

Poly(alcian blue) Modified Carbon Paste Electrode for the Determination of Catechol in Presence of Hydroquinone: A Voltammetric Study

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Abstract

The carbon paste electrode (CPE) was modified by electropolymerisation of alcian blue in 0.2 M phosphate buffer solution (PBS) of pH 7.4 by using cyclic voltammetric (CV) technique. The fabricated electrode was employed for the electrochemical analysis of catechol (CC) and hydroquinone (HQ). The effect of scan rate suggests the adsorption controlled electrode process. A good analytical performance was observed in terms of sensitivity, selectivity, linearity and observed detection limits. The lower limit of detection of CC and HQ was found to be 0.104 μ M and 0.142 μ M by cyclic voltammetric technique. Because of the catalytic capability of the fabricated electrode the simultaneous separation was observed in a binary mixture containing CC and HQ.

Keywords: Catechol; Hydroquinone; Poly(alcian blue); Cyclic voltammetry; Pulse voltammetry

Introduction

Phenolic compounds are formed during the biological degradation processes; they are widely used as raw materials in the production of dyes, photostabilizer, plasticizers, cosmetics, pesticides and some pharmaceuticals [1,2]. Catechol (CC) and hydroquinone (HQ) are two simple electroactive molecules, belongs to the class of dihydroxybenzene isomers. Since their wide spread applications in day to day life, they are the major cause for environmental pollutions [3,4]. HQ and CC are highly toxic and even at very low concentrations can be harmful to animals and plants [5]. Therefore, sensitive and selective analytical methods are necessary for their determination. Several methods are proposed [6-10] including chromatography [11,12], spectrophotometry [13], pH-based flow injection analysis [14], synchronous fluorescence [15], and voltammetry [16-21]. Among the various fabrication methodologies in getting the new chemically modified electrodes, electropolymerisation is a conveniently simple and powerful method by easy modification of different types of electrodes with desired matrices. The easy synthesis and deposition of desired electroactive polymers onto the conductive surface from monomer solutions and the formation rate and thickness can be precisely controlled by electrochemical input parameters. These electroactive polymers have useful properties such as electronic conductivity and ionic conductivity [3,22-25]. Most of all the bare carbon paste electrodes suffer from a fouling effect due to surface accumulation of the oxidized products, and because of the similar structure and properties the oxidation of dihydroxy benzene isomers at bare electrodes was undistinguishable. Swamy et al. developed an electrochemical sensor for the electroanalysis of CC and HQ by electropolymerising brilliant blue on the surface of carbon paste electrode (CPE) [26]. J He et al. reported the modification of the glassy carbon electrode by electropolymerised film of eosin Y and used for the voltammetric separation of CC and HQ [27]. Wang et al. studied the application of simple amino acids in the fabrication of a new modified glassy carbon electrode for the qualitative determination of CC and HQ in a binary mixture [3,22,23].

Alcian Blue is a phthalocyanine dye contains copper metal and used in the cationic form. The alcian blue has many positive charges on the molecule and it is thought to work by forming reversible electrostatic bonds between the cationic dye and the negative sites on the polysaccharide. Alcian Blue is a group of polyvalent basic water soluble compound which imparts blue color in the solution form

due to the presence of copper ion in the molecule [28]. We proposed a modification of CPE by weight ratio method using alcian blue as a modifier for the determination of dopamine [29]. The present work gives a detailed work for the modification of carbon paste electrode by electropolymerising alcian blue followed by its characterization for the voltammetric determination of catechol and hydroquinone by cyclic voltammetric and differential pulse voltammetric techniques. The fabricated Poly(alcian blue) modified carbon paste electrode shows catalytic capability in the oxidation of both CC and HQ. The sensitivity, selectivity, stability and reproducibility in the result were obtained at the fabricated electrode. The structure of alcian blue was shown in the Scheme 1 (Scheme 1).

Experimental Section

Reagents and apparatus

Hydroquinone (HQ), catechol (CC) and alcian blue were purchased from Himedia. The stock solutions of 25 $\times 10^{-4}$ M HQ, 25 $\times 10^{-4}$ M CC and 25 $\times 10^{-3}$ M alcian blue was prepared in double distilled water. Phosphate buffer solution (PBS) of same ionic strength was maintained (0.2 M) and the desired pH was obtained by mixing appropriate ratio of NaH₂PO₄·H₂O and Na₂HPO₄. Graphite powder of 50 μ m particle size was purchased from Merck and silicone oil from Himedia was used to prepare the carbon paste electrode (CPE). All the chemicals are of analytical grade used as received without any further purification.

