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An electrochemical Study of Phenol Oxidation in Acidic Medium

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This work addresses the electrooxidation of phenol on platinum electrodes applying cyclic voltametry. The effect of different parameters on the electrooxidation of phenol, such as the scan rate, the inversion potential, the phenol concentration, the sulphuric acid concentration, and the stirring of the solution, were investigated using a conventional three-electrode cell. The results show the presence of an oxidation peak in the region around 1V *vs* Ag/AgCl to all conditions evaluated. In cyclic voltametric experiments a gradual decrease of the oxidation peak with the number of cycles was observed, and after about four cycles there was no more evidence of a peak. This behavior was repeated for all phenol and sulphuric acid concentrations studied. This suggests the deactivation or blockage of the electrode surface by the adsorption of substances and/or phenoxy radical polymerization.

Keywords: Electrochemical oxidation, phenol, cyclic voltammetry, wastewater treatment

1. INTRODUCTION

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 microbubbles [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]. Comminellis and Pulgarim [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 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. [19] investigated the oxidation and polymerization of amino-phenolic compounds in neutral solutions and they proposed a mechanism of substitution reaction, followed by oxidation and polymerization. Pacheco et al. [20] 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. [21] 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 react with other phenol molecules producing a dimer 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 (maleic and oxalic) 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].

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:

$$PtO_x + H_2O \rightarrow PtO_x(\bullet OH) + H^+ + e^- \qquad (1)$$

In a second step, the hydroxyl radical can react with the oxygen present on the anodic oxide, producing a super oxide, as follows:

$$PtO_x(\bullet OH) \rightarrow PtO_{x+1} + H^+ + e^- \quad (2)$$

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).

$$PtO_x(\bullet OH) \rightarrow \frac{1}{2} O_2 + PtO_x + H^+ + e^- \quad (3)$$

$$PtO_{x+1} \rightarrow \frac{1}{2} O_2 + PtO_x \quad (4)$$

In the presence of organic radicals (R) it is possible to produce the complete mineralization, by the action of the hydroxyl radical, or selective oxidation products (R_{ox}) can be obtained, by the interaction with the active oxygen chemically adsorbed, as shown in reactions (5) and (6).

$$R + PtO_x(\bullet OH)z \rightarrow PtO_x + zH^+ + ze^- + CO_2 \quad (5)$$

$$R + PtO_{x+1} \rightarrow PtO + R_{ox} \quad (6)$$

This work addresses the electrooxidation of phenol on platinum electrodes applying cyclic voltametry, in conditions that should not favored the polymerization in a way that the oxidation reaction occurs mainly according to reaction (5). Arslan et al. [18] observed that at low phenol concentrations and low pH values, the oxidation of phenol according to the route shown in reaction (5) has a higher probability. Nevertheless it was not possible in their studies to obtain a satisfactory result due to the blockage of the platinum electrode surface.

2. EXPERIMENTAL

Table 1 presents the solutions used at this work. All solutions were prepared using analytical grade reagents. Solutions containing phenol (Panreac) in five different concentrations of 0.5, 1, 6.25, 12.5 and 25 mM and sulphuric acid (J. T. Baker) in four different concentrations of 0.01, 0.05, 0.5 and 1 M were used. All solutions were prepared with distilled water. Acidic pH values were selected in order to prevent the undesirable phenomenon of phenol polymerization. The effect of different parameters on the electrooxidation of phenol, such as the scan rate, the phenol concentration, the sulphuric acid concentration, and the stirring of the solution, was investigated by cyclic voltametry using a conventional three-electrode cell.

The working electrode (WE) was a platinum rotating disc electrode (RDE), enclosed in Teflon, with a surface area of 0.058 cm^2. An Ag/AgCl saturated KCl electrode was used as the reference electrode (RE) and a platinum electrode was used as the counter electrode (CE). All potentials reported here are expressed with respect to the Ag/AgCl electrode. Before each electrochemical experiment, the solution was deoxygenated for 10 minutes with ultrapure nitrogen. This inert atmosphere was maintained during the whole measurement. The electrochemical experiments were controlled using a Potentiostat/Galvanostat PGSTAT20. The scan rate was varied from 10 to 200 mVs^{-1}. The initial potential was the open circuit potential, and the polarization was first in the positive direction.

Table 1. Working solutions, pH and conductivity.

H_2SO_4 Concentration (M)	Phenol Concentration (mM)	Conductivity (mS)	pH
0.01	25.0	4.25	1.92
	12.5	4.25	1.92
	6.25	4.37	1.91
	1.0	4.50	1.89
	0.5	4.31	1.92
0.05	25.0	14.65	1.10
	12.5	13.73	1.14
	6.25	13.68	1.15
	1.0	13.21	1.18
	0.5	12.10	1.23
0.5	25.0	14.75	0.45
	12.5	14.57	0.44
	6.25	14.94	0.42
	1.0	15.14	0.42
	0.5	14.60	0.47
1.0	25.0	16.34	0.21
	12.5	16.54	0.20
	6.25	16.86	0.20
	1.0	17.12	0.19
	0.5	17.71	0.19

All experiments were carried out at room temperature with a solution volume of 25 mL. Prior to each experiment, the Pt surface was mechanically polished with emery paper down to 4000 grit, and then with alumina, being the electrode finally washed with distilled water.

