

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

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Abstract Electrochemical oxidation of phenol in acidic aqueous solution was studied on a vitreous carbon electrode at different temperatures in the range of 25–85 °C by cyclic voltammetry and chronoamperometry. The kinetic aspect of the phenol oxidation was investigated as a function of its concentration and temperature. The electrode deactivation by formation of an adherent, compact, and insulating polymeric film was examined by monitoring the decrease in the peak current of phenol oxidation during the course of successive potential scans. Repeated potential scans in the region of water stability did not reactivate the electrode whatever the temperature used. Chronoamperometric curves recorded at different potentials in the region of water decomposition shown that the electrochemical activity of the electrode was partially restored even when performed at low temperature (25 °C).

Keywords Acid media · Cyclic voltammetry · Chronoamperometry · Electropolymerization · Phenol · Temperature · Vitreous carbon

1 Introduction

Highly toxic organic compounds such as phenols can be electrochemically mineralized on high oxygen over-potential anodes such as SnO₂ [1–6], PbO₂ [1, 7–12], and boron-doped diamond (BDD) [13–17]. However, this technique is not yet used in industrial wastewater treatment mainly owing to the high energy consumption which results from the large number of electrons involved in the complete mineralization of organic pollutants into carbon dioxide and water. However, it appears that partial oxidation could be used as a pretreatment ahead of bio-treatment rather than complete mineralization on the express understanding that toxic intermediaries are completely eliminated [18, 19]. On the other hand, low reaction rates are observed with some aromatic organic compounds such as phenols due to electrode fouling [2, 20]. For example, phenol is well-known for its ability to foul anodes and the tarry deposit formed during its oxidation was ascribed to polymerization products [5, 18, 20–26]. The first step of the oxidation of phenolic compounds produces reactive phenoxy radicals which form, by coupling, oligomeric and polymeric compounds [20–24, 27–29]. Electropolymerization reaction involves less than two electrons per phenol molecule transformed into polymer [27, 30] while 28 electrons are involved for the complete mineralization of a phenol molecule into CO₂ and H₂O. Therefore, the electrochemical approach to remove phenols from waste waters by anodic polymerization could be advantageous compared to a complete mineralization. The challenge is to find the operating conditions that simultaneously favor the electropolymerization reaction and avoid the resulting electrode passivation. It has been reported that formation of the polymeric film depends strongly on the operating conditions; low potential [26, 31], high temperature, and alkaline media [26] favor film

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formation. On the contrary, electrode fouling was lowered at high potential [14, 18, 31, 32], high temperatures [18], and low pH [33]. From these results it appeared that the use of a high temperature is favorable to both polymeric film formation and electrode fouling hindrance. In regard to potential, an optimum value should exist to favor polymerization without electrode deactivation.

Techniques using anodes of large specific area [30, 34–36], high concentration of NaCl [37], or surfactant [38] were used to eliminate phenols from solution by electropolymerization.

In our previous study [39, 40], 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 and high temperature have shown that 39% of the starting phenol was removed as polymer under the best operating conditions [39, 40]. It was also shown that the fraction of starting phenol converted into polymers increased substantially with temperature and that no electrode passivation (in that no noteworthy tension-cell increase happened) was observed over electrolysis [40].

We have also investigated the electrochemical behavior of phenol on vitreous carbon by cyclic voltammetry and chronoamperometry in basic aqueous solution at temperatures comprised between 25 and 85 °C [41]. Cyclic voltammetry performed in the potential region of water stability has shown that: (1) vitreous carbon electrode passivated as earlier as the second potential scan, (2) electrode activity was progressively restored over successive potential scans only at high temperatures (≥ 60 °C). Chronoamperometric measurements conducted at potential situated in the region of water stability have shown that polymeric film did not deactivate the electrode when working at high temperatures (≥ 60 °C).

