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**ELECTROSYNTHESIS AND CHARACTERIZATIONS OF SOME
POLY(DYES)**

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ABSTRACT

The electrochemical polymerization and characterization studies were made for monomers: malachite green, neutral red, aniline, and methylene blue using GC working electrode with respect to Ag wire reference electrode. The electrochemical properties of their corresponding polymers were also studied in monomer free solution using cyclic voltammetry.

Copolymer films were electropolymerized from malachite green and neutral red, and aniline and neutral red where neutral red plays a role of electrocatalysis. In addition, PB film was also deposited potentiostatically from 2mM $K_3[Fe(CN)_6]$ and 2mM $FeCl_3$ solution on to GC/Polymer modified electrode at a potential of +0.4 V for 60 s. GC/Polymer/PB modified electrodes were also characterized using cyclic voltammetry where the presence of PB film together with GC/Polymer modified electrode enhances the peak currents of the GC/Polymer modified electrode indicating PB film also plays a role of electrocatalysis.

Key words: Electrosynthesis, poly(neutral red), poly(malachite green), poly(aniline), poly(methylene blue), and Prussian blue.

1. Introduction

1.1. General about conducting polymers

Conducting polymers are salts of inorganic acceptors and organic donors consisting of large, cyclically conjugated electron systems [1, 2].

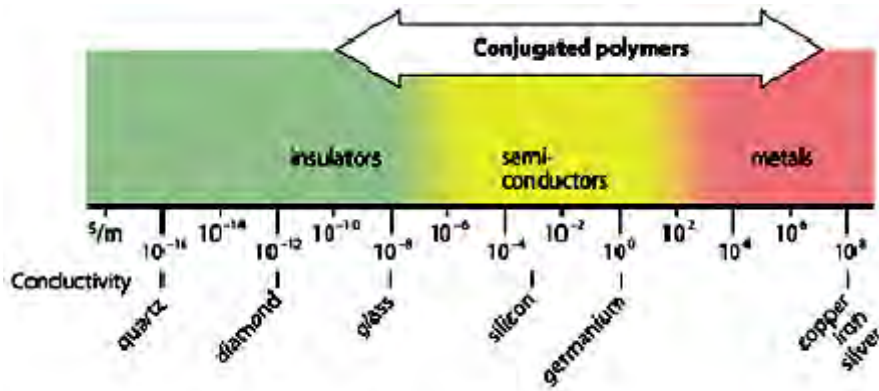


Figure 1. Conductivity of conducting polymers compared to those of other materials, from quartz (insulator) to copper (conductor). Polymers may also have conductivities corresponding to those of semiconductors.

There are generally four main types of conducting polymers. The first and most commercially important are composites, in which the filling of polymer matrix, which is originally nonconducting, with a powdered conductive medium such as metal or carbon, gives rise to conductivity. These composite polymers are used as antistatic coatings, substitutes for solder and many other applications. The second group of polymers is called ionically conducting polymers. They are organic polymers in which electric charge is carried by ions. Polyethylene oxides, in which lithium ion is mobile, are an example. These polymers are gaining importance in the battery industry. The third group of polymers is called redox polymers. These contain immobilized electroactive centers (or redox centers), which, although not in direct contact with one another, can exchange

electrons by a “hopping” mechanism. The fourth type is electrically conducting polymers, or conjugated polymers (CPs). 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 rather than the hopping observed in redox polymers. Structures of the most common CPs are depicted in figure 2 [1].

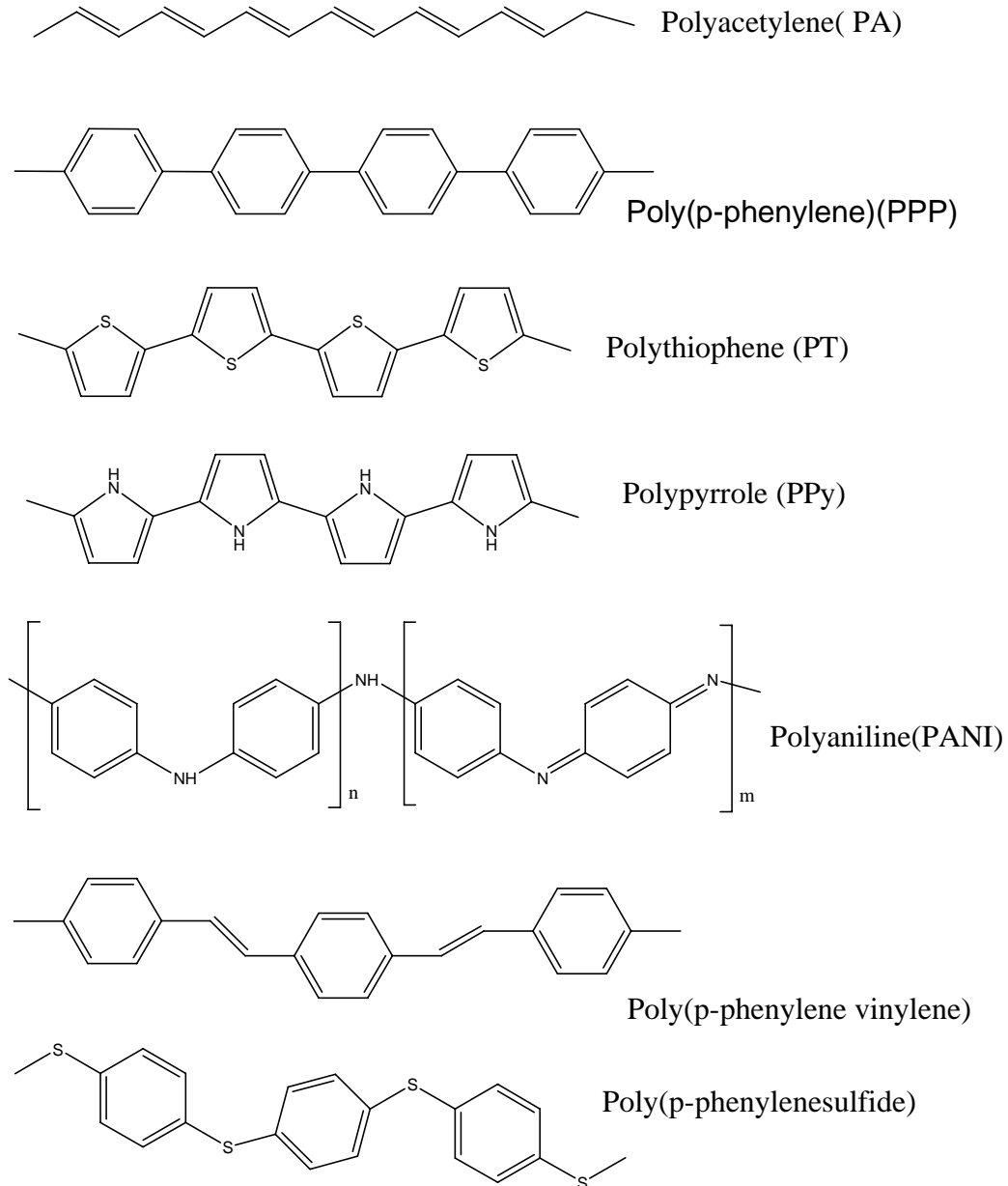


Figure 2. Structures for the most common CPs

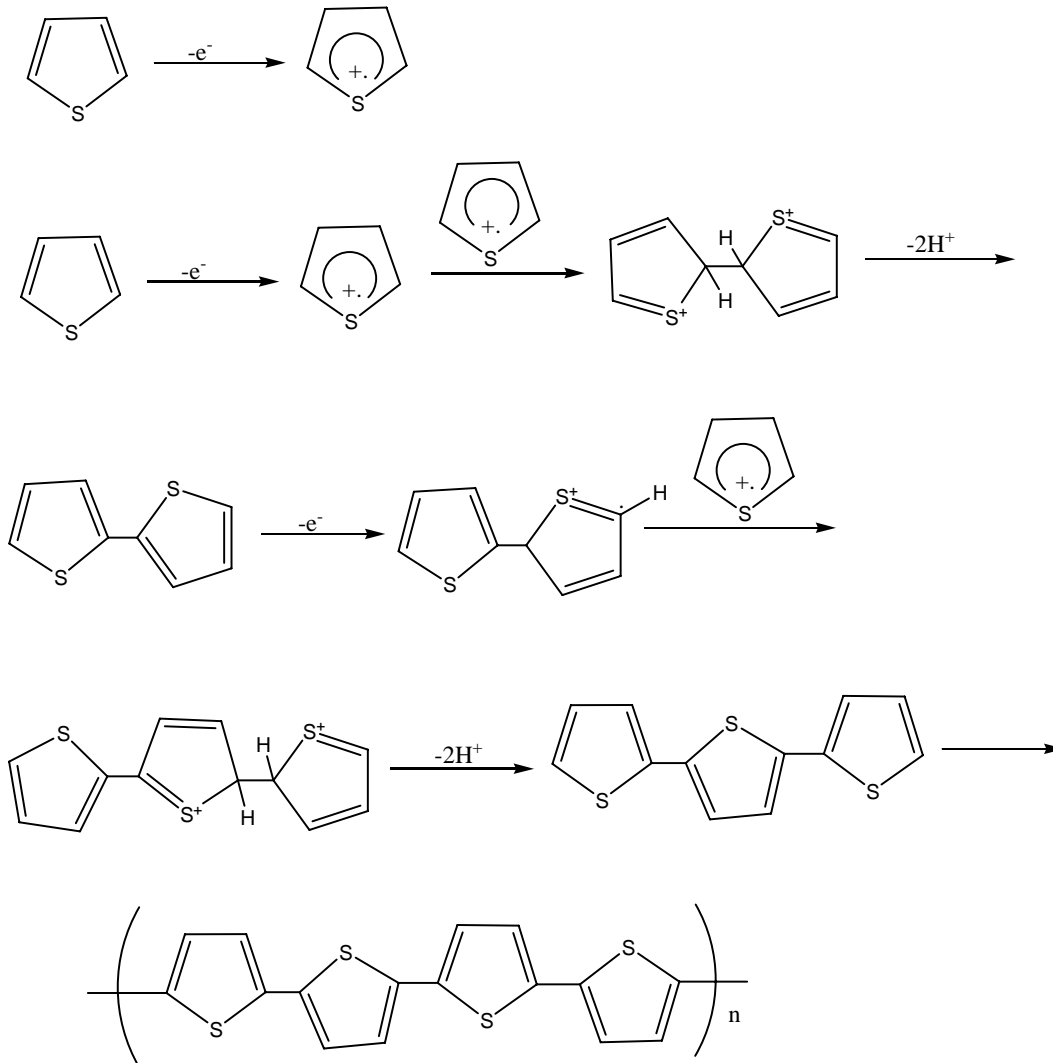
1.2. Conducting polymer synthesis

Conducting polymer syntheses fall broadly into two categories: Chemical and electrochemical syntheses. Nearly all electrochemical syntheses are radical coupling polymerizations, and many chemical syntheses are condensation polymerizations. Radical coupling polymerizations involve the well-known chain initiation generally occurring through generation of a highly reactive, radical ion. Condensation polymerization generally involves loss or elimination of a chemical species resulting from the reaction of end groups on monomer chains [1].

Electrochemical synthesis of polymers occurs via radical intermediates with the aim to stabilize the species generated in the electrode/solution interface. Therefore, applying an adequate electrochemical perturbation, it should be possible that the progressive elongation of polymeric chains, and with that, the control over the structure and polydispersity of the deposit [3]. The electropreparation and electrochemical stability of conducting polymers are of major importance for their use in different electrochemical systems such as batteries, electrocatalysis materials, sensor devices and electronic components [4, 5].

Electrochemical synthesis is a powerful tool for development of modified electrodes. Among certain advantages of this technique one should point out that the electropolymerization provides simplicity of targeting for selective modification of multielectrode arrays. In addition the electropolymerized materials usually possess some unique properties which are not peculiar to the corresponding monomers [6].

Mechanism of electrosynthesis of thiophene is shown in scheme 1 below as an example.



Scheme 1. Mechanism of electrosynthesis of thiophene

1.3. Basic concepts of conducting polymers

1.3.1. The reason for conduction in CPs

The reason that CPs are conducting can be found by the molecular orbital theory: The bonding of ethylene, which is a typical CP, can be given here as an example. One carbon atom has six electrons, of which four can be used to create bonds to other atoms. One sp^2

orbital forms a bond with the hydrogen atom overlapping with its 1s orbital and the other two form σ -bonds with adjacent carbon atoms along the chain (overlapping the sp^2 orbitals) as in Figure 3 (a) [1].

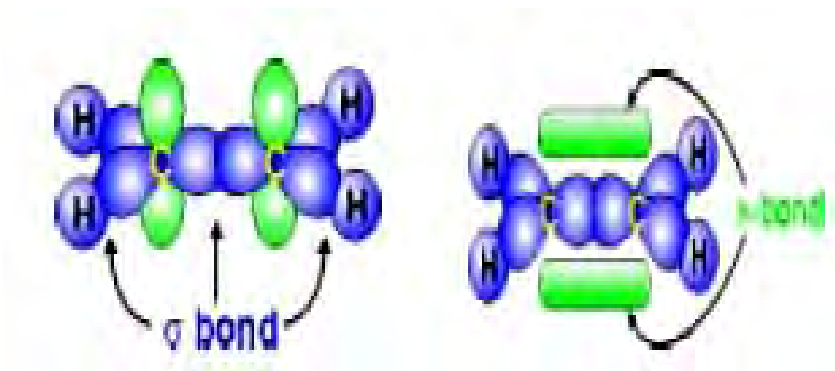


Figure 3. (a) σ -bond in C₂H₄

(b) π -bond in C₂H₄

In forming the sp^2 orbital, one $2p$ orbital on carbon has not been used. The remaining p orbital (p_z) is oriented perpendicular to the plane of sp^2 orbitals as in Figure 3(b). Along the polymer chain the p_z orbitals of two adjacent carbon atoms can overlap and form a π -bond. The π -bonds have smaller binding energy than the σ -bonds. That is the reason why electrons will move more easily, which is called delocalization. This system of interacting p_z -orbitals is called the conjugated π -system and is the reason for the unique electronic and optical properties of conjugated polymers. Extended overlap of the π -orbitals, intrinsic to CPs, develops broad valence and conduction bands. The valence and conduction bands can be classified as π and π^* orbital bands, respectively [1].