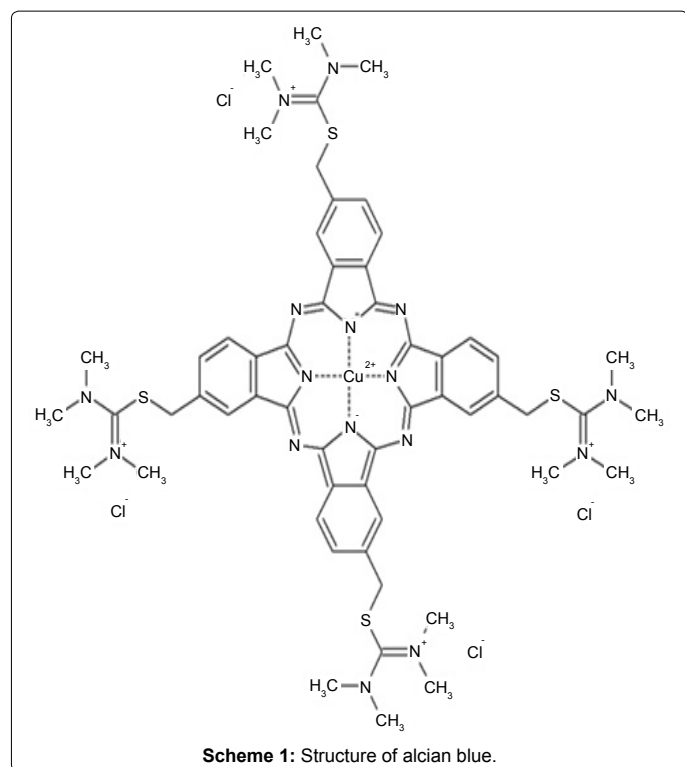
All electrochemical experiments were performed using a model CHI-660c (CH Instrument-660 electrochemical work station). A conventional three electrode system was used in an electrochemical cell with a saturated calomel electrode (SCE) as a reference, a platinum

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wire counter electrode and bare carbon paste electrode (BCPE) or poly(alcian blue) modified carbon paste electrode as a working electrode. Oxidation potentials of all the analytes were recorded versus SCE at an ambient temperature of $25 \pm 0.5^\circ\text{C}$.

Preparation of the bare carbon paste electrode

The BCPE was prepared by homogeneously mixing graphite powder and silicone oil in a ratio of 70:30% for about 45 minutes. The paste was then packed into a PVC tube with homemade cavity of 3 mm internal diameter and the surface was smoothed on a weighing paper. Unless otherwise stated, the paste was carefully removed prior to pressing a new portion into the electrode after every measurement. The electrical contact was provided by a copper wire connected to the end of the tube.

Result and Discussion

Electropolymerisation of alcian blue on BCPE

The poly(alcian blue) MCPE was fabricated by cyclic voltammetric technique by potential sweeping the bare carbon paste electrode between the potential window of -0.8 V to $+1.8\text{ V}$ with scan rate 0.1 Vs^{-1} for 5 multiple cycles in 0.2 M PBS of pH 7.4 until a stable cyclic voltammogram was observed. During this process of recording the multiple cycles the voltammogram was slowly increased with increasing in cyclic times as shown in Figure 1a and later becomes constant [30,31]. This indicates that a thin polymer layer of alcian blue was formed and deposited on BCPE. As the extent of thickness can vary the electrocatalytic performance of the fabricated electrode, it was subjected for the oxidation of 0.2 mM CC in 0.2 M PBS of pH 7.4 with the scan rate of 0.05 Vs^{-1} as shown in the Figure 1b. A better catalytic performance was observed for the electrode which was modified by five consecutive cycle scans. Therefore, the Poly(alcian blue) MCPE was fabricated by considering all the above mentioned parameters (Figures 1a and 1b).

Characterization of BCPE and poly(alcian blue) MCPE

The convenient redox probe of $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ was used for the electrochemical characterization of the fabricated electrodes. The freshly prepared stock solutions of 1 mM potassium ferrocyanide in 1 M KCl as a supporting electrolyte were placed in an electrochemical cell. Figure 2 shows the cyclic voltammograms obtained for the redox behavior of $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ at both BCPE (dotted line) and Poly(alcian blue) MCPE (solid line) at the scan rate 0.05 Vs^{-1} . A poor catalytic performance was observed at BCPE with low redox current response. On the other hand, Poly(alcian blue) MCPE has shown the capability of enhancing the redox peak currents with improved electrocatalytic effect. The electrochemical results obtained at Poly(alcian blue) MCPE suggests that the surface property was significantly changed. This remarkable change in the surface of the Poly(alcian blue) MCPE is a platform for the analysis of the targeted

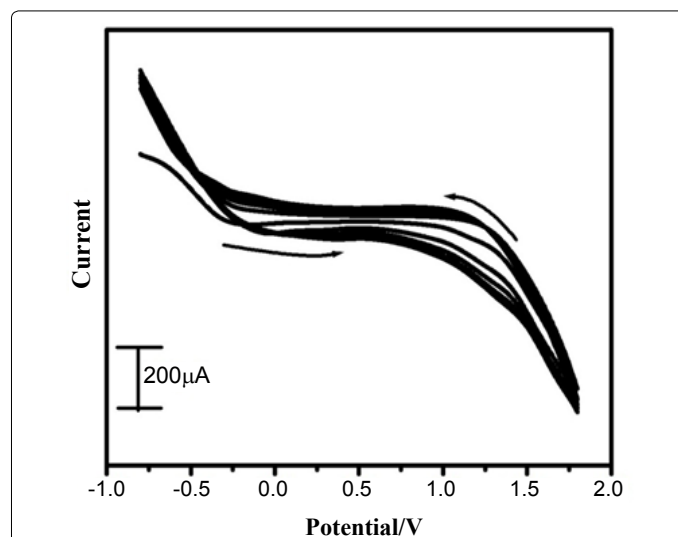


Figure 1a: Cyclic voltammograms of preparation of poly(alcian blue) MCPE. 1 mM solution in 0.2 M PBS of pH 7.4 at 5 cycles with scan rate 0.1 Vs^{-1} .

