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Electropolymerization of phenol on a vitreous carbon electrode in alkaline aqueous solution at different temperatures

Noureddine Belhadj Tahar^a, André Savall^{b,*}

^a Département de Chimie, Faculté des Sciences de Monastir, Université de Monastir, Route de Kairouan, 5000 Monastir, Tunisia

^b Laboratoire de Génie Chimique, CNRS, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse, France

A B S T R A C T

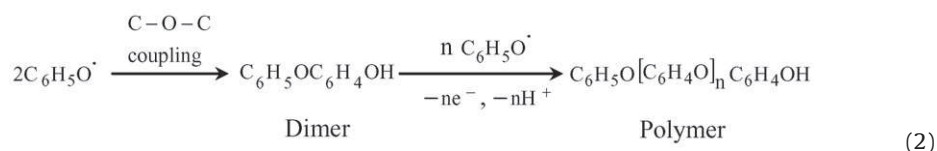
Electrochemical oxidation of phenol in basic aqueous solution has been studied on a vitreous carbon electrode at different temperatures in the range of 25–85 °C by cyclic voltammetry and chronoamperometry techniques. The electrochemical oxidation of phenol led to a complete deactivation of the electrode, whatever the temperature used, as a result of the deposition of an adhesive and insulating polymeric film. The electrochemical activity of the electrode was progressively restored by repeated potential scans in the range of water stability only when conducted at high temperatures; electrode reactivation was explained by an increase in the polymeric film permeability for both electrons (electron tunneling) and phenol molecules (diffusion). Chronoamperometric measurements carried out in the potential region of water stability have shown that electrode passivation was reduced or prevented at high temperatures. For chronoamperometry performed at the onset of oxygen evolution, the electrode remained active even at low temperatures because the discharge of water involved the production of hydroxyl radicals that destructively oxidized the polymeric film. The effect of temperature on electrode reactivation was determined by the measurement of current at an electrolysis time of 300 s; an increase of the temperature from 25 to 85 °C amplified the current from 0.212 to 5.373 mA.

1. Introduction

The formation of a passivating polymeric film on the electrode surface during anodic oxidation of phenols is of great importance since it interferes with the electrochemical process of oxidation involved in the treatment of phenolic wastes. Electropolymerization of phenols, occurring by direct electron transfer in the potential region of water stability, involves less than 2 electrons per molecule of monomer a value much lower than that required for a complete mineralization (28 e⁻ per molecule in the case of phenol) [1]. Therefore, the removal of phenols based on anodic polymerization could be taken into consideration for waste water treatment as an alternative to the mineralization technique. Taking into account that electrochemical electropolymerization can be carried out at a lower

potential than that of oxygen evolution, this technique appears as low demanding in energy.

It has been reported that electropolymerization of phenols occurs on different electrodes such as Au [2], glassy carbon [3], Pt [1,4–8], PbO₂ [9–11] and boron doped diamond (BDD) [12–14]. Polymer formation has been studied in several investigations [6,7,15–18] and a global reaction mechanism is commonly accepted. Oxidation of phenol can be used as a model reaction; at pH value higher than pK_a (9.89), during the first step of oxidation, the phenate anion gives rise to a phenoxy radical which can react with another radical or with an unreacted phenate anion monomer, according to C–C or C–O–C couplings, to form dimeric products and then polymers. For example:



The film of polymer was considered by Bruno et al. [18] and Koile and Johnson [19] to be composed of a tightly adsorbed layer of products of oxidation and polymerization covered with polymeric and oligomeric layers; the tightly adsorbed layer was unaffected by

* Corresponding author. Tel.: +33 5 61556110; fax: +33 5 61556139.
E-mail address: savall@chimie.ups-tlse.fr (A. Savall).

oxygen evolution while the upper layers can be disrupted by gas evolution. Therefore, oxygen evolution is considered as beneficial to prevent complete deactivation of the electrode by a thick polymeric film; however, electron transfer remains hindered by a barrier at the electrode surface.

