

**ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY**

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**SIMULTANEOUS DETERMINATION OF CATECHOL
AND HYDROQUINONE AT POLY-p-(ASA)/MWCNT
COMPOSITE MODIFIED GLASSY CARBON
ELECTRODE**

BY

YAZACHEW ALEMU

JUNE 2010

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HYDROQUINONE AT POLY-p-(ASA)/MWCNT COMPOSITE
MODIFIED GLASSY CARBON ELECTRODE**

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TO THE MEMORY OF MY MOTHER
TIRUEHELE ASMARE

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LIST OF ABBRVIATIONS

CC	Catechol	A	ampere
HQ	hydroquinone	t	time
GCE	glassy carbon electrode	v	Scan rate
p-(BPB)	poly-Bromophenol Blue	V	volt
MWCNT	Multiwalled carbon nanotube	E	potential
CMK	mesoporous carbon	i	current
PASA	poly-amido sulfonic acid	ΔE_p	change in potential
SWCNT	single-walled carbon nanotube	$E_{1/2}$	half wave potential
P-(PA)	poly-phenyl aniline	n	number of electron
P-(GA)	poly- gulatamic acid	S	second
P-(GI)	poly-glycine	μ	Micro
Asp	aspartic acid	M	molar
P-(PABA)	poly-para-amino benzoic acid	R^2	correlation coefficient
P-(ASA)	para-amidosalicyclic acid	i_{pa}	anodic peak current
CV	cyclic Voltammetry	i_{pc}	cathodic peak current
DPV	differential pulse Voltammetry	E_{pa}	anodic peak potential
CNT	carbon nanotube	E_{pc}	cathodic peak potential
CME	chemically modified electrode		
NPV	normal pulse voltammetry		
PBS	phosphate buffer solution		

ABSTRACT

A simple and highly selective electrochemical method for simultaneous determination of hydroquinone and catechol has been developed at a glassy carbon electrode modified with multiwalled carbon nanotubes (MWCNT) and poly-para-amidosalicylic acid (poly-p-ASA). It was found that the oxidation peak potential separation and the oxidation currents of hydroquinone and catechol highly increase at the polymer and MWCNT modified glassy carbon electrode in 0.10 M phosphate buffer solution (pH 7.0). The oxidation peak potential of hydroquinone and catechol merge into a large peak at 430.71 mV at bare glassy carbon electrode. The two well-defined oxidation peaks of hydroquinone in the presence of catechol at poly-p-(ASA), MWCNT and composite modified electrode occur at 136.52 mV and 228.04 mV, 161.29 mV and 262.82 mV and 172.12 mV and 286.85 mV respectively. Under the optimized condition, the oxidation peak current of hydroquinone is linear over a range from 2.0×10^{-5} M to 7.0×10^{-4} M hydroquinone in the presence of 1.0×10^{-3} M catechol with the detection limit of 1.2×10^{-6} M and the oxidation peak current of catechol is linear over a range from 2.0×10^{-5} M to 6.0×10^{-4} M catechol in the presence of 1.0×10^{-3} M hydroquinone with the detection limit of 1.4×10^{-7} M. The proposed method has been applied to the simultaneous determination of hydroquinone and catechol in a water sample and the results are satisfactory.

KEYWORDS

Electrochemistry, Electropolymerization, Multiwalled carbon Nanotubes, chemically modified electrode, Hydroquinone, Catechol and para-amidosalicylic acid

1. INTRODUCTION

1.1. General properties of catechol and hydroquinone

Catechol and hydroquinone are called benzenediols or dihydroxybenzenes, which are aromatic chemical compounds and polyphenols in which two hydroxyl groups are substituted onto a benzene ring; because they have at least one hydroxyl group covalently bonded directly to a carbon atom in a benzene ring. They belong to a class of organic compounds called phenols. There are three isomeric of benzenediols, with the chemical formula $C_6H_6O_2$ and molar mass 101.11 g/mol. Each form has its own particular name as 1, 2-di-hydroxybenzene or ortho-di-hydroxybenzene (Catechol), 1, 3-di-hydroxybenzene or meta-di-hydroxybenzene (resorcinol) and 1, 4-di-hydroxybenzene or Para-di-hydroxybenzene (hydroquinone) as indicated by the structures in Fig.1 below. The general physical properties of catechol and hydroquinone are summarized in table 1.

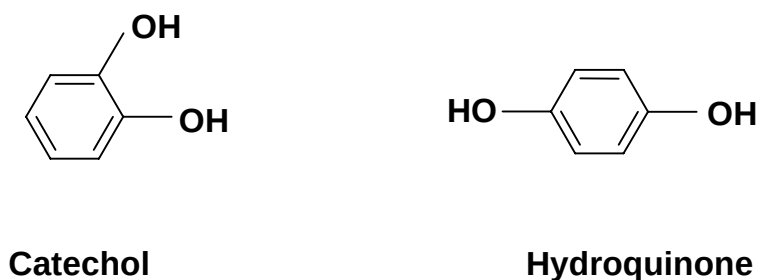


Fig.1 The chemical structure of catechol and hydroquinone [1]

All the above isomeric compounds are strong reducing agents and are colorless to white granular solids at room temperature and pressure, but if exposed to air (oxygen) or any oxidizing agent, they get easily oxidized (into the corresponding quinone) i.e. hydroquinone and catechol can undergo mild oxidation to be converted to benzoquinone ($C_6H_4O_2$) often called quinone. Reduction of quinone reverses this reaction back to hydroquinone or catechol [1]. The hydroxyl groups on the aromatic ring of a benzenediol are weakly acidic. Each benzenediol can lose an H^+ from one of the hydroxyls to form a type of phenolate ion (semiquinone) that can serve as intermediate for complete oxidation as shown in Fig.2, 3.

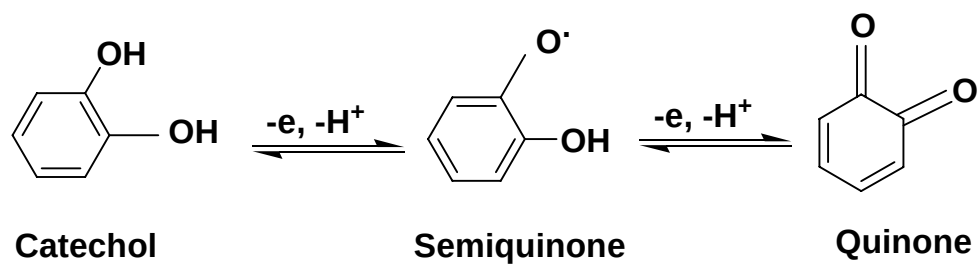


Fig.2 Formation of semiquinone and quinone from catechol

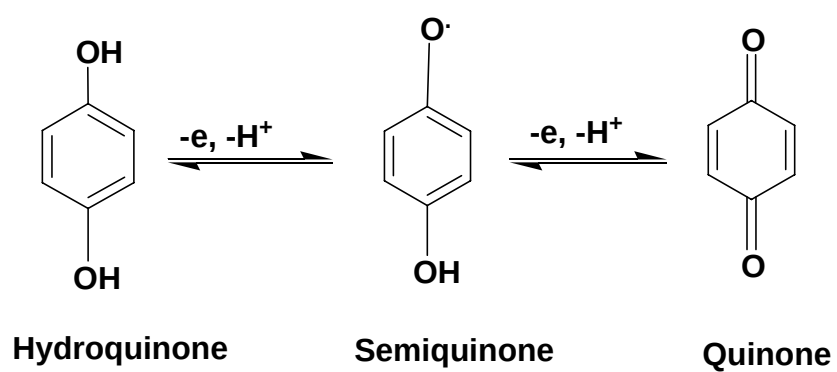


Fig.3 Formation of semiquinone and quinone from hydroquinone

Table 1 General physical properties of benzenediols [1]

Benzenediols	Properties	Value
Catechol	Appearance	White crystalline solid
	Density	1.344 g/cm ³
	Melting point	105 °C
	Boiling point	245.5 °C
	Solubility	Soluble in water
Hydroquinone	Appearance	White granular solid
	Density	1.3 g/cm ³
	Melting point	172 °C
	Boiling point	287 °C
	Solubility	Soluble in water

1.2. Natural occurrence of hydroquinone and catechol

Hydroquinone (HQ) and catechol (CC) are found in a variety of forms as natural products from plants and animals. HQ and CC have been identified in roasted coffee beans [2] and in the leaves of blueberry, cranberry, cowberry and bearberry plants [3]; in addition, tea is prepared from these leaves that have been reported to contain HQ and CC at concentrations up to 1% of total ingredients [4]. The hazardous substances data bank (HSDB) in 1993 reported CC is found in onions, apples, and even in the leaves or branches of oak and willow trees. HQ was observed in the tissue cultures of *Antennaria-microphylla* and *Euphorbia-esula* [5]. HQ is also found in the explosion chamber of beetle [6] that is ready to shoot toward the enemy in the form of hot

quinone cloud and also it is present in tobacco smoke and occurs naturally in trace amounts in some fruits, vegetables, grains, dairy products, coffee, tea, beer, and wine.

1.3. Uses of catechol and hydroquinone

HQ and CC are used in many fields including graphic arts, photographic developers, antioxidants, polymerization inhibitors and pharmaceuticals. The use of hydroquinone for film developing is common. They are used in cosmetics and medical skin preparations as depigmenting agents to lighten small areas of hyper-pigmented skin [3] or as ingredient of permanent hair dyes and color preparations [7]. HQ and CC are used also in medical and industrial X-ray films [8] as well as developer in black-and-white photography or related graphic arts such as lithography and rotogravure [3, 8]. They are widely used in the manufacture of rubber antioxidants, monomer inhibitors and food antioxidants to prevent deterioration in many oxidizable products [3]. HQ and CC are very useful in our life; on the other hand, they are also very harmful if we misuse them.

1.4. Toxic effects of catechol and hydroquinone

Cigarette smoking is the leading cause of preventable death in the United States, claiming more than 400,000 lives per year [6, 7]. A typical smoker receives more than 100 μg of HQ or CC per cigarette [9]. Environmental Protection Agency (EPA) database in U.S. (revised in January 2000) reported vapor pressure of CC is 0.03 mmHg, at 20 °C while HQ exhibits a much lower vapor pressure of 1.9×10^{-5} mmHg at 25 °C; however, they can be oxidized in the presence of moisture to form quinone, which is more volatile. Inhalation of HQ or CC has been shown to induce coughing, burning sensations, labored breathing in humans [10] as well as reduced bone marrow and corneal damage in mice [11].

Concentration of HQ or CC as low as 10 μM inhibits ribo-nucleotide reductase that causes an immediate cessation of DNA synthesis in proliferating lymphocytes [12]; even worse, 50 μM of HQ or CC instantaneously block more than 90 % DNA synthesis [13]. The major concern is HQ and CC may exist as semiquinone radical form causing cancer, mutations and many health

symptoms in our life. Furthermore, if we handle HQ improperly, it poses short- and long-term damage and danger to the health of human beings and the natural environment. It can enter into the human body via the respiratory and digestive organs or by direct contact to affect skin, mucous membranes, digestive, hepatic and renal systems. High concentration of HQ may incur headache, fatigue, tachycardia, decompensation, kidney damage and even death. Long-term respiration in the atmosphere containing low concentration of HQ may cause coughing, dizziness, anorexia, nausea, vomiting and the pigmentation of the eye [13, 14].

1.5. Methods of determination of catechol and hydroquinone

Besides their importance they are very much toxic and create serious water pollution problems in many localities. There are varieties of methods available in the literature for the determination of hydroquinone and catechol using colorimetry [15], titrimetry [16], spectrofluorimetry [17], spectrophotometry [18], high-performance liquid chromatography (HPLC) with different detectors [19] and gas chromatography- mass spectrometry (GC-MS) [20].

Due to simple instrumentation, low cost, high selectivity and sensitivity, better reproducibility, broad linear dynamic range and easy sample preparation procedure, voltammetric techniques such as differential pulse voltammetry have clear edge over the other techniques for the quantitative determination of environmentally toxic organic compounds in complex matrices [21]. The determination of hydroquinone and catechol in different samples have been reported by voltammetry using various chemically or biologically modified electrode which act as an intermediary in their oxidation process [22]; but the maintenance and the procedures for the preparation of such type of electrodes is cumbersome and time consuming.

Due to high rate of electrode processes, wide anodic potential window, glassy carbon electrode is considered to be the most suitable sensor for the oxidation of various substrates and extensively being used in electrochemistry for the analysis of various important electroactive substances and as a template for the modification of electrodes [23].

1.6. Conducting polymers

Polymers are macromolecules produced by the union of many (10^2 - 10^6) small repeating units called monomers. Many polymers are strong, elastic, plastic, tough, friction-resistant and insulating. We encounter them in our day-to-day life in a wide range of products from most consumer goods to highly specialized applications.

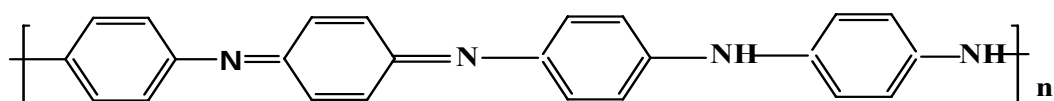
Conducting polymers contain π -electron backbone responsible for their universal electronic properties such as electrical conductivity, low energy optical transitions, low ionization potential and high electron affinity. Conducting polymers have potential applications in various fields such as fuel cells, biosensors, electroanalysis, electrocatalysis, electrochromic displays and others [24]. In recent years, electrochemically synthesized polymer films on electrode surface are considered for potential applications in electroanalysis of biological molecules. A recent review by Cosnier [25], deals with recent advances and scientific progress in electrochemical immobilization procedures for biological macromolecules on electrodes via electrogenerated polymer films. Electrochemical synthesis and some properties of nano-structured conducting polymers and nanocomposites derived from conducting polymers and metals, carbon and inorganic and organic materials and their potential applications in batteries, supercapacitors, energy conversion systems, corrosion protection and sensors have been reviewed by Malinauskas et al [24].

