte volume.

We can define also the volume fraction (V^*) in which reaction takes place:

$$V^* = \frac{V_\mathrm{R}}{V} = A_\mathrm{SP}\delta_\mathrm{r} \tag{9}$$

The thickness of the reaction layer δ_r depends on the reaction rate constant k_i (δ_r decreases with increasing k_i) but in this case it is always smaller than the diffusion layer (which depends on the hydrodynamic conditions).

Considering a value of $\delta_\mathrm{r} = 10^{-5}$ m (a value close to the diffusion layer) and $A_\mathrm{SP} = 100\,\mathrm{m}^{-1}$ (for a filter-press electrochemical reactor) we obtain, from Relation 9, $V^* = 10^{-3}$ indicating that under these conditions the reaction volume is about 0.1% of the total electrolyte volume.

In case (b), the reaction between organics and ClO^- occurs far from the anode in a volume V (electrolyte volume). The concentration of ClO^- in the electrolyte in this case is given by the relation.

$$[\mathrm{ClO}^-] = \frac{I}{2FVk_i[\mathrm{Org}]_i} \tag{10}$$

3. Experimental details

3.1. *Determination of the current efficiency*

The chemical oxygen demand (COD) method [7–9] was used for the determination of the current efficiency for the anodic oxidation of phenol in the presence of NaCl. In this method, the COD was measured (COD, Hach Dr/2000) during electrolysis and the instantaneous current efficiency (ICE) was calculated using the relation

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

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

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

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

where τ is the time of electrolysis at which *ICE* is almost zero (*ICE* $\sim$ 0.01). *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.

3.2. *Electrochemical cell*

Two electrochemical cells were used, a two compartment cell (cell I) and a one compartment cell with electrolyte circulation (cell II).

Cell I: This was a two compartment cell of $150\,\mathrm{cm^3}$ capacity; the anode was a titanium sheet (of $35\,\mathrm{cm^2}$ surface) coated with $\mathrm{IrO_2}$ or $\mathrm{SnO_2}$ and the cathode was a platinum spiral ($4\,\mathrm{cm^2}$) enclosed in a 10 ml porous porcelain pot; stirring was provided by a magnetic bar.

Cell II: This was a one compartment parallel plate cell, constructed in two halves each with electrodes inlayed in polypropylene blocks. The electrode dimensions were 180 mm x 55 mm with an interelectrode gap of 5 mm, the cathode was made of titanium and the anode was a titanium plate coated with iridium dioxide ($60\,\mathrm{g\,IrO_2/m^2}$).

On one of the halves, inlet and outlet were provided for circulation of the electrolyte through the parallel plate cell using a magnetic pump (Iwaki MD 50 R). The electrolyte flow rate was measured with a magneto hydrodynamic flow meter (Deltaflux), and the temperature was maintained at 50 °C using a heat exchanger.

Details of the hydraulic equipment are given in Fig. 1.

3.3. *Preparation of the anodes*

The $\mathrm{Ti/IrO_2}$ electrode ($60\,\mathrm{g\,IrO_2/m^2}$) was prepared by the thermal decomposition technique [10, 11] which consisted of the following steps: dissolution in isopropanol of $\mathrm{H_2IrCl_6}$ (10% solution); varnish application on the pretreated titanium base; drying at

