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# The Electro-Catalytic and Redox-Mediator Effects of Nanostructured PDMA-PSA Modified-Electrodes as Phenol Derivative Sensors

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Phenol derivatives in laboratory prepared solutions were determined with a platinum electrode coated with poly2, 5-dimethoxyaniline phenanthrene sulphonic acid (PDMA-PSA) polymer layer. The electrically-conducting polymers were prepared by synthetic polymerisation of monomer solutions of 2, 5 dimethoxyaniline and phenanthrene sulphonic acid. Scanning Electron Microscopy (SEM) analyses of the Pt-PDMA-PSA coated electrodes have shown that nanostructured materials have formed with diameters of nanorods or nanowires at approximately 50 -200 nm. Cyclic voltammetry (CV) and Differential Pulse Voltammetry (DPV) were used to study a solution composed of $1 \times 10^{-6}$ M phenol derivatives, in the presence of the Pt/PDMA-PSA polymer sensor electrode. Amperometric phenol derivative sensors constructed with PDMA-PSA on a platinum electrode gave sensitivities from 13.65 to 63.00 mA/M and the detection limit ranged from $7.152 \times 10^{-5}$ to $1.434 \times 10^{-2}$ M for the different phenol derivatives. The data obtained for the determination of the phenol derivatives was consistent with the electro catalytic Michaelis-Menten model, giving apparent Michaelis-Menten constants ($K'_m$) values range from 6.13 to 320.80 µM for the different phenol derivatives.

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**Keywords:** PDMA-PSA modified electrodes, phenol derivative sensors, electrocatalysis, Michaelis-Menten constant.

## 1. INTRODUCTION

Phenolic compounds and their derivatives are considered priority pollutants because they are harmful to living organisms, even at low concentration (ppb) levels. Phenols are produced as wastes in a variety of industries, including dyes, plastics, pharmaceutical, oil refineries, and coke plants [1, 2]. If released into the environment, they may accumulate in the soil, ground water, or surface water, thus constituting environmental menace. It is therefore important to assess the fate of these compounds in the environment and develop effective methods to detect and remove them from water [3, 4].

There is thus an increasing demand to monitor phenol (derivatives) in the environment in real time which has been brought about by our increasing concerns with pollution, health and safety. Also, at the same time, there is the need to determine phenol (derivatives) contaminants at lower detection levels (ppb) and to improve the accuracy and precision at these levels. As a result, many methods for phenol determination have been developed in recent years, namely spectroscopic, chromatographic and electrochemical detection. These methods are however expensive, needs pre-treatment, required skilled operators and can’t get to the sample sites [5, 6]. Thus the desire to monitor real time phenol concentrations has led to the development of sensors for phenol (derivatives) detection. The end result provided us with an inexpensive, portable, miniature and intelligent sensing device to monitor phenol (derivatives) [7, 8]. The use of enzymes tyrosinase, horseradish peroxidase, etc for phenol detection and measurements has been well documented. However, these enzymes are expensive, are liable of losing its liability under operative conditions and needs to be kept at a certain storage temperature. For these reasons the enzyme route has not been widely accepted [9].

Biosensors using polyaniline (derivatives) conductive polymers are well known as electro catalyst in different enzyme electrode reactions. The goal of the electrode modification with ECP are to; (i) improve sensitivity, (ii) impart selectivity, (iii) suppress the effect of the interfering reactions and (iv) in addition the polymer membrane may serve as a support matrix for immobilized indicator molecule [10-13]. Organic polymers are normally insulators, so it can be presumed that an electrically conducting polymer must have an unusual structure. Conducting polymers i.e. polyenes or polyaromatics contain a series of conjugated single ($\sigma$- bond) and double ($\pi$- bond). The $\pi$-electrons are highly delocalized along the polymer back bone and are easily polarizable. This ability of electronic delocalization of conjugated polymers provides them the high way for the charge mobility along the polymer back bone [14-16].

In this study phenol derivatives in laboratory prepared solutions were determined with a platinum electrode coated with poly2,5-dimethoxyaniline phenanthrene sulphonic acid (PDMA-PSA) polymer layer.

## 2.EXPERIMENTAL

### *2.1. Materials*

The phenolic compounds: Phenol (Ph), 2.4-Dichlorophenol (2.4DCP), 4-Chloro-3-methylphenol (4C3MP), 2.4.6 Trichlorophenol (2.4.6TCP), 2.6-Dinitro-4-methylphenol (2.6DN4MP), 4-Nitophenol (4NP), 4-Chlorophenol (4CP), Pentachlorophenol (PCP), 2,4 Dinitrophenol (2.4DNP) and 2.4-Dimethylphenol (2.4DMP) were all obtained from Aldrich (Germany). The reagents 2,5 dimethoxyaniline (DMA), ammonium persulphate (APS) and dimethyl ether were also purchased from Aldrich (Germany). Merck’s hydrochloric acid (HCl) and methanol (MeOH) were used in the experiments. The chemicals were of analytical grade, used without further purification and were all purchased in Cape Town, South Africa.

