FULL LENGTH ARTICLE

Electrochemical oxidation behavior of some hazardous phenolic compounds in acidic solution

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Abstract The electrochemical oxidation of phenol, resorcinol and pyrogallol was investigated in sulfuric acid solution. Cyclic voltammetry and electrochemical impedance spectroscopy, EIS, were used. The mechanism of the electrochemical oxidation process was proposed and discussed. The process includes a selective oxidation and PtO_x formation. EIS measurements were carried out to further examine the reaction kinetics involved in the phenolic compounds electro-oxidation. The EIS responses were found to be strongly dependent on electrode potentials. The result showed the presence of an oxidation peak in the region around 1 V *vs* SCE to all conditions evaluated. In cyclic voltammetric experiments a gradual decrease of the oxidation peak with the number of cycles was observed. This suggests the deactivation or blockage of the electrode surface by the adsorption of substances and/or phenoxy radical polymerization.

1. Introduction

The electrochemical oxidation of hazardous organic species is a promising method for wastewater remediation. Phenols are a large group of pollutants in industrial effluents and, due to their low degradability by conventional effluent treatment, even at low concentrations they present toxicity and bioaccumulation problems [1]. Phenolic compounds are present in effluents from coke production, food industries, chemical industries, such as those associated to the production of resins and pesticides, and petroleum refineries [2]. Many different technologies are in use or have been proposed for the recovery or destruction of phenols [3,4]. Among these technologies, there are processes dealing with collapse of micro bubbles [5], anodic polymerization [6–8], oxidation by photocatalysis or by hydrogen peroxide [9–12], as well as electrooxidation with various electrode materials [13–16].

The electrochemical oxidation of organic substances is a promising technique for the treatment of industrial effluents and the electrooxidation of phenol has been evaluated by different authors [17–21]. Comninellis and Pulgarin [17] studied the anodic oxidation of phenol on platinum and concluded that the most important parameters for this study are the phenol concentration and pH. They have not reported any blocking effect on the electrode surface. Arslan et al. [18] studied, besides the effect of temperature and pH, the influence of the phenol concentration in the process of phenol electrooxidation

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on platinum. They found a dependence of the peak potential on concentration and on temperature, and this dependence was more pronounced for the highest values of concentration and temperature studied. The authors reported the blocking of the electrode surface for high concentrations of phenol in alkaline medium and a phenol polymerization on the electrode surface explained this process. Kennedy et al. [20] investigated the oxidation and polymerization of aminophenolic compounds in neutral solutions and they proposed a mechanism of substitution reaction, followed by oxidation and polymerization. Pacheco et al. [21] evaluated the degradation of phenol, catechol and cresol on boron doped diamond electrodes and concluded that the degradation process increases with increasing current densities. The effect of the solute concentration was also investigated; the results have shown that under conditions of diffusive control the degradation is independent of the concentration. Li et al. [19] investigated the electrochemical degradation of phenol on platinum electrodes in comparison with oxide electrodes, obtaining similar results for platinum and Ti/RuO$_2$ electrodes.

Although different works are associated to the electrooxidation of phenols, the study of this process is still a matter of research, since this technique is able to achieve good destruction rates. The electrooxidation of phenol occurs through the formation of the phenoxy radical, which either reacts with other species present in the solution generating products, or reacts with other phenol molecules producing a dimeric radical. This radical can be oxidized following two different paths: the formation of polymers or quinones, depending on the conditions used. For high phenol concentrations and basic medium, polymerization is favored, while for low phenol concentrations and acid medium the formation of quinones is privileged [22]. From the oxidation reaction of quinone, carboxylic acids are obtained. These products are difficult to oxidize, but are biodegradable compounds, and therefore the electrooxidation process can be associated to a biological process [23,24]. Electropolymerization of phenol beings with the formation of the phenoxy radical, or it can react with a molecule of phenol to give predominantly a para-linked dimeric radical. This radical may be further oxidized to form a neutral dimmer or it may attach another molecule. The dimer may be further oxidized create oligomers to polymers. Formation of the insoluble polyphenol results in deactivation of electrode surface. The relative rates of the two pathways (polymerization and forming quinonic structure) depend on the phenols concentration, the nature of electrode, pH, solvent, additives, electrode potential and current density [25]. Electropolymerization of phenols occur on different electrodes, such as Fe, Cu, Ni, Ti, Au, Pt and other type of electrodes [26]. Deactivation of electrode due to the phenol polymerization is more characteristic in alkaline medium. Insoluble high molecular weight species blocks the electrode surface and prevents effective electrooxidation of phenol.

It is well known that cyclic voltammetry is one of the primary research means for the oxidation of organisms in electrochemical oxidation. Iotov and Kalcheva adopted cyclic voltammetry technology exclusively to study the oxidation of phenol at a platinum/gold electrode in an acid medium [27]. The electrode behavior of aniline at several conditions was investigated on a platinum, glassy carbon, and carbon fiber electrode using voltammetry techniques [28]. Kuramitz et al.

investigated the electrochemical behavior of p-nonylphenol by voltammetric techniques [29].

This work is aimed to study the electrochemical oxidation behavior of phenol, resorcinol and pyrogallol at platinum electrode in of 0.5 M H$_2$SO$_4$ solution.

