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# Electrochemical polymerisation of phenol in aqueous solution on a Ta/PbO<sub>2</sub> anode

Noureddine Belhadj Tahar · Ridha Abdelhédi ·  
André Savall

**Abstract** This paper deals with the treatment of aqueous phenol solutions using an electrochemical technique. Phenol can be partly eliminated from aqueous solution by electrochemically initiated polymerisation. Galvanostatic electrolyses of phenol solutions at concentration up to 0.1 mol dm<sup>-3</sup> were carried out on a Ta/PbO<sub>2</sub> anode. The polymers formed are insoluble in acidic medium but soluble in alkaline. These polymers were filtered and then dissolved in aqueous solution of sodium hydroxide (1 mol dm<sup>-3</sup>). The polymers formed were quantified by total organic carbon (TOC) measurement. It was found that the conversion of phenol into polymers increases as a function of initial concentration, anodic current density, temperature, and solution pH. The percentage of phenol polymerised can reach 15%.

**Keywords** Waste water treatments · Electrochemical polymerisation · Phenol · PbO<sub>2</sub> anode

## 1 Introduction

Industrial effluents containing toxic and/or biorefractory compounds cause serious environmental problems owing to the lack of a general method of treatment. Furthermore, legislation has increased the acceptable concentration

limits for effluents. Among aqueous industrial effluents, those containing organic pollutants are problematic due to the high activation energy barrier for chemical oxidation. For organic pollutants ranging between 2 and 20 g dm<sup>-3</sup>, electrochemical oxidation can be used as a method of treatment either by direct electron or by atomic oxygen transfer [1–6]. Transfer of oxygen atoms is the fundamental process in the course of mineralization of organics. It is now assumed that the step preceding the transfer of an oxygen atom in the oxidation mechanism in aqueous solution is the discharge of a water molecule, involving only one electron, leading to a hydroxyl radical [1, 5–13]:



Then, hydroxyl radicals react, by electrophilic attack on the organic compound diffusing to the electrode surface.

The electrochemical reactivity of organic compounds depends on the anode material used. Anodic oxidation reactions by oxygen transfer are characterised by low rate constants when carried out on electrode materials such as Pt or Au. This relative slowness of the oxygen atom transfer is due to the competing reaction forming molecular oxygen [1, 5–11]. Thus, materials having high oxygen overpotential (SnO<sub>2</sub>, PbO<sub>2</sub>, boron-doped diamond) should be used as anode to degrade organic compounds in aqueous solution. Oxidations of organics on these anode materials, in the potential region of water decomposition, are non-selective; the anodic oxidation can go to carbon dioxide and water via successive oxidation steps. In the case of phenol more than 90% of the starting material can be converted into CO<sub>2</sub> on these anode materials [5, 10, 14–17]. However, the current efficiency decreases during electrolysis as phenol and its oxidation products are oxidised; current efficiency values less than 30% at the end of the treatment penalize the process from the energy point of view [5, 14, 18, 19].

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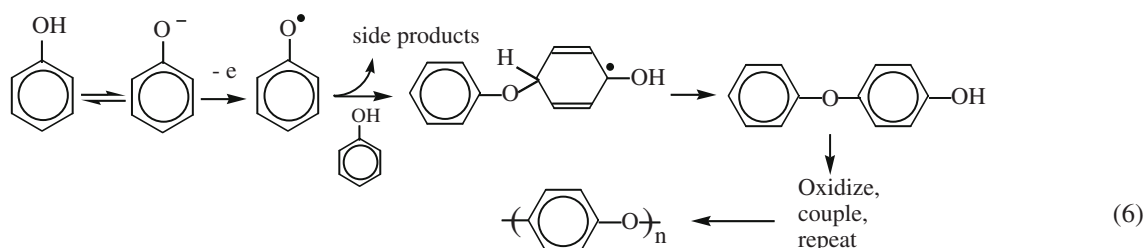
N. Belhadj Tahar · R. Abdelhédi  
UR Electrochimie et Environnement, Ecole Nationale  
d'Ingénieurs de Sfax, BPW, 3038 Sfax, Tunisia

A. Savall (✉)  
Laboratoire de Génie Chimique, CNRS, Université Paul  
Sabatier, 118, Route de Narbonne, 31062 Toulouse cedex,  
France  
e-mail: savall@chimie.ups-tlse.fr

Therefore, techniques reducing the energy consumption and/or the concentration of the toxic compounds are of interest.