Electrochemical removal of phenols from aqueous solution based on anodic polymerization was attempted in batch type cell using carbon fiber [20–22] and granular activated carbon [23] as anodes having large surface areas; bulk electrolyses were carried out at a constant applied potential (around 50 mV more positive than the phenols oxidation peak potential) [20–22] and at very low constant anodic current density (0.017 mA cm^{-2}) [23]. The electropolymerized phenols were immobilized on the anode surface. This method can be applied only for the removal of phenols present at very low concentration in water [20–23]. Unfortunately, the anode used in this treatment of phenols must be regenerated or else disposed of by incineration or land filing. Otherwise, Zareie et al. [24] have shown that the removal of phenol from wastewater in the form of polymer suspended in the reactor can be achieved using carbon electrode and high anodic current density in the presence of NaCl (120 g dm^{-3}); the authors suggested that the renewal of the oxidizing agent formed at the electrode by agitation caused most of the phenol oxidation to occur in the bulk solution without electrode fouling. However, this process uses a large amount of salt and would form toxic organohalogen compounds.

In previous works [9–11], we have studied the electrochemical removal of phenol from aqueous solution based on anodic polymerization as a possible route that could improve the electrochemical wastewater treatment process. Results of bulk electrolysis conducted on Ta/ β -PbO₂ at high anodic current density (200 mA cm^{-2}) and temperature (86°C) have shown that 39% of the starting phenol can be removed as polymers dispersed in the reactor under the best operating conditions used [9,10]. Using a high anodic current density (in the potential region of water decomposition) avoids anode fouling but simultaneously favors the oxidation of the polymeric film and oxygen evolution leading to current yield around 20% [9,10]. It was also shown that the fraction of starting phenol converted into polymer increased substantially with temperature and that no electrode passivation (in that no noteworthy tension-cell increase was observed) occurred during electrolysis [10]. Gattrell and Kirk [3] have also observed during bulk electrolysis of phenol aqueous solution that passivation on Pt anode was reduced or prevented by increasing the temperature.

In the aim to find operating conditions that favor electropolymerization whereas avoiding anode fouling we have investigated phenol oxidation on a vitreous carbon electrode surface in alkaline aqueous solution at different temperatures [25–85 °C] using cyclic voltammetry and chronoamperometry. Our objective was to provide a better understanding of the effect of temperature and potential as the key factors in the film passivity.

2. Experimental

Cyclic voltammetry and chronoamperometry measurements were carried out in a conventional three-electrode cell (200 ml) using a computer controlled Eco Chemie Autolab Model 30 (Utrecht, The Netherlands). The working electrode was vitreous carbon disk with a geometric area of 0.0707 cm^2 . The counter and reference electrodes were respectively platinum spiral and Hg/Hg₂Cl₂/Cl⁻ (sat.). Before each experiment, the working electrode was polished to a mirror with $1 \mu\text{m}$ alumina slurries on polishing sheet (3M 262X IMPERIAL Lapping Film) and subsequently washed with distilled water.

Cyclic voltammetry and chronoamperometry were performed at different temperatures (25, 40, 60, 75 and 85°C) in aqueous solution containing 1 M potassium hydroxide and phenol at a con-

centration of 5 or 10 mM. Chronoamperometric measurements were carried out at 0.5 and 1.1 V vs. SCE.