2. Experimental details

Phenol, resorcinol and pyrogallol were obtained from Sigma and were used without further purification. The chemical structure of the different compounds is shown in Fig. 1. Deionized water was used for the preparation of the different solutions. Stock solutions of the different investigated materials were prepared by dissolving an appropriate amount in deionized water. Temperatures were kept constant by water circulation trough the double wall of the cell. The electrochemical cell was a three-electrode all-glass cell, the counter and working electrodes were platinum and the reference electrode was saturated calomel electrode (SCE), whose all potentials were referred. The electrolyte solutions were 0.5 M H$_2$SO$_4$ containing different concentration of phenols (0, 1, 5, 10, 15 and 20 mM). The cyclic voltammograms experiments and electrochemical impedance spectroscopic investigations were performed using a Voltalab PGZ 100 ''All-in-one'' Potentiostat/Galvanostat. The cyclic voltammetry measurements were carried out using a different potential scan rate (10, 25, 50, 75, 100, 150 and 200 mV/s). The total impedance, Z, and phase shift, θ, were measured in the frequency range from 0.1 to 10^5 Hz. The superimposed ac-signal amplitude was 10 mV peak to peak.

3. Results and discussion

3.1. Cyclic polarization measurements

Typical examples of cyclic voltammograms recorded for clean bright platinum sheet in 0.5 M H$_2$SO$_4$ solution in absence and presence 10 mM of phenol, resorcinol and pyrogallol are shown in Fig. 2. In 0.5 M H$_2$SO$_4$ solution, monolayer oxide formation occurred in the region above 0.60 V on the anodic swept and the reduction of oxide gives cathodic peak at about 0.47 V on the reverse scan. When phenolic compounds are added to 0.5 M H$_2$SO$_4$ solution, phenol and resorcinol oxidation displays one oxidation peak at potential range of 0.7–1.2 V, while pyrogallol displays two oxidation peaks at potential range of 0.4–0.55 V (Peak A1) and of 0.7–1.1 V (Peak A2).
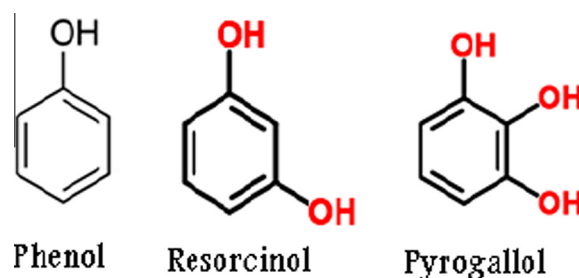

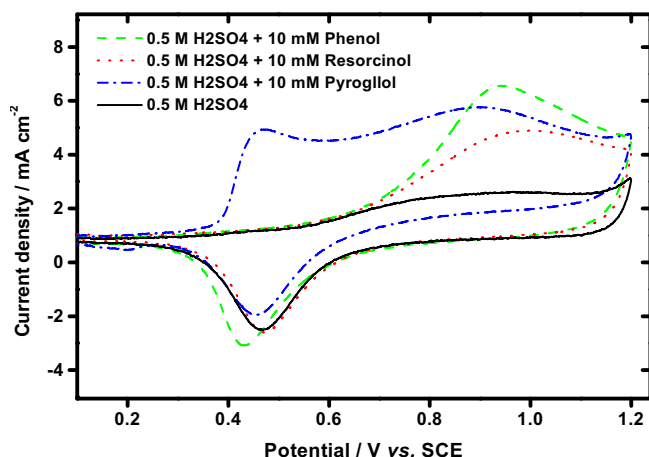**Figure 1** Structure of phenolic compounds.

Figure 2 Cyclic voltammogram of Pt in 0.5 M H$_2$SO$_4$ (—) containing 10 mM of phenol (----), resorcinol (•••••) and pyrogallol (-•-•-•) at scan rate 10 mVs^{-1}.

The electrooxidation of organic compounds on platinum electrodes can take place through the formation of an oxide film of the anode material on the electrode surface. The adsorption of the hydroxyl radical on the anode surface occurs as the first step according to the reaction [18]:

$$PtO_x + H_2O \rightarrow PtO_x(\cdot OH) + H^+ + e^- \qquad (1)$$
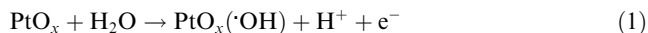
The hydroxyl radical can react with the oxygen present on the anodic oxide, producing a super oxide,

$$PtO_x(\cdot OH) \rightarrow PtO_{x+1} + H^+ + e^- \qquad (2)$$
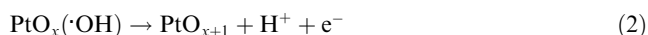
Therefore, the coexistence of two states of active oxygen on the electrode surface can be considered, a chemically adsorbed state, and a hydroxyl radical physically adsorbed. In the lack of organic material, both active oxygen stages produce O$_2$ according to reactions (3) and (4) [18].