Cyclic voltammetry and chronoamperometry measurements on phenolic compounds have shown that electrode materials such as Pt, Au, C are rapidly deactivated under anodic polarisation in the region of water stability, even at low concentration [14, 19–23]. It has also been reported that oxidation of phenols achieved by direct electron transfer on a BDD anode in the potential gap of water stability gives rise to rapid anode deactivation [14–17, 19–25]. This has been ascribed to electrode fouling by a polymeric film. These studies have shown that the electrode surface

phenoxonium cations can react to form polymeric products in acidic medium while phenoxy radicals initiate polymerisation in alkaline medium. Phenoxonium cations and phenoxy radicals generated at the anode are electrophiles capable of reacting with either the starting phenol molecule or another radical by C–C and/or C–O coupling, giving dimers [30]. An example of reaction path is given in Eq. 6: the electrogenerated phenoxy radical reacts with a phenol molecule which yields a predominantly *para*-linked dimer radical; subsequent reactions produce neutral dimers, oligomers, and finally polyphenol films and insoluble polymers [29–32]:



can be reactivated by anodic polarisation in the potential range of water decomposition; it was suggested that oxygen evolution in addition to oxidation by OH radicals avoids electrode fouling by polymeric products.

Vermillion and Pearl [26] have proposed that the first stage of the anodic oxidation of phenol on PbO<sub>2</sub> occurs according to two different mechanisms depending on the pH. They have suggested that, at pH values below the pK<sub>a</sub> (9.89), the bielectronic discharge of phenol molecules leads to the formation of phenoxonium cations:



By hydrolysis, the phenoxonium cation gives catechol and hydroquinone:



In basic solution (pH > 9.89), the predominant form is the phenate anion which undergoes a one-electron anodic oxidation leading to the formation of a phenoxy radical:



The phenoxy radical then, undergoes a second electron transfer leading to the phenoxonium cation which gives catechol and hydroquinone by hydrolysis:



Several authors have suggested that polymers are formed during anodic oxidation of phenolic compounds [14–16, 19–23, 25–29]. According to Vermillion and Pearl [26],

The initial activity of the anode can be restored by anodic polarisation in the potential region of water discharge because the hydroxyl radicals produced at these high overvoltages oxidize the polymeric film on the surface. In addition, the parallel oxygen evolution:



can mechanically break the polymer film.

The formation of polymers implies a consumption of less than one electron per monomer molecule (Eq. 6) while complete combustion of phenol involves a higher number of electrons exchanged (i.e., 28 electrons per molecule for the complete degradation into water and carbon dioxide). Thus, a possibility for improving the treatment of polluted wastewater is opened up by optimizing the polymer formation as well as its separation. However, accurate data on the efficiency of phenol conversion into polymers by electrochemical oxidation of aqueous solutions of phenol are sparse.

In this work we have investigated the effect of operating parameters on the efficiency of phenol elimination from aqueous solution by electrochemical polymerisation on a Ta/PbO<sub>2</sub> anode. By this treatment a part of the phenol can be eliminated from the solution in the form of insoluble polymers. In order to characterize qualitatively the proportion of phenol transformed into insoluble polymers, phenol solutions have been electrolysed under various conditions of initial concentration, pH, anodic current density, and temperature. Measurements of the total organic carbon were used to quantify the phenol transformed into insoluble polymers.

## 2 Experimental details

### 2.1 Preparation of Ta/PbO<sub>2</sub>

#### 2.1.1 Surface treatment

The tantalum plates (70 mm × 10 mm × 1 mm) were first roughened to increase the adhesion of the PbO<sub>2</sub> deposit. The surface of the tantalum plates was subjected to mechanical abrasion by sand blasting with grains of 0.3 mm average diameter at a pressure of 5 bar (Brasfanta 037/320 Bremor, Switzerland). The tantalum substrate was then cleaned using ultrasound for 10 min in order to remove any sand particles lodged on its surface. The average loss in mass per unit area due to the sand blasting was  $0.55 \pm 0.12$  mg cm<sup>-2</sup>. The tantalum substrate was then chemically stripped for 30 s in 40% hydrofluoric acid at room temperature. This chemical treatment dissolves the layer of tantalum oxide, which is formed spontaneously with oxygen in the air. The substrate was then washed with distilled water. The loss in mass per unit area due to this chemical stripping was  $0.18 \pm 0.06$  mg cm<sup>-2</sup>.