In this study, we have undertaken the study of the influence of concentration, temperature, and applied potential on phenol electropolymerization in acidic aqueous solution on a vitreous carbon electrode. The objective is to evaluate if working at high temperature and low applied potential, which are prerequisite conditions that assure high current yields for electrochemical wastewater treatments, could prevent electrode deactivation during bulk electrolysis. Cyclic voltammetry and chronoamperometry techniques were used to study the electrochemical oxidation of phenol and the resulting fouling of a vitreous carbon electrode in acidic aqueous solution.

2 Experimental details

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 a vitreous carbon disk with a geometric area of 0.0707 cm². The counter and reference electrodes were platinum spiral and Hg/Hg₂Cl₂/Cl⁻ (sat.), respectively. Before each experiment, the working electrode was polished to a mirror with 1 μ m alumina slurries on polishing sheet (3 M 262 \times 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 mol L⁻¹ of sulfuric acid and 1 or 4 mmol L⁻¹ of phenol. Chronoamperometric measurements were carried out at constant potentials chosen either in the region of water stability or oxygen evolution.

3 Results and discussion

3.1 Cyclic voltammetry

3.1.1 Influence of phenol concentration

Figure 1a shows cyclic voltammograms recorded on vitreous carbon electrode at 25 °C in 1 mol L⁻¹ of H₂SO₄ containing phenol concentrations ranging from 0.5 to

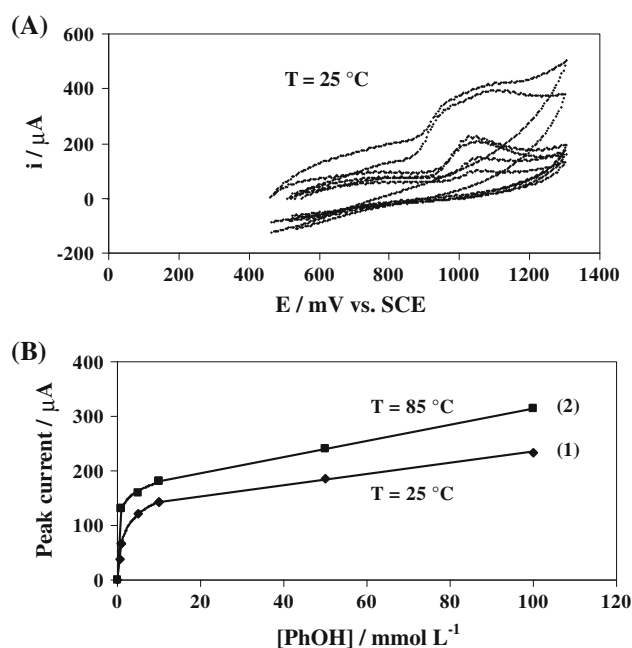


Fig. 1 a Cyclic voltammograms (first cycles) of phenol on vitreous carbon electrode in 1 mol L⁻¹ of H₂SO₄ aqueous solution. $T = 25$ °C; scan rate: 200 mV s⁻¹; [PhOH] (from inner to outer): 0.5, 1, 5, 10, 50, and 100 mmol L⁻¹. b Relationship between phenol concentration and the oxidation peak current

100 mmol L⁻¹. In the first positive going scan, an anodic peak, involving a direct electron transfer, corresponding to the oxidation of phenol is observed at $E_{\text{peak}} = 1041$ mV versus SCE in the potential region of water stability while no reduction peak appears on the reverse scan. Figure 1a shows that above 10 mmol L⁻¹, phenol oxidation is expressed as a wave. The peak potential shifts toward low values by increasing concentration; the peak current increases rapidly with phenol concentration up to 1 mmol L⁻¹ then tends to stabilize around 150 μA (Fig. 1b; curve 1).

