

Full Paper

Voltammetric Investigation of Catechol at Zinc Oxide Poly(Congo Red) Modified Carbon Paste Electrode

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Abstract- Here, the synthesized zinc oxide nanoparticle and characterized with XRD and SEM techniques. The carbon paste electrode was modified by using prepared nanoparticles with electrochemically polymerized by treating with 25mM Congo red and sensing environmental pollutants. The Poly (Congo red) Zinc oxide modified carbon paste [PCRZOMCPE] brings an enhanced sensitivity at electrochemical detection of catechol (CC) by using cyclic voltammetry (CV); the parameters like pH, sweep rates and concentration study was carried out, the PCRZOMCPE is applied for the simultaneous determination of CC and hydroquinone (HQ) then the detection limit and quantification value for CC is established to be 9.39 μ M and 31.30 μ M respectively and the electrode showed excellent sensitivity and selectivity towards electrochemical examination of CC.

Keywords- Congo red; Catechol; Hydroquinone; Poly(Congo red) Zinc oxide modified carbon paste electrode; Zinc oxide nanoparticle

1. INTRODUCTION

From past few years, the modification of the carbon paste electrode has constructed which has high attention in the electro analysis of environment pollutant. The voltammetric technique has excellent, simple and cost-effective method to investigation of environmental pollutant. Congo red is a dye utilized in many food industries and textiles. The improper using and discard of these can cause environment pollution and many respiratory abnormal diseases [1-4].

Catechol (CC) and hydroquinone (HQ) are isomers and extremely employed intermediates in the department of pesticides, pharmaceutical, dyes and various industries [5-8]. They are known as environmental pollutants due to their discharging from the different sources, having toxicity and less degradability in nature which cause harmful to the environment [9-13]. Therefore, the detection in biological system makes a significant role in environmental study. Different techniques have been developed to determination of HQ and CC. As analogize to these methods, the determination of CC and HQ by electrochemical method has significant because of very low cost, high sensitivity, quite simple to operate. But other methods had liability of these [14-20].

Nanoscience has a more importance in all the fields because of their individual physical and chemical properties. Metal oxide brings a good thermal and electric conductivity with high surface area like zinc oxide (ZnO), copper oxide (CuO) and magnesium oxide (MgO) nanoparticles (NPs) [21-24]. Zinc oxide nanoparticle (ZnO/NPs) was utilized in industrial area such as electronic devices and medical curative. From some literature survey brings us that among all the nanoparticles the ZnO NP's has better electrochemical activity and brings very good surface area of the BCPE [25-28]. The obtained ZnO/NPs utilized in as modified carbon paste electrode for the application as sensor and examine its electrochemical parameter; by virtue of their excellent bio compatibility and high surface area.

Here, the poly (Congo red)/ ZnO are constructed and employed for the concurrent detection of HQ and CC in existence of 0.2 M PBS (pH 7.4) at a sweep rate of 0.05 Vs⁻¹. Here the electrode shows good sensitivity and stability towards the sensing of CC and HQ by cyclic voltammetry techniques.

2. EXPERIMENTAL SECTION

2.1. Chemicals Utilized

CC and HQ having 99% purity and Congo red powder were obtained from Hi-media and utilized without further purification. 0.1 M NaOH and 25×10⁻⁴ M each stock solution and 25×10⁻⁴ M Congo red is prepared in DD water. Zinc chloride tetra hydrate [ZnCl₂.4H₂O]; KCl, K₄[Fe(CN)₆], sodium hydroxide (NaOH), di-sodium hydrogen ortho phosphate (Na₂HPO₄), Mono sodium hydrogen ortho phosphate (NaH₂PO₄) were purchased from Merck. pH 7.4 (0.2 M PBS) was utilized as supporting electrolyte. From Fluka the fine graphite powder and silicone oil are used for carbon paste and water of DD was utilized for preparation of solutions throughout the experiments.

2.2. Apparatus

Cyclic voltammetry (CV) study were carried out by utilizing a model CHI-660d with typical three electrode junction, specifically reference (Ag/AgCl), the platinum wire as counter electrode and working were carbon paste electrode (CPE), bare CPE and PCRZOMCPE.

