

## Electrochemical detection of phenol in aqueous solutions

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Phenol oxidation in aqueous solutions was carried out in a pH range of 7-12 using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) studies on a glassy carbon electrode. Peak potentials are found to be distinct for each pH value. A linear relationship is observed between the peak current and the concentration ranging from micro- to millimolar levels. The peak current is found to be proportional to the concentration of phenol up to 5  $\mu\text{M}$  that allows determination of unknown concentrations of phenol down to 5  $\mu\text{M}$ . Using DPV technique, the phenol concentration is detected up to a concentration of 0.5  $\mu\text{M}$ .

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Among the organic pollutants encountered in water, phenol and its derivatives are important and a number of industrial processes contribute to it<sup>1,2</sup>. The US EPA has listed some of the phenols as priority pollutants<sup>3</sup> due to their serious detrimental effects on aquatic organisms. The electrochemical oxidation of phenol has been attempted as a means to treat the wastewaters containing phenols and these methods are gaining increased acceptance now-a-days<sup>4-8</sup>.

In aqueous media the oxidation process is a complex one and is known to inactivate the electrode via deposition of electropolymerised films. The accumulation of reaction products, which leads to the loss of electrode activity, is a problem in analytical applications of electrode surfaces. Due to this effect, the peak current falls to negligible values immediately after the first cycle. However, it has been possible to obtain a reproducible current signal for the oxidation of phenol using the first cycle for the electroanalysis of phenol. Any electroanalytical method needs measurement of reproducible current or potential signal as a function of analyte concentration.

In electrochemical oxidation, phenol is allowed to undergo oxidation on a working electrode. Because of its attractive electrocatalytic character, platinum has been widely tried as the electrode. The investigations on Pt and Pt-alloys have shown that the electro-oxidation is often hampered by the adsorption of phenol on the electrode surface<sup>9-12</sup>. 'Will

carbonaceous surfaces, whose electronic characteristics are vastly different from that of the Pt, offer themselves as better candidates?' is a moot question. Even the electrodes like Boron Doped Diamond (BDD) that have been projected for this type of analysis have not proved useful<sup>13</sup>. Studies on carbon electrodes<sup>14,15</sup> are scarce and the present efforts are aimed to investigate the electro-oxidation behaviour of phenol on glassy carbon electrodes. The oxidation is studied using cyclic voltammetry as the analytical tool. The phenol is known to have a slightly acidic nature and hence its oxidation will be influenced by the pH of the medium in which it is oxidized. So, the effects of pH and potential sweep rate have been examined in this study to investigate the best conditions for electroanalysis.

Moreover, pollution abatement procedures can be effective and successful only when efficient methods for monitoring phenol content in water samples are available. Here too, electroanalytical methods can be used conveniently. Based on the above investigations the possibility of using CV and DPV for monitoring phenol in aqueous solutions has been carried out.

### Experimental Procedure

Electrochemical experiments were carried out using a Potentiostat-Galvanostat Autolab<sup>®</sup> PGSTAT-30 (Eco-Chemie B.V., Netherlands). A standard three electrode cell consisting of a glassy carbon (GC) disc electrode of 3 mm diameter (Bio Analytical Systems Inc.) as the working electrode, a large surface area platinum sheet as the counter electrode and a normal

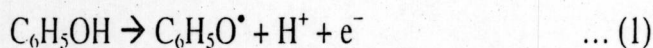
calomel electrode (potentials mentioned throughout the text are with reference to NCE only) as reference was employed for the voltammetric measurements.

All solutions were prepared using Milli-Q water and chemicals of pure and analytical grade were used. Prior to the measurements, the electrolyte solutions were prepared by appropriate dilution of the stock solution with the standard buffer solution. The standard buffer solutions used in these studies were prepared as follows: pH=12; 50 mL of 0.05 M disodium hydrogen orthophosphate and 26.9 mL of 0.1 M NaOH were mixed and made up to 100 mL. pH=9; 50 mL of 0.025 M borax and 4.6 mL of 0.1 M HCl were mixed and made up to 100 mL. pH = 7; 50 mL of 0.1 M potassium dihydrogen phosphate and 29.1 mL of 0.1 M NaOH were mixed and made up to 100 mL.