$$PtO_x(\cdot OH) \rightarrow 1/2O_2 + PtO_x + H^+ + e^- \qquad (3)$$

$$PtO_{x+1} \rightarrow 1/2O_2 + PtO_x \qquad (4)$$
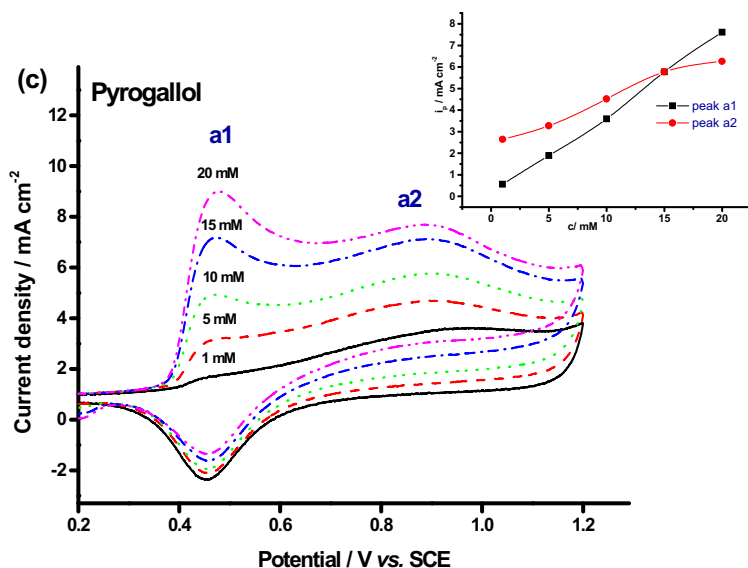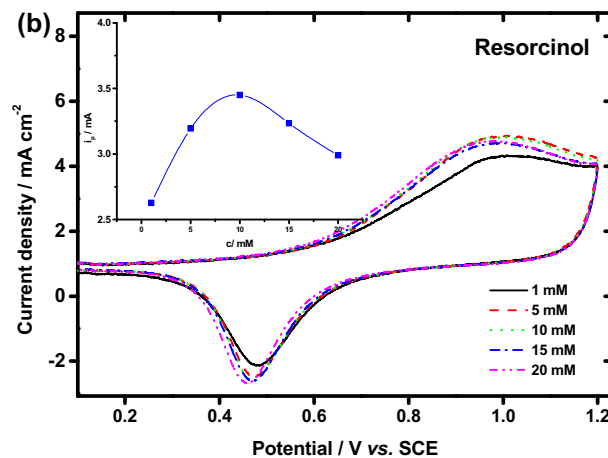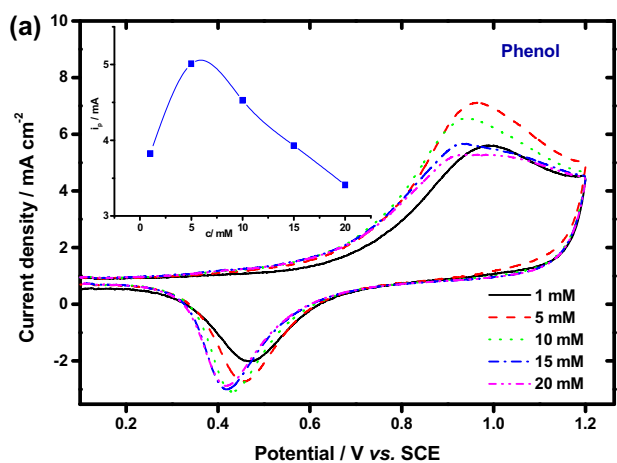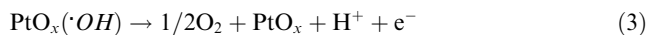
Figure 3 Cyclic voltammogram of Pt in 0.5 M H$_2$SO$_4$ solution with different concentrations of phenol (a), resorcinol (b) and pyrogallol (c). Scan rate = 10 mVs^{-1}. (inset). Dependence of the catalytic currents on the phenol (A), resorcinol (B) and pyrogallol (C) concentrations.

Scheme 1 Suggested mechanism of phenol electro oxidation.

Scheme 2 Suggested mechanism of resorcinol electro oxidation.

Thus, we can consider at the anode surface two states of "active oxygen". In the presence of oxidizable organics (R) the physisorbed "active oxygen" ('OH) should cause predominantly the complete combustion of organics, and chemisorbed "active oxygen" (PtO_{x+1}) participate in the formation of selective oxidation products [18]:

$$R + PtO_x(\text{'}OH)z \rightarrow CO_2 + PtO_x + zH^+ + ze \qquad (5)$$

$$R + PtO_{x+1} \rightarrow R_{ox} + PtO_x \qquad (6)$$

It is said that PtO and PtO_2 are formed on Pt anode surfaces. As can be seen in Fig. 2 the PtO_x formation takes place in potential range 0.4–1.2 V (SCE) in acidic 0.5 M H_2SO_4 med-

ium. At all conditions phenol, resorcinol and pyrogallol oxidation peaks are seen at potential range, which belong to PtO and PtO_2 formation region (0.4–1.2 V in H_2SO_4). Phenol oxidizes with the formation of oxide film in all worked solution. These results indicated that phenolic compounds oxidize on platinum oxide film not on Pt.

3.1.1. Effect of phenolic compounds concentration

Fig.3 shows the cyclic voltammograms of phenol (A), resorcinol (B) and pyrogallol (C) at different concentrations (0, 1, 5, 10, 15 and 20 mM) in the presence of 0.5 M H_2SO_4 solution recorded at a scan rate of 10 mV s^{-1}. The comparison of the

Scheme 3 Suggested mechanism of pyrogallol electro oxidation.