2.3. Preparation ZnO nanoparticles

The ZnO NP's was prepared by using co-precipitation method. Zinc chloride tetra hydrate [ZnCl₂.4H₂O] and sodium hydroxide (NaOH) are the utilized chemicals. The 0.25 M [ZnCl₂.4H₂O] is prepared in 50 mL DD water separately and solution is stirred for about 45 min at a magnetic stirrer, then added dropwise 0.5 M NaOH solution, after again stirred it for about 60 min finally, it is stirred again for 150min, filtered and dried. Obtained product was calcined at 723.15 K for 120 min [29-33] and finally obtained NP's was utilized as modifier.

2.4. Preparation of BCPE and PCRZOMCPE

The Bare CPE was constructed by homogeneous hand mixing 70:30 ratio fine graphite powder and silicon oil mixture respectively. The ZnO/MCPE was prepared by adding of synthesized ZnO/NPs and the similar action as follow in BCPE. The preparation of PCRZOMCPE Through electrochemical polymerization of 1ml of 25×10⁻⁴ M Congo red at different cycles (2 to 12) by utilizing 0.1 M NaOH as supporting electrolyte here for 4 cycles maximum current appeared. Finally, the PCRZOMCPE was selected for further evaluation.

3. RESULTS AND DISCUSSION

3.1. Characterization

Figure 1A brings the XRD pattern of synthesized ZnO NP's. The diffraction peaks obtained at 31.74°, 32.96°, 36.17°, 36.28°, 47.46°, 56.53°, 62.96°, 68.13° and 69.99° have been neatly indexed with the JCPDS card number: 36-1451 and it also confirms that the synthesized NP's was not containing any impurities. The size of NPs was calculated by Debye-Scherrer equation i.e. $d=0.89\lambda\beta\cos\theta$, where λ is X-ray wavelength, θ is angle of diffraction and β is the FWHM. The average crystalline size of the NP's is 16.54 nm. Figure 1B is the SEM data reveals that the wurtzite structure was formed.

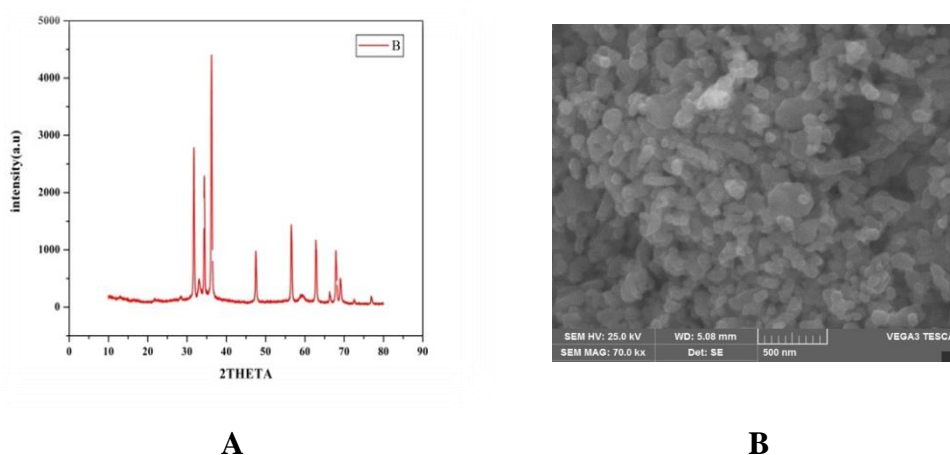


Figure 1. A) X-ray pattern of synthesized ZnO nano particles; B) SEM image of synthesized ZnO nano particles

3.2. Electro polymerization of poly (Congo red) on ZnO/CPE

The poly (Congo red) modified CPE was fabricated through electropolymerization on a bare carbon paste electrode by utilizing aqueous Congo red (0.1 mM) with NaOH (0.1 M) in electrochemical cell at the potential range from 0.5 to 1.5 V having scan rate 50 mVs⁻¹ for different cycles. The thickness of the film and variety weight of synthesized ZnO NPs have significantly effects on response of PCRZOMCPE which is shown in Figure 2A and a maximum current response was occurred at 4 polymerized cycles after that later became constant, which confirms that aqueous Congo red was cleanly deposited on the surface of ZnO/MCPE.