The GC electrode was polished with alumina suspensions (1  $\mu\text{m}$  and then 0.05  $\mu\text{m}$  size from BAS), washed with water and finally sonicated in water for 5 min. Cyclic voltammograms were recorded at potentials scanning from 0.0 to 1.2 V. Differential pulse voltammetry (DPV) experiments were performed in the potential range of 0.0 to 1.2 V with the following parameters: scan rate, 20 mV/s; pulse amplitude, 50 mV; pulse width, 500 ms; and sample width, 50 ms. All measurements were performed at room temperature ( $25 \pm 1^\circ\text{C}$ ).

## Results and Discussion

The phenol molecule readily undergoes electro-oxidation. Primarily, it is oxidized to phenoxy radical according to Eq. (1),



and hence is pH dependence. This radical intermediate subsequently undergoes polymerization leading to the formation of a film on the electrode surface.

Figure 1 shows the cyclic voltammogram of 50  $\mu\text{M}$  phenol in phosphate buffer (pH  $\sim$  7.0) at a scan rate of 0.02  $\text{Vs}^{-1}$ . It could be seen from Fig. 1, that the oxidation peak occurs at 0.55 V and this agrees well with the peak potential for phenol oxidation reported earlier<sup>15</sup>. During the reverse scan, no reduction peak was observed. This is attributed to the rapid polymerization reaction that consumes the oxidation product formed during the forward scan.

Cyclic voltammetric experiments reveal, that, during the second cycle the oxidation peak current

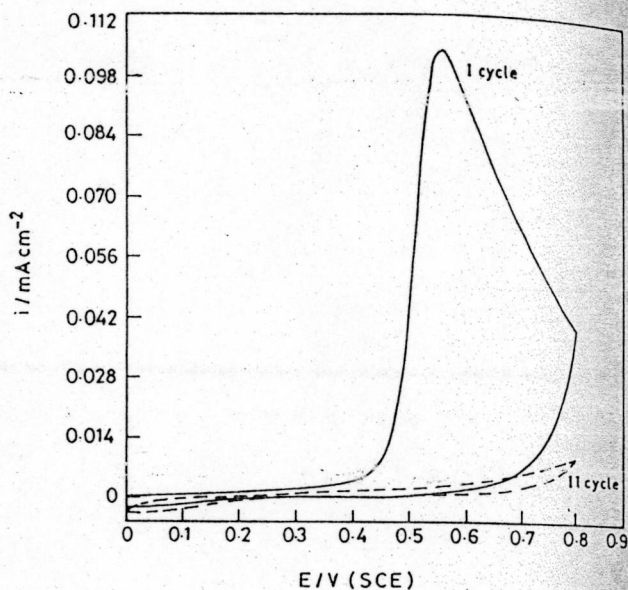


Fig. 1—Cyclic voltammogram for the electro-oxidation of 0.05 mM phenol in phosphate buffer of pH 7.0 at a glassy carbon electrode at a scan rate of 0.02  $\text{Vs}^{-1}$ .

decreases significantly. This behaviour arises due to the blocking of the electrode surface with the phenolic oxidation products. Phenol undergoes electro-oxidation possibly leading to the formation of phenoxy radical, which then undergoes polymerization with other phenol molecules<sup>16,17</sup>. This polymeric product tends to stick to the electrode surface as a film. The polymeric film, thus formed on the electrode surface, hinders/prevents diffusion of further phenoxide ions to the electrode surface for oxidation, thereby causing a significant decrease in the anodic peak current<sup>18-20</sup>. Since the polymeric film is not chemically bound to the electrode surface (*i.e.* physically stuck), its removal can be achieved by merely physically rubbing against a tissue paper.

In view of the film formation and its impact on the voltammetric behaviour during the second and subsequent cycles, the investigations in this study were confined to the CVs obtained in the first cycle under different experimental conditions, *viz.*, scan rate, concentration and pH.

The electrooxidation of phenol (50  $\mu\text{M}$ ) at pH  $\sim$  7.0 was studied at different scan rates varying from 0.005 to 0.200  $\text{Vs}^{-1}$  under experimental conditions same as in Fig. 1. The voltammetric data calculated from the CVs are presented in Table 1.

It can be seen that the peak potential shifts anodically with the increase in sweep rate which indicates that the oxidation behaves quasi-reversibly.