Figure 4 Successive cyclic voltammograms recorded on Pt electrode for 10 mM of phenol in 0.5 M H_2SO_4 aqueous solution at 25 °C. Scan rate: 10 mV s^{-1}.

cyclic voltammograms of the electrode obtained in the presence and absence of different compounds shows that oxidation of phenol and resorcinol takes place at an electrode potential of about 1 V, while the first oxidation peak of pyrogallol takes place at an electrode potential of about 0.45 V and the second oxidation peak takes place at 0.9 V. The peak potential of phenol is proportional to concentration and is shifted to less positive potentials as the concentration increases. The cyclic voltammograms of all investigated solutions containing phenol have the same shape. The peak potential of resorcinol and pyrogallol is not affected by increasing the concentration and voltammograms of all investigated solutions have the same shape. The oxidation peak current density versus phenol, resorcinol and pyrogallol concentration is plotted and presented in Fig. 3a–c inset. This figure shows that the peak current density increases with phenol and resorcinol concentration, reaches a maximum value and then decreases for phenol and resorcinol concentrations. This behavior may be due to a decreased activity of the electrode at high phenol concentrations, probably due to competition for active sites on the electrode surface or to the formation of a larger amount of phenoxy radicals. These radicals are involved in electropolymerization processes, causing faster deactivation of the electrode with the increase in phenol or resorcinol concentration. Since the voltammograms of phenol and resorcinol have the

same shape and the same behavior, the reaction mechanism is thought to be the same for both mediums. And the higher current values observed in phenol solutions could be explained with higher phenoxide concentration due to the higher activity of phenol. In the first step of electrooxidation of phenol phenoxy radicals are generated from phenoxide ion. The possible electrooxidation pathways for phenol are shown in Scheme 1. Rate determining step for phenolic compounds is one electron reaction, such as phenoxy radical forming.

Scheme 1 is the pathway for oxidation of phenol in acidic medium. The main oxidation peak in Fig. 3a is the oxidation of phenol resulting in phenoxy radicals (cf. Scheme 1). Further oxidation to benzoquinone of such radicals can occur, assisted by hydroxyl radicals (that are formed from water) adsorbed on the anode surface [30]. In an alternative pathway, however, phenoxy radicals undergo polymerization, this process being responsible for the fouling of the electrode. Wang and Lee [31] have observed that the fouling of the electrode by the phenolic oxidation products is more prominent at higher concentrations. Similar results have been found by other authors studying the oxidation of phenolic compounds both in acidic and in alkaline media [18,32]. In this way, for phenol concentrations below 10 mM, the peak current density increases with the concentration of phenol, while for higher phenol concentrations, the peak current density remains constant or decrease with the concentration of phenol. The analogous reaction for resorcinol is shown in Scheme 2. The radical so formed then reacts to form dimers (see Scheme 2). These dimers are more easily oxidized than the monomer [33]. Oxidation of these dimers results in oligomer formation, leading to polymer growth causing faster deactivation of the electrode. The dimers that will predominate are those which are ether linked and those that are carbon linked. The peroxide linked dimers will be highly unstable and will break up as soon as they are formed [34]. The bond dissociation energies of oxygen–oxygen bonds are less than half that of carbon–carbon bonds. For phenol the predominant form of bonding in the polymer would be carbon–carbon, but for more highly substituted phenols a greater proportion of the bonds tend to be of the ether variety [35]. Hydroxyl groups in a meta orientation interact in the same fashion as amine groups meta to each other. That is to say that one group exerts influence on the other via induction effects but not via resonance effects. Since induction effects will be minimal over the distance of three carbon atoms the groups can effectively be viewed as being isolated from each other. As before the meta orientation of the groups leads to a high degree of cross-linking in the polymer film produced
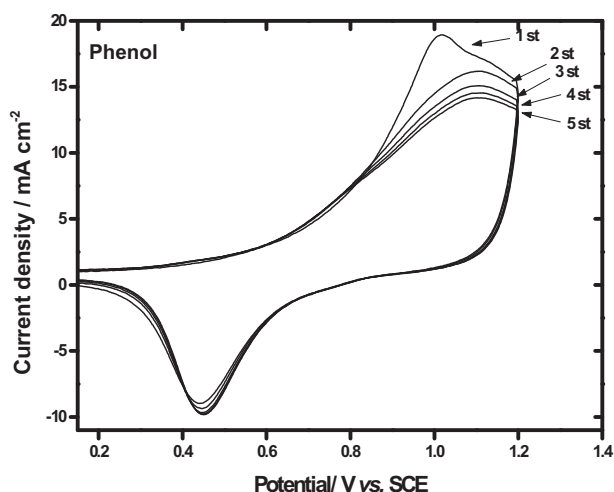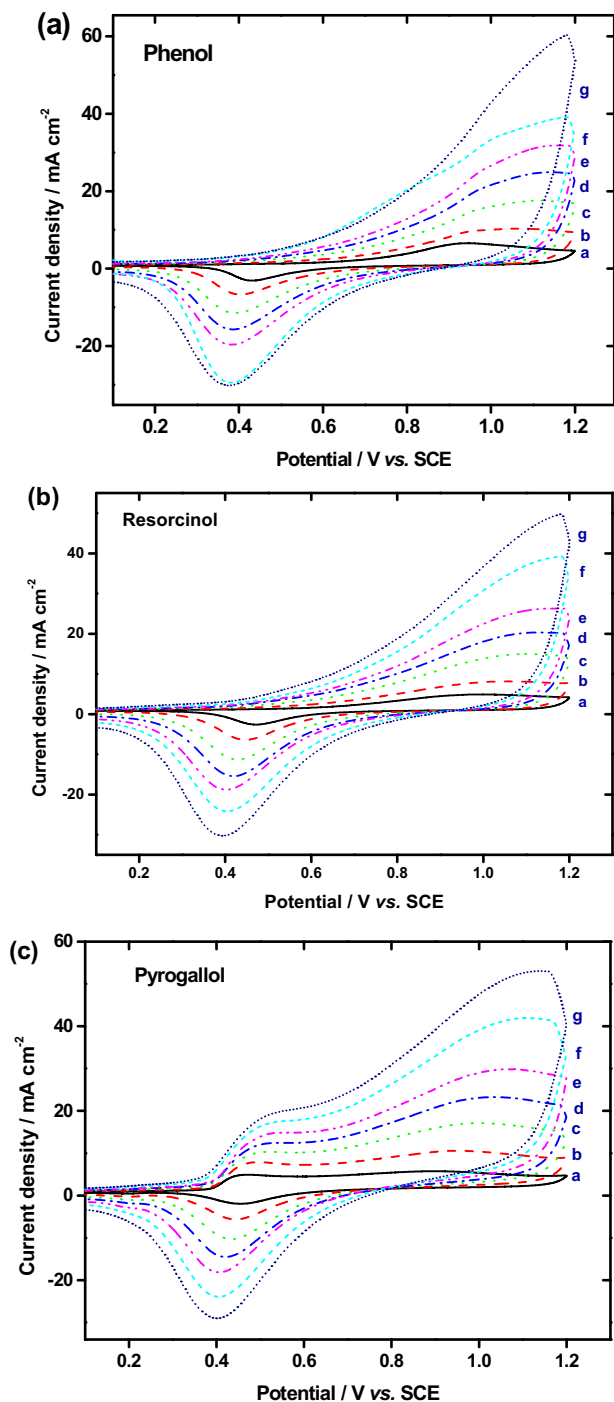
Figure 5 Cyclic voltammograms of Pt electrode in 0.5 M H$_2$SO$_4$ solution containing 10 mM of Phenol (a), resorcinol (b) and pyrogallol (c) at different scan rates. Scan rates = (a) 10, (b) 25, (c) 50, (d) 75, (e) 100, (f) 150 and (g) 200 mV s^{-1}.