At last, in order to verify the possible blocking of the electrode surface due to phenol polymerization, a series of six cycles without cleaning the electrode were carried out.

3. RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltammograms of phenol at different concentrations (0, 0.5, 1, 6.25, 12.5 and 25 mM) in the presence of sulphuric acid 0.05M recorded at a scan rate of 60 mV·s^{-1}. The comparison of the cyclic voltammograms of the electrode obtained in presence and absence of phenol shows that oxidation of phenol takes place at an electrode potential of about 1 V. This peak is not proportional to concentration and is shifted to less positive potentials as the concentration increases. The presence of only an anodic oxidation peak, without cathodic counter part, suggests that the electrochemical process of phenol is totally irreversible. The cyclic voltammograms of all investigated solutions containing phenol have the same shape.

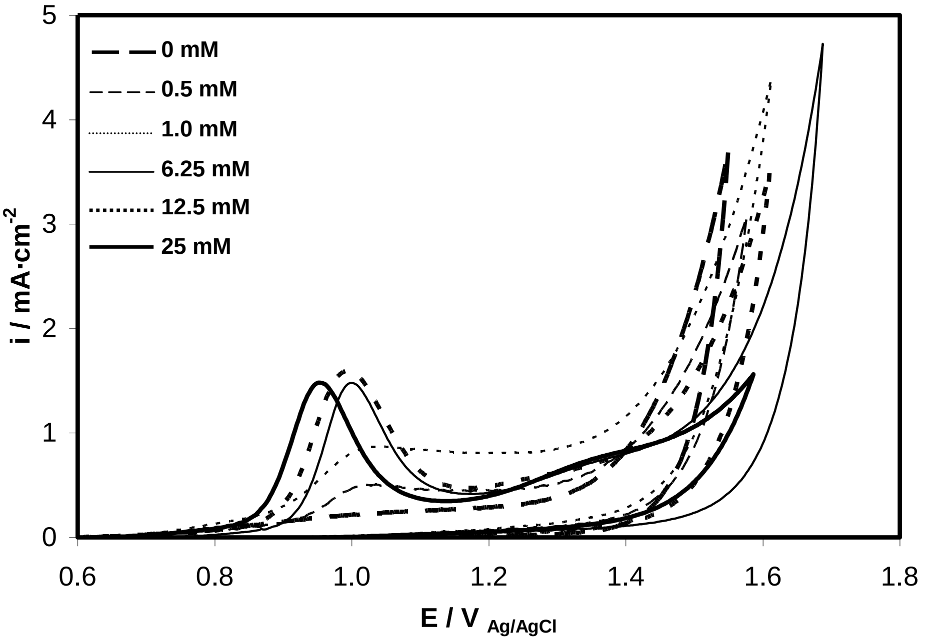


Figure 1. Cyclic voltammogram of Pt in 0.05 M H_2SO_4 solution with different phenol concentrations. Scan Rate = 60 $mV\cdot s^{-1}$. (WE = Pt, CE = Pt, RE = Ag/AgCl).

The oxidation peak current density versus phenol concentration is plotted in Figure 2 for different concentrations of sulphuric acid. This figure shows that the peak current density increases with phenol concentration, reaches a maximum value and then decreases for phenol concentrations higher than 12.5 mM. 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 concentration. Wang and Lee [25] 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, 26-28]. In this way, for phenol concentrations below 10 mM, the peak current density increases linearly with the concentration of phenol, while for higher phenol concentrations, the peak current density remain constant or decrease with the concentration of phenol. On the other hand, as can be seen in Figure 2, for a given phenol concentration, the peak current density increases with the increase of sulphuric acid concentration since the polymerization of phenol is less favored at low pH [17, 19].

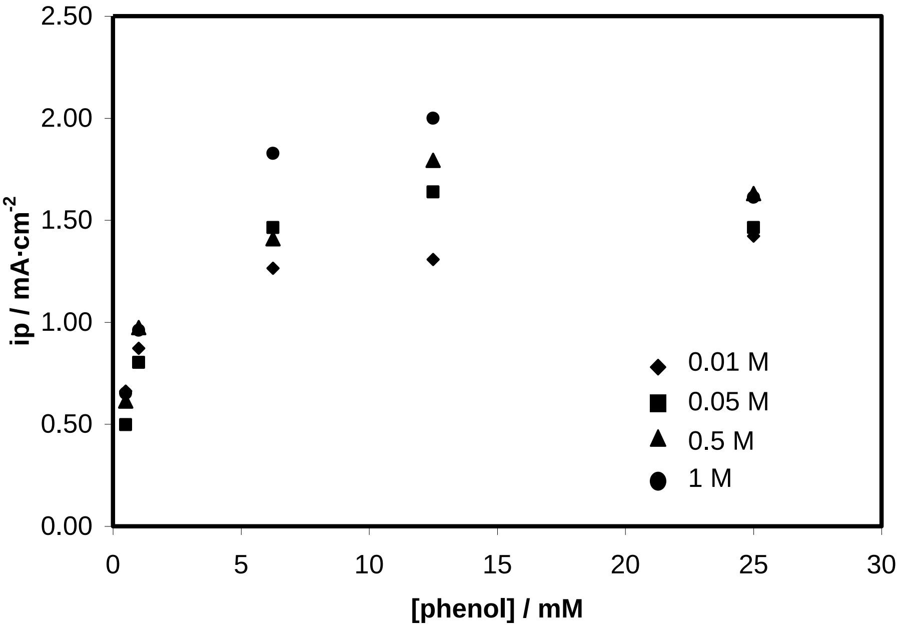


Figure 2. Peak current density as a function of phenol concentration for different concentrations of sulphuric acid.