1.3.2. Doping of conjugated polymers

The chemical oxidation of CP by anions, or its reduction by cations, was originally called “doping”. The associated anions/cations, i.e. the counterions, were called “dopants”. The concept of doping is the unique, central, underlying, and unifying theme, which distinguishes conducting polymers from all other types of polymers. During the process, an organic polymer, either an insulator or semiconductor having a small conductivity, typically in the range from 10^{-10} to 10^{-5} S/cm, is converted to a polymer, which is in the ‘metallic’ conducting regime ($1\sim 10^4$ S/cm). The controlled addition of usually small ($\leq 10\%$ w/w) nonstoichiometric quantities of chemical species causes dramatic changes in the electronic, electrical magnetic, optical, and structural properties of polymer. Doping is reversible with little or no degradation of the polymer backbone. Both doping and undoping processes, involving dopant counterions which stabilize the doped state, may be carried out chemically or electrochemically [1, 7].

p-Doping

p-Doping is partial oxidation of the π -backbone of an organic polymer; it was first discovered by treating trans-(CH)_n with an oxidizing agent such as iodine. During the p-doping (oxidation) of a CP, an electron is removed from the polymer film and structural relaxation causes a local distortion in the polymer chain around the charge and the dopant being an anion. The twisted benzoid-like structure of the affected segments transforms into a quinoid-like structure. This form is energetically favorable, and functions to stabilize the charge. The quinoid structure possesses a slightly higher energy than the benzoid structure and the CP is said to have a non-degenerate ground state [1, 7].

n-Doping

n-doping is partial reduction of the backbone of π -system of an organic polymer and the dopant being a cation. It was also discovered using trans-(CH)_n by treating it with a reducing agent such as liquid sodium amalgam or preferably sodium naphthalide. In all chemical and electrochemical p- and n-doping processes discovered for conducting polymers, counter 'dopant' ions are introduced to stabilize the charge on the polymer backbone [1, 7].

The magnitude of the conductivity change of electrically conducting polymers depends on the doping level which can be controlled by the applied potential in the case of electrochemical doping. The doping mechanism of a fully conjugated poly(3, 4-propylenedioxythiophene) (PProDOT) is given in Figure 4. Neutral polymer (a) is a typical semiconductor and it exhibits an aromatic form with alternating double bonds. After removal of an electron from the polymer chain (oxidative doping), a radical cation (polaron) is generated, and the polymer assumes a quinodial state that facilitates charge transfer along the backbone. To maintain electroneutrality, anions diffuse into the polymer film. With increasing doping levels, more than one electron can be removed from the chain which results in formation of a dication (bipolaron) [7].

One of the greatest advantages of organic polymers compared with inorganic materials is their flexibility: they can be chemically modified and easily shaped according to the requirements of a particular device, their versatility and compatibility, coupled with ease of fabrication and light weight, make them useful materials for electronic devices. The potential applications of these conjugated polymers derived from both their conducting or neutral (non-conducting) forms [1, 8].

Other potential applications of conducting polymers are as corrosion inhibiting coatings, in sensors, photocells, solar batteries, electronic devices (diodes, transistors, and capacitors), memory devices, optical display devices, and recording. Conducting polymers are candidates for application in electrochemical cells. In particular, polyheterocycles have been cycled thousands of times. Conducting polymers may find applications in non-linear optical devices, particularly, e.g., signal processing and optical processing, and optical communication. These applications benefit from polymer flexibility, mechanical strength and high damage threshold [1, 8].

1.5. Electrochemical Method: Cyclic Voltammetry (CV)

Cyclic voltammetry is a reversal technique and is a potential scan equivalent of double potential step chronoamperometry. Cyclic voltammetry has become a very popular technique for initial electrochemical studies of new systems and has proven very useful in obtaining information about fairly complicated electrode reactions [9].

Cyclic voltammetry was used both to polymerize the monomers and to characterize the resultant polymers electrochemically. The method consists basically of measuring the current resulting from an applied triangular potential waveform. 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 [1, 9].

The current i is proportional to the gradient slope imposed ($i \propto dc/dx$). 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) [1, 9].

The peak current consists of two components. As in Figure 5, 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). 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 [1, 9].

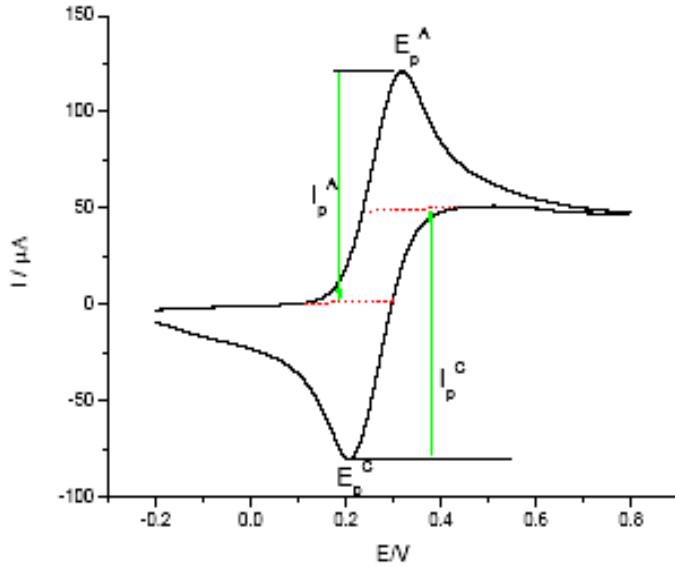


Figure 5. Cyclic voltammogram for a reversible reaction

1.5.1. Reversible Reactions

To understand what form voltammograms take, let us first consider a simple reversible reaction: $O + ne^- \leftrightarrow R$. It is assumed that, under steady state conditions, concentrations above a certain distance from the electrode are maintained uniform by natural convection. On the other hand, within the region next to the electrode, known as the Nernst diffusion layer, the concentration gradients are essentially linear. In order to determine the exact form of the cyclic voltammogram, it is again necessary to solve Fick's second law for O and R, as equations (1) and (2)

$$\partial C_O / \partial t = D_O \partial^2 C_O / \partial x^2 \quad (1)$$

$$\partial C_R / \partial t = D_R \partial^2 C_R / \partial x^2 \quad (2)$$

C_O : Concentration of oxidant. C_R : Concentration of reductant. D_O : Diffusion coefficient of oxidant. D_R : Diffusion coefficient of reductant.

For planar diffusion at 25⁰C, the final equation deduced is called Randles-Sevcik equation.

$$I_p = - (2.69 \times 10^5) n^{3/2} C_{O^\infty} D^{1/2} v^{1/2} \quad (3)$$

Where I_p , the peak current density (measured as shown in Figure 5) is in $A\text{cm}^{-2}$, D is in cm^2s^{-1} , scan rate v is in Vs^{-1} , and bulk concentration of oxidant C_{O^∞} is in mol cm^{-3} . Thus we can see that the peak current density is proportional to the concentration of electroactive species and to the square roots of the sweep rate and diffusion coefficient. Sometimes, because the potential peak is so broad, it is difficult to locate E_p accurately. Then the potential at $i_p/2$ is recorded and called $E_{p/2}$ [1].

In the case of reversible system, the electron transfer rates at all potentials are significantly greater than the rate of mass transport to the electrode, and therefore Nernstian equilibrium is always maintained at the electrode surface.

1.5.2. Irreversible Systems

In contrast with reversible system, when the rate of electron transfer is insufficient to maintain the Nernstian equilibrium at the electrode surface, the slope of the cyclic voltammogram changes. At lower potential sweep rates the rate of electron transfer is greater than that of mass transfer, and a reversible cyclic voltammogram is recorded.

When the sweep rate is increased, however, the rate of mass transfer increases and becomes comparable to the rate of electron transfer. The most noticeable effect of this is to increase the peak separation. In the limit for a totally irreversible process the shape of the cyclic voltammogram can again be obtained mathematically by solution of the differential equations, and yields the following equation for the peak current density at 25°C [1].

$$I_p = - (2.99 \times 10^5) n (\alpha_c n_a)^{1/2} C_o^\infty D_o^{1/2} v^{1/2} \quad (4)$$

The factor $(\alpha_c n_a)$ is deduced from solving the differential equations. n_a in the equation is the number of electrons transferred, and including, the rate determining step. Thus, for the reversible case, the peak current density is proportional to the concentration and to the square root of the transfer coefficient α_c . Probably the most marked feature of a cyclic voltammogram of a totally irreversible system, for example $O + ne^- \rightarrow R$, is the total absence of a reverse peak. However, such a feature itself does not necessarily imply an irreversible electron transfer process, but could also be due to a fast following chemical reaction.

1.5.3. Application of CV on CPs

Besides the instrumental simplicity of cyclic voltammetry, a considerable amount of information about the CPs can be obtained on the basis of recording a single CV. Cyclic voltammetry is one of the first methods to be applied to an electrode coated with a CP film. Electrochemical monitoring of the electropolymerization process is primarily

performed using cyclic voltammetry. In the first potential cycle, during anodic electropolymerization by potential cycling, the oxidation peak corresponds to formation of radical monomer cations. On the reverse scan, the reduction peak corresponding to this oxidation is not always observed. This indicates that in the time scale of the experiment, the intermediate reactive radical monomer cations dimerize in the subsequent chemical reaction. Starting with the second potential scan a current peak at lower potential than the monomer oxidation peak is observed. This corresponds to oxidation of the formed oligomer chains. On the reverse scan, a peak current due to reduction of the oxidized oligomer species is observed. During subsequent potential scans oxidation and reduction of the growing CP film can be followed. The redox current peak increases until the polymer stops growing on the electrode [1, 9].

2. Literature of Review

2.1. Poly(neutral red)

Neutral red (NR) (3-amine-7-dimethylamine-2-methylphenazine) is a phenazine dye with the molecular structure shown in figure 6 [10].

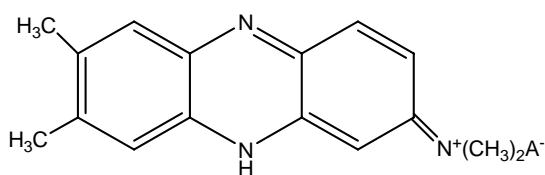
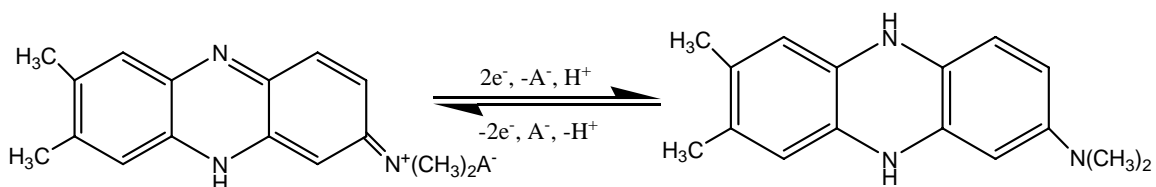


Figure 6. The molecular structure of Neutral Red (NR)

NR has a pair of redox peaks, which is attributed to the electrochemical redox process of C=N group in its structure. The electrode reaction process can be expressed with the following equation [11]:



Neutral red can be used for developmental studies of living roots [12], as pH indicator, changing from red to yellow between the pH 6.8-8.0 in aqueous media [13-14], as an electronophore for electricity generation in microbial fuel cells [15], for the fabrication of an amperometric hydrogen peroxide sensor [16], and for distinguishing double strand DNA (dsDNA) and single strand DNA (ssDNA) [10]. Moreover, the chemical and electrochemical properties of neutral red dye make it an ideal substance as an electronic mediator in the construction of enzymatic electrodes [17].

Poly(neutral red) is a polyaniline derivative. Polyaniline and its derivatives have attracted much attention for both theoretical reasons and potential applications in sensors, rechargeable batteries and potential applications in electronic devices. Due to its conjugative ring structure, phenazine may be a promising block for building high quality conducting polymers. In fact, the electrochemical oxidation of phenazine neutral red (3-amine-7-dimethylamine-2-methylphenazine), an aniline derivative, has been studied extensively in weak acidic, neutral and basic solutions. It has been proved and reported in

the literature that NO_3^- is the best dopant for phenazine-type polymers. The poly(neutral red) film produces useful electrode transfer mediators and it is used as immobilization of enzymes. This polymer also exhibits electrocatalytic activity, e.g. electro-oxidation of NADH [18], and electroreduciton of NO_2^- , IO_3^- and BrO_3^- , and also for the development of new biosensors for glucose and pyruvate [19-20]. Somewhat surprisingly, to date, there have been a few studies concerning the polymerization reaction of neutral red in strong acidic solutions, and the structures and electrochemical properties of poly(neutral red) (PNR) have not yet been studied in detail [19].

2.2. Poly(malachite green)

Malachite green is a synthetic dye used to color silk, wool, leather, cotton and paper. The name comes from the similarity of color of malachite green to the mineral, malachite [5]. Poly (malachite green) can be generated by electrochemical polymerization of malachite green, the chemical structure of which is illustrated in figure 7. Malachite green has an opened but ionized structure and hence the resulting polymer is promising in exhibiting interesting features like fast rate of charge transfer and ion transport and nice catalytic ability towards small biomolecules [10].

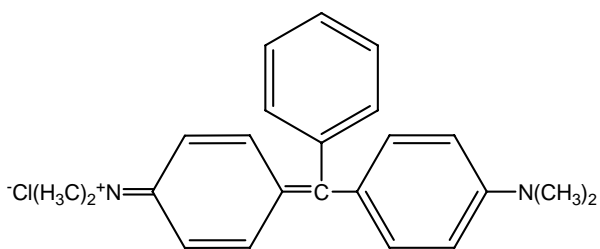
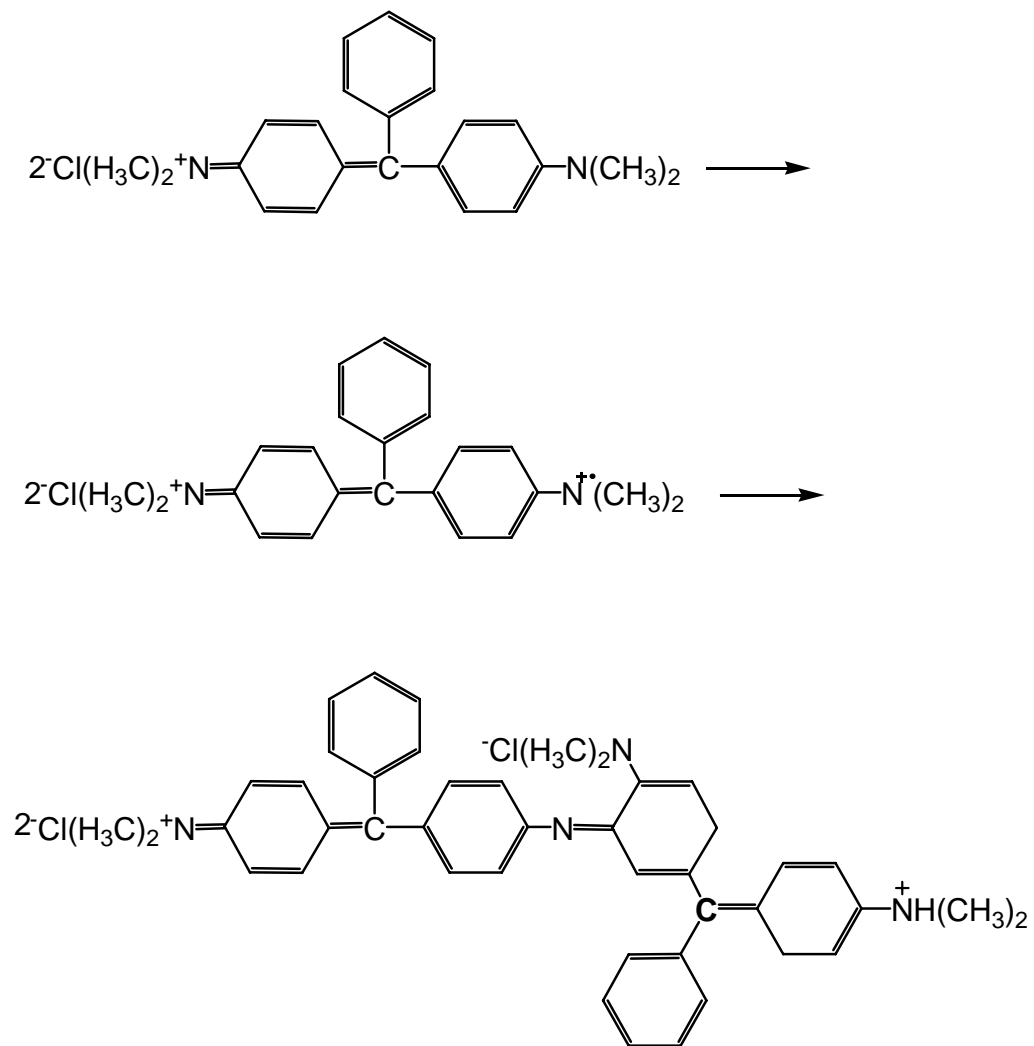


Figure 7. Chemical structure of malachite green

Therefore, the polymerization of malachite green is carried out potentiodynamically on the glassy carbon electrode, and the possible growth mechanism of poly (malachite green) film is investigated as shown in scheme 3 below [10].



