

Voltammetric and Impedance studies of Phenols and Its Derivatives at Carbon Nanotubes/Prussian Blue Films Platinum Modified Electrode

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ABSTRACT

The electrochemical oxidation of phenol (Ph), 4-chlorophenol (4-CIPh) and 4-nitrophenol (4-NPh) at a platinum electrode modified with and without multi-walled carbon nanotubes/Prussian blue nanocomposite was investigated by cyclic voltammetry (CV) and impedance measurements. The modified electrodes were characterized using transmission electron microscopy (TEM), electron X-ray dispersive spectroscopy (XRD), cyclic voltammetry (CVs) and electrochemical impedance spectroscopy (EIS). Pt-MWCNT-PB electrode gave the highest electro-oxidation current compared to the other electrodes studied. The oxidation of the phenol was characterized by some level of adsorption. The degree of adsorption was depicted by the Tafel values of 4292.4, 663.2 and 203.8 mVdec⁻¹ for Ph, 4-CIPh and 4-NPh respectively. The limits of detection were in the micro molar range and the Gibbs free energy change (ΔG°) due to adsorption was estimated as -33.8, -35.8 and -36.0 kJmol⁻¹ for Ph, 4-CIPh and 4-NPh.

Keywords: Phenols, Platinum electrode, Prussian blue nanoparticles, Adsorption, Impedance measurement.

1.0 INTRODUCTION

Phenols and the chlorinated and alkylated derivatives are classified as priority pollutants due to the health risk associated with their toxicity [1]. Industrial effluents containing phenols as pollutants include effluents or waste from pharmaceuticals, dyes, plastic, food, oil, detergents, pesticide and herbicide, coal, pulp and paper industry, textiles, chemical synthesis, etc. [2,3]. They are extremely dangerous since they are harmful to organisms even at low concentrations [4]. Due to their constant presence in

industrial waste and consequently their carcinogenic risk for humans, methods for the detection of phenol and its derivatives are important. Phenol and chlorophenols can be detected by means of spectrophotometric [5], chromatographic [6] and electrochemical methods [7] but the electrochemical method is the most efficient since it takes a shorter time with no chemical derivatization and gives very reproducible results [2]. In fact, electrochemical oxidation of phenol is reported to be the effective and attractive method from the economical point of view of removal of phenolic compounds from waste water [8]. However, electrochemical oxidation of phenols on solid surface is usually associated with adsorbed oxidation intermediates which poison the surface due to polymer formation during the oxidation process. Prussian blue (PB) is an iron cyanide complex (Fe₄(III)[Fe(II)(CN)₆]₃) often used as an electron-transfer mediator on modified electrodes during electrochemical processes. Therefore, the objective of this study was to explore the resistance of the platinum electrode modified with multi-walled carbon nanotubes/Prussian blue nanocomposite (Pt-MWCNT-PB) towards poisoning by phenols oxidation.

2.0 EXPERIMENTAL

2.1 Materials and reagents

Multi-walled carbon nanotubes were purchased from Sigma Aldrich Chemicals and were acid treated to introduce sulphonic functional group (SO₃²⁻) using a known procedure [9]. FeCl₃, K₄[Fe(CN)₆], KCl, Phenol (Ph), 4-chlorophenol (4-CIPh) and 4-nitrophenol (4-NPh) and other chemicals and reagents were of analytical grade and sourced from Sigma-Aldrich chemicals. Ultra pure water of

resistivity 18.2 MΩcm was obtained from a Milli-Q Water System (Millipore Corp., Bedford, MA, USA) and was used throughout the experiments. A phosphate buffer solution (0.1 M PBS) of pH 7.3 was prepared with appropriate amount of NaH₂PO₄·2H₂O and Na₂HPO₄·2H₂O, and the pH was adjusted with 0.1 M H₃PO₄ or NaOH.

2.2 Electrode Modification and Pretreatments

A platinum electrode was cleaned by gentle polishing in aqueous slurry of alumina powder, Sigma-Aldrich (grain size <100 nm) on a SiC-emery paper, mirror finished on a Buehler felt pad and was subjected to ultrasonic vibration in absolute ethanol and water successively. Pt-MWCNT was prepared by a drop-dry method using 10 μL drop of the MWCNT solution (0.1 mg MWCNT in 1 ml DMF). The Pt-MWCNT electrode was dried in an oven at 50 °C for about 2 min. Electrodeposition of Prussian blue on the Pt-MWCNT and its activation was done by adopting a method earlier reported [10]. The modified electrode was denoted as Pt-MWCNT-PB. Other electrodes investigated are bare Pt and Pt-PB.