Figure 6 Dependence of anodic peak current (i$_p$) on the square root of potential scan rate (v). Phenol (a), resorcinol (b) and pyrogallol (c).

[36]. It has to be said that phenol itself produces a highly cross-linked stable polymer film, indicating that the meta orientation is not as critical for 1,3-dihydroxybenzene.

Cyclic voltammograms of Pt electrode in 0.5 M H$_2$SO$_4$ aqueous solution for various concentrations of pyrogallol at a fixed scan rate of 10 mV s^{-1} at 25 °C are shown in Fig. 3c. It can be seen that the pyrogallol concentration is an important factor for oxidation. The oxidation peaks current of pyrogallol increased with the increase of concentration (cf. Fig. 3c inset) and the peak current value was proportional to the concentration. This is due to the species that formed not adhering to the electrode surface. The peak potential is less affected by increas-

(a) $\ln i_p = \{0.79 \ln v\ (V\ s^{-1})\}mA + 5.099\ mA$
$R^2 = 0.995$

(b) $\ln i_p = \{0.74 \ln v\ (V\ s^{-1})\}mA + 4.77\ mA$
$R^2 = 0.994$

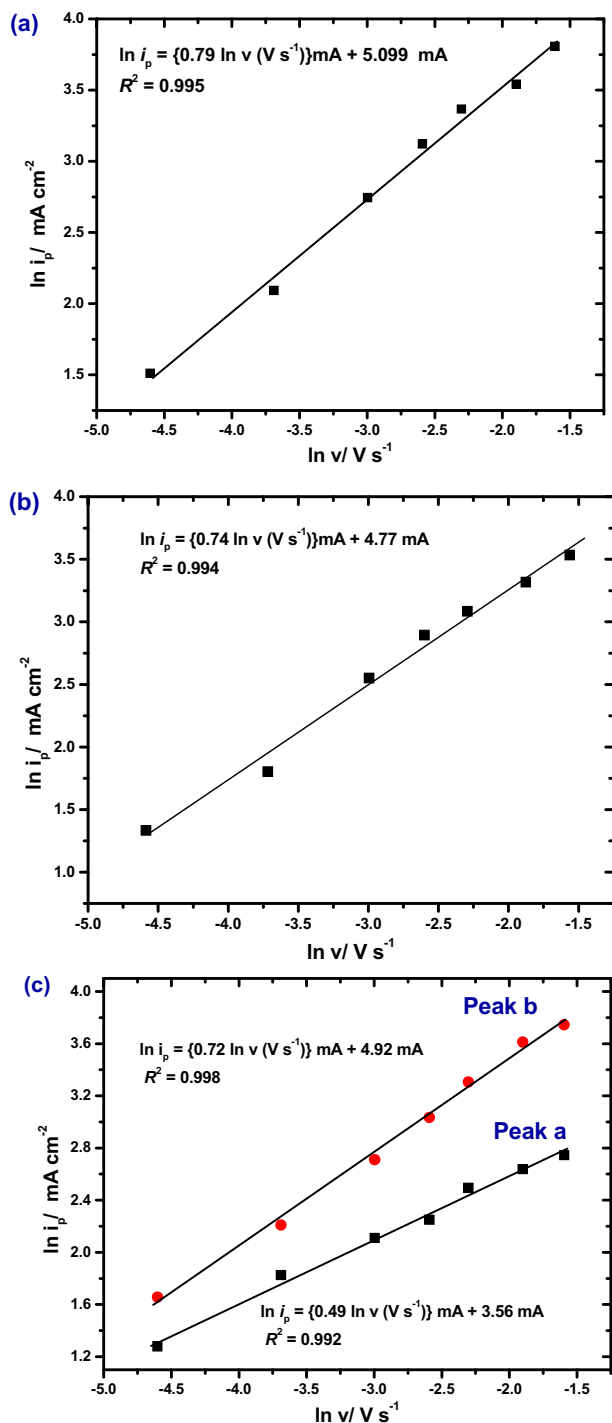**(c)** Peak b
$\ln i_p = \{0.72 \ln v\ (V\ s^{-1})\}\ mA + 4.92\ mA$
$R^2 = 0.998$

