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Polyaniline and its Derivatives for Environmental Analysis

A thesis

presented to

the faculty of the Department of Chemistry

East Tennessee State University

In partial fulfillment

of the requirements for the degree

Master of Science in Chemistry

by

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August, 2006

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Keywords: Polyaniline, Carbon Nanotubes, Poly-(*ortho*-phenylenediamine), Poly-(*meta*-phenylenediamine), Poly-(*para*-phenylenediamine), Electropolymerization, Heavy metals, Environment

ABSTRACT

Polyaniline and its Derivatives for Environmental Analysis

by

Atogho Jude Abia

Electrooxidation has been used to deposit thin film polyaniline as well as its derivative – thin film poly (ortho-phenylenediamine) (POPD) and poly (meta-phenylenediamine) (PMPD) on carbon electrodes, which are subsequently used to monitor the environmental heavy metal ions (Hg^{2+} , Pb^{2+} , Cd^{2+}) through a rather unusual “blocking” of anodic stripping for these metals. Using Hg^{2+} as a model, its cyclic voltammogram for a modified glassy carbon electrode with the resultant polymer shows an enhanced cathodic peak that increases linearly with the analyte ion concentration. POPD also exhibits unique selective detection for organic species. Acetaminophen and uric acid can be preferentially detected over ascorbic acid from a mixture of these three compounds. In addition, the effect of carbon nanotubes incorporated in polyaniline (PAN) film is observed to have enhanced electrochemical catalytic activities on the remedy of environmental dichromate.

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CHAPTER 1

INTRODUCTION

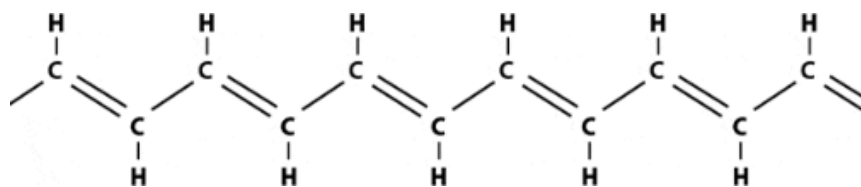
The Conducting Polymer

Conducting polymers (CPs) can be defined as large cyclically conjugated electroactive polymers, that is, they are capable of undergoing oxidation/reduction themselves [1].

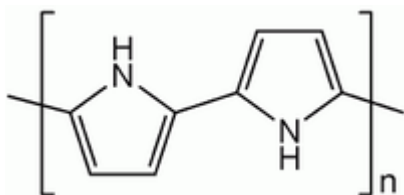
Generally, there are considered to be four primary types of conducting polymers [2]. The first and most widely used commercial conducting polymers are composites in which an originally non-conducting polymer matrix is filled with a powdered conductive medium such as carbon or metal to give rise to its conductivity. Applications for such composites are varied and could be used for solder substitutes and antiseptic. The second group of polymers is called ionically conducting polymers. Here, electrical conductivity is as a result of movement of ions. An example of such a polymer is polyethylene oxide, in which lithium ions are mobile. These kinds of polymers find application in the battery industry. The third group of polymers is called redox polymers. These contain immobilized redox centers (electroactive centers). These centers are not necessarily in contact with one another, but can conduct charge by electron transfer from one center to another by what is known as a “hopping” mechanism. In this mechanism, electrons

tunnel from one redox center to another through an insulating barrier. There must be a large number of redox centers so as to increase the probability of such tunneling. The fourth group is conjugated polymers. These polymers consist of alternating single and double bonds, creating an extended π -network. Electron movement within this π -framework is the source of conductivity. Polyaniline (PAN), of which more information will be presented on later in this work, is an example of such a polymer. Other common examples of conjugated polymers are shown in Figure 1.

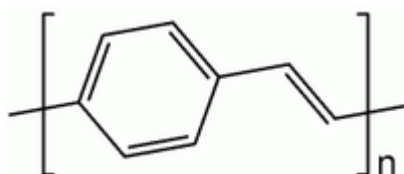
The difference between redox polymers and conjugated polymers may be subtle. However, in conjugated polymers, conduction within one polymer chain is based on the conjugated nature of the polymer molecules and the resulting mobility of π -electrons and not on immobilized redox centers.



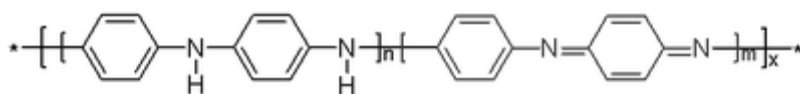
Polyacetylene (PA)



Polypyrrole (PPY)



Poly (p-phenylene vinylene)



Polyaniline (PAN)

Figure 1: Structures of Some Common Conjugated Polymers

Synthesis of Conducting Polymers

There are two main methods of synthesizing CPs, namely[3]; chemical synthesis and electropolymerization. The electrochemical synthesis, which I used for my work, is a more preferred method due to its reproducibility and simplicity. The synthesis is carried out at room temperature, and the desired polymer film thickness can be achieved by simply varying the potential or current with time. Most electrochemical synthesis proceeds through radical coupling polymerizations, while chemical syntheses are condensation polymerizations. Condensation polymerization generally involves loss or elimination of a chemical species resulting from the reaction of end groups on monomer molecules.

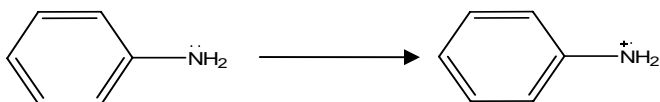
Electrochemical Methods. Constant potential (or potentiostatic), constant current (or galvanostatic) and potential sweep methods are usually used for electropolymerization of PAN and its derivatives. These procedures are advantageous for controlling the amount of product because the polymerization can proceed only when the monomer is oxidized at the electrode. Standard electrochemical techniques, which employ a divided cell containing a working electrode, a counter electrode and a reference electrode generally, produce the required films. The commonly used working electrodes are conducting substrates such as gold, carbon, platinum, and indium-tin oxide coated glass plates. Semi-

conducting materials including n-doped silicon, gallium arsenide, and cadmium sulfide and semi-metal graphite are also employed for the growth of polymer films. It is important to remember that many CPs synthesized by electrochemical methods are oligomers, with chain lengths ranging from about 8 monomer units to 50 units, which is much less than the typically portrayed 100,000 units of some anilines [3]. Even for the best CPs, morphology is poor, nowhere approaching the morphology routinely obtained in common organic polymers such as polyethylene.

Polyaniline (PAN)

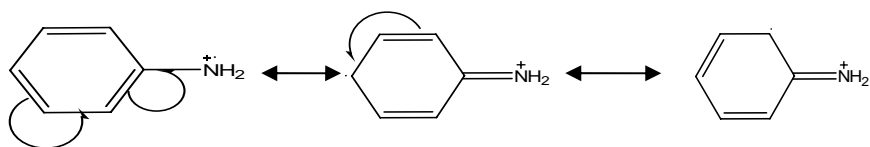
Mechanism of Polymerization

As early as 1962, Mohilner et al. [4] investigated the kinetics of the electrochemical oxidation of aniline in sulfuric acid and deduced that the initial oxidation requires the formation of aniline radical. Since then the nature of the intermediates of PAN synthesis have been proposed based on cyclic voltammograms. The first stage of the PAN synthesis was found to be the formation of $C_6H_5-NH_2^+$ cation radical through the transfer of electron from an sp^3 orbital of nitrogen atom to the electrode during electrochemical oxidation.



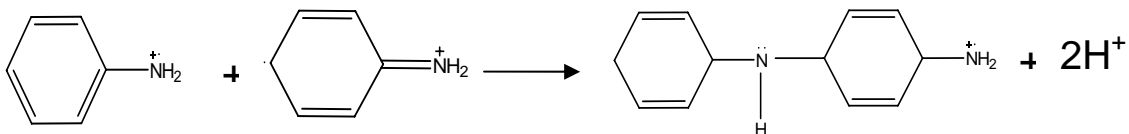
1.1

The aniline radical is resonance stabilized as shown:



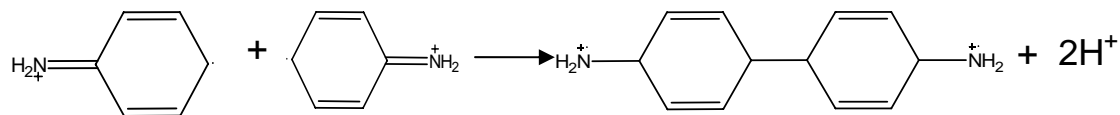
1.2

These radicals may then combine in different ways to form polyaniline. Head to tail coupling or 1, 4-substitution is believed to predominate and produce p-aminodiphenyl amine.



1.3

A competing reaction involves tail-tail coupling of aniline, which forms benzidine.



1.4

Kinetics studies led Mohilner et al. [4] to the conclusion that the oxidation of aniline occurs *via* a free radical mechanism that produces the emeraldine octamer as the primary product. A more detailed mechanism as proposed by Wei and coworkers [5] is presented below in Figure 2.

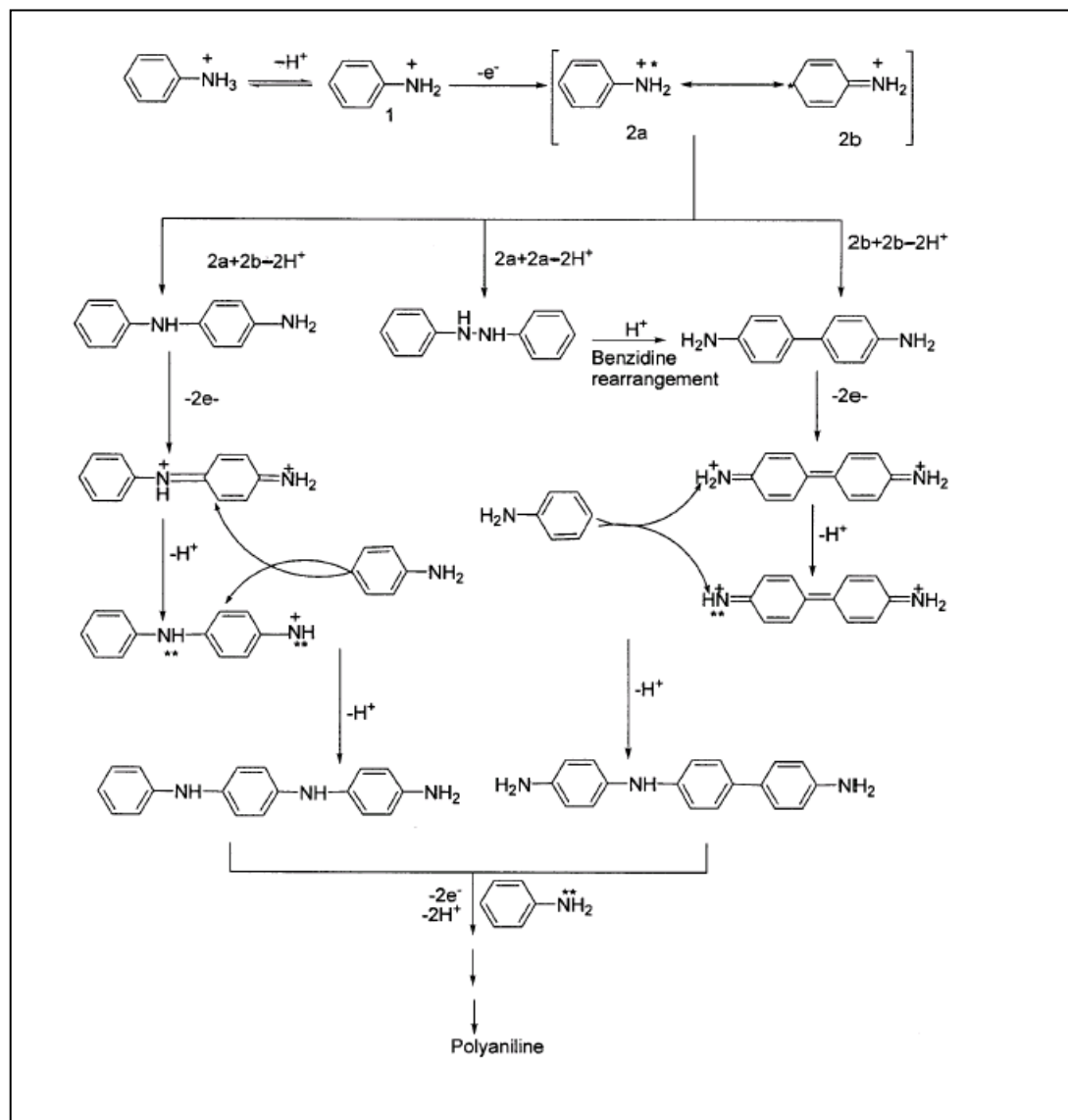
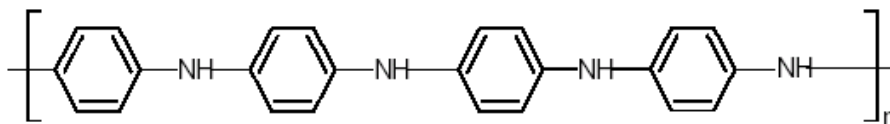