Scheme 3. Possible growth mechanism of poly (malachite green) film

2.3. Polyaniline

Polyaniline (PANI) has been known and studied extensively since the 1980s [21]. Polyaniline (PANI) is synthesized by electrochemical polymerization in a medium of proton acid of small molecular size, such as HCl or H₂SO₄ via a radical cation mechanism [21] from its monomer aniline, whose structure is shown in figure 8. The interest in this material and its derivatives is mainly due to its interesting electrical and optical properties together with its chemical tunability, ease of derivatization, solubility in a variety of solvents, processability into fibers and films, and its stability [21-23].

During the past two decades, the chemical and physical properties of polyaniline have been studied extensively under different conditions and, together with polypyrrole; this material has become one of the most popular conducting polymers. A complete review of the tremendous advances in the chemistry, electrochemistry, physics, theory, and processing of polyaniline has been given by MacDiarmid.

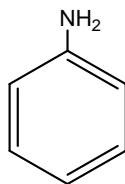


Figure 8. Chemical structure of aniline

Polyaniline has three main stable oxidation states: the fully reduced “leucoemeraldine” (LE) form, the 50% oxidized “emeraldine base” (EB) form and the fully oxidized “pernigraniline” (PN) form. Each of these can exist in the form of its base or in the form

of its protonated (doped) salt [1, 21]. The only electrically conducting one is, however, the emeraldine salt form (ES: half oxidized), which is protonated from emeraldine base (EB). The different fundamental forms of PANI structures are shown below (figure 9).

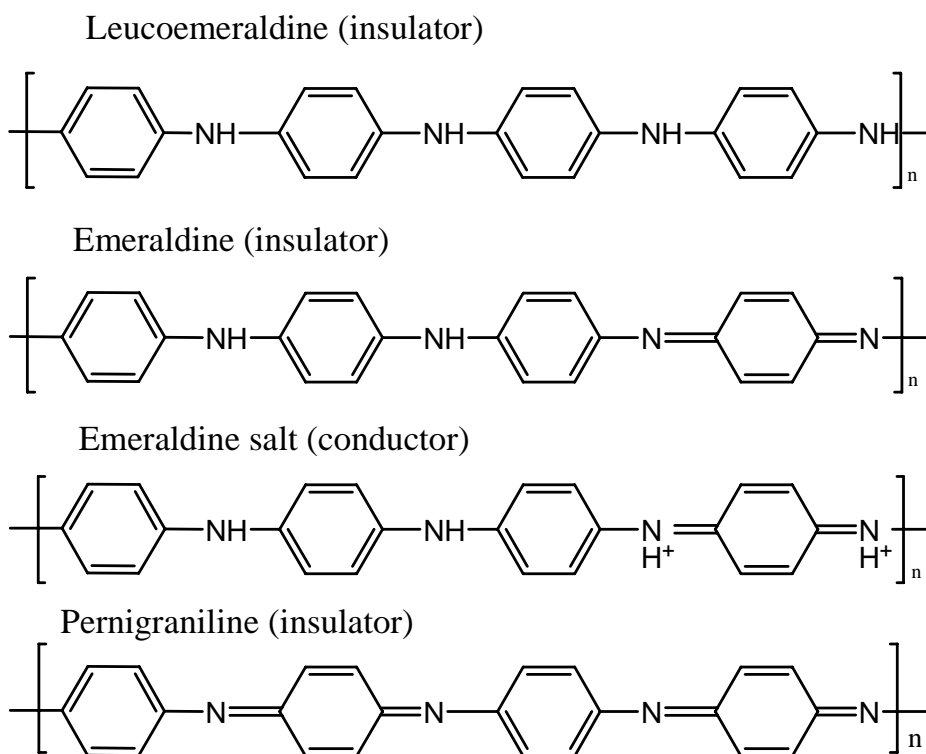


Figure 9. Fundamental forms of PANI structures

2.4. Poly(methylene blue)

Methylene blue is widely used as a redox indicator in analytical chemistry. Solutions of this substance are blue when in an oxidizing environment, but will turn colorless if exposed to a reducing agent. The redox behavior of the phenothiazine methylene blue (MB), whose structure is shown in the figure 10 below, has been under study for nearly 60 years. Karaykin et al. found that an electroactive surface layer was formed at high

positive potentials only in neutral and basic solutions [6, 24-25]. This is in contrast with the electropolymerization of the widely familiar conducting polymers (e.g. Polyaniline) in which strong acidic solution is necessary for polymerization. It was observed that the rate of polymerization of methylene blue increased with increasing pH indicating that basic solutions are the optimal media for polymerization of methylene blue [6, 24]. These unique properties of methylene blue electropolymerization and the structure of the monomer molecule allowed one to expect poly(methylene blue) as one of a representative of a new group of electroactive polymers [6]. Despite the extensive study, the linkage of the polymer is still in question. Three different linkage schemes, viz., “nitrogen-to-ring” (“N-to-ring”), “ring-to-ring”, and “nitrogen-to-nitrogen” (“N-to-N”) have been proposed in the literature [24]. Among these, demethylation followed by “nitrogen-to-ring” coupling is the dominant reaction during the electropolymerization of MB on the basis of the mass spectrometry results [24].

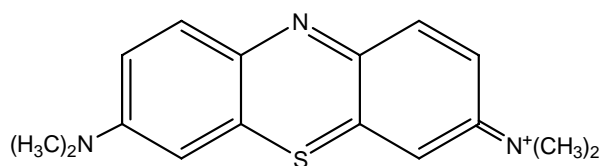


Figure 10. Chemical structure of methylene blue

Electropolymerized Methylene Blue is used as an electrocatalyst of NADH oxidation. It was found that electropolymerization could be considered as a good method of mediator immobilization on the electrode surface. The main advantage of using electropolymerized Methylene Blue as catalyst of NADH oxidation was its improved long-term stability [26].

2.5. Prussian blue

Prussian blue (PB) is the historic name of an ancient pigment that today is recognized as belonging to a very important family of functional inorganic materials: the transition metal hexacyanoferrates. PB is the simplest representative for which the metal ion centers are both iron. The unique structural arrangement and its route to compositional variation by metal substitution lead to a combination of properties not readily found in other inorganic materials. The fabrication of metal hexacyanoferrate thin films for device applications is particularly attractive. This has been approached only recently; for many years these materials were available only as friable particles that could not be formed or cast. Electrochemical methods introduced by Neff and co-workers allowed the first straight forward formation of PB films [23].

There exist two well-known forms of the PB crystal: the so called “insoluble” PB with the formula $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$ and the “soluble” $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$. In truth, both forms are completely insoluble in water and most common solvents [23-24]. PB is one of the most extensively studied due to the electrochromic properties and the electrocatalytic activity and stability in aqueous solutions. PB has been used in the electrocatalytic reduction of CO_2 , hydrogen peroxide, hydrazine, and the oxidation of ascorbic acid and dopamine. The presence of two well distinct redox couples ascribes it selectively with respect to the redox processes that can or can not be electrocatalysed by an electrode modified by PB [27-29].

3. Objective of the study

The main objective of this study is to electrosynthesize and characterize poly(dyes) such as poly(neutral red), poly(malachite green), poly(aniline), and poly(methylene blue) using cyclic voltammetry.

In addition, the objective is also to study the effect of neutral red on electropolymerizations of malachite green and aniline (copolymerization) compared with electropolymerizations of malachite green and aniline in the absence of neutral red i.e. to study the electrocatalytic effect of neutral red during the electropolymerizations of poly(dyes), malachite green and aniline, and characterizations of the films and compare with electropolymerizations of the poly(dyes) and characterizations of the films in the absence of neutral red.

Furthermore, the electrocatalytic effect of Prussian blue (PB) on some poly(dyes) such as poly(neutral red), poly(aniline), and poly(methylene blue) will also be studied.

4. Experimental Section

4.1. Chemicals and solutions

Neutral red, malachite green, and methylene blue are analytical grade reagents and were used without further purification. Aniline (Aldrich) was distilled before use for further purification. Other chemicals like sulfuric acid (H_2SO_4) (Riedel-de Haen), hydrochloric acid (HCl) (BDH), sodium hydroxide (NaOH) (BDH), dipotassium orthophosphate (K_2HPO_4) (Fluka), potassium dihydrogenorthophosphate (KH_2PO_4) (Fluka), disodium orthophosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) (BDH), sodium dihydrogenorthophosphate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) (BDH), potassium chloride (KCl) (BDH), FeCl_3 (BDH), potassium hexacyanoferrate ($\text{K}_3[\text{Fe}(\text{CN})_6]$) (Merck), sodium nitrate (NaNO_3) (Riedel-de Haen) and sodium sulphate (Na_2SO_4) (NICE) were also used without special treatment. All the solutions were prepared with doubly distilled water.

4.2. Instrumentation

All the electrochemical experiments were carried out using a computerized electrochemical analyzer (BAS CV-50W) with a conventional three electrode system at room temperature. Film coated glassy carbon electrode or a bare glassy carbon electrode 3 mm in diameter was employed as the working electrode. A platinum metal foil and silver wire were used as auxiliary electrode and reference electrode respectively. The potentials mentioned throughout this paper were against the above reference electrode.

4.3. Procedure

Before each electrochemical test the surface of the working electrode was polished subsequently with alumina powder to a mirror finish, treated for several cycles in sulfuric acid solution to activate it and finally rinsed with doubly distilled water. Several buffer solutions were prepared in doubly distilled water and their pHs were adjusted by a pH/ION meter level 2. Before the electrochemical polymerizations and characterizations the appropriate working potential windows were selected using the supporting electrolyte solutions. Prussian blue film was deposited on to the working electrode potentiostatically at +0.4 V for 60s [27-29]. Then electrochemical polymerizations of the dyes and voltammetric characterizations of the films produced were studied.

5. Results and Discussion

5.1. Electropolymerization of Neutral Red

The generation of the poly (neutral red) on conducting materials requires the application of a positive potential to the working electrode immersed in a monomer solution in order to generate a neutral red radical cation, which is the precursor of the polymer [11]. The cyclic voltammograms of film growth during the electrolysis of neutral red is shown in figure 5. The experimental conditions are described in the caption of figure 11.

The polymerization of neutral red takes place when the potential reaches about 0.85 V vs Ag wire. At that potential an oxidation peak (A) is recorded (Figure 11). The absence of the corresponding reduction peak cause one to assign the peak to the formation of

monomer radical cation that reacts with itself to form a dimer. The dimer can also give a radical cation when oxidized, and react with other radicals, forming a polymeric structure. The peak system (BC) corresponds to the reduction and reoxidation of the polymer.

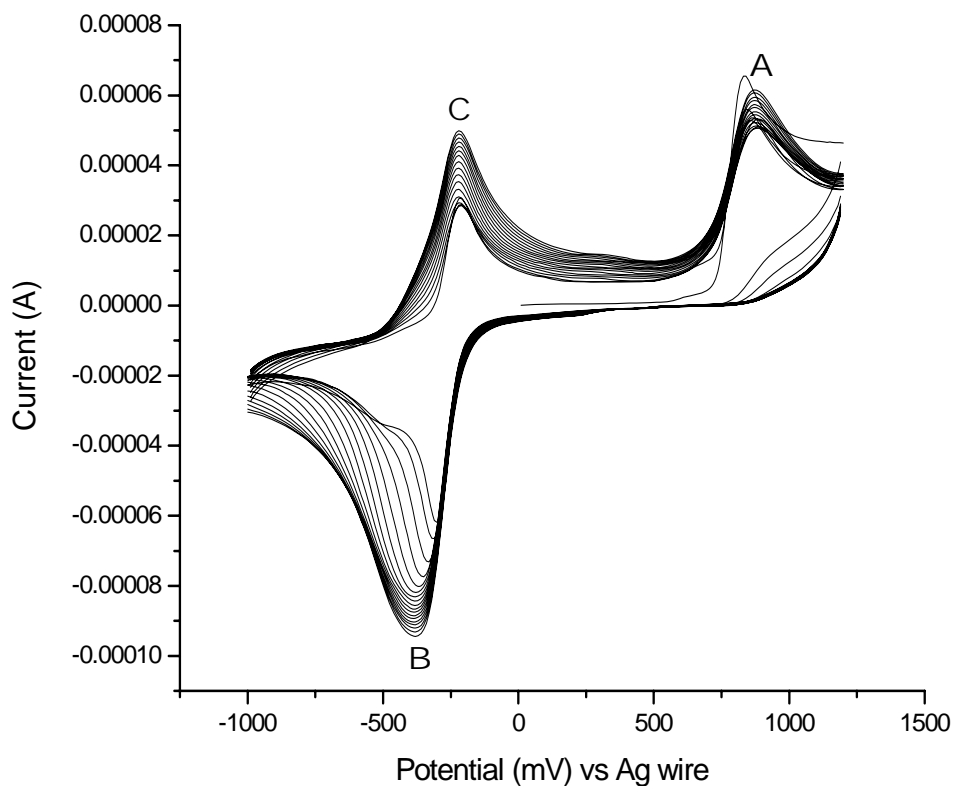


Figure 11. Cyclic voltammograms of electropolymerization of 5 mM Neutral Red in 0.5 M H₂SO₄ solution on glassy carbon electrode in the potential range from -1.0 V to 1.2 V at a scan rate of 100 mVs⁻¹. Number of cycles 18.