### *2.1.2. Synthesis of phenanthrene sulfonic acid (PSA)*

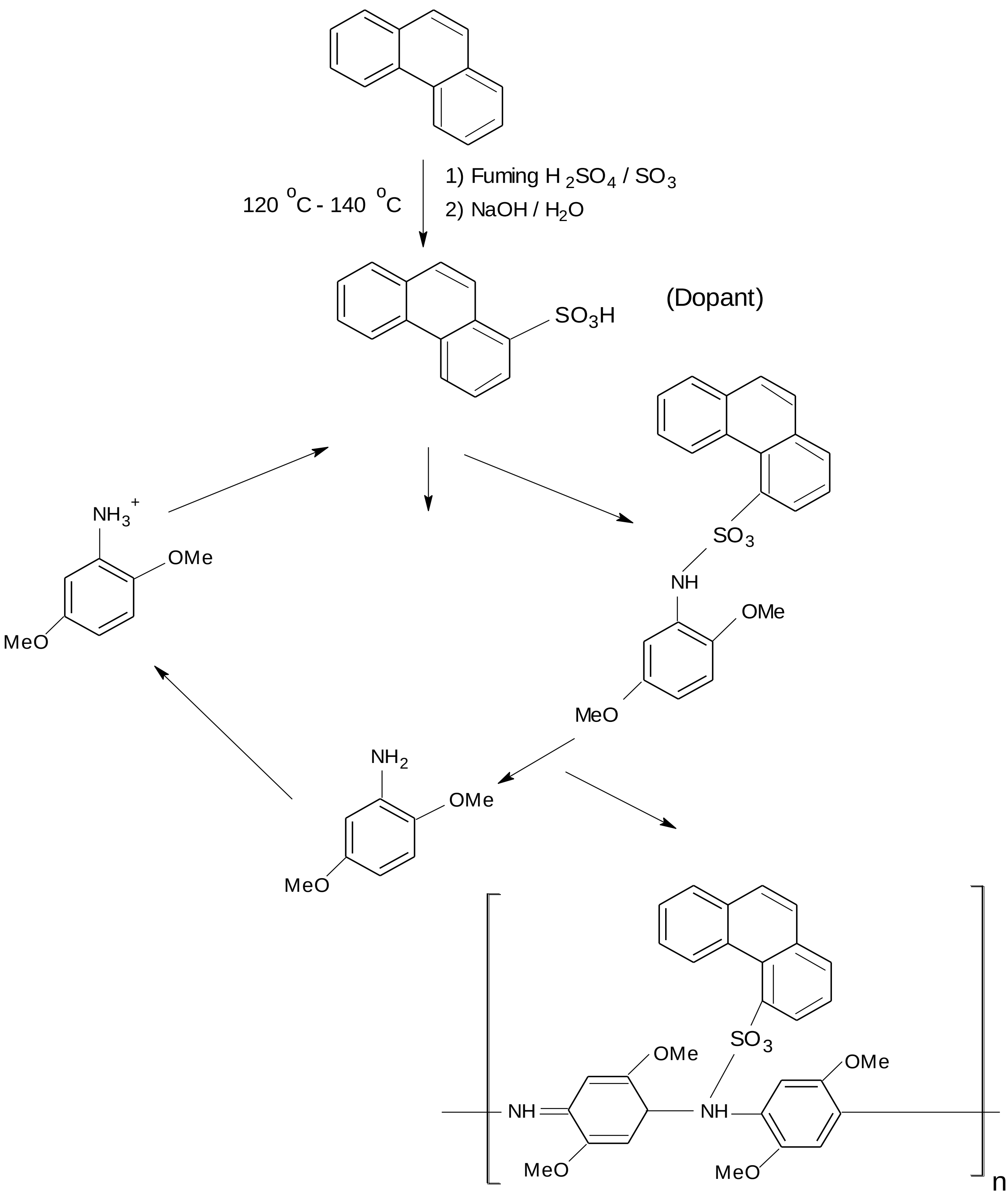

**Figure 1.** Schematic representation of the synthesis and incorporation of phenanthrene sulphonic acid (PSA) in the polymerization of 2,5 dimethoxyaniline (DMA)

10 mL of fumic $H_2SO_4$ was diluted with 10 mL $H_2SO_4$ (6 M) and the mixture was diluted to 100 mL in a volumetric flask. 50 mL of the solution was then added to 2 g of phenanthrene in a round bottom flask. The contents were heated to boiling in an oil bath (temperature between 120 – 140 °C) fitted with a condenser and thermometer.

The mixture was refluxed for 2-3 hours with constant shaking to immerse reactants into solution. The mixture was then poured into crushed ice for 20 minutes and the unreacted phenanthrene was filtered off. 10 mL 50% NaOH was added to the mixture and put in a refrigerator to crystallize, forming white phenanthrene sulfonic salt. The salt was then hydrolysed to form phenanthrene sulfonic acid (Figure 1) [15].

### *2.1.3. Synthesis of poly (2,5 dimethoxyaniline)(PDMA)-Phenanthrene sulfonic acid (PSA) nanostructures*

The procedure for the synthesis of PDMA-PSA was a modification of a typical oxidation polymerisation method. 2,5 dimethoxyaniline (0.0334 g), 20 mL of deionized water and phenanthrene sulphonic acid (0.2592 mL) were placed in a 100 mL beaker. The mixture was heated for 30 min at 50 $^{o}$C while stirring vigorously.

An aqueous solution of ammonium persulphate (APS) (0.1 M) was added dropwise to the hot solution. The mixture was cooled down to room temperature while continuously stirred for 15 hrs. The product was filtered and washed with deionised water, methanol and dimethyl ether 3 times respectively, to remove impurities such as APS, free PSA and unreacted 2,5 dimethoxyaniline [17–18].

### *2.1.4. Construction of Phenol (derivative) Chemical sensor*

Prior to use, a platinum disc electrode was first etched for about 5 min in a hot ‘Piranha’ solution {1:3 (v/v) 30% $H_2O_2$ and concentrated $H_2SO_4$}. It was then polished on aqueous slurries of 1, 0.3 and 0.05 micron alumina powder, respectively.

After thorough rinsing with deionized water followed by acetone, the electrodes were cleaned electrochemically by cycling it between -200 and 1500 mV in 0.05 M $H_2SO_4$ at a scan rate of 10 mV/s for 10 min or until the CV characteristics for a clean Pt electrode were obtained. The redox mediator was formed by dissolving 0.001 g of PDMA/PSA polymer in 0.1 mL of methanol (MeOH). 10 µL of the polymer solution was then put on top of a Pt-disk electrode and the MeOH solvent was allowed to evaporate.

