

ELECTRO-OXIDATION OF PHENOL IN ACID AND NEUTRAL MEDIA*L JOHN BERCHMANS, SHEELA BERCHMANS and R VIJAYAVALLI*

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Phenolic compounds are the major pollutants in waste water from coal and petroleum industries and their concentrations even go up to 7000 ppm. Treatment of such waste water has been a problem so long, since the tolerance limit for disposal is 1 ppm phenol. Investigations are carried out on the anodic oxidation of phenol at graphite electrode in acid and sodium chloride media using various electrochemical techniques such as linear sweep voltammetry, cyclic voltammetry and controlled potential electrolysis. The extent of oxidation was determined by electrolysis at controlled potential of + 0.98 V which corresponds to final oxidation peak. In acid medium the peak heights varied quantitatively with concentration of phenol. There is a scope of using linear sweep voltammetry as an analytical method for the estimation of phenol in acid medium.

Key words: Electro-oxidation, phenol, pollution

INTRODUCTION

It is very well known that phenolic compounds when present in water are highly toxic and contact with large quantities of phenol or even continuous contact with such polluted water can cause defects in the nervous system causing paralysis of the central nervous system and ultimate death. Even a range of 0.1 to 1 ppm in the marine environment causes considerable damage by tainting the taste of fish. Hence these compounds are necessarily to be removed for maintaining healthy environment. The tolerance limit for phenol is 1 ppm for discharging the effluent in inland surface water [1]. Hence it has become necessary to treat this water prior to discharging the same into water streams. Phenolic compounds generally are present in coal and petroleum industry effluents and the concentrations vary from 15 to 500 ppm.

Attempts have earlier been made to purify industrial waste water by anaerobic circulation biofilter [2] and activated sludge system [3]. In the latter, the efficiency of removal of phenol in a model pilot plant had been approximately 99.5%. Electrocoagulation of phenol has been tried with steel electrodes and has been found to be possible to reduce the concentration of phenol in waste water from 100 ppm to 5.6 ppm [4]. Use of ferrate ion for the treatment of waste waters containing organic compounds has been found to yield encouraging results [5]. Purification of bio-oxidized waste water containing phenol from city sewage and solid fuel processing industries has been carried out using titanium anodes coated with magnetite [6]. The electro-oxidation of phenol containing waste water has been investigated using a graphite anode for a phenol concentration of 150 ppm and a correlation between the current density to be employed and concentration of phenol has been worked out [7]. Anodic oxidation of various phenols has been investigated at a constant current on a packed bed PbO₂ electrode with electrolyte recirculation. Though the phenols are largely destroyed, their organic degradation products are found to remain in solution. 50% reduction of BOD and 96% destruction of phenolics were observed in this [8].

Anodic oxidation of phenol has been studied in aqueous sulphuric acid using platinum electrode by chronopotentiometric

method. At low concentrations of phenol the anode itself was found to be oxidized forming two kinds of products, one water soluble and the other adhering to the electrode, whereas increasing concentration resulted in the formation of the latter only, which was explained on the basis of interaction of the intermediate products with platinum oxide [9]. The passivation that resulted from such a formation was counteracted by polarisation to one to three volts for several minutes [10]. The oxidation of phenol was improved by using lead anode containing 0.5 to 2% thallium [11]. Voltammetric investigations on the oxidation of 0.3M solution has been carried out in the pH range 2-12 at a graphite electrode. The various products were identified corresponding to different pH regions [12]. Electro-oxidation of phenol in presence of sodium chloride was investigated at a graphite electrode with a view to probe the possibility of using the same for treatment of waste water. During some stages of the process, formation of tarry products and foam was observed [13]. Studies have also been reported on the anodic oxidation of phenol at various electrodes in 0.01 to 3M sodium hydroxide and it was observed that the rate of oxidation depended on the intermediates and the effective area of the anode. Silver and platinum were found to be more suitable than others [14]. The voltammetric studies on the oxidation of phenol at a platinum electrode in NaOH showed that phenol was oxidized in the potential region where oxides of platinum were formed. Formation of a dimerization product of quinone type has been suggested based on the product analysis [15]. For effective treatment of waste water different cell designs have been attempted [16,17]. Estimation of phenol in oil refining waste water has been carried out by U.V. and I.R. spectroscopy using extinction measurements at 268 or 270 nm [18].