Table 1—Parameters derived from CV curves for electro-oxidation of phenol—Scan rate at pH~7.0

Scan rate ( $v$ ), V/s	Peak potential ( $E_p$ ), V	Peak current ( $i_p$ ), A	Square root of scan rate ( $\sqrt{v}$ )	Current function $i_p/ACv^{-1/2}$
0.005	0.518	$4.13 \times 10^{-6}$	0.07071	$5.84 \times 10^{-5}$
0.010	0.530	$4.54 \times 10^{-6}$	0.10000	$4.54 \times 10^{-5}$
0.020	0.549	$6.13 \times 10^{-6}$	0.14142	$4.34 \times 10^{-5}$
0.050	0.569	$1.21 \times 10^{-5}$	0.22361	$5.41 \times 10^{-5}$
0.080	0.576	$1.74 \times 10^{-5}$	0.28284	$6.13 \times 10^{-5}$
0.100	0.608	$2.00 \times 10^{-5}$	0.31623	$6.32 \times 10^{-5}$
0.150	0.635	$2.30 \times 10^{-5}$	0.38730	$5.94 \times 10^{-5}$
0.200	0.591	$2.70 \times 10^{-5}$	0.44721	$6.04 \times 10^{-5}$

Further, the peak-current is found to increase with the increase in scan rate, in conformity with Eq. (2).

$$i_p \propto n(\alpha n)^{1/2} D_{\text{red}}^{1/2} A C_{\text{red}} v^{1/2} \quad \dots (2)$$

where  $i_p$  is peak current in amperes,  $n$  = number of electrons,  $\alpha$  = symmetry factor (usually 0.5),  $D_{\text{red}}$  = diffusion coefficient in  $\text{cm}^2\text{s}^{-1}$ ,  $A$  = electrode area in  $\text{cm}^2$ ,  $C_{\text{red}}$  = concentration of electroactive species in  $\text{mol cm}^{-3}$  and  $v$  = potential scan rate in  $\text{Vs}^{-1}$ .

The plot of  $i_p$  versus  $v^{1/2}$  (Fig. 2,a) is linear thereby indicating that the electrooxidation of the phenol is diffusion-controlled. Moreover, the calculated current function values ( $i_p/ACv^{1/2}$ ) are seen to be constant over the range of sweep rates, which again shows that the oxidation process is diffusion-controlled.

Subsequently, the influence of phenol concentration on the CV behaviour was studied. In view of the limited solubility of phenol at neutral pH, the voltammetric experiments were restricted to a maximum phenol concentration of 10 mM and the data obtained from CVs are given in Table 2.

It can be seen from Table 2, that, the peak current increases linearly with the increase in phenol concentration up to 0.5 mM. This is obvious due to the increased availability of the electroactive species, phenol in solution, which is again in accordance with Eq. (2). At higher concentrations, no noticeable increase in peak current was observed. This suggests that, at higher concentrations, the oxidation reaction is not limited by diffusion alone. It is likely, that, at higher concentrations of phenol in solution, phenol gets adsorbed on the electrode surface and the adsorbed layer predominantly undergoes oxidation. This behaviour is possibly responsible for the absence of proportionate current increase at higher concentrations. It may be noted, that, adlayers of phenol are easily formed on platinum. Of course, Pt is

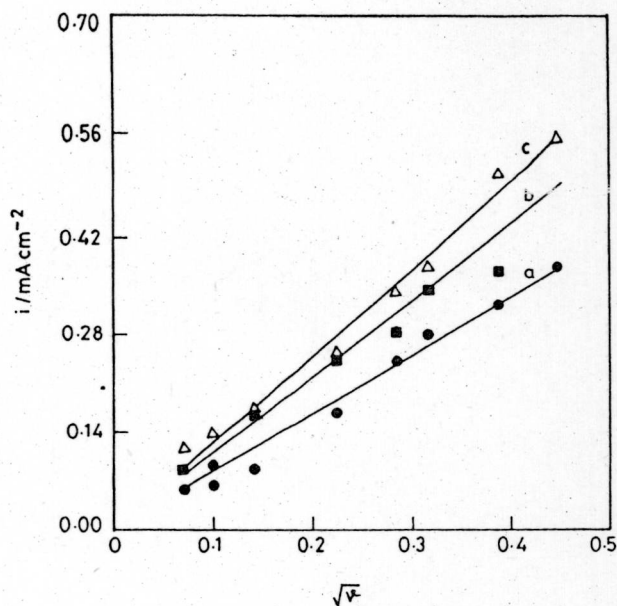


Fig. 2—Plot of variation of peak current with square root of sweep rate for phenol in buffer solution of pH (a) 7.0. (b) 9.0 and (c) 12.0.

known to favour adsorption of organics<sup>21</sup>. However, such favourable conditions do not exist for GC. Nevertheless, the restricted solubility of phenol in neutral solutions will promote the adsorption of phenol on GC surface. This supposition is corroborated from the observation of the peak potential shifting cathodically with the increase in concentration (Table 2).