Figure 2: Mechanism of Electropolymerization of Aniline

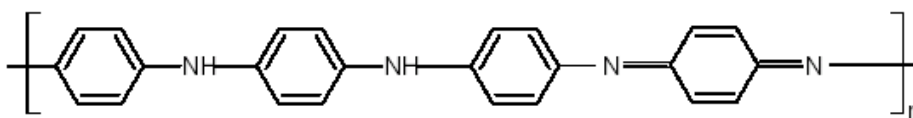
It is well known that PAN has a variety of oxidation states that are both pH and potential dependent. It is generally agreed that PAN has three different fundamental forms: leucoemeraldine (LE: fully reduced), emeraldine base (EB: half oxidized), and pernigraniline (PN: fully oxidized). The only electrically conducting one is, however, the emeraldine salt form (ES: half oxidized), which is the protonated form of EB.

The four forms are as follows:

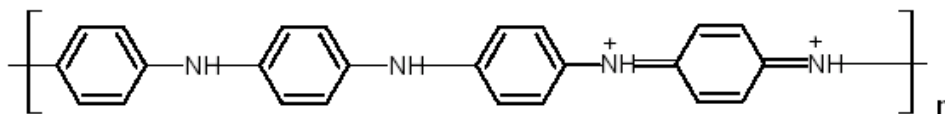
Leucoemeraldine (insulator): Light yellow / transparent



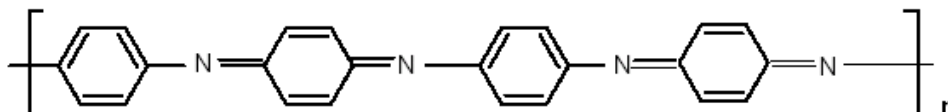
Emeraldine base (insulator): Blue



Emeraldine Salt Conductive form (Good conductor): Green



Pernigraniline (insulator): Blue-black



Carbon Nanotubes Incorporation into PAN

Carbon nanotubes (CNTs) are molecular-scale tubes of graphitic carbon with outstanding properties. They are among the stiffest and strongest fibers known, and have remarkable electronic properties and many other unique characteristics. For these reasons they have attracted a lot of attention in academia and industries. The use of CNTs for commercial applications has been slow, due primarily to the high production costs of high quality nanotubes. CNTs could be either single-walled (SWCNT) or multi-walled (MWCNT). To date, only a few papers have been reported on PAN/CNTs composite [6]. Here, we report the preparation and use of PAN/SWCNT for environmental analysis.

Polyaniline Derivatives

Introduction

Whereas many papers have been devoted to the electropolymerization of aniline and the characterization of the polyaniline-modified electrodes, not a lot of information is available about the properties of the polymeric films formed by the electrooxidation of the aniline derivatives [7]. Among those derivatives, *ortho*-phenylenediamine and its polymer poly (o-phenylenediamine) (POPD) have shown interesting properties and thus promising application in various aspects [8]. POPD

can be obtained as a thin layer of self-limiting thickness on different conducting substrates *via* anodic electropolymerization processes [9].

Properties of Poly-*ortho*-Phenylenediamine (POPD)

POPD is a solid. In the reduced form, the film is colorless, and its oxidized form is red. This is contrary to the usual green-blue color of other polyaniline films [7]. Two interesting properties of POPD, different from those that are characteristic for usual conducting polymers like polyaniline makes it promising for applications in electrochemical and bioelectrochemical sensors:

- 1) As opposed to PAN, the conducting form of POPD is its reduced state, whereas its oxidized state is insulating.
- 2) POPD film is permselective. Permselectivity is a term used to define the preferential permeation of certain ionic species through ion-exchange membranes.

This permselectivity of POPD is different from other PAN polymers. When deposited onto an electrode, POPD permits the diffusion of some redox active species to the electrode surface, whereas other species with are retarded at the polymer/solution interface. This useful property of POPD has been widely exploited for the development of sensors [8].

Mechanism of Polymerization of POPD. POPD can be prepared electrochemically in acidic, neutral, and alkaline solutions. It is very stable in both aqueous solutions and air [10]. POPD easily dissolves in organic solvents such as dimethyl sulfoxide. This ease of dissolution makes it one of the so-called soluble electroactive polymers and provides more flexibility in its *ex-situ* structural studies. In the first step of the polymerization process, oligomers are formed, and in acidic medium, only a small portion of oligomers are polymerized and deposited on the electrode surface [10, 11]. The polymerization process is not an autocatalytic one. The electrochemical polymerization of o-phenylenediamine is a self-limiting process because poly (o-phenylenediamine) is an insulating polymer [12]. Barbero et al. [12] have studied the structure and the mechanism of the electropolymerization of o-phenylenediamine and have proposed the following scheme as shown in Figure 3.

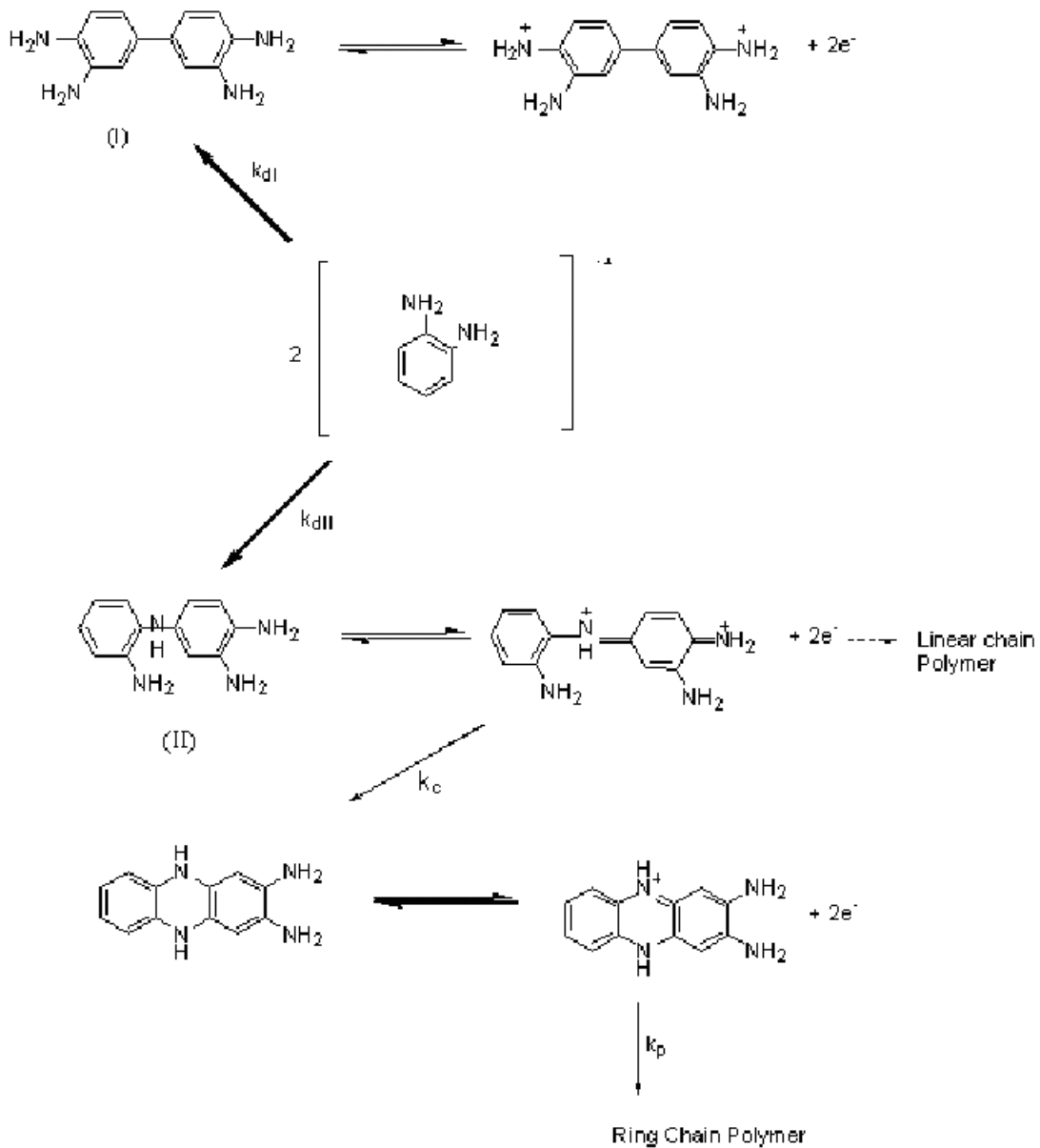
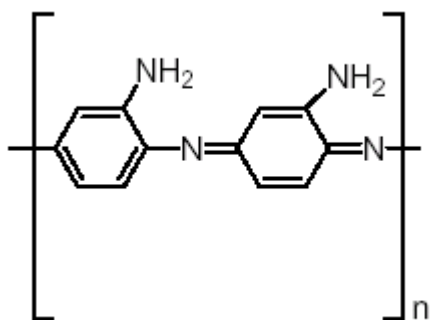
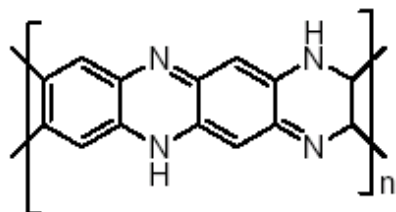


Figure 3: Mechanism of Polymerization of POPD

Based on the above scheme, the monomer, o-phenylenediamine, is initially oxidized anodically to give the mono-cationic radical. As is known for aromatic amine, cation radicals may dimerize by either C-C coupling to give the dimer I, or by C-N coupling and they give the dimer II. These dimers are then oxidized to their respective dication, with the formation of two products. One of the products can undergo a linear polymerization to form a linear chain polymer as below [7]:



The other product can undergo a cyclization reaction to give a ladder structure [13]:



It was found that the rate of cyclization is greater than that of the linear polymerization [12]. Thus at the outset, the polymer is composed of linear

conducting chains; however, it is later dominated by the insulating ladder structure [10, 13].

A similar mechanism of polymerization is observed for *meta*-phenylenediamine. However, only linear polymer chains are formed for *para*-phenylenediamine, because coupling of monomers can only be either head-to-head or tail-to-tail.

Methodology

Voltammetry

A general definition for the term voltammetry is an electrochemical technique that involves controlling the potential of an electrode while at the same time measuring the current flowing at that electrode. The graph generated from such measurements is called a voltammogram. The electrode in question is referred to as the working electrode so it can be distinguished from other electrodes that are present in the electrochemical cell [14].

Voltammetry is usually performed by connecting an electrochemical potentiostat to an electrochemical cell. The cell contains a test solution and three electrodes: the working, reference, and auxiliary electrodes. Special electronic circuitry in the potentiostat permits the working electrode potential to be controlled with respect to the reference electrode that has no any appreciable current flowing

through it. Rather, the current is forced to flow between the working electrode and the auxiliary electrode. This unusual arrangement has two principle benefits. First, the reference electrode is protected from internal electrochemical changes caused by current flow. Second, measurement errors related to the resistance of the test solution are kept to a minimum.