The oxidation of phenol at a graphite electrode has now been investigated using the voltammetric techniques and the results are presented in this paper.

EXPERIMENTAL

Investigations have been carried out using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) in the oxidation of phenol. The oxidation was carried out on a specpure graphite anode with

Pt as the counter electrode. The studies were carried out from 0 to 1.2V vs saturated calomel electrode (SCE). The voltammograms were recorded on an X-Y recorder.

An airtight cell with provisions for bubbling the gas and inserting various electrodes was used. The electrolyte was 1N H₂SO₄ with varying concentrations of phenol. For finding out the effect of chloride media, NaCl (1N) was used instead of sulphuric acid. The electrolyte was deaerated by bubbling nitrogen and proper precautions were taken to avoid errors due to atmospheric oxidation of phenol prior to electrolysis. All the solutions were prepared using analar grade chemicals and triple distilled water. The electrode surface was polished prior to each experiment, to get uniformly reproducible surface.

For CV studies the scan rate was varied from 10 to 160 mV.s⁻¹ and two different concentrations of phenol namely 120 ppm (0.0012M) and 500 ppm (0.1005 M) were used.

For linear sweep voltammetry the concentration of phenol was varied from 5 to 500 ppm maintaining a constant potential scan rate of 100 mV.s⁻¹.

In order to get an idea about the reaction mechanism, coulometry was employed using 500 ppm phenol solution at + 980 mV vs SCE.

RESULTS AND DISCUSSION

Fig. 1 shows typical cyclic voltammograms obtained in 1N H₂SO₄ for a phenol concentration of 500 ppm at various scan rates.

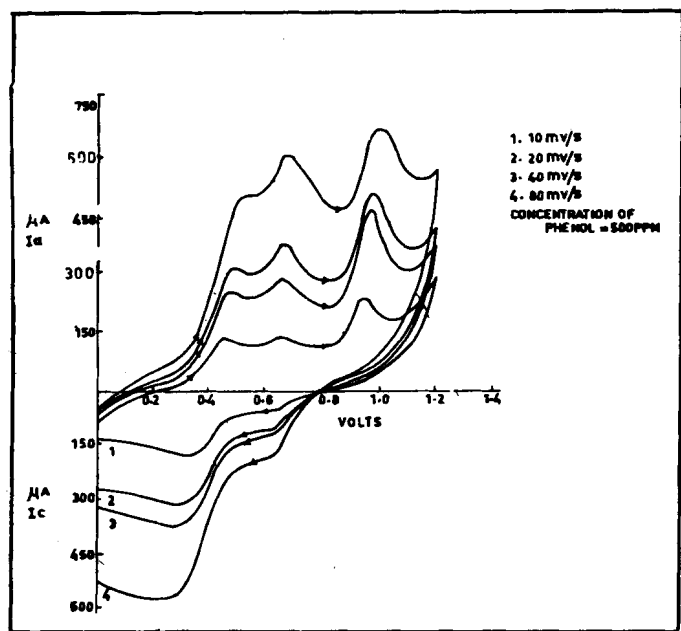


Fig. 1: Cyclic voltammograms of phenol in 1N H₂SO₄ for various scan rates (mV.s⁻¹). (1) 10 (2) 20 (3) 40 (4) 80 (concentration of phenol 500 ppm)

