

The effect of pH, temperature and concentration on electrooxidation of phenol

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Abstract

The electrochemical oxidation of phenol on Pt electrode has been investigated in 1 M NaOH and 0.5 M H₂SO₄ solutions at different temperature and different phenol concentration. A simplified mechanism for the electrochemical oxidation of phenol is proposed which includes a selective oxidation parallel with PtO_x formation. Activation energy, which was obtained from the experimental data, was almost same in studied mediums. This means that electrooxidation mechanism for phenol must be same. Other thermodynamic values such as ΔS , ΔH were calculated from the experimental data.

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1. Introduction

The electrochemical oxidation of hazardous organic species is a promising method for wastewater remediation [1–13]. Phenols constitute a large group of organic pollutants due to their slow degradation, bioaccumulation and toxicity. The quantitation of phenolic compounds in environmental, industrial and food samples is currently of great interest, which can be found in soils and groundwater [14]. Also, these compounds are important synthesis intermediates in chemical industry such as resins, preservatives, pesticides, etc. [15]. Another, the main sources of phenolic waste are in glass fiber insulation manufacture on petroleum refineries. Phenol and substituted phenolic compounds such as catechol, chlorophenol are hydroquinones and discharged in the effluent from a number of chemical process industries.

Today, these compounds are found in relatively high amount in domestic and industrial wastewater, discharged mainly from the mechanical industries. Many treatment technologies are in use or have been proposed for phenol recovery or destruction.

The electrooxidation of phenolic compounds can be occurs as follows: in the first step of electrooxidation of phenol and its derivatives, phenoxy radicals are generated, then these species can be either oxidized further or be coupled, forming ether and quinone-type oligomeric or polymeric compounds [16–33]. Electropolymerization of phenol beings with the formation of the phenoxy radical and follows with the reaction with other species present in the solution forming side products, or it can react with a molecule of phenol to give predominantly a para-linked dimeric radical. This radical may be further oxidized with a loss of proton to form a neutral dimer or it may attach another molecule. The dimer may be further oxidized a 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 phenolic compounds concentration, higher concentration favoring polymerization on the electrode surface, and lower concentration the oxidation to quinonic species and the nature of electrode, pH, solvent, additives, electrode potential and current density [17]. Electropolymerization of phenols occur on different electrodes, such as Fe, Cu, Ni, Ti, Au, Pt and other type of electrodes [22–32]. Deactivation of electrode due to the phenol polymerization is more characteristic in

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alkaline medium. Insoluble high molecular weight species block the electrode surface and prevent effective electrooxidation of phenol. A weaker electrode fouling occurs on the metal oxide or boron – doped diamond [32].

The effect of pH, temperature and concentration are important parameter on electrooxidation of phenol. In this study, we have focused on a CV study of phenol in alkaline (1 M NaOH) and acidic (0.5 M H₂SO₄) medium on a Pt electrode in order to investigate thermodynamic parameters (ΔH , ΔG , ΔS , E_0) of electrooxidation reaction both mediums. Potentiodynamic cyclic voltammetry measurements provide important information on the electrochemical characterization of the species under study and are a simple method for screening the processes occurring in a wide potential range though a constant current or potential electrolysis is used more often for the practical purposes.

2. Experimental studies

Electrochemical experiments were carried out using an experimental set up consisting of CHI 604A instrument. Prior to any electrochemical experiment a standard voltammogram was recorded to check the purity of the system. All the experiments were performed at 288, 298, 313 and 333 K, under an atmospheric condition. Temperatures were kept constant by water circulation through the double wall of the cell. Cyclic voltammograms were obtained by using potentiostat in all investigated solution with different potential scan rate (30, 50, 60, 80 and 100 mV/s).

The electrolyte solutions were 0.5 M H₂SO₄ and 1 M NaOH containing with different concentration of phenol (0, 0.1, 0.05, 0.025 and 0.0125 M).