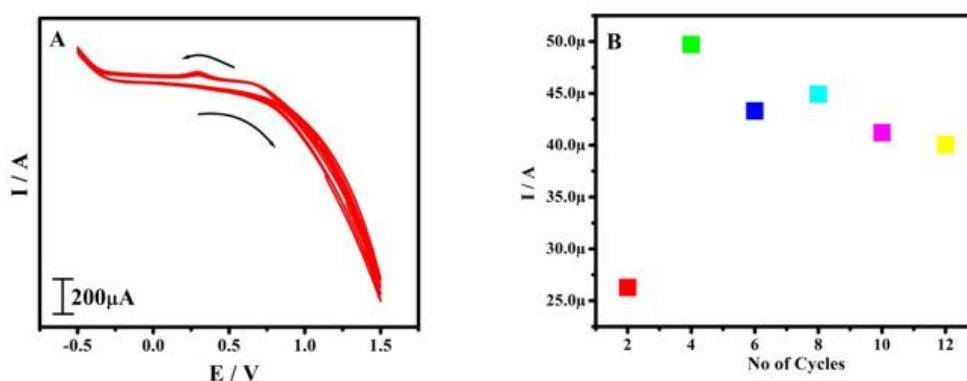


Figure 2. A) Tentative CVs for the preparation of ZnO/poly (Congo red); the electrolytic cell contains 1 mM Congo red in 24 mL 0.1 M NaOH at 4 multiple cycles with scan rate of 0.05Vs⁻¹; B) Relationship between anodic peak current and number of polymerization cycles.

3.3. Influence of multiple cycles

By varying cycles from 2 to 12 on the ZnO/CPE the oxidation peak of 25×10^{-4} M $K_4[Fe(CN)_6]$ in 1 M KCl solution was examine and at the 4 multiple cycles there is enhanced peak current was observed as compared to other variety of cycles, that is presence in Figure 2B. Therefore the 4 multiple cycles were selected for electro polymerization of poly (Congo red) at ZnO/CPE.

3.4. Electrochemical investigation of PCRZOMCPE in standard $K_4[Fe(CN)_6]$ system

The CV technique was performed with typical three electrode arrangement. The obtained cyclic voltammogram for the 1 mM $K_4[Fe(CN)_6]$ at bare CPE (red dotted line) and PCRZOMCPE (blue colored) with 1 M KCl with a sweep rate of 50 mVs⁻¹ was noted in Figure 3A. The PCRZOMCPE displays rising in peak currents with increasing in the transfer of electrons (Figure 3B). By utilizing Randles-Sevcik equation (A) the surface area of MCPE and BCPE can be denoted.

$$I_p = 2.69 \times 10^5 n^{3/2} A D_0^{1/2} C_0 v^{1/2} \text{ ----- (A) [34]}$$

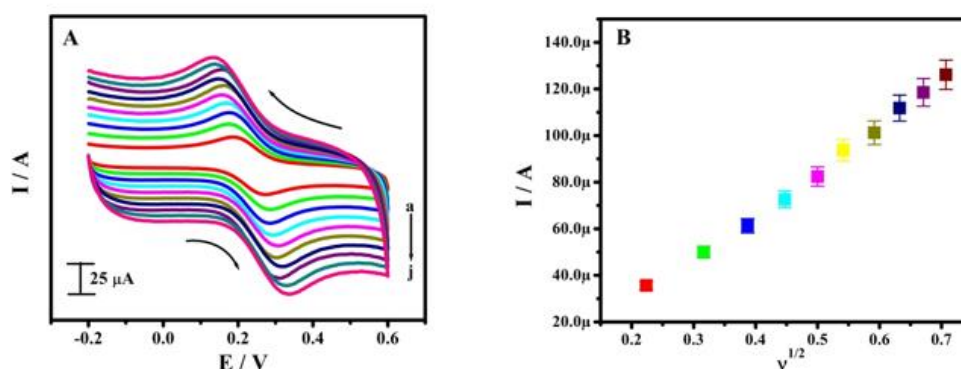


Figure 3. A) Electrochemical investigation of PCRZOMCPE in standard $K_4[Fe(CN)_6]$ system in 1 M KCl at different scan rate of $0.05\text{-}0.5\text{ Vs}^{-1}$; B) plot of scan rate versus peak current