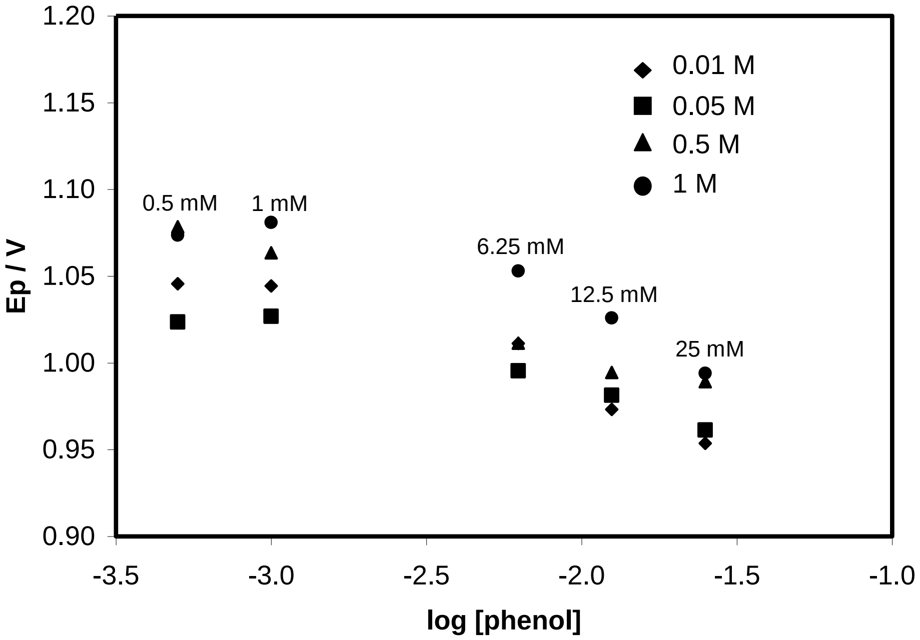


Figure 3. Peak potential as a function of phenol concentration for different concentrations of sulphuric acid.

Peak potentials are also related to phenol concentration. Figure 3 shows the variation of the peak potential with respect to the logarithm of phenol concentration for different concentrations of sulphuric acid. For phenol concentrations lower than 1 mM, the peak potential is found to be practically unchanged with the phenol concentration. However, for phenol concentrations higher than

1 mM the peak potential shifts to less anodic values, from 1 to 0.9 V, with increasing phenol concentration. Singh et al. [28] found that for phenol concentrations lower than 5 mM the peak potential was practically unchanged with the phenol concentration, while Arslan et al. [18] found that when the phenol concentration was increased to 0.1 M, the peak potential shifted to negative values both in acidic and in alkaline media. This behaviour could be explained by a more availability of phenoxy radical associated to a higher phenol concentration, which favors the oxidation reactions that occur at less anodic potentials [18].

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 electrode stability, repetitive cyclic voltammograms in a solution containing 0.5 mM of phenol in 0.5 M H_2SO_4 at a scan rate of 60 $mV\cdot s^{-1}$ were performed. The current involved in the oxidation of phenol drops gradually with increasing the number of cycles until almost zero after about four cycles as can be seen in Figure 4. However, the peak potential (E_p) 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 [28-35]. So, in subsequent studies, the oxidation peak current density of the first anodic cycle was considered for analysis of results.