Linear Sweep Voltammetry. In linear sweep voltammetry (LSV), a fixed potential range is employed and voltage is scanned from a lower to an upper limit, as shown below in Figure 4.

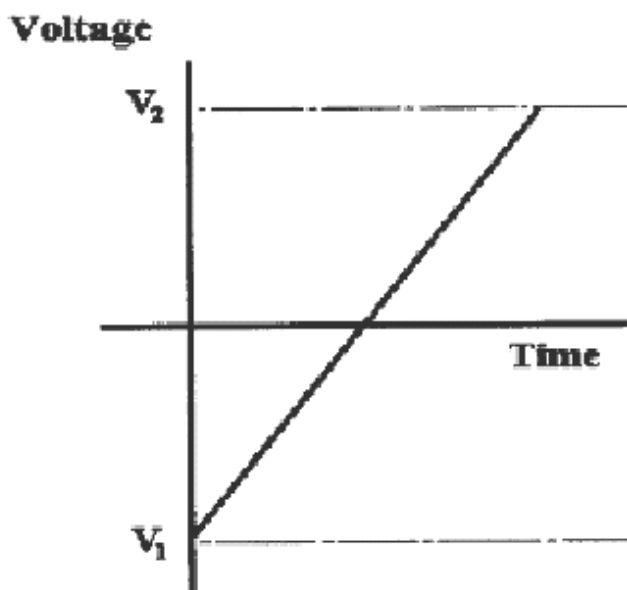


Figure 4: Potential Wave Generation Form in Linear Sweep Voltammetry

The voltage scan rate (v) is calculated from the slope of the line. Besides the

voltage scan rate, other characteristics of the linear sweep voltammogram recorded depend on a number of factors including the rate of the electron transfer reaction, and the chemical reactivity of the electroactive species. In LSV measurements, the current response is plotted as a function of voltage rather than time. For example, in the system $\text{Fe}^{3+}/\text{Fe}^{2+}$ the following graph, Figure 5, (called a voltammogram) would be seen for a single voltage scan:

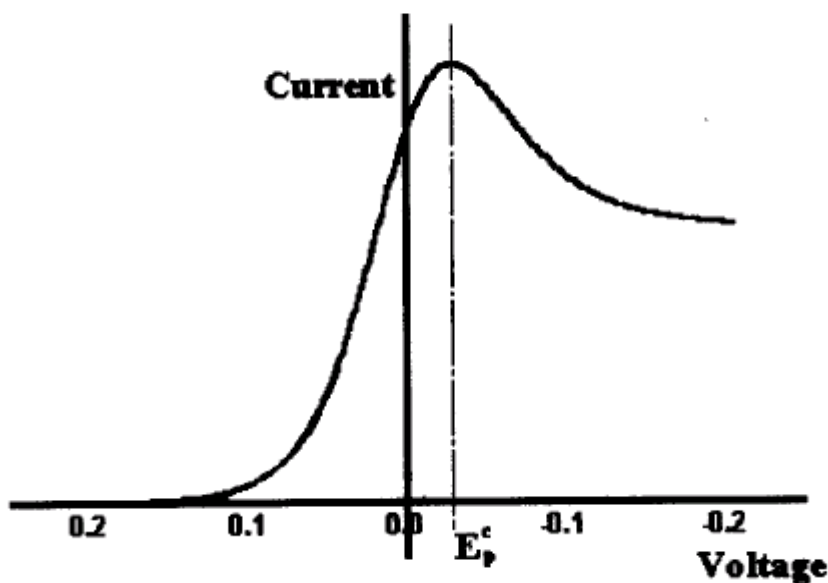


Figure 5: Single Voltage Scan

The scan begins from the left hand side of the current voltage plot where no current flows. As the voltage is swept further to the right (to more reductive values)

a current begins to flow and eventually reaches a peak before dropping. To rationalize such behavior it is necessary to consider the influence of voltage on the equilibrium established at the electrode surface. Considering the electrochemical reduction of Fe^{3+} to Fe^{2+} , the rate of electron transfer is fast in comparison to the voltage sweep rate. Therefore, at the electrode surface equilibrium is established identical to that predicted by thermodynamics. The relationship between concentration and voltage is given by the Nernst equation [15 – 21] shown below:

$$E = E^0 + (RT/nF) (\ln[\text{Fe}^{3+}]/[\text{Fe}^{2+}]) \quad 1.5$$

Here, E is the applied potential difference and E^0 is the standard electrode potential. So, as the voltage is swept from V_1 to V_2 the equilibrium position shifts from no conversion at V_1 to full conversion at V_2 of the reactant at the electrode surface.

Cyclic Voltammetry. A related technique, cyclic voltammetry, consists of measuring the current resulting from an applied potential waveform [21.] The potential is cycled within a given potential range at a constant rate and the current is measured as a function of the potential. The rate can vary from less than 1 mV/s to several hundred V/s. When a high enough potential is applied at an electrode surface to cause oxidation or reduction of species in solution, a current arises due to the depletion of the species in the vicinity of the electrode surface. As a

consequence, a concentration gradient appears in the solution. The current i is proportional to the gradient slope imposed. In the case of cyclic voltammetry, however, the potential does not stay constant. It rises at a constant rate until it reaches a chosen maximum and then decreases again at the same rate. The current does not reach a maximum immediately after imposition of the potential, as the potential is not immediately great enough to give rise to any reaction. The current starts to rise as the potential enters the area where oxidation or reduction can occur. It then continues to rise rapidly as the surface concentration of the species becomes smaller and smaller (the concentration gradient increases). The peak current consists of two components. In addition to the diffusion-controlled current, there is also a contribution from the initial current surge required to adjust the surface concentration of the reactant to its equilibrium concentration as given by the Nernst equation. The current then decays rapidly as the diffusion layer begins to extend further and further away from the electrode surface (gradient slope decreases and, therefore, so does the current). The same progression is seen on the negative scan as well, but in the opposite direction. As shown in Figure 6, when scanning towards positive potential (E_p^A), the current is denoted “anodic” (with corresponding peaks ‘anodic peaks’ I_p^A), and when towards negative potential (E_p^C), the current “cathodic” (I_p^C).

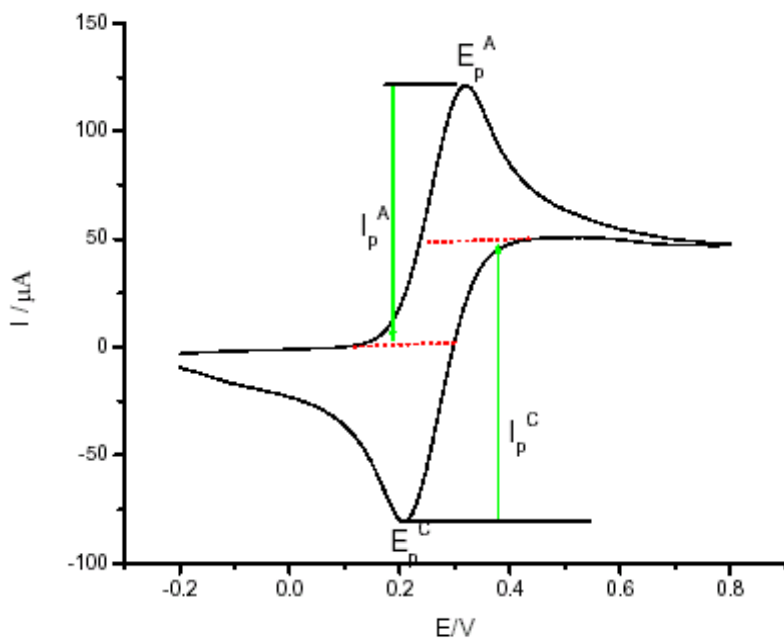


Figure 6: CV for a Reversible Reaction

From the anodic and cathodic peak currents and potentials, important parameters characterizing chemical materials can be calculated, such as rate constants for oxidation/reduction processes and the doping /dedoping within a polymer film.

Anodic Stripping Voltammetry. Anodic Stripping Voltammetry (ASV) is an electrolytic method in which a mercury (Hg) electrode is held at a negative potential to reduce metal ions in solution and form an amalgam with the electrode. The solution is stirred to carry as much of the analyte metal(s) to the electrode as

possible for concentration into the amalgam. After reducing and accumulating the analyte for some period of time, the potential on the electrode is increased to reoxidize the analyte and generate a current signal. The concentration of the analyte in the Hg electrode, C_{Hg} , is given by:

$$C_{\text{Hg}} = \frac{i_l t_d}{n F V_{\text{Hg}}} \quad 1.6$$

where i_l is the limiting current during reduction of the metal,

t_d is the duration of accumulation,

n is the number of moles of electrons transferred in the half reaction,

F is the Faraday constant (96,487 coulombs/mole of e^-), and

V_{Hg} is the volume of the electrode.

The expression for current produced by anodic stripping depends on the particular type of Hg electrode but is directly proportional to the concentration of analyte concentrated into the electrode. The main advantage of stripping analysis is the preconcentration of the analyte into the electrode before making the actual current measurement. Anodic stripping can achieve detection of concentrations as low as 10^{-10} M.

However, it should be noted that while the signal (cathodic peak) for metal

reduction is less sensitive than the corresponding anodic stripping (anodic peak), the former can still be correlated to the analyte concentration through calibration. In this work, we seek to detect and quantify some heavy metal ions by eliminating the anodic stripping while at the same time enhancing the cathodic peak. This was achieved using thin polymer film of *ortho*-phenylenediamine.

Some Environmental Concerns

Chromium

Chromium is a hard, steel-gray metal that is highly resistant to oxidation, even at high temperatures. It is the sixth most abundant element in the earth's crust, where it is combined with iron and oxygen in the form of chromite ore. Chromium is used in three basic industries: metallurgical, chemical, and refractory (heat-resistant applications), and these industries are the second largest source of ambient chromium. Chromium exists in a series of oxidation states from -2 to +6 valence; the most important stable states are 0 (elemental metal), +3 (trivalent), and +6 (hexavalent). Chromium in chromite ore is in the trivalent state; industrial processes also produce the elemental metal and hexavalent chromium. The health effects of chromium are at least partially related to the valence state of the metal at the time of exposure [22]. Trivalent and hexavalent compounds are thought to be the most biologically significant. Cr(III) is an essential dietary mineral in low

doses. Certain compounds of Cr(VI) appear to be carcinogenic, but insufficient evidence exists to determine whether Cr(III) or chromium metal can be human carcinogens. Cr(VI) is generally considered 1,000 times more toxic than Cr(III).

Workers in industries that use chromium, especially stainless steel welding, chromate production, chrome plating, and chrome pigment industries, where exposure *via* inhalation of aerosols is primarily of hexavalent chromium are at increased risk of chromium's effects. Occupational exposure to Cr(VI) has been associated with increased incidence of lung cancer. Residents near chromate production facilities might be exposed to higher than background levels of Cr(VI). Groundwater contamination might increase exposure in persons using well water as a source of drinking water. The content of chromium in tap water in U.S. households is from 0.4 to 8.0 micrograms per liter ($\mu\text{g/L}$). (EPA's maximum contaminant level for chromium in drinking water is $100\ \mu\text{g/L}$.) Thus, an objective of this work is to electrocatalyze the reduction of Cr(VI) to the less toxic Cr(III) using PAN/CNTs film.

Mercury

Mercury is the most powerful neurotoxin on the planet [23]. Mercury (Hg) is a shiny liquid metal that is a widespread environmental contaminant [23]. Especially a problem is methyl or ethyl mercury, or mercuric chloride, which is very

poisonous. Modern humans have much higher body levels of mercury than did our ancestors because of its greater use in recent times. It has been used for more than 2,000 years. Nowadays, mercury is employed daily by medical and dental practices in thermometers, drugs (more so in the past), and amalgam for fillings; by agriculture in fungicides and pesticides; and by the cosmetics industry. Mercury in industrial waste has polluted our waters and contaminated our fresh- and salt-water plants and fish.