3.5. Electrochemical investigation of CC at PCRZOMCPE

Figure 4 illustrates the voltammograms obtained for CC ($10\text{ }\mu\text{M}$) having 0.2 M PBS (pH 7.4) at a bare CPE (red dotted) and PCRZOMCPE (blue colored) with scan rate of 50 mVs^{-1} . The oxidation peak was noted at 0.16 V for bare CPE, here poor peak current response was observed because of slow electron transfer in BCPE. But at a modified CPE brings an increase in I_{pa} having $31.30\text{ }\mu\text{A}$ under same conditions. This reveals that the PCRZOMCPE is an excellent towards electrochemical activity of CC (Scheme 1).

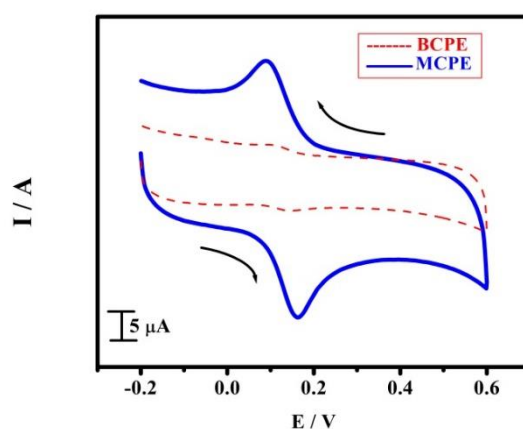
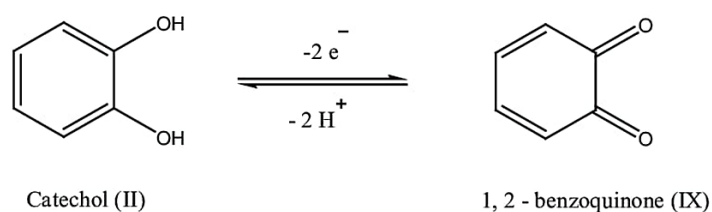


Figure 4. A) Cyclic voltammograms of $10\text{ }\mu\text{M}$ CC in 0.2 M PBS solution of pH 7.4 at BCPE (red colored dotted line) and PCRZOMCPE (blue colored) at scan rate of 0.05 Vs^{-1}



Scheme 1. Oxidation scheme of catechol

3.6. Effect of pH on CC at PCRZOMCPE

The effect of pH from 6.2-7.8 of PBS was examined on CC oxidation at PCRZOMCPE. The CV noted for 25×10^{-4} M CC at PCRZOMCPE with variety PBS pH with scan rate 50 mVs^{-1} , by raise in pH, the E_{pa} of CC moves towards negative potential displayed in Figure 5A. A graph between pH against pH was constructed, which brings that peak potential is pH dependent (Figure 5B). The regression linear equation can be indicated as $E_{\text{pa}}(\text{V}) = 0.54642 - 0.05183 (\text{pH})$, ($r^2 = 0.995$). The earned slope was 52 (Figure 5B) is nearer to the nearest value 59 mV/pH , which illustrates that the number of electrons and protons transferred in oxidation and reduction mechanism are equally. The highest peak current was obtained at pH 7.4, therefore the physiological pH 7.4 was picked for additional examines.

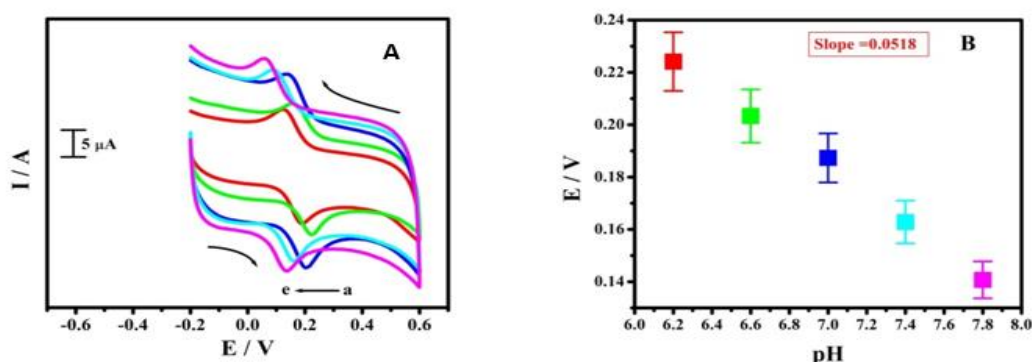


Figure 5. A) Cyclic voltammogram of the PCRZOMCPE in 0.2 M PB solution containing $10 \mu\text{M}$ CC with different pH (a-e: 6.2-7.8) at a scan rate of 0.05 Vs^{-1} ; B) the linearity plot of E_{pa} versus varied pH values