3. Results and discussion

3.1. Cyclic voltammetry

Fig. 1 displays cyclic voltammograms (first, second and sixth cycles) recorded at 25°C on a vitreous carbon electrode in electrolytic aqueous solution containing potassium hydroxide at 1 M and phenol at 5 mM. The voltammogram obtained under the same experimental conditions but in the absence of phenol is also given for comparison in Fig. 1 (curve (1')). Curve (1) shows the first positive direct scan; an anodic current peak corresponding to the oxidation of phenol is observed at 483 mV vs. SCE. This phenol oxidation which takes place in the potential region of water stability occurs by direct electron transfer. There is no reduction peak on the reverse scan. Fig. 1 shows that, in the second scan (curve (2)) at $E_{\text{peak}} = 483 \text{ mV}$, the anodic current decreases substantially compared to that of the first scan (from 160 to $40 \mu\text{A}$). As the number of successive cycles increases, the anodic peak current diminishes continuously until obtaining of a steady state after six cycles (Fig. 1). This rapid loss of electrode activity is due to the formation of an electroinactive polymeric film which entirely covers the electrode surface. After the first scan of potential the polymeric film is already formed. Visual inspection of the electrode surface revealed that a brown polymer layer was deposited once the potential of the vitreous carbon electrode was scanned past 0.5 V. The decrease of the anodic peak current at $E_{\text{peak}} = 483 \text{ mV}$ with successive potential scans suggests that the electroinactive polymeric film coated on the electrode hinders the direct electron transfer and/or the diffusion of phenol molecules to the anode surface. This behavior is consistent with previous observations of electrode fouling of Au [2,5], Pt [6–9], PbO₂ [9,11,25], carbon [17] and BDD [14,25,26].

An increase of temperature resulted in two distinct changes (Fig. 2): (i) the anodic peak current increases (Table 1) and (ii)

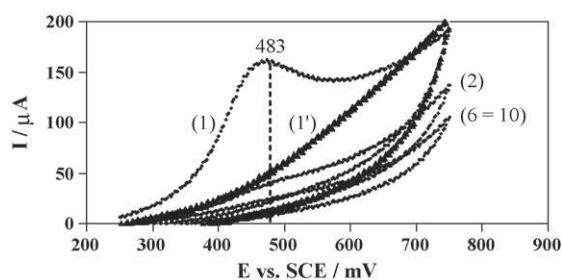


Fig. 1. Cyclic voltammograms recorded between 0.25 and 0.75 V in the potential range of water stability on vitreous carbon electrode in 5 mM phenol in 1 M KOH: (1) first cycle; (2) second cycle; (6) sixth cycle; (10) tenth cycle; (1') represents the ground current in 1 M KOH. Scan rate 100 mV s^{-1} , $T = 25^\circ\text{C}$.

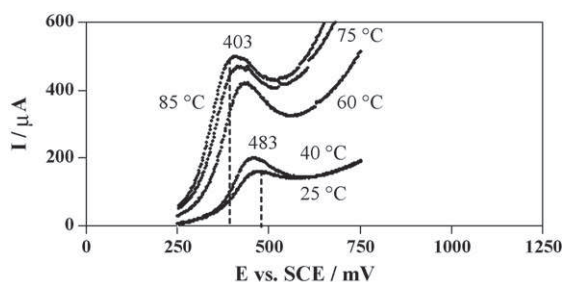


Fig. 2. Cyclic voltammograms (first cycles) recorded at different temperatures (25, 40, 60, 75, 85°C) on vitreous carbon electrode in 5 mM phenol in 1 M KOH. Scan rate 100 mV s^{-1} .

Table 1

Variation of the anodic peak current and anodic peak potential as functions of temperature for cyclic voltammetry conducted on a vitreous carbon electrode (0.0707 cm²) in aqueous solution of 5 mM phenol in 1 M KOH.

T (°C)	25	40	60	75	85
$E_{\text{peak}}^{\text{first cycle}}$ (mV)	483	463	434	405	403
$i_{\text{peak}}^{\text{first cycle}}$ (μA)	160	202	421	464	500
$i_{\text{peak}}^{\text{tenth cycle}}$ (μA)	20	30	110	250	400

the peak potential shifts towards lower values of the potential (Table 1). Similar results for oxidation of phenol on platinum have already been reported in the literature [7,27]. Table 1 shows also that the oxidation peak current increases substantially between 40 and 60 °C while the peak potential does not practically change beyond 75 °C. This shift of the oxidation peak potential might be explained by the decrease of adsorption of the phenate anion arising from the temperature increase. In fact, we have verified that the peak current of phenol (10 mM) oxidation in 1 M KOH aqueous solution is a linear function of the square root of the potential scan rate both at 25 and 85 °C; therefore, under these conditions (pH = 14), phenol oxidation has a kinetic limitation by diffusion. We assume that phenate ions are not adsorbed on the vitreous carbon electrode surface in the temperature range 25–85 °C. Thus, the shift of the oxidation peak towards lower values of the potential as the temperature increased may be explained by an increase of the diffusion coefficient of phenol with temperature leading to a higher oxidation current flow (Fig. 2).