The curve shows three peaks at 0.45V, 0.66V, 0.98V on the anodic side and are well defined. It can be very well seen that I and II peaks do not shift whereas there is a shift observed in the case of III peak with increase in scan rate. A shift of 60 mV has been observed by increasing the scan rate from 10 to 80 mV.s⁻¹. This indicates that the reactions corresponding to anodic peaks I and II are reversible whereas that corresponding to peak III is irreversible. Two peaks have been observed in the cathodic cycle at 0.38V and 0.61V respectively. Cathodic peak I shifts with increase in scan rate to the extent of 80mV when the scan rate is increased from 10 to 80 mV.s⁻¹, while EpcII does not seem to have been altered by change in sweep rate. Difference in potential of EpaI and EpcI works out to 60 mV which suggests the reaction involves one electron transfer. On examination of peak II on anodic and cathodic side it is observed that the peak occurs exactly at the same potential at both anodic and cathodic side thereby indicating that in this process both oxidant and reactant are adsorbed.

Fig. 2 shows the cyclic voltammogram for oxidation of phenol in presence of 1N NaCl as supporting electrolyte at three different scan rates namely 10, 40 and 80 mV.s⁻¹

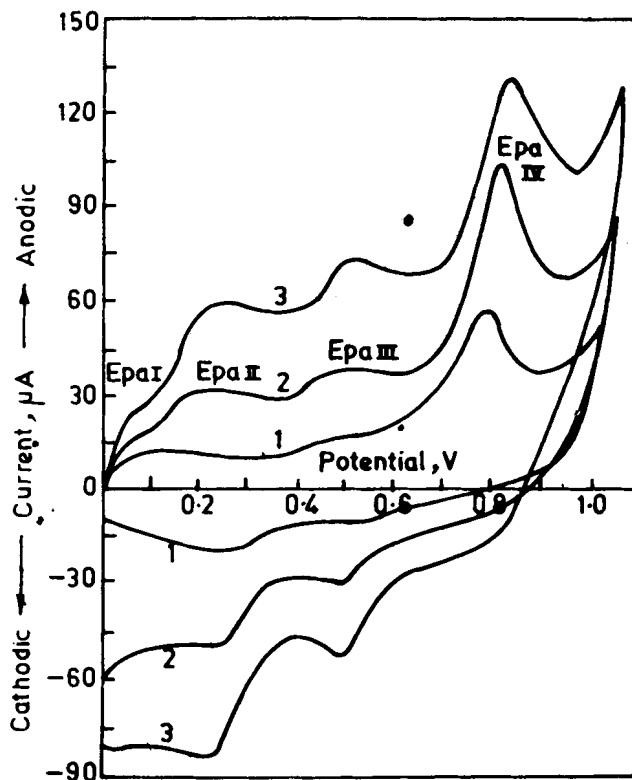


Fig.2: Cyclic voltammograms of phenol in 1N NaCl for different scan rates (mV.s⁻¹) (1) 10 (2) 40 (3) 80 (concentration of phenol 300 ppm)

It can be seen from the figure that there are four peaks on the anodic side at potentials of +0.09V, 0.24V, +0.54V and +0.850V.

The resolution of the peaks is more precise on increasing the scan rate. At low scan rates, namely, $10 \text{ mV}\cdot\text{s}^{-1}$ the peak II is absent and peak III is not very well defined. Peak I corresponds to the background, namely, sodium chloride and hence in further discussions only the three peaks corresponding to phenol will be taken into consideration. Unlike the previous case, there is a slight shift in all the three peaks with increasing scan rate and the shifts in peak potentials (E_p) for peaks II, III and IV work out to 40, 30 and 20 mV respectively when the scan rate is altered from 40 to $80 \text{ mV}\cdot\text{s}^{-1}$. On the cathodic side, there are two peaks at 0.29V and 0.52V. Both the peaks do not show any shift in potential with change in scan rate. E_{pII} and E_{pIII} have corresponding peaks on the cathodic side whereas E_{pIV} does not have any such peak.