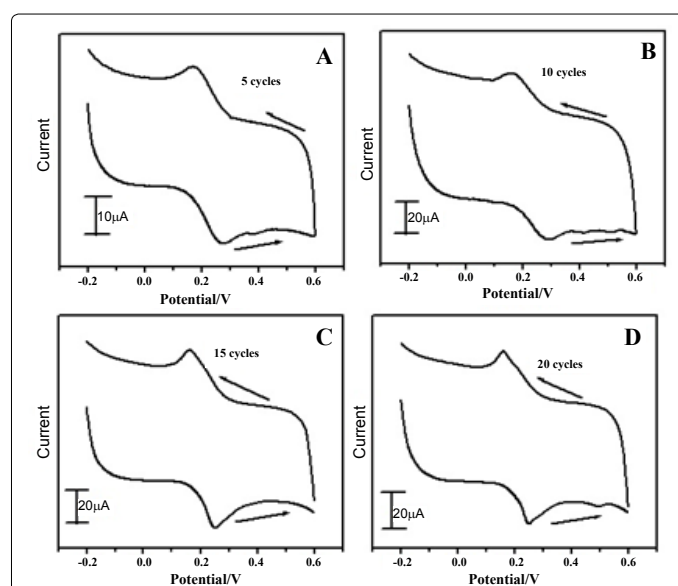


Figure 1b: Cyclic voltammograms recorded for the oxidation of 0.2 mM catechol in 0.2 M PBS of pH 7.4 at poly(alcian blue) MCPE at scan rate of 0.05 Vs^{-1} . (A-5cycles B-10cycles C-15 cycles D-20 cycles).

molecule. The total active surface area available for reaction of species in solution can be estimated by the Randles–Sevcik equation (1) [26,31].

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C_0 \nu^{1/2} \quad (1)$$

where, I_p is the peak current in A. C_0 is the concentration of the electroactive species (mol cm^{-3}), n is the number of electron exchanged, D is the diffusion coefficient in $\text{cm}^2 \text{s}^{-1}$, ν is the scan rate (Vs^{-1}) and A is the electroactive surface area (cm^2). As calculated, the electroactive surface is maximum for Poly(alcian blue) MCPE (0.0358 cm^2) as compared with BCPE (0.0279 cm^2).

Scanning electron microscopy (SEM) images of BCPE and Poly(alcian blue) MCPE are shown in the Figure 2b, which reveals that the surface of BCPE is of irregular shape (A) with less available surface area. After the electropolymerisation the electrode surface is covered by a thin polymer layer of alcian blue (B), with uniform aligned surface. This morphological feature is entirely different from BCPE (Figures 2a and 2b).

Electrochemical response of CC at Poly(alcian blue) MCPE

The Figure 3 shows the cyclic voltammograms recorded for the oxidation of 0.1 mM CC in 0.2 M PBS of pH 7.4 with the scan rate of 0.05 Vs^{-1} at BCPE and poly(alcian blue) MCPE. The CC shows quasi-reversible behavior at BCPE with a broad voltammetric response and the oxidation peak potential was located at around 0.230 V versus SCE. On the other hand, an improved current response was obtained at Poly(alcian blue) MCPE (solid line) with a slight shifting in the anodic peak potential towards the positive side comparing to BCPE. The anodic peak potential was observed at 0.176 V versus SCE. This

refinement in the voltammetric response shows the catalytic capability of fabricated Poly(alcian blue) MCPE towards the oxidation of CC. The oxidation mechanism of CC and HQ was shown in Scheme 2 (Figure 3 and Scheme 2).

The effect of scan rate on peak current of CC

The effect of variation of applied scan rate for 0.1 mM CC in 0.2 M PBS of pH 7.4 was examined by cyclic voltammetric technique at poly(alcian blue)MCPE as shown in Figure 4A. The experimental results obtained at Poly(alcian blue) MCPE suggests the peak current and scan rate are proportional to each. It can be observed that, there is a slight positive shift of anodic peak potential (E_{pa}) and negative shift in the cathodic peak potential (E_{pc}). In order to evaluate the electrode phenomenon, the graph of peak current (I_p) versus scan rate (ν) was plotted and the obtained graph is a straight line with good linearity in the range from 0.01 to 0.14 Vs^{-1} as shown in Figure 4B with the correlation coefficient of (r^2) 0.9973 and 0.9992. On other hand, the I_p versus square roots can rate ($\nu^{1/2}$) was plotted as shown in Figure 4C with the correlation coefficient (r^2) 0.9911 and 0.9949. This suggests

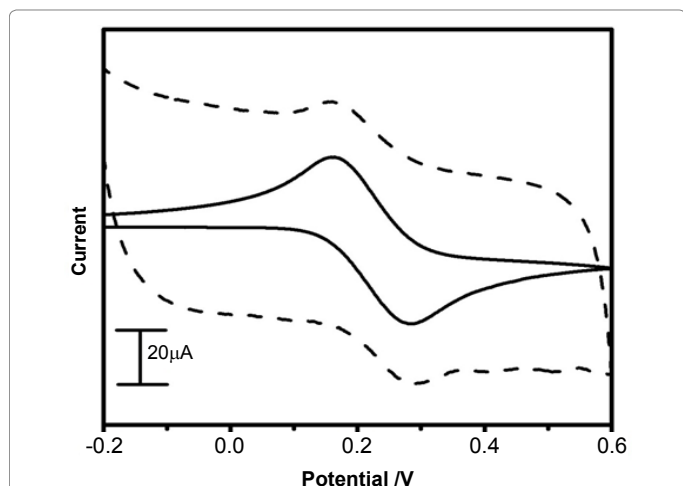


Figure 2a: Cyclic voltammograms of 1 mM potassium ferrocyanide in 1M KCl at BCPE (solid line) and poly(alcian blue) MCPE (dashed line) at scan rate of 0.05 Vs^{-1} .