On the other hand, the adsorption of phenol on the vitreous carbon electrode was investigated according to a procedure already proposed by Gattrell and Kirk [3] for the study of phenol oxidation on platinum. The vitreous carbon electrode was dipped during 30 min at 25 °C in 1 mol L⁻¹ of H₂SO₄ aqueous solutions containing phenol at different concentrations (5, 10, 50, and 100 mmol L⁻¹), then rinsed with distilled water and immediately subjected to potential cycling in phenol free 1 mol L⁻¹ of H₂SO₄ at 25 °C. The voltammograms (not shown) reveal an anodic peak situated at 1095–1125 mV corresponding to the oxidation of the adsorbed phenol molecules and which is typical of an irreversible reaction; the adsorption peak potential is shifted toward lower potential values by increasing phenol bulk concentration. Moreover, the variation of the adsorption peak current with phenol bulk concentration shows two linear parts with very different positive slopes; the transition occurs at concentrations between 5 and 10 mmol L⁻¹.

3.1.2 Influence of the potential scan rate

Figure 2 shows cyclic voltammograms of 5 mmol L⁻¹ of phenol in 1 mol L⁻¹ of H₂SO₄ aqueous solution at 25 °C recorded at scan rates comprised between 100 and 500 mV s⁻¹. The oxidation peak current i_p varies linearly with the potential scan rate v (inset in Fig. 2) according to the following equation [42]:

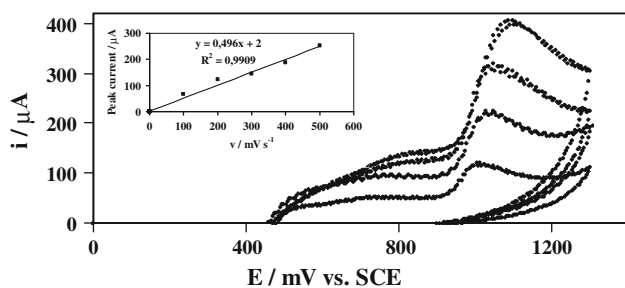


Fig. 2 Cyclic voltammograms (first cycles) recorded on vitreous carbon electrode in 1 mol L⁻¹ of H₂SO₄ aqueous solution containing phenol at a concentration of 5 mmol L⁻¹. $T = 25$ °C. Scan rate (from inner to outer): 100, 200, 300, 400, and 500 mV s⁻¹

$$i_p = \frac{n^2 F^2}{4RT} Sv\Gamma \tag{1}$$

where Γ is the superficial concentration (mol cm⁻²) of the adsorbed phenol.

We verified the same behavior for phenol concentrations of 0.5 and 50 mmol L⁻¹ (not shown) indicating that the oxidation kinetics at 25 °C is controlled by phenol adsorption at the vitreous carbon electrode surface whatever the phenol bulk concentration used in the range 0.5–50 mmol L⁻¹. According to Eq. 1, as the phenol bulk concentration increases, the oxidation peak current increases then tends to stabilize when Γ reaches its limiting value (at a phenol bulk concentration of around 1 mmol L⁻¹) (Fig. 1b; curve 1).

According to the same procedure described in Sect. 3.1.1, we have verified from cyclic voltammograms (not shown), recorded in 1 mol L⁻¹ of H₂SO₄ aqueous solution at 25 °C with various scan rates, of adsorbed phenol (adsorption during 30 min in 1 mol L⁻¹ of H₂SO₄ aqueous solution containing 100 mmol L⁻¹ of phenol at 25 °C) that the peak current is proportional to the potential scan rate.

3.1.3 Influence of the temperature

Figure 3 shows cyclic voltammograms (first cycles) of 10 mmol L⁻¹ of phenol in 1 mol L⁻¹ of H₂SO₄ aqueous solution at different temperatures in the range 25–85 °C recorded at 500 mV s⁻¹ while cyclic voltammograms recorded on vitreous carbon electrode for blank solution at 25 and 85 °C are given in Fig. 4. The peak current increases linearly with temperature between 25 and 75 °C then tends to stabilize (inset in Fig. 3). Furthermore, an increase of temperature results in a shift of the peak potential toward the lower values (Fig. 3).

Figure 1b shows that the relationship between the oxidation peak current and the phenol bulk concentration is the same at 25 (curve 1) and 85 °C (curve 2) except that the limiting value is higher at 85 than 25 °C.