3.7. Influence of sweep rate on oxidation of CC

For investigation of the redox behavior of CC on PCRZOMCPE was either adsorption controlled or diffusion, the sweep rates was examined from 50-500 mV/s on PCRZOMCPE surface in pH 7.4 (PBS) was investigated by CV technique as displayed in Figure 6A.

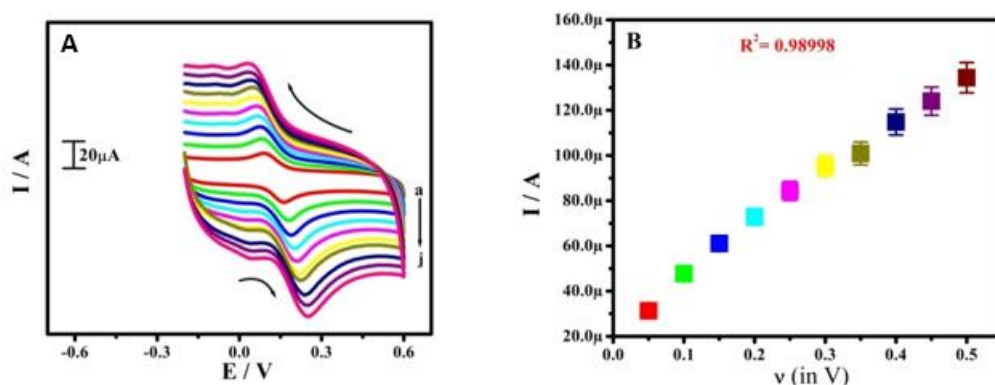


Figure 6. A) Cyclic voltammogram of $10 \mu\text{M}$ CC in 0.2 M PBS of pH 7.4 at PCRZOMCPE with different scan rate (a-j: $0.05\text{-}0.5 \text{ Vs}^{-1}$); B) Graph of anodic peak current versus scan rate

The I_{pa} of CC raises with raise in the sweep rates, by Randles Sevcik relation. The E_{pa} of CC is shifted towards positive side and E_{pc} was towards negative. To examine the process of electrode, plotted a graph of I_{pa} versus sweep rate v of CC was constructed, Figure 6B. A better linearity was gained and $I_{pa}(\mu A) = 2.37016E^{-5} v (V/s) + 2.17342E^{-4}$ with a correlation coefficient value (r^2) 0.998.

3.8. Effect of CC concentration on its oxidation

The influence of CC concentration was examined for CC at PCRZOMCPE by applying CV technique it is varied from 10-100 μM shows in Figure 7A. From Figure 7B illustrates that the raise in the CC concentration the current response is going to be raises. The corresponding equation of linear regression was explained as,

$$I_{pa}(\mu A) = 0.01246 (C_0 \mu M/L) + 1.4280, (r^2 = 0.9993) \text{ for CC}$$