Conducting polymers are a natural choice for preparing arrays of voltammetric sensors because they have a rich electrochemical behavior and their electrochemical properties can be modulated by introducing chemical modifications in the sensitive materials [26].

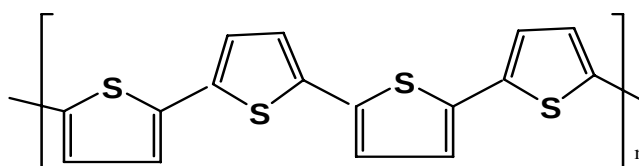
Electropolymerization is a good approach to prepare polymer modified electrodes (PMEs) as adjusting electrochemical parameters can control film thickness, permeation and charge transport characteristics. PMEs have many advantages in the detection of analytes because of their selectivity, sensitivity and homogeneity in electrochemical deposition, strong adherence to electrode surface and chemical stability of the film [27].

The electronically conducting polymers (ECPs) which cover several types of polymeric materials with electronic and/or ionic conductivity, including: (i) doped conjugated polymers, (ii) redox

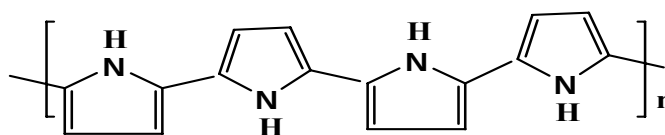
polymers, (iii) polymer composites and (iv) polymer electrolytes. ECPs as ion selective membrane and their applications in solid-state ion selective electrodes have been reviewed [28]. The most popular members of ECPs such as polyaniline, polythiophene, polypyrrole and polyphenylene are p-type semiconductors as shown in Fig.4 [29, 30]. Stability of polymers, conductivity and doping nature has been discussed in several reviews [31]. Conducting polymers are promising materials for a large variety of chemical sensors, their preparation and applications in several aspects have been discussed in many reviews [32 –34].



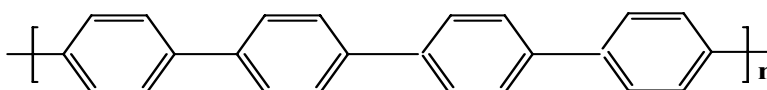
Polyaniline (conductivity 1-100 S/cm)



Polythiophene (conductivity 10-100 S/cm)



Polypyrrole (40-100 S/cm)



Polyphenylene (conductivity 100 – 500 S/cm)

Fig.4 Some popular conducting polymers [32]

1.7. Carbon nanotubes

Since their discovery [35-36], carbon nanotubes (CNTs) have found applications in various fields of science and nanotechnology. They have attracted much attention because of their high electrical conductivity, mechanical strength and chemical stability [37]. The unique properties of CNTs make them extremely attractive for electrochemical sensors and biosensors [38]. Recent investigations demonstrated that CNTs show strong electrocatalytic activity and minimization of surface fouling if employed to improve the electrochemical response of some important bioactive molecules. Recently, methods based on electrochemical deposition [39] and electrochemical polymerizations [40] have been employed for loading CNTs onto electrodes. CNT-based electrodes have been demonstrated to reduce the over-potential significantly [38, 39]. The ability of carbon nanotubes to promote electron-transfer reactions suggests great promise for amperometric sensors [38]. Chemically modified carbon nanotubes for use in electroanalysis have been reviewed in detail by Gregory et al [41].

Depending of the arrangement of their grapheme cylinders, there are two types of nanotubes: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs).

1.7.1. Single-walled carbon nanotubes

Single-walled carbon nanotubes have only one single layer of grapheme cylinders; as shown in Fig.5. Most single-walled carbon nanotubes have a diameter of close to 1 nanometer, with a tube length that can be many millions times longer. The structure of a SWCNT can be conceptualized by wrapping a one-atom-thick layer of graphite called grapheme into a seamless cylinder.

Single-walled carbon nanotubes are an important variety of carbon nanotubes; because they exhibit electric properties that are not shared by the multi-walled carbon nanotube (MWCNT) variants. In particular, their band gap can vary from zero to about 2 eV and their electrical conductivity can show metallic or semiconducting behavior, whereas MWCNTs are zero-gap metals. Single-walled carbon nanotubes are the most likely candidate for miniaturizing electronics beyond the micro electromechanical scale currently used in electronics.

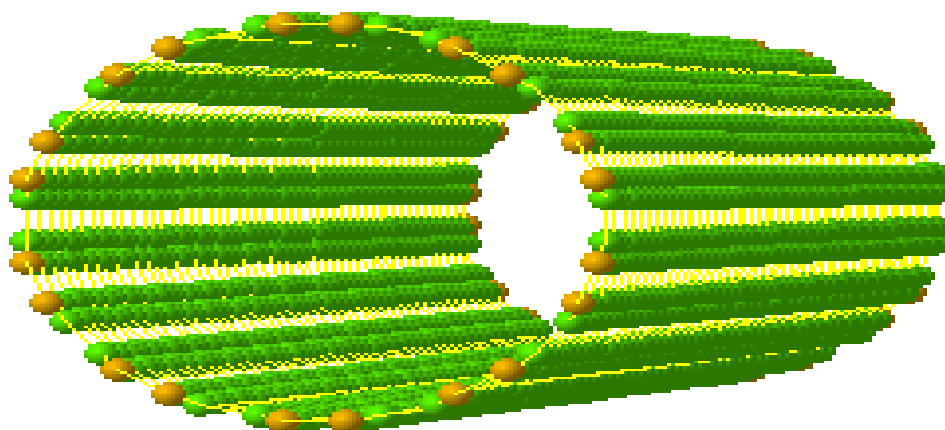


Fig.5 The structure of single-walled carbon nanotubes [37]

1.7.2. Multi-walled carbon nanotubes

Multi-walled carbon nanotubes (MWCNTs) are the type of carbon nanotubes which are composed of concentric and closed grapheme tubules, each with a rolled-up grapheme sheet, formed with a range of diameters, typically from 2 nm to 25 nm with many layers (approximately 50) as shown in Fig.6. MWCNTs have been employed to fabricate carbon nanotubes modified electrodes by casting MWCNT on conventional electrode surface [42] or by mixing MWCNT with bromoform, mineral oil, liquid paraffin, or Teflon composite to form MWCNT paste electrode [43]. The resulting carbon nanotube electrodes have been successfully utilized in the bioelectrochemical reactions [44-47] and electrocatalysis of gas [48, 49]. The performances of MWCNT modified electrodes have been found to be superior to the performance of other conventional carbon electrodes in terms of electron transfer rate, reversibility and conductivity [50]. The simultaneous determination of isomers is an interesting subject in electroanalysis [51, 52]. The increasing demand for the simultaneous determination of isomers have led to the development of a rapid, simple and non-separation method for the simultaneous determination of isomers where a chemically modified electrode (CME) has

emerged as an efficient and versatile approach and has attracted considerable interest over the past two decades due to the advantages in terms of reduced costs, automatic and fast analysis, high sensitivity and selectivity [53–54]. Recently, CME with MWCNT has been used to simultaneously determine isomers, such as catechol and hydroquinone [55] and nitrophenol isomers [56]. A high potential difference between redox peaks and an electrocatalytic effect on isomers are obtained at CME with MWCNT. These results show that CME with MWCNT is a promising approach for the simultaneous determination of isomers.

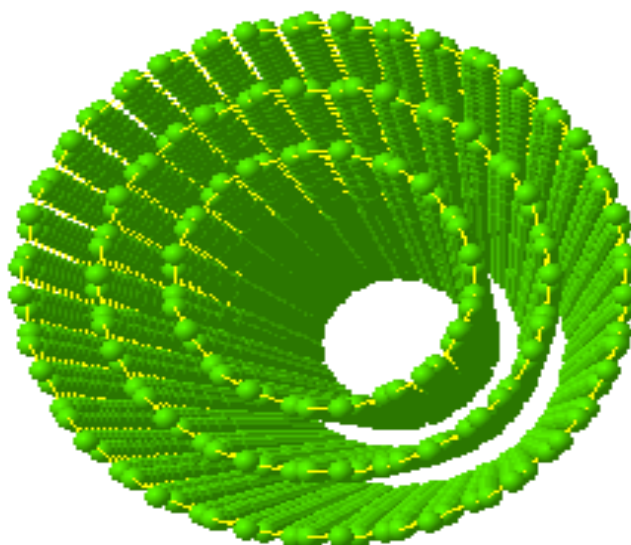


Fig.6 The structure of multi-walled carbon nanotubes [42]

1.8. Chemically modified electrodes

The beauty of electrochemical (EC) techniques is to utilize a tailor made chemically modified electrode (CME) for sensitive and selective analytical applications. The electrode itself can act as a reactant to pump (reduction)/withdraw (oxidation) electron in the reaction, which cannot be expected in spectroscopic characterization methods. In combination with CMEs, EC techniques can also be turned into important applications in electrosynthetic organic chemistry and material characterization. To prepare the CME, most often a thin film of selected chemical is either bound

or coated onto the electrode surface to endow desirable properties of the film in rationally and chemically designed manners.

The motivations behind the modifications of the electrode surface are: (i) improved electrocatalysis, (ii) freedom from surface fouling and (iii) prevention of undesirable reactions competing kinetically with the desired electrode process, in addition irreversible adsorption or covalent attachment, or, in the form of organized assemblies are some common possible routes for the preparation of CME's by in which monolayer's can be formed on electrode surfaces [57].

One typically modifies an electrode when the electrode materials given by nature will not allow the desired electron transfer reaction to occur under the selected experimental conditions. To overcome such obstacles, the region near the electrode surface can sometimes be altered to make the desired reaction more facile. There are many different types of applications of modified electrodes, among them particularly electrocatalysis has been attracted much attention among the researchers [57].

2. THEORETICAL BACKGROUND

2.1. The electrodes and cell

2.1.1. The cell

A typical electrochemical cell consists of the sample dissolved in a solvent, an ionic electrolyte and three electrodes directly connected to electroanalyzer. Cells (i.e., sample holders) come in variety of sizes, shapes and materials. The type used depends on the amount and type of sample, the technique and the analytical data to be obtained. The material of the cell (glass, Teflon and polyethylene) is selected to minimize reaction with the sample. To avoid contamination, it is necessary to place the reference electrode in a separate compartment as shown in the Fig.7.

In predominately aqueous systems, the supporting electrolyte is typically a Group I (alkali) metal salt added in excess to the solution containing the metal ions, an example being potassium chloride (KCl). This is known not to undergo chemical reaction with the commonly used working electrodes at the potentials used for measurement.

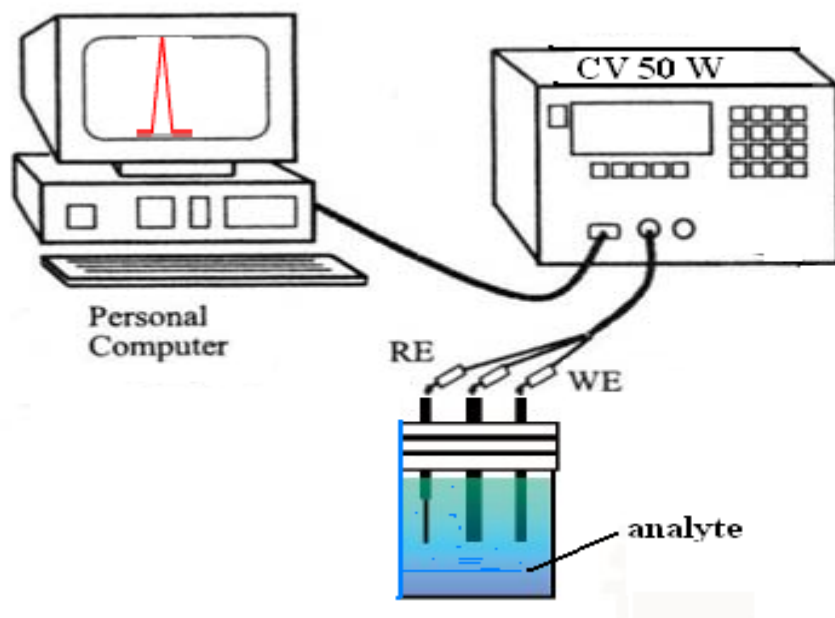


Fig.7 a typical set up of an instrument for voltammetric measurements [58]

2.1.2. The electrodes

Electrochemical measurements initially involved two electrodes: the working electrode, where the electrochemical reactions in the form of oxidation or reduction occurred, and a counter electrode which was large enough not to be polarized during the measurement. The potential of the working electrode was thus calculated from the difference between the applied potential and the potential of the counter electrode. However, distorted voltammogram were obtained when the resistance of the electrolyte was high. A third electrode was thus introduced whose potential remained constant throughout the entire measurement. This was known as the reference electrode.

2.1.2.1. Reference electrodes

Reference electrodes, as their name suggests, are electrodes which have a stable and well known electrode potential and used to give a value of potential to which other potentials can be referred in terms of a potential difference, (as potentials can only be registered as differences with respect to a chosen reference value.) They should provide a reversible half-reaction with Nernstian behavior, be constant over time and easy to assemble and maintain. They consist of a half cell with a known reduction potential as shown in table 2 below. Their only role is to act as reference in measuring and controlling the working electrodes potential and at no point do they pass any current [58].

Table 2 Half-reactions for some common reference electrodes in aqueous media [59]

Half reactions	E°/V
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00
$\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$	0.222
$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$	0.268

2.1.2.2. Counter electrodes (or Secondary or Auxiliary electrodes)

The counter electrode must be inert in the conditions to which it is exposed in order to avoid contamination of the solution. Typically platinum or graphite is used. It is often specified that the counter electrodes should have a large area compared to the working electrode, but this may not be necessary in many cases. The fundamental requirement is that to pass sufficient current into the solution without needing an excessive cell voltage or creating a non-uniform current distribution on the working electrode.