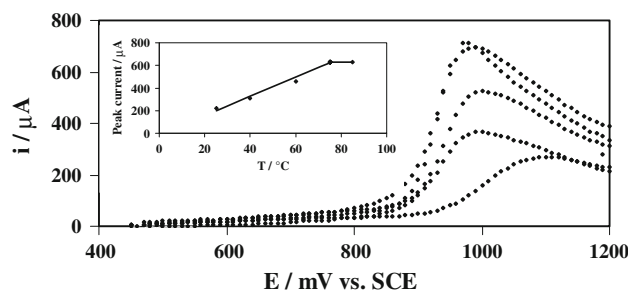


Fig. 3 Cyclic voltammograms (first cycles) recorded on vitreous carbon electrode in 1 mol L⁻¹ of H₂SO₄ aqueous solution containing 10 mmol L⁻¹ of phenol. Scan rate 500 mV s⁻¹; temperature (from inner to outer): 25, 40, 60, 75, and 85 °C

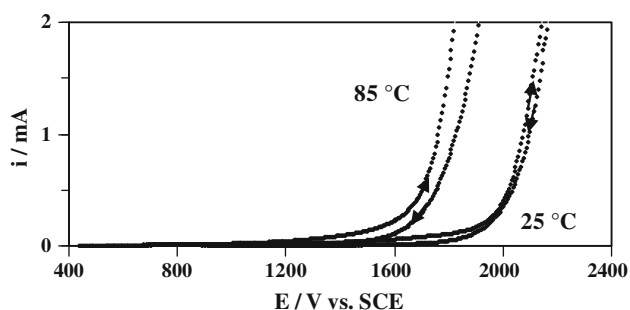


Fig. 4 Cyclic voltammograms recorded between 450 and 2500 mV on vitreous carbon electrode in 1 mol L⁻¹ of H₂SO₄ aqueous solution. Scan rate: 100 mV s⁻¹

To investigate the kinetic aspect of phenol oxidation at 85 °C on a vitreous carbon electrode, cyclic voltammograms (first cycles) were recorded for solution of H₂SO₄ at 1 mol L⁻¹ for concentration of phenol up to 100 mmol L⁻¹ at different scan rates in the range 50–500 mV s⁻¹. Figure 5a shows that for solution containing 1 mmol L⁻¹ of phenol, the peak current is proportional to the square root of the scan rate; so, under these conditions, the electrode process for phenol oxidation is controlled by diffusion. This result may be brought closer to the following experiment: the cyclic voltammogram (first cycle) recorded on vitreous carbon at 500 mV s⁻¹ in 1 mol L⁻¹ of H₂SO₄ at 85 °C after adsorption of phenol under the same condition described in

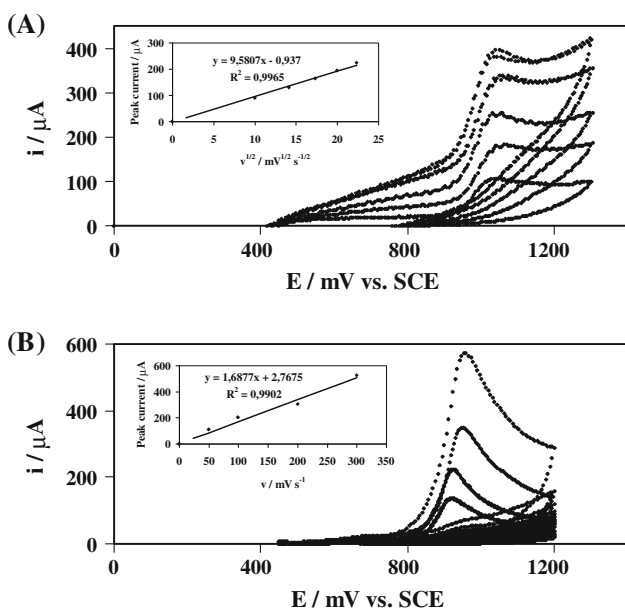


Fig. 5 Cyclic voltammograms (first cycles) recorded on vitreous carbon electrode in 1 mol L⁻¹ of H₂SO₄ aqueous solution containing phenol at a concentration of: **a** 1 and **b** 10 mmol L⁻¹. *T* = 85 °C. Scan rate (from inner to outer): **a** 100, 200, 300, 400, and 500 mV s⁻¹ and **b** 50, 100, 200, and 300 mV s⁻¹