The experiments were carried out in undivided electrolytic cell. A three-electrode cell was utilized: the counter and working electrodes were platinum and the reference electrode was saturated calomel electrode (SCE), which all potentials were referred. The working and counter electrode was prepared from bright platinum sheet that have 1 cm² area and 0.5 mm thickness sealed into a glass tube with polyester. Electrochemical measurements were carried out on freshly prepared electrodes that were cleaned in chromic acid solution (3 g K₂Cr₂O₇ + 100 ml H₂SO₄).

3. Results and discussion

Typical examples of cyclic voltammograms recorded for clean bright platinum sheet in 1 M NaOH solutions, one at 288 K the others at 298, 313 and 333 K are shown in Fig. 1. In the hydrogen adsorption region (region A, -0.85 to -0.62 V) two peaks were observed on the positive sweep at all temperature and occur approximately at same potentials. B is double layer region. Double layer starts from -0.67 V and ends at about -0.30 V. At all temperature oxide formation commenced at -0.22 V (region C) and the reduction

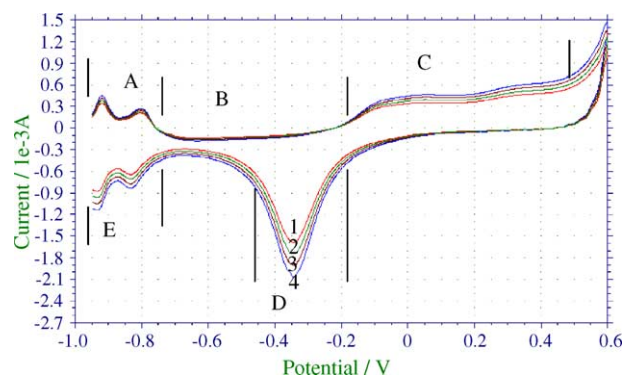


Fig. 1. Cyclic voltammogram of Pt in 0.5 M NaOH solution at different temperature. 1, 2, 3 and 4 are represents 288, 298, 313 and 333 K, respectively.

of oxide film gave rise to a peak on the negative sweep with an approximately the same potential (region D, -0.38 V) (Fig. 1). And two hydrogen adsorption peaks appeared on the subsequent negative sweep (region E): these are usually attributed to the reaction of strongly bound and weakly bound hydrogen, respectively. The maximum of these peaks shifted slightly to more positive potentials on raising the temperature.

A typical cyclic voltammogram for platinum in 0.5 M H₂SO₄ solutions at different temperatures are shown in Fig. 2. The usual two peaks (region A) can be seen at -0.20 to 0.05 V potential range on the anodic sweep. Hydrogen desorption peaks are usually seen the same region of the cathodic sweep (H_1 , H_2). Monolayer oxide formation occurred in the region above 0.80 V on the anodic sweep and the reduction of oxide gives cathodic peak at about 0.42 V on the reverse scan. Oxide reduction peak grow with the increasing temperature (Fig. 2).

When phenol is added to 1 M NaOH and 0.5 M H₂SO₄ solution, hydrogen adsorption and desorption peaks completely disappear at anodic and cathodic potential range and phenol oxidation peak occurs at potential range of 0.4 – 0.7 V

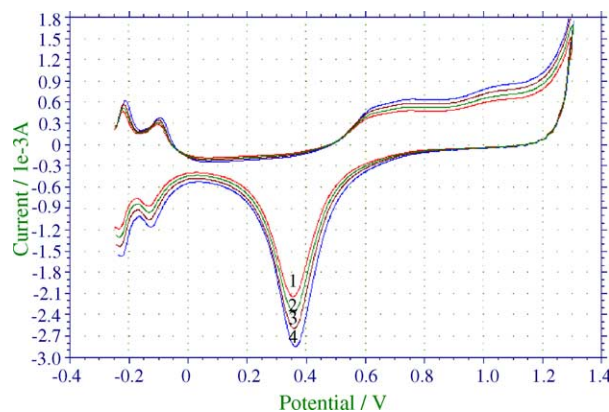


Fig. 2. Cyclic voltammogram of Pt in 0.5 M H₂SO₄ solution at different temperature. 1, 2, 3 and 4 are represents 288, 298, 313 and 333 K, respectively.