Inorganic mercury toxicity occurs in several forms: metallic mercury (Hg), mercurous mercury (Hg_2^{2+}), or mercuric mercury (Hg^{2+}). Toxicity from inorganic mercury can result from direct contact through the skin or gastrointestinal tract or from inhalation of mercury vapors. Detection and quantification of inorganic mercury has been the focus of many papers. Common techniques currently used for such assays are stripping voltammetry (where anodic stripping is correlated to metal concentration) and inductively coupled plasma (ICP). An important aspect of my work is the development and use of thin film POPD for quantitative analysis of Hg^{2+} through cathodic peak enhancement.

CHAPTER 2

EXPERIMENTAL

Instrumentation

The analytical experiments were conducted using cyclic voltammetry. The studied system consists of a 10mL cell (beaker) in which three electrodes was connected to the electrochemical analyzer QCM 400. The electrochemical analyzer was then connected to a computer for readout. The three electrodes are:

Reference electrode: Ag/AgCl

Counter electrode: Platinum (Pt)

Working electrode: Glassy carbon (GC)

These electrodes are separated from each other and are physically held in place by a three compartment holder clamped to a stand.

The electrode setup for all experiments is shown below in Figure 7.

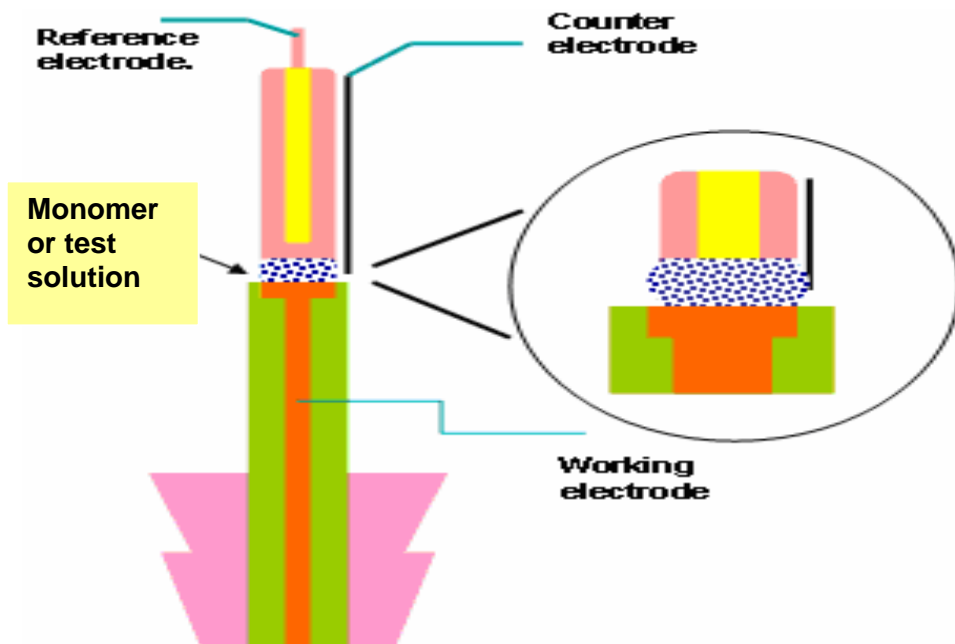


Figure 7: Electrode Setup

Chemicals

The chemicals used in this work are listed in Table 1.

Table 1: List of Chemicals Used

Chemical	Producer	Assay
Aniline	Aldrich Chemical	99%
<i>ortho</i> -phenylenediamine dihydrochloride	Aldrich Chemical	99%
<i>meta</i> -phenylenediamine dihydrochloride	Aldrich Chemical	99%
<i>para</i> -phenylenediamine dihydrochloride	Aldrich Chemical	99%
Single-walled carbon nanotubes	Aldrich Chemical	99+ %
Sulfuric acid	Sigma	
Hydrochloric acid	Sigma	
water		distilled
Ascorbic acid	Fisher Scientific	100.6%
Uric acid	Aldrich Chemical	99+ %
Acetaminophen	Aldrich Chemical	99+ %
Mercuric nitrate	Fisher Scientific	98.0%
Cadmium nitrate	Fisher Scientific	99.8%
Lead (II) nitrate	Fisher Scientific	99.8%
Potassium dichromate	Fisher Scientific	
Alumina powder	CH Instruments Inc.	0.05micron

Procedures

Electrode Preparation

Cleaning of Working Electrode. Several cleaning procedures are used for cleaning the glassy carbon electrode when it is used for the first time. The first step should always be the removal of macroscopic impurities, like old polymer film, from the electrode by polishing it against an abrasive material. The polishing agent used here was alumina (Al_2O_3 , particle size 0.05micron). Usually, this is the most effective way of removing impurities on the electrode. However, it has its shortcomings too. Frequent scrubbing of the GC and the Teflon around it may speed up its wear. Additionally, the overuse of alumina can lead to an alumina modified GC. To overcome these shortcomings, the cleaning procedure consisted of just removing the old polymer film from the electrode surface with 0.05 micron alumina powder. To remove the remaining amounts of impurities such as the alumina, the polished electrode was put into distilled water and then cleaned using a polishing cloth. To verify the cleanness of the GC (as well as the other electrodes), we run a cyclic voltammogram (CV) of a 1mM solution of ferricyanide and compare the result to the characteristic CV of ferricyanide.

Reference Electrode Preparation. Here, we used a commercial reference electrode (Ag/AgCl). Whenever necessary, 1 M aqueous solution of KCl was used to fill the electrode.

Sample Preparation

Here, four monomer solutions were used to make polymer films. These are: Phenyleneamine (aniline), *ortho*-phenylenediamine, *meta*-phenylenediamine, and *para*-phenylenediamine. It should be noted that each of these monomers (except aniline) has two moles of HCl. The primary solvents used for these studies were 1M H₂SO₄ and 1M HCl. These solvents also serve as a supporting electrolyte in the electropolymerization process.

Preparation of PAN/CNTs. A 97 μ L of 10.3M aniline was dissolved in 10mL of 1M H₂SO₄ in a 10mL cell to make a 0.1M solution, then 0.05g of single-walled CNTs was added to this mixture. The polymerization was done using cyclic voltammetry with the following parameters; 0~1.0V, 100 mV/s, 4 scanning cycles.

Preparation of Aniline Derivatives. The aniline derivatives used were *ortho*-phenylenediamine dihydrochloride, *meta*-phenylenediamine dihydrochloride, and *para* phenylenediamine dihydrochloride. The procedure described here applies to all three of these monomers. First, 0.1900g of monomer was dissolved in 1M HCl to make a 0.1M solution in a 10mL cell. Using cyclic voltammetry, a thin film of

polymer was deposited on the surface of a GC electrode with the following parameters; 0~1.0V, 100 mV/s, 3 scanning cycles.

Preparation of Test Solutions. All test samples used for this work were solids. These samples included: potassium dichromate, mercuric nitrate, cadmium nitrate, lead nitrate, ascorbic acid, uric acid, and acetaminophen. An appropriate amount of the respective sample was dissolved to make a 1M stock solution. For potassium dichromate, the solvent used was 1M H₂SO₄ and samples of varying concentrations were made with the least being 1mM. The same is true for the other samples, the only difference being that the solvent used was 1M HCl. More on the exact concentration of each test sample, as well as polymer film used for analysis, will be presented in the next chapter of this work.

CHAPTER 3

RESULTS AND DISCUSSION

Electropolymerization of PAN

One part of this project involved the electrosynthesis of thin film PAN/CNTs and use of the resulting film to remedy environmental dichromate. First, the PAN/CNTs film was synthesized using cyclic voltammetry in 1M H₂SO₄ as solvent. Second, the electrocatalytic effect of the film was investigated in the reduction of dichromate. Finally, results obtained will be discussed after each experiment.

Figure 8 shows the cyclic voltammogram (CV) of the electropolymerization of a 0.1 M aniline solution in 1M H₂SO₄ solution. The resultant polymer film is PAN.

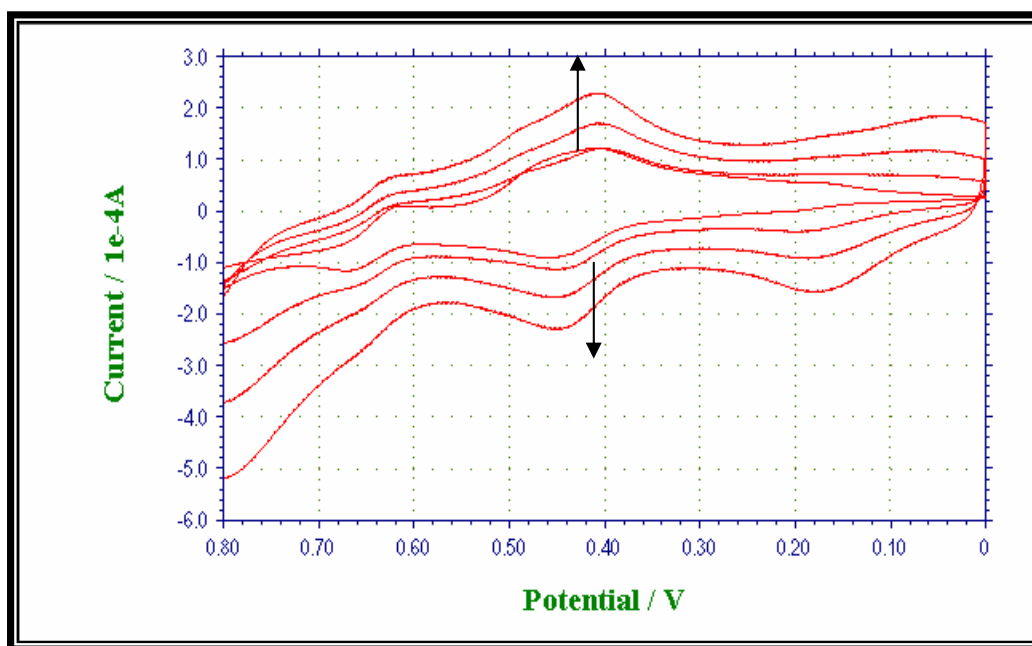


Figure 8: CV of PAN

There are four distinguishable peak pairs in this CV: The first peak appears between 0.10 V and 0.20 V in the region of oxidation and the formation of the radical cation. The second peak appears between 0.40V and 0.50 V in the region of conducting state where a partial hydrolysis and a formation of benzoquinone can occur. The third peak is at 0.65 V and it is due to the oxidation of the dimers. The last peak at 0.78 V corresponds to the conversion of emeraldine to the pernigraniline. These four peaks are typically characteristic of the voltammogram of the polyaniline. The positions of the peaks change depending on the acidity of

the media and the potential window applied. The gradual growth of voltammetric currents (as indicated by the arrows) represent the accumulation of polymer formed on the surface of the GC. As a general practice, the resultant film from the electropolymerization is voltammetrically scanned in blank electrolyte to confirm its electroactivity.

Incorporation of CNTs into PAN

The CV for the electropolymerization of PAN/CNTs is shown on Figure 9, and the overlapping of the two CVs (PAN and PAN/CNTs) is shown in Figure 10.