Sect. 3.1.1 does not show any oxidation peak. This means that the phenol adsorbed at 25 °C was completely desorbed at 85 °C. Since (i) the vitreous carbon electrode was immediately subjected to potential cycling as soon as the phenol adsorption step was achieved and (ii) potential scan was conducted in unstirred electrolytic solution, we assume that at 85 °C the desorbed phenol molecules have rapidly diffused toward the bulk of the solution; as a result, the concentration of dissolved phenol at the electrode surface was so much low that no oxidation peak was detectable.

By increasing phenol concentration at 10 mmol L⁻¹, cyclic voltammograms recorded at 85 °C shown that the peak current became proportional to the scan rate (Fig. 5b) indicating an oxidation reaction controlled by adsorption. The same behavior was obtained for phenol concentration of 100 mmol L⁻¹ (not shown). In accordance with this observation, Fig. 1b shows that the variation of the peak current with the phenol bulk concentration at 25 °C (curve 1) and 85 °C (curve 2) is typical of an oxidation process limited by adsorption (for phenol concentration higher than 1 mmol L⁻¹).

3.1.4 Influence of the successive potential scans at different temperatures

In order to better understand the influence of temperature on electrochemical activity of phenol on vitreous carbon electrode in acidic medium, successive cyclic voltammograms were recorded at 25 and 85 °C. Figure 6 shows that electrode passivation occurred after the first cycle whatever the temperature used; the voltammetric response was characterized by a decrease of the current, measured at the potential of the phenol oxidation peak, upon continuous scanning until a stationary state was reached at the eighth scan (Fig. 6). The decrease of the current with successive potential scans suggests that coating of the electrode surface by the electroinactive polymeric film blocks both direct electron transfer and diffusion of phenol molecules toward the anode surface. This behavior is consistent with previous observations of electrode fouling of Au [21, 22], Pt [20, 23, 24, 39], PbO₂ [32, 39], BDD [17, 32, 43], and vitreous carbon [41]. The decrease of current observed as the scan number increased is likely due to film oxidation reaction as already suggested by Gattrell and Kirk [23]. Once the polymeric film is oxidized to unreactive forms, the electrode grow effectively blocked for further reaction and a stationary state is reached with oxidation currents falling to 0. Similar results of phenol oxidation on vitreous carbon electrode were previously obtained in basic aqueous solution (1 mol L⁻¹ of KOH) at 25 °C except for the corresponding anodic peak which appeared at a lower potential $E_{\text{peak}} = 483$ mV [44]. However, beyond 60 °C, successive voltammograms recorded in acidic aqueous

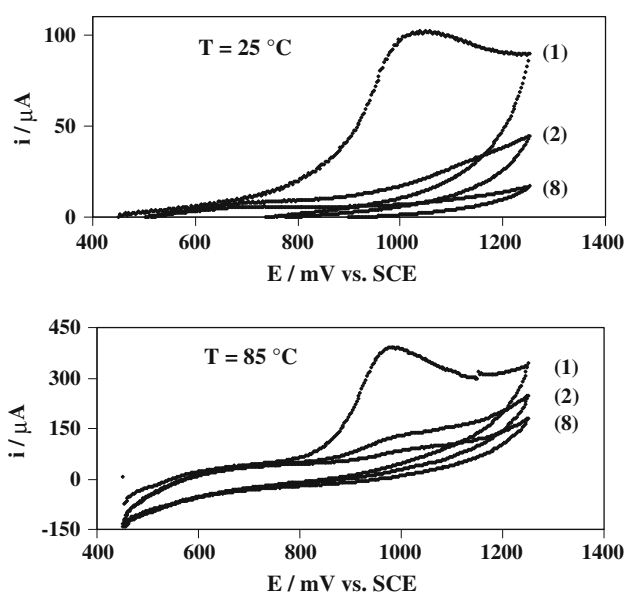
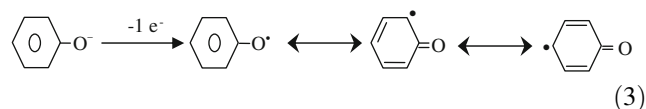