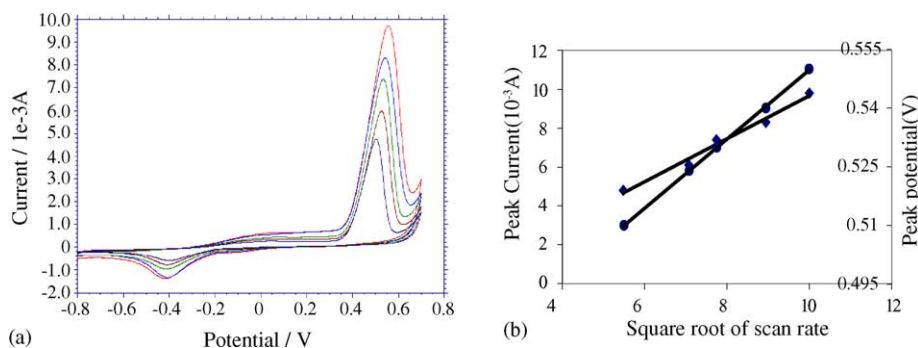
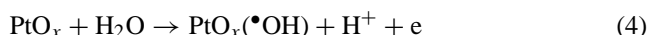


Fig. 3. (a) Cyclic voltammogram of Pt at different scan rate (100, 80, 60, 50 and 30 mV/s), (b) (◆) plot of the anodic peak current and (●) peak potential versus square root of the scan rate in 1 M NaOH + 0.0125 M phenol.

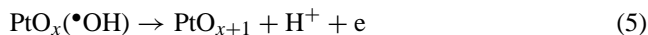
in NaOH (Figs. 3a and 5a) and 0.7–1 V in H₂SO₄ depending on temperature and phenol concentration (Figs. 4a and 6a).

Electrochemical conversion/combustion of organics on oxide anode (MO_x) can be occurs as follows (10).

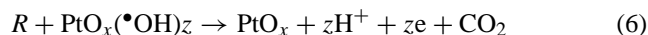
The first step is discharge at the anode to produce adsorbed hydroxyl radicals according to the equation:



In the second step, the adsorbed hydroxyl radicals may interact with the oxygen already present in the oxide anode:



Thus, we can consider that at the anode surface two states of “active oxygen” (adsorbed hydroxyl radicals and chemisorbed “active oxygen”). In the presence of oxidizable organics (*R*) the pysisorbed “active oxygen” (•OH) should cause predominantly the complete combustion of organics, and chemisorbed “active oxygen” (PtO_{x+1}) participate the formation of selective oxidation products (12):



It is said that PtO and PtO₂ are formed on Pt anode surfaces and the reactions are as follows:

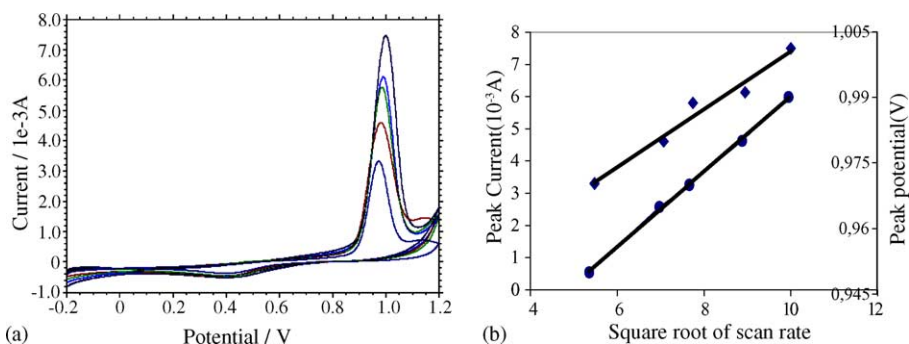


Fig. 4. (a) Cyclic voltammogram of Pt at different scan rate (100, 80, 60, 50 and 30 mV/s), (b) (◆) plot of the anodic peak current and (●) peak potential versus square root of the scan rate in 0.5 M H₂SO₄ + 0.0125 M phenol.