Peak a
$\ln i_p = \{0.49 \ln v\ (V\ s^{-1})\}\ mA + 3.56\ mA$
$R^2 = 0.992$

Figure 7 Dependence of anodic peak current on the potential scan rate in double logarithm coordinates for the oxidation of phenol (a), resorcinol (b), and pyrogallol (c) at Pt electrode in 0.5 M H$_2$SO$_4$.

ing pyrogallol concentration. Reaction course scheme is expressed in Fig. 2. It was found that the solution after electrolysis changed from colorless to deep yellow (see Scheme 3)

Noble electrodes usually exhibit short-lived activity for phenol oxidation as a consequence of surface fouling by adherent films, generated by polymerization of the phenoxy radicals produced in the oxidation. Then, in order to examine the elec-
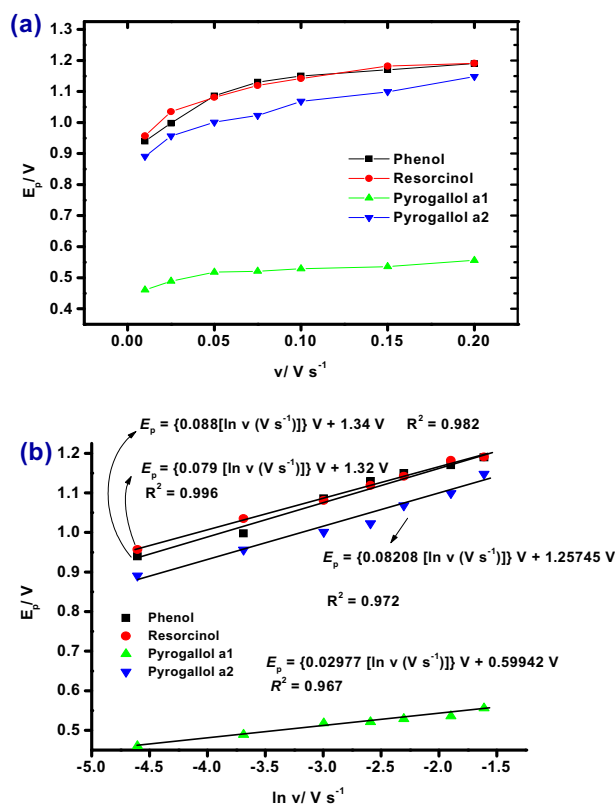

(a)

(b) $E_p = \{0.088[\ln v\ (V\ s^{-1})]\}\ V + 1.34\ V \quad R^2 = 0.982$
$E_p = \{0.079\ [\ln v\ (V\ s^{-1})]\}\ V + 1.32\ V$
$R^2 = 0.996$
$E_p = \{0.08208\ [\ln v\ (V\ s^{-1})]\}\ V + 1.25745\ V$
$R^2 = 0.972$
$E_p = \{0.02977\ [\ln v\ (V\ s^{-1})]\}\ V + 0.59942\ V$
$R^2 = 0.967$

Figure 8 (a) Dependence of peak potential, E_p, on the potential scan rate, v, for the oxidation of phenol, resorcinol and pyrogallol (10 mM) in 0.5 M H$_2$SO$_4$ at Pt electrode. (b) Dependence of peak potential on the ln v for the oxidation of phenol, resorcinol and pyrogallol in 0.5 M H$_2$SO$_4$ at Pt electrode.

trode stability, repetitive cyclic voltammograms in a solution containing 10 mM of phenol in 0.5 M H$_2$SO$_4$ at a scan rate of 10 mV s^{-1} were performed. The current involved in the oxidation of phenol drops gradually with increasing the number of cycles as can be seen in Fig. 4. However, the peak potential, Ep, value corresponding to the oxidation peak does not change with the number of cycles. This inhibition process might be attributed to the electrode fouling produced by the formation of a nonconductive polymeric product coming from phenol oxidation that blocks the electrode surface. Phenoxy radicals produce a polymer layer that inhibits the direct oxidation of phenol at the anode surface. Similar deactivation of different electrodes in the presence of aromatic organic substrates such as phenol, chlorophenols and safrole has already been reported in the literature [37–41]. So, in subsequent studies, the oxidation peak current density of the first anodic cycle was considered for analysis of results.