The dried Pt/PDMA-PSA modified electrode was then characterised in 1 M HCl (pH 0 – 1) at different scan rates using Cyclic Voltammetry (CV).

### *2.1.5. Determination of Phenol and Phenol derivatives*

The Pt/PDMA-PSA electrochemical sensor was placed in 1 ml 1 M HCl (pH 0 -1) solution to which 10 µL additions of the phenol derivatives were added. Differential Pulse Voltammetry (DPV) was performed after each addition of the phenol (derivatives) up to maximum concentration. The increase in current due to the phenol (derivatives) oxidation was recorded.

### *2.2. Instrumentation*

Scanning electron microscopy (SEM) was performed with a Hitachi X650 scanning electron microscope which has a operating voltage window of 5 – 40 kV. All electrochemical experiments were carried out and recorded on a BAS50/W electrochemical analyser (Bioanalytical Systems, Lafayette, IN, USA). Alumina micro polish and polishing pads (Buehler, IL, USA) were used for the Pt electrode polishing. A paste of the PDMA-PSA (0.1 g) in 2 mL HCl (1 M) was first prepared. The paste cell was degassed with argon for 20 minutes to exclude any oxygen from the paste. A conventional three electrode system was employed: working electrode (WE) was a platinum disc electrode, silver/silver chloride (Ag/AgCl) and a platinum wire were used as reference and auxiliary electrodes, respectively. Voltammograms were recorded at 25 $^{o}$C, anodically at potential scan rates of 10 – 70 mV/s. For convention, a negative oxidation current was used for the display of all figures.

## 3. RESULTS AND DISCUSSION

### *3.1. Morphology of PDMA/PSA structures*

The morphology and structure of poly (2,5 dimethoxyaniline) (PDMA) with phenanthrene sulphonic acid (PSA) were investigated.

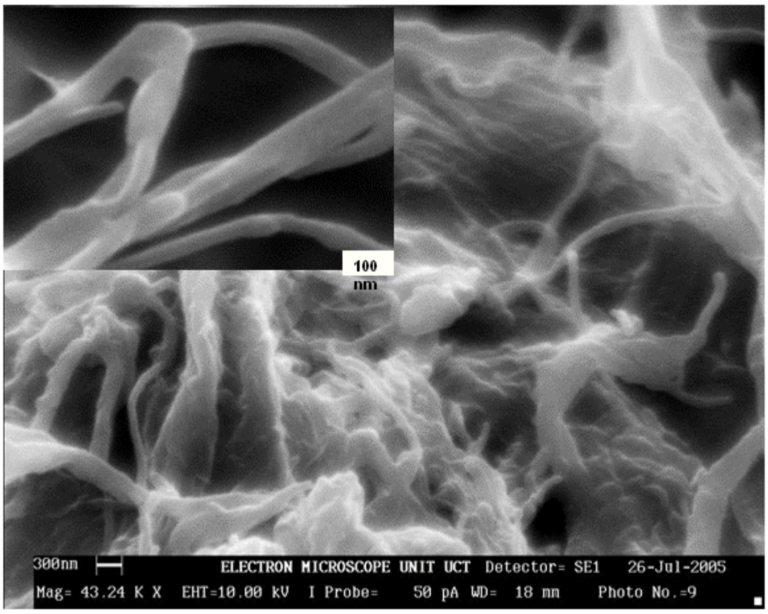

**Figure 2.** SEM micrograph of Poly (2,5 dimethoxyaniline) (PDMA) doped with phenanthrene sulfonic acid (PSA)

Figure 2 and insert shows SEM micrograph of PDMA doped with PSA. Nanostructured wires were observed when PDMA was doped with PSA. The observed diameters were between 100 and 300 nm at 100 000 x magnification [19].

### *3.2. Electrochemistry*

#### *3.2.1. CV characterization of PDMA/PSA on platinum*

Figure 3 illustrates multi-scan voltammograms of PDMA/PSA on Pt electrode in HCl (1M) solution with scan rates 5, 10, 15, 30, 40 and 50 mV/s. Analysis of the voltammograms showed that the peak potentials and corresponding currents vary with the scan rates.