It is pertinent to note, that, in solutions of high phenol concentrations (*ca.* 0.5 mM and above), the fall in peak current during the second cycle is very rapid and falls to nearly zero. On the other hand, in solutions of low phenol concentrations, the fall in peak current is gradual and becomes negligible after a few cycles. This could be attributed to complete blocking of the electrode surface by the oxidation products of the adsorbed phenol at high

Table 2—Parameters derived from CV curves for electro-oxidation of phenol – Peak current variation with phenol concentration

Phenol concentraion in mM	pH 7.0		pH 9.0		pH 12.0	
	Peak current in $\mu\text{A}$	Peak potential (V)	Peak current in $\mu\text{A}$	Peak potential (V)	Peak current in $\mu\text{A}$	Peak potential (V)
0.001	0.94	0.591	0.77	0.488	0.82	0.432
0.005	1.50	0.601	2.14	0.466	1.85	0.403
0.010	3.89	0.645	3.93	0.457	4.06	0.400
0.020	4.89	0.564	6.14	0.449	7.12	0.393
0.050	6.13	0.549	11.76	0.437	12.50	0.391
0.100	10.76	0.515	16.82	0.408	27.24	0.366
0.200	15.68	0.491	20.92	0.388	31.44	0.349
0.500	19.66	0.469	24.13	0.366	32.33	0.327
1.000	16.79	0.432	23.90	0.342	35.22	0.310
2.000	19.44	0.410	23.96	0.330	26.55	0.288
5.000	16.26	0.391	17.24	0.315	21.76	0.278
10.000	16.22	0.359	14.94	0.303	20.08	0.281

concentrations, which causes the rapid fall in peak current during the second cycle itself. At lower concentrations, the blocking effect due to oxidation products is not that much rapid as in high concentrations, but the film formation tends to be complete over a few cycles.

Figure 3b shows the cyclic voltammetric response of 50  $\mu\text{M}$  phenol at pH = 9.0 at a scan rate of 0.02  $\text{Vs}^{-1}$ . The peak potential for the phenol oxidation occurs at 0.45 V. It is seen, that, the oxidation peak potential at pH~9.0 has shifted to a less anodic value when compared to the peak potential (0.55 V) at pH~7.0. This suggests, that, at higher pH, the oxidation is energetically favoured. This observation stands in conformity with Eq. (1). As observed earlier, at this pH also, the peak current falls rapidly during the second cycle and becomes negligible upon further cycling. Similarly, no peak is observed during the reverse scan indicating the absence of any reduction process.

The oxidation of phenol at pH~9.0 was studied using 50  $\mu\text{M}$  concentration at scan rates ranging from 0.005 to 0.2 V/s and the voltammetric data are presented in Table 3. The results show that the peak current increases with the increase in scan rate, as predicted by Eq. (2). Further the plot of  $i_p$  versus  $\sqrt{v}$  exhibits a linear dependence (Fig. 2,b) indicating that the oxidation process is diffusion controlled. Also, the value of the current function [ $i_p/(ACv^{-1/2})$ ] is found to be constant over the range of sweep rates studied (Table 3).

The influence of varying the concentration of phenol on its oxidation behaviour was studied at this pH also employing a constant scan rate of 0.02  $\text{Vs}^{-1}$ . The phenol concentration was varied from 0.001 to