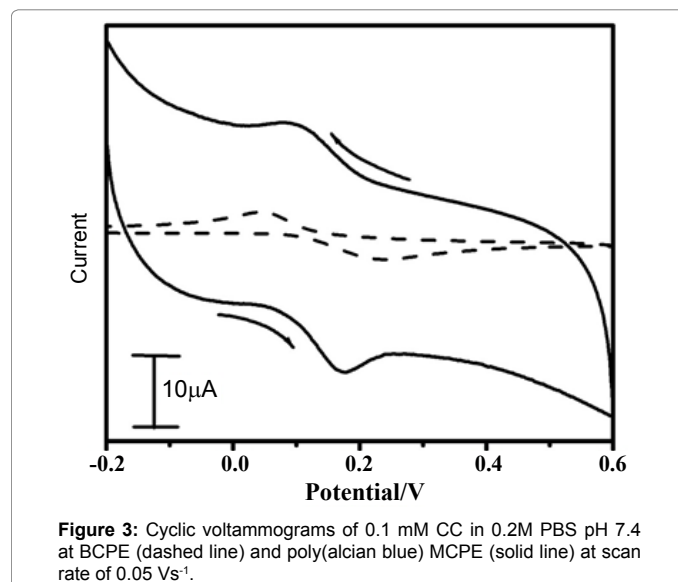


Figure 3: Cyclic voltammograms of 0.1 mM CC in 0.2M PBS pH 7.4 at BCPE (dashed line) and poly(alcian blue) MCPE (solid line) at scan rate of 0.05 Vs^{-1} .

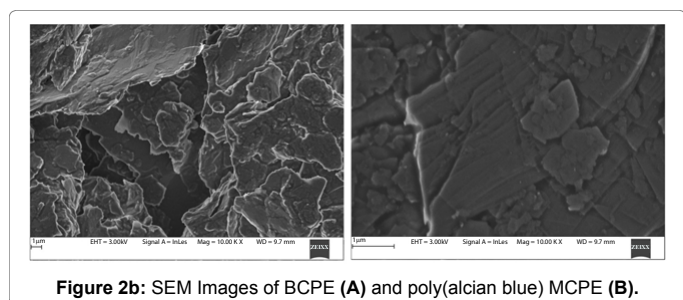
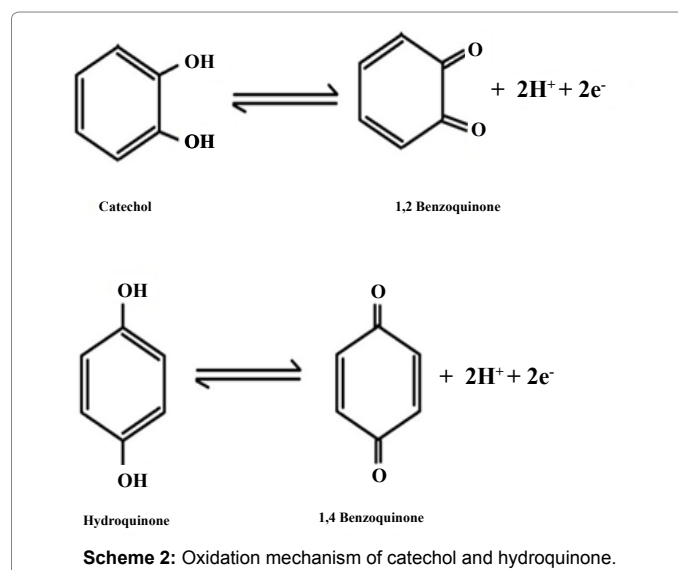


Figure 2b: SEM Images of BCPE (A) and poly(alcian blue) MCPE (B).



the electrode phenomenon was an adsorption-controlled [32]. The heterogeneous rate constant (k^0) values was determined from the experimental peak potential difference (ΔE_p) data's, Eq.(2) was used for the voltammograms whose ΔE_p values are greater than 10 mV [26,31].

$$\Delta E_p = 201.39 \log(v/k^0) - 301.78 \quad (2)$$

From the experimental ΔE_p values and corresponding k^0 values for the oxidation of catechol and hydroquinone was tabulated in Table 1 (Figure 4 and Table 1).

Effect of CC concentration

Differential pulse voltammetry (DPV) shows better defined peaks at lower concentrations than those obtained by cyclic voltammetry. The variation of concentration of CC at Poly(alcian blue) MCPE was conducted by DPV technique. The Figure 5A shows by increasing the concentration of CC from 10 to 60 μM the I_{pa} and I_{pc} goes on increasing with a small shifting in the peak potentials. The graph of I_{pa} versus concentration of CC was plotted as shown in the Figure 5B and it shows a straight line with good linearity. The linear regression equation is $I_{pa} (\mu\text{A}) = 0.1172(C_0 \mu\text{M/L}) + 0.4275$, ($r^2=0.9872$). The limit of detection

was calculated as previously reported [24,26]. The poly(alcian blue) MCPE shows a limit of detection of 0.104 μM for CC by DPV technique, which is relatively lower compared to other reported as shown in Table 2 [8,33-39] (Figure 5 and Table 2).