Table 1
Reversible potentials of platinum oxides (PtO_x)

Solutions	E (V)			
	vs./SHE		vs./SCE	
	PtO	PtO ₂	PtO	PtO ₂
1 M NaOH	0.213	0.278	-0.028	0.037
0.5 M H ₂ SO ₄	0.920	0.986	0.679	0.745



$$E = 0.980 - 0.059 \text{ pH (vs./SHE)} \quad (8)$$



$$E = 1.045 - 0.059 \text{ pH (vs./SHE)} \quad (9)$$

In our working conditions, the calculated formation potentials for PtO_x are given in Table 1

As can be seen in Figs. 1 and 2 that PtO_x formation takes place in potential range -0.25 to 0.50 V (SCE) in alkaline (1 M NaOH) and 0.5–1.2 V (SCE) in acidic (0.5 M H₂SO₄) medium. At all conditions phenol oxidation peak seen at potential range, which belongs to PtO and PtO₂ formation region (-0.30 to 0.7 V in NaOH and 0.5–1.2 V in H₂SO₄) (Figs. 1 and 2). Phenol oxidizes with the formation of oxide film in all worked solution. This results indicated that phenol oxidize on platinum oxide film not on Pt.

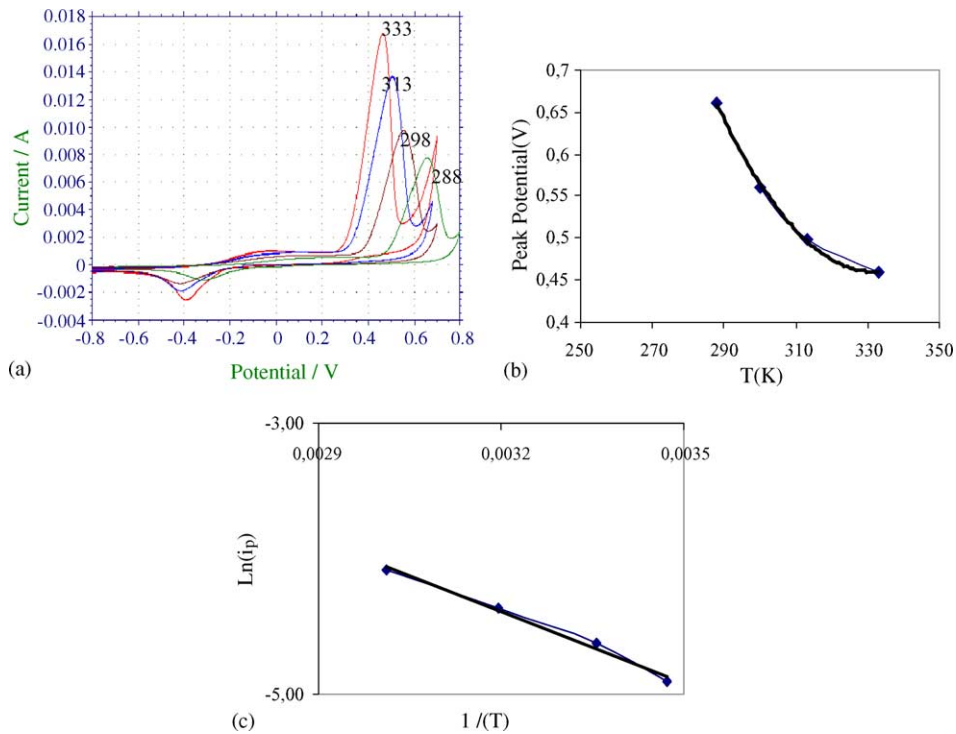


Fig. 5. (a) Cyclic voltammogram of Pt at different temperature (298, 313, 333 and 353 K), (b) the anodic peak potential versus absolute temperature and (c) logarithm of peak current versus square root of the scan rate in 1 M NaOH + 0.0125 M phenol.