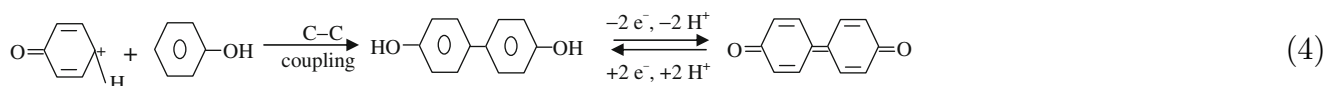
Fig. 6 Successive cyclic voltammograms recorded on vitreous carbon electrode for 4 mmol L⁻¹ of phenol in 1 mol L⁻¹ of H₂SO₄ aqueous solution at 25 and 85 °C. (1) first cycle; (2) second cycle; (8) eighth cycle. Scan rate: 100 mV s⁻¹

solution (Fig. 6) are quite different to those obtained in alkaline one [41] where after the second cycle, the oxidation peak current begins to grow continuously as the scan number increases. Therefore, the electrode deactivation at



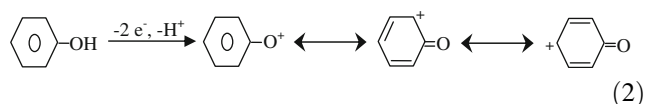
These two different oxidation pathways could be ascribed to different orientations of the phenol molecules at the electrode surface as a function of the electrolytic solution pH. Neutral phenol can be adsorbed due to π -electron interaction between the aromatic ring and the electrode leading to a flat orientation of the molecule with respect to the electrode surface. On the contrary, phenoxide anions are either oriented vertically or be inclined at an oblique with respect to the electrode surface. This inclined position may result from (i) π -electron interaction conducting to a parallel orientation and (ii) electrostatic interaction between the negative charged oxygen and the electrode leading to vertical orientation [48]; the latter orientation reduces the interaction of the aromatic ring with the electrode and hinders the anodic oxidation of phenol [20]. These two pathways are in agreement with our results in that phenol oxidation is found to be limited by adsorption in acidic medium (Figs. 2 and 5) and diffusion in alkaline one (1 mol L⁻¹ of KOH) [41].

Phenoxonium ion is a reactive electrophile which participates in a C–C coupling reaction with the starting phenol to form dimer [45]:



temperatures higher than 60 °C is more pronounced in acidic medium than in alkaline one. This result indicates that the properties of the polymeric film depend on whether the medium is acidic or basic.

According to literature [44–47], phenol oxidation occurring in acidic medium (pH < 9.89 (pKa)) involves two electrons per molecule to give a mesomeric phenoxonium ion (reaction 2) while in basic solution (pH > 9.89) it corresponds to a one-electron exchange from phenoxide anion to give a mesomeric phenoxy radical (reaction 3).



3.2 Chronoamperometry

Chronoamperometric curves were registered at different applied potentials in 1 mol L⁻¹ of H₂SO₄ aqueous solution containing 4 mmol L⁻¹ of phenol at different temperatures. Figure 7a shows that for chronoamperometry performed at 25 °C and 1100 mV situated in the potential range of water stability and slightly above the peak potential of phenol oxidation (see Fig. 4), the current falls rapidly to reach a stationary value less than 5 μ A. This rapid deactivation is due to the formation of an adherent and compact polymeric film that blocks further access of phenol molecules to the electrode surface (low permeability for phenol molecules). Under these conditions, increasing temperature from 25 to 85 °C did not reactivate the electrode vis-à-vis of phenol oxidation since although the stationary current at 85 °C is