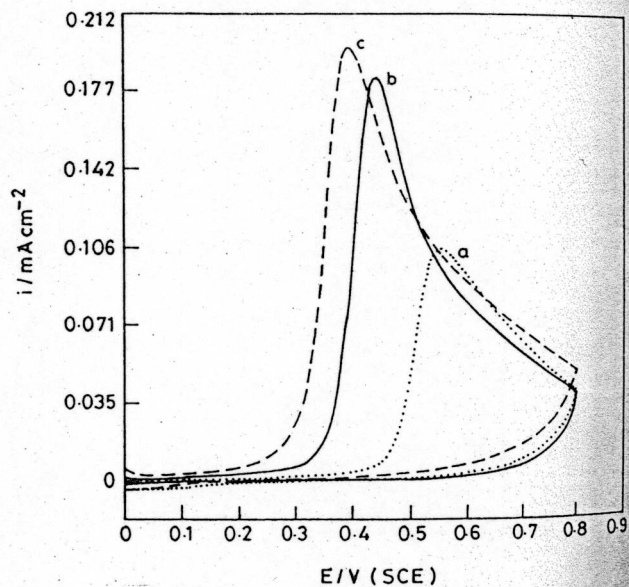


Fig. 3—First cycle cyclic voltammogram of the electro-oxidation of 0.05 mM phenol at a glassy carbon electrode at scan rate of 20  $\text{mVs}^{-1}$  in buffer solution of pH (a) 7.0, (b) 9.0 and (c) 12.0.

10.00 mM. The values of peak currents and peak potentials at different concentrations of phenol, estimated from the voltammograms are given in Table 2.

As observed earlier at pH~7.0, the anodic peak current at pH~9.0 also was found to increase with the increase of phenol concentration. However, the peak current increase was found to be linear up to 0.5 mM and at concentrations above 0.5 mM, increase in peak current could not be noticed.

The voltammetric behaviour of phenol (50  $\mu\text{M}$ ) in pH=12.0 phosphate buffer was also studied and the cyclic voltammogram obtained at 0.02  $\text{Vs}^{-1}$  is depicted in Fig. 3c. At this pH also, no reduction peak

Table 3—Parameters derived from CV curves for electro-oxidation of phenol—Effect of scan rate at pH~9.0

Scan rate (mV)	Square root of scan rate ( $\sqrt{v}$ )	Peak current ( $i_p$ )	$i_p/\sqrt{v}$	Peak potential ( $E_p$ )
0.005	0.07071	$6.00 \times 10^{-6}$	$8.48 \times 10^{-5}$	0.410
0.010	0.10000	$6.53 \times 10^{-6}$	$6.53 \times 10^{-5}$	0.422
0.020	0.14142	$1.18 \times 10^{-5}$	$8.32 \times 10^{-5}$	0.437
0.050	0.22361	$1.75 \times 10^{-5}$	$7.81 \times 10^{-5}$	0.454
0.080	0.28284	$2.01 \times 10^{-5}$	$7.12 \times 10^{-5}$	0.464
0.100	0.31623	$2.44 \times 10^{-5}$	$7.73 \times 10^{-5}$	0.471
0.150	0.38730	$2.64 \times 10^{-5}$	$6.81 \times 10^{-5}$	0.479
0.200	0.44721	$4.00 \times 10^{-5}$	$8.94 \times 10^{-5}$	0.483

Table 4—Parameters derived from CV curves for electro-oxidation of phenol – effect of scan rate at pH~12.0

Scan rate (mV)	Square root of scan rate ( $\sqrt{v}$ )	Peak current ( $i_p$ )	$i_p/\sqrt{v}$	Peak potential ( $E_p$ )
0.005	0.07071	$8.36 \times 10^{-6}$	$1.18 \times 10^{-4}$	0.361
0.010	0.10000	$9.87 \times 10^{-6}$	$9.87 \times 10^{-5}$	0.376
0.020	0.14142	$1.25 \times 10^{-5}$	$8.84 \times 10^{-5}$	0.391
0.050	0.22361	$1.83 \times 10^{-5}$	$8.18 \times 10^{-5}$	0.405
0.080	0.28284	$2.44 \times 10^{-5}$	$8.63 \times 10^{-5}$	0.410
0.100	0.31623	$2.69 \times 10^{-5}$	$8.51 \times 10^{-5}$	0.413
0.150	0.38730	$3.64 \times 10^{-5}$	$9.40 \times 10^{-5}$	0.413
0.200	0.44721	$3.96 \times 10^{-5}$	$8.85 \times 10^{-5}$	0.422

was observed during the reverse scan. The phenol oxidation occurs at a peak potential of 0.39 V. During second and subsequent cycles the anodic peak current decreases rapidly, analogous to the behaviour noted earlier at other pH. The peak potential shifted to a less anodic value (0.391 V) at this pH, when compared to the peak potentials of 0.55 and 0.45 V at pH~7.0 and 9.0 respectively. The  $pK_a$  for phenol<sup>22</sup> is 10.0. Hence, at pH~12.0, phenol will readily dissociate and be present mostly as phenolate anion. The oxidation of the anion, as indicated by Eq. (3) should be relatively easier compared to the undissociated phenol molecule.