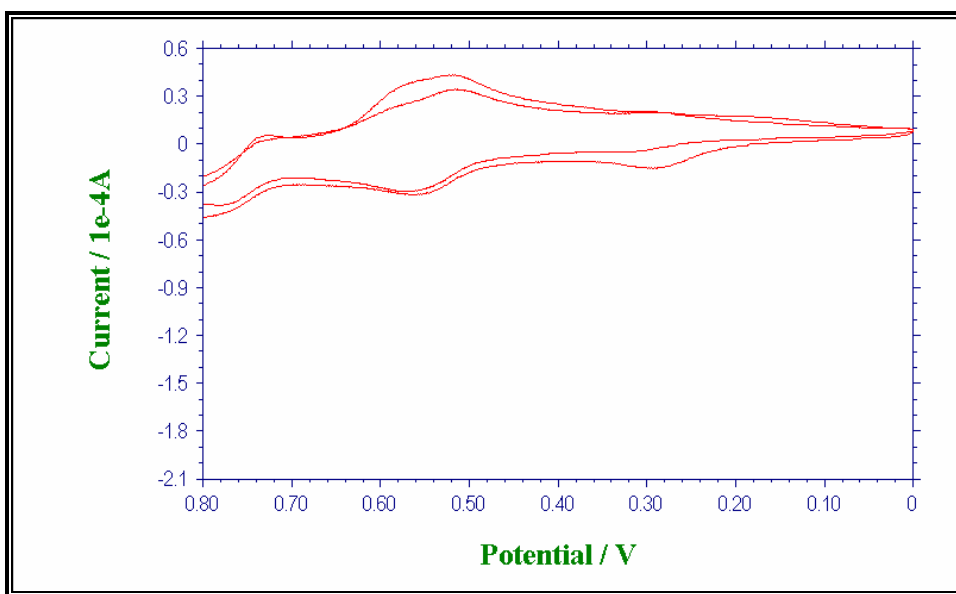


Figure 9: CV of PAN/CNTs; Only Two Representative Cycles Shown

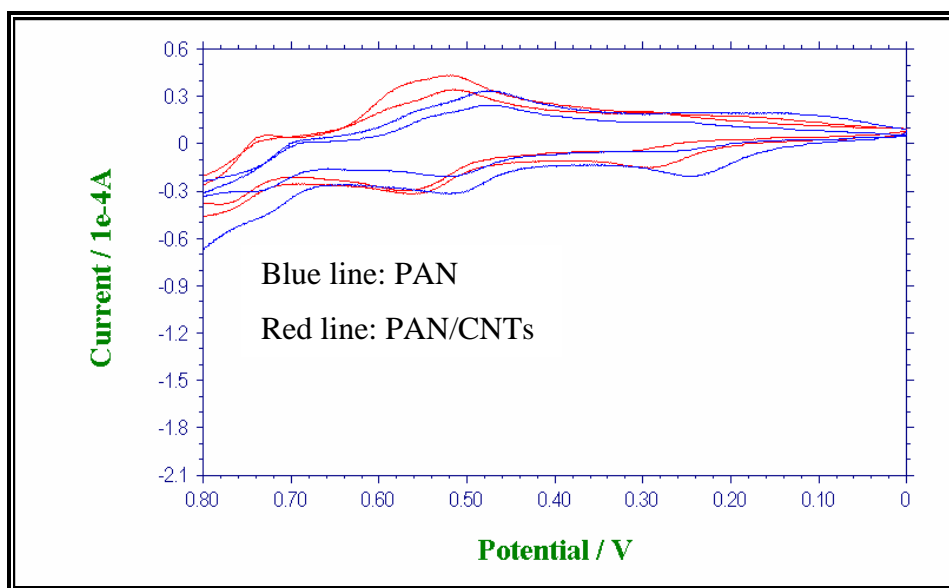


Figure 10: The overlapping of the CVs of PAN and PAN/CNTs

The CV of PAN/CNTs has the same shape as that of PAN. While the current has remained the same; however, the coordinates of this new CV obtained for PAN/CNTs have changed; the potentials have been shifted to a slightly positive value. The difference is an illustration of the CNTs effect. Hence, the CNTs introduced into the polyaniline have favored a more reduced state of aniline. The voltammetric method has served as an indication of the growth of the PAN/CNTs complex in comparison of the growth of PAN.

Application of PAN/CNTs for Dichromate Reduction

Using an unmodified (bare) GC, the reduction of 1mM dichromate (Cr [VI])

to Cr (III) in 1M H₂SO₄ occurs at 0.20V, 4.8 x 10⁻⁵A. This is shown in Figure 11.

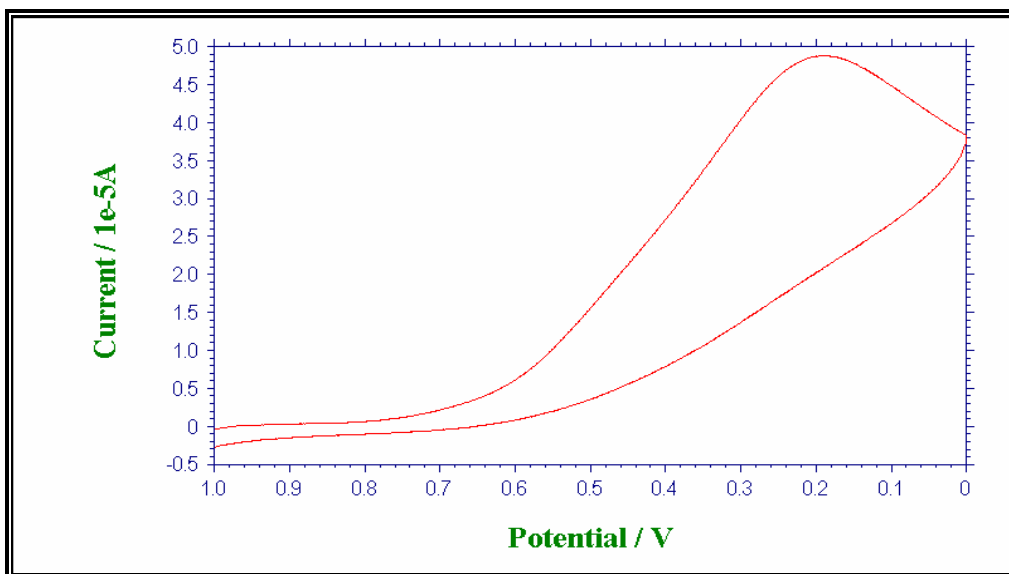


Figure 11: CV of Cr (VI) Using Bare GC

However, for a modified GC with PAN/CNTs film, the same signal for the reduction of Cr (VI) now occurs at 0.65V, 7.0 x 10⁻⁵A as shown in Figure 12.

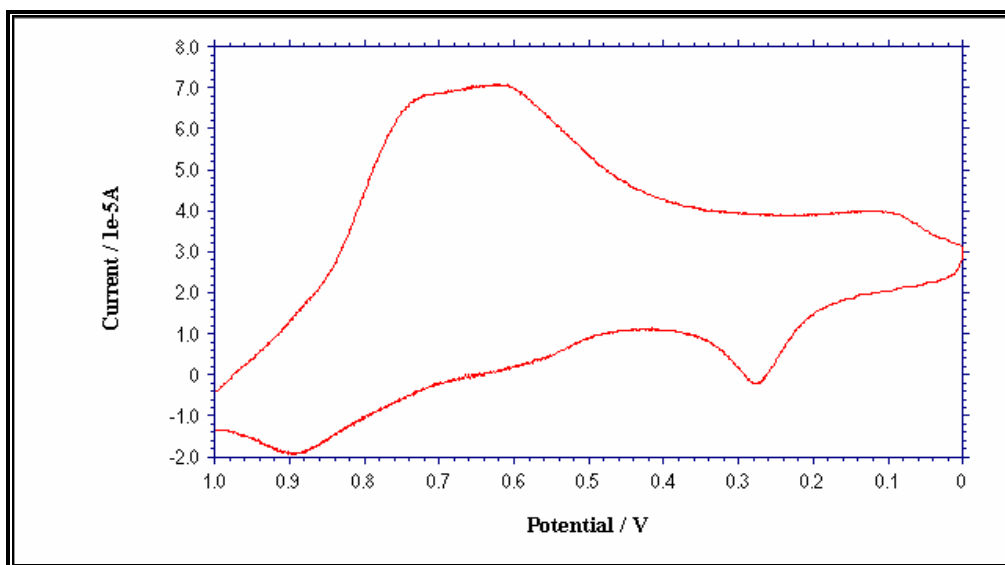


Figure 12: CV of Cr (VI) Using PAN/CNTs

Discussion of Result

When the PAN/CNTs GC is used, the reduction of Cr (VI) is greatly enhanced, not only does the signal occur at a higher peak or current value but also at a more positive potential. The potential shift is to the value of +0.45V. This is a substantial difference, and in electrochemistry, a shift to a more positive potential translate as a more favored reduction process. Therefore, we conclude that PAN/CNTs show catalytic properties for the reduction of Cr (VI). An electrocatalytic scheme that explains this reduction processes (both at the surface of the bare GC and PAN/CNTs modified GC) is indicated below in Figure 13.

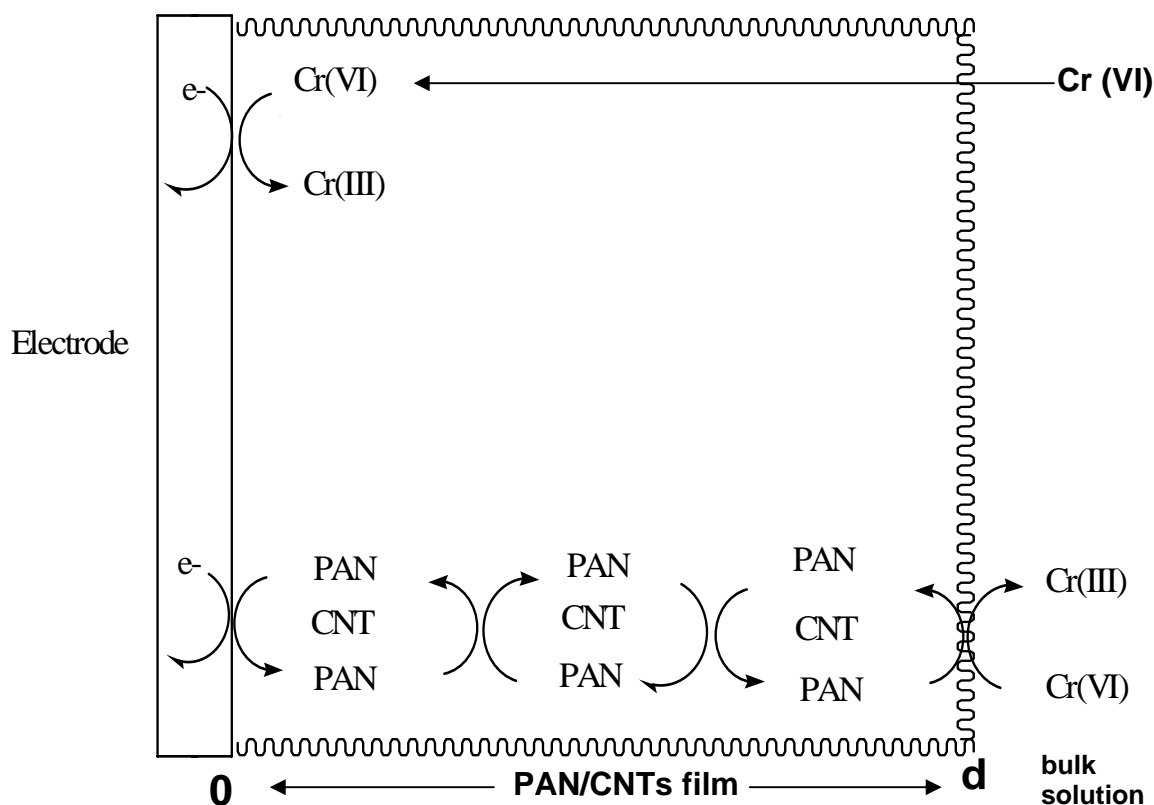
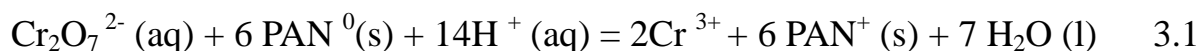


Figure 13: Electrocatalytic Scheme for Dichromate Reduction

Overall equation:



At the surface of a bare GC, electrons are passed on to Cr (VI) in bulk solution, reducing it to Cr (III). In the presence of PAN/CNTs, a series of coupled reaction involving $\text{PAN}^+/\text{PAN}^0$ is set into motion. The electron is eventually passed on to reduce Cr (VI). The exact nature of this electronic process involving PAN has remained elusive; however, it is the responsible factor for the enhanced

electrocatalytic effect of PAN/CNTs for the remediation of environmental dichromate.

Preparation and Use of POPD

The CV for preparation of POPD from a 0.1M monomer solution in 1M HCl is shown in Figure 14.