4. Effect of scan rate

The potentiodynamic profiles of all investigated (which contain phenol) solutions and temperature have the same shape. The currents at the potential that the electrocatalytic

oxidation of phenol occurs grow as the concentration of phenol increase also peak current increases with temperature. However, small differences occur, depending on the concentration and temperature range. At low phenol concentrations, and low temperature peaks potentials have more

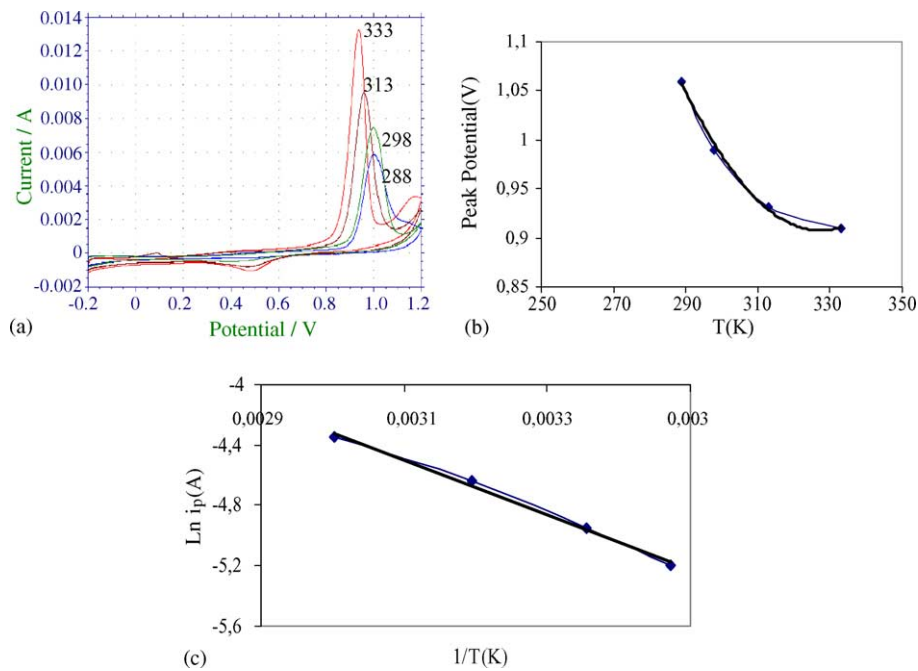


Fig. 6. (a) Cyclic voltammogram of Pt at different temperature (288, 298, 313 and 333 K), (b) the anodic peak potential versus absolute temperature and (c) logarithm of peak current versus square root of the scan rate in 0.5 M H_2SO_4 + 0.0125 M phenol.

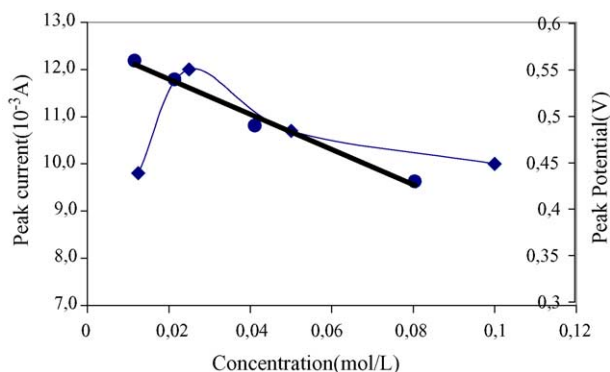


Fig. 7. (◆) Plot of the anodic peak current and (●) peak potential versus concentration of phenol in 1 M NaOH + 0.0125 M phenol.

positive value than the other. When temperature and phenol concentration increase, peak potentials shifts more negative potentials (Figs. 5a, 6a, 7 and 8).