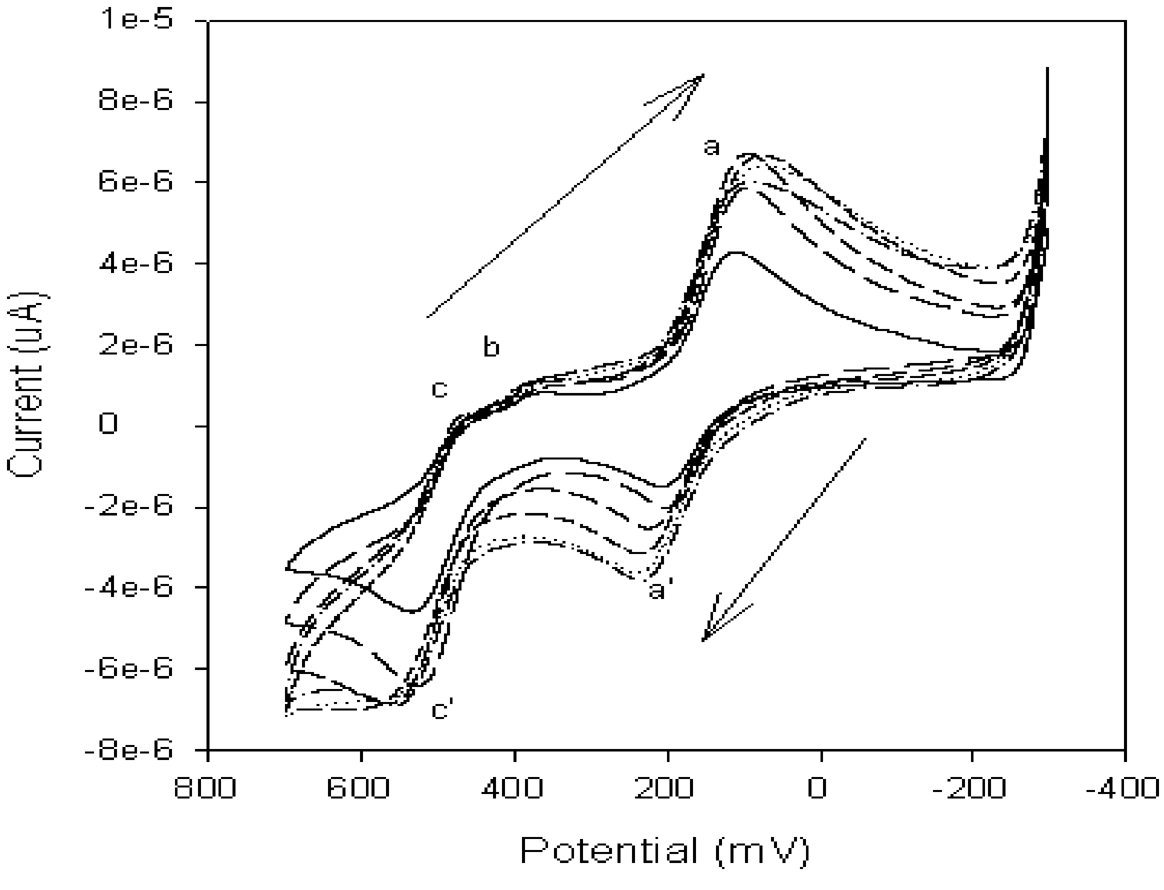

**Figure 3.** Multi-scan cyclic voltammograms (CV) of Pt/PDMA-PSA in 1 M HCl at 25 °C

This indicates that the polymer nanostructure is electro-active and the electron transfer processes are coupled to a diffusion process namely, charge transportation along the polymeric nanostructure. Analysis of the cyclic voltammograms established 2 anodic and 3 cathodic peaks. The first oxidation peak at +172.1 mV is the emaraldine (peak a′), which is further oxidized at higher potential +577.0 mV (peak c′). On the cathodic peak scan, pernigraniline cation radical at +354.0 mV (peak c) is reduced to the fully reduced leucoemaraldine at +119.3 mV (peak a) [19 - 21].

### *3.2.2. Kinetic studies of PDMA-PSA on Pt electrode in 1M HCl*

The number of electrons transferred was estimated from the CV and was calculated for PDMA/PSA (peak (a), using the equation:

$$/E_p - E_{p1/2}/ = 2.20\ R\ T/\ n\ F = 56.5\ /\ n \qquad (1)$$

where $E_p$ is the maximum peak potential, $Ep_{1/2}$ is half the maximum peak potential, R is the gas constant (8.314 J.(mol. $K^{-1}$)), T is the absolute temperature (298 K) of the system, F is the Faraday constant (96.584 C/mol) and n represents the number of electrons transferred. It was found to be a one electron transfer system for PDMA-PSA [20, 21].

The linear dependence of peak current on the scan rate for PDMA-PSA showed that we have a stationary paste of conducting electro-active polymers on the electrode, which undergo rapid charge transfer reactions.

This is typical of a Nernstian reversible reaction of a surface confine species. The surface concentration (Γ*) of the absorbed electro active species could therefore be estimated from a plot of Ip versus υ in accordance with the Brown Anson model [16] using the equation:

$$Ip = n^2\ F^2\ \Gamma^*\ A\ \nu\ /\ 4\ R\ T \qquad (2)$$

where Ip represents the peak current, A is the surface area of the electrode (0.0177 $cm^2$), ν is the scan rate (V/s), Γ* is the surface concentration of the absorbed electro-active species, and F, R, T are the same as in equation (1). The surface concentration of PDMA-PSA (peak c) was estimated to be $2.960 \times 10^{-2}$ mol/$cm^2$.

The Randel-Sevcik equation of analysis of voltammetric data was used to determine the rate of charge transport coefficient (D) along the polymer chain.

The Randel-Sevcik behaviour of the cyclic voltammetric peak currents has been used to evaluate D from the slope of the straight line obtained from the Ip versus $\nu^{1/2}$. D value was estimated to be $2.008 \times 10^{-9}$ $cm^2$/s for PDMA-PSA (peak a′). Mathebe et al.[21] and Iwuoha et al.[20] reported $D_e$ values for PANI ($8.68 \times 10^{-9}$ $cm^2$/s) and PANI/PVS ($6.46 \times 10^{-8}$ $cm^2$/s) in 1 M HCl. These findings were further confirmed by calculation of the standard rate constant ($k^o$) of to PDMA/PSA, peak a, ($5.593 \times 10^{-5}$ cm/s) [22, 23].

### *3.2.3. Characterisation of PDMA-PSA electrode*

Figure 4 shows the cyclic voltammogram (CV) of a clean Pt electrode in comparison with the same electrode coated with PDMA/PSA polymer. The voltammograms show that there is a change in sensitivity of the Pt electrode surface characterised by an increase in $\Delta E_p$ when PDMA/PSA was coated on the electrode surface. PDMA/PSA thus provides a template upon which oxidation and reduction reactions can take place.