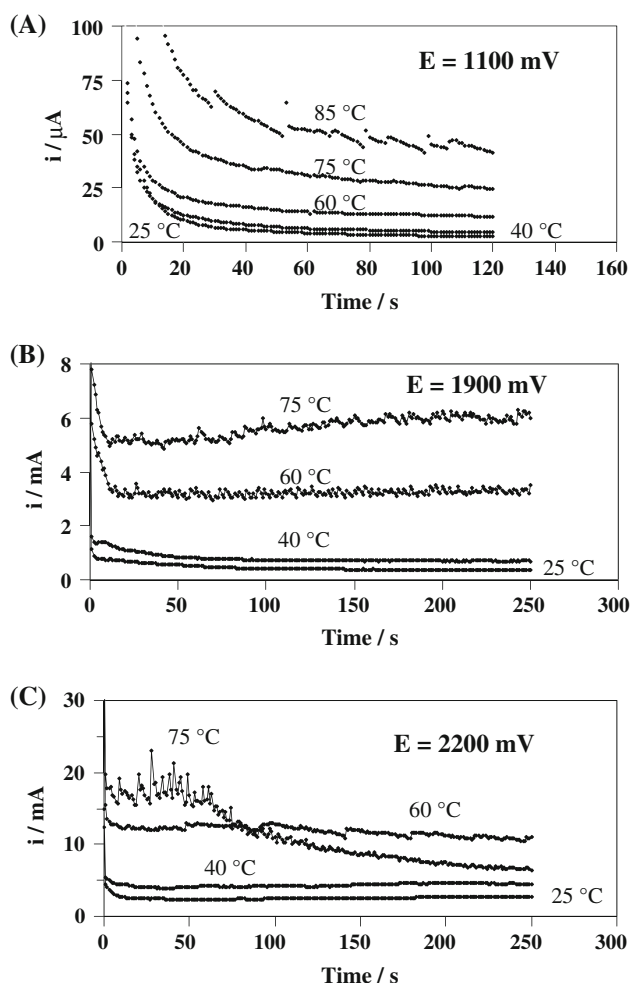


Fig. 7 Potentiostatic *i-t* curves recorded on vitreous carbon electrode in unstirred solution containing 1 mol L⁻¹ of H₂SO₄ and 4 mmol L⁻¹ of phenol at different temperatures. Applied potential: a 1100; b 1900; c 2200 mV

around 15 times greater than that obtained at 25 °C its value remains less than 50 μA . These results are in agreement with those already found by cyclic voltammetry (Fig. 6) performed in the potential region of water stability in that ten successive cycles between 450 and 1250 mV did not reactivate the electrode even at 85 °C. On the contrary, in alkaline medium, it has been shown that the electrode passivation is more and more prevented by increasing temperature [41]. For chronoamperometry performed at 1900 mV situated at the onset of oxygen evolution (Fig. 7b) and at 2200 mV with a significant oxygen evolution (Fig. 7c), the stationary currents were higher than 0.7 mA and increased substantially with temperature.

Visual observation of the electrode surface revealed that brown layers were deposited on the vitreous carbon electrode after anodic polarization even under simultaneous oxygen evolution whatever the temperature used in the range 25–85 °C. Thus, the significant enhancement of current with