Figs. 3a and 4a indicated that cyclic voltammogram of phenol in 1 M NaOH and 0.5 M H₂SO₄ at 298 K and cyclic voltammograms obtained at different potential scan rate. Anodic oxidation of phenol occurs during positive potential scan in the range of platinum oxide formation both alkali (0.4–0.6 V) and acidic medium (0.7–1 V). Phenol oxidation peak current is increase 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 (Figs. 3a and 4a). The dependence of the peak current and potential on the square root of the scan rate ($\gamma^{1/2}$) are shown in Fig. 3b (in NaOH) and Fig. 4b (in H₂SO₄). Under potentiodynamic conditions, the following equations described the scan rate dependence of the peak maximum [33,34].

$$I_0 = \left(\frac{nFpK}{M} \right)^{1/2} A_0(1 - Q_p)\gamma^{1/2} \quad (10)$$

$$E_p = E_0 + \left(\frac{nFpK}{M} \right)^{1/2} \left[\left(\frac{d}{\kappa} \right) + R_0 A_0(1 - Q_p) \right] \gamma^{1/2} \quad (11)$$

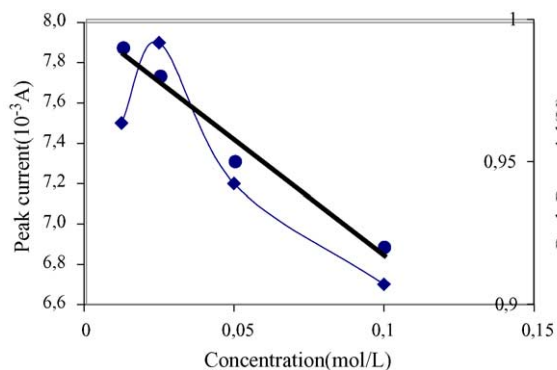


Fig. 8. (◆) Plot of the anodic peak current and (●) peak potential versus concentration of phenol in 0.5 M H₂SO₄ + 0.0125 M phenol.

The anodic peak current (i) varied linearly with the square root of the potential scan rate ($\gamma^{1/2}$) (Fig. 3b in NaOH and Fig. 4b in H₂SO₄). A linear dependence was also found between the peak potential (E_p) and $\gamma^{1/2}$, which is extrapolated to a zero scan rate gave a standard phenol oxidation potential (E_0). This E_0 values are found as 0.46 V in NaOH (Fig. 3b) and 0.90 V in H₂SO₄ (Fig. 4b).

5. Effect of temperature

Cyclic voltammograms are obtained in 0.0125 M phenol + 1 M NaOH (Fig. 5a) and 0.0125 M phenol + 0.5 M H₂SO₄ (Fig. 6a) at different temperature (288, 298, 313 and 333 K). Phenol oxidation peak grow with increasing temperature and peak potentials shifted more positive value. Peak currents are 7.4 mA at 288 K, 9.8 mA at 298 K, 14 mA at 313 K, 17.2 mA at 313 K and peak potential values are 0.66, 0.56, 0.51, 0.46 and 0.43 V, respectively at given temperatures in 1 M NaOH solution (Fig. 5a). In acidic medium, peaks currents are smaller and oxidation peaks are seen at more positive potential region than alkali medium. As seen in Fig. 6a the peak current is 5.1 mA at 1.06 V at 288 K. The phenol oxidation peak current values are at other temperatures (288, 313 and 333 K) are 7.5, 9.7 and 13.1 mA at 0.99, 0.96 and 0.93 V, respectively.