3.0 RESULTS AND DISCUSSION

3.1 Comparative FTIR, XRD, SEM, TEM, and EDX spectra

Figure 1 shows the comparative FTIR spectra of the MWCNT-SO₃⁻, PB and MWCNT-PB. In the MWCNT-SO₃⁻ spectrum, the bands at 1384, 1044 cm⁻¹ are respectively attributed to S=O and S-O stretching modes of the sulphonic acid group (-SO₃⁻) in MWCNT-SO₃⁻. Also, the band at around 1653 cm⁻¹ is due to the vibration mode of C=C bonds of the CNT structure. As can be seen in the MWCNT-PB spectrum, upon modification, all these peaks (1384, 1044, 1653 cm⁻¹) drastically reduced in intensities, indicating that the MWCNT-SO₃⁻ had now been modified with PB. Further evidence of modification of MWCNT-SO₃⁻ with PB can be seen in the MWCNT-PB spectrum, the sharp band at 2078 cm⁻¹ is attributed to PB C≡N str band found in MWCNT-PB and PB spectra but absent in MWCNT-SO₃⁻ spectrum.

The corresponding XRD spectra for the MWCNT-SO₃⁻, PB and the MWCNT-PB nanoparticles are shown in Figure 2. The XRD spectrum for MWCNT-PB gave peaks with a higher intensity than PB alone due to large surface area created by the MWCNT-SO₃⁻ supports for more deposition of uniformly and evenly distributed PB nanoparticles.

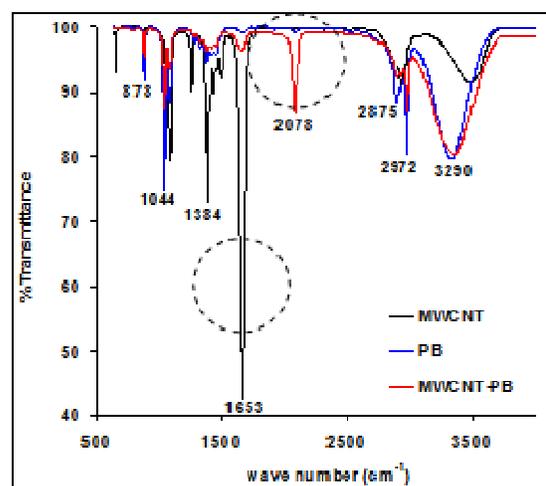


Figure 1: Comparative FTIR spectra of MWCNT-SO₃⁻, PB and MWCNT-PB nanoparticles

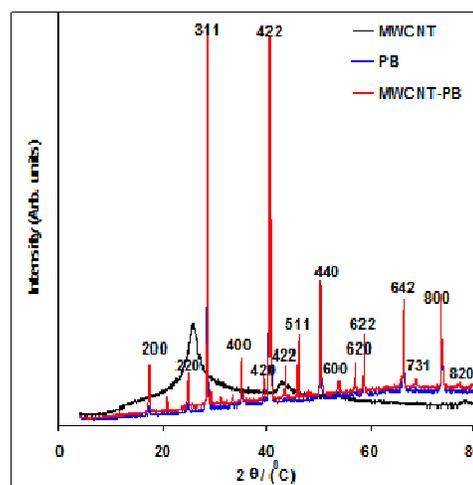


Figure 2: Comparative XRD spectra of MWCNT-SO₃⁻, PB and MWCNT-PB nanoparticles.

The crystal sizes of the PB particles were estimated from three prominent peaks to be ~ 17.5 nm using Debye-Scherrer formula [11]:

$$d = \frac{K\lambda}{B \cos \theta} \quad (1)$$

where d is the average crystal size; K is a constant (0.89); λ is the wavelength (1.78901 nm) used; B is the full width at half maximum of the peak, θ is the Bragg's angle of the XRD peak.

Figures 3 (a) shows the transmission electron microscope (TEM) images of the PB nanoparticles and the images confirm the crystalline nature of the PB nanoparticles. From

TEM, PB nanoparticle sizes of the 15–35 nm range were obtained which agreed with the particle size obtained from the XRD result. The EDX profile (Fig. 3b) revealed the presence of Fe peaks which represent Fe^{2+} and Fe^{3+} of the PB nanoparticles.