2.1.2.3. Working electrodes

The working electrode is the electrode in an electrochemical system on which the reaction of interest occurs [59]. The working electrode is often used in conjunction with an auxiliary electrode and a reference electrode in a three electrode system. Depending on whether the reaction on the electrode is a reduction or an oxidation, the working electrode can be referred to as either cathodic or anodic.

An electrode that serves as a transducer responding to the excitation signal and the concentration of the substance of interest in the solution being investigated and that permits the flow of current sufficiently large to effect appreciable changes of bulk composition within the ordinary duration of a measurement [60]. The working electrodes commonly employed are highly conductive and inert materials such as mercury (in the form of a dropping mercury electrode (DME)), carbon, gold and platinum, with which the potential is varied to induce a redox reaction.

The most important properties of glassy carbon electrode are high temperature resistance, hardness, low density, low electrical resistance, low friction, low thermal resistance, extreme resistance to chemical attack and impermeability to gases and liquids. Glassy carbon is widely used as an electrode material in electrochemistry, as well as for high temperature crucibles and as a component of some prosthetic devices.

Table 3 Variety, features and applications of some working electrodes [60]

Variety of working electrodes	features and applications
Platinum electrode (PTE)	Conventional electrode, which has hydrogen adsorptive wave, used for H ₂ O ₂ and oxides detection.
Gold electrode(AUE)	Conventional electrode, which has no hydrogen adsorption wave, used for thiols detection.
Glassy carbon electrode (GCE)	Chemically stable electrode despite its relatively large over-potentials of oxygen and hydrogen evolutions.
Silver electrode (AGE)	For cyanide and sulfide detection.
Carbon paste electrode (CPE)	Mixed with enzyme etc. to make modified electrodes.

Compared to metal electrode, the glassy carbon electrode (GCE) has been widely used, which is due to its biocompatibility with tissue, has low residual current over a wide potential range and has minimal tendency to show deteriorated response as a result of electrode fouling.

2.2. Voltammetry

Voltammetry is defined as “a method based on the measurement of current as a function of the potential applied to an electrode” (Skoog *et al.*, 1996). It originates from polarography which is a measure of current as a function of potential when the working electrode is comprised of a liquid conductor such as mercury implying that polarography is a reductive process. It was discovered by Jaroslav Heyrovsky in the 1920s. Voltammetry has now become widely used in biological, physical and inorganic chemistry where processes such as electron transfer, adsorption, oxidation and reduction are studied.

Voltammetry is an analytical technique which works based on the measurement of the current flowing through the electrochemical cell containing electroactive substances, while the potential is applied to an electrode. In voltammetry a time dependent potential is applied to an electrochemical cell and the current flowing through the cell is measured as a function of that

potential. A plot of current as a function of applied potential is called a voltammogram. They are considered to be active techniques because the applied potential forces a change in the concentration of the electroactive species at the electrode surface by electrochemically reducing or oxidizing it [61, 62].

In voltammetric measurements, a time dependent potential excitation signal is applied to the working electrode, changing its potential relative to the fixed potential of the reference electrode. The resulting current between the working and auxiliary electrode is measured. In many cases, the applied potential is varied and the current is monitored over a period of time (t). Therefore all voltammetric techniques can be described as a function of E , i and t . Since the reaction of interest occurs at the working electrode, the classification of current is based on this reaction. A current due to the analyte's reduction is called a cathodic current and by convention is considered positive. Anodic currents are due to oxidation reactions and carry a negative value.

Voltammetric techniques are preferred for their benefits such as excellent sensitivity with a very large useful linear range for both inorganic and organic species (10^{-12} to 10^{-1}), a very large number of useful solvents and electrolytes, wide range of temperature, rapid analysis (in seconds), simultaneous determinations of several analytes, the ability to determine kinetics and mechanistic parameters, a well developed theory and the ability to estimate the value of unknown parameters and the ease with which different potential can be generated and small currents measured [63].

These techniques have wide applications in several fields of science. Analytical chemists routinely use them for quantitative determinations of a variety of dissolved inorganic and organic substances. Inorganic, physical and biological chemists widely use them for variety of purposes such as fundamental studies of oxidation and reduction process in various media, adsorption process at surfaces, electron transfer process and transport, speciation and thermodynamic properties of solvated species. They are also applicable in the determination of compounds of pharmaceutical interest.

2.2.1. Cyclic voltammetry

Cyclic Voltammetry (CV) is one of the first electroanalytical techniques reported in 1938 and described theoretically in 1948 by Randles and Sevcik. It has grown enormously in popularity over the past few decades, so much so that obtaining CV is often the first experiment performed by the electrochemist, giving invaluable information as to the presence of electroactive species in solution or at the electrode surface. The basis of voltammetry is the current-voltage relationship exhibited by an indicator electrode immersed in a solution of an electroactive species. Cyclic voltammetry (CV) is a modification of linear sweep voltammetry (LSV). The effectiveness of CV results from its ability for rapidly observing redox behavior over the entire potential range available [64].

CV is an essential technique for initial electrochemical studies of new systems and has proven very useful in obtaining mechanistic information about fairly complicated electrode reactions. Although CV is particularly useful in qualitative studies of electrode processes, it is less well suited for quantitative determinations. Its merits are thus; largely in qualitative experiments. Quantitative measurements are best obtained by employing other (step or pulse) techniques [65].

CV consists of scanning linearly the potential of a stationary working electrode, using a triangular potential wave form as shown in Fig.8. Depending on the information sought, single or multiple cycles can be used. During the potential sweep, the triangular potential excitation signal causes the potential of the working electrode to sweep between two designated values called the switching potentials. During the potential sweep, the potentiostat measures the current resulting from the applied potential. The resulting plot of current vs. potential is termed a cyclic voltammogram as shown in Fig.9 below.

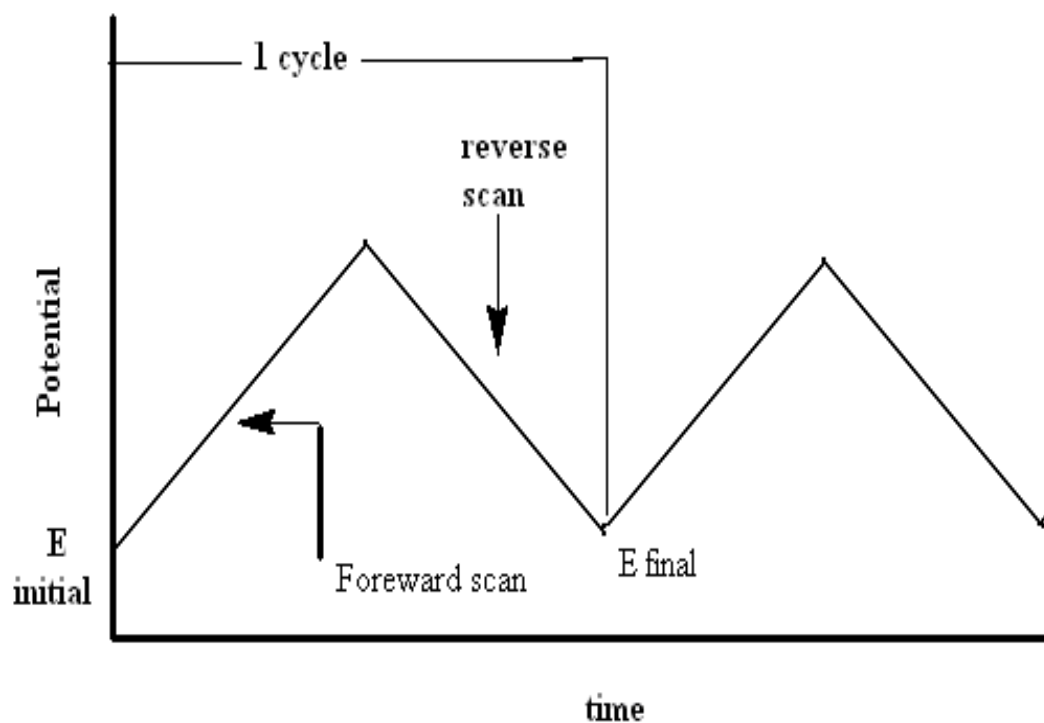


Fig.8 Typical excitation signal for cyclic voltammetry [64]

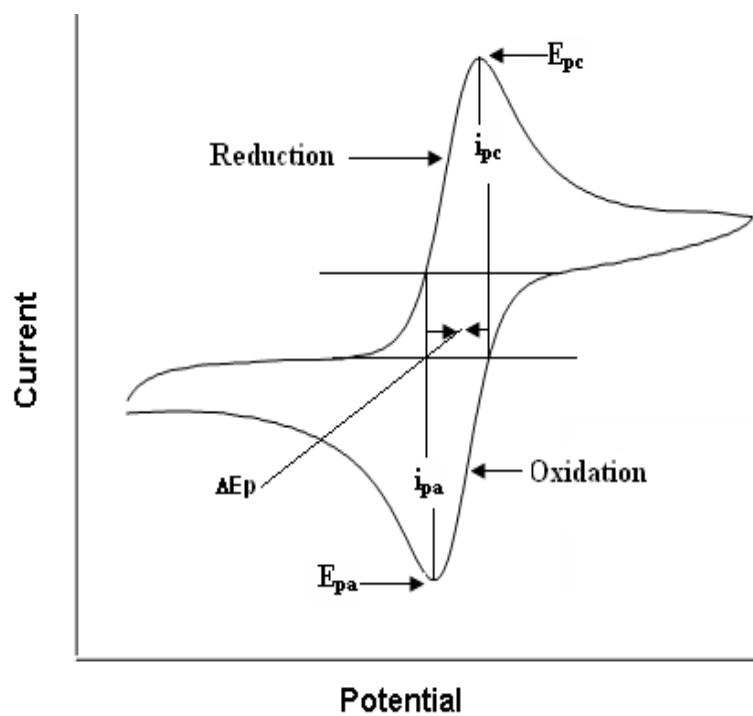


Fig.9 The current versus potential response in a cyclic voltammograms [64]

2.2.1.1. Reversible systems

A redox couple in which both species rapidly exchange electrons with working electrode is termed a reversible system. The redox reaction taking place in the solution can be expressed as: $O + ne^- \leftrightarrow R$; where O and R are the oxidized and reduced forms of the redox couple respectively. When the electron transfer rate in both the forward and reverse directions at the electrode is high, the process is described as reversible, and the cathodic and anodic peaks are separated by a potential of approximately $59/n$ mV at 25°C , where n is the number of electrons transferred. If n electrons are transferred in a reaction that is reversible, the peak separation is:

$$\Delta E_p = |E_{pa} - E_{pc}| = 2.23 \frac{RT}{nF} = \frac{57}{n} \text{ mV} \text{-----} (1)$$

Where E_p^{ox} and E_p^{red} are the potentials at which the oxidation and reduction processes occur, R is the universal gas constant, T is absolute temperature and F is Faraday's constant. Thus, the peak separation can be used to determine the number of electrons transferred, and as a criterion for a Nernstian behavior. Accordingly, a fast electron process exhibits ΔE_p of about 59 mV.

The expression of the peak current for a reversible couple (at 25°C) is given by the Randles-Sevcik equation:

$$i_p = (2.69 \times 10^5) n^{3/2} A C D^{1/2} v^{1/2} \text{-----} (2)$$

where, i_p is the peak current, n is the number of electron exchanged during the redox process, A is the active area of the working electrode, v is the scan rate, D and C are the diffusion coefficient and the bulk concentration of the electroactive species respectively.

Accordingly, the peak current is directly proportional to the concentration and increases with the square root of scan rate. The relation of i_p to bulk concentration is particularly important in analytical applications and in studies of electrode mechanisms. The values of i_{pa} and i_{pc} are similar in magnitude for a simple reversible electron transfer reaction, i.e. their ratio is unity. However, the ratio of the peak current can be significantly influenced by the chemical reactions

coupled to the electrode process. For example, if there is a chemical reaction following the electron transfer reaction, the peak current on the reverse scan is decreased.

The position of the peaks on the potential axis (E_p) is related to the formal potential of the redox process. The formal potential for a reversible couple is centered between E_{pa} and E_{pc} .

$$E^o = \frac{E_{pa} + E_{pc}}{2} \text{-----(3)}$$

The diagnostic criterion of a single electron transfer reversible reaction is often sufficient to get qualitative as well as quantitative information about the thermodynamic and kinetic parameters of the system. The important quantities are peak potentials, E_{pa} , E_{pc} and $E_{p/2}$, which provide a direct estimate of the electrode reversibility process. These indicate that for a given system the electrochemical equilibrium is always maintained at the electrode surface. The separation of peak potentials permits determination of $E_{1/2}$ of the measured redox system.

$$E_{pa} = E_{1/2} + \frac{0.0285}{n} \text{V} \text{-----(4)}$$

The oxidation half peak potential is determined by the equation:

$$E_{p/2} = E_{1/2} - \frac{28.5}{n} \text{mV} \text{-----(5)}$$

2.2.1.2. Irreversible systems

When the charge transfer reaction is slow the shape of the response is determined by the rate of the charge transfer reaction and not by diffusion of the analyte to the electrode surface. As equilibrium cannot be attained at the electrode surface during the time of measurement, the Nernst equation doesn't apply and instead the appropriate rate expression must be used to obtain the relationship between the current and the surface concentration of the analyte. Since the rate constants are potential dependent an increase in the potential causes the reaction rates to increase, so that eventually a diffusion controlled limiting current region is reached. For the case of an irreversible reaction, the potential current relationship is given by:

$$E_p = E_{1/2} - \frac{RT}{nF} 0.78 + \frac{RT}{2nF} \ln \lambda \text{-----} (6)$$

where:

$$\lambda = \frac{KRT}{nFv}$$

Where α is the transfer coefficient, i_d diffusion limited current and n_a is the number of electrons involved in the charge transfer step. The potential E_p occurs at a higher value than E^o with the over potential related to k^o and α . The peak potential and the half peak potential (at 25°C) differ by $48/\alpha n$ mV. Hence the voltammogram becomes more drawn out as αn decreases. The peak current is given by:

$$i_p = (2.99 \times 10^5) n^{3/2} (\alpha D v)^{1/2} \text{-----} (7)$$

Still, the peak current is proportional to the bulk concentration. Assuming α value of 0.5, the ratio of reversible to irreversible current peaks is 1.27 (i.e. the peak current for the irreversible process is about 80% of the peak for a reversible one).