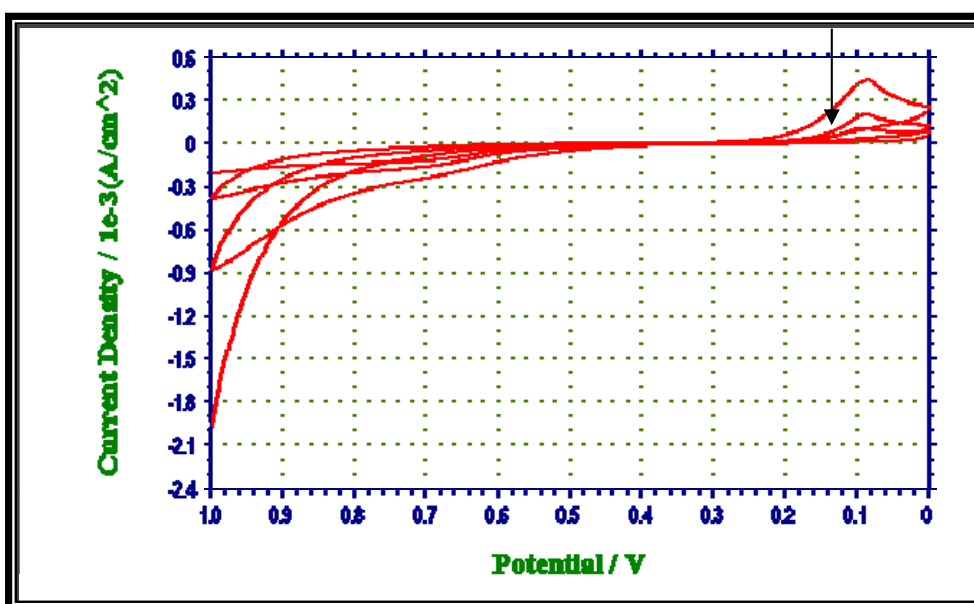


Figure 14: CV for Preparation of POPD

The arrow in the diagram above indicates a downward trend in the peak heights. Successive polymer layers that are deposited have conductivities less than that of the GC surface and this shows as a decrease in peak heights. This is indicative of the overall insulating property of POPD.

Application of POPD for Water Quality Analysis

Hg²⁺ Ion Detection and Quantification. Using a 1mM Hg²⁺ sample in 1M HCl, a CV can be obtained for a bare GC and a POPD modified GC. For easy comparison, these two CVs has been overlapped and shown below in Figure 15.

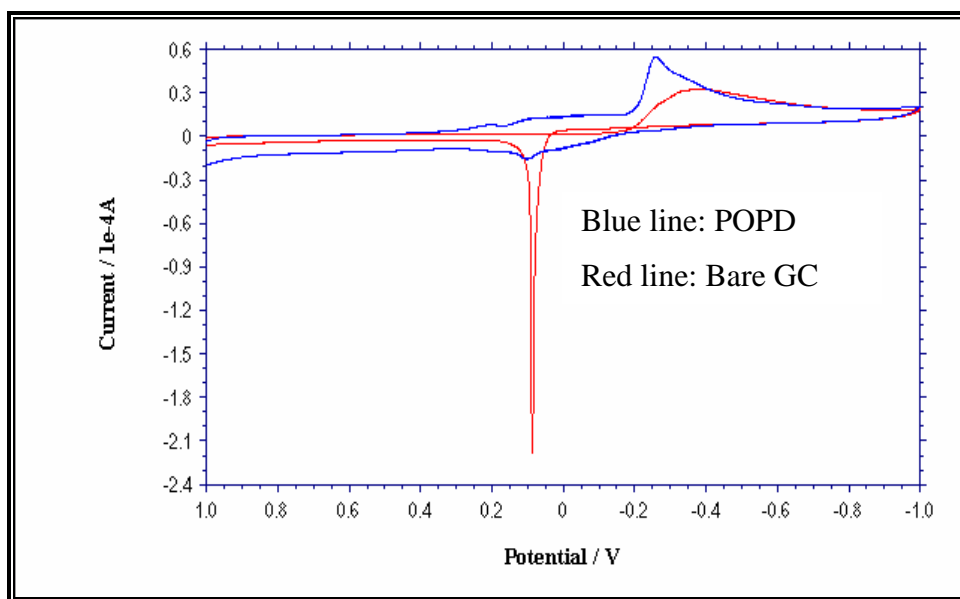


Figure 15: The Overlapping of the CVs of Hg²⁺ Using Bare and POPD GC

Discussion of Results. In the case of a bare GC, a negative potential scan reduces Hg²⁺ to Hg⁰ at the surface of the GC. This shows as a cathodic peak at -0.35V, 3.0×10^{-5} A. A positive scan does the reverse. Hg⁰ is oxidized to Hg²⁺ and is stripped off the surface of the GC. The corresponding peak (anodic peak) that is observed occurs around 0.10V. This peak is sharp and is characteristic of such

stripping processes for heavy metal oxidation.

On the other hand, when the GC is modified with the POPD film, the anodic peak is completely blocked, while the cathodic peak is enhanced; it has been shifted to a slightly more positive potential (around -0.25V) and a higher current value (around 5.0×10^{-5} A). This enhanced cathodic peak increases linearly with Hg^{2+} concentration. As shown in Figure 16, a correlation (R^2) of 0.9822 is obtained.

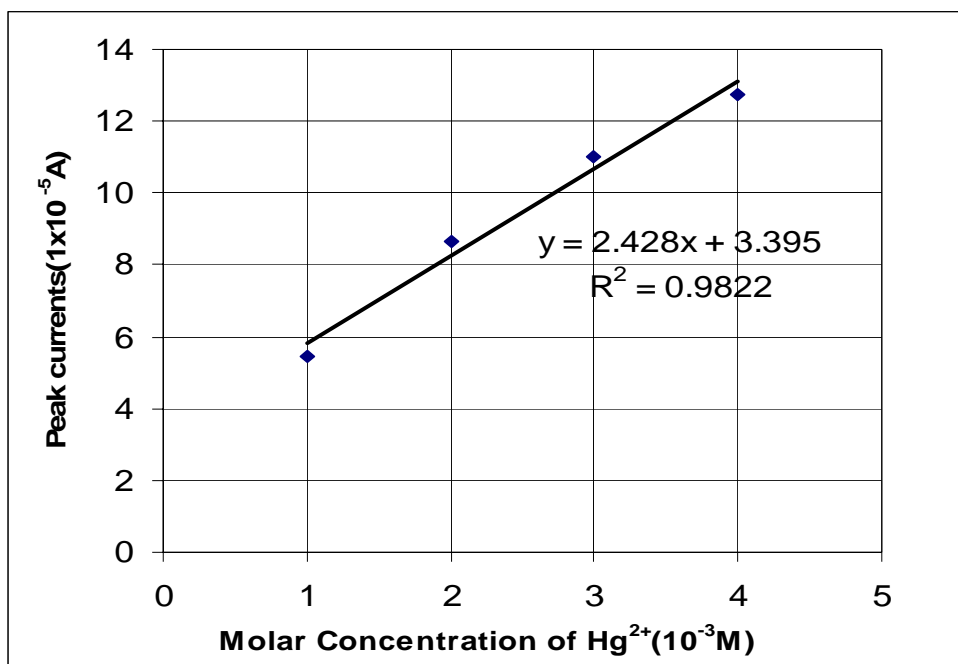
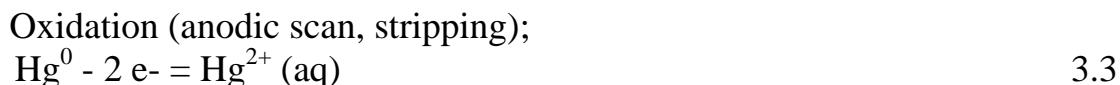
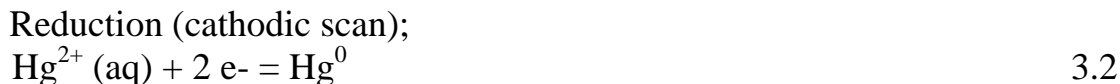


Figure 16: Graph of Peak Current Versus Concentration of Hg^{2+}

Proposed Mechanism of Redox Reactions of Hg^{2+} . A mechanism for the

redox processes occurring at the surface of the electrode can be proposed as follows:

For bare GC:



For POPD:

1. Accumulation/extraction of Hg (II) via complexation reaction (through the amine coordination from POPD network).



2. Reduction (cathodic scan);
$$\text{Hg}^{2+} / \text{POPD} + 2 \text{e}^- = \text{Hg}^0 / \text{POPD} \quad 3.5$$

The formation of this surface complex results in the enhanced cathodic peak.

3. Oxidation (anodic scan);
$$\text{Hg}^0 / \text{POPD} - 2 \text{e}^- = \text{Hg}^{2+} (\text{aq}) \quad 3.6$$

This process is hindered or blocked, because of the impermeable POPD film. Only a small anodic peak is observed.

Application of POPD for Simultaneous Qualitative Analysis

For a mixture of heavy metal ions in solution, POPD is observed to block the anodic stripping of such metals. Here we used a mixture composed of 1mM each of Hg^{2+} , Pb^{2+} , and Cd^{2+} in a 1M HCl solvent. The result is shown in Figure 17.

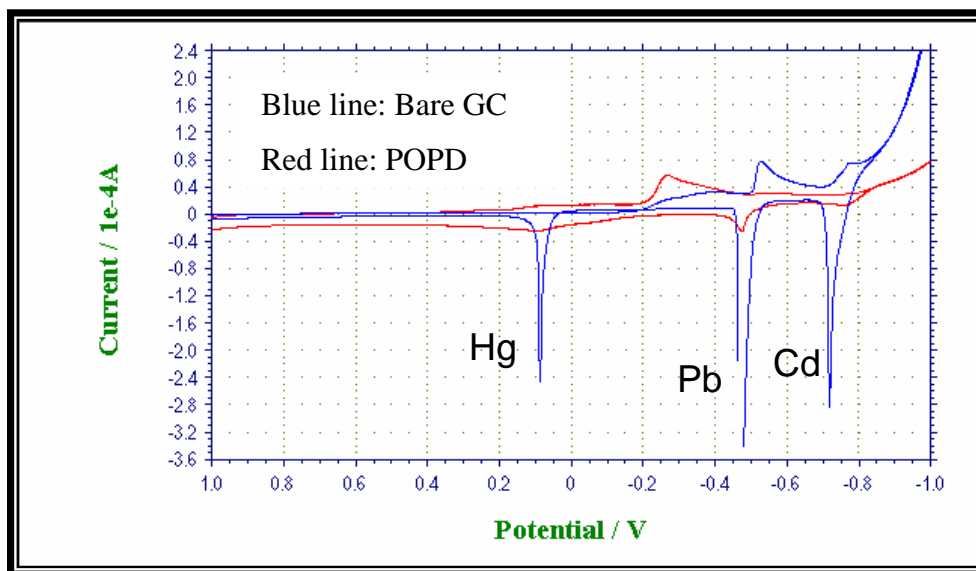


Figure 17: CV for a Mixture of Metal Ions Using Bare and POPD GC

The three sharp anodic peaks corresponds to Hg^{2+} (around +0.12V), Pb^{2+} (around -0.48V) and Cd^{2+} (around -0.72V). On the other hand, for POPD, the sharp anodic peaks corresponding to these metals is no longer observed because it is blocked by POPD, and this serves as a qualitative test for the presence of these metals in solution.

Interference from Other Ions in Hg^{2+} Analysis

Water samples are usually composed of several inorganic ions. The effectiveness of testing for one component of a sample can be compromised by the presence of other species in solution besides the analyte. Here, several ions were tested for their possible interference in Hg^{2+} analysis.