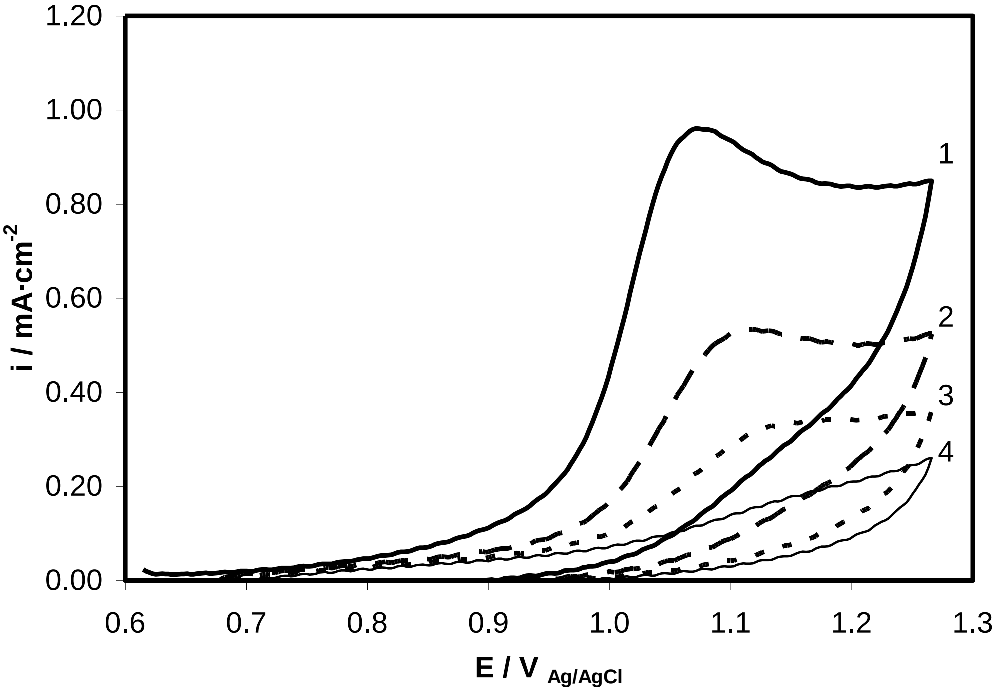


Figure 4. Cyclic voltammograms with a solution containing 0.5 mM phenol and 0.5 M H_2SO_4. Scan Rate = 60 $mV\cdot s^{-1}$. (WE = Pt, CE = Pt, RE = Ag/AgCl).

Chronoamperometry was used further to show the stability of the Pt electrode. Figure 5 displays the potentiostatic i-t curve obtained in a stirred solution of 0.5 mM of phenol at an applied potential of 1.1 V on the Pt electrode. It can be seen that the current density decreases to very low values after a few minutes due to blocking of the electrode surface by the deposition of polymeric adhesive products, as was already found in cyclic voltammetry measurements.

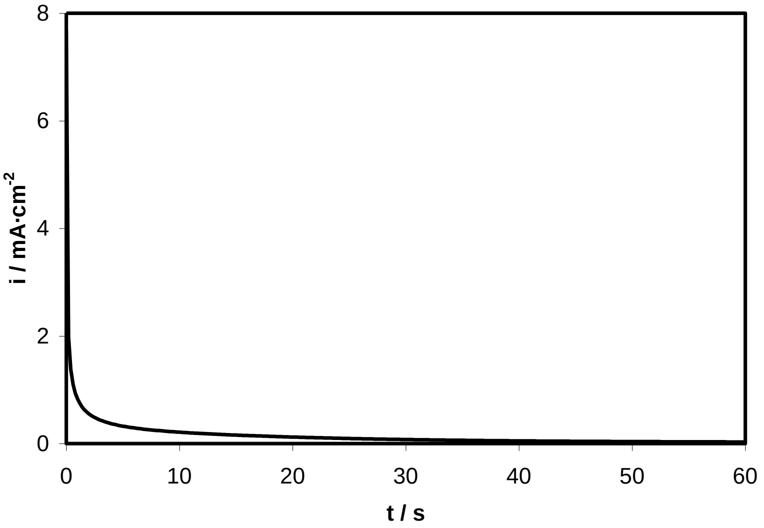


Figure 5. Potentiostatic *i-t* curves recorded at 1.1 V in a solution of 0.5 mM phenol and 0.5 M H_2SO_4. Scan Rate = 60 $mV\cdot s^{-1}$. (WE = Pt, CE = Pt, RE = Ag/AgCl).

A comparison of the cyclic voltammograms obtained at different RDE rotation rates for a phenol concentration of 12.5 mM and two sulphuric acid concentrations of 0.05 M and 0.5 M is shown in Figure 6 A and B respectively. The RDE rotation rate has no important influence on the peak height or peak potential.

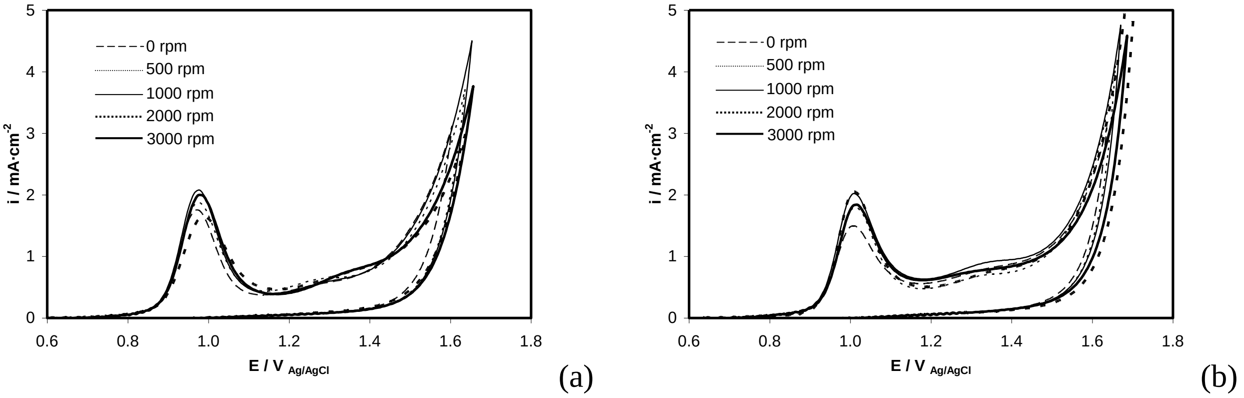
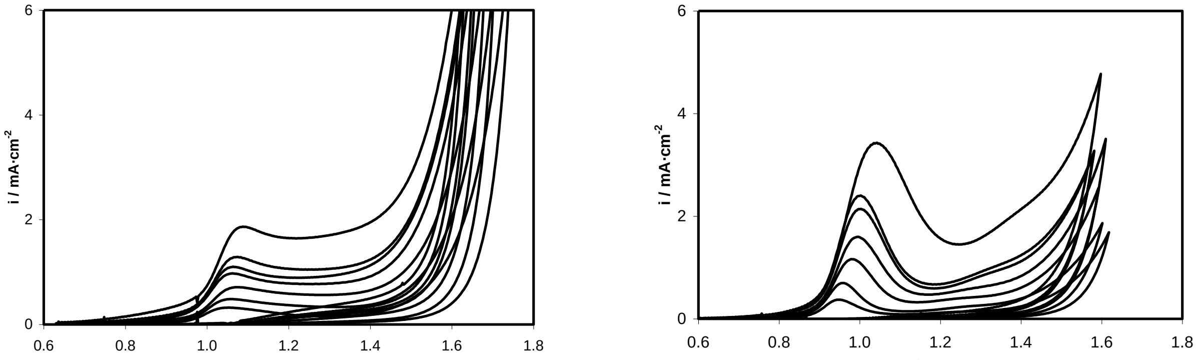