#### 2.1.2 Electrochemical deposition of PbO<sub>2</sub>

The lead dioxide was galvanostatically deposited on the tantalum substrate using a two compartment cell ( $V = 200$  cm<sup>3</sup>) thermoregulated at 65 °C. The anolyte was an aqueous solution containing only lead nitrate at a concentration of 1 mole dm<sup>-3</sup>; the cathodic compartment contained a solution of sulphuric acid at 1 mole dm<sup>-3</sup>. A porous ceramic separator (Norton, RA 84) was used to prevent short-circuits by lead dendrites formed on the cathode. The deposition of PbO<sub>2</sub> was carried out for 2.5 h using an anodic current density of 20 mA cm<sup>-2</sup>. The average mass of PbO<sub>2</sub> deposited per unit area was  $0.23 \pm 0.04$  mg cm<sup>-2</sup>. The deposit obtained was mat grey, adherent, regular, and uniform.

### 2.2 Electrolyses

Electrolyses of aqueous phenol solutions ( $V_0 = 0.14$  dm<sup>3</sup>) were carried out, at constant temperature, using magnetic stirring, in a two-compartment cylindrical reactor. The pH of the solution was adjusted to a constant value, before and during electrolyses, by adding concentrated solutions of either sulphuric acid or sodium hydroxide (5 mol dm<sup>-3</sup>). The anode was made up of four identical plates symmetrically arranged around the cathode; the side of each plate not facing the cathode was covered with a protective film (transparent polyethylene type, Scotch TM 480, 3M). The working area of each plate was 5 cm<sup>2</sup>. The cathode was a graphite rod ( $\phi = 1$  cm;  $L = 6$  cm) placed in a porous

**Table 1** Influence of the anodic current density on the proportion of phenol transformed into insoluble polymers, CO<sub>2</sub> and intermediary products. [PhOH]<sub>0</sub> = 105 mmol dm<sup>-3</sup>, pH = 2 and T = 65 °C. Q is the charge passed during the electrolysis

$J$ (mA cm <sup>-2</sup> )	$Q$ (Ah dm <sup>-3</sup> )	$r(\text{polymers})$ (%)	$r(\text{CO}_2)$ (%)	$r(\text{intermediary products})$ (%)
100	70	2	72	26
150	60	5	65	30
200	60	9	56	35

**Table 2** Influence of the initial phenol concentration on the proportion of phenol transformed into insoluble polymers, CO<sub>2</sub> and intermediary products.  $J = 200$  mA cm<sup>-2</sup>, pH = 2 and T = 65 °C

[PhOH] <sub>0</sub> (mmol dm <sup>-3</sup> )	$Q$ (Ah dm <sup>-3</sup> )	$r(\text{polymers})$ (%)	$r(\text{CO}_2)$ (%)	$r(\text{intermediary products})$ (%)
42	30	4	30	66
63	40	6	35	59
105	60	9	56	35

**Table 3** Influence of the pH on the proportion of phenol transformed into insoluble polymers, CO<sub>2</sub> and intermediary products. [PhOH]<sub>0</sub> = 105 mmol dm<sup>-3</sup>,  $J = 200$  mA cm<sup>-2</sup> and T = 65 °C

pH	$Q$ (Ah dm <sup>-3</sup> )	$r(\text{polymers})$ (%)	$r(\text{CO}_2)$ (%)	$r(\text{intermediary products})$ (%)
2	60	9	56	35
13	60	15	47	38

**Table 4** Influence of the temperature on the proportion of phenol transformed into insoluble polymers, CO<sub>2</sub> and intermediary products. [PhOH]<sub>0</sub> = 105 mmol dm<sup>-3</sup>,  $J = 200$  mA cm<sup>-2</sup> and pH = 13

T (°C)	$Q$ (Ah dm <sup>-3</sup> )	$r(\text{polymers})$ (%)	$r(\text{CO}_2)$ (%)	$r(\text{intermediary products})$ (%)
25	140	3	78	19
35	115	4	77	19
50	80	13	59	28
65	60	15	47	38

ceramic cylinder (Norton, RA 84) containing sulphuric acid at 1 mol dm<sup>-3</sup>. The phenol solutions were electrolysed galvanostatically.

All electrolyses were carried out with anodes freshly prepared and were continued until the complete disappearance of the starting phenol. This electrolysis time defines the electrical charge values Q shown in Tables 1, 2, 3, 4; these charge values depend on the operating conditions.