Table 2: List of Selected Ions and their Possible Effect on Hg²⁺ Analysis

Ions	Effect on Hg ²⁺ Analysis
1-fold NO ₃ ⁻	Interferes with POPD network
1-fold dichromate	Interferes for qualitative analysis
10-fold Cl ⁻	No interference
100-fold SO ₄ ⁻	No interference
Group I and II cations	No interference
Heavy metal ions	No interference for qualitative analysis

Preparation of Poly-*meta*-Phenylenediamine (PMPD)

A preparative CV for poly-*meta*-phenylenediamine (PMPD) is shown in Figure 18. The monomer solution is of 0.1M concentration in 1M HCl.

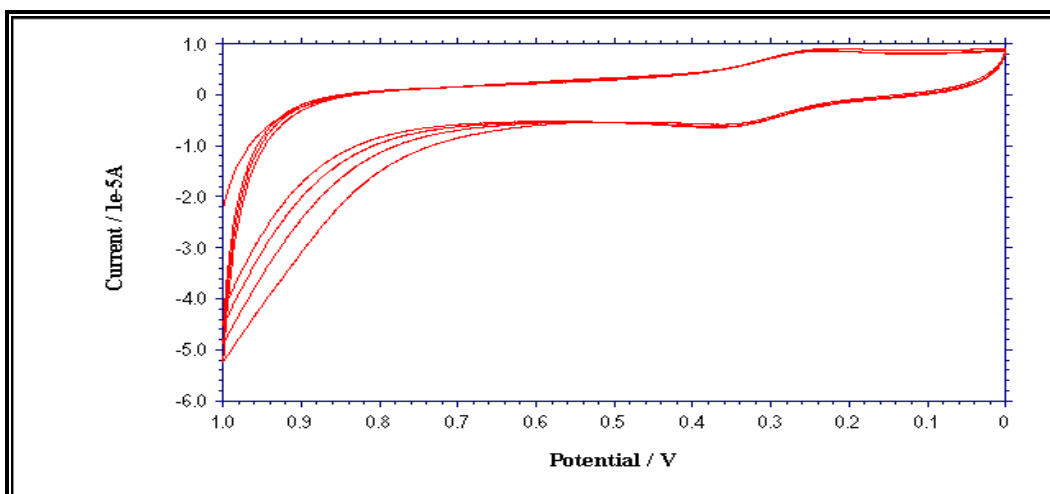


Figure 18: CV for the Preparation of PMPD

Successive scans do not produce any significant growth in the peak heights. This is indicative of the insulating nature of POPD

Application of PMPD for Hg^{2+} Analysis

For a 1mM Hg^{2+} solution, a CV is obtained using PMPD modified GC and is compared to that of a bare GC. These two CVs are overlapped and shown in Figure 19.

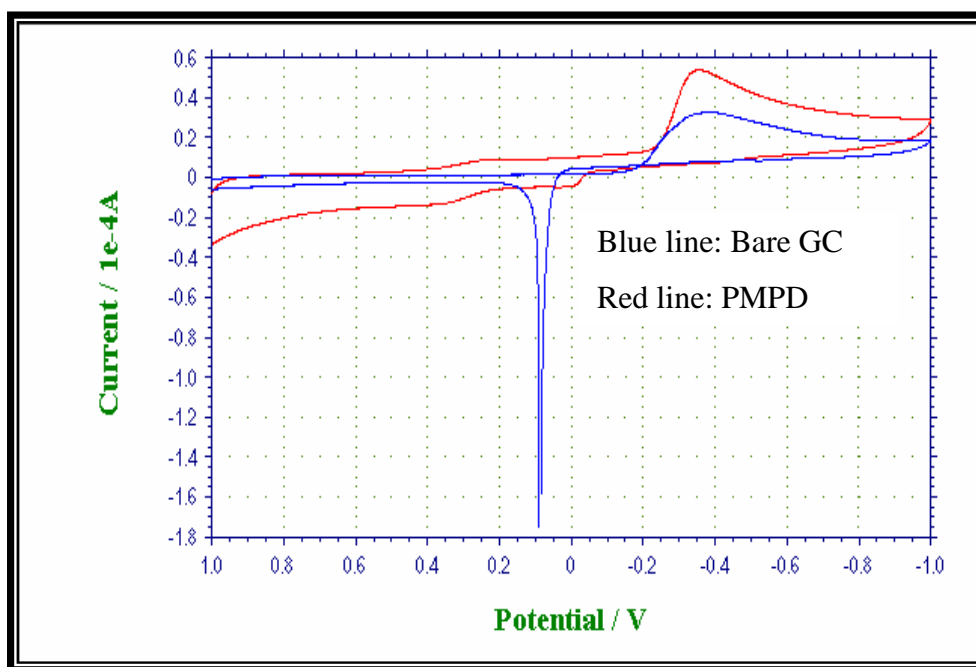


Figure 19: The Overlapping of the CVs of Hg^{2+} Using Bare and PMPD GC

Similar to the observation for POPD, here, in the case of bare GC, a negative potential scan reduces Hg^{2+} to Hg^0 at the surface of the GC. This shows as a

cathodic peak at -0.35V , $3.0 \times 10^{-5}\text{A}$. For the reverse scan, Hg^0 is oxidized to Hg^{2+} and is stripped off the surface of the GC. The corresponding anodic peak occurs around 0.10V .

However, when the GC is modified with the PMPD film, the anodic peak is completely blocked, while the cathodic peak occurs at a higher peak current (around $5.5 \times 10^{-5}\text{A}$). Unlike POPD, however, the cathodic peak is not shifted to a more positive potential.

Preparation and Use of Poly-*para*-Phenylenediamine (PPPD)

Unlike POPD and PMPD where branching during polymerization produces the non-conducting ladder network, for poly-*para*-phenylenediamine (PPPD), only head-to-head or tail-to-tail combination of monomers is possible. The result is the formation of linear conducting chains of PPPD. The CV for the preparation of thin film PPPD is shown in Figure 20.

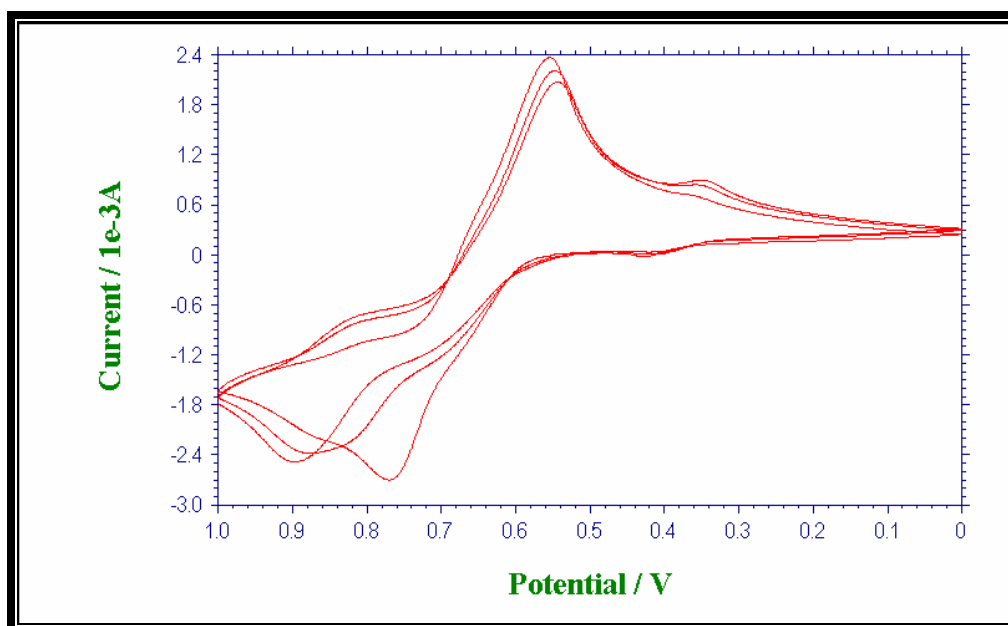


Figure 20: CV for PPPD

PPPD is observed to show the least blocking of anodic stripping for heavy metal ions. This was demonstrated using 1mM Hg^{2+} solution. The result is shown in Figure 21 below. Again, for easy comparison, this result has been overlapped with the CV for the same solution using bare GC.

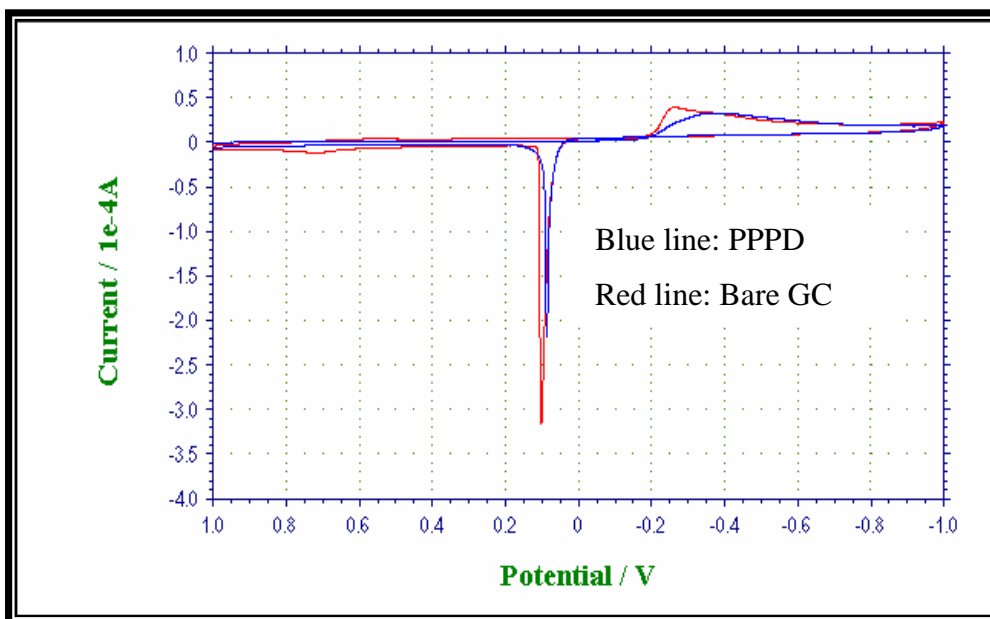


Figure 21: The Overlapping of the CVs of Hg^{2+} Using Bare and PPPD GC

Thus, even when PPPD is used, a considerable amount of stripping is observed. A comparison of the blocking effect of the three polymer films; POPD, PMPD, and PPPD are listed in Table 3. Included in this Table is the film's ability to enhance the cathodic peak. The model used for this comparison is Hg^{2+} .

Table 3: Comparison of Anodic Blocking and Cathodic Enhancement by Different Polymer Films

Polymer film	Blocking of anodic stripping	Cathodic peak enhancement
POPD	Greater than 95%	Shift to a more positive potential and higher current value
PMPD	Greater than 95%	Shift to higher current value
PPPD	Less than 40%	No significant enhancement

Comparison of This Approach to Traditional Method for Heavy Metal Analysis

Traditionally, anodic stripping voltammetry (ASV) has been used for quantitative analysis of heavy metal ions. The stripping of metal ions from the surface of an electrode during oxidation produces a sharp anodic peak. This peak is then correlated to the concentration of the metal ions in solution. However, my approach deals primarily with the intensity of the cathodic peak obtained during

the reduction of metal ions. Other aspects of comparison between the ASV approach and mine are listed in Table 4.

Table 4: Comparison of my Approach to Traditional Approach for Heavy Metal Ion Analysis

	Traditional Approach	My Approach
Technique	Anodic Stripping Voltammetry	Cyclic Voltammetry
Peak of interest	Anodic peak	Cathodic peak
Sensitivity	More sensitive; ppb range	Less sensitive; ppm range
Hg amalgam formation	Yes	No
Environmental friendliness	Less friendly; requires use of Hg	More friendly; no use of Hg

Permselectivity of POPD

The preparation of permselective thin films produced on electrode surface by electropolymerization of suitable organic molecules has gained a growing interest

from a technological and analytical point of view. As a result, they display properties like size exclusion, ion exchange, and hydrophobic interaction, which offer them the required permselective behavior. Electropolymerization of *ortho*-phenylenediamine offers the advantages of producing a very thin and self-insulating film that can be coated on a conducting surface.