The growth of the polymer on the electrode can be seen in the increase of all the peaks, and it is more evident at the reduction one. The increase of the radical formation peak (peak A) indicates that both the monomer and the deposited polymer can also be oxidized

[11, 17-19]. It was observed that the monomer anodic peak potentials shift slightly towards positive values with the increase in the number of cycles. These potential peaks displacements are caused by the increase of the ohmic drop across the film [17-19]. The cathodic peak current of the polymer increases rapidly and its peak potential shifts towards more negatively a little with increasing the number of potential cycles while its anodic peaks remain nearly constant. This reason is that the film thickness of the poly(neutral red) on the glassy carbon electrode was gradually growing during the electrolysis and causes potential drop.

5.1.1. Voltammetric characterization of GC/PNR modified electrode

5.1.1.1. Scan rate effect

The voltammogram shape of the polymer film is affected by the scan rate as shown in figure 12. The peak intensities (both the cathodic and the anodic) depend linearly on the scan rate. The cathodic and anodic peak potentials move to more negative and positive potentials respectively as the sweep rate is increased. This behavior is characteristic of multi-layer modified electrodes, where mass transfer is done through the film, and also of the processes with slow electron transfer or influenced by an ohmic drop effect.

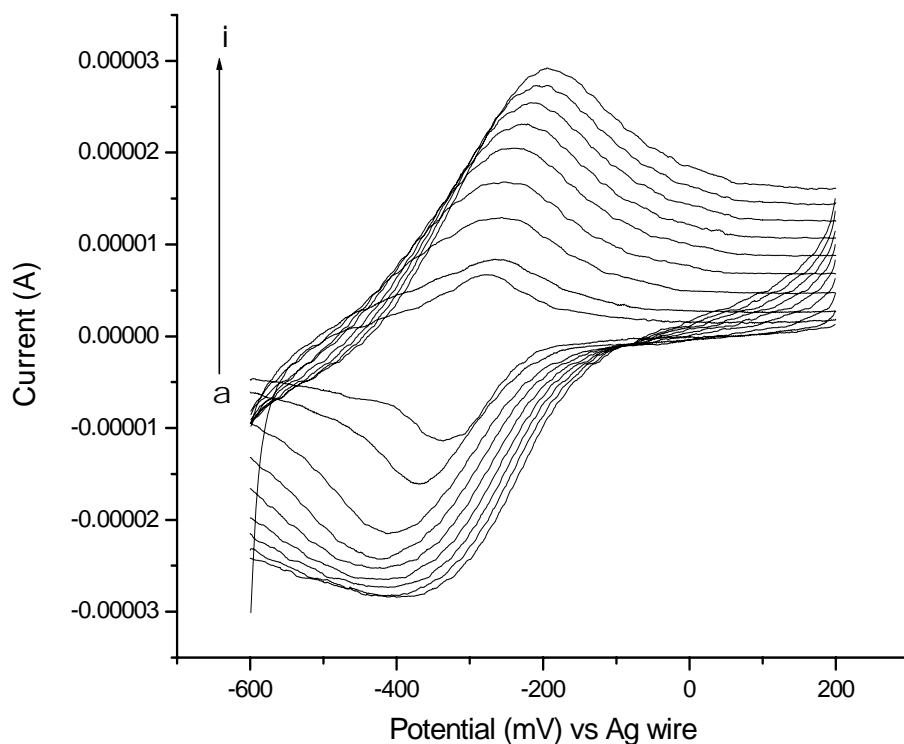


Figure 12. Cyclic voltammograms of poly(neutral red) film on glassy carbon electrode at scan rates of: a) 10, b) 20, c) 40, d) 60, e) 80, f) 100, g) 120, h) 140, and i) 160 mVs^{-1} in 0.1 M H_2SO_4 solution.

5.1.1.2. pH effect

In general, one of the most interesting characteristics of electroactive polymers is the dependence of their electrochemical properties on the pH [19]. Figure 13 shows the variation of the cyclic voltammetry of the modified electrode with pH. There are several interesting features in this dependence. It can be seen that the peak potential moves to more negative potentials as pH increases, suggesting that a protonation, previous to the electron transfer, must occur in the reduction, as well as a deprotonation in the oxidation [11].

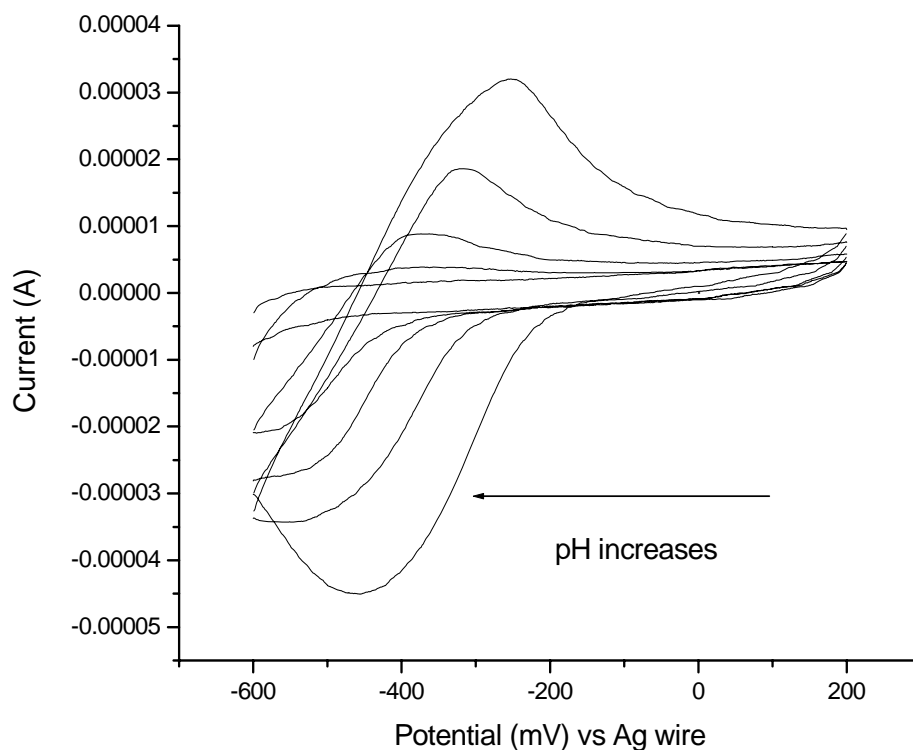


Figure 13. Cyclic voltammograms of the poly(neutral red) film coated glassy carbon electrode at a scan rate of 100 mV s^{-1} in $0.5 \text{ M Na}_2\text{SO}_4$ solutions with various pH values ranging from 1.09 to 5.3. From right side to left side, the pH values were 1.09, 2.24, 3.29, 4.07, and 5.30.

The peak intensities are also greatly affected by the pH. Both the anodic and cathodic peak intensities decrease with increase in the values of pH. The intensity decrease is associated with a decrease of the hydrogen ion concentration. The increase in pH also increases the peak width, that is to say, to increase the irreversibility of the peak; this effect is more acute in the cathodic peak when the pH is increased. That increase in the irreversibility can also be seen as an increase in the peak-to-peak separation when pH increases.

From the plot of both cathodic and anodic peak potentials vs the pH, it is observed that both potentials vary linearly with the pH (figure 14). The slope of the cathodic peak potential dependence (43.8 mV/pH) is almost equals to the slope of the anodic one (52.7 mV/pH). This result points out the participation of one hydrogen ion in the electrochemical reaction associated to both the cathodic peak and the anodic one.

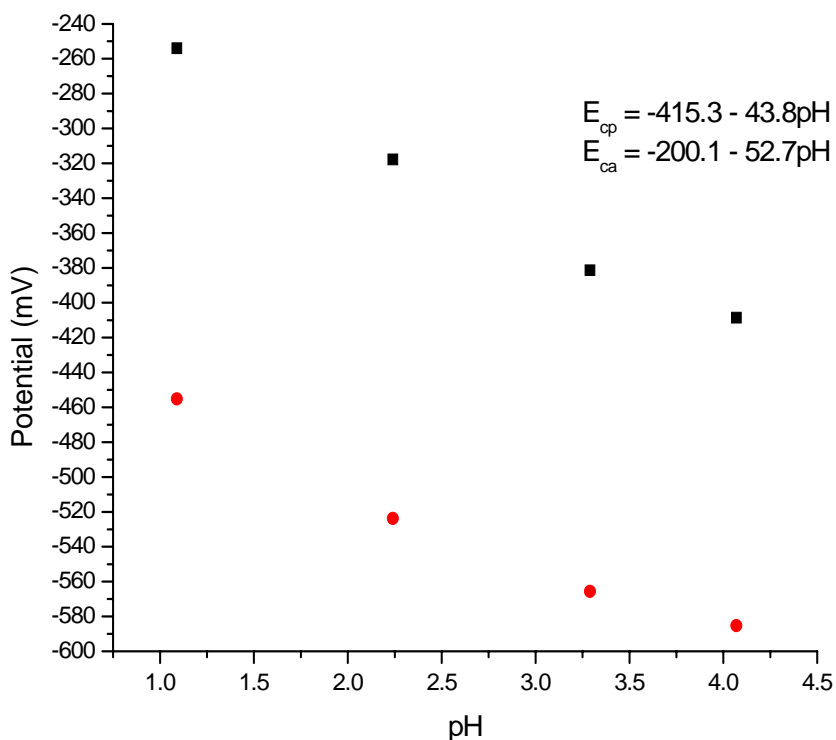


Figure 14. Peak potentials dependence of the redox couple of PNR on the pH in 0.5 M Na_2SO_4 solution. Anodic (top); cathodic(bottom).

It must be taken into account that the hydrogen ion acts not only as a reactant in the electrochemical reaction, but also as counter ion to the electrons, and then a decrease in its concentration in the film (proportional to the solution pH) will diminish the electrical conductivity through the film and make the process more irreversible [11, 17-19].

5.2. Electropolymerization of Malachite Green

Figure 15 shows cyclic voltammograms of electropolymerization of malachite green on glassy carbon electrode through scanning at a sweep rate of 100 mV s^{-1} in a 10 mM malachite green aqueous solution containing 0.5 M NaNO_3 and 0.025 M K_2HPO_4 - KH_2PO_4 buffer solution in the potential range from -1400 to 1800 mV for 12 cycles.

As observed from electropolymerization voltammograms one anodic peak at 1.5 V and a cathodic wave at -0.4 V were noticed. The peak currents of these waves enlarged with increase cycling numbers although with a little shift of peak potentials. From the cyclic voltammograms of electropolymerization of malachite green solution, the peak at around -0.4 V indicates the reduction of the poly(malachite green) (PMG) film formed at the surface of the glassy carbon electrode. Similarly the peak at around 1.5 V is responsible for the oxidation of malachite green monomer. The increase in both peaks with potential cycles shows the development of polymer film on the surface of the electrode [3].

The high increment of current at far positive potential with increase of potential cycles during the electropolymerization of malachite green is most probably due to two superposition processes: the oxidation reactions of the monomer and poly(malachite green) film.

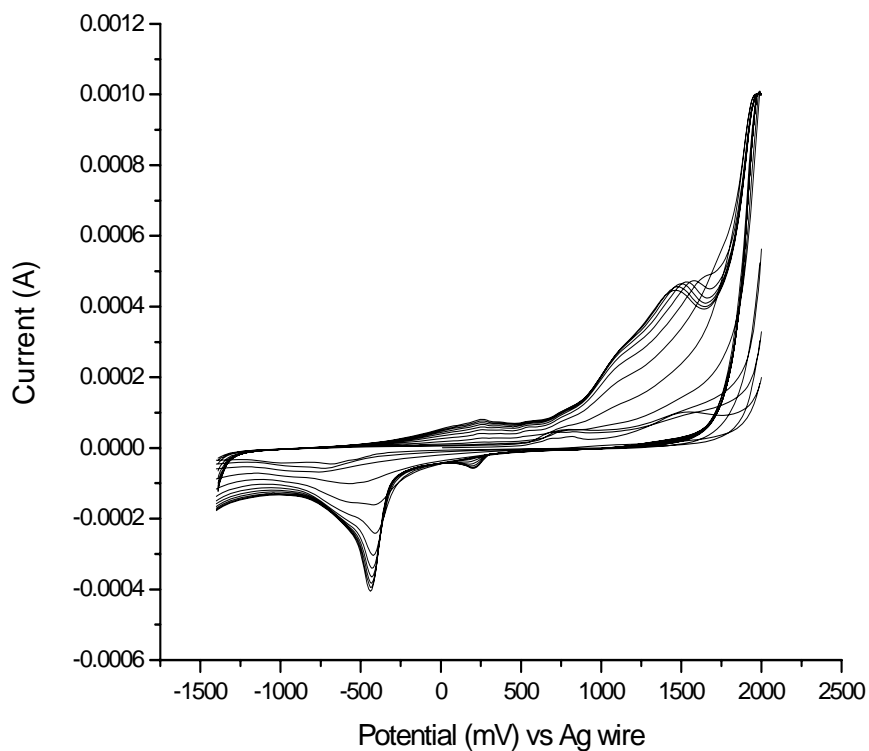


Figure 15. Cyclic voltammograms of electropolymerization of malachite green on glassy carbon electrode in the potential range from -1.4 V to 1.8 V at a scan rate of 100 mVs^{-1} . The polymerization solution was 10 mM malachite green aqueous solution containing 0.5 M NaNO_3 and 0.025 M $\text{K}_2\text{HPO}_4\text{-KH}_2\text{PO}_4$ buffer solutions. Number of cycles 12.

5.2.1. Voltammetric characterization of the GC/PMG modified electrode

5.2.1.1. Scan rate effect

Electrochemical activity (redox behavior) of the poly(malachite green) film on the glassy carbon electrode was investigated in 0.1 M H_2SO_4 at various scan rates. Figure 16 shows cyclic voltammograms of the poly(malachite green) film coated glassy carbon electrode in 0.1 M H_2SO_4 in the potential range of -0.2 to 0.8 V at various scan rates ranging from 10 to 160 mV s^{-1} .