## 2.3 Analyses

### 2.3.1 High-pressure liquid chromatography

Analyses of phenol were carried out using a Hewlett Packard 1090 HPLC apparatus. Phenol and its oxidation products were separated thanks to a Hamilton PRP X 300 column and quantified by measurement of optical density at 220 nm by using a diode array detector. The mobile phase was a binary mixture of methanol with a 0.05 mol dm<sup>-3</sup> sulphuric acid solution. The volume ratio of methanol varied linearly with time as follows: from 2 to 25% for the first 10 min then from 25 to 40% up to 20 min and finally from 40 to 60% up to 40 min. The mobile phase flow rate was fixed at 1.3 ml min<sup>-1</sup>.

### 2.3.2 Total organic carbon

TOC was measured using a Model 700 TOC Analyser (purchased from O. I. Analytical). Before analysis, each sample was diluted to bring its concentration into the working range of the apparatus.

### 2.3.3 Determination of the proportion of phenol transformed into insoluble polymers

During electrolyses of acidic phenol solutions, polymers were formed and precipitated in the form of solid, black particles. Polymers formed during electrolyses conducted in basic medium were soluble; at the end of the electrolysis they were precipitated by adding concentrated sulphuric acid. Polymer particles were recovered on a filter (Millipore type GV; 0.22 μm) and then dissolved in a sodium hydroxide solution at 1 mol dm<sup>-3</sup> ( $V = 1 \text{ dm}^3$ ).

The proportions of phenol transformed respectively into insoluble polymers, carbon dioxide, and intermediary products are defined as follows:

$$r(\text{polymers}) = \frac{[\text{TOC}]_2 \times V}{[\text{TOC}]_0 \times V_0} \times 100 \quad (8)$$

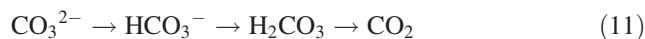
$$r(\text{CO}_2) = \frac{[\text{TOC}]_0 - [\text{TOC}]_1}{[\text{TOC}]_0} \times 100 - r(\text{polymers}) \quad (9)$$

$$r(\text{intermediary products}) = 100 - r(\text{polymers}) - r(\text{CO}_2) \quad (10)$$

where  $[\text{TOC}]_0$  is the total organic carbon of the aqueous phenol solution before electrolysis (mg dm<sup>-3</sup>),  $[\text{TOC}]_1$  is the total organic carbon of the electrolysed solution after recovery of polymers by filtration (mg dm<sup>-3</sup>),  $[\text{TOC}]_2$  is the total organic carbon of the aqueous sodium hydroxide solution in which the polymers were dissolved (mg dm<sup>-3</sup>),  $V_0$  and  $V$  were respectively the volumes of the electrolysed solution and of the sodium hydroxide solution in which

polymers were dissolved (dm<sup>3</sup>). Intermediary products in Eq. 10 designate all the oxidation products other than insoluble polymers and CO<sub>2</sub>.

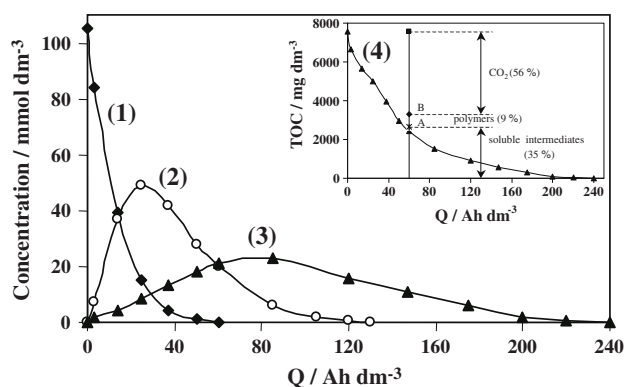
Addition of concentrated sulphuric acid to the electrolysed solution was accompanied by a carbon dioxide evolution, which was particularly strong for electrolyses performed under alkaline conditions, and which can be interpreted by considering the following steps:



## 3 Results and discussion

### 3.1 Oxidation products of phenol

As shown in Fig. 1, the main intermediary products formed during the electrochemical oxidation of phenol in aqueous solution at pH = 2 on a Ta/PbO<sub>2</sub> anode are 1,4-benzoquinone (curve 2) and maleic acid (curve 3). The other soluble intermediary products (not shown in Fig. 1), present in the solution at very low concentration (less than 0.5 mmol dm<sup>-3</sup>) are hydroquinone, catechol and fumaric, glyoxalic and formic acids. Curve 4 of Fig. 1 (inset) shows the TOC variation calculated from the compounds quantified by HPLC. Points A and B (Inset) represent the experimental TOC values measured at a charge  $Q$  equal to 60 Ah dm<sup>-3</sup> for which the phenol is completely oxidized. The TOC value at point A is slightly higher than that given by curve (4) since the latter is only relative to the soluble species quantified by HPLC; the difference corresponds to the non-identified soluble oxidation intermediates. The TOC value at point B corresponds to the sum of soluble intermediates and insoluble polymers. The charge  $Q$



**Fig. 1** Variation of the concentration of phenol, 1,4-benzoquinone, maleic acid and total organic carbon during the electrolysis of an aqueous phenol solution ( $V = 0.14 \text{ dm}^3$ ) on a Ta/PbO<sub>2</sub> anode ( $S = 20 \text{ cm}^2$ ). Supporting electrolyte: H<sub>2</sub>SO<sub>4</sub> (pH = 2), initial phenol concentration: 105 mmol dm<sup>-3</sup>, applied anodic current density: 200 mA cm<sup>-2</sup>,  $T = 65 \text{ }^\circ\text{C}$ . (1) phenol, (2) 1,4-benzoquinone, (3) maleic acid. Inset: (4) TOC calculated from the compounds quantified by HPLC

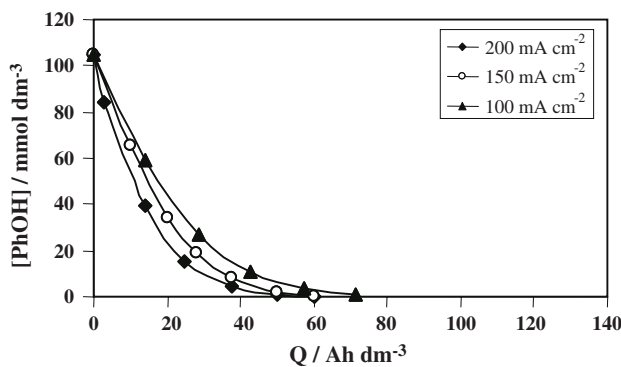
measured at the almost complete disappearance of the phenol depends on the electrolysis operating conditions (initial concentration of phenol, anodic current density, and temperature) [3, 5, 22]. It is assumed that polymer is formed mainly at the beginning of the electrolysis when the phenol concentration has its highest value (Eq. 6). However, considering that polymerization can occur as long as phenol is present in solution, all experiments performed in this work were continued up to the complete disappearance of the initial phenol; values of the charge  $Q$ , measured at this point, for different experimental conditions are given in Tables 1, 2, 3, 4.

### 3.2 Influence of the anodic current density

Figure 2 shows the decrease in phenol concentration as a function of the charge  $Q$  injected during electrolyses performed on Ta/PbO<sub>2</sub> for three values of the anodic current density.

Table 1 shows that, in acidic medium, the proportion of phenol transformed into insoluble polymers increases from 2 to 9% when the anodic current density increases from 100 to 200 mA cm<sup>-2</sup> whereas, the proportion of phenol converted into CO<sub>2</sub> decreases slightly (from 72 to 56%). At the same time the yield in intermediary products increases to some extent (26 to 35%).

Under the experimental conditions used in this study, phenol oxidation is a process limited by diffusion-convection [5]. It has been shown that an increase in the anodic current density amplifies the concurrent oxygen evolution (Reaction 7) [5]. Now, when gas evolution occurs at the electrode surface, the mass transfer coefficient can be significantly raised due to formation and detachment of bubbles [33]. So, increasing the anodic current density increases the diffusion-convection flux of phenol molecules towards the electrode surface. Precisely, Fig. 2 shows that the rate of



**Fig. 2** Variation of the concentration of phenol during the electrolysis of an aqueous phenol solution ( $V = 0.14 \text{ dm}^3$ ) performed on a Ta/PbO<sub>2</sub> anode ( $S = 20 \text{ cm}^2$ ) for three applied anodic current densities. Supporting electrolyte: H<sub>2</sub>SO<sub>4</sub> (pH = 2), initial phenol concentration: 105 mmol dm<sup>-3</sup>,  $T = 65 \text{ }^\circ\text{C}$