This is obvious from the fact that the oxidation peak potential at pH~12.0 is cathodically shifted compared to the values noticed at lower pH conditions.

At pH 12.0, the oxidation of phenol (50  $\mu$ M) was studied at different sweep rates and the voltammetric data are presented in Table 4. The results show a linear dependence of peak current on square root of scan rate (Fig. 2,c), indicating that the oxidation is diffusion-controlled. Also, the calculated values of current function tending to be a constant at the entire

sweep rates studied support the diffusion-controlled nature of the oxidation.

The effect of phenol concentration on its electro-oxidation at pH=12.0 was studied at a constant sweep rate of 0.02  $Vs^{-1}$  and the concentration was varied from 0.001 to 10.00 mM. The results obtained at different concentrations are presented in Table 2. The oxidation current was found to increase with the increase of phenol concentration. However, as noticed earlier, the peak current increase was found to be linear in the range of 0 to 0.5 mM and thereafter tends to be concentration-independent. This is analogous to the behaviour observed earlier in other pH conditions.

#### Effect of pH

The results of the electro-oxidation of phenol at three different pH conditions presented in Table 2 reveal, that, as pH is increased, the oxidation peak potential shifts cathodically indicating that the oxidation is facilitated. Phenol is known to be weakly acidic in character, increase of pH would facilitate the abstraction of  $H^+$  from the phenol molecule [Eq. (1)], which in turn will help to bring down the overpotential for oxidation reaction. Further, it is seen that this cathodic shift is more pronounced at lower concentrations of phenol. Typically at 10  $\mu$ M solution,  $E_{pa}$  shifts from 0.645 to 0.400 V, while at

10 mM concentration it shifts from 0.359 to 0.281 V. This possibly arises from the oxidation reaction being progressively dominated by adsorbed phenol molecules at higher concentration, while at lower concentrations it is almost diffusion-controlled.

Also, the data in Table 2 shows, that, at any pH, the  $E_{pa}$  shifts cathodically as concentration is increased. As discussed earlier, it could be attributed to the oxidation of adsorbed phenol predominating over that of bulk species. Moreover, it could be noticed that this cathodic shift is more pronounced at lower pH. Typically, at pH~7.0, the peak potential shifts from 0.591 to 0.359V as concentration is increased from 0.001 to 10 mM. However, at pH~12.0, the shift is from 0.432 to 0.281 V only. This suggests that the tendency for the adsorbed phenol predominating over bulk molecules in oxidation reaction decreases as pH is increased and is comparatively less at higher pH conditions. This is understood that, because of its acidic character, increase of pH enhances the solubility of phenol in solution. This, in other words would decrease the tendency for adsorption.

The variation of oxidation peak currents also supports this view. At low concentrations, typically below 10  $\mu\text{M}$ , the solubility is not influenced by pH and thus the peak current values are nearly the same under three pH conditions. At higher concentrations (above 5.0 mM), the oxidation of adsorbed molecules tends to dominate and hence no significant changes in peak current are seen, as pH is varied. In the intermediate concentration range, where the oxidation process is predominantly diffusion-controlled, increase of pH yields enhancement of peak current.

#### Estimation of phenol by CV and DPV

The above studies have shown that the electro-oxidation of phenol, especially at low concentrations, follows diffusion-controlled kinetics and the oxidation behaviour, as evidenced by the voltammograms, gets inhibited in the second and subsequent cycles. In view of the above observation, the electroanalytical estimation of phenol in solution could reliably be carried out using the characteristics of the first cycle voltammogram. Further, the present investigations have also shown that the voltammetric peaks are well-defined only at concentrations above 5  $\mu\text{M}$ . The limitations in determining concentrations below this limit are obviously caused by the capacitive background currents. Hence, in order to explore the possibility of approaching lower detection limits, differential pulse voltammetry (DPV) measurements

were attempted. The typical DPV curve obtained for 1.0  $\mu\text{M}$  phenol concentration at pH~7.0 in phosphate buffer solution is depicted in Fig. 4. The DPV measurements were carried out at different pH conditions of 7.0, 9.0 and 12.0. Based on these results the calibration plots obtained at the three pH values are given in Fig. 5. The studies have shown that DPV enables estimation of phenol down to 0.5  $\mu\text{M}$ , one order lower than by the normal voltammetric method.