3.1.2. Influence of scan rate

Scan rate is one of parameters significantly affecting electrooxidation of various compounds. Thus, an effect of the scan rate on phenol, resorcinol and pyrogallol electrooxidation was investigated in the range from 10 to 200 mV s^{-1} using cyclic voltammetry method (Fig. 5). Anodic oxidation of the different compounds occurs during positive potential scan in the range of platinum oxide formation in acidic medium. Phenol, resorcinol and pyrogallol oxidation peaks current is increase
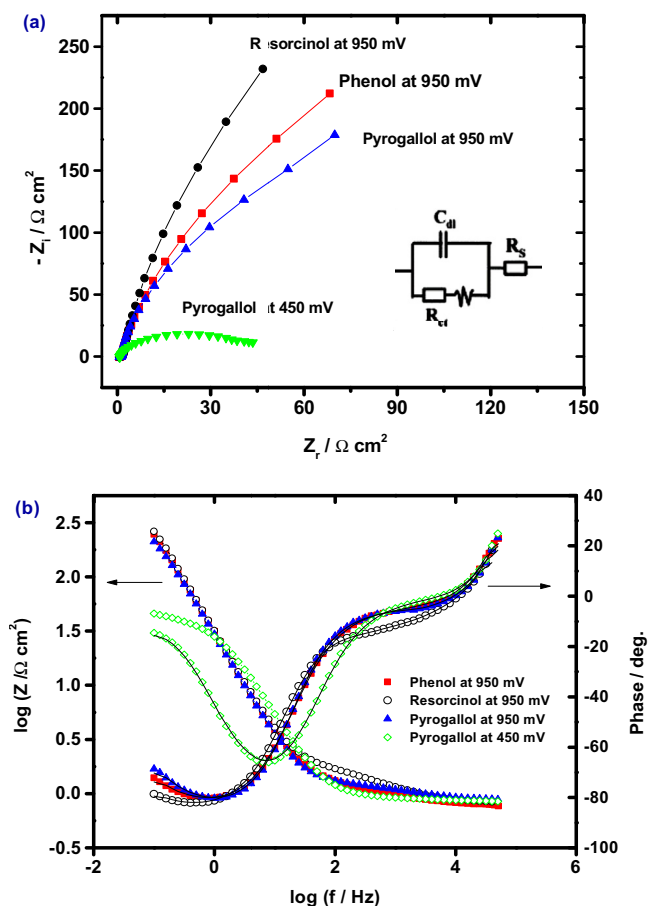
Figure 9 Presents (a) Nyquist plots and (b) Bode plots for the Pt electrode during the oxidation of 10 mM of phenol, resorcinol and pyrogallol in 0.5 M H$_2$SO$_4$. Inset in Figure 9a is the electrical circuit used in the fitting of the impedance data.

with scan rate. Anodic peak potentials, as well as the corresponding peak currents, changed with the scan rate. An increase in scan rate shifted the anodic peak to more positive potentials (Fig. 5a–c). Cyclic voltammograms were used in determination of peak current and potential for the phenols electrooxidation. Two approaches widely used to study the reversibility of reactions and to determine whether a reaction is adsorption or diffusion controlled consist of the analyses of dependences: i_p on $v^{1/2}$ and ln i_p on ln v. Figs. 6 and 7 shows these plots for the oxidation peak of phenol (Figs. 6a and 7a), resorcinol (Figs. 6b and 7b) and pyrogallol (Figs. 6c and 7c) in 0.5 M H$_2$SO$_4$. For reversible or irreversible systems without kinetic complications, i_p varies linearly with $v^{1/2}$, intercepting the origin [42]. Although, the plot of i_p on $v^{1/2}$ presented in Fig. 6 is linear, it does not cross the origin of the axes. This is characteristic for the electrodic process preceded or followed by a homogenous chemical reaction. In the scan rate range from 10 to 200 mV s^{-1}, peak current, i_p, of phenol, resorcinol and pyrogallol electrooxidation depends linearly on square root of the scan rate, v, and is described by the following equation:

For phenol

$$i_p = \left\{117.9\left[v(\text{Vs}^{-1})\right]^{\frac{1}{2}}\right\}\text{mA} - 9.4\,\text{mA} \quad (R^2 = 0.988) \qquad (7)$$

Resorcinol

$$i_p = \left\{116.4\left[v(\text{Vs}^{-1})\right]^{\frac{1}{2}}\right\}\text{mA} - 11.9\,\text{mA} \quad (R^2 = 0.988) \qquad (8)$$

Pyrogallol

$$i_p = \left\{34.63\left[v(\text{Vs}^{-1})\right]^{\frac{1}{2}}\right\}\text{mA} + 0.45\,\text{mA} \quad (R^2 = 0.995) \quad \text{Peak}A1 \qquad (9)$$

$$i_p = \left\{128.6\left[v(\text{Vs}^{-1})\right]^{\frac{1}{2}}\right\}\text{mA} - 11.55\,\text{mA} \quad (R^2 = 0.950) \quad \text{Peak}A2 \qquad (10)$$

This dependence does not cross the origin (Fig. 6a–c). This fact can suggest that the electrode process of phenol, resorcinol and pyrogallol electrooxidation is controlled by diffusion and can be preceded by chemical reaction [18]. On the other hand, a dependence of ln i_p on ln v is linear (Fig. 7) and is described by the following equation:phenol

$$\ln i_p = \left\{0.78587\ \ln v(\text{Vs}^{-1})\right\}\text{mA} + 5.094\,\text{mA} \quad (R^2 = 0.995) \qquad (11)$$

Resorcinol

$$\ln i_p = \left\{0.74\ \ln\ v(\text{Vs}^{-1})\right\}\text{mA} + 4.77\,\text{mA} \quad (R^2 = 0.995) \qquad (12)$$

Pyrogallol

$$\text{Peak}A1 \quad \ln i_p = \left\{0.49\ \ln v(\text{Vs}^{-1})\right\}\text{mA} + 3.56\,\text{mA} \quad (R^2 = 0.992) \qquad (13)$$

$$\text{Peak}A2 \quad \ln i_p = \left\{0.72\ \ln v(\text{Vs}^{-1})\right\}\text{mA} + 4.92\,\text{mA} \quad (R^2 = 0.998) \qquad (14)$$

The slopes for the different compounds are around 0.5 and indicate diffusion control of the electrode process. A slope close to 0.5 is expected for diffusion-controlled electrode processes and close to 1.0-for adsorption-controlled processes [43–45].