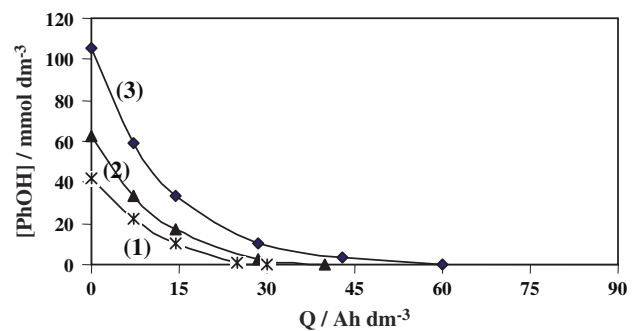
phenol oxidation increases as the anodic current density increases; nevertheless, the different values of the charge  $Q$  are not significantly affected (Table 2). The polymer yield increase may be explained by considering the competitive reactions: i.e., polymer formation (Reaction 6) and hydroquinone and catechol production (Reaction 3). By assuming that Reaction 3 is a chemical limiting step, it results that an increase of the diffusion flux of phenol increases the rate of electrochemical polymerisation (Reaction 6) while rates of production of hydroquinone and catechol are not clearly affected.

Table 1 shows that values of  $r(\text{CO}_2)\%$  are relatively significant proving that polymer formation occurs mainly at the beginning of the electrolysis when phenol concentration is still high (Reaction 6). Furthermore, when current intensity is increased, polymer formation is favoured to the detriment of phenol degradation into CO<sub>2</sub>. This may be explained as follows: at the higher current densities, the strong oxygen evolution induces the thin polymer film to come unstuck and to scatter as small particles throughout the solution; these conditions are not suitable for a strong conversion of polymeric phenol into CO<sub>2</sub>.

### 3.3 Influence of the initial phenol concentration

Electrolyses were carried out at pH = 2 on Ta/PbO<sub>2</sub> using an applied anodic current density of 200 mA cm<sup>-2</sup> for initial phenol concentrations of 42, 63, and 105 mmol dm<sup>-3</sup>. Figure 3 shows the variation of phenol concentration as a function of the charge  $Q$  for these electrolyses; values of the charge  $Q$  corresponding to the complete disappearance of phenol molecules from the solution are equal to 30, 40, and 60 Ah dm<sup>-3</sup> respectively for initial phenol concentrations of 42, 63, and 105 mmol dm<sup>-3</sup>.

Table 2 shows that an increase in the initial phenol concentration favours polymer formation as well as mineralization. This result is understandable if we consider



**Fig. 3** Variation of the concentration of phenol during the electrolysis of aqueous phenol solutions ( $V = 0.14 \text{ dm}^3$ ) performed on a Ta/PbO<sub>2</sub> anode ( $S = 20 \text{ cm}^2$ ). Supporting electrolyte: H<sub>2</sub>SO<sub>4</sub> (pH = 2), initial phenol concentration: (1) 42, (2) 63, and (3) 105 mmol dm<sup>-3</sup>. Applied anodic current density: 200 mA cm<sup>-2</sup>,  $T = 65 \text{ }^\circ\text{C}$

again that the initial step in phenol oxidation into the phenoxonium ion is limited by mass transport. At a constant anodic current density, an increase in the initial phenol concentration causes an increase in its diffusion flux, which speeds up generation of the phenoxonium ion. As the phenol flux and phenoxonium ion flux at the electrode surface both increase at the same time, this can explain the increase in the phenol converted into insoluble polymers (Reaction 6).

The increase in phenol concentration produces a higher surface concentration of oxidation intermediates that adsorb onto the electrode. For electrolyses carried out at constant current, hydroxyl radicals are generated at steady rate; however, given that hydroxyl radicals have non-selective reactivity regarding the oxidation of organic compounds, it is the adsorbed intermediates that are oxidised rather than new phenol molecules. On the contrary, at low concentration and high anodic current density, as soon as phenol molecules reach the electrode surface, they are rapidly mineralized rather than being converted into polymer [5].