Figure 6. Cyclic voltammograms using a Rotating Disk Electrode in Solutions: (A) 12.5 mM phenol and 0.05 M H_2SO_4 and (B) 12.5 mM phenol and 0.5 M H_2SO_4. Scan Rate = 60 $mV\cdot s^{-1}$. (WE = Pt, CE = Pt, RE = Ag/AgCl).

Figure 7 shows a comparison of the cyclic voltammograms of phenol as a function of scan rate recorded at Pt working electrode for a sulphuric acid concentration of 0.05 M and two phenol concentrations of 1.0 mM and 6.25 mM (Figures 8A and 8B, respectively). Anodic peak potentials, as well as the corresponding peak currents, changed with the scan rate. An increase of potential scan rate (ν) increases the peak current density (i_p) and shifts the peak potential (E_p) in the positive direction as is typical of totally irreversible systems [27]. This effect was more pronounced for the highest phenol concentration (Figure 7 B). In all cases, the difference in the value of $|E_p – E_{p/2}|$ is much higher than the value required for a reversible process (24.7 mV at 373K) [36], indicating that, in the range of the experimental conditions used in this work, the oxidation of phenol in sulphuric acid at Pt electrode is not only controlled by diffusion but also by charge transfer kinetics.



(a) (b)

Figure 7. Cyclic voltammograms at different scan rate (10, 20, 40, 60, 80, 100 and 200 mV/s): (A) 1.0 mM phenol and 0.05 M H_2SO_4 and (B) 6.25 mM phenol and 0.05 M H_2SO_4. (WE = Pt, CE = Pt, RE = Ag/AgCl).

Experiments were performed for different sulphuric acid concentrations, since studies on this subject emphasize the influence of pH on the process of electrooxidation of phenol, and found that in strongly acidic media the oxidation reaction would be favoured.

The effect of sulphuric acid on the electrooxidation of phenol is shown in Figure 8 which represents the cyclic voltammograms obtained for two phenol concentrations of 1 mM and 6.25 mM (A and B, respectively) and different concentrations of sulphuric acid at a scan rate of 60 mVs^{-1}. As shown in Figure 8, under the conditions investigated in this work, the concentration of sulphuric acid has little effect on the peak current density, especially for pH values ranging between 0.2 and 0.4, corresponding to sulphuric acid concentrations of 1 M and 0.5 M respectively.

However, there is a significant shift in the peak potential towards more positive values at the highest sulphuric acid concentration of 1 M (pH = 0.2) for all phenol concentrations studied in this work. This shift towards more positive potential values observed at pH 0.2 may be due to a weaker influence of the polymerization phenomena and adsorption on the electrode surface in strongly acidic solutions [18].

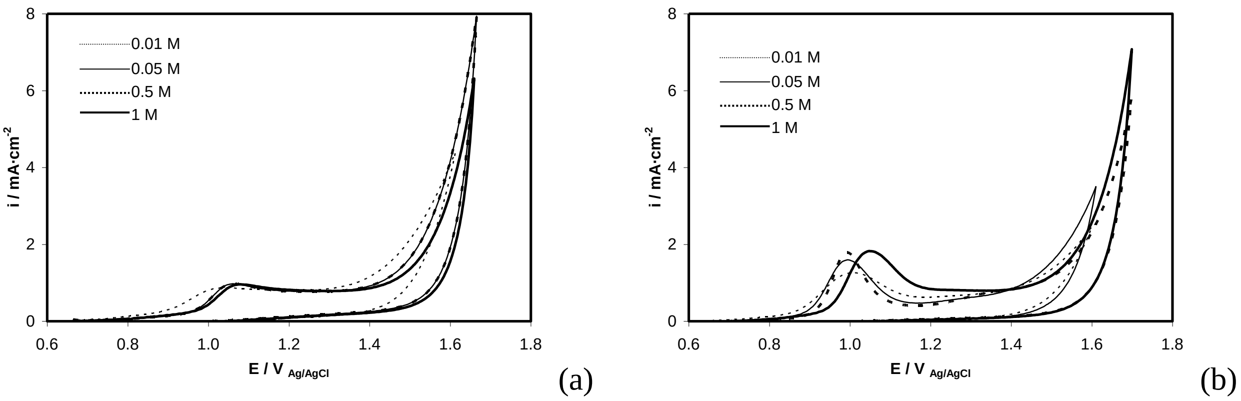


Figure 8. Cyclic voltammograms with 4 different H_2SO_4 concentrations in solutions: (A) 1.0 mM phenol and (B) 6.25 mM phenol. Scan Rate = 60 $mV \cdot s^{-1}$. (WE = Pt, CE = Pt, RE = Ag/AgCl).