Influence of solution pH on the determination of CC at Poly(alcian blue) MCPE

The pH of the phosphate buffer solution plays a key role in the oxidation of the electroactive molecules, and it was evaluated at Poly(alcian blue) MCPE by cyclic voltammetric technique. The effect of phosphate buffer pH value at Poly(alcian blue) MCPE for the determination of CC was evaluated in a pH range of 5.5-8.0. Figure 6A shows cyclic voltammograms recorded for 0.1 mM CC at Poly(alcian blue) MCPE. It is clear that as the pH increases the oxidation peak potential shifts to a negative potential. The linear relationship was observed between anodic peak potential (E_{pa}) versus pH with a slope of 0.0588 V/pH as shown in inset Figure 6B. The result suggests the involvement of equal number of electrons followed by equal number of protons in the redox mechanism [24,26] (Figure 6).

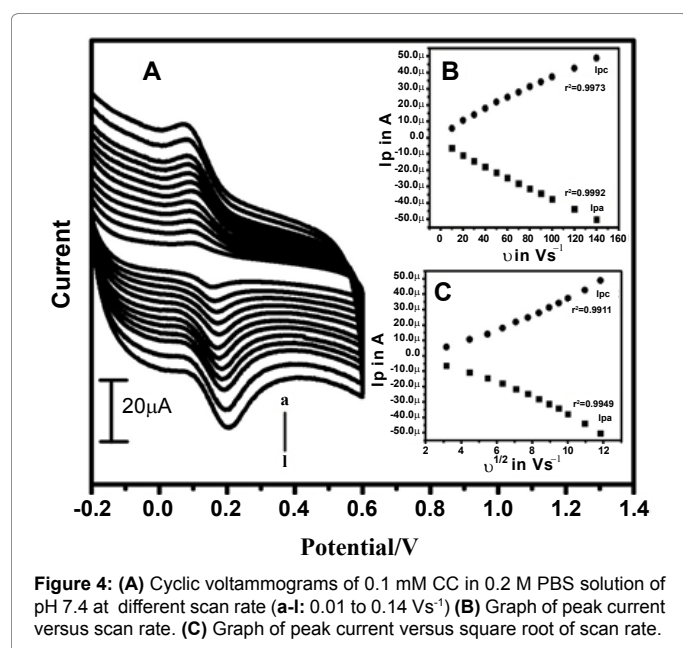


Figure 4: (A) Cyclic voltammograms of 0.1 mM CC in 0.2 M PBS solution of pH 7.4 at different scan rate (a-f: 0.01 to 0.14 Vs^{-1}) (B) Graph of peak current versus scan rate. (C) Graph of peak current versus square root of scan rate.

| v/ mVs^{-1} | $\Delta E_p/\text{mV}$ | | k^0/ s^{-1} | |
|----------------------|------------------------|-------------------|----------------------|-------------------|
| | Catechol (CC) | Hydroquinone (HQ) | Catechol (CC) | Hydroquinone (HQ) |
| 10 | 0.0388 | 0.0403 | 0.3172 | 0.3280 |
| 20 | 0.0393 | 0.0425 | 0.6344 | 0.6212 |
| 30 | 0.0425 | 0.0445 | 0.9515 | 0.9008 |
| 40 | 0.0434 | 0.0458 | 1.2680 | 1.2242 |
| 50 | 0.0426 | 0.0462 | 1.5852 | 1.4828 |
| 60 | 0.0398 | 0.0466 | 1.9028 | 2.0012 |
| 70 | 0.0424 | 0.0468 | 2.2202 | 2.1098 |
| 80 | 0.0412 | 0.0462 | 2.5368 | 2.4880 |
| 90 | 0.0422 | 0.0458 | 2.8516 | 2.7102 |
| 100 | 0.0430 | 0.0478 | 3.1717 | 3.1882 |
| 120 | 0.0436 | 0.0460 | 3.8053 | 3.6022 |
| 140 | 0.0446 | 0.0468 | 4.4401 | 4.2202 |

Table 1: Voltammetric parameters gathered from Figures 4 and 8.

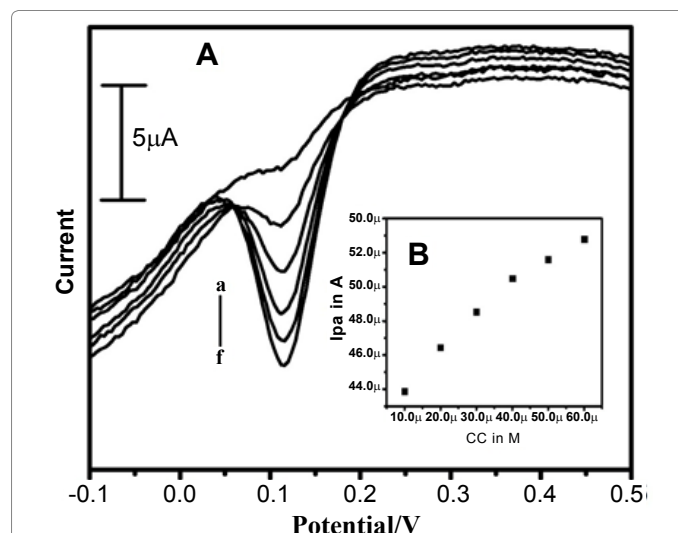


Figure 5: (A) Differential pulse voltammograms of CC in 0.2 M PBS solution of pH 7.4 at poly(alcian blue) MCPE with different concentrations (a-f: 10-60 μM). (B) Graph of anodic peak current versus concentration.