2.2.2. Pulse Voltammetric Techniques

The basis of all pulse techniques is the difference in the rate of the decay of the charging and the faradaic currents following a potential step (or "pulse"). The charging current decays exponentially, whereas the faradaic current (for a diffusion-controlled current) decays as a function of $(t)^{-1/2}$ that is, the rate of decay of the charging current is considerably faster than the decay of the faradaic current.

The important parameters for pulse techniques are pulse amplitude, pulse width, sample period and the pulse period or drop time

For some pulse techniques pulse period or drop time must also be specified. This parameter defines the time required for one potential cycle, and is particularly significant for polarography (i.e., pulse experiments using a mercury drop electrode), where this time corresponds to the lifetime of each drop (i.e., a new drop is dispensed at the start of the drop time, and is knocked

off once the current has been measured at the end of the drop time. It should be note that the end of the drop time coincides with the end of the pulse width).

A number of different pulse techniques are available on the epsilon, which differ in their potential pulse wave forms, the number of sampling points, and whether a solid electrode (voltammetry) or a mercury drop electrode (polarography) is used. The discrimination against the charging current that is inherent in these techniques leads to lower detection limits (when compared to linear sweep techniques), which makes these techniques suitable for quantitative analysis.

2.2.2.1. Differential Pulse Voltammetry (DPV)

This technique is similar to the normal pulse voltammetry in that the potential is also scanned with a series of pulses; however it differs from NPV because each potential pulse is fixed, of small amplitude (10 to 100 mV) and is superimposed on a slowly changing base potential.

Current is measured at two points for each pulse, the first point just before the application of the pulse and the second at the end of the pulse. These sampling points are selected to allow for the decay of the non-faradic (charging) current. The difference between current measurements at these points for each pulse is determined and plotted against the base potential. For a reversible process the peak current is proportional to analyte concentration and it is given by:

$$i_p = \frac{nFAD^{1/2}C}{(\pi tp)^{1/2}} \left(\frac{1-\sigma}{1+\sigma} \right) \text{-----} (8)$$

where:

$$\sigma = \exp\left(\frac{nF\Delta E}{2RT}\right)$$

And the peak potential occurs at:

$$E_p = E_{1/2} - \frac{\Delta E_p}{2} \text{-----} (9)$$

Where: t_p and ΔE_p are pulse duration and amplitude of the voltage respectively. For small values ΔE_p , the peak half width that is the width at $i = i_{p/2}$ is 90.4 mV, but for larger pulse amplitude it approaches the pulse amplitude.

Differential pulse voltammetry has the following characteristics:

Reversible reactions show symmetrical peaks and irreversible reactions show asymmetrical peaks, the peak potential is equal to $E_{1/2} - \Delta E/2$ in reversible reactions, the peak current is proportional to the concentration and the detection limit is about 10^{-8} M.

The potential wave form consists of small pulses (of constant amplitude) superimposed upon a staircase wave form. The current is sampled twice in each pulse period (once before the pulse, and at the end of the pulse), and the difference between these two current values is recorded and displayed.

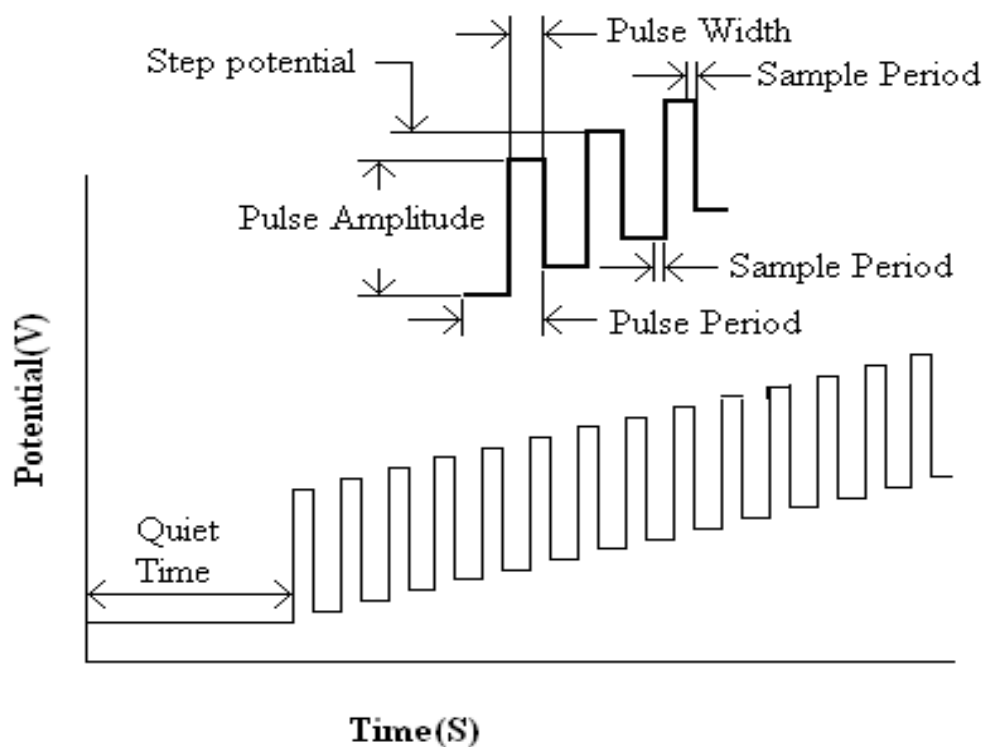


Fig.10 Potential wave form for differential pulse voltammetry [65]

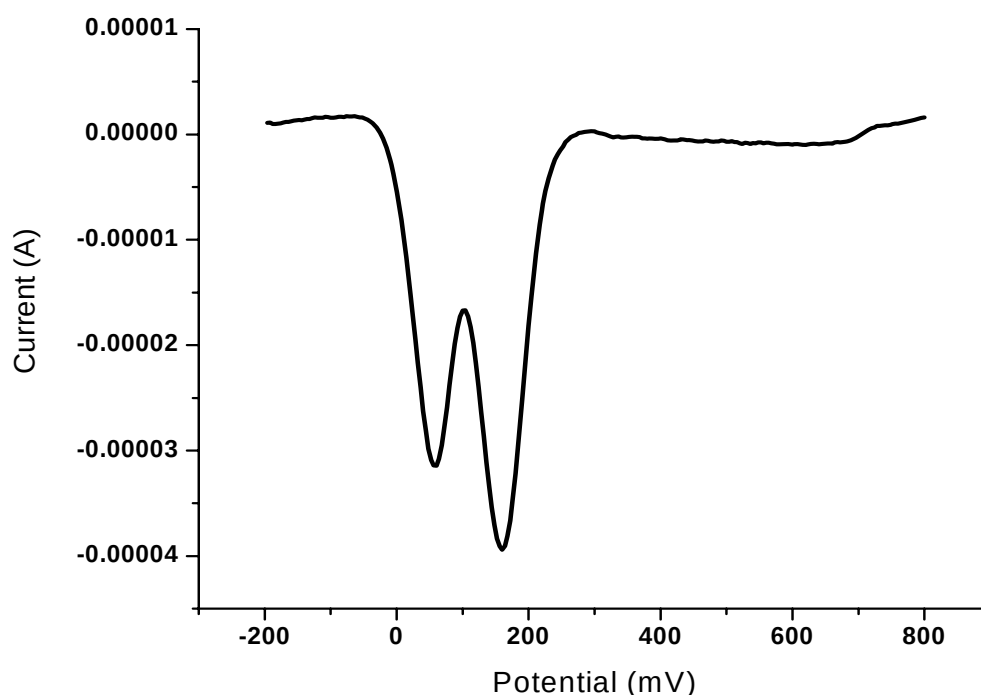


Fig.11 A typical current-potential response in differential pulse voltammetry [65]

2.2.2.2. Advantages of pulse voltammetric techniques

In order to increase speed and sensitivity, many forms of potential modulation have been tried over the years. The various pulse voltammetric techniques are all based on the difference in the rate of the decay of the double layer charging currents and the faradic currents following a potential step. After the potential is stepped, the charging currents, i_c decay exponentially with time which is faster than the faradic currents, i_f , which decays as a function of the square root of time. Since the current is sampled late in the pulse life; an effective discrimination against the charging current is achieved. Therefore, in pulse voltammetric techniques the measured current is mainly of the faradic current. The discrimination against the charging current that is inherent in these techniques leads to lower detection limits and higher sensitivity compared to linear sweep techniques, and this makes the pulse techniques more suitable for quantitative analysis.

3. OBJECTIVE OF THE STUDY

3.1. General objective

HQ and CC are two isomers of dihydroxy benzenes. They widely exist in the environment as a kind of pollutants and hazardous to human health. Because HQ and CC have similar structures and properties, they usually coexist in products. Therefore it is very important to develop simple and rapid analytical methods for dihydroxybenzenes isomers.

But, there are many difficult in simultaneously determining HQ and CC. The major difficulty is that the voltammetric peaks corresponding to oxidation and reduction of two phenol isomers are in many highly overlapping.

So, this paper employed a glassy carbon electrode which was covalently modified with a polymer and MWCNT to develop a voltammetric method for the simultaneously selective and sensitive determination of HQ and CC. To the best of our knowledge, the covalently modified glassy electrode with poly-(p-ASA) and MWCT for the determination of HQ and CC has not been reported.

3.2. Specific objective

To improve the linear range, sensitivity and detection limit of the simultaneously differential pulse voltammetric determination of catechol and hydroquinone by using poly-para-amino salicylic acid and multiwalled carbon nanotube modified glassy carbon electrode

4. EXPERIMENTAL

4.1. Reagents

The chemicals used were of analytical reagent grade and were used without further purification. Para-amidosalicylic acid (p-ASA) was obtained from Wulian Chemical Industry Factory (Shanghai, China) and MWCNTs (obtained from Aldrich) were treated with conc. HNO_3 and H_2SO_4 during purification processes. HQ and CC were obtained from (B.D.H. laboratory chemical divisions) England, Phosphate buffer solutions (PBS) were prepared from KH_2PO_4 and K_2HPO_4 and pH was adjusted with KOH and H_3PO_4 . The pH value of phosphate buffer solutions (PBS) was adjusted by using pH meter (Leici instrument factory, Shanghai, China). All experiments were carried out at the room temperature and all solutions were prepared from distilled water

4.2. Apparatus

Electrochemical measurements were performed with a system BAS-50 W electrochemical analyzer. A conventional three-electrode system was employed with a bare GCE or poly-(p-ASA)/MWCNT modified GCE (3 mm in diameter) as the working electrode, a saturated silver-silver chloride as the reference electrode and a platinum wire electrode as the counter electrode was used.

4.3. Preparation of the glassy carbon electrodes

The GCE surface is cleaned with high purity of alumina powder on a polishing cloth to obtain a mirror-like, slurry electrode surface and the washed with distilled water. The electrochemical pretreatment has done by using cyclic voltammetry for ten cycles with a potential scanning between -0.8 to +0.8 V at 100 mV/s in 0.05 M H_2SO_4 until a stable voltammograms was obtained. The cyclic voltammograms response was comparable with the electrochemical pretreatments of GCE in pH 7.0 PBS. These processes were done before every experiment.

4.4. Acidification of MWCNT

Purification of common MWCNTs is of great importance since most CNT applications require materials of high quality. Nitric acid and sulfuric acid is a common reagent for purification of CNTs and constitutes the first step in many different schemes. HNO_3 and H_2SO_4 treatments are usually employed to remove metal catalysis, together with some of the amorphous carbon [66].

1.0 mg Multi-walled carbon nanotubes (MWCNTs, purity >95%, diameter 30-10 nm, length 5-20 μm , NanoLab, Inc., Brighton, MA, USA) were purified by refluxing in a mixture of concentrated sulphuric and nitric acids (1:1, v/v) for 2 h at 55 $^\circ\text{C}$ and then for 3 h at 80 $^\circ\text{C}$, respectively. Afterwards, the nanotubes were washed with deionized water by centrifugation (10 min) repeating it for several times until the filtrate became neutral. Finally, the MWCNTs were dried under vacuum for 15 h [67]; the resulting dispersion was sonicated for 30 min to give a 1 mg mL^{-1} homogeneous black suspension. Thus, acid-oxidized MWCNT samples acquired hydroxyl or carboxylic functional group as shown in Fig.12.