Fig. 3 shows cyclic voltammograms (first cycles) recorded at different temperatures (40, 60, 75 and 85 °C) on the vitreous carbon electrode in 1 M KOH aqueous solution in absence (1) and presence (2) of phenol at 5 mM. Fig. 3 shows that in the range of 40–60 °C and for potentials higher than that of the oxidation peak (after electrode passivation), the gap between curves (1) and (2) increases with temperature; we assume that this results from a difference in film thickness; larger current passed before electrode passivation leads to thicker polymeric film. Beyond 60 °C, the cyclic voltammetric scans are characterized by smaller and smaller gap between curves (1) and (2) as the temperature increases; higher temperature (see for 85 °C and potential higher than 600 mV) seems then to reduce or prevent electrode passivation.

In order to better understand the influence of temperature on electrochemical activity of the vitreous carbon electrode in 1 M

KOH aqueous solution containing 5 mM phenol, successive cyclic voltammograms (Fig. 4) were recorded at different temperatures (40, 60, 75, 85 °C) between 0.25 and 0.75 V in the potential range of water stability. Fig. 4 shows that electrode passivation occurs after the first cycle, whatever the temperature, up to 85 °C. Successive cyclic voltammograms obtained at 40 °C are similar to those shown in Fig. 1 (for a temperature of 25 °C) except for the steady state which was obtained as soon as the third cycle (Fig. 4); this fact shows that oxidation of the polymeric film formed at the electrode surface was not possible by direct electron transfer in the potential range 0.25–0.75 V at temperatures below 40 °C. However, beyond 60 °C and after the second cycle, the oxidation peak current begins to grow continuously as the number of successive cycles increases; the oxidation peak current increases as a function of the temperature (Fig. 4 and Table 1). The normalized peak currents ($i_{\text{peak}}^{\text{tenth cycle}} / i_{\text{peak}}^{\text{first cycle}}$, where $i_{\text{peak}}^{\text{first cycle}}$ and $i_{\text{peak}}^{\text{tenth cycle}}$ are the peak currents of phenol oxidation respectively at first and tenth cycles) are 0.26, 0.54 and 0.80, respectively at 60, 75 and 85 °C. This means that 26, 54 and 80% of the initial electrochemical activity of the vitreous carbon electrode was restored after the tenth cycle respectively at 60, 75 and 85 °C. It is important to note that an adherent polymeric film covering completely the electrode surface was always observed to the naked eye after each experience (10 cycles) whatever the temperature used in the range of 25–85 °C. Taking into account this observation, the partial reactivation of the electrode obtained at temperatures higher than 60 °C could be interpreted in terms of changes in the polymeric film properties with temperature over cyclic scanning. We assume that an adherent, compact (pinholes-free) and insulating polymeric film, blocking both direct electron transfer and access of phenol molecules, was formed on the electrode surface at lower temperatures (below 60 °C). At temperature higher than 60 °C, these compact and insulating layers, formed during the first cycle, began probably to over-oxidize slowly after the second cycle and/or started to progressively disrupt by the decrease of the adsorption strength at the electrode. In summary, the temperature increase leads the initial blocking film to be more permeable for both electrons (tunnel effect) and phenol molecules (diffusion).