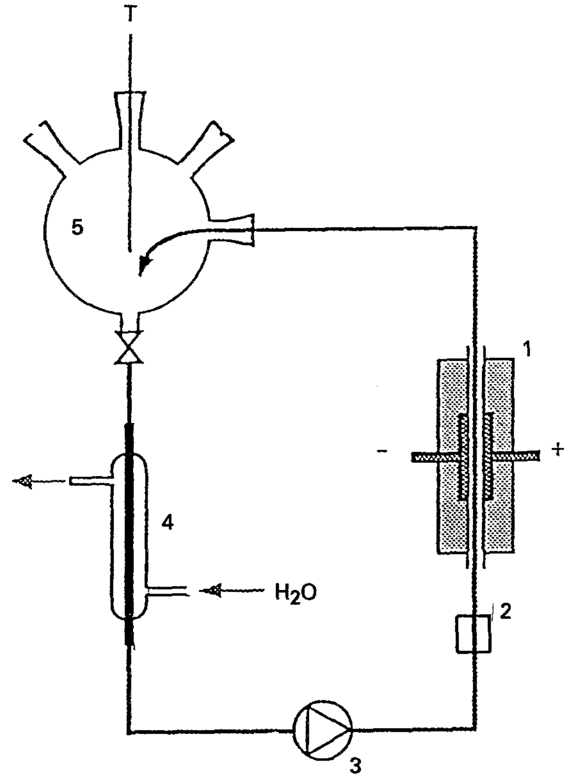

Fig. 1. Equipment used for the anodic oxidation of phenol. (1) Electrolytic cell, (2) flow meter, (3) recirculation pump, (4) heat exchanger, (5) $4\,dm^3$ reactor.

80 °C; thermal decomposition at 530 °C; cooling and repeating the above operation 10 times, finally post-heat treatment for 2 h at 530 °C. More detail concerning anode preparation and characterization are given elsewhere [13, 14].

The Ti/SnO_2 electrode doped with Sb_2O_5 was prepared by the standard spray hydrolysis method [3]. In this technique, alcoholic solution containing the coating components ($SnCl_4$ and $SbCl_3$) was sprayed on a heated (at 550 °C) titanium substrate.

3.4. *Analysis*

The disappearance of phenol during anodic oxidation was monitored by HPLC (Shimazu 8A) using a spherisorb 5 ODS-2 reversed phase column with a mobile phase of acetic acid/water 7% (v/v) at a flow rate of $0.8\,ml\,min^{-1}$ and a column temperature of 25 °C. The formation of hypochlorite was determined by iodometric titration and the organochlorinated compounds in the electrolyte and in the evolved gases were determined using standard equipment (Organochlortest APE, Burger, Bern).

4. Results and discussion

4.1. *Influence of the anode material*

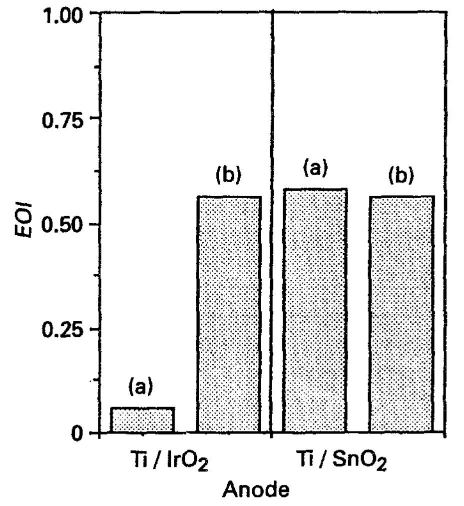

Fig. 2. Influence of the anode material on *EOI* values for the anodic oxidation of phenol. (a) $150\,g\,dm^{-3}$ Na_2SO_4; (b) $150\,g\,dm^{-3}$ $Na_2SO_4 + 85\,mM$ NaCl. Conditions: $i = 0.05\,A\,cm^{-2}$, $T = 50\,°C$, pH 12.2 and initial phenol concentration: 10 mM.

The influence of the anode material (Ti/IrO_2, Ti/SnO_2) on *EOI* values for the electrochemical oxidation of phenol in $Na_2SO_4 + NaCl$ solution (using cell I) is given in Fig. 2. The presence of NaCl in the electrolyte results in an increase of *EOI* values for the Ti/IrO_2 anode, in contrast to the Ti/SnO_2 anode for which the presence of NaCl does not influence the *EOI* value.

This specific catalytic action of NaCl on the Ti/IrO_2 anode can be explained by the mechanism of phenol oxidation at Ti/IrO_2 (selective oxidation with IrO_3) and Ti/SnO_2 (combustion with $^{\bullet}OH$ radicals) [8]. In the case of Ti/IrO_2, the direct oxidation product at the anode (hydroquinone, benzoquinone, catechol ...) are further oxidized near the anode surface by electrogenerated ClO^-, in contrast to the Ti/SnO_2 anode for which phenol is oxidized with electrogenerated $^{\bullet}OH$ radicals to carboxylic acids and CO_2; these oxidation products are stable toward ClO^- oxidation. To study this catalytic action of NaCl on the Ti/IrO_2 anodes, electrolysis of phenol was effected under different conditions using the electrochemical cell II (in which the hydrodynamic conditions were controlled).