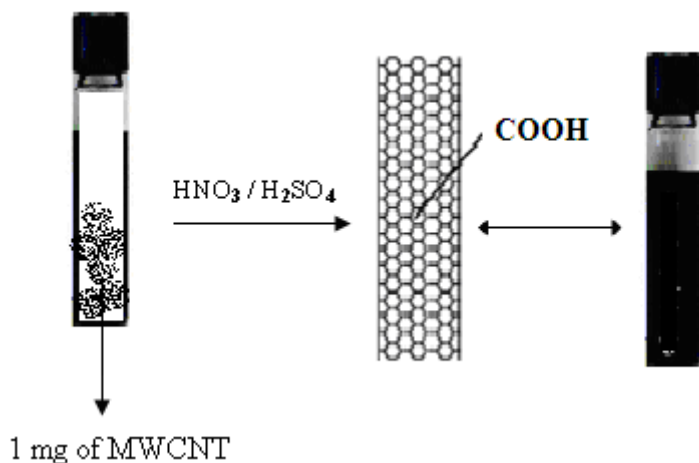


Fig.12 The oxidation of MWCNT

It is possible to conclude from Fig.12 is that that the oxidation of MWCNT with concentrated acid mixtures of $\text{H}_2\text{SO}_4/\text{HNO}_3$ (1:1, V/V) could make the relative significant amount of hydroxyl functional groups present on the surface of nanotubes. These nanotubes-bound hydroxyl groups

at the surface were used as the reaction sites to further functionalize MWCNT by esterification with the polymer used.

4.5. Modification of GC electrode by MWCNT

The bare GCE was polished successively with 0.3 and 0.05 μm Al_2O_3 slurry on emery paper before modification. Then it was rinsed with distilled water. To yield a thin, well dispersed a MWCNT/GC electrode 5 μL black suspension of functionalized MWCNT was casted on the surface of the cleaned GC electrode surface as shown in Fig.13 and then the solvent was evaporated from the electrode surface at room temperature.

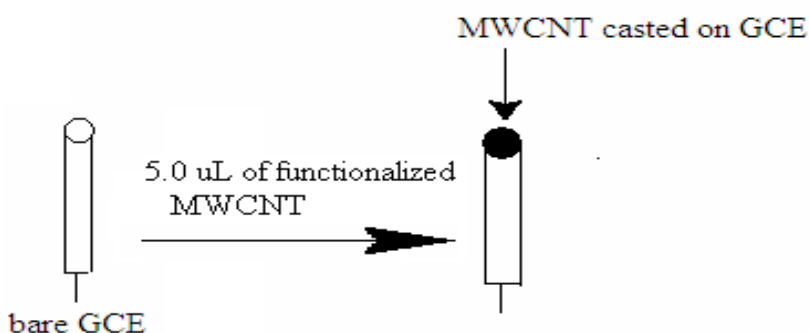


Fig.13 The modification of GCE by MWCNT

4.6. Modification of GCE by poly-(p-ASA)

Prior to electrochemical modification, the bare glassy carbon with a diameter 3 mm was polished with Al_2O_3 slurry down to 0.05 μm on a polishing cloth. After being cleaned, the electrode was then placed in 2 mM p-ASA solution. The electrode was treated with cyclic scanning between -1.0 V to 2.0 V at a scan rate of 100 mV/s, for ten scans, adherent polymer was found on the glassy carbon electrode surface. The electrooxidation of p-ASA to its analogous cation radicals to form a chemically stable covalent linkage between the nitrogen atom of the amine group and the edge plane sites of the GCE [68], as shown in Fig.14.

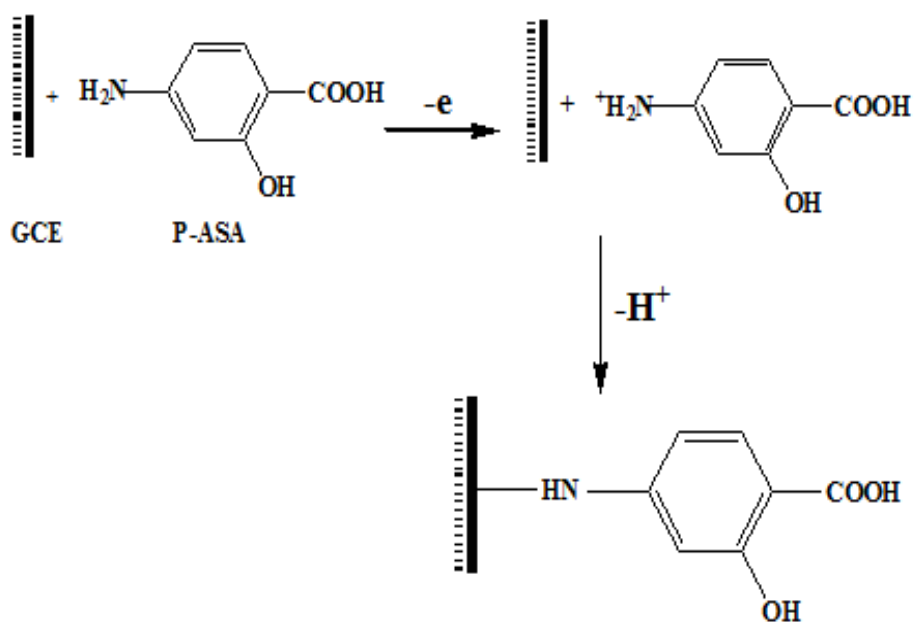


Fig.14 Covalent attachment of p-ASA on the surface of GCE

4.7. Preparation of poly (p-ASA) film on the MWCNT/GCE

The MWCNT modified glassy carbon electrode was immersed in $2.0 \times 10^{-3} \text{ molL}^{-1}$ p-ASA solution and was conditioned by cyclic sweeping between -8.0 V and $+2.0 \text{ V}$ at 100 mVs^{-1} for 24 segments.

5. RESULTS AND DISCUSSION

5.1. Electropolymerization of poly-(p-ASA) on the MWCNT/GCE surface

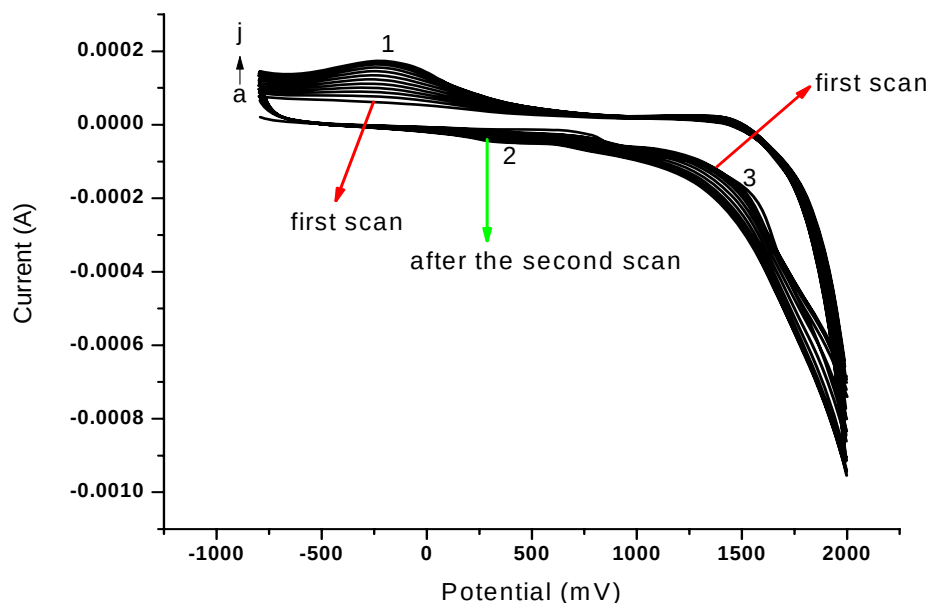


Fig.15 Cyclic voltammograms for the electropolymerization of poly-(p-ASA) film on the MWCNT modified glassy carbon electrode in a 0.1 mM p-ASA solution

If the positive potential value for polymerization was under +1500 mV or the negative potential was above -450 mV, the polymerization reaction did not occur. When the positive and negative potential value reached +2000 and -800 mV, the electropolymerization was observed on the CVs as shown in Fig.15 above. The experimental result showed that a better conductive polymeric film could be formed when the potential scan window was from -450 mV to +1500 mV.

Fig.15 shows cyclic voltammograms of $2.0 \times 10^{-3} \text{ molL}^{-1}$ p-ASA on the MWCNT/GCE. In the first scan, anodic peak 3 and cathodic peak 1 were observed around a peak potential value at +800 mV and -450 mV, respectively. From the second cycle onwards, new anodic peaks 2 appeared at +250 mV; then larger peaks were observed upon continuous scanning, reflecting the continuous growth of the film. It can also be observed that the film growth was faster during the

first six cycles than during the other cycles. From the cycle tenth and onwards, the film hardly grew; these facts indicated that p-ASA was deposited on the surface of MWCNT/GCE by electropolymerization.

5.2. Electrochemical behavior of HQ and CC on the GC electrodes

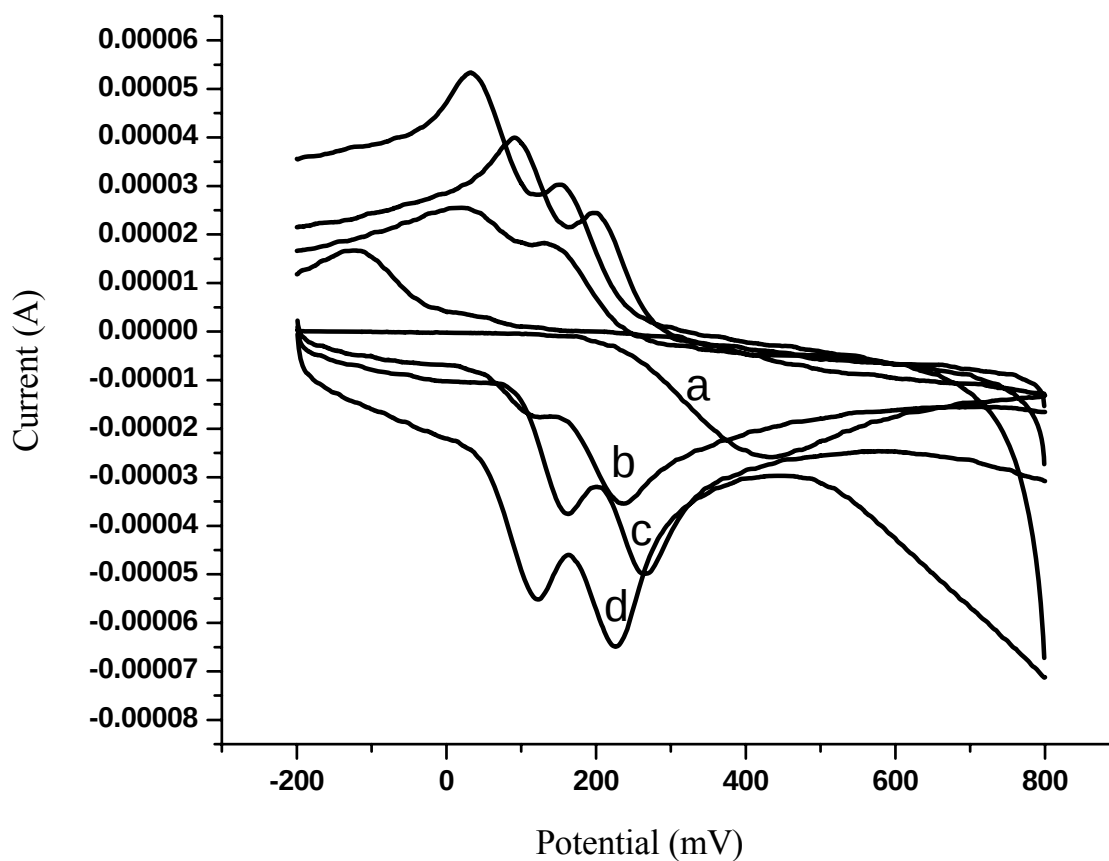


Fig.16 Cyclic voltammograms of 1 mM CC and HQ at different electrodes (a) bare GCE, (b) poly-p-ASA/GCE, (c) MWCNTs/GCE and (d) poly-p-ASA/ MWCNTs/GCE at a scan rate of 20 mVs^{-1} in 0.1 M PBS solution (pH 7.0)

Table 4 Comparison of GCE, Poly-(p-ASA)/GCE, MWCNT/GCE and poly-(p-ASA)/MWCNT/GCE

Electrode composition	HQ		CC	
	E _{pa} , mV	i _{pa} , μ A	E _{pa} , mV	i _{pa} , μ A
Bare GCE	430.71	25.25	430.71	25.25
Poly-(p-ASA)/GCE	136.52	26.89	228.04	35.08
MWNT/GCE	161.52	37.54	262.82	49.84
Poly-(p-ASA)/MWCNT/GCE	172.12	54.75	286.85	64.59

5.2.1. Electrochemical behavior of HQ on the GC electrodes

From Fig.16 (a) it can be seen that at the bare electrode, the oxidation and reduction of HQ result in broad waves with the corresponding peak potentials of 430.71 mV and -131 mV. Hence it shows irreversible behavior with ($\Delta E_p = 561.75$ mV). However, at the polymer modified electrode in (Fig.16 (b)), the reversibility of HQ is slightly improved together with the current signal increase. The oxidation peak potential negatively shifts to 136.17 mV and the reduction peak positively shifts to 25.00 mV with ($\Delta E_p = 111.17$ mV). In addition At the MWCNT/GCE in (Fig.16 (c)) the reversibility of HQ is improved. The oxidation peak potential negatively shifts to 161.52 mV and the reduction peak positively shifts to 92.12.mV from bare electrode with ($\Delta E_p = 69.40$ mV). But the composite modified electrode consisting of poly-(p-ASA)/MWCNT at the GCE in (Fig.16 (d)) the oxidation peak potential negatively shifts to 172.12 mV and the reduction peak positively shifts to 114.30 mV with ($\Delta E_p = 57.82$ mV) where the reversibility of HQ is significantly improved.