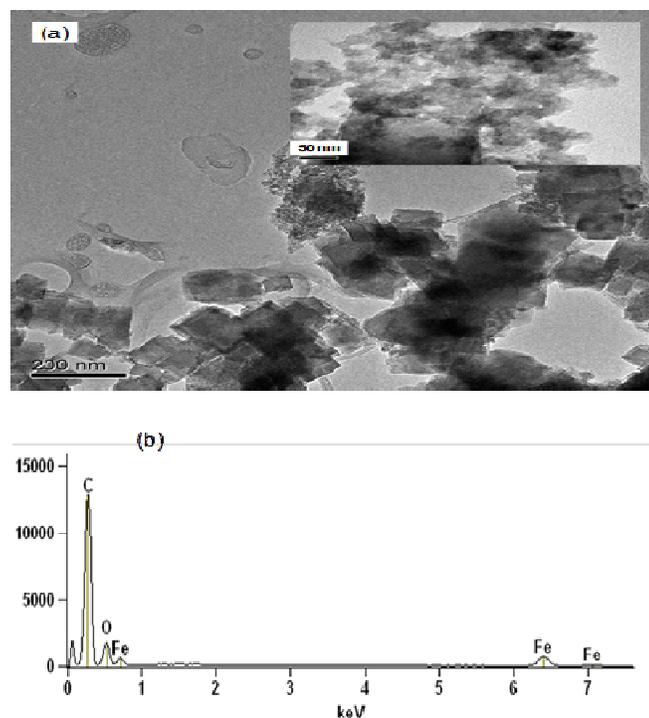


Figure 3:(a) HRSEM image of PB nanoparticles (b) EDX spectrum PB nanoparticles.

3.2 Electrocatalytic oxidation of Ph, 4-CIPh and 4-NPh at the electrodes

Figure 4a compares the current response (1st scan) of the modified electrode in phosphate buffer solution (pH 7.3) containing 10 mM Ph, 4-CIPh and 4-NPh respectively at 25 mVs^{-1} . In all the analytes, Pt-MWCNT-PB electrode gave the highest oxidation current of 108.0, 128.0 and 162.0 μA in Ph, 4-CIPh and 4-NPh respectively, which was almost 12 and 9 times greater than current recorded for the analytes on bare Pt electrode. The results obtained were consistent with other literature reports on enhanced phenols oxidation current on modified electrodes [2,4,]. However, after the second scan, a complete loss in oxidation signals of the analytes was observed on the bare Pt electrode (not shown), while a relatively small drop (7-14%) in the analytes oxidation currents was noticed on the Pt-MWCNT-PB electrode. This finding further suggests the capability of Pt-MWCNT-PB modified electrode to withstand electrode fouling that is due to the formation of polymerised Ph, 4-

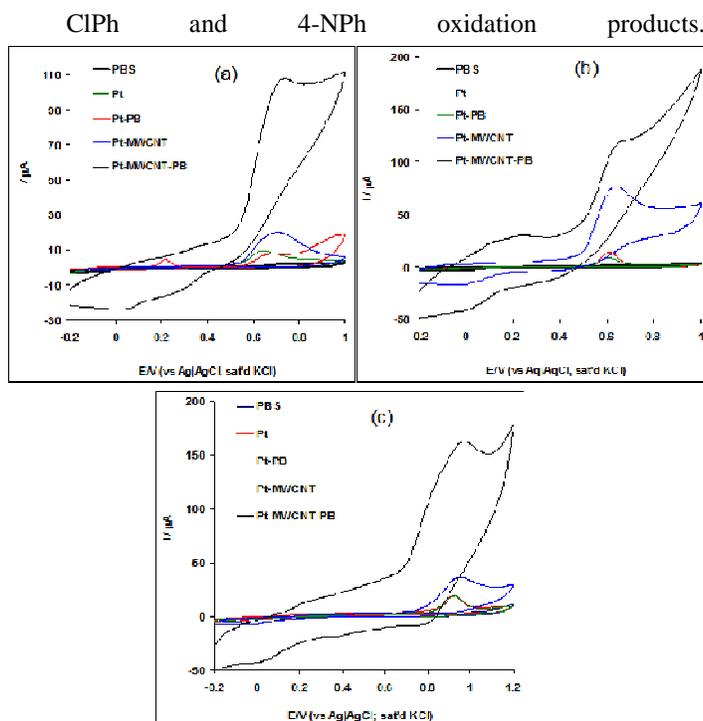


Figure 4: Comparative current response (1st and 2nd scan) showing the effect of passivation on (a) bare Pt electrode in PBS (pH 7.3) containing 10 mM Ph, (b) Pt-MWCNT-PB electrode in PBS (pH 7.3) containing 10 mM Ph, (c) Pt-MWCNT-PB electrode in PBS (pH 7.3) containing 10 mM 4-CIPh and (d) Pt-MWCNT-PB electrode in PBS (pH 7.3) containing 10 mM 4-NPh.

The Pt-MWCNT-PB electrode was run repetitively (30 cycles) in 10 mM solution of the analytes at 50 mVs^{-1} . Noteworthy, the oxidation signal of the analytes could still be observed even after the 20 scans. This is an indication that the electrode exhibited higher stability. Conducting polymers such as PBT (poly(2,2'-bithiophene)), PMT (poly(3-methylthiophene)), and PBSBT (poly[4,4'-bis(butylsulphonyl)-2,2'-bithiophene]) coating on Pt electrode led to the loss of the phenol oxidation signal after the second scan and beyond [1].