3.2. Chronoamperometry

The electrochemical oxidation of phenol at 5 mM in aqueous solution on vitreous carbon electrode was studied by chronoam-

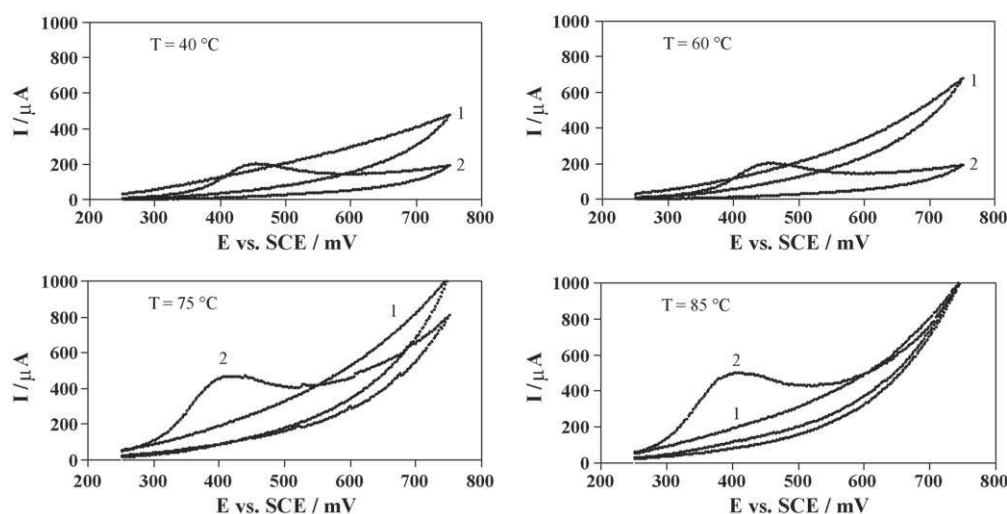


Fig. 3. Cyclic voltammograms (first cycles) recorded at different temperatures (40, 60, 75, 85 °C) on vitreous carbon electrode in 1 M KOH in the absence (1) and presence (2) of 5 mM phenol. Scan rate 100 mV s⁻¹.

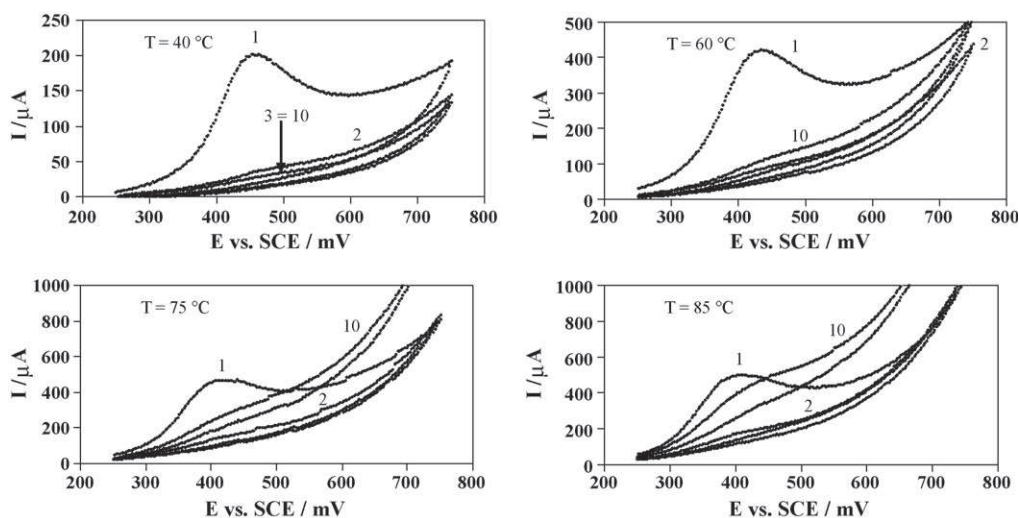


Fig. 4. Cyclic voltammograms recorded on vitreous carbon electrode in 5 mM phenol in 1 M KOH at different temperatures (40, 60, 75, 85 °C): (1) first cycle; (2) second cycle; (3) third cycle; (10) tenth cycle. Scan rate 100 mV s⁻¹.

perometry at different temperatures (25, 40, 60, 75 and 85 °C). Chronoamperometric measurements were firstly conducted at a potential of 0.5 V situated in the region of water stability (Fig. 5) but at 50 mV beyond the phenol peak potential (Fig. 3). Other chronoamperometric scans were recorded at a potential of 1.1 V in the region of water decomposition and at the onset of oxygen evolution (Fig. 5).