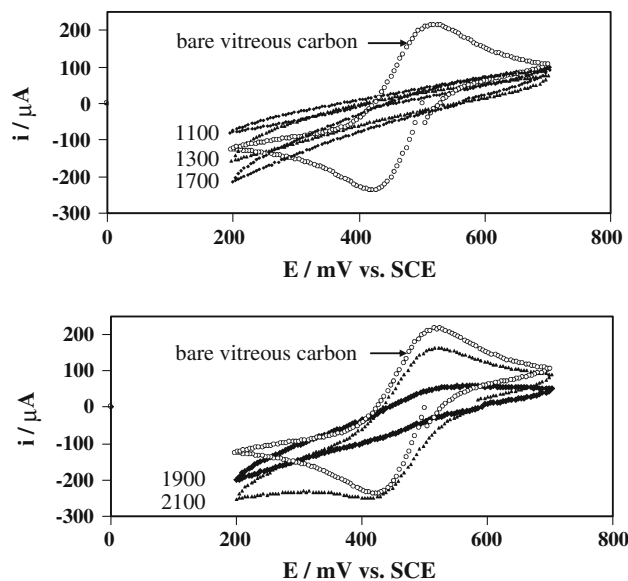


Fig. 8 Cyclic voltammograms of 10 mmol L⁻¹ of potassium ferricyanide in 1 mol L⁻¹ of H₂SO₄ aqueous solution recorded at 25 °C on bare vitreous carbon and polymer-coated vitreous carbon electrodes prepared by anodic polarizations at different potentials (1100–2100 mV) for 10 min in 1 mol L⁻¹ of H₂SO₄ aqueous solution containing 1 mmol L⁻¹ of phenol at 85 °C. Scan rate: 500 mV s⁻¹

applied potential (Fig. 7) is likely due to an increase in the permeability of the film which maintains its electrochemical activity. We dismiss the action of hydroxyl radicals conducting to a chemical degradation of the polymer. This was confirmed from voltammograms of potassium ferricyanide (Fig. 8) performed on vitreous carbon electrode preliminary treated at 85 °C by anodic polarization at different potentials during 10 min in 1 mol L⁻¹ of H₂SO₄ containing 1 mmol L⁻¹ of phenol. Figure 8 shows that ferricyanide was not reduced on polymer-coated vitreous carbon electrode prepared by anodic polarization at a potential below 1700 mV; however, the voltammogram recorded on a polymer-coated vitreous carbon electrode prepared by anodic polarization at 2100 mV was almost similar to that recorded on a bare electrode. From these results and chronoamperometric measurements, we assume that polymeric film formed during anodic polarization at a potential in the region of water stability has very low permeability for phenol molecules while that formed in the presence of a simultaneous oxygen evolution is more permeable. Furthermore, chronoamperometric results show that the vitreous carbon electrode conserves its electrochemical activity under anodic polarization in the region of water decomposition at 25 as well as 85 °C. However, at present, it is difficult to know whether it is better for the treatment of phenols in acid medium by electropolymerization to use high applied potential and low temperature or lower potential and high temperature since in the two cases electrode deactivation by the polymeric film seems to be

avoided. To answer this question, work is in progress to study the permeability for phenol molecules of the polymeric film formed under different experimental conditions. To treat phenolic compounds at high concentration by electropolymerization, the polymeric film formed at the electrode surface must have the highest permeability for phenol molecules in order to proceed by electropolymerization as long as a current is supplied to the electrode.

4 Conclusions

Electrochemical oxidation of phenol on a vitreous carbon electrode was studied by cyclic voltammetry and chronoamperometry in acidic aqueous solution as a function of phenol concentration, applied potential and temperature. It was confirmed by cyclic voltammetry that phenol oxidation performed in acidic media is controlled by adsorption except at both low concentration (1 mmol L^{-1}) and high temperature ($85 \text{ }^\circ\text{C}$) where it is limited by diffusion. Visual observation of the electrode surface revealed the formation of an adherent polymeric film (brown layers) when the potential was scanned past 1000 mV ; as a result, no phenol oxidation peak was observed after the first scan indicating that the electrode was completely passivated. Repeated potential scans or anodic polarization in the potential region of water stability were not able to restore the electrochemical activity of the electrode even using a higher temperature. However, electrode deactivation was partially prevented during anodic polarization at a constant potential in the region of water discharge. The thin polymeric film endured at the electrode surface even after anodic polarization inducing simultaneous oxygen evolution. Thus, we reasonably believe that the polymeric film formed in this way becomes permeable rather by the physical effect of the concomitant oxygen evolution than by its degradation by chemical reaction with hydroxyl radicals.

Results presented in this study show evidence on the possibility to form a permeable polymeric film by electrochemical oxidation of phenol on condition that the working electrode potential is situated at the onset of oxygen evolution. Work is in progress for verification by extensive electrolyses.

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