| Working Electrode | Limit of detection in μM | | Technique | Reference |
|--|-------------------------------------|-------|-----------|------------------|
| | CC | HQ | | |
| Zn/Al Layered Double Hydroxide Film MGCE | 1.2 | 9 | DPV | [33] |
| Glassy carbon electrode in CPB and SDBS | 3 | 8 | DPV | [34] |
| Silsesquioxane-MCPE | 10 | 10 | DPE | [8] |
| Graphene oxide and multiwall carbon nanotubes | 1.8 | 2.6 | DPV | [35] |
| [Cu(Sal- β -Ala)(3,5-DMPz) ₂]/SWCNTs/GCE | 3.5 | 1.46 | DPV | [36] |
| Poly(calmagite) MCPE | 2.55 | 1.70 | DPV | [37] |
| PEDOT/GO modified Electrode | 1.6 | 1.6 | DPV | [38] |
| PASA/MWNTs/GCE | 1.0 | 1.0 | DPV | [39] |
| Poly(alcian blue) MCPE | 0.104 | 0.142 | DPV | This work |

Table 2: Comparison table of limit of detection obtained at poly(alcian blue) MCPE with other electrodes.

Electrocatalytic oxidation of HQ at Poly(alcian blue) MCPE

The Figure 7 shows the oxidation of 0.1 mM HQ at BCPE (dotted line) and Poly(alcian blue) MCPE (solid line) in 0.2 M PBS of pH 7.4 at the scan rate of 0.05 Vs⁻¹. From the Figure 7 it is observed that the oxidation potential of HQ at BCPE was broad and poor in sensitivity, the anodic peak potential was located at around 0.126 V. However, at poly(alcian blue) MCPE the oxidation peak potential was shifted towards negative side by minimizing the over potential with enhancement in redox peak current, the anodic peak potential was situated at -0.0585 V. Therefore, by this it came to know that the fabricated poly(alcian blue) MCPE can catalyze the favorable oxidation process of HQ.

The effect of applied potential scan rate for 0.1 mM HQ in 0.2 M PBS of pH 7.4 was examined by CV technique at poly(alcian blue) MCPE as shown in Figure 8A. The applied scan rate was proportional to the redox peak current, with a small shift in the anodic peak potential (E_{pa}) towards more positive side and cathodic peak potential (E_{pc}) to the less negative side. The graph I_p versus v and I_p versus $v^{1/2}$ was plotted in the range from 0.01 to 0.14 Vs⁻¹ as shown in Figure 8B and Figure 8C. As the obtained correlation coefficient is more linear with I_p versus v , suggesting electrode phenomenon was an adsorption-controlled [40].

The electrocatalytic oxidation of HQ was conducted by varying its concentration in the range 10 to 60 μM at Poly(alcian blue) MCPE as shown in the Figure 9A. A linear relationship was established between the I_{pa} and concentration of HQ as shown in the Figure 9B, with a linear regression equation of I_{pa}(μA)=0.3563(C₀ μM/L)+0.55407, (r²=0.9753). The limit of detection for HQ at Poly(alcian blue) MCPE was calculated in the lower concentration range was found to be 0.142 μM by DPV technique.

The effect of phosphate buffer pH value on the cyclic voltammetric determination of 0.1 mM HQ at poly(alcian blue) MCPE was shown in the Figure 10A. The oxidation peak potential shifts to a more negative potential with increasing pH. The E_{pa} versus pH (Figure 10B) graph clearly indicated the depends of E_{pa} with pH in the range of 5.5–8.0 with a slope of 0.0634V/pH (r²=0.9939). This was consistent with the reported literature [24, 26] (Figures 7-10).

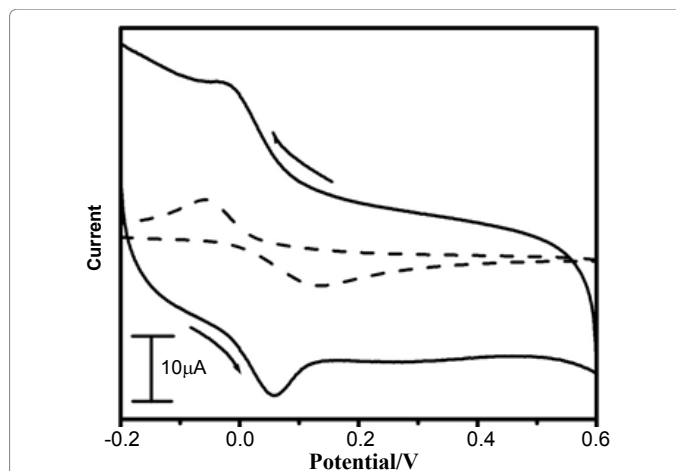


Figure 7: Cyclic voltammograms of 0.1 mM HQ in 0.2 M PBS pH 7.4 at BCPE (dashed line) and poly(alcian blue) MCPE (solid line) at scan rate of 0.05 Vs⁻¹.