Electrochemical rate can be given as follows:

$$I = nFkC e^{-\alpha F\eta/RT} \quad (12)$$

Reaction activation energy calculated from Arrhenius equation. The dependence of rate constant on temperature over a limited range can usually be represented by an empirical equation proposed by Arrhenius

$$k = A e^{-E_a/RT} \quad (13)$$

where A is the frequency factor and E_a is activation energy. Eq. (13) may be written in the logarithmic form

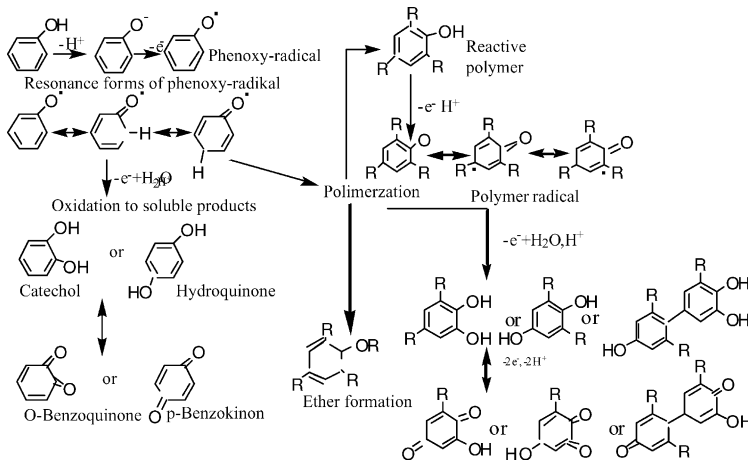
$$\ln k = \ln A - \frac{E_a}{RT} \quad (14)$$

Substituting (12) into (14) gives:

$$\ln i_p = \text{constant} - \frac{\Delta G}{RT} \quad (15)$$

When the logarithm of the peak current is plotted against the reciprocal of the absolute temperature (Fig. 5c in NaOH and Fig. 6c in H₂SO₄) a straight line is obtained and the activation energy values calculated from the slope of these lines are 14.6 and 15.2 kJ/mol in sequence. Since the activation energy values calculated for these two mediums are almost equal, the reaction mechanism is thought to be the same for both mediums. And the higher current values observed in alkaline solutions could be explained with

higher phenoxide concentration due to the pH of the solution. In the first step of electrooxidation of phenol phenoxy radicals are generated from phenoxide ion. The possible electrooxidation pathways for phenol are given below (19):



Polymerization reaction pathways of phenol (where R=hydrogen or an adjacent ring in the polymer structure)

Rate determining step for phenolic compounds is one electron reaction, such as phenoxy radical forming. The oxidation peak potential (E_p) is plotted against to temperature (Fig. 5b in NaOH and Fig. 6b in H_2SO_4); curve obtained gives slope corresponding to a thermal coefficient (dE_p/dT) equal to $-2.27 \times 10^{-2} + 6 \times 10^{-5}T$ in 0.0125 M phenol + 1 M NaOH and $-2.33 \times 10^{-2} + 6 \times 10^{-5}T$ 0.0125 M phenol + 0.5 M H_2SO_4 . Peak potential, temperature relation can be given as below for studied temperature range (288–333 K).

$$E = 4.4960 - 2.27 \times 10^{-2}T + 3 \times 10^{-5}T^2 \quad (16)$$

(for alkaline medium)

$$E = 4.9164 - 2.33 \times 10^{-2}T + 3 \times 10^{-5}T^2 \quad (17)$$

(for acidic medium)

From the measured peak potential at studied temperatures some thermodynamic properties (ΔG , ΔH , ΔS) can be calculated and are given as follows.

$$\Delta G = -nFE \quad (18)$$

$$\Delta S = nF \left(\frac{\partial E}{\partial T} \right)_p \quad (19)$$

$$\Delta H = \Delta G + T \Delta S \quad (20)$$

Thermodynamical properties of phenol oxidation reaction are calculated from Eqs. (18)–(20) for different temperatures (temperature range 100–500 K) and are plotted against temperature and shown in Fig. 9a and b at studied temperatures (288–333 K) ΔG , $T \Delta S$ and ΔH values increase with temperature. Free enthalpy change for the oxidation reaction increases with the temperature up to 378 K in alkaline solution, 388 K in acidic solution and starts to decrease after these temperatures, because, after these temperatures the main reaction tends to be the degradation of phenol and the polymer film performed in the surface and this reaction is spontaneous. $T \Delta S$ changes for the two mediums show a minimum at 189 and 194 K, respectively. This means that polymerization process takes place without any side reaction (e.g. degradation) at that temperature because the stability of the system is maxima, as the temperature increases entropy changes increase for the system. $T \Delta S$ value is negative up to 378 K in alkaline solution, 388 K in acidic medium and phenol oxidation path way is mainly polymerization (Fig. 9a and b).