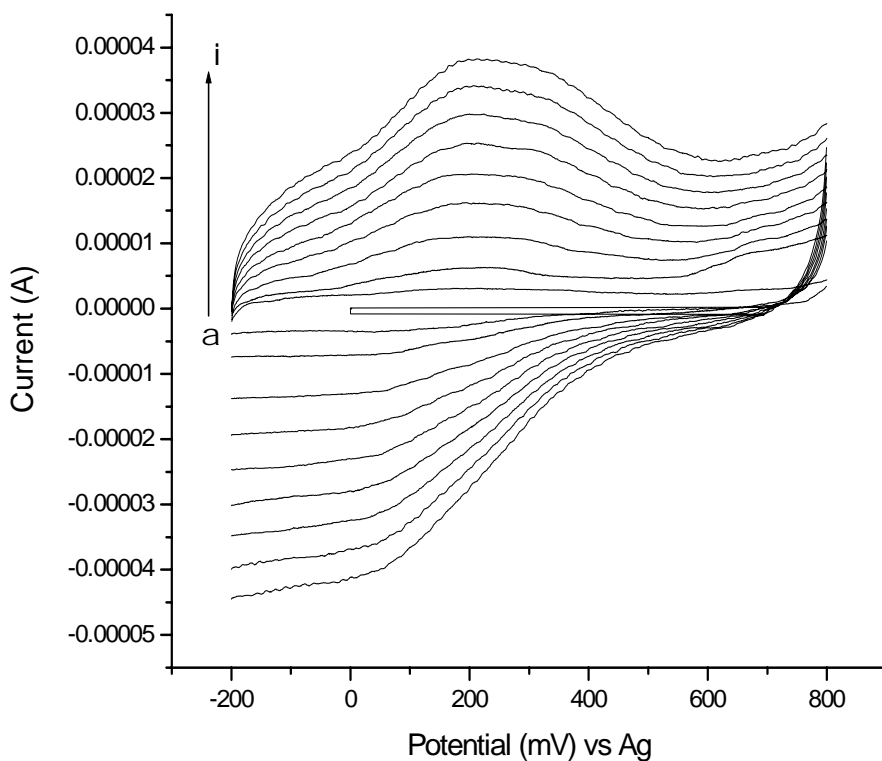


Figure 16. Cyclic voltammograms of poly(malachite green) film on glassy carbon electrode at scan rates of: a) 10, b) 20, c) 40, d) 60, e) 80, f)100, g) 120, h) 140, and i) 160 mVs^{-1} in 0.1 M H_2SO_4 solution.

One couple of redox waves appeared at potentials of around 0.05 and 0.2 V for the cathodic and anodic one, respectively. The peak potentials did not alter with increased scan rates while both of the peak currents enhanced proportionally with scan rates. The independence of peak potentials on scan rates demonstrates that the redox reaction is a reversal process controlled by adsorption [3].

5.2.1.2. pH effect

Figure 17 shows cyclic voltammograms of the poly(malachite green) film coated glassy carbon electrode in a solution with different pH values ranging from 1.09 to 5.3 at scan rate of 100 mVs^{-1} .

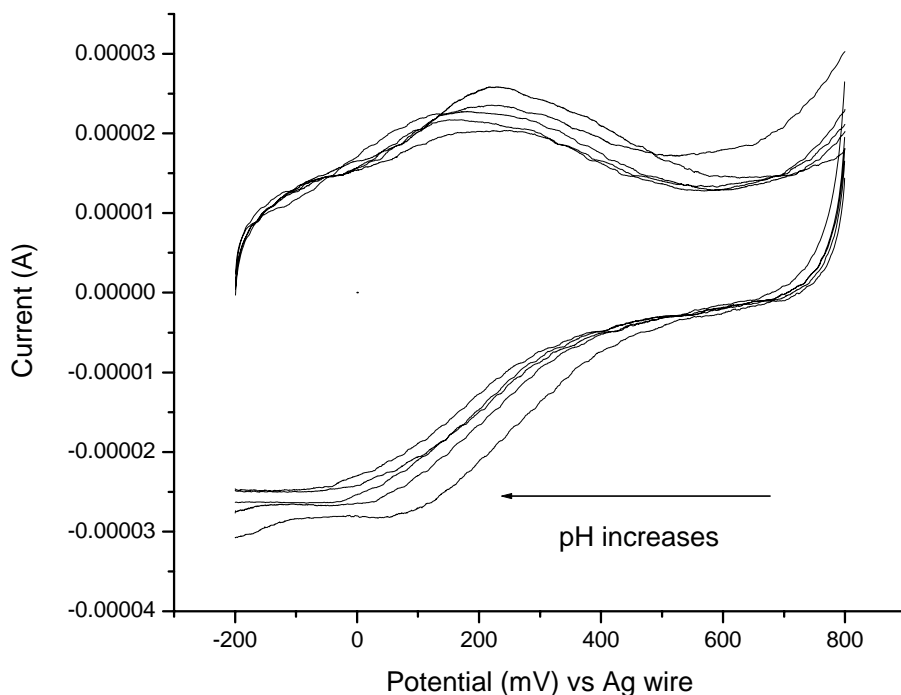


Figure 17. Cyclic voltammograms of the poly(malachite green) film coated glassy carbon electrode at a scan rate of 100 mV s^{-1} in $0.5 \text{ M Na}_2\text{SO}_4$ solutions with various pH values ranging from 1.09 to 5.3. From right side to left side, the pH values were 1.09, 2.24, 3.29, 4.07, and 5.30.

The shape of voltammograms obtained in $0.5 \text{ M Na}_2\text{SO}_4$ buffer solution was much worse than those obtained in $0.1 \text{ M H}_2\text{SO}_4$ (figure 10) and the currents are close to each other at the same scan rate. Both anodic and cathodic peak potentials shifted negatively while the peak current decreased with an increase in pH values. The decreased peak current results

from a decade of the concentration of proton in the solution [3-4, 11, 17-19]. The effect of pH on poly(neutral red) film is more pronounced than its effect on poly(malachite green) film under the same solution condition. This is most probably due to the primary amine group present in neutral red that might also be present in its polymer form that could not be expected in poly(malachite) green film.

5.3. Electropolymerization of malachite green in the presence of neutral red

Before electropolymerization of malachite green in the presence of neutral red, optimum mole ratio of the two dyes was determined from four different mole ratios as shown below (figure 18). Maximum current is produced when the mixture contains 1:1 mole ratio of the two dyes.

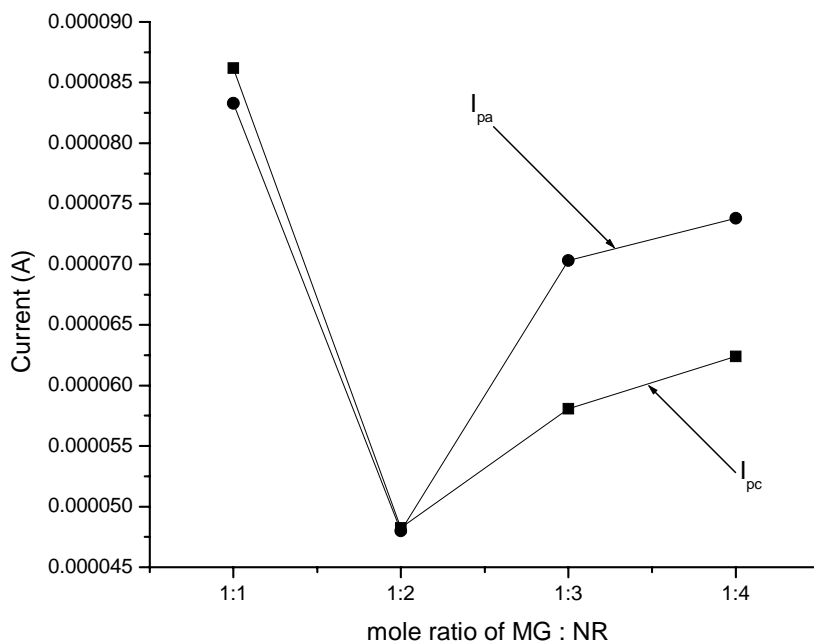


Figure 18. Effect of composition of neutral red on copolymerization of mixture of malachite green and neutral red.

Figure 19 shows cyclic voltammograms of copolymerization of malachite green and neutral red on glassy carbon electrode in the potential range from -1.4 to 2.0 V at a scan rate of 100 mV s^{-1} .

From the cyclic voltammograms of the copolymerization of 5mM neutral red in 0.5 M H_2SO_4 and 10 mM malachite green in 0.5 M NaNO_3 and 0.025 M $\text{K}_2\text{HPO}_4\text{-KH}_2\text{PO}_4$, the cathodic peak current observed at around -0.4 V is almost doubled when compared with that of the peak current observed during the electropolymerization of malachite green in the absence of neutral red at about the same peak potential. However, the anodic peak currents at around peak potential of 1.5 V and the high currents observed at far positive potential are almost equal for the electropolymerization of both malachite green and malachite green in the presence of neutral red.

Hence, the presence of neutral red enhances the rate of polymerization of malachite green at the surface of glassy carbon electrode. From this one can conclude that neutral red has catalytic effect for the electropolymerization of malachite green as it increases the rate of polymerization of malachite green.

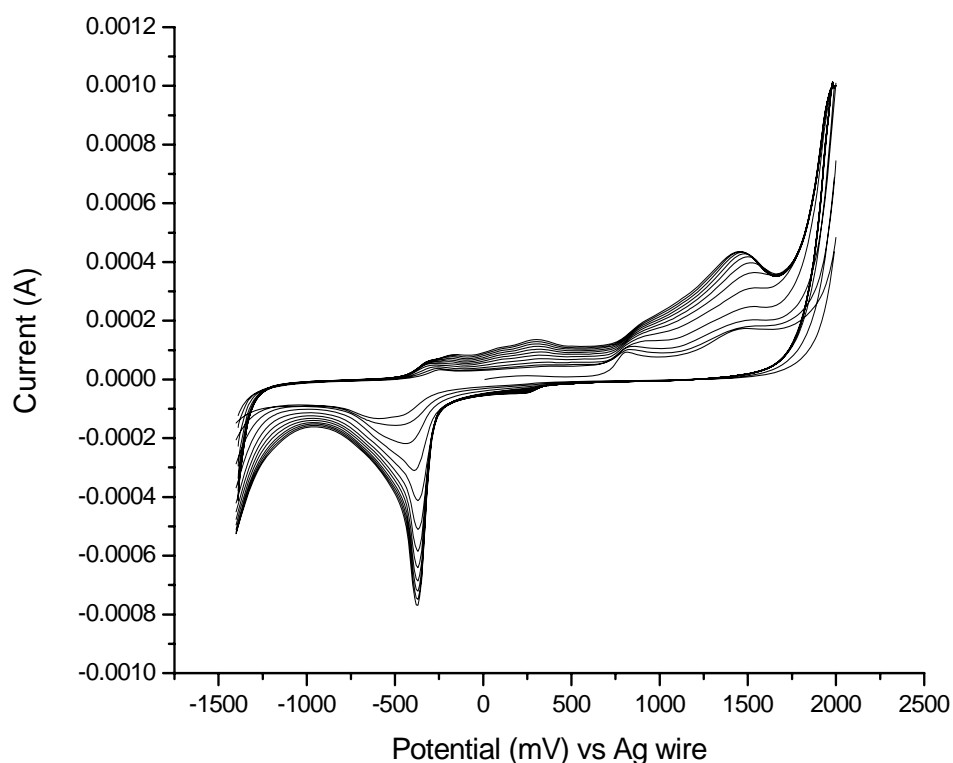


Figure 19. Cyclic voltammograms of copolymerization of malachite green and neutral red on glassy carbon electrode in the potential range from -1.4 to 2.0 V at a scan rate of 100 mVs^{-1} . The polymerization solution was a mixture of 10 mM malachite green aqueous solution containing 0.5 M NaNO_3 and 0.025 M $\text{K}_2\text{HPO}_4\text{-KH}_2\text{PO}_4$ buffer solutions and 5 mM neutral red in 0.5 M H_2SO_4 . Number of cycles 12.

5.3.1. Voltammetric characterization of the GC/copolymer modified electrode

5.3.1.1. Scan rate effect

Figure 20 shows Cyclic voltammograms of film formed from copolymerization of 5 mM neutral red in 0.5 M H_2SO_4 and 10 mM malachite green in 0.5 M NaNO_3 and 0.025 M $\text{K}_2\text{HPO}_4\text{-KH}_2\text{PO}_4$ at scan rates ranging from 10 to 160 mV.

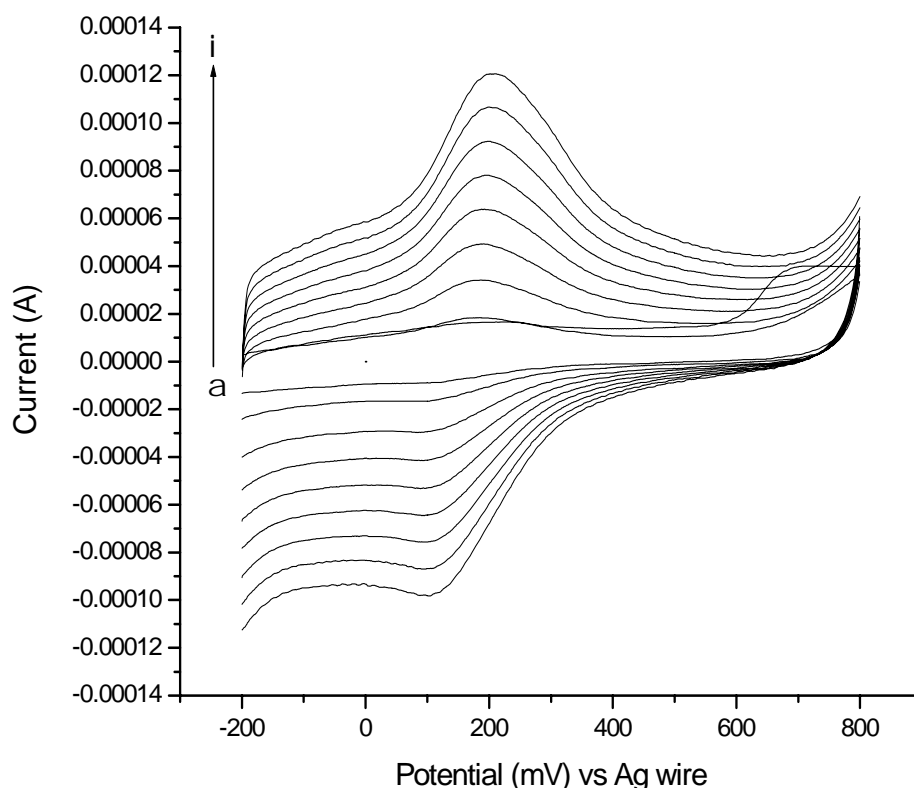


Figure 20. Cyclic voltammograms of copolymer formed from electropolymerization of 5 mM neutral red in 0.5 M H₂SO₄ and 10 mM malachite green in 0.5 M NaNO₃ and 0.025 M K₂HPO₄-KH₂PO₄ at scan rates of: a) 10, b) 20, c) 40, d) 60, e) 80, f) 100, g) 120, h) 140, and i) 160 mVs⁻¹ in 0.1 M H₂SO₄ solution.

Like poly(neutral red) and poly(malachite green) films on glassy carbon electrode, the peak currents of the copolymer increase with increase in scan rate. The cathodic and anodic peak potentials show no shift upon increasing the sweep rate. This indicates that the redox reversal process is adsorption controlled as in poly(malachite green) film.