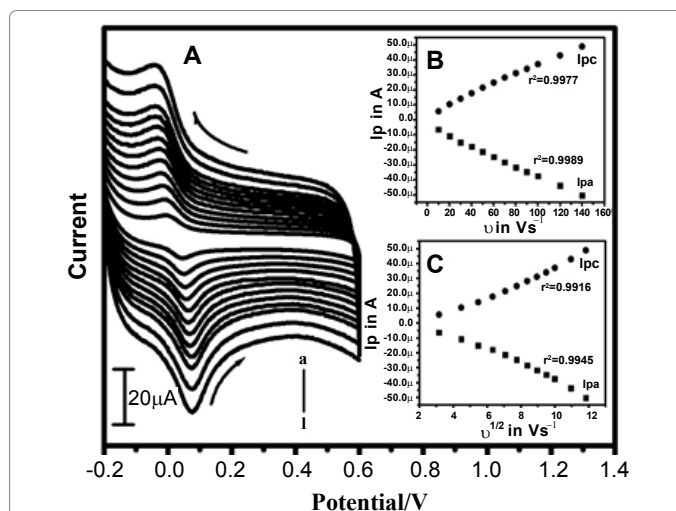


Figure 8: (A) Cyclic voltammograms of 0.1 mM HQ in 0.2 M PBS solution of pH 7.4 at different scan rate (a-l: 0.01 to 0.14Vs⁻¹) (B) Graph of peak current versus scan rate. (C) Graph of peak current versus square root of scan rate.

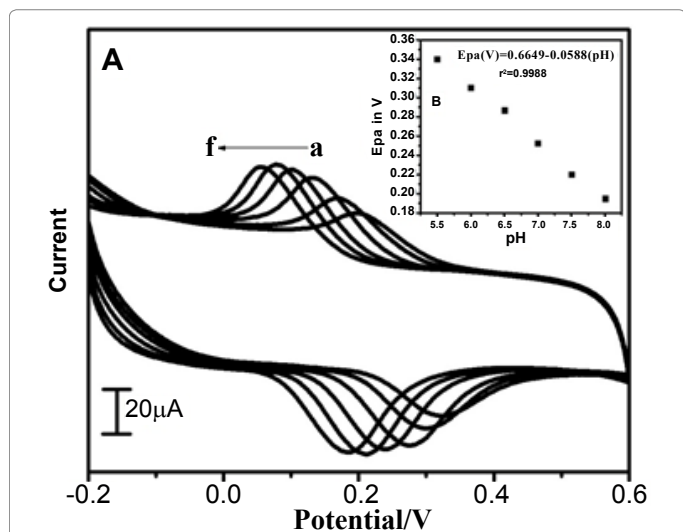


Figure 6: (A) Cyclic voltammograms of 0.1 mM CC at poly(alcian blue) MCPE in 0.2 M PBS solution with different pH values (a-f: 5.5 to 8.0) at scan rate of 0.05 Vs⁻¹. (B) Graph of anodic peak potential versus pH.

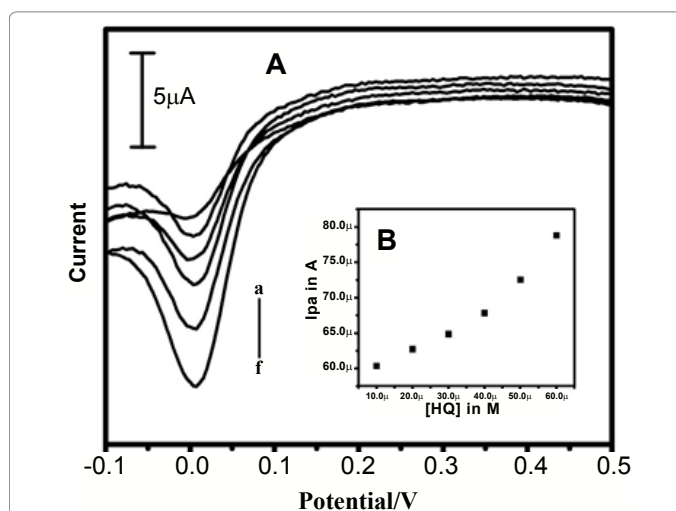


Figure 9: (A) Cyclic voltammograms of 0.1 mM HQ at poly(alcian blue) MCPE in 0.2 M PBS solution with different pH values (a-f: 5.5 to 8.0) at scan rate of 0.05 V s⁻¹ (B) Graph of anodic peak potential versus pH.

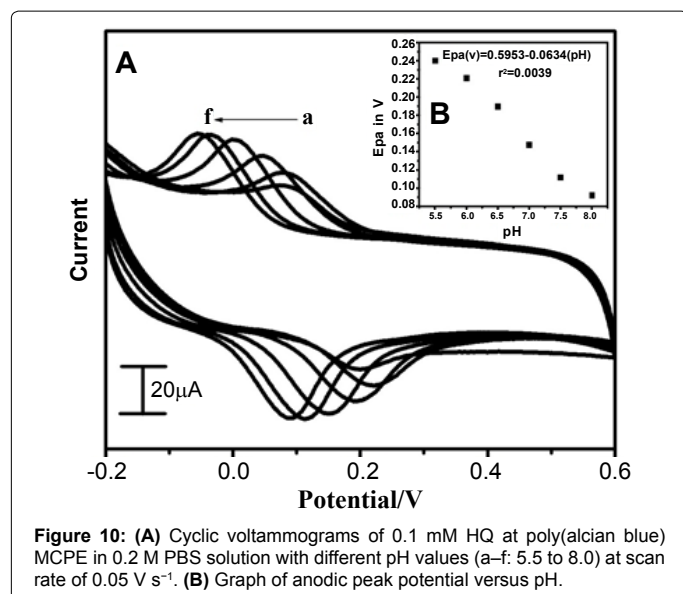


Figure 10: (A) Cyclic voltammograms of 0.1 mM HQ at poly(alcian blue) MCPE in 0.2 M PBS solution with different pH values (a–f: 5.5 to 8.0) at scan rate of 0.05 V s⁻¹. (B) Graph of anodic peak potential versus pH.