Figs. 3A and 3B show the linear sweep voltammograms for the oxidation of phenol in $1N \text{ H}_2\text{SO}_4$. The voltammograms are obtained for different concentrations of phenol varying from 5 ppm. As observed in the CV - studies there are three peaks, out of which I_{p1} and I_{p3} have been found to depend on the concentration of phenol in solution over the range studied. However, I_{p2} has been found to slightly deviate in the low concentration range. Fig. 4 gives a plot I_p vs concentration of phenol in the concentration range from 150 ppm to 400 ppm. The curves show a linear variation for all the three peaks. Fig. 5 shows the variation of peak current for the peaks I and III for the concentration range 0-120 ppm. Though there is linearity in the peak current the slopes change remarkably when dealing with very dilute solutions (< 20 ppm). Hence it is implied that the correlation of peak currents to the concentration of phenol in presence of sulphuric acid can be used for the estimation of phenol with proper calibration curves covering the different ranges of concentration.

The electro-oxidation of phenol has been extensively studied both in the preparative organic chemistry as well as mechanistic studies of organic reactions [19-22]. Two mechanisms have been suggested [23].

Mechanism I involves a $2e$ transfer reaction and the product is 4', 4' biphenyl quinone.

Mechanism II involves a $4e$ transfer reaction and the product is p- benzoquinone.

In order to decide the final product formed at the E_{pIII} coulometric analysis was carried out at $+0.98 \text{ V}$ vs SCE in H_2SO_4 medium. The results indicate that the reaction involves four electron transfer. Hence it is evident that under the conditions of study the final product of oxidation of phenol is p- benzoquinone. It is also well known that p-benzoquinone is less toxic than phenol which can be used to advantage in the treatment of effluents containing phenol.

CONCLUSION

It is concluded that electro-oxidation of phenol can be successfully carried out as a possible method of treatment of phenolic effluents either in acid medium or near neutral solutions. The linear sweep voltammetry can be adopted for the estimation of phenol

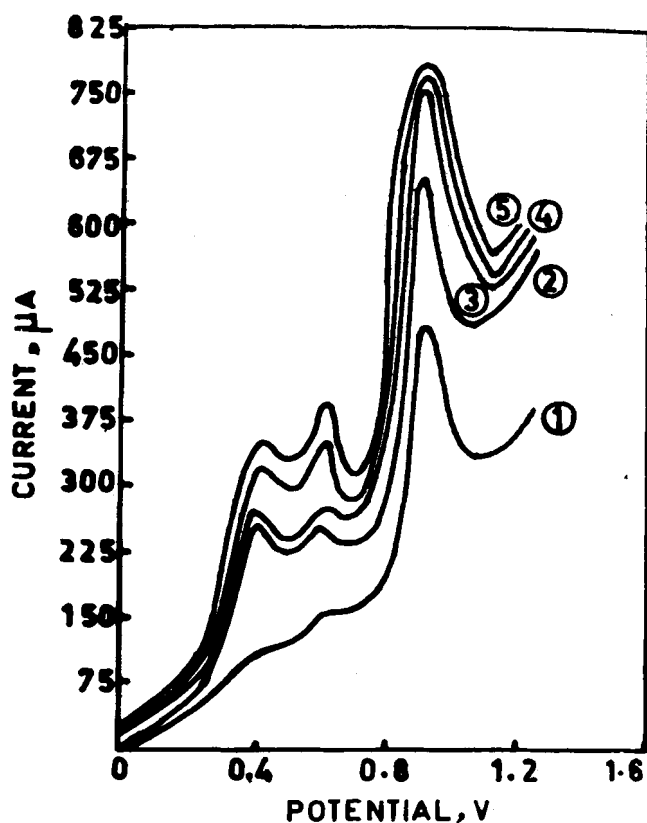


Fig. 3A: Linear sweep voltammograms for phenol in $1N \text{ H}_2\text{SO}_4$, concentration of phenol (ppm) (1) 160 (2) 250 (3) 350 (4) 450 (5) 500