Selective Oxidation of Acetaminophen over Hg^{2+}

Acetaminophen is a major ingredient in numerous cold and flu medications and many prescription analgesics.

As discussed earlier, POPD effectively hinders the anodic stripping of Hg^{2+} , however, for a 1mM mixture of Hg^{2+} and acetaminophen in 1M HCl, POPD was found to allow the oxidation of acetaminophen over Hg^{2+} . This result is shown in Figure 22.

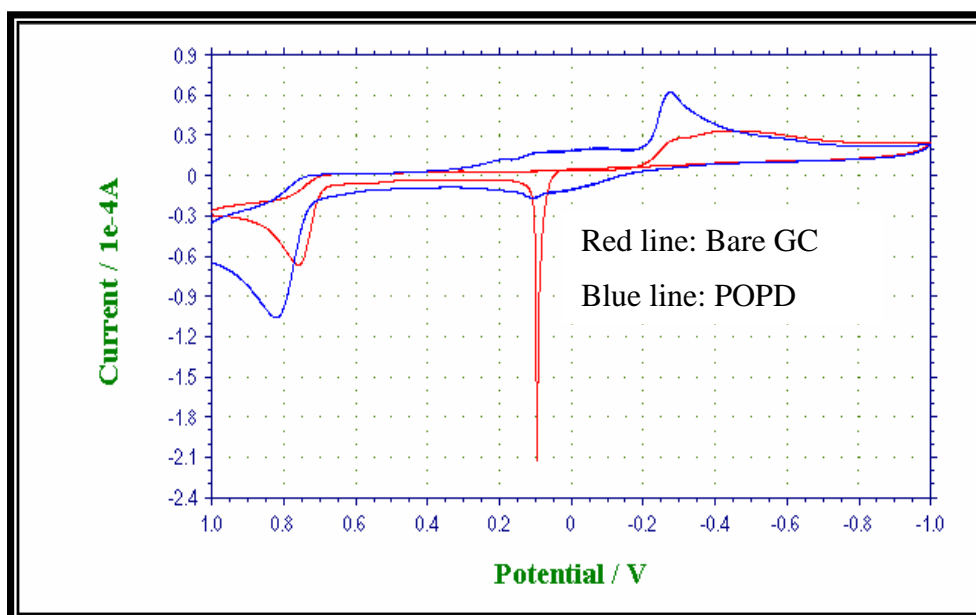


Figure: 22. CV for a Mixture of Acetaminophen and Hg^{2+}

In the case of bare GC, both the oxidation peaks of Hg^{2+} (around 0.10V) and acetaminophen (around 0.75V) are observed. When the modified POPD GC is used, we now observe only the oxidation peak for acetaminophen (around 0.82V). As a general practice, a CV is obtained for the individual analyte for the same medium. This helps to ascertain the assignment of the analyte signal when found in a mixture. Analyte signal can also be confirmed by increasing the analyte concentration and observing for a corresponding increase in its signal intensity.

Selective Oxidation of Bioorganic Species

Selective Oxidation of Acetaminophen Over Ascorbic Acid. Ascorbic acid

(Vitamin C) is an organic acid with antioxidant properties. It is a water-soluble nutrient essential for life, and is used by the human body for many purposes.

For a 1mM mixture of acetaminophen and ascorbic acid in 1M HCl, POPD selectively oxidizes acetaminophen. This result is reported in Figure 23.

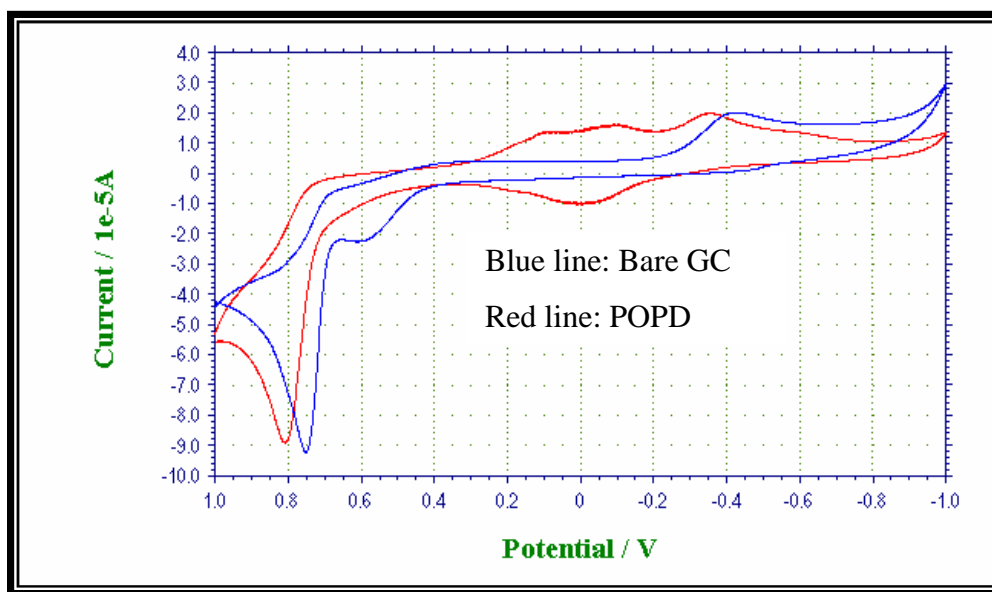


Figure 23: CV for a Mixture of Acetaminophen and Ascorbic Acid

For bare GC, the oxidation peak for ascorbic acid is the little hump that occurs at 0.55V, while that for acetaminophen is at 0.75V. When POPD is used, notice the peak for ascorbic acid is absent while that for acetaminophen is present (around 0.82V). Thus, POPD preferentially detects acetaminophen over ascorbic acid for a mixture containing both species.

Also investigated for this mixture was the response of acetaminophen's signal to an increase of its concentration. As shown in Figure 24, this response was found to be linear, with a correlation (R^2) of 0.9809.

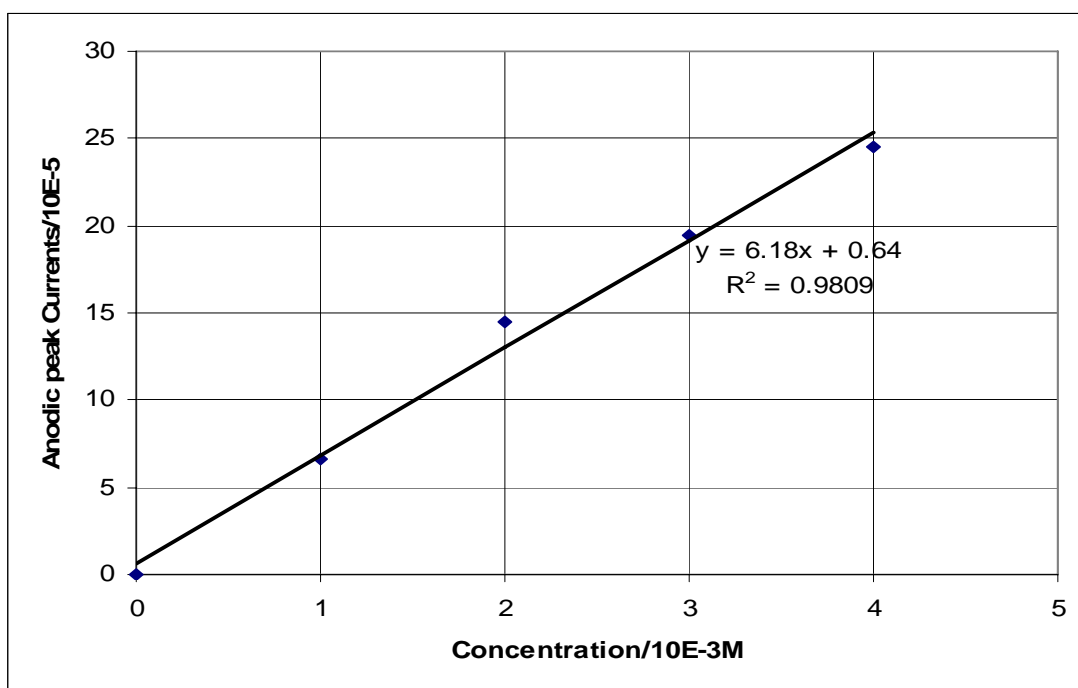


Figure 24: Graph of Peak Current Versus Concentration of Acetaminophen

Selective Oxidation of Uric Acid Over Ascorbic Acid. Uric acid is the final oxidation product of purine metabolism in the human body and is found in small amounts in urine.

Similar to the response observed for acetaminophen and ascorbic acid, for a

1mM mixture of uric acid and ascorbic acid in 1M HCl, POPD preferentially allows the oxidation of uric acid (Figure 25).

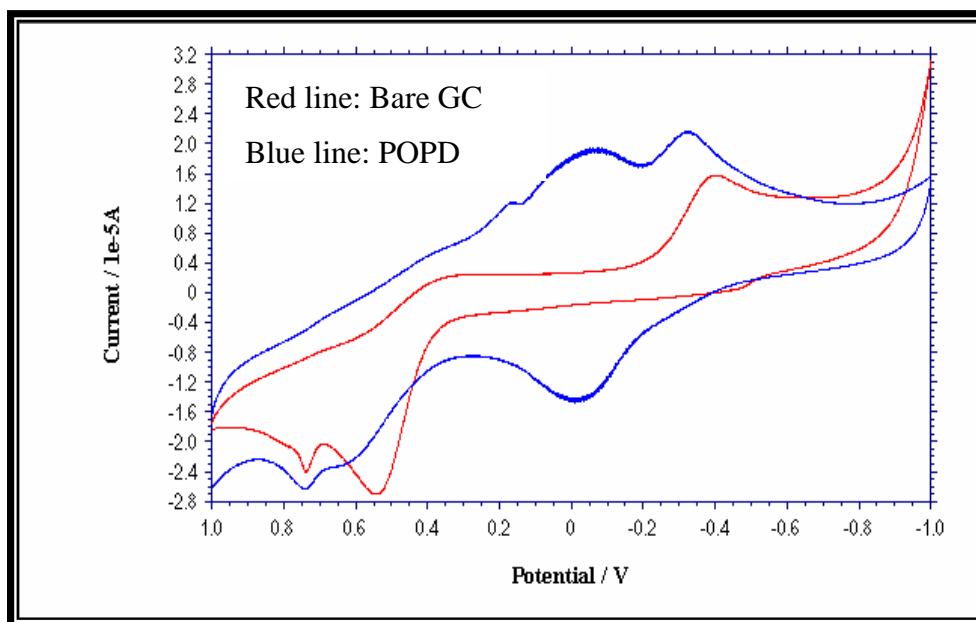


Figure 25: CV of a Mixture of Uric Acid and Ascorbic Acid

Again, notice that for bare GC, the oxidation peak that was present for ascorbic acid (around 0.55V) is absent when POPD is used. On the other hand, the anodic peak for uric acid is observed, both when bare GC and POPD are used.

Discussion of Results on Selective Oxidation of Bioorganic Species. The selective response towards acetaminophen and uric acid by POPD has potential to discriminate different active species within biofluid samples. It is my opinion that the exact responsive mechanism might be related to the difference in net charge

carried by the preferentially detected compound and the non - detected one when penetrating the laddered structure of the POPD network.

CHAPTER 4

CONCLUSIONS

PAN/CNTs polymer film is observed to show enhanced catalytic effect on the remedy of environmental dichromate. With the use of PAN/CNTs, the reduction potential of Cr (VI) is shifted to more positive potential (more enhanced reduction) when compared to that of a bare GC.

Thin, less conducting POPD film is observed to effectively block the anodic stripping for Hg^{2+} . The corresponding cathodic peak is enhanced and increases linearly with ion concentration.

The blocking of anodic stripping for by POPD and PMPD provides a conclusive qualitative test for heavy metal ions.

The permselective property of POPD was exploited for selective detection of some active bioorganic species. The selective response of POPD towards acetaminophen and uric acid over ascorbic acid has potential to discriminate different active species within biofluid samples. The exact responsive mechanism might be related to the difference in net charge carried by such species when penetrating the ladder structure of the POPD network.

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