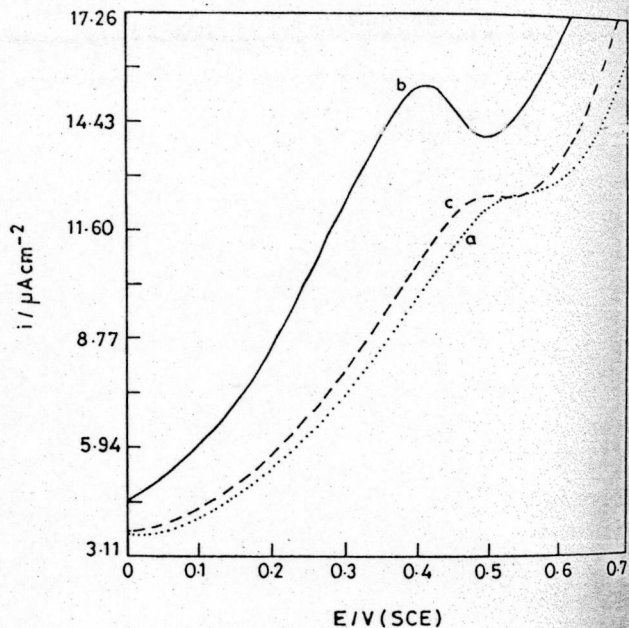


Fig. 4—Differential pulse voltammogram of phenol (concentration = 0.5  $\mu\text{M}$ ) in buffer solution of pH (a) 7.0, (b) 9.0 and (c) 12.0.

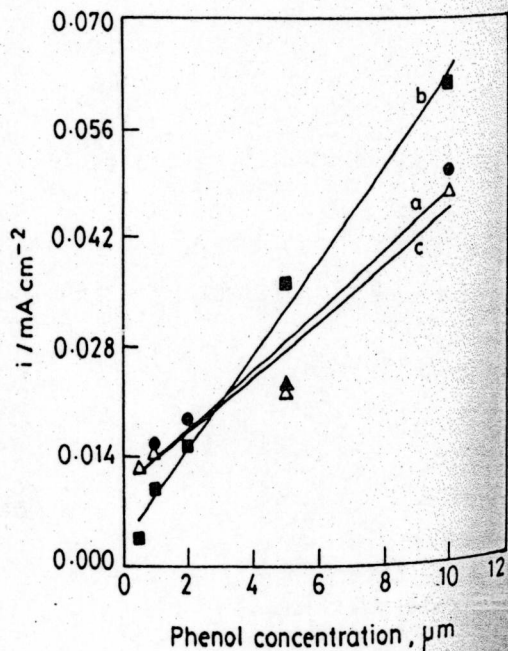


Fig. 5—Calibration curves for phenol obtained using DPV at pH (a) 7.0, (b) 9.0 and (c) 12.0.

The calibration plot was found to be linear with a correlation coefficient of 0.95-0.99 and slopes of 0.3-0.4  $\mu\text{A} \cdot \mu\text{M}^{-1}$  at pHs 7-12. It is interesting to note that the relationship between the peak current and the concentration at pH 9.0 is linear passing through origin and for which the reasons are not known at present.

### Conclusions

Electrochemical oxidation of phenol is feasible on glassy carbon electrode in a potential window of 0.0-1.0 V in aqueous media. Reproducible voltammetric features for the oxidation reaction are obtained in the first cycle. During the second and subsequent cycles, the oxidation reaction is significantly inhibited due to polymeric products blocking the electrode surface. Increase of pH makes the oxidation facile by shifting the oxidation peak potential to more and more cathodic values. At low concentrations, the oxidation is diffusion-controlled and at high concentrations adsorption of phenol becomes predominant. Electroanalytical estimation of phenol is achieved down to 5.0  $\mu\text{M}$  using the peak current in the first cycle of the voltammogram and DPV enables estimation down to 0.5  $\mu\text{M}$  (correlation coefficient = 0.95-0.99 and slope = 0.3-0.4  $\mu\text{A} \cdot \mu\text{M}^{-1}$ ). At pH 9.0, the plot of peak current versus concentration yields a straight line passing through origin, rendering it amenable for electroanalysis.

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