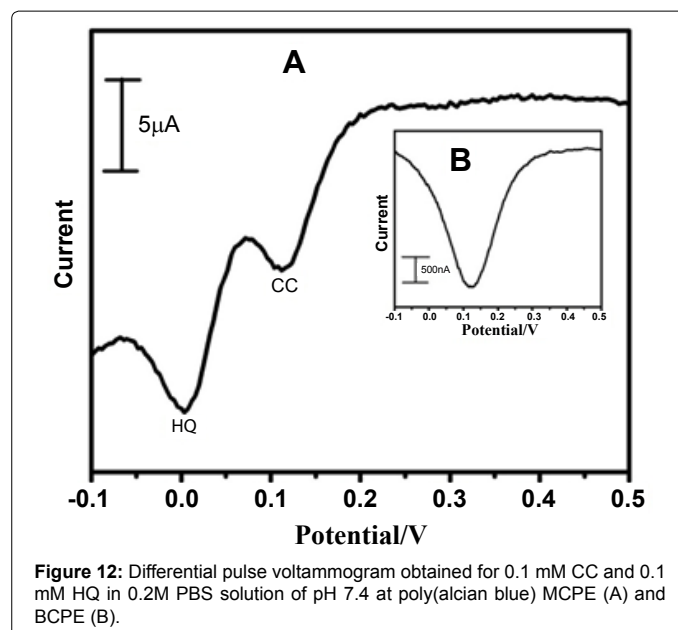


Figure 12: Differential pulse voltammogram obtained for 0.1 mM CC and 0.1 mM HQ in 0.2 M PBS solution of pH 7.4 at poly(alcian blue) MCPE (A) and BCPE (B).

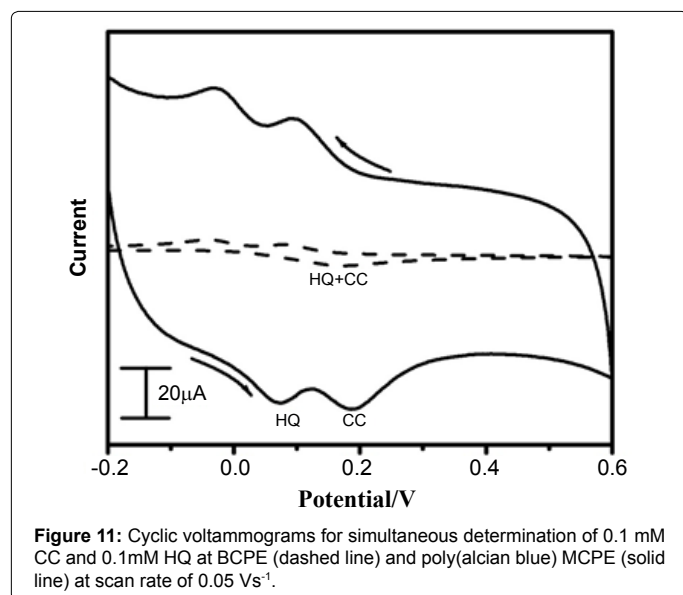


Figure 11: Cyclic voltammograms for simultaneous determination of 0.1 mM CC and 0.1 mM HQ at BCPE (dashed line) and poly(alcian blue) MCPE (solid line) at scan rate of 0.05 Vs⁻¹.

Simultaneous determination of CC and HQ

The cyclic voltammetry was employed for the simultaneous electrochemical determination of CC and HQ. The Figure 11 shows the cyclic voltammograms obtained for the equimolar (0.1 mM) mixture of CC and HQ in 0.2 M PBS of pH 7.4 at the scan rate of 0.05 Vs⁻¹. The dotted line shows cyclic voltammogram obtained at BCPE, on the other hand the solid line for poly(alcian blue)MCPE and the oxidation potential of CC and HQ were observed at the same potential as determined individually, this voltammetric resolution of CC and HQ at poly(alcian blue) MCPE has great significance in the simultaneous analysis. Differential pulse voltammetry has some advantages like higher current sensitivity and absence of background current, The Figure 12 shows the DPV curves recorded for the equimolar mixture of CC and HQ at BCPE and poly(alcian blue) MCPE. Therefore, the discrimination of oxidation potentials of CC and HQ was achieved at Poly(alcian blue) MCPE (Figures 11 and 12).

Conclusion

A simple and convenient method for the modification of bare carbon paste electrode was proposed by the electropolymerisation of alcian blue followed by its electrochemical and scanning electron microscopic characterization. The strong electrocatalysis in the oxidation of catechol and hydroquinone has made the fabricated electrode as a promising analytical sensor in the simultaneous analysis of both the isomers by cyclic voltammetric and differential pulse voltammetric techniques. Overall, the sensitivity, selectivity, antifouling property, reproducibility, stability was shown by the electrode.

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