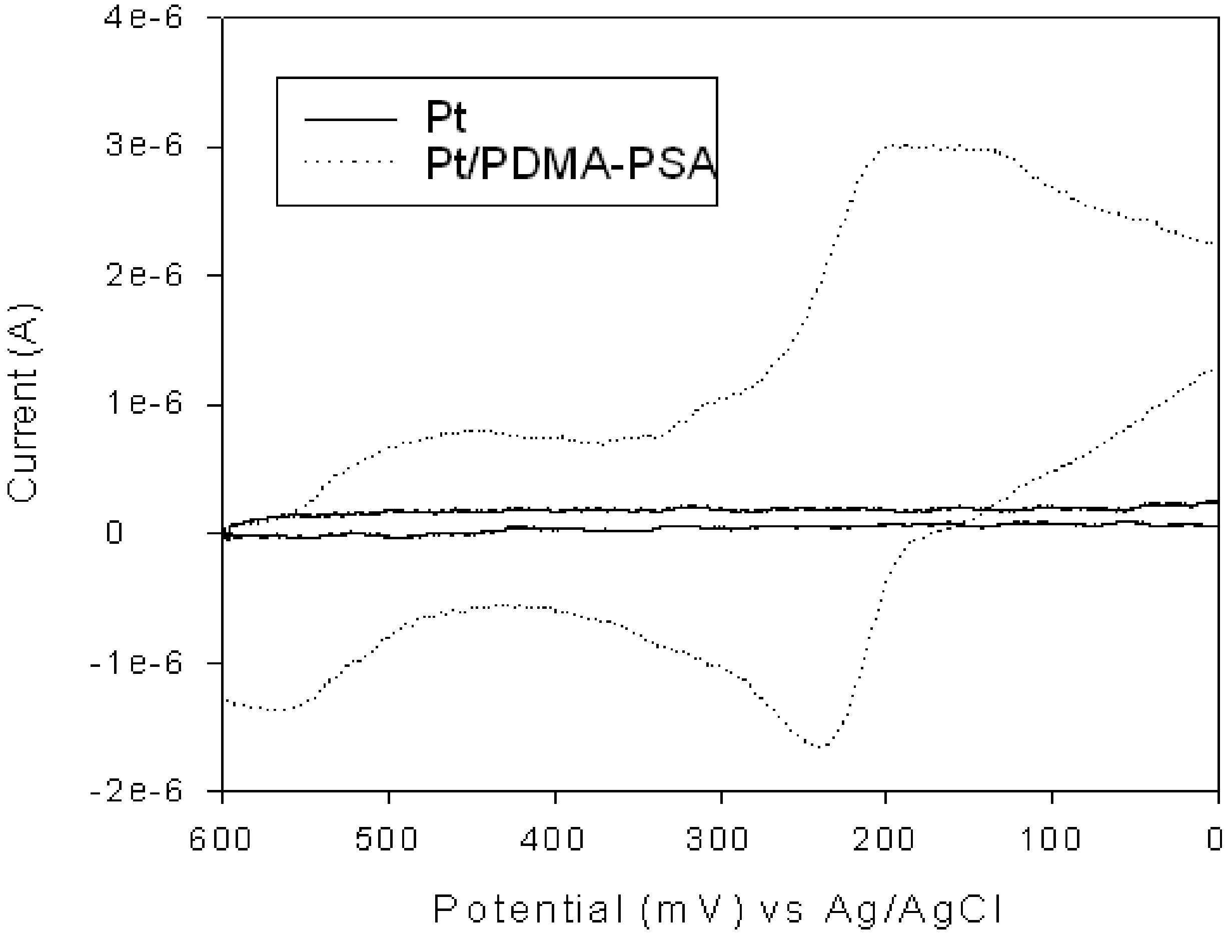

**Figure 4.** Cyclic voltammograms of — clean Pt electrode and ····· Pt/PDMA/PSA electrode in1 M HCl (pH 0 – 1) at a scanrate of 10 mV/s

### *3.2.4. Reactivity of Pt/PDMA/PSA to phenol (derivatives)*

Figure 5 is a schematic representation of the reactions of the Pt/PDMA/PSA chemo sensor system. The figure shows that one of two pathways of phenol oxidation may occur at the electrode surface. It is generally considered that the oxidation of phenol begins with electron transfer that leads to phenoxic radicals.

In pathway 1, the phenoxic radicals results in the formation of polymeric phenols, this leads to poisoning of the electrode surface. In pathway 2, the phenoxy radicals results in the formation of benzoquinone and hydroquinone and can be further degraded with ring breakage to form various aliphatic acids, which is then further degraded to carbon dioxide and water [24].