Fig. 8a presents a dependence of E_p on scan rate determined from cyclic voltammograms recorded for the phenol, resorcinol and pyrogallol electrooxidation. If electrochemical reaction is reversible, then E$_p$ is independent on v. Thus, it can be concluded that heterogeneous electron transfer in phenols electrooxidation is irreversible because E$_p$ increases with an increase in the scan rate. In addition, the value of the overall electron transfer coefficient for the reaction can be obtained from the following equation [45,46]:

$$E_p = \left(\frac{RT}{2\beta n_\beta F}\right)\ln v + const \qquad (15)$$

where E_p-peak potential (V), R-universal gas constant (8.314 J K^{-1} mol^{-1}), F-Faraday constant (96,487 C mol^{-1}), T-Kelvin temperature (298 K), βn_β anodic transfer coefficient, v-scan rate (V s^{-1}). This is valid for a totally irreversible diffusion-controlled process. Using the dependence of anodic peak potential on the logarithm of the potential scan rate (Fig. 8b), the value of the overall electron transfer coefficient (βn_β) was obtained as 0.146, 0.163, 0.431and 0.157 for phenol, resorcinol, pyrogallol peak A1 and peak A2 electrooxidation.

Table 1 Equivalent circuit parameters for the Pt electrode in 0.5 M H_2SO_4 solution containing 10 mM of phenol, resorcinol and pyrogallol at 25 °C.

Compounds	R_s/Ω	$R_{ct}/\Omega\ cm^2$	$C_{dl}/\mu F\ cm^{-2}$	α
Phenol at 0.95 V	1.1	551.6	722	0.98
Resorcinol at 0.95 V	1.4	673.1	945	0.92
Pyrogallol at 0.45 V	1.0	44.2	4533	0.99
Pyrogallol at 0.95 V	1.1	499	797	0.99

3.2. Electrochemical impedance spectroscopy

EIS experiments were conducted to characterize the oxidation of phenol, resorcinol and pyrogallol on the Pt electrode in 0.5 M H_2SO_4. Fig. 9a and b shows the Nyquist and Bode plots for Pt electrode during phenol, resorcinol and pyrogallol oxidation at 0.95 V. The Nyquist impedance plot (Fig. 9a) for the different compounds in acid solution at oxidation half wave potential, displayed Warburg impedance, indicating a diffusion effect. In fact the impedance diagram gives a capacitive loop and a Warburg impedance, which implies that coverage on the electrode surface with adsorbed species is low and oxidation process is still proceeding on uncovered sites. The impedance spectra with Warburg impedance and capacitive loop may be analyzed using the electrical circuits shown by Fig. 9a inset respectively. Inset in Fig. 9a is the electrical circuit used in the fitting of the electrochemical impedance data, where: R_s represents the solution resistance, R_{ct} is charge transfer resistance, W is Warburg impedance, C_{dl} represents double layer capacitance. The values of elements of circuit are calculated and presented in Table 1. In addition, only one arc can be observed on the Nyquist plot, which suggested that the electro-oxidation reaction appears to be a simple electrode process [47]. At high frequencies, the Warburg impedance becomes unimportant in relation to Rct. Also, the low value of the charge transfer resistance of the oxidation for pyrogallol and phenol at applied potential of 0.95 V than resorcinol, which means that fast electron transfer reaction. This represents the first step of the reaction which is followed by polyphenol formation on the electrode surface. It is clear that the size of the arc radius on the EIS Nyquist plot is increased by increasing the applied potential from 0.45 to 0.95 V. The lower Rct for the Pt electrode at 0.45 V compared with that of the Pt electrode at 0.95 V for pyrogallol oxidation (Table 1) indicating faster electron transport at the first oxidation than the second oxidation. Bode plot of –phase angle vs log (f/Hz) obtained for the different solutions (Fig. 9b) gave phase angles approach to −90° which is expected in ideal capacitive behavior confirming the presence of capacitive behavior of Pt electrode toward phenol, resorcinol and pyrogallol. Also, the n values obtained (Table 1) were 1.0, indicating the real-capacitive nature of the electrodes in the analyte.

4. Conclusion

The electrochemical oxidation of phenol, resorcinol and pyrogallol on Pt electrode in 0.5 M H_2SO_4 was carried out using cyclic voltammetry and electrochemical impedance spectroscopy techniques. Electrochemical oxidation of phenol

and resorcinol species is stopped due to electropolymerization and quinone- type polymeric non- soluble compounds are formed as a result of the coupling of phenoxy radicals generated in the initial oxidation step. These non-soluble solid polymeric compounds block the electrode surface and lead to electrode deactivation and prevent effective total phenol deactivation,while the oxidation of pyrogallol is not affected by the formed species. For all phenolic compounds concentrations, the presence of a peak in the anodic oxidation was verified and this peak is proportional to the scan rate and to the phenol concentration. Oxidation of phenol occurs in the range of PtO_x formations in all investigated medium.

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