5.2.2. Electrochemical behavior of CC on the GC electrodes

Similarly, from Fig.16 (a) it can be seen that at the bare electrode, the oxidation and reduction of CC result in broad waves with the corresponding peak potentials of 430.71 mV and 24.90 mV. Hence it shows irreversible behavior with ($\Delta E_p = 405.81$ mV). However, at the polymer modified electrode in (Fig.16 (b)), the reversibility of CC is slightly improved together with the current signal increase. The oxidation peak potential negatively shifts to 228.04 mV and the reduction peak positively shifts to 137.13 mV with ($\Delta E_p = 90.91$ mV). In addition At the MWCNT/GCE in (Fig.16 (c)) the reversibility of CC is improved. The oxidation peak potential negatively shifts to 262.82 mV and the reduction peak positively shifts to 188.59 mV with ($\Delta E_p = 81.23$ mV). But the composite modified electrode consisting of poly-(p-ASA)/MWCNT at the GCE in (Fig.16 (d)) the oxidation peak potential negatively shifts to 286.85 mV and the reduction peak positively shifts to 231.76 mV with ($\Delta E_p = 55.09$ mV) where, the reversibility of CC is significantly improved.

At the bare glassy carbon electrode as shown in (Fig.16 (a)) HQ and CC showed a poor electrochemical response. Their response merged to the same large peak potential of ($E_{pa} = E_{pc} = 430.71$ mV); indicating it is impossible to separate the two voltammetric signals of isomeric compounds at bare GCE.

But the peak currents for HQ and CC increased highly and the oxidation peak potentials were shifted negatively. The voltammogram yielded two defined oxidation peak potentials, with anodic peak potential for HQ and CC 136.52 mV and 228.04 mV respectively with a peak potential separation of ($\Delta E_p = 91.52$ mV). It can also be seen that the oxidation peak potentials of HQ and CC shifted negatively from 430.71 mV at the bare GCE to 136.52 mV and 228.04 mV at the polymer modified GC electrode. The oxidation peak current for HQ and CC at the polymer modified electrode was 1.06 and 1.39 times higher than that of HQ and CC at the bare GCE respectively. This result indicates that the polymer can accelerate the electron transfer of HQ and CC on the electrode surface.

At the MWCNT/GCE in (Fig.16 (c)) HQ and CC yielded two well defined oxidation peaks not clearly observed with the polymer modified GCE, of 161.52 and 262.82 mV respectively. This gives a peak potential separation of ($\Delta E_p = 101.30$ mV). It can also be seen that the oxidation peak potentials of HQ and CC are shifted more negatively from 430.71 mV at the bare GCE to 161.52 mV and 262.82 mV at the MWCNT modified GC electrode. The oxidation peak current of HQ and CC at the MWCNT modified GC electrode was 1.48 and 1.97 times higher than that of HQ and CC at the bare GCE respectively. The increase in peak currents and separation between peaks potentials compared to bare and polymer modified GCE can be explained by the high surface area of the MWCNT possessing abundant acidic sites which can offer special approach to the simultaneously electrochemical determination of HQ and CC.

The composite modified electrode consisting of poly-(p-ASA)/MWCNT at the GCE in (Fig.16 (d)) while HQ and CC at GCE yielded two further well defined oxidation peaks for HQ and CC more clearly observed than (b) and (c). The oxidation peak potentials were 172.12 and 286.85 mV respectively, giving a peak potential separation of ($\Delta E_p = 114.73$ mV). Here also the oxidation peak potentials of HQ and CC shifted more negatively from 403.17 mV compared to the bare GCE and the polymer/MWCNT modified GC electrode to 172.12 mV and 286.85 mV respectively. The oxidation peak currents of HQ and CC at the polymer/MWCNT modified GC electrode were 2.17 and 2.56 times higher than that of HQ and CC at the bare GCE respectively.

Therefore it is possible to conclude that; the poly-p-ASA/MWCNT/GCE (composite) showed excellent electrocatalytic activity and the best selectivity for HQ and CC, the difference in the oxidation peak potentials between HQ and CC and the oxidation peak currents were higher than with the other electrodes. It can also be conclude that the poly-(p-ASA)/MWCNT (hybrid) GC electrode shows a synergic effect of the electrocatalytic properties and high active surface area of both the conducting polymer and multi-walled carbon nanotubes, which gives rise to a remarkable improvement for the oxidation of HQ and CC compared to the polymer modified electrode (PME) alone and multiwalled carbon nanotube (MWCNT) alone modified electrodes.

5.3. Effect of scan rate on the peak current in the binary mixture of HQ and CC

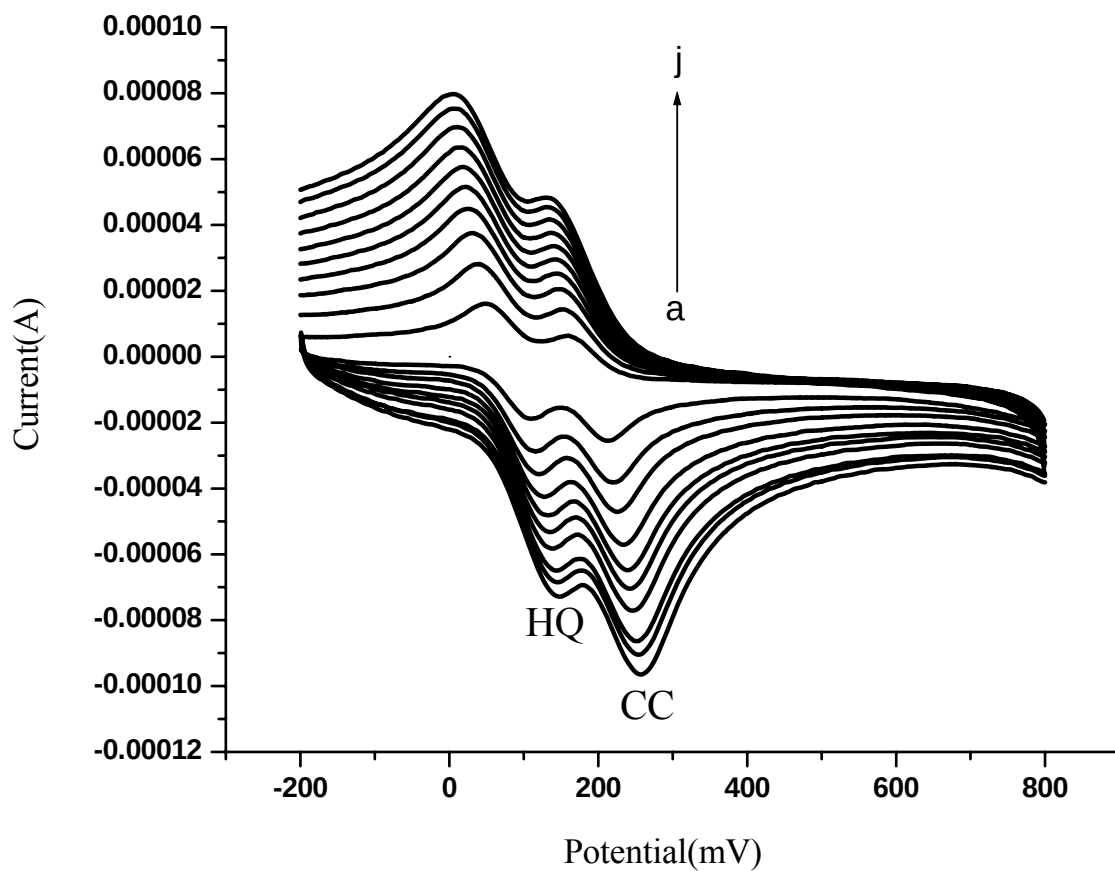


Fig.17 cyclic voltammograms for a binary mixture of 1 mM CC and HQ in 0.1 M PBS solution (pH 7.0) on poly-p-ASA/MWCNT/GCE at different scan rates of (a) 10 ,(b) 20, (c) 30, (d) 40, (e) 50, (f) 60, (g) 70, (h) 80, (i) 90 and (j) 100 mVs⁻¹

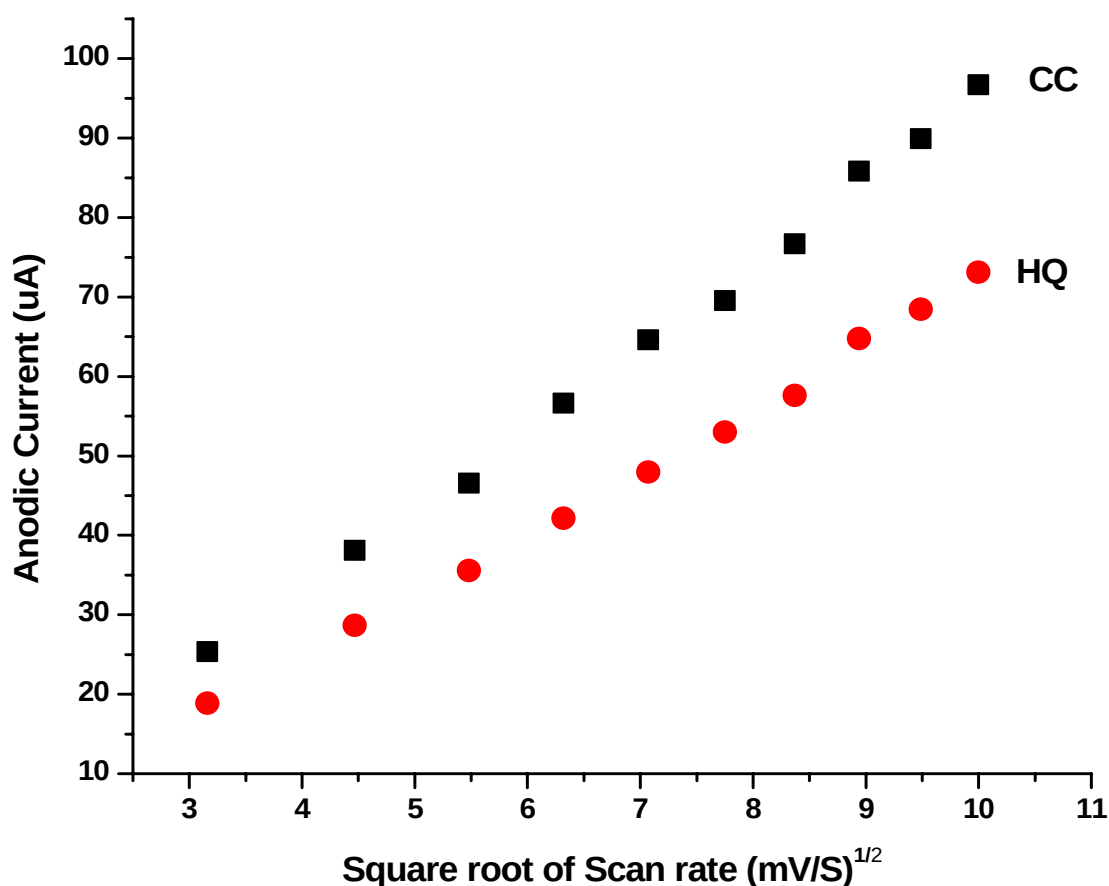


Fig.18 Effect of scan rate on the anodic peak current of 1 mM of CC and HQ in 0.1 M phosphate buffer at a pH 7.0 at a scan rate of 100 mV/s

Fig.17 shows the cyclic voltammograms for a binary mixtures of 1 mM HQ and CC in 0.1 M PBS (pH =7.0) at the poly-p-ASA/MWCNT/GCE at different scan rates. From table 5 below it can be observed that the scan rate affects the position of oxidation peaks. Inspection of the curve shows increase in the scan rates increases the current of oxidations of CC and shifts the anodic peak potential toward more negative potentials, whereas the cathodic peak potential shifts toward more positive potentials. In addition the oxidation peak current for the oxidation of HQ exhibited a linear relation to the square root of scan rate, in the range from 10 to 100 mVs^{-1} with a linear regression equation $i_{pa}/\mu\text{A} = -7.27102 + 7.92048 v^{1/2}$ with correlation coefficient, $R^2 = 0.99837$ and also the oxidation peak current for the oxidation of CC also exhibited a linear relation to the square root of scan rate as $i_{pa}/\mu\text{A} = -9.01081 + 10.41546 v^{1/2}$ with correlation coefficient, $R^2 =$

0.99827. The relationship between the oxidation peak current and square root of the scan rate indicates that the oxidation of HQ and CC at the composite modified electrode is a diffusion-controlled process.

Table 5 The corresponding oxidation potential of different scan rate

Scan rate (mV/s)	Oxidation potential peak (E_{pa} , mV)	
	CC	HQ
10	218	113
20	225	117
30	232	128
40	236	131
50	243	135
60	246	139
70	250	142
80	254	146
90	257	147
100	258	149

5.4. Effect of pH on the oxidation of HQ and CC in the binary mixtures

The effect of pH on the peak potentials and the peak currents of hydroquinone and catechol at poly-p-ASA/MWCNT/GCE were examined by using DPV between -200 mV and +800 mV in 0.1 M phosphate buffer solution of different pH. The results showed that both the cathodic and anodic peak potentials of HQ and CC shifted negatively with increase in pH from 4.0 to 9.0 as shown in Fig.20 and are presented in table 6.