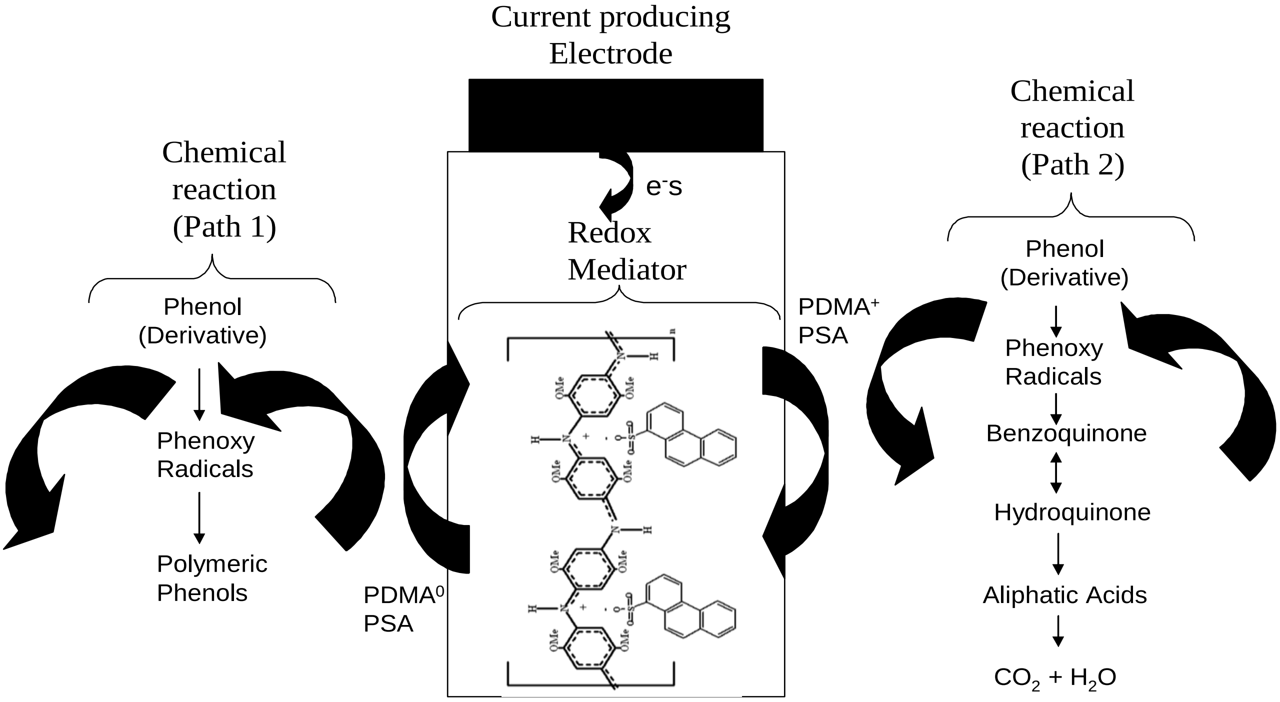

**Figure 5**. A schematic representation of the Pt/PDMA/PSA/Phenol chemosensor reactions occurring at the Pt electrode

### *3.2.5. Detection of phenol, 2,4 dichlorophenol and 2,4,6 trichlorophenol*

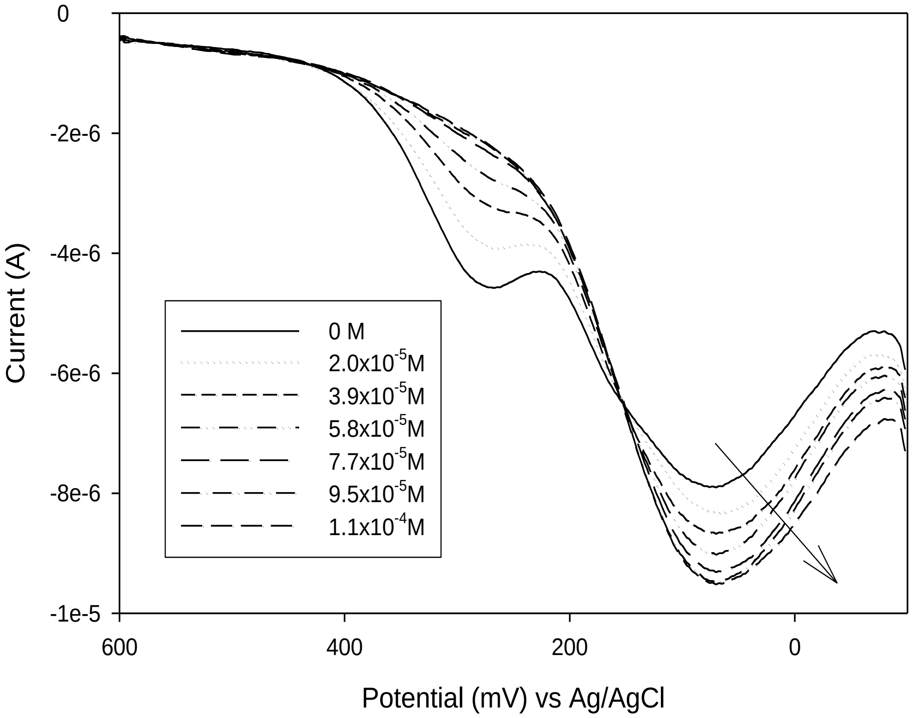

**Figure 6.** Differential pulse voltammograms of Pt/PDMA/PSA chemosensor responses to phenol in 1 M HCl, with the potential scanned between -100 mV to +600 mV at a frequency of 10 Hz. Arrow indicates increase in catalytic current

Figure 6 shows the anodic DPV responses of Pt/PDMA/PSA chemo sensor to phenol in cell solution containing 1 M HCl. There was a negligible shift in the differential pulse peak potential on addition of phenol. An increase in the catalytic current was observed at a potential of +100 mV, most conducting emeraldine state of PDMA, upon addition of phenol.