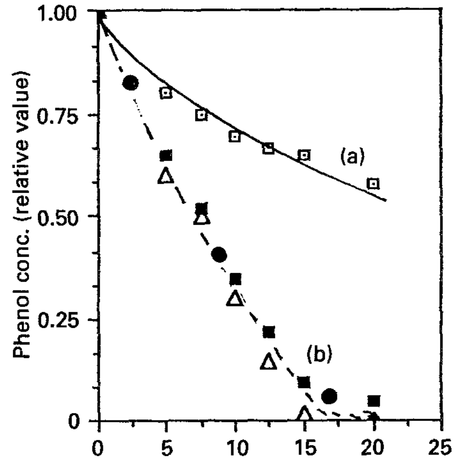

Fig. 3. Influence of NaCl concentration on the rate of phenol elimination. (a) $150\,g\,dm^{-3}$ Na_2SO_4; (b) $150\,g\,dm^{-3}$ $Na_2SO_4 + NaCl$. NaCl concentration: (△) 433, (●) 85 and (■) 17 mM. Conditions: $i = 0.1\,A\,cm^{-2}$, $T = 50\,°C$, pH 12.2 and initial phenol concentration: 10 mM.

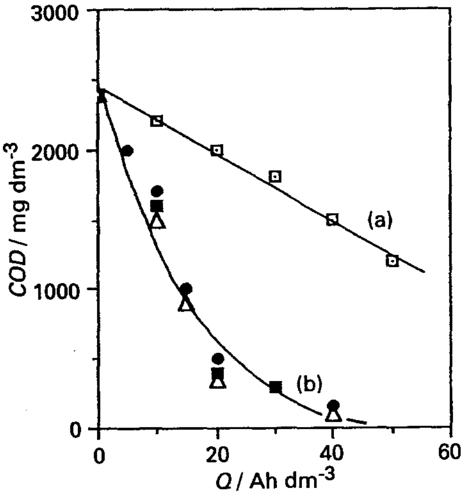

Fig. 4. Influence of NaCl concentration on the rate of chemical oxygen demand (COD) elimination. (a) 150 g dm^{-3} Na_2SO_4; (b) 150 g dm^{-3} Na_2SO_4 + NaCl. NaCl concentration: (△) 433, (●) 85 and (■) 17 mM. Conditions: as in Fig. 3.

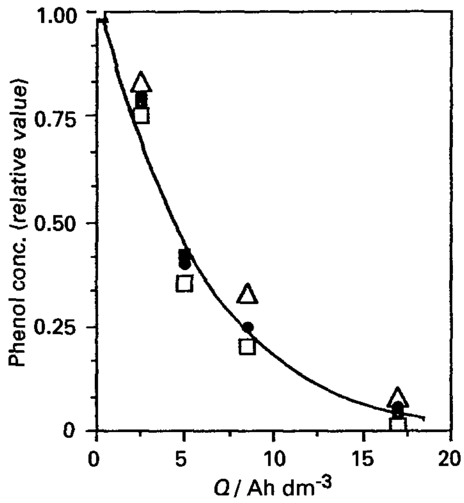

Fig. 6. Influence of current density on the rate of phenol elimination by anodic oxidation in presence of NaCl (85 mM). Key: (△) 0.1, (●) 0.18, (□) 0.2 and (■) 0.3 A cm^{-2}. Conditions: as in Fig. 5.

4.2. *Influence of NaCl concentration*

Some tests were run at different NaCl concentrations using a Ti/IrO_2 anode. Other conditions were kept constant; initial phenol concentration (10 mM), current density (0.1 A cm^{-2}), temperature (50 °C), pH during electrolysis (12.2 ± 0.3) and hydrodynamic conditions (electrolyte velocity: 0.55 m s^{-1}). The results reported in Figs 3 and 4 show that the enhancement in the rate of phenol and COD elimination is independent of NaCl concentration and occurs even in the presence of catalytic amounts of NaCl (17 mM).

4.3. *Influence of current density*

The current density was changed within the technically reasonable limits of 0.05 to 0.3 A cm^{-2}. As the working temperature has only a small effect on EOI values in the temperature range 20 to 50 °C, all experiments were performed at 50 °C. Figure 5 shows the influence of current density on EOI values for the anodic oxidation of phenol in the presence of NaCl. Increasing current density results in a slow decrease in EOI values.