From the results discussed previously, it can be concluded that under the conditions used in this work, sulphuric acid concentration has little effect on the electrooxidation of phenol, while there is a higher influence of phenol concentration in the peak current density, peak potential and in the shape of the oxidation peak. It has also been observed an increase in peak current density and a shift of the peak potential towards more anodic values with the scan rate, which may indicate an irreversible mechanism in the oxidation process of phenol.

In order to carry out a more detailed analysis of the influence of the different parameters used in this work, on the process of phenol electrooxidation, a study about the variation of the peak potential and the peak current density, associated to the scan rate, for different phenol and sulphuric acid concentrations, was accomplished.

A plot of the anodic peak potential (E_p) as a function of the logarithm of the scan rate (log ν) for the oxidation of phenol at Pt electrode is shown in Figure 9 for a sulphuric acid concentration of 0.05 M and different phenol concentrations.

For phenol concentrations below 1 mM, phenol concentration does not affect the peak potential, while for concentrations above 1 mM, the peak potential decreases with the phenol concentration. This behaviour may be due to the availability of the phenoxy radical. Thus, for low phenol concentrations, the availability of phenoxy radical is lower, so that the polymerization phenomenon, or adsorption of phenoxy radical on the electrode surface, is either less probable or slower. As a consequence, a higher peak potential will be necessary to produce the electrode surface blockage. This same behaviour was observed by Arslan et al. [18] in their studies on the electrooxidation of phenol.

The anodic peak current varied linearly with the square root of the potential scan rate, as shown in Figure 10 for a 0.05 M sulphuric acid solution with different phenol concentrations, showing that the electrode process is diffusion controlled [27, 31, 37]. It can be seen that for phenol concentrations below 6.25 mM, the peak current density increases with phenol concentration, while for concentrations higher than 6.25 mM, the peak current density does not vary with phenol concentration.

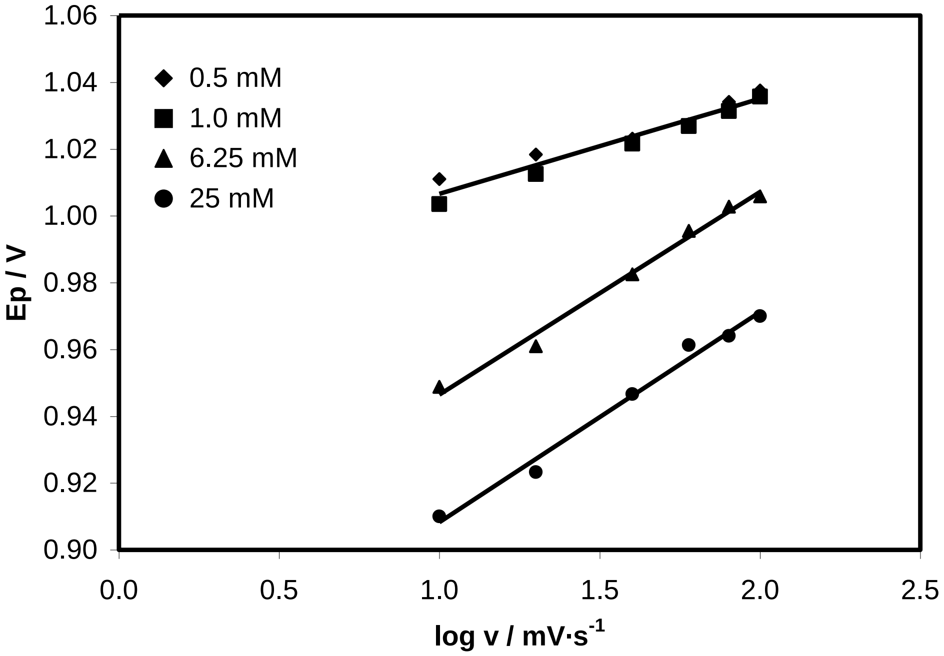


Figure 9. Peak potential as a function of the logarithm of the scan rate for different concentrations of phenol in 0.05 M H_2SO_4 solution.