3.3 Electrochemical impedance studies

To further examine the electron transfer or capacitive behaviour of the Pt-MWCNT-PB electrode in the analytes, electrochemical impedance spectroscopy (EIS) experiment was conducted at 0.7 V vs Ag|AgCl, sat'd KCl. The impedance data (not shown) was fitted with a circuit model containing elements R_s , the solution/electrolyte resistance; R_{ct} the charge-transfer resistance, C_{film} describes the high pseudocapacitive nature of the system while CPE relates to the porous nature of the electrode.

Table 1: Impedance data for Pt and Pt-MWCNT- PB electrodes in PBS (pH 7.3) containing 10 mMPh, 4-CIPh and 4-NPh respectively, at 0.70 V vsAg|AgCl|sat'dKCl. Note that the values in parentheses are the percent errors of data fitting.

Electrode	Impedimetric parameters					
	R _e /KΩ	C/nF	R _{ct} /KΩ	Q/μF	n	C/μF
Phenol						
Pt	0.585 (6.416)	20.23 (5.26)	2.016 (6.50)	3.066 (1.210)	0.558 (0.610)	-
Pt-MWCNT-PB	185.6 (38.632)	9780.0 (6.087)	0.578 (18.044)	74.0 (4.180)	0.2802 (9.621)	-
4-chloroPhenol						
Pt	0.573 (13.209)	24.47 (13.33)	1.566 (14.99)	3.685 (2.859)	0.564 (1.387)	-
Pt-MWCNT-PB	0.372 (4.940)	265.7 (12.949)	0.453 (15.611)	124.8 (4.141)	0.4244 (4.507)	-
4-nitroPhenol						
Pt	0.632 (7.115)	1413.0 (9.785)	9.11 (14.087)	-	-	6.74 (9.808)
Pt-MWCNT-PB	0.328 (2.394)	91400.0 (5.893)	2.050 (6.367)	-	-	748.0 (15.419)

The result of the fitting is presented in Table 1. The lower R_{ct} for the Pt-MWCNT- PB electrode in all the analytes compared the bare Pt suggest faster electron transport and more favorable oxidation of the analytes on the formal electrode, enabled by the porous and the high electroactive surface area of the electrode for easy contact with the analytes. Bode plot of -phase angle vs. log (f/Hz) obtained for the different PB layers in the analyte (not shown) gave phase angles less than -90° which is expected in ideal capacitive behavior confirming the presence of CPE and pseudo-capacitive behavior of Pt-MWCNT-PB electrode towards Ph, 4-CIPh and 4-NPh. This behavior has also been related to adsorption of reaction intermediates at the electrode [12].

3.4 Electroanalysis of Ph, 4-CIPh and 4-NPh

From the scan rate study (v) (not shown), plots of E_p versus log v gave a linear relationship with Tafel values (b) of 4292.4, 663.2 and 203.8 mVdec⁻¹ for Ph, 4-CIPh and 4-NPh respectively higher than the theoretical value of 118 mVdec⁻¹ for a one-electron process in the rate-determining step, suggesting adsorption of phenol oxidation product on the electrode. Similarly, adsorptive stripping voltammetry (LSV) was used to investigate the impact of varying concentrations of the analytes to current response at the Pt-MWCNT-PB platform. From the plots of I_p versus concentration (not shown), the values of the limit of detection (LoD = 3.3 δ/m, where δ is the relative standard deviation of the intercept of the y-coordinates from the line of best fit, and m the slope of the same line) were 7.04, 4.71 and 11.76 μM for Ph, 4-CIPh and 4-NPh respectively. The

LoD value obtained for phenol (7.04 μM) in this study is a lot less compared to 500 μM reported for the analyte on PEDOT/NaPSS platinum electrode using similar technique. Also from from Langmuir adsorption isotherm plots, the adsorption equilibrium constant for the Pt-MWCNT-PB electrode in the analytes was estimated to be β (0.83± 0.05), (1.86 ± 0.05) and (2.06 ± 0.02) × 10³ M⁻¹ for Ph, 4-CIPh and 4-NPh oxidation. Thus, using Eqn. 2, the Gibbs free energy change due to adsorption was estimated as -33.8, -35.8 and -36.0 kJmol⁻¹.

$$\Delta G^{\circ} = -RT \ln \beta \quad (2)$$

4.0 CONCLUSION

This study showed that the Pt-MWCNT-PB electrode displayed higher stability and enhanced anti-fouling effects over other electrodes towards phenol oxidation. Oxidation of the analytes on the electrode was characterised by adsorption of polyphenols intermediate products.

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