3.2.1. Chronoamperometry at 0.5 V

Fig. 6 shows that for chronoamperometry performed at 25 and 40 °C at 0.5 V the electrode was rapidly deactivated (current less than 0.1 mA at the stationary state). This deactivation is due to electrode fouling by a compact, adherent and insulating polymeric film, as already found in cyclic voltammetry (Figs. 1 and 4). The

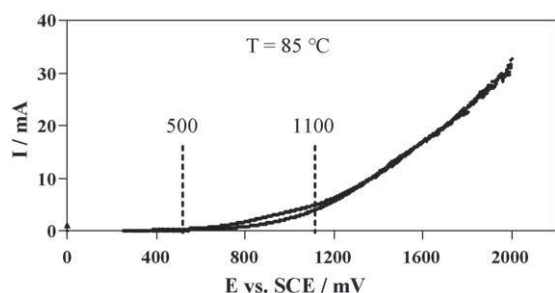


Fig. 5. Cyclic voltammogram recorded between 0.25 and 2.0 V in 1 M KOH on vitreous carbon electrode. Scan rate 100 mV s⁻¹, T = 85 °C.

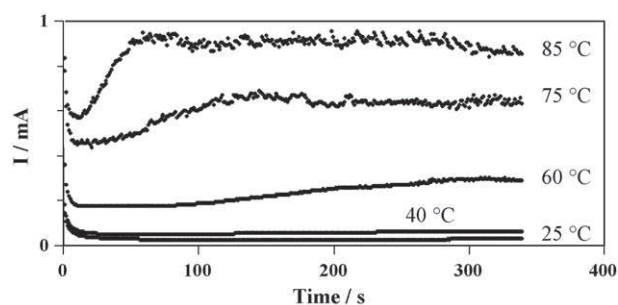


Fig. 6. Potentiostatic *I-t* curves recorded at different temperatures (25, 40, 60, 75, 85 °C) in unstirred solution containing 5 mM phenol in 1 M KOH on vitreous carbon electrode at 0.5 V.

fouling effect was clearly observed right from the first 10 s (Fig. 6) since polymer was initiated by direct electron transfer (Eqs. (1) and (2)). At 60 and 75 °C, the current decreased rapidly during the first 10 s then inclined to rise slowly. However, at higher temperature (85 °C), the current slowed down quickly during the first seconds (passivation) then increased rapidly (depassivation) and reached a stationary state at a relatively high value (1 mA). Table 2 shows current values measured at the stationary state (300 s); these values indicate that the electrode passivation was more and more prevented by increasing temperature; the anodic current (at *t* = 300 s) was 31.5 times greater at 85 °C than at 25 °C. These results show clearly that the electrode reactivation is stable for temperatures higher than 75 °C and are in agreement with those already found by cyclic voltammetry when partial reactivation of the electrode was observed during consecutive potential scans in the potential range of water stability (Fig. 4). Taking into account that at 85 °C the ground current at *E* = 0.5 V is practically nil (Fig. 5), it is clear that the oxidation current measured at the stationary state, at the same temperature, corresponds to the oxidation of phenol.

Inhibition of electrode fouling at high temperature could be related to polymer over-oxidation by direct electron transfer in the potential region of water stability. Gattrell and Kirk [6] and Papouchado et al. [17] have reported that oligomers and polymers are oxidized by direct electron transfer at lower potential than for phenol to new radicals leading to more complex polymeric structures which include cross-linking. We assume that such oxidation occurring at temperatures higher than 75 °C could modify the polymer permeability to phenol and electrons (tunnel effect) that leads to electrode reactivation.

3.2.2. Chronoamperometry at 1.1 V

During chronoamperometric measurements at the onset of oxygen evolution (1.1 V), anodic current values were much higher than

Table 2

Variation of the anodic current *I* with temperature; *I* is measured 300 s after starting a potentiostatic electrolysis at *E* = 0.5 or 1.1 V vs. SCE on a vitreous carbon anode in aqueous solution of 5 mM phenol in 1 M KOH.