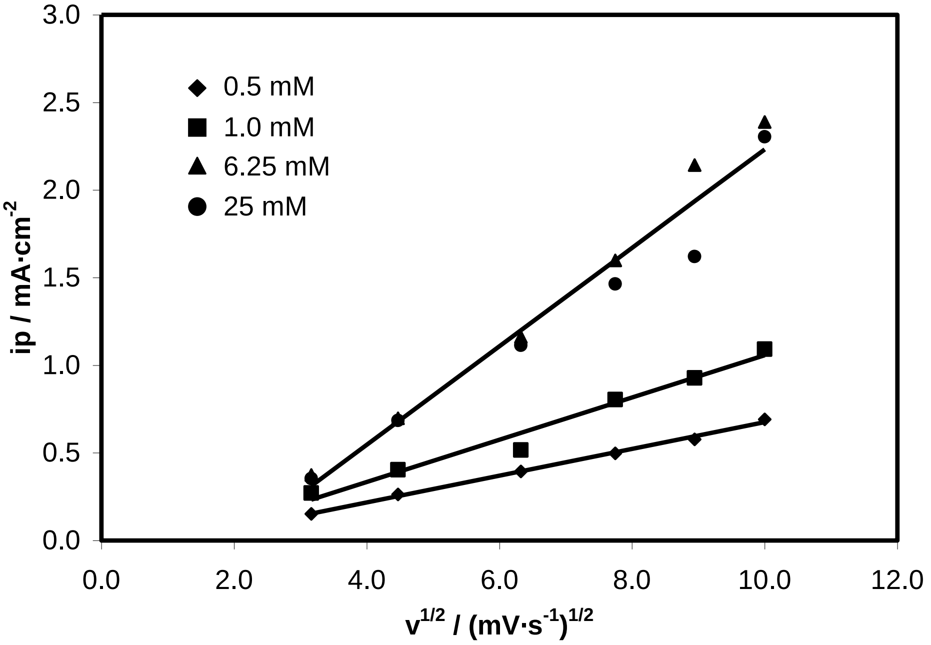


Figure 10. Peak current density as a function of the squared root of the scan rate for different concentrations of phenol in 0.05 M H_2SO_4 solution.

A plot of the anodic peak potential (E_p) as a function of the logarithm of the scan rate (log ν) is shown in Figure 11 for two different phenol concentrations (1 mM and 6.25 mM) and sulphuric acid concentrations varying from 0.01 to 1M. For both phenol solutions it can be seen that the higher the acid concentration is, the higher the peak potential is. It is also possible to see two different ranges of variation, one for the two highest sulphuric acid concentration (0.5 and 1 M), and another for the other two acid solutions, that can be associated to a weaker influence of the polymerization phenomena and adsorption on the electrode surface in strongly acidic solutions, as was commented previously.

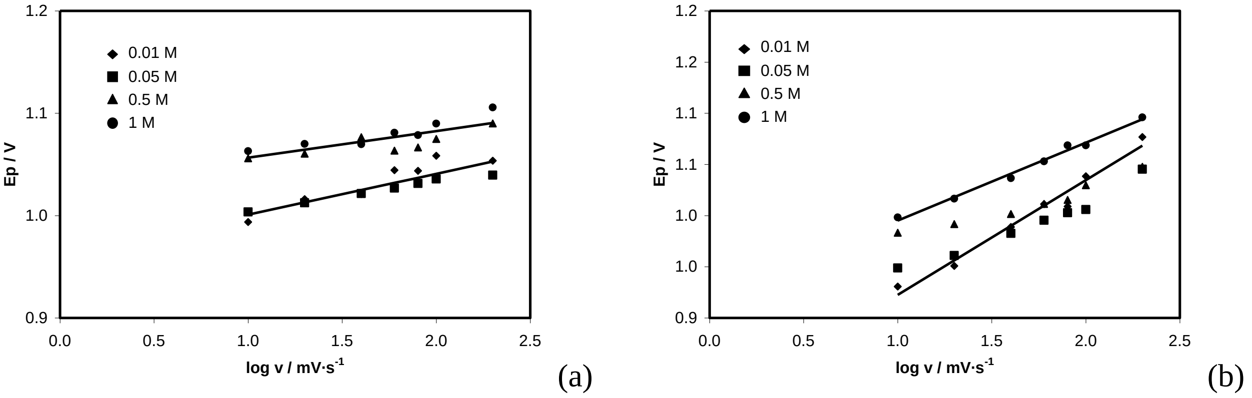


Figure 11. Peak potential as a function of the logarithm of the scan rate for different H_2SO_4 concentrations with two different concentrations of phenol: (A) 1 mM and (B) 6.25 mM.

Figure 12 shows the peak current density as a function of the square root of the scan rate for two different phenol concentrations (1 mM and 6.25 mM) and sulphuric acid concentrations varying from 0.01 to 1M. It can be seen that for both phenol concentrations the peak current density increases with the squared root of the scan rate and with the concentration of sulphuric acid.