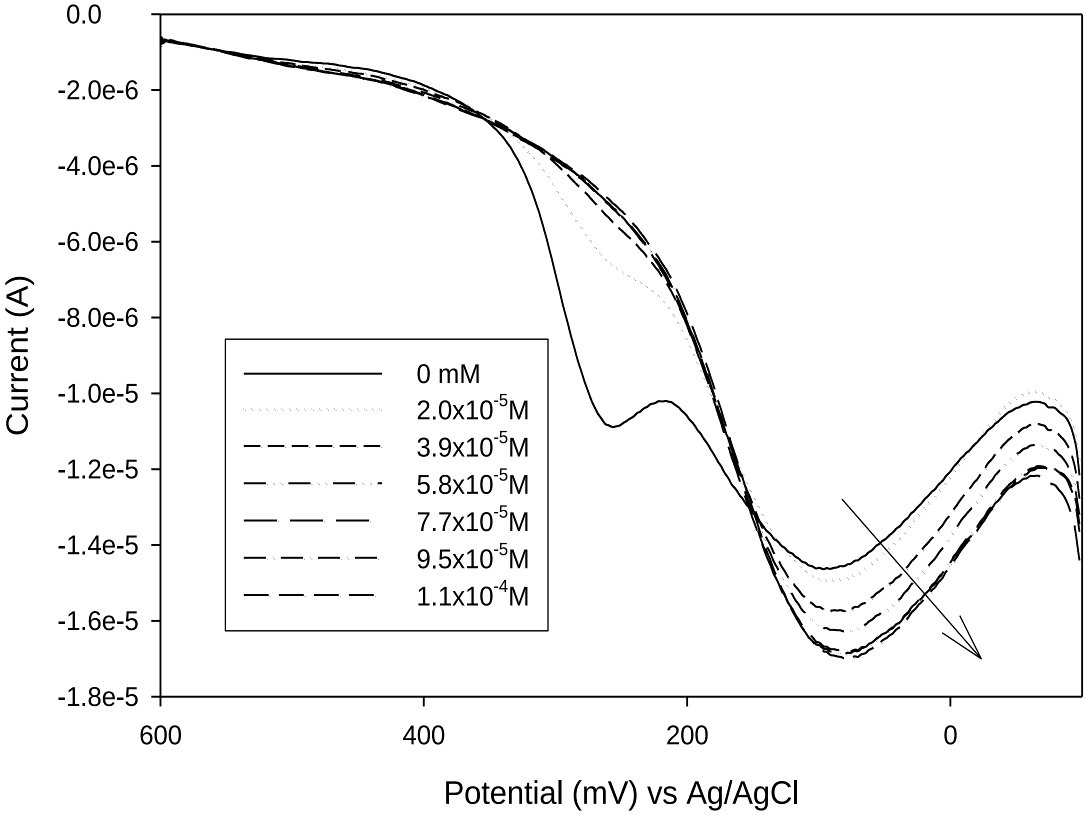

**Figure 7.** Differential pulse voltammograms of Pt/PDMA/PSA chemosensor responses to 2,4 Dichlorophenol in 1 M HCl, with the potential scanned between -100 mV to +600 mVat a frequency of 10 Hz

The increase in current can be explained as resulting from the formation of the phenol oxidation products. A decrease of catalytic current was observed around +300 mV, which was attributed to the less conducting pernigraniline state of PDMA. Similar results were obtained for 2,4 dichlorophenol (Figure 7) and 2,4,6 trichlorophenol (Figure 8).

Figure 9 represents the Pt/PDMA-PSA chemo sensor calibration curves in 1 M HCl when 4-CP, 2.4-DCP, 2.4-DNP, 2.4-DMP and 2.4.6-TCP were added to the electrochemical cell. An increase in current responses was detected at low concentration of the phenolic compounds. A maximum current was reached where the activity of the chemo sensor is decreased at high concentrations of the phenolic compounds, which was probably due to the competition for active sites on the chemo sensor surface [24].

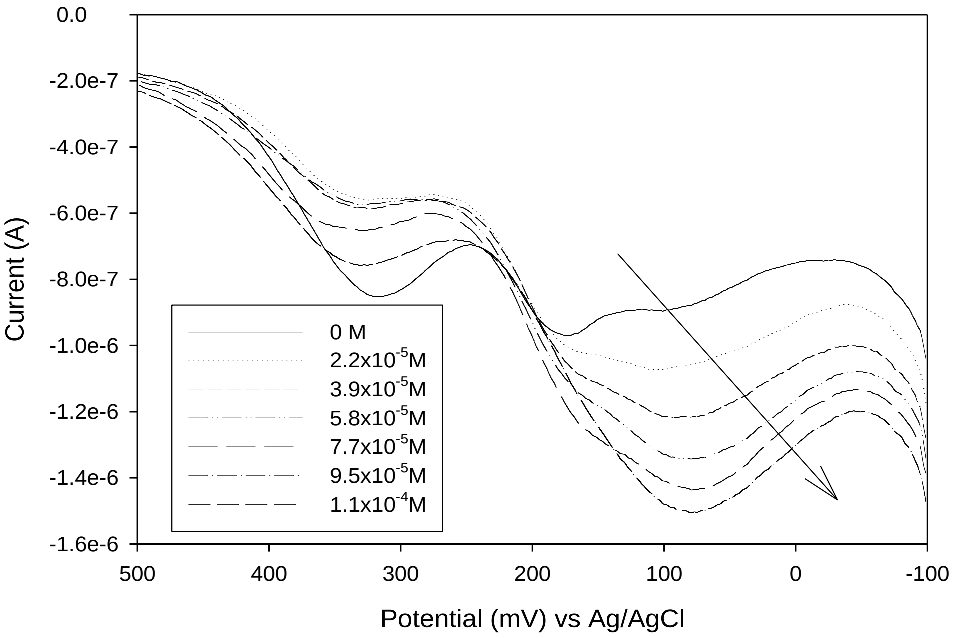

**Figure 8**. Differential pulse voltammograms of Pt/PDMA/PSA chemosensor responses to 2,4,6 Trichlorophenol in 1 M HCl, with the potential scanned between -100 mV to +600 mVat a frequency of 10 Hz