<i>T</i> (°C)	25	40	60	75	85
<i>E</i> vs. SCE = 0.5 V					
<i>I</i> (mA)	0.028	0.064	0.297	0.615	0.891
<i>E</i> vs. SCE = 1.1 V					
<i>I</i> (mA)	0.212	0.636	2.100	4.758	5.373

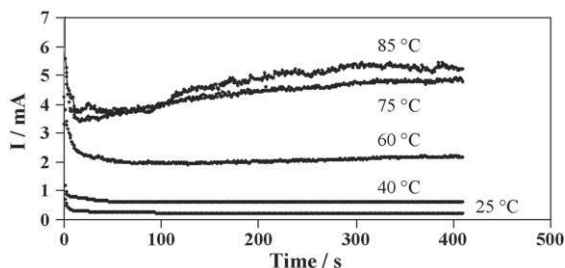


Fig. 7. Potentiostatic $I-t$ curves recorded at different temperatures (25, 40, 60, 75, 85 °C) in unstirred solution containing 5 mM phenol in 1 M KOH on vitreous carbon electrode at 1.1 V.

those at 0.5 V for all studied temperatures (Fig. 7 and Table 2). We suggest that, at 1.1 V, the polymeric film begins to decompose by reaction with active intermediates (hydroxyl radicals) electrogenerated from water oxidation; simultaneously, the fouling film can be mechanically removed by the underneath oxygen evolution. A progressive disruption of the polymeric film results from these two actions and restores the initial activity of the electrode. Table 2 shows that by increasing the temperature from 25 to 85 °C the current, measured at the stationary state ($t = 300$ s), was increased from 0.21 to 5.4 mA. This result shows again the positive role played by temperature in the hindrance of electrode passivation. In the view to avoid fouling of the electrode, it appears from Table 2 that whatever the potential chosen either in the domain of water stability or at the onset of oxygen evolution it is better to work at high temperature (85 °C) than at low temperature (25 °C).

From cyclic voltammetry and chronoamperometry results, we believe that current yield for electropolymerization could be improved and at the same time electrode fouling could be avoided during bulk electrolysis of phenol in alkaline solution by using a low anodic current density and a high temperature.

4. Conclusions

Electrochemical oxidation of phenol in alkaline aqueous solution has been studied on vitreous carbon electrode in the temperature range of 25–85 °C by cyclic voltammetry and chronoamperometry. The main results are as follows:

1. One irreversible anodic peak is observed in the potential region of water stability corresponding to phenol oxidation by direct electron transfer. The potential shift of this peak towards the lower potential values and its height increase as the temperature increases are interpreted by the increase of phenol diffusivity.
2. A compact, adherent and insulating polymeric film is formed as earlier as the first cycle leading to a complete deactivation of the electrode whatever the temperature; both direct electron transfer and phenol diffusion at the electrode are completely blocked

owing to this film. However, successive cycles between 0.25 and 0.75 V vs. SCE, conducted at temperature higher than 75 °C, progressively restore the electrode activity probably in reason to disruption of the polymeric film by its electrochemical oxidation and/or decrease of its adsorption on the electrode.

3. Chronopotentiometry carried out in the potential region of water stability (0.5 V), where oxidation occurs by direct electron transfer, have shown that the electrode is completely deactivated when electrolyses are conducted at low temperatures (25 and 40 °C) while electrode passivation is reduced or prevented at high temperatures (60, 75 and 85 °C).
4. Electrolyses carried out at the onset of oxygen evolution (1.1 V) show that the anode remains active even at low temperature because water discharge involves the production of hydroxyl radicals that oxidize the polymeric film, but a mechanical removal of the polymeric film by the underneath oxygen evolution could also be evoked. The positive effect of temperature is again observed here since the stationary current is multiplied by a factor 25 for a temperature increase from 25 to 85 °C.
5. Selective oxidation of phenol into polymer could be profitable for waste water treatment by using mild potentials and high temperatures. The main advantage of this method is that the polymerization process can be performed at potentials below that of oxygen evolution without deactivation; by this way it could be possible to reach a high current efficiency.

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