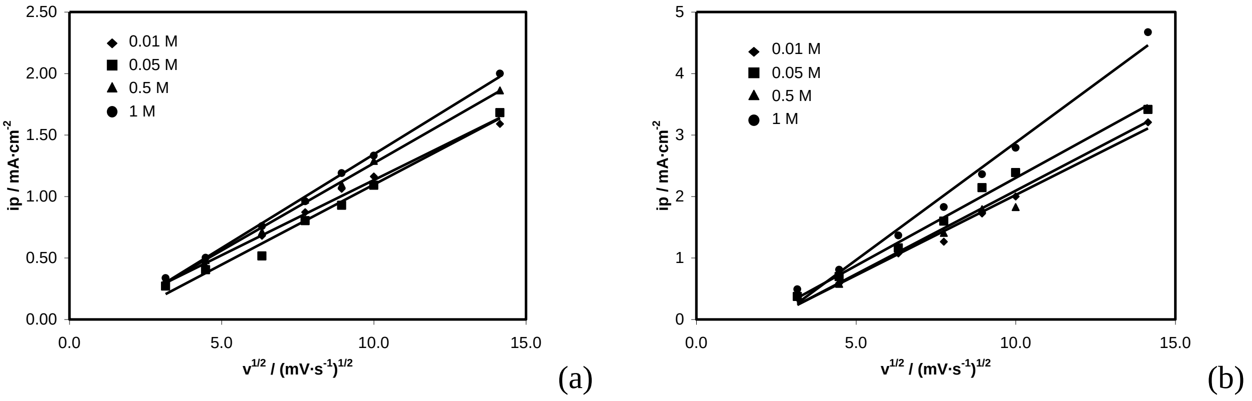


Figure 12. Peak current density as a function of the squared root of the scan rate for different H_2SO_4 concentrations with two different concentrations of phenol: (A) 1 mM and (B) 6.25 mM.

For a non-reversible process, under potentiodynamic conditions, the shift in E_p per a 10-fold increase in scan rate by is given by the following equation [36]:

$$\Delta E_p = \frac{1.15RT}{\alpha \cdot n_\alpha F} \tag{7}$$

where α is the charge transfer coefficient and represents a measure of symmetry barrier in a non-reversible electrode process, n_α is the number of electrons involved in the rate determining step, F the Faraday constant and T is the absolute temperature in K.

On the other hand, the relationship between the anodic peak current density (i_p) and the scan rate (ν) for an irreversible process is given by the following equation [36, 38]:

$$i_p = 0.496nFCD^{1/2}\left(\frac{(\alpha \cdot n_\alpha)F\nu}{RT}\right)^{1/2} \tag{8}$$

where n_α is the number of electrons transferred, D is the diffusion coefficient of the species being oxidized in $cm^2 \cdot s^{-1}$, C is the phenol concentration in the bulk solution in $mol \cdot cm^{-3}$ and ν is the scan rate in $V \cdot s^{-1}$. As can be seen in Figures 10 and 12, the peak current density is proportional to the square root of the scan rate but doesn’t pass through origin, which is also a feature of the irreversibility of the phenol oxidation process [39].

Form the slope of the linear variation of E_p with respect to the logarithm of the scan rate of the data presented in Figures 9 and 11, the value of $\alpha \cdot n_\alpha$ can be determined using equation (7). Once the value of $\alpha \cdot n_\alpha$ is known, the diffusion coefficient of phenol can be estimated from the slope of the straight lines presented in Figures 10 and 12 using equation (8). The values of $\alpha \cdot n_\alpha$ and the diffusion coefficient of phenol are presented in Table 2.

Table 2. Values of $\alpha \cdot n_\alpha$ and Diffusion coefficient of phenol.

[H_2SO_4] (M)	**0.01**		**0.05**		**0.5**		**1**	
[Phenol] (mM)	$\alpha \cdot n_\alpha$	D×10^9 ($m^2 \cdot s^{-1}$)	$\alpha \cdot n_\alpha$	D×10^9 ($m^2 \cdot s^{-1}$)	$\alpha \cdot n_\alpha$	D×10^9 ($m^2 \cdot s^{-1}$)	$\alpha \cdot n_\alpha$	D×10^9 ($m^2 \cdot s^{-1}$)
0.5	0.64	23.16	0.97	8.02	0.93	10.18	1.92	7.93
1	0.58	7.16	1.01	4.69	1.35	4.19	0.97	6.68
6.25	0.26	1.87	0.42	1.41	0.60	0.88	0.39	2.71
12.5	0.27	0.42			0.56	0.36		
25	0.29	0.12	0.36	0.10	0.53	0.12	0.56	0.13

The values of $\alpha \cdot n_\alpha$ decrease with the increase of phenol concentration and with the decrease of sulphuric acid concentration because the oxidation of phenol is favored at low phenol concentrations and in acidic solutions, where the polymerization is not favored. The calculated diffusion coefficients decrease with the increase of phenol concentration, probably due to the blockage of the electrode surface with increasing the concentration of phenol. The values obtained in this work are similar to those obtained by other authors [40], and to phenol diffusivity in water calculated as $8.47 \cdot 10^{-10}$ $cm^2 \cdot s^{-1}$ from Wilke and Chang equation [41].

4. CONCLUSIONS

In this work the electrooxidation of phenol on platinum electrodes was carried out. For all phenol concentrations and pH ranges evaluated, 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.

The peak current density is not affected by the pH variation, in the pH range studied at this work. Nevertheless there is a strong relationship between the peak current density and phenol concentration, as well as scan rates, the peak current density presenting a linear behavior related to the square root of the scan rate, which is typical of diffusion controlled processes.

Considering that the peak current density increases with the scan rate increase and is non-linear regarding to phenol concentration and that the peak potential shrinks in the positive direction with the scan rate increase, it is not possible to envisage whether the electrode blockage occurs as a function of reagents or reaction products adsorption.

On cyclic voltametry experiments there is a gradual decrease of the oxidation peak with the cycles, probably due to the adsorption of substances on the electrode surface.

Given the results of this research work, in the range of pH and phenol concentration evaluated, it is not recommended the use of platinum electrodes for phenol oxidation.

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