From this and the appearance of the redox peaks of the copolymer film at about the same peak positions with that of the poly(malachite green) film under the same sweep rate

variation leads one to conclude that the copolymer possesses more of the properties of the poly(malachite green) than that of poly(neutral red) film. From figure 21 below one can appreciate the effect of the presence of neutral red on the peak current of poly(malachite green) film.

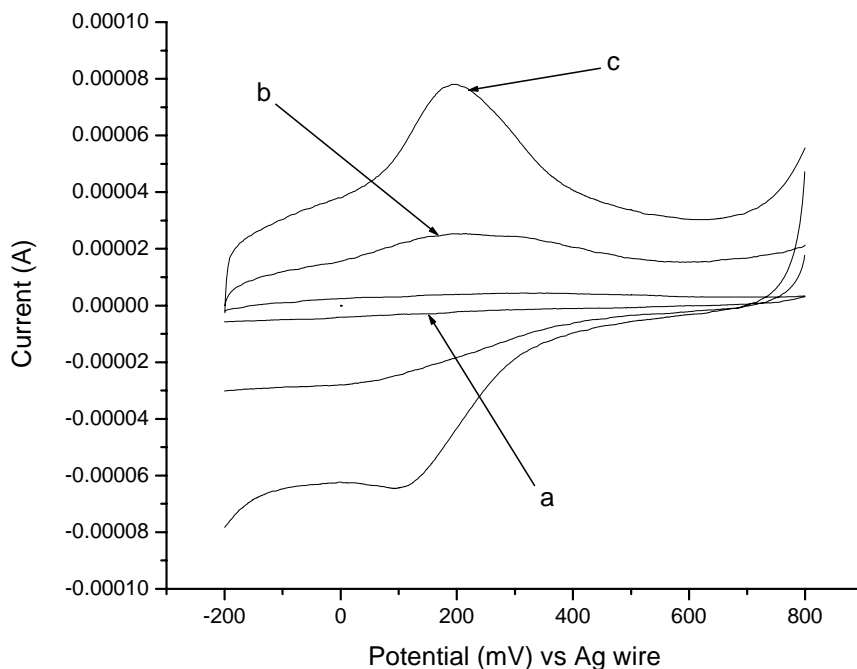


Figure 21. Cyclic voltammograms of: a) bare GC, b) Poly(malachite green) film and c) the copolymer in 0.1 M H_2SO_4 at a scan rate of 100 mVs^{-1} .

5.3.1.2. pH effect

Figure 22 shows the cyclic voltammograms of the copolymer film at different pH values in 0.5 M Na_2SO_4 solutions at a scan rate of 100 mVs^{-1} .

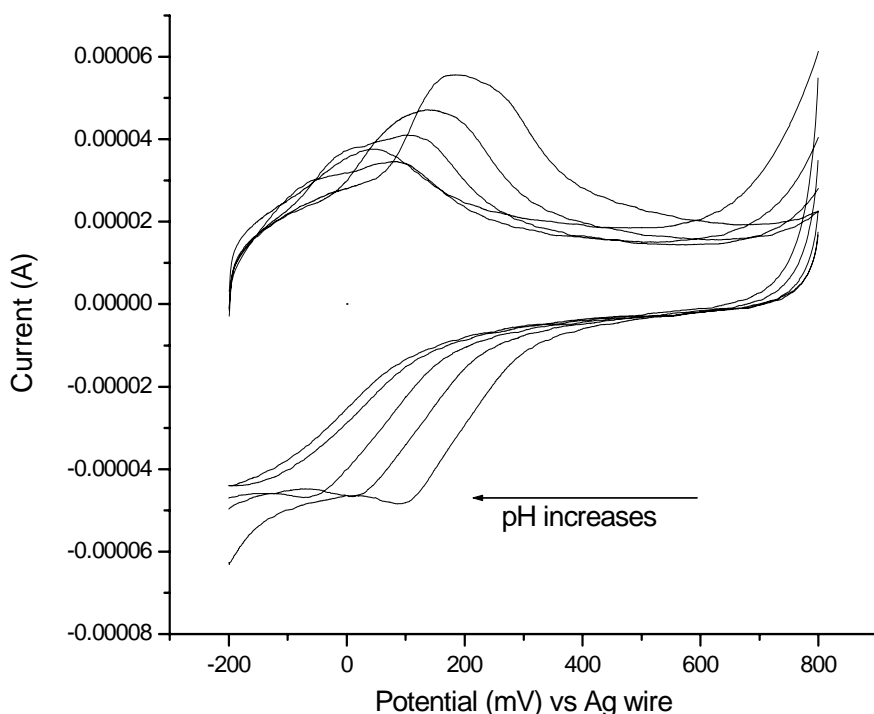


Figure 22. Cyclic voltammograms of the copolymer film coated glassy carbon electrode at a scan rate of 100 mV s^{-1} in $0.5 \text{ M Na}_2\text{SO}_4$ solutions with various pH values ranging from 1.09 to 5.3. From right side to left side, the pH values were 1.09, 2.24, 3.29, 4.07, and 5.30.

As observed from figure 22, both anodic and cathodic peak potentials of the cyclic voltammograms of the copolymer film at different pH values shifted negatively; while the peak intensity decreased with an increase in pH values for the same reason stated above for poly(neutral red) and poly(malachite green) films. Similar to that of the scan rate effect, the current generated by the copolymer film in different pH values is about twice of that of the poly(malachite green) film. In addition, the shape of the cyclic voltammograms and the peak positions of the copolymer in different pH values resemble that of poly(malachite green) than poly(neutral red) film. This further leads one to

conclude that the copolymer film possesses more of the properties of the poly(malachite green) than the poly(neutral red) film.

However, as it is observed from figure 21 above the area of the copolymer is much greater than that of the poly(malachite green) film under the same conditions. From this one can also derive other conclusion that eventhough the copolymer possesses more of the properties of poly(malachite green) film, it is not exactly the same with that of poly(malachite green) film in structure.

When both cathodic and anodic peak potentials are plotted vs the pH, it is observed that both potentials vary linearly with the pH (figure 23). The difference between both peaks is that the slope of the cathodic peak potential dependence (84 mV/pH) is roughly twice larger than the slope of the anodic one (35.1 mV/pH). This result points out the participation of two hydrogen ions in the electrochemical reaction associated to the cathodic peak and only one proton in the anodic one.

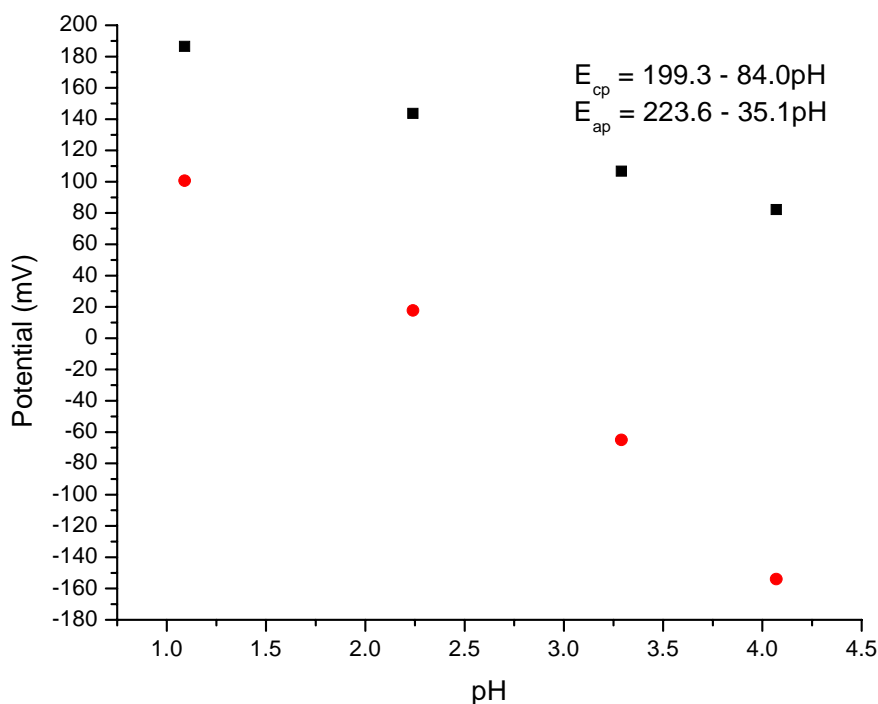


Figure 23. Peak potentials dependence of the redox couple of the copolymer on the pH in 0.5 M Na₂SO₄ solution. Anodic (top); cathodic (bottom).

5.4. Electropolymerization of aniline

The electrodeposition of polyaniline proceeds via a radical cation mechanism [1, 21]. Electrochemical polymerization of aniline on the GC electrode surface was achieved by applying potential cycling between -0.3 and +1.0 V at a scan rate of 60 mVs⁻¹. The cyclic voltammograms (CV) obtained during the electropolymerization is shown in figure 24.

The first redox process at about 0.05 V in the positive scan and -0.2 V in the negative scan corresponds to the electron transfer from/to the electrodeposited polyaniline film. The second redox process, 0.45 and 0.25 V for the oxidation and reduction respectively, probably corresponds to side reactions such as decomposition of the polymer [1, 21].

The rising in currents observed at the positive end of the CV during electropolymerization are due to the superposition of two distinct processes: one is the electron transfer from the PANI film corresponding to the oxidation of the PANI film and the other is the electron transfer from the aniline monomer to the electrode corresponding to the oxidation of the aniline monomer to produce a precursor for the PANI film [1, 21].

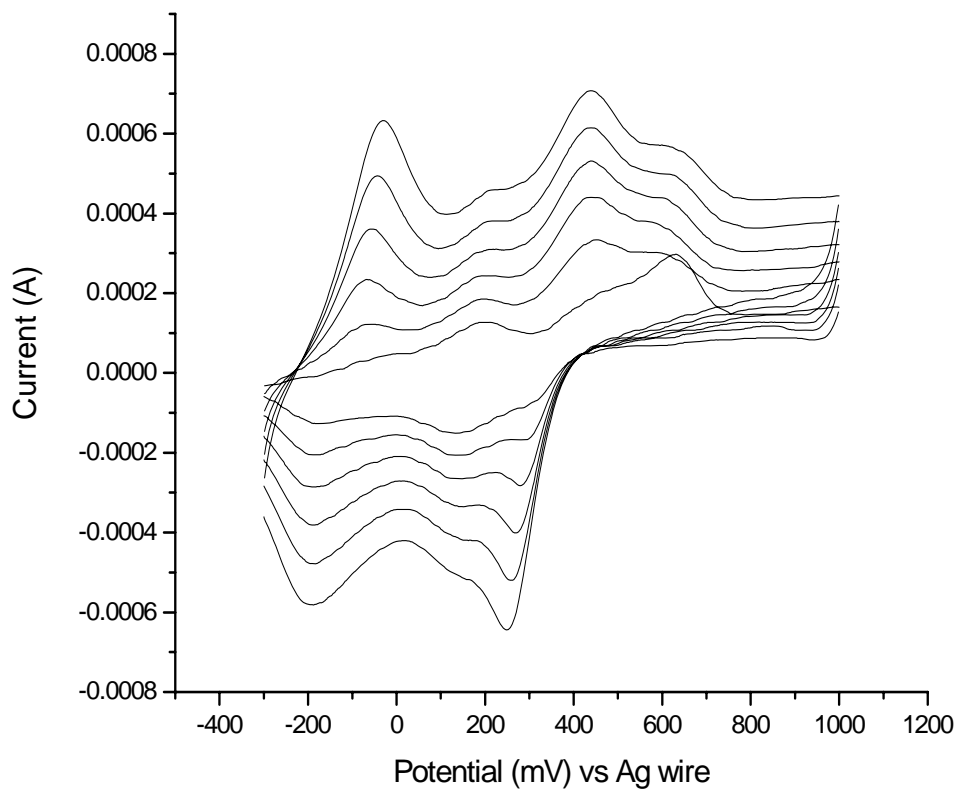


Figure 24. Cyclic voltammograms of polymerization of aniline during electrolysis of the solution consisting of 0.3 M H₂SO₄ and 0.4 M aniline at a scan rate of 60 mVs⁻¹. Number of cycles 6.

The cyclic voltammetry curve of a deposited PANI film in monomer-free solution is shown in figure 25. The cyclic voltammetry was scanned between -0.3 and +1.0 V at a scan rate of 100 mV/s in a monomer-free 0.5 M H₂SO₄ solution.

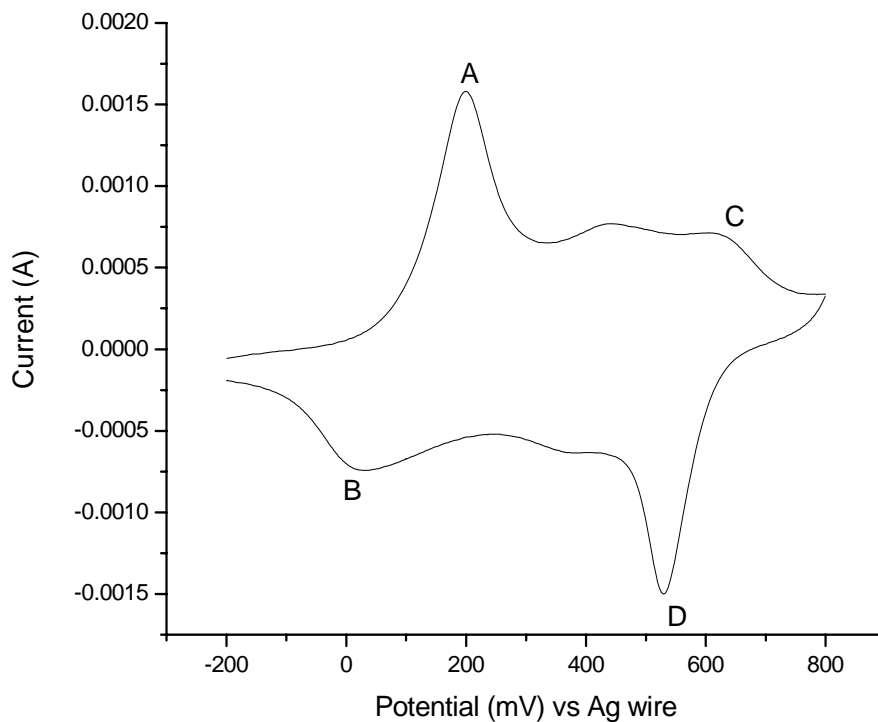


Figure 25. Cyclic voltammogram of poly aniline film in 0.3 M H₂SO₄ (pH 1) solution at a scan rate of 100 mVs⁻¹.