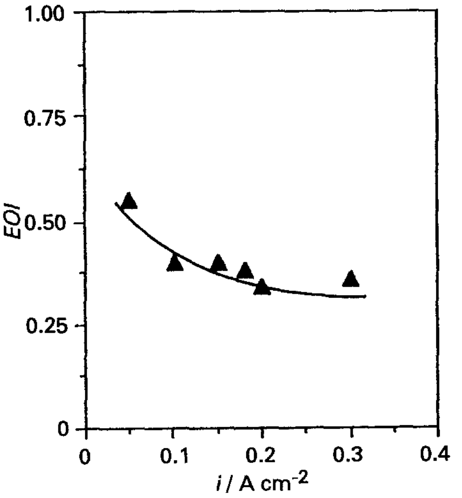

Fig. 5. Influence of current density on EOI values for the anodic oxidation of phenol in presence of NaCl (85 mM). Conditions: $T = 50$ °C, pH 12.2 and initial phenol concentration: 10 mM.

The influence of current density on the rate of phenol elimination is given in Fig. 6. This figure shows that the rate of phenol elimination is independent of current density and depends only on the specific electrical charge passed (Q). Thus, almost complete phenol elimination can be achieved after the passage of an electrical charge, Q^*, of 17–20 A h dm^{-3}.

Concerning the evolution of ClO^- concentration in the electrolyte during electrolysis, Fig. 7 shows that for any electrical charge $Q < Q^*$ the concentration of ClO^- in the electrolyte is virtually zero; this is due to the fact that phenol reacts very rapidly with the electrogenerated ClO^- in a reaction volume near the anode surface (case (a), Section 2). For higher electrical charges, $Q > Q^*$, the ClO^- initially increases slowly with time, then a rapid increase of ClO^- is observed (for $Q > Q^{**}$). The slow increase of ClO^- in the electrolyte indicates that oxidation of organics with ClO^- occurs far from the anode in the

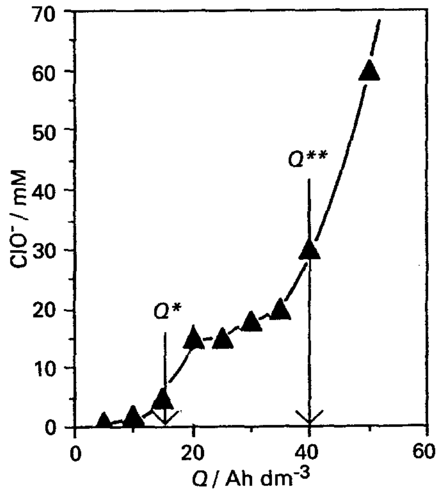

Fig. 7. Evolution of ClO^- concentration in the electrolyte during anodic oxidation of phenol in presence of NaCl (85 mM), $i = 0.18$ A cm^{-2}. Conditions as in Fig. 5.

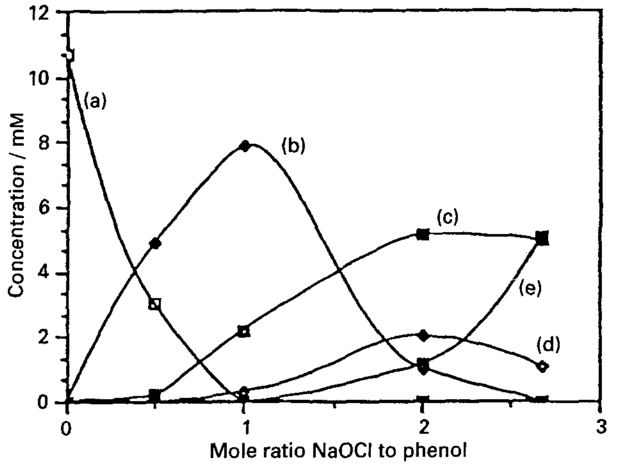

Fig. 8. Chemical oxidation of phenol with NaOCl. Reaction products as a function of the molar ratio R = NaOCl/phenol. (a) phenol, (b) 2-chlorophenol, (c) 4-chlorophenol, (d) 2,4 dichlorophenol and (e) 2,4,6 trichlorophenol. Conditions: $T = 50\,^{\circ}C$, pH 12.2 and initial phenol concentration: 10 mM.