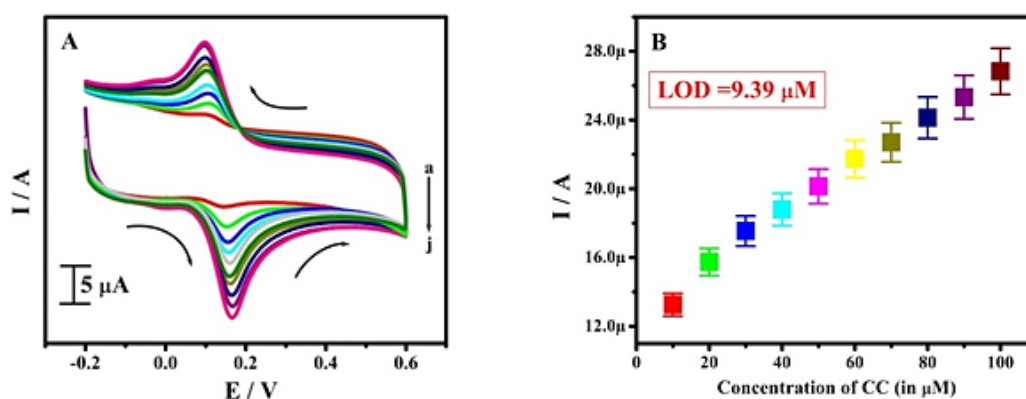


Figure 7. A) Cyclic voltammogram of CC in 0.2 M PBS of pH 7.4 at PCRZOMCPE with varied concentration (a-j: 10-100 μM) at a scan rate of 0.05 Vs^{-1} ; B) Graph of anodic peak current versus concentration.

Table 1. Comparison of LOD with other reported modified electrodes for CC

Sl. No.	Electrodes	Reaction	Method	LOD=3 σ /M (μM)	Ref.
1	GNPs/CNF/Au	Oxidation	DPV	9	[35]
2	Influence of micelles/GCE	Oxidation	DPV	8.0	[36]
3	GCE/Pt-MnO ₂	Oxidation	DPV	15	[37]
4	LDH/GCE	Oxidation	DPV	9	[38]
5	MWCNT-NF-PMG-GCE	Oxidation	CV	31.0	[39]
6	Poly (Congo red) ZnO/MCPE	Oxidation	CV	9.39	This work

The detection limit and quantification were examined for CC at PCRZOMCPE by utilizing relations b and c:

$$\text{LOD} = 3\sigma/P \text{ ----- (b)}$$

$$\text{LOQ} = 10\sigma/P \text{ ----- (c)}$$

where P is the slope and σ is the value of standard deviation. The LOD was established to be 9.39 μM and LOQ was 31.307 μM for CC. The corresponding detection limit of CC is compared with different electrode was tabulated in Table 1 [35-37].

3.9. Simultaneous detection of HQ and CC

The proper detection of HQ and CC has examined at PCRZOMCPE by CV technique. The separation peaks for HQ and CC were not neatly observed, almost merged (red dotted line) E_{pa} was revealed at 0.17 V for bare CPE. But at PCRZOMCPE, two well elucidated peaks were noticed (red colored line) shows in Figure 8, at various E_{pa} detected that is 0.042 V and 0.145 V having a potential difference between HQ and CC is 0.103 V respectively. This confirms that it is enough to detect CC in the existence of HQ at PCRZOMCPE.

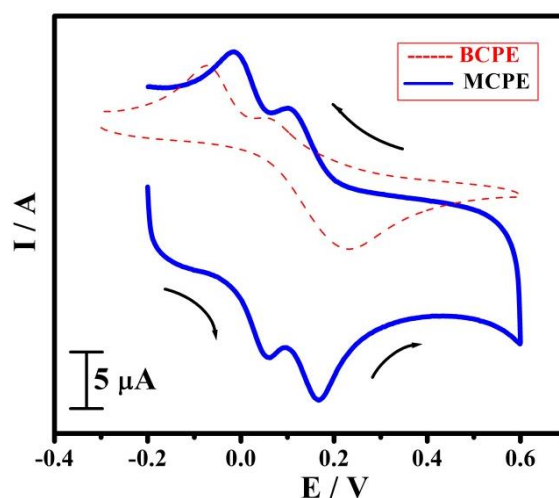


Figure 8. Cyclic voltammogram for simultaneous determination of 10 μM CC and 10 μM HQ at bare carbon paste electrode (red dotted line) and PZOCR modified carbon paste electrode (blue colored line) at scan rate of 0.05 Vs^{-1}

4. CONCLUSION

PCRZOMCPE shows excellent sensitivity and selectivity having notable electrochemical nature towards determination of CC and it shows an adsorption-controlled process by the electrode. The modification of BCPE done via by utilizing different weight of synthesized ZnO NPs. The modified electrode has excellent performance as compared with the different

modified electrodes which are already published to investigate CC and HQ separately. It brings detection values are LOD 9.39 μM and LOQ 31.307 μM . Thus, the PCRZOMCPE is an excellent tool for detection of CC and other environmental contaminants also.

Declarations of interest

The authors declare no conflict of interest in this reported work.

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