### 3.4 Influence of the solution pH

Phenol was oxidized in acid solutions (pH = 2; neutral molecules) and alkaline solutions (pH = 13; phenoxide anions) under a constant anodic current density (200 mA cm<sup>-2</sup>). Table 3 shows that the charge Q needed for the complete elimination of phenol from the solution is independent of the pH. Table 3 shows also that electrochemical polymerisation of phenol is more favoured in alkaline than in acidic solution. This result can be interpreted by considering that a homogeneous and adherent polymer film is formed on the electrode surface [19–23]. Furthermore, these polymers (which have OH substituents; see Eq. 5) are insoluble in acidic medium but soluble in alkaline. Though the concomitant production of oxygen bubbles discourages insoluble polymers formed in acidic medium from adhering to the anode surface, this film makes it more difficult for phenol to diffuse towards the electrode surface and may slow down electron transfer; consequently, the rate of polymer formation decreases (Reaction 6). On the other hand, in alkaline medium, polymers (in phenate form) are soluble, thus completely avoiding anode fouling.

Table 3 shows also that phenol mineralization was more favoured in acidic solutions than in alkaline. Nevertheless, production of hydroxyl radicals according to Reaction 1 should be thermodynamically favoured in alkaline solution. In a previous work [3], it was shown that an increase in pH reduces the current efficiency of phenol oxidation due to parasitic oxygen evolution (Reaction 7). Furthermore, in basic medium the total carbonate concentration rises with pH by the reactions opposite to those presented in Eq. 11.

Carbonate anions are easily oxidized by hydroxyl radicals [34]. This last reaction is concurrent to the mineralization process.

### 3.5 Influence of the temperature

Electrolyses of 105 mmol dm<sup>-3</sup> phenol solutions (pH = 13) on Ta/PbO<sub>2</sub> at an applied anodic current density of 200 mA cm<sup>-2</sup> were carried out at different temperatures in the range 25–65 °C. Increasing the temperature considerably reduces the charge Q necessary for the complete elimination of phenol molecules from the solution (Table 4). Table 4 shows that, for basic solutions, phenol oxidation at temperatures below 35 °C is very slow as indicated by the high charge required for the complete removal of phenol (Q = 140 Ah dm<sup>-3</sup> at 25 °C); the main product formed at low temperature from phenol oxidation is carbon dioxide (r(CO<sub>2</sub>) = 78% at 25 °C). In addition, the proportion of phenol converted into polymer is relatively low and temperature independent up to 35 °C; on the other hand, bigger amounts of polymer are formed at temperatures above 50 °C; moreover, there is a sudden transition between 35 and 50 °C, the amount of polymer increasing by a factor 3 in this temperature gap.

All these results are understandable if we consider again that phenol oxidation described by Reaction 2 (or 4) is limited by mass transport. At low temperature (below 35 °C), phenol diffusion is slower because of the relatively high viscosity of the electrolytic solution and its flux at the electrode surface is low. Therefore, for electrolyses carried out at constant and high anodic current density (200 mA cm<sup>-2</sup> in this case), phenol molecules are oxidised into carbon dioxide, owing to the high production rate of hydroxyl radicals. In previous work [5], it was concluded that a phenol molecule adsorbed onto a catalytic site of a Ta/PbO<sub>2</sub> anode undergoes a succession of very rapid oxidation steps, without desorption of the intermediate products, by transfer of oxygen atoms, leading to the formation of CO<sub>2</sub>; this probably reduces the possibility of polymer formation by a coupling reaction (Reaction 6).

Furthermore, the fact that a rise in temperature increases the fraction of phenol that ends up as polymer could possibly be explained if we consider the oxidation of both adsorbed and dissolved forms of phenol. Gattrell and Kirk [23], using cyclic voltammetry with a platinum electrode, have shown that the dissolved phenol is oxidised at a potential lower than that for the oxidation of the adsorbed form and have concluded that the dissolved form is oxidised by electron transfer through the adsorbed layer. These authors have also shown that the oxidation of the dissolved phenol produces phenoxy radicals leading to the formation of polymers and quinones while that of the adsorbed form, because of the strong adsorption, is more complete giving simple organic



acids and/or CO<sub>2</sub>. Therefore, one implication of our results is that at lower temperature (25 and 35 °C) it is the adsorbed layer, rather than the dissolved phenol, that is oxidised into simple organic acids and/or CO<sub>2</sub>. On the other hand, operation at higher temperature (50 and 65 °C) enhances desorption of reaction products from the electrode surface resulting in a continuous predominance of the oxidation of the dissolved phenol molecules into polymers and quinones (Table 4).

A more detailed study of the effect of temperature and of the nature of the anode material on the electrochemical polymerisation of phenol in aqueous solution is required and will be the subject of future investigations.