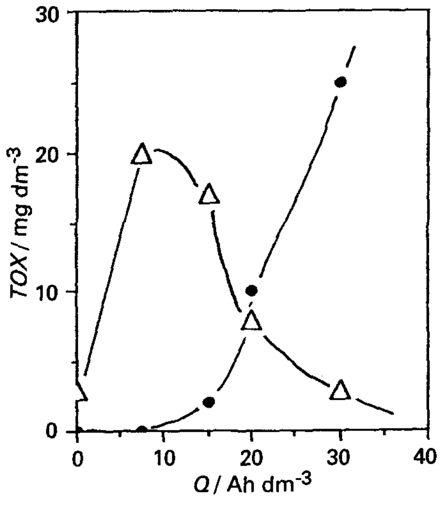

Fig. 9. Evolution of the organochlorinated compounds (*TOX*) during anodic oxidation of phenol in presence of NaCl (85 mM). (△) *TOX* in the electrolyte; (●) *TOX* in the evolved gases. Conditions as in Fig. 7.

bulk of the electrolyte (case (b), Section 2) and the rapid increase of ClO^- (for $Q > Q^{**}$) indicates that the rate of oxidation of organics present in the electrolyte is almost zero.

This model was confirmed by cyclic voltammetry measurements which showed that the reduction peak of ClO^- observed in the reverse scan of the cyclic voltammogram obtained in 1 M NaCl solution completely disappeared in the presence of phenol (due to a fast reaction between phenol and ClO^-) and remains almost unchanged in the presence of oxalic acid (with a very slow reaction between carboxylic acids and ClO^-).

4.4. *Comparison between electrochemical and chemical oxidation*

For better understanding of the mechanism of the electrochemical oxidation of phenol in the presence of NaCl, a comparative study between electrochemical and chemical oxidation of phenol with NaOCl was undertaken.

For the chemical oxidation of phenol with NaOCl, different molar ratios, R = NaOCl/phenol, were used and for each molar ratio, R, the composition of the reaction medium was analyzed after completion of the reaction. The results (Fig. 8) showed that monochlorophenols (2-chlorophenol and 4-chlorophenol) are the principal reaction products for $R \leqslant 1.5$, and for high R values ($R \geqslant 2$) trichlorophenol is also formed to a considerable extent.

The situation was completely different for the electrochemical oxidation of phenol in the presence of NaCl; here, chlorinated phenols were not detected during electrolysis.

The absence of chlorinated phenols during electrochemical oxidation of phenol in the presence of NaCl can be explained by the fact that the reaction between phenol and ClO^- occurs in a reaction volume near the anode surface; the chlorinated phenols formed in this reaction volume are further oxidized (with ClO^- or/and at the anode) to aliphatic acids.

4.5. *Analysis of organochlorinated compounds*

The total organochlorinated compounds (*TOX*) were measured in the electrolyte and in the evolved gases during electrolysis.

The results show that *TOX* (mg dm^{-3}) in the electrolyte first increases, reaching a maximum, and then decreases to a very low value. In contrast to the *TOX* in the evolved gases (calculated as *TOX* in the electrolyte) which is initially zero and then increases rapidly (Fig. 9), analysis of the organochlorinated compounds by gas chromatography showed that chloroform is the main organic compound present in the evolved gases during electrolysis.

On the basis of these results, a reaction scheme is proposed in which phenol is first oxidized to nonvolatile organochlorinated compounds (chlorinated aliphatic acids) which are further oxidized to volatile chlorinated compounds ($CHCl_3$).

5. Conclusions

The anodic oxidation of phenol in the presence of NaCl, for wastewater treatment, has been investigated under different experimental conditions; the results show that:

(i) The presence of NaCl in the electrolyte catalyses the oxidation of phenol only at the Ti/IrO_2 anode (their is no catalytic action at the Ti/SnO_2 anode).

(ii) The catalytic action of NaCl has been attributed to the participation of electrogenerated ClO^- in the oxidation of organics (phenol and its oxidation products) near to the anode or/and in the bulk of the electrolyte.

(iii) Analysis of the reaction products during electrolysis has shown that chlorinated phenols are absent and the chlorinated aliphatic acids formed are further oxidized to $CHCl_3$ which escapes with the evolved gases during electrolysis.

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