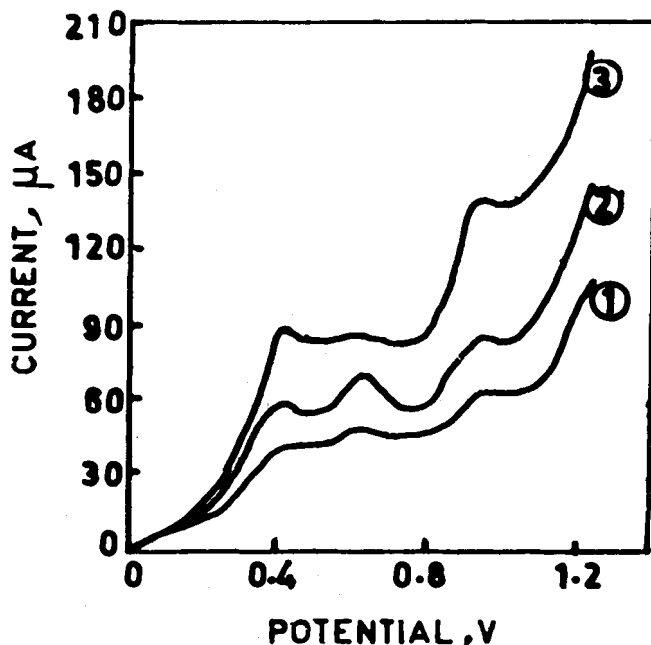


Fig. 3B: Linear sweep voltammograms for phenol in $1N \text{ H}_2\text{SO}_4$, concentration of phenol (ppm) (1) 5 (2) 10 (3) 20

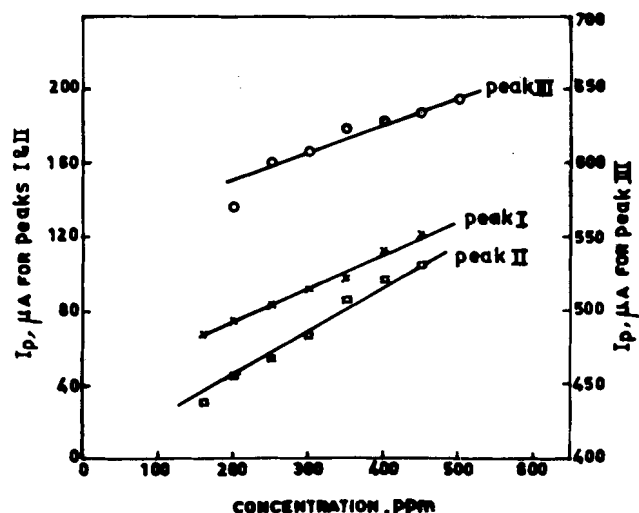


Fig. 4: Variation of peak current with concentration of phenol (150-400 ppm)

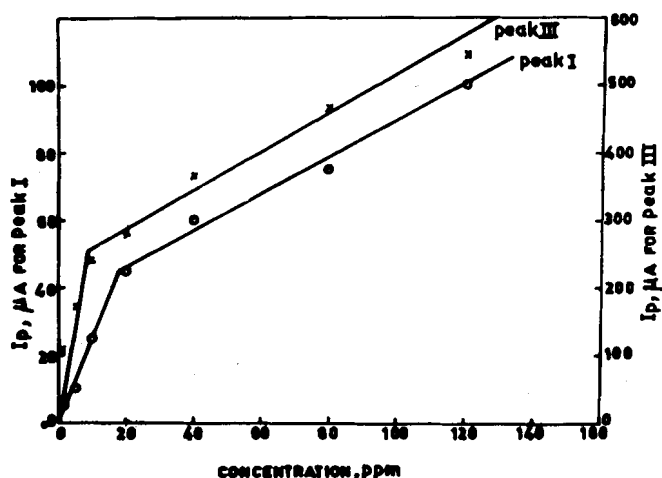


Fig. 5: Variation of peak current with concentration of phenol (0-120 ppm)

for very low concentration with the help of calibrations for different concentration ranges. This will be advantageous while considering tedious methods of estimation by chromatography or other forms of chemical analysis.

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