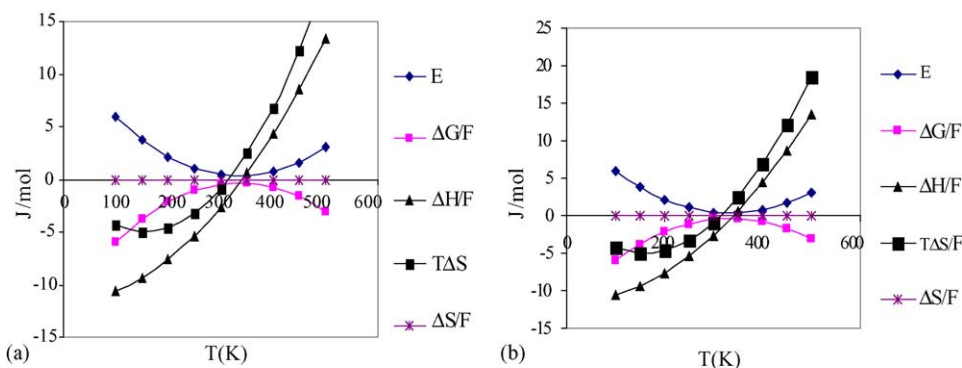


Fig. 9. Thermodynamic properties of phenol oxidation reaction and temperature relation; (a) for NaOH solution (b) for H_2SO_4 solution.

6. Effect of the phenol concentration

The cyclic voltammogram obtained for different phenol concentration (0.0125, 0.025, 0.05 and 0.1) in NaOH and H₂SO₄ at 298 K. The oxidation peak current versus *C* are plotted in Figs. 7 and 8 the increase of the peak current do not follow a linear law. The highest current value was observed for 0.025 M phenol concentration in both alkaline and acidic medium (12.0 and 7.9 mA, respectively). This can be explained by an increase in phenol concentration enables formation of a larger amount of phenoxy radicals, which are involved in electropolymerization processes, causing faster deactivation of the electrode. Peak potentials also related to phenol concentration. Peak potential more positive when the solution containing 0.0125 M phenol (0.56 V in NaOH and 0.99 V in H₂SO₄) at 298 K and phenol concentration is increased to 0.1 M, peak potential shift to negative potential value in both medium (0.43 and 0.93 V, respectively) (Figs. 7 and 8).

7. Conclusion

1. The potentiodynamic profiles of all investigated (which contain phenol) solutions and temperature have the same shape. The currents at the potential, which the electrocatalytic oxidation of phenol occurs, change with the concentration of phenol and peak current increases with temperature. However, small differences occur, depending on the concentration and temperature. At low phenol concentrations, and low temperature peaks potentials have more positive value than the other conditions. When temperature and phenol concentration increase, peak potentials shifts more negative values.
2. Oxidation of phenol occurs in the range of PtO_x formations in all investigated medium.
3. Although activation energy of phenol oxidation almost same in both medium (alkaline and acidic), phenol oxidation rate is bigger in NaOH. It can be explained that surface concentration of phenoxide ion.
4. The highest current value was observed for 0.025 M phenol concentration in both alkaline and acidic medium (12.0 and 7.9 mA, respectively). This can be explained by an increase in phenol concentration enables formation

of a larger amount of phenoxy radicals, which are involved in electropolymerization processes, causing faster deactivation of the electrode.

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