Table 6 The potential shift on different pH values of 1 mM CC and 1 mM HQ 0.1 M phosphate buffer

pH	E_{pa} (mV)		E_{pc} (mV)	
	HQ	CC	HQ	CC
4	320	435	213	341
5	260	380	158	280
6	210	317	102	220
7	134	245	33	155
8	71	182	-18	103
9	30	130	-60	66

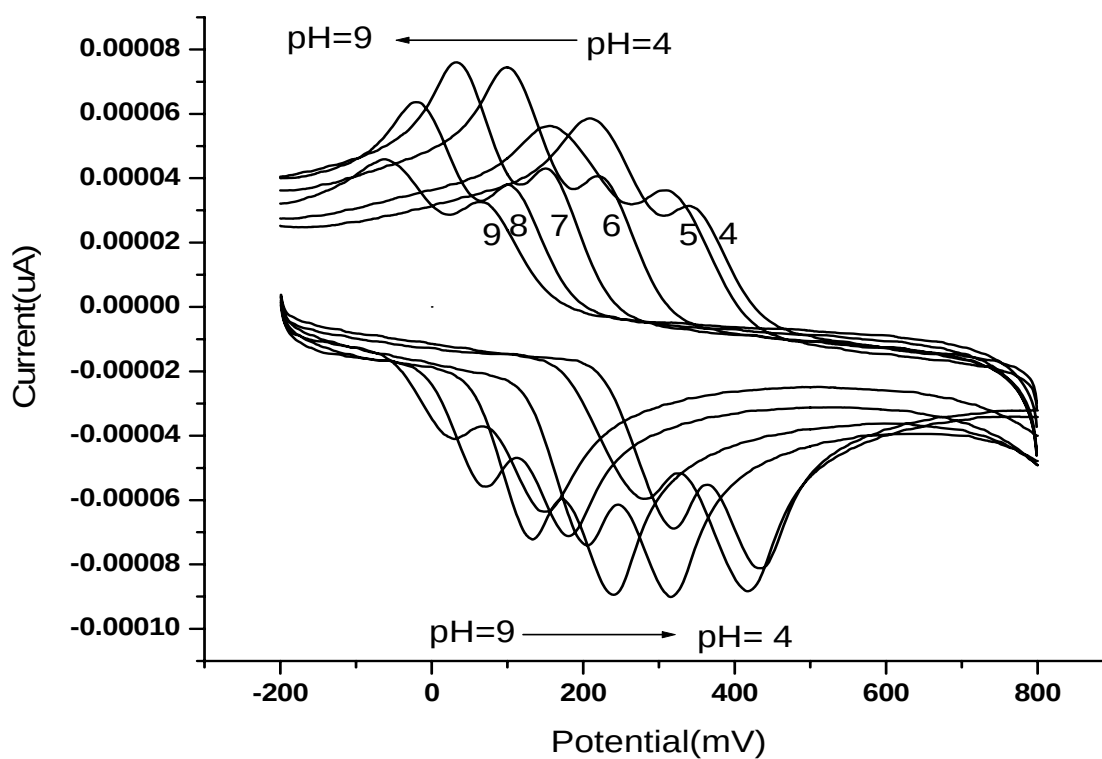


Fig.19 Cyclic voltammograms of 1 mM CC and 1 mM HQ 0.1 M phosphate buffer solution at different pH values

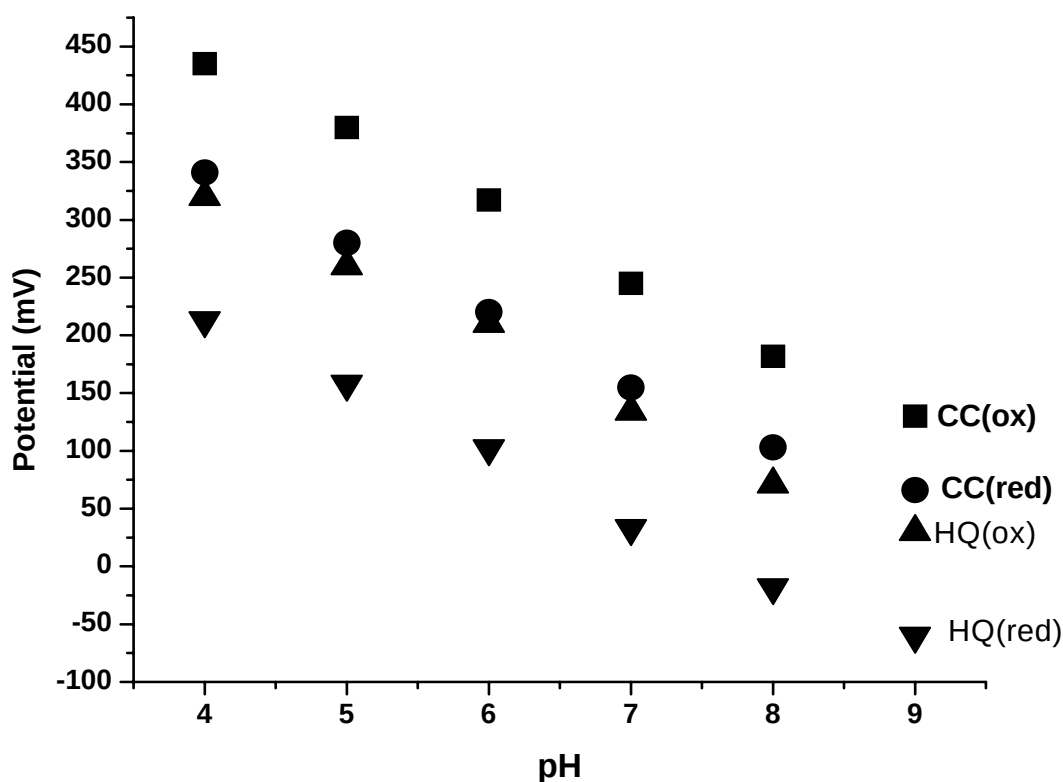


Fig.20 The relationship between anodic peak potentials of the two benzadiols vs. solution pH

The anodic peak potential (E_{pa}) and cathodic peak potential is proportional with the solution pH in the range of 4.0 to 9.0 as shown in Fig.20 above. The results showed that both the cathodic and anodic peak potentials of hydroquinone and catechol shifted negatively with increase in pH from 4.0 to 9.0.

For hydroquinone: the equation for the dependence of peak potential on the pH obtained were: E_{pa} (mV) = 559.53 - 59.8pH ($R^2=0.99752$), E_{pc} = 435.70 - 56.05pH ($R^2=0.99784$) and for catechol: E_{pa} (mV) = 688.4 - 62.64pH ($R^2=0.99904$), E_{pc} (mV) = 560.21 - 56.31pH ($R^2=0.99669$).

The slopes of E vs. pH suggest that two protons take part in the two-electron redox reaction of both hydroquinone and catechol, or, the anodic potentials shift negatively with increasing pH, indicating that protons take part in the redox process of HQ and CC at the poly-p-ASA/MWCNT/GCE modified electrode.

From Fig.21 it can be seen that the oxidation peak current of hydroquinone and catechol increased with increasing solution pH until it reached 7.0. The anodic peak current decreased when the $\text{pH} > 7$. The mechanism for pH effect on the composite modified glassy carbon electrode was studied. The negative carboxylate group on the electrode surface is decreased with decreasing pH, the probable reason may be at low pH, H^+ concentration is high enough so that the nitrogen atoms of the polymer and the hydroxyl of HQ and CC are protonated in the forms of NH_3^+ and OH_2^+ , so more HQ and CC are attracted to the composite electrode surface.

The HQ and CC anodic peak current increased with the increase of pH over the range 4.0-7.0. Then the degree of protonation HQ and CC decreases with increasing pH, because the hydroxyl group of HQ and CC are easily oxidized. When pH of the solution is higher than 7, the negative carboxylate group of the composite electrode surface is increases, but the protonation of HQ and CC decreases more, therefore the static attraction between HQ and CC with the composite electrode film decreases. The anodic peak current of HQ and CC decreases with increase of pH over the range 7-9. Moreover hydroquinone and catechol are known to be protic aromatic molecules and can become deprotonated as anions at higher pH. Since pH 7.0 is the physiological pH value, 7.0 was chosen for the electrochemical determination of HQ and CC.

Therefore, with increase in pH, those oxygen-containing functional groups at the poly-(p-ASA)/MWNT-modified GC electrode may become deprotonated and possess negative charges. Electrostatic repulsion between the analytes and the electrode might be one of the reasons for the adsorptions of analytes on the electrode at higher pH are inefficient.

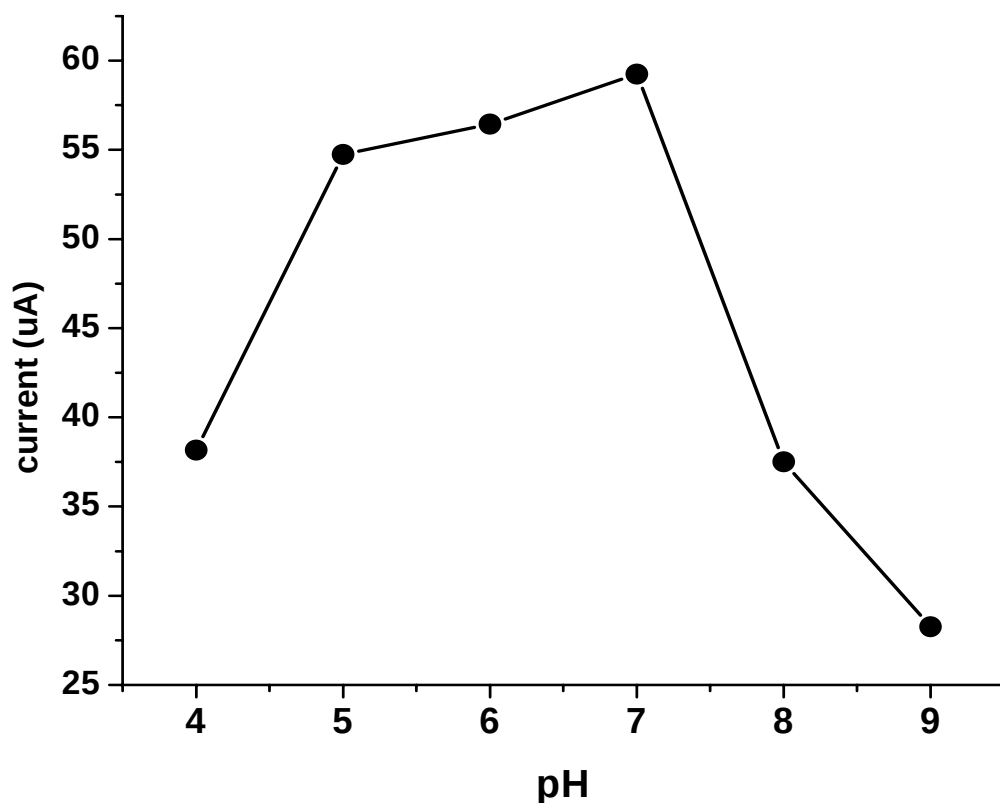


Fig.21 The plot of anodic current vs. pH

5.5. Simultaneous determination of HQ and CC

The results in Fig.16 above indicate that the composite modified electrode showed an excellent electrocatalytical effect on the oxidation of HQ and CC. In DPV measurements, the oxidation potential of HQ at the composite modified electrode was found to be more negative by 114.73 mV than that of CC. Therefore, this fact encouraged us to apply the composite modified electrode for the simultaneous determination of HQ and CC.

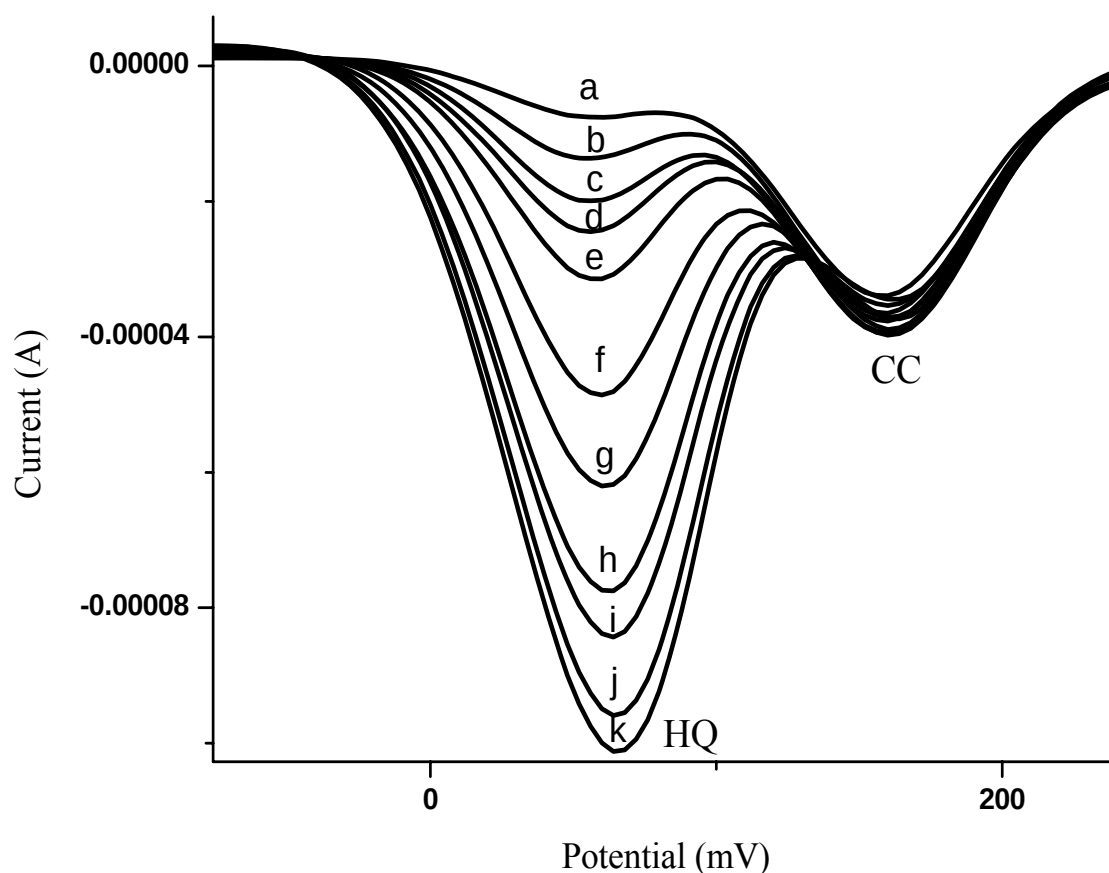


Fig.22 DPVs of the binary mixtures of (a) 20, (b) 40, (c) 60, (d) 80, (e) 100, (f) 200, (g) 300, (h) 400, (i) 500, (j) 600 and (k) 700 μM of HQ in the presence of 0.1mM CC

Thus attempt was made to determine HQ and CC simultaneously by using the composite modified electrode with DPV. Fig.22 above represents the DPVs at different concentration of HQ where the concentration of CC was kept constant. As shown in Fig.23 below the oxidation peak current for HQ increased linearly increasing in HQ concentration in the range of 2.0×10^{-5} – 7.0×10^{-4} M. the linear regression equation was $i_{pa}(\mu\text{A}) = 1.26252 + 0.30569 C (\mu\text{M})$ with correlation coefficient (R^2) = 0.99982 and the detection limit was 1.23×10^{-6} M in the present of 1.0 mM CC. Furthermore, while HQ peak current increased with increase in HQ concentration, the peak current of CC remained almost constant. Thus, it is confirmed that the responses of HQ and CC at the composite modified electrode are independent.