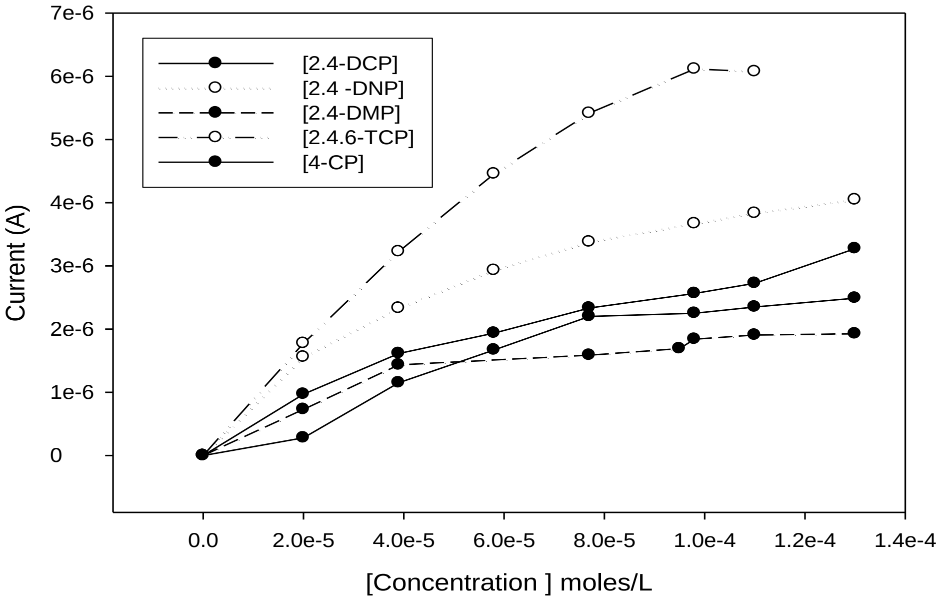

**Figure 9**. Calibration curves of the Pt/PDMA-PSA modified electrode for 4-CP, 2.4-DCP, 2.4-DNP, 2.4-DMP and 2.4.6-TCP

### *3.2.6. Chemosensor Kinetic Parameters for Phenol (derivatives) detection*

The kinetic parameters of the Pt/PDMA-PSA nanostructure polymer for phenolic compounds are presented in Table 1. The calibration curves all displayed non-linear responses of current with phenolic compound concentration and was modelled according to the Michaelis-Menten paradigm [20-22]. The sensitivities, measured by the slope of the calibration curves, followed the order 2.4.6-TCP > PCP > 2.4-DNP > 2.6DN4MP > 2.4.6TCP > 4-CP > 2.4-DCP > 4-C3MP > Ph > 2.4-DMP. Thus indicating that the electron-withdrawing phenolic compounds are more soluble in the PDMA-PSA matrix than the electron donating phenolic compounds [22]. The Michaelis-Menten constant ($K'_m$) in this case predicts the ease with which an analyte interact with the polymer and followed the order 2.4-DMP > 4-CP > 2.4-DCP > 2.4.6-TCP > Ph > 2.4-DNP > 2.6-DN4MP > 4-C3MP > PCP. This means that 2.4-DMP stays longer in the solvent medium than PCP, with the result that the sensor requires a large amount of the 2.4-DMP to saturate its activity [20]. The apparent turnover rate constant ($k'_{cat}$) of the chemo-sensor is directly proportional to the total analyte concentration in the sensing nanostructured polymer and it therefore determines the maximum current, realizable from the sensor at saturation concentration of the analyte. The $k'_{cat}$ followed the order 2.4.6-TCP > 2.4-DNP > 4-CP > PCP > 2.4-DCP > 2.6-DN4MP > 2.4-DMP > Ph > 4-C3MP, which suggest faster reaction rate and higher currents for Pt/PDMA-PSA as a chemosensor for 2.4.6-TCP compare to Pt/PDMA-PSA as a chemosensor for 4-C3MP. A high detection limit was observed for the Pt/PDMA-PSA electrode as a chemosensor for phenol (derivatives) at an estimated signal to noise (S/N) ratio of 3 [21].

**Table 1.** Kinetic parameters of the Pt/PDMA-PSA chemosensor for various phenol (derivatives)

| Analyte | Sensitivity (mA/M) | $K'_m$ (µM) | $k'_{cat}$ ($nmol.cm^{-2}.s^{-1}$) | Detection Limit (M) |
|---|---|---|---|---|
| Phenol | 13.65 | 86.50 | 0.691 | $2.089 \times 10^{-3}$ |
| 4-CP | 22.54 | 145.00 | 1.916 | $1.434 \times 10^{-2}$ |
| 4-NP | nd | nd | nd | nd |
| 2.4-DCP | 20.50 | 121.50 | 1.458 | $2.526 \times 10^{-3}$ |
| 2.4.6-TCP | 63.00 | 97.05 | 3.58 | $7.152 \times 10^{-5}$ |
| 2.4-DNP | 42.00 | 80.43 | 1.978 | $6.347 \times 10^{-4}$ |
| 2.4-DMP | 6.00 | 320.80 | 1.127 | $3.708 \times 10^{-3}$ |
| PCP | 48.00 | 6.13 | 1.721 | $6.089 \times 10^{-4}$ |
| 4-C3MP | 17.70 | 18.3 | 0.1897 | $1.045 \times 10^{-3}$ |
| 2.6-DN4MP | 31.00 | 79.19 | 1.437 | $7.89 \times 10^{-4}$ |

nd = not determined

The voltammetric responses obtained by the Pt/PDMA-PSA modified electrode obtained in the presence of phenolic compounds is proposed to be representative of the catalytic current results from the redox mediation reactions of the PDMA-PSA conducting polymer and the oxidation of the phenolic compounds as schematically represented in Figure 5 (path 2). The diagram shows that the phenol is firstly oxidised to phenoxy radicals, which is further converted to benzoquinone and hydroquinone, as the reaction proceeds the aliphatic acids was formed and then eventually converted to carbon dioxide and water [25].

## 4. CONCLUSION

This study shows that the dopant phenanthrene sulfonic acid (PSA) could be incorporated into the poly (2,5 dimethoxyaniline) [PDMA] polymer backbone. The redox characteristics of phenol derivatives at Pt electrode coated with a poly (2,5 dimethoxyaniline) phenanthrene sulphonic acid [PDMA-PSA] has been investigated. Cyclic Voltammetric characterization of the polymer pastes showed distinctive redox couples representing various redox states measurable in the polymer. Thus, by applying appropriate potential the polymeric nanotubes can be stabilized at required oxidation states. SEM analyses of the PDMA-PSA polymer coated electrodes have shown that nanostructured materials were obtained. Lastly, it was found that the sensors has a detection limits of $1.434 \times 10^{-2}$ to $7.152 \times 10^{-5}$ M which is within the range of other phenol sensors quoted in literature [22].

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