As mentioned before, the first redox couple (A, B) is commonly assumed to correspond to the electron transfer from/to the PANI film i.e., the partial oxidation of leucoemeraldine to emeraldine form. The second redox couple (C, D) corresponds to a deprotonation and protonation process i.e., the complete oxidation of emeraldine to pernigraniline. The small peak at around 0.4 V is probably due to a side reaction in the polyaniline film [1, 21].

5.5. Electropolymerization of aniline in the presence of neutral red

Figure 26 shows the cyclic voltammograms of electropolymerization of solution consisting of 0.3 M H_2SO_4 , 5 mM neutral red and 0.4 M aniline at a scan rate of 60 mV/s. As can be seen, the cyclic voltammograms of the copolymer in figure 25 behave differently from cyclic voltammograms of electropolymerization of neutral red and aniline.

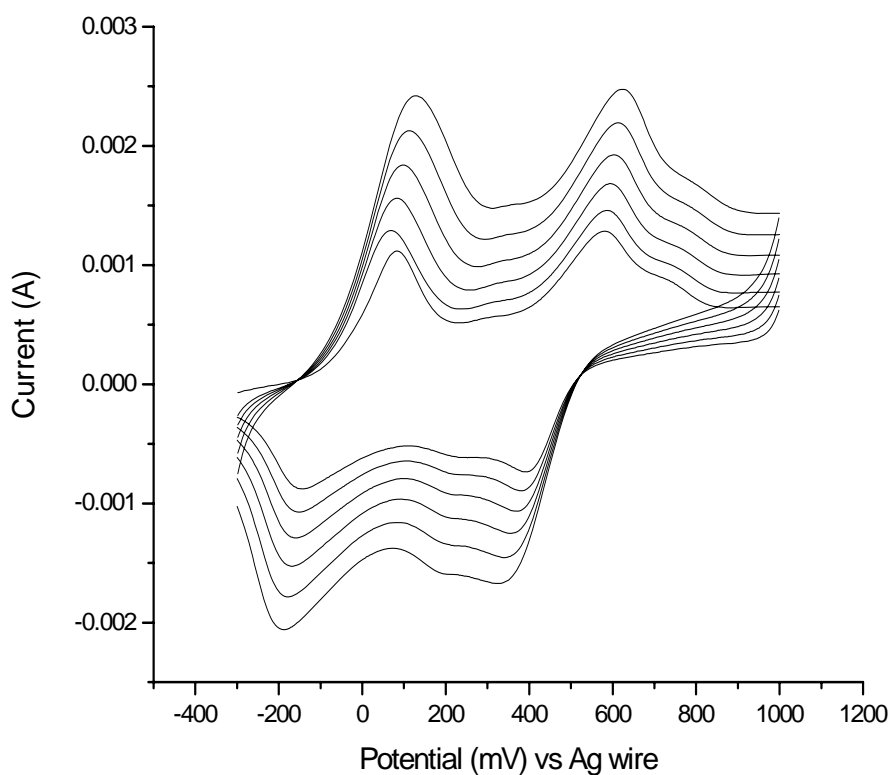


Figure 26. Cyclic voltammograms of copolymerization of aniline and neutral red during electrolysis of the solution consisting of 0.3 M H_2SO_4 , 5 mM neutral red and 0.4 M aniline at a scan rate of 60 mVs^{-1} . Number of cycles 6.

During the electropolymerization of the copolymer, the change in current is similar with that of the voltammograms of electropolymerization of aniline; however, the former produces high current than that of the later. This result indicates that neutral red may play some role in electrochemical catalysis. In addition, the presence of neutral red caused anodic peak potentials to shift to more positive values during the electropolymerization of the copolymer when compared with aniline in the absence of neutral red. This is most probably because of the IR-drop at the surface of the working electrode due to the thickness of the film which is in agreement with the increase in the rate of electropolymerization of the copolymer.

Figure 27 below shows the cyclic voltammograms of polyaniline (curve a) and copolymer (curve b) films in 0.5 M Na₂SO₄ (pH 1) respectively. The scan potential was controlled between -0.3 and +1.0 V. Three redox couples are observed in each of the curves a and b (figure 27), and the curves are similar to each other. The area of the cyclic voltammogram of curve b is larger than that of curve a. This result is in agreement with the film growth rate of aniline and the copolymer. This means that the copolymer is not quite the same as polyaniline in structure.

The first redox couple, observed at more negative potentials, is most probably responsible for electron transfer from to the copolymer like that of polyaniline, and the second redox couple, observed at more positive potentials, is responsible for deprotonation/protonation reaction of the copolymer film.

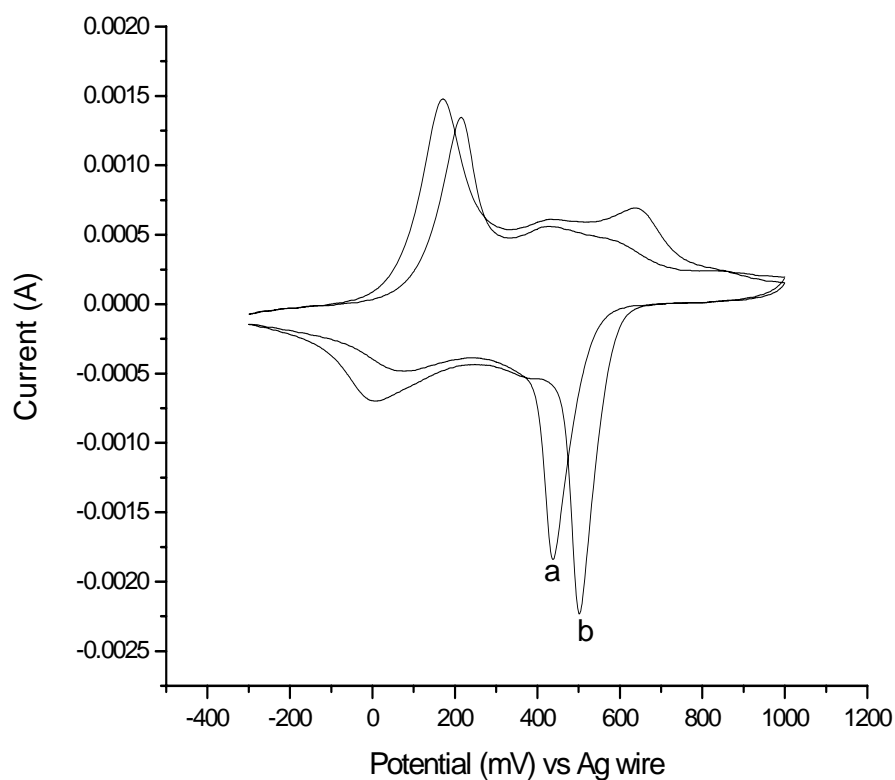


Figure 27. Cyclic voltammograms of: a) poly aniline film and b) the copolymer film in 0.5 M Na₂SO₄ (pH 1) solution at a scan rate of 100 mVs⁻¹.

5.6. Electropolymerization of methylene blue

Figure 28 shows the cyclic voltammograms of electropolymerization of methylene blue from a solution consisting 2mM methylene blue monomer, 0.1 M phosphate buffer (pH 8.2), and 0.1 M Na₂SO₄ at a scan rate of 100 mV s⁻¹. The potential range was from -0.65 to +1.0 V.

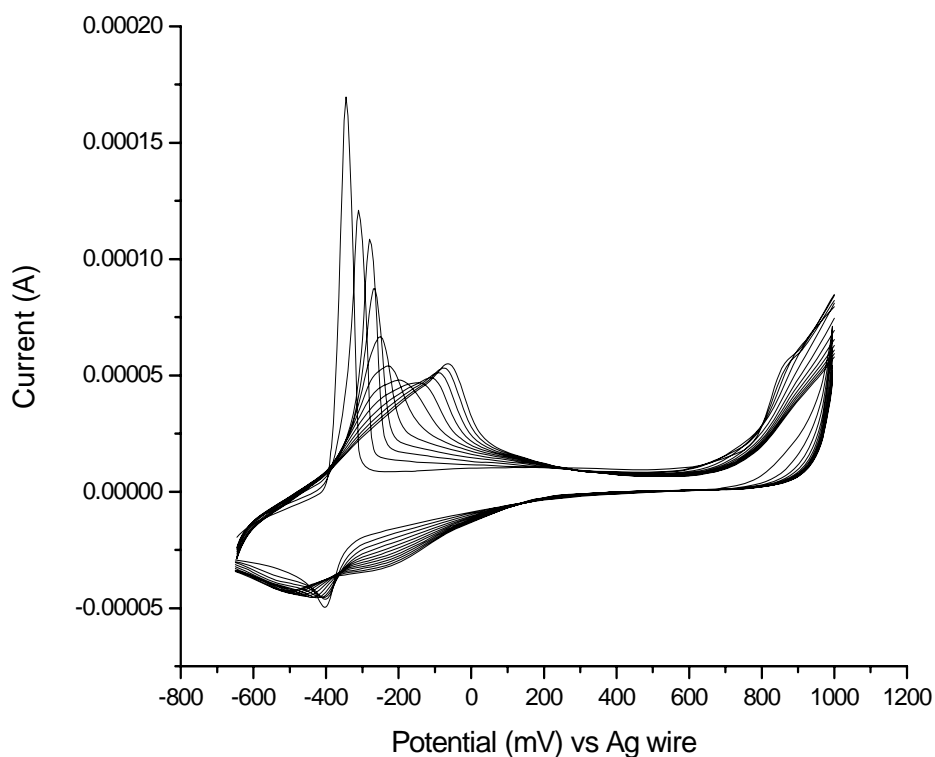


Figure 28. Cyclic voltammograms of electropolymerization of methylene blue from a solution consisting of 2mM methylene blue monomer, 0.1 M phosphate buffer (pH 8.2), and 0.1 M Na_2SO_4 at a scan rate of 100 mV s^{-1} . The potential range was from -0.65 to +1.0 V. Number of cycles 12.

As can be seen from the cyclic voltammograms of the film growth, beyond about +0.8 V the rapidly rising in current originates from the oxidation of methylene blue and in part from the oxidation of water [19], which results in the electropolymerization of the monomer. The current peak for the oxidation of the methylene blue at about -0.3 V continuously decreased, while the peaks for poly(methylene blue), observed at around -0.1 V, increased during the cycles.

The increase in peaks at around -0.1 and beyond +0.8 V with increase with cycles is an indication for film growth during electropolymerization. Hence, electropolymerization of methylene blue causes the appearance of set of peaks in cyclic voltammograms that represent polymer type redox activity which is shifted to more positive region compared with the redox activity of the monomer [6].

Figure 29 shows cyclic voltammograms of poly(methylene blue) in a monomer free buffer solution at a scan rate of 100 mV s^{-1} .

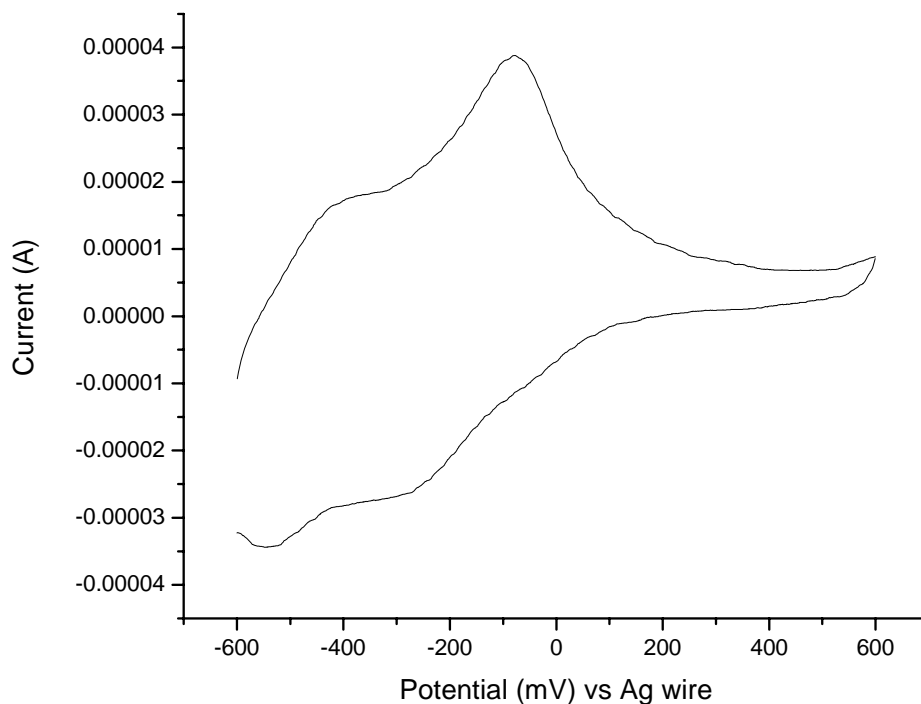


Figure 29. Cyclic voltammogram of poly(methylene blue) film in monomer free 0.1 M phosphate buffer at a scan rate of 100 mVs^{-1}

As one can see from the cyclic voltammogram, electropolymerized methylene blue exhibited two sets of peaks. The redox couple at more negative potential seemed to be a monomer-type redox activity; while the one at more positive potential appears only in polymer. This indicates that poly(methylene blue) consists of phenothiazine units covalently linked to each other [26].

5.7. Voltammetric characteristics of some GC/Polymer/PB modified electrodes

Figure 30 shows the cyclic voltammogram of Prussian blue film on GC electrode in 0.1 M KCl + 0.01 M HCl solutions at a scan rate of 100 mVs⁻¹. PB was deposited on to the glassy carbon (GC) electrode by potentiostatic method at a potential value of +0.4 V, from an aqueous solution containing 2 mM K₃[Fe(CN)₆] and 2 mM FeCl₃ in 0.1 M KCl + 0.01M HCl. The electrolysis was prolonged for 60 s [28-29]. After electrodeposition, the modified electrode was rinsed with doubly distilled water and immersed in to a solution containing 0.1 M KCl + 0.01 M HCl, where the electrode potential was cycled between -0.1 and +1.00 V at a scan rate of 100 mV s⁻¹, until a stable voltammetric response was obtained [29].