#### 4 Conclusions

This work has shown that the proportion of phenol converted into insoluble polymer depends on the experimental conditions such as anodic current density, initial concentration, pH, and temperature. It was found that the electrochemical polymerisation is favoured by high values of phenol concentration, anodic current density, temperature, and pH. The electrochemical polymerisation technique is able to eliminate up to 15% of the initial phenol in the form of polymers by a process involving the exchange of less than one electron per phenol molecule. The electrochemical polymerisation could compete interestingly with the electrochemical combustion process in waste-water treatment. Work is in progress to improve the contribution of electrochemically initiated polymerisation in the treatment of waters polluted by phenolic compounds.

#### References

- Vitt JE, Johnson DC (1992) *J Electrochem Soc* 139:774
- Comninellis Ch, Pulgarin C (1993) *J Appl Electrochem* 23:108
- Belhadj Tahar N (1996) Thesis. Université Paul Sabatier, Toulouse
- Belhadj Tahar N, Savall A (1997) In: Weaver RD, Fisher F, Kalhammer FR, Mazur D (eds) *Fundamentals and potential applications of electrochemical synthesis*, Electrochemical Society, Pennington, NJ
- Belhadj Tahar N, Savall A (1998) *J Electrochem Soc* 145:3427
- Belhadj Tahar N, Savall A (1999) *J Appl Electrochem* 29:277
- Fleszar B, Ploszynska J (1985) *Electrochim Acta* 30:31
- Chang H, Johnson DC (1989) *J Electrochem Soc* 136:17
- Yeo IH, Kim S, Jacobson R, Johnson DC (1989) *J Electrochem Soc* 136:1395
- Comninellis Ch (1994) *Electrochim Acta* 39:1857
- Feng J, Hook LL, Johnson DC (1995) *J Electrochem Soc* 142:3626
- Trasatti S, Lodi G (1981) In: Trasatti S (eds) *Electrodes of conductive metallic oxides*, Elsevier, Amsterdam
- Trasatti S (1994) In: Lipkowski J, Ross PN (eds) *The electrochemistry of novel materials*, VCH, Weinheim
- Iniesta J, Michaud PA, Panizza M, Cerisola G, Aldaz A, Comninellis Ch (2001) *Electrochim Acta* 46:3573
- Rodrigo MA, Michaud PA, Duo I, Panizza M, Cerisola G, Comninellis Ch (2001) *J Electrochem Soc* 148:D60
- Panizza M, Michaud PA, Cerisola G, Comninellis Ch (2001) *J Electroanal Chem* 507:206
- Codognoto L, Machado SAS, Avaca LA (2003) *J Appl Electrochem* 33:951
- Sharifian H, Kirk DW (1986) *J Electrochem Soc* 133:921
- Comninellis Ch, Pulgarin C (1991) *J Appl Electrochem* 121:703
- Papouchado L, Sandford RW, Petrie G, Adams RN (1975) *J Electroanal Chem* 65:275
- Fleischmann M, Hill IR, Mengoli G, Musiani MM (1983) *Electrochim Acta* 28:1545
- Gattrell M, Kirk DW (1990) *Can J Chem Eng* 68:997
- Gattrell M, Kirk DW (1993) *J Electrochem Soc* 140:1534
- Canizares P, Garcia-Gomez J, Saez C, Rodrigo MA (2003) *J Appl Electrochem* 33:917
- Canizares P, Saez C, Lobato J, Rodrigo MA (2004) *Ind Eng Chem Res* 43:1944
- Vermillion FJ, Pearl IA (1964) *J Electrochem Soc* 111:1392
- Mengoli G, Musiani MM (1987) *J Electrochem Soc* 134:643 C
- Ronlan A, Parker VD (1971) *J Chem Soc (C)* 19:3214
- Bruno F, Pham MC, Dubois JE (1977) *Electrochim Acta* 22:451
- Wang J, Jiang M, Lu F (1998) *J Electroanal Chem* 444:127
- Panizza M, Cerisola G (2003) *Electrochim Acta* 48:3491
- Li X, Cui Y, Feng Y, Xie Z, Gu JD (2005) *Water Res* 39:1972
- Vogt H (1983) In: Yeager J, JO'M Bockris, Conway BE, Sarangapani S (eds) *Comprehensive treatise of electrochemistry*. Plenum Press, New York
- Buxton GV, Wood ND, Dyster S (1988) *J Chem Soc, Faraday Trans 1*(84):1113