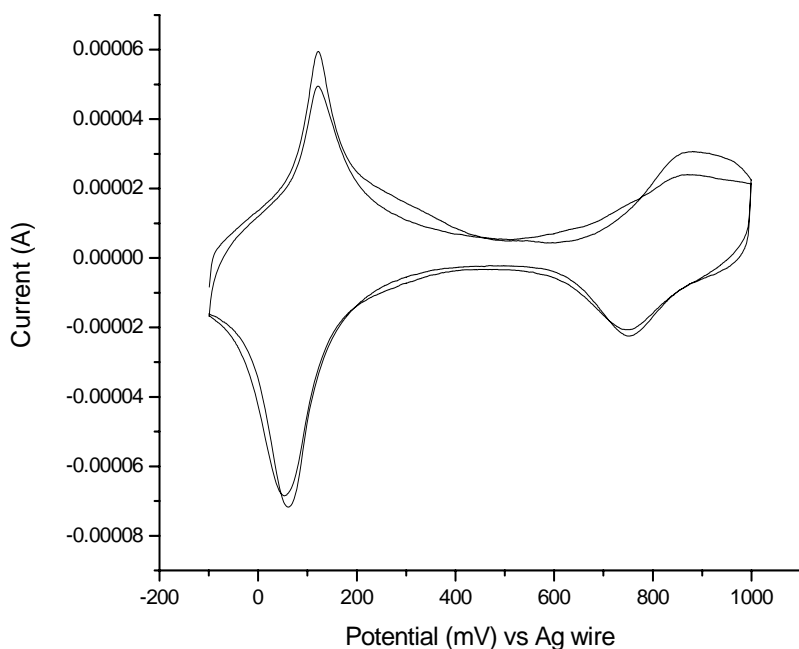
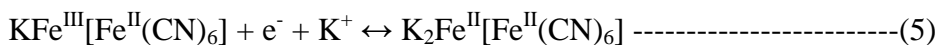


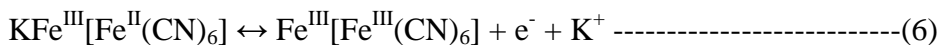
Figure 30. Cyclic voltammogram of Prussian blue film (PB) on glassy carbon electrode in 0.1 M KCl + 0.01 HCl solutions at a scan rate of 100 mVs⁻¹.

The signals in figure 30 are ascribed to the following processes:

- Peak system at about +0.1 V:



- Peak system at about +0.9 V:



PB was preferred as an outer layer in GC/Polymer/PB modified electrode since it produced better current than when it was used as an inner layer during the experiment.

5.7.1. GC/PNR/PB modified electrode

The inner polymer i.e., poly(neutral red) (PNR) was prepared by direct electrochemical polymerization-deposition on to GC electrode, carried out in the solution containing 5 mM neutral red monomer in 0.5 M H₂SO₄ supporting electrolyte. The polymer film was grown by cycling the electrode potential in the range from -1.0 to +1.2 V, at a scan rate of 100 mV s⁻¹.

After electrochemical deposition, the polymer was rinsed with doubly distilled water and its voltammogram was recorded in 0.1 M KCl + 0.01 M HCl aqueous solution in the potential range from -0.6 to +0.6 V, at a scan rate of 100 mV s⁻¹ (figure 31b). PB film was then electrodeposited on to the GC/PNR modified electrode as an outer layer potentiostatically from aqueous solution containing 2 mM K₃[Fe(CN)₆] and 2 mM FeCl₃ in 0.1 M KCl + 0.01M HCl and the cyclic voltammogram of the GC/PNR/PB modified electrode was recorded at the same condition as for GC/PNR modified electrode (figure 31c).

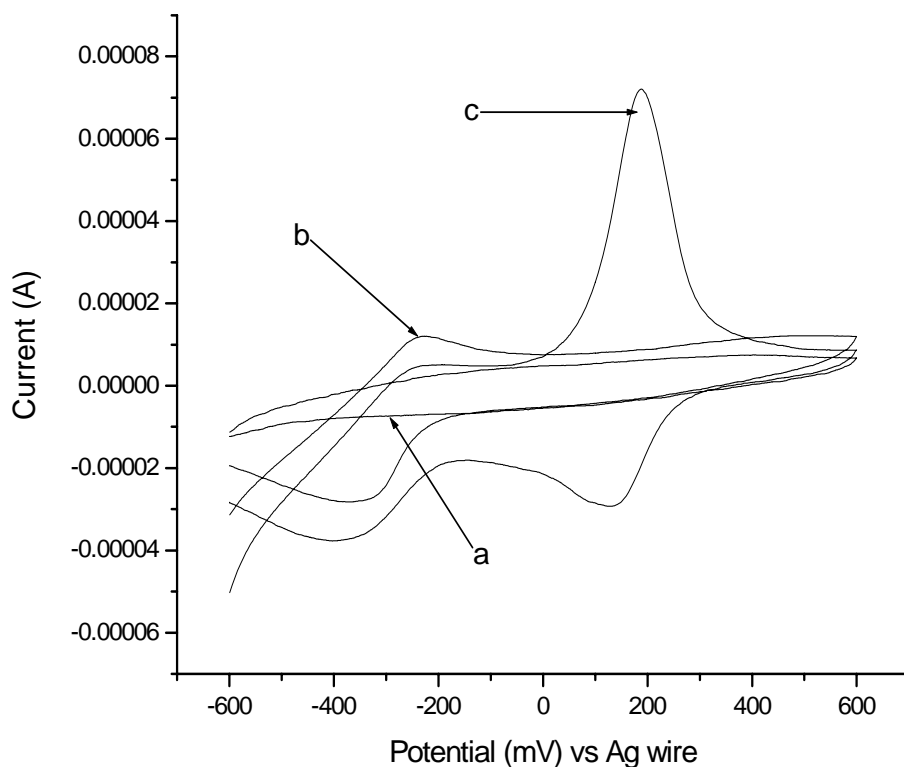


Figure 31. Cyclic voltammogram of: a) bare GC, b) GC/PNR, and c) GC/PNR/PB film modified electrodes in 0.1 M KCl + 0.01 HCl solutions at a scan rate of 100 mVs^{-1} .

As observed from figure 31b and c, the presence of PB film increases the reduction peak and decreases the oxidation peak currents of PNR with slight shifting of the cathodic peak potential to more negative value. The shift of peak potential position is mostly due to the increase in film thickness which causes potential drop. Hence, PB film catalyses the reduction reaction with peak potential shift to more negative value while inhibiting the oxidation reaction of PNR with almost no peak potential shift. On the other hand, the redox couple of PB at about +0.1 V shows some change when compared with GC/PB voltammogram (figure 30) at about the same peak position in the presence of PNR film.

That is, the oxidation peak of PB (the backward reaction of equation 5), is enhanced while its reduction (the forward reaction of equation 5) peak is decreased in the presence of PNR (figure 31 c) with slight shift of peak potentials to more positive values.

In general the presence of PB film together with PNR catalyses the reduction reaction of PNR film while the oxidation reaction of PB is catalyzed in the presence of PNR film with peak potentials shift to more negative and positive values respectively.

5.7.2. GC/PANI/PB modified electrode

PANI was also prepared as inner layer by electrochemical polymerization-deposition on to GC electrode, carried out in the solution containing 0.4 M aniline monomer in 0.3 M H₂SO₄ supporting electrolyte.

The polymer film was grown on to GC electrode by cycling the electrode potential in the range from -0.2 to +1.0 V, at a scan rate of 100 mVs⁻¹. Like PNR, the PANI film deposited was rinsed with doubly distilled water and its voltammogram was recorded in 0.1 M KCl + 0.01 M HCl aqueous solution in the potential range from -0.2 to +0.8 V, at a scan rate of 100 mV s⁻¹ (figure 32b). PB was deposited on to GC/PANI modified electrode as an outer layer in the same manner as for GC/PNR modified electrode stated above and the voltammogram of GC/PANI/PB modified electrode was recorded at the same condition as for GC/PANI modified electrode (figure 32c).

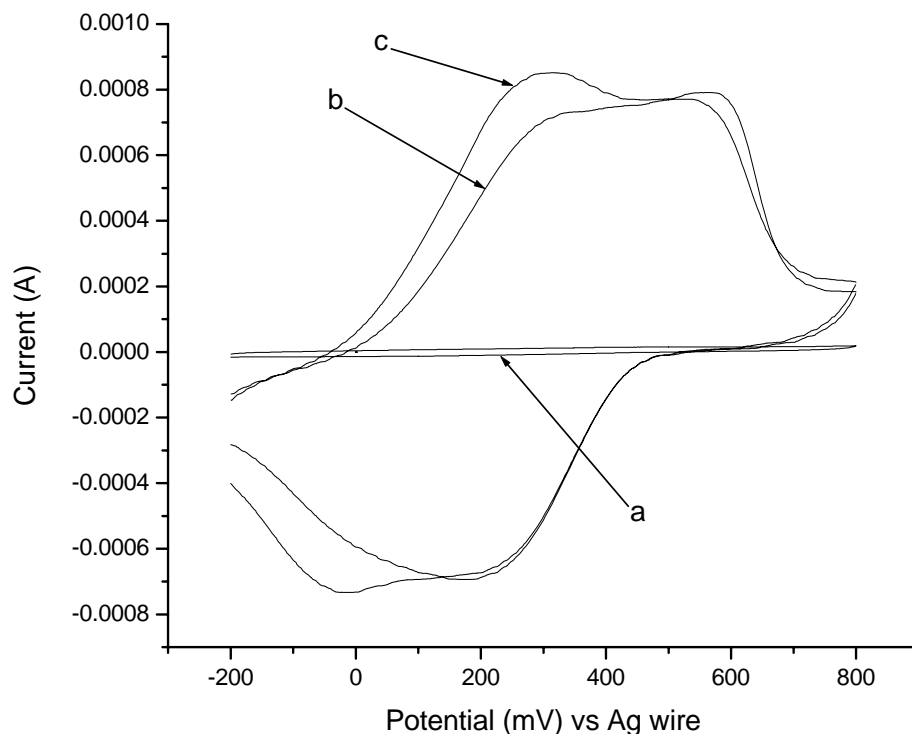


Figure 32. Cyclic voltammogram of: a) bare GC, b) GC/PANI, and c) GC/PANI/PB modified electrodes in 0.1 M KCl + 0.01 HCl solutions at a scan rate of 100 mVs^{-1} .

As one can see from figure 32b and c, the presence of PB increases the oxidation and reduction peak currents of PANI responsible for the electron transfer from/to PANI film, observed at more negative potential region, better than the redox reaction responsible for deprotonation/protonation reactions of PANI film redox couple, observed at more positive potential region. The presence of PB also caused the peak potentials responsible for the electron transfer from/to PANI film to shift to more negative values while shifting the peak potentials responsible for deprotonation/protonation reactions slightly to more positive values.

5.7.3. GC/PMB/PB modified electrode

PMB was also prepared as an inner layer by electrochemical polymerization-deposition on to GC electrode as that of PNR and PANI, carried out in the solution containing 2 mM methylene blue monomer in 0.1 M phosphate buffer (pH 8.2) and 0.1 M Na₂SO₄ supporting electrolyte [25]. The polymer film was grown on to the electrode by cycling the electrode potential in the range from -0.65 to +1.0 V, at a scan rate of 100 mVs⁻¹.

The electrodeposited polymer was rinsed with doubly distilled water and its cyclic voltammogram was recorded in 0.1 M KCl + 0.01 M HCl aqueous solution in the potential range from -0.6 to +0.6 V, at a scan rate of 100 mV s⁻¹ (figure 33b). PB film was electrodeposited in the same manner as for GC/PNR and GC/PANI modified electrodes and the voltammogram of the GC/PMB/PB modified electrode was recorded at the same condition as for GC/PMB modified electrode (figure 33c).

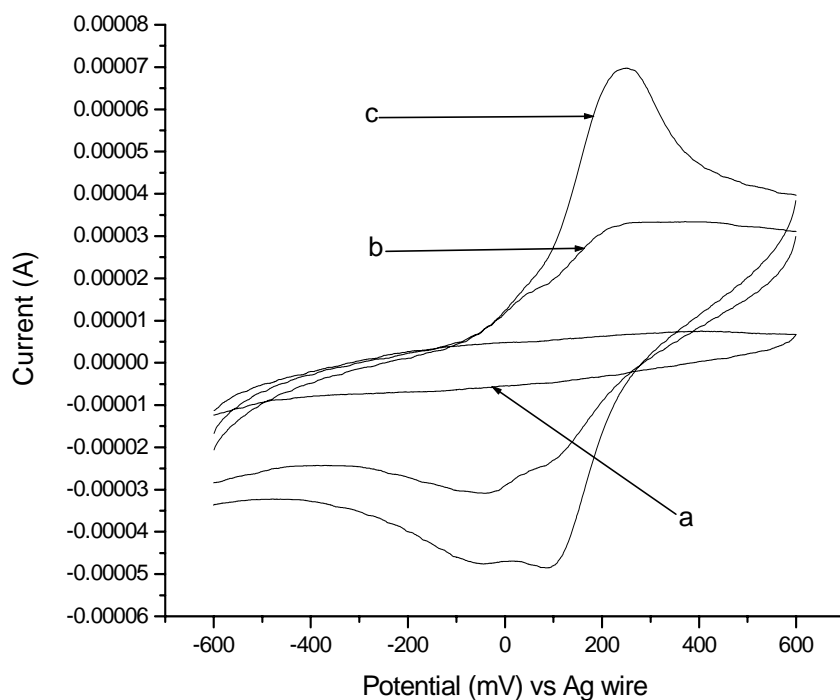


Figure 33. Cyclic voltammogram of: a) bare GC, b) GC/PMB, and c) GC/PMB/PB film modified electrodes in 0.1 M KCl + 0.01 HCl solutions at a scan rate of 100 mVs^{-1} .

As can be seen from figure 33b and c, the presence of PB film increases both the reduction and oxidation peak currents of the PMB film, with almost no peak potentials shift. When it is carefully observed, the oxidation peak enhancement is greater than the reduction peak enhancement. Hence, one can say PB film catalyses more of oxidation reaction than reduction reaction of PMB film. Moreover, PB increases the peak currents of PMB film more than the other two, PNR and PANI.

The redox couple of the prussial blue (PB) film that changes the peak currents of poly(neutral red) (PNR), poly(aniline) (PANI), and poly(methylene blue) (PMB) modified electrodes is the one which is observed at about +0.1 V potential. This is

because the potential of this redox couple of PB is more closer than the potential of the other redox couple of PB, at +0.9 V, to the potentials where the polymer films show redox reactions.

6. Conclusions

The electrochemical polymerization and characterization studies of neutral red, malachite green, aniline, and methylene blue were made successfully on glassy carbon (GC) electrode using silver wire as a reference electrode.

The presence of neutral red during the electropolymerizations of malachite green and aniline highly increases the rate of electropolymerizations and hence their peak currents compared with their electropolymerizations in the absence of neutral red. Hence neutral red plays the role of electrocatalysis in the electropolymerization of malachite green and aniline.

The copolymer electropolymerized from malachite green and neutral red, possesses more of the properties of poly(malachite green) than poly(neutral red)film. Similarly, the copolymer electropolymerized from aniline and neutral red possesses more of the properties of poly(aniline) than poly(neutral red) film.

Finally, the potentiostatically deposited PB film as an outer layer on GC/Polymer modified electrodes like: GC/PNR, GC/PANI, and GC/PMB increases the peak currents of the polymer films. When observed carefully, the effect of PB on the peak currents of

PMB is more pronounced than its effect on the other two .i.e., PNR and PANI. Generally, one can conclude that PB is an inorganic film that enhances the peak currents (acts as a catalyst) of polymer films like poly(neutral red) (PNR), poly(aniline) (PANI), and poly(methylene blue) (PMB).

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