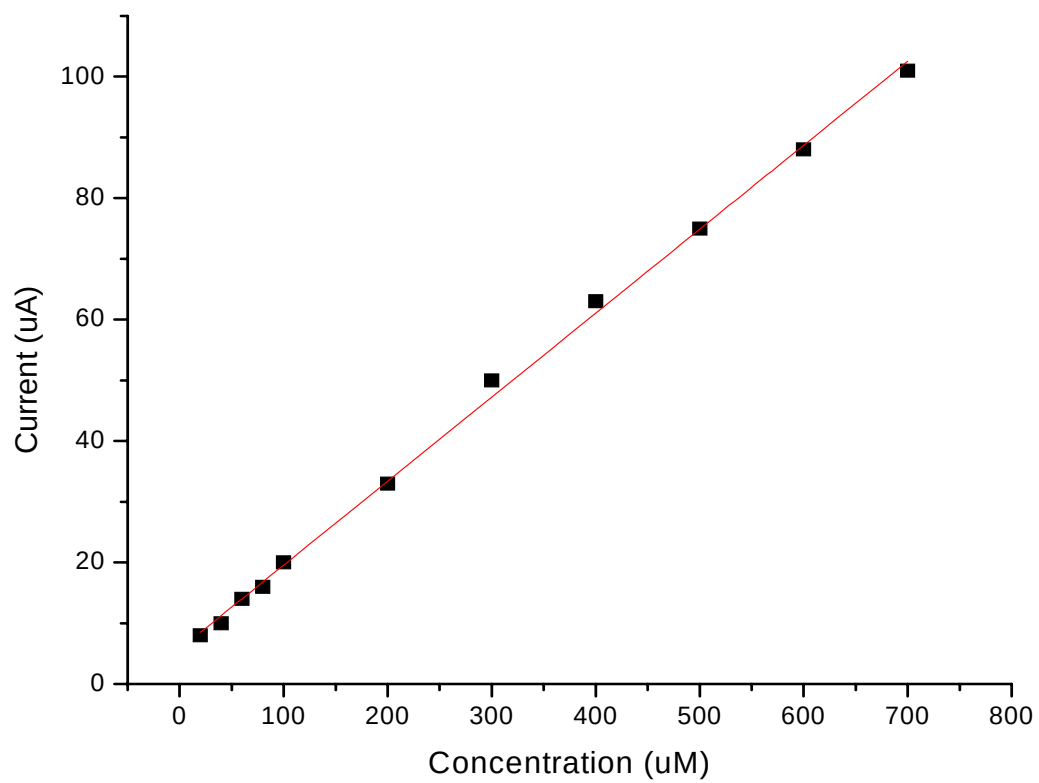


Fig.23 Calibration plot of hydroquinone in the presence of 0.1 mM catechol

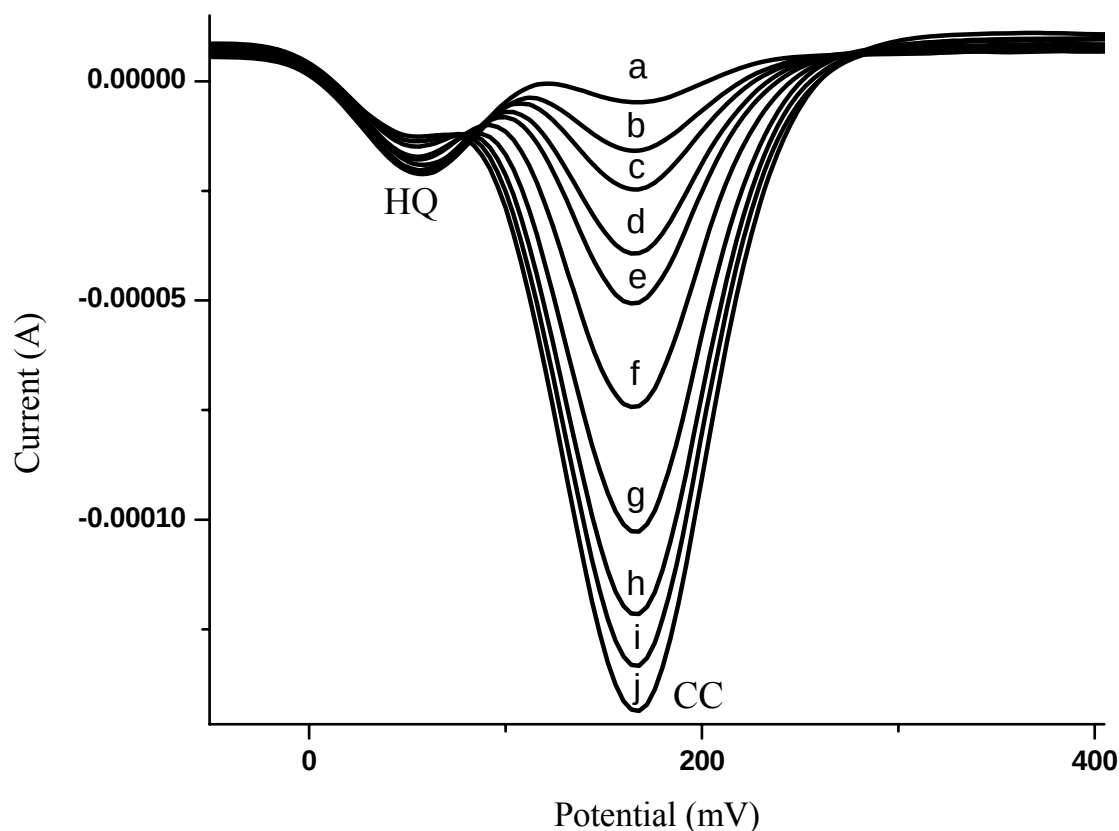


Fig.24 DPVs for the binary mixtures of (a) 20, (b) 40, (c) 60, (d) 80, (e) 100, (f) 200, (g) 300, (h) 400, (i) 500, (j) 600 μM of CC in the presence of 0.1mM HQ

Fig.24 above represents the DPV recordings at different concentrations of CC where the concentration of HQ was kept constant. Here also the oxidation peak current for CC increased linearly with increase in CC concentration in the range of $2.0 \times 10^{-5} - 6.0 \times 10^{-4}$ M as shown in Fig.25 below. The linear regression equation was $i_{pa}/\mu\text{A} = -4.96902 + 0.51502 C (\mu\text{M})$ with correlation coefficient (R^2) = 0.99985 and the detection limit was 1.4×10^{-7} M in the presence of 1 mM HQ. Furthermore, while the peak current for CC increased with the increase in the concentration of CC, the peak current of HQ remained almost constant. This suggests that the fouling effect by the oxidized product of HQ on the response of CC does not occur at the composite modified electrode. Thus, the simultaneous selective and sensitive determination of HQ and CC was achieved at the composite modified glassy carbon electrode.

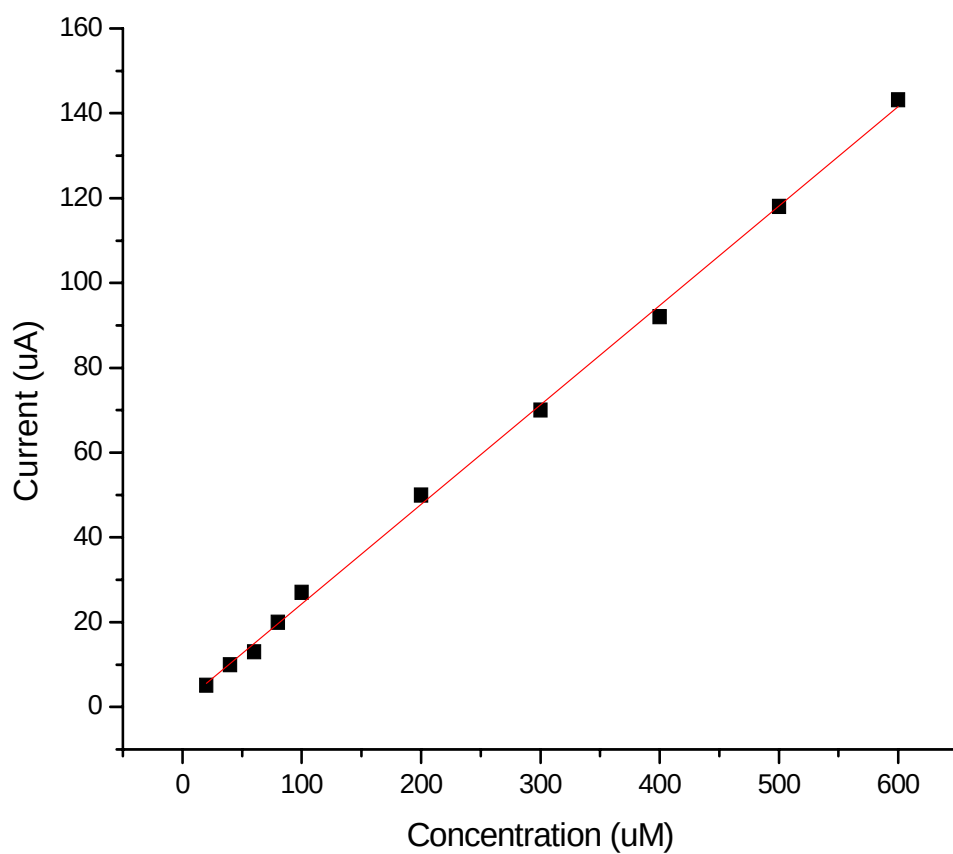


Fig.25 Calibration plot of catechol in the presence of 0.1 mM hydroquinone

Table 7 Comparison of different modified electrodes used for simultaneous determination of HQ and CC

Electrodes	Linear range (molL ⁻¹)		Detection limit (molL ⁻¹)		Met.	Ref.
	HQ	CC	HQ	CC		
P-(BPB)/MWNT/GCE	10 ⁻⁶ - 10 ⁻⁴	1x10 ⁻⁶ -1x 10 ⁻⁴	3x10 ⁻⁷	3x10 ⁻⁷	LSV	69
CMK-3-Nafion/GCE	10 ⁻⁶ - 3x10 ⁻⁵	5x10 ⁻⁷ -3.5x10 ⁻⁵	1x10 ⁻⁷	1x10 ⁻⁷	CV	70
PASA/MWNTs/GCE	6x10 ⁻⁶ - 4x10 ⁻⁴	6x10 ⁻⁶ - 7x10 ⁻⁴	1.0x10 ⁻⁶	1.0x10 ⁻⁶	DPV	71
MWNT/GCE	10 ⁻⁶ - 10 ⁻⁴	6x10 ⁻⁷ – 1x10 ⁻⁴	2x10 ⁻⁷	7.5x10 ⁻⁷	DPV	72
P-(PA)/GCE			1x10 ⁻⁶	7x10 ⁻⁷	DPV	73
P-(GA)/GCE	5x10 ⁻⁶ - 8x10 ⁻⁵	1x10 ⁻⁶ - 8x10 ⁻⁵	1x10 ⁻⁶	8x10 ⁻⁷	DPV	74
P-(GI)/GCE			1x10 ⁻⁶	5x10 ⁻⁷	DPV	75
Asp/GCE			9x10 ⁻⁷	5x10 ⁻⁷	DPV	76
Micelles/GCE	8x10 ⁻⁷ - 4x10 ⁻³	3x10 ⁻⁷ - 4x10 ⁻⁴	5x10 ⁻⁷	3x10 ⁻⁶	DPV	77
P-(PABA)/GCE	1.2x10 ⁻⁶ -6x10 ⁻⁴	2x10 ⁻⁶ - 9x10 ⁻⁴	4x10 ⁻⁷	5x10 ⁻⁷	DPV	78
P-(ASA)/MWNT/GCE	2x10 ⁻⁵ -7x10 ⁻⁴	1x10 ⁻⁵ - 6x10 ⁻⁴	1.2x10 ⁻⁶	1.4x10 ⁻⁷	DPV	this work

Table 8 The current produced from concentration of CC and HQ in tap water

Conc.(μM)	CC/HQ(μA)	HQ/CC(μA)
40	15.63	15.83
80	33.66	27.36
100	41.23	28.37

Table 9 Simultaneous determination of CC in local tap water containing HQ

Sample No.	HQ (μM)	CC(added) μM	CC(found) μM	Recovery (%)
1	100	40	39.62	99.05
2	100	80	74.23	92.79
3	100	100	88.85	88.85

Table 10 Simultaneous determination of HQ in local tap water containing CC

Sample No.	CC (μM)	HQ added	HQ found	Recovery (%)
1	100	40	47	117.5
2	100	80	84.19	105.24
3	100	100	87.45	87.45

5.6. Analytical applications

In order to assess the possible applications of the proposed method for direct simultaneous determination of HQ and CC, synthetic samples consisting of HQ and CC in local tap water were tested. The determination of HQ and CC in the samples was carried out using DPV at the poly-(p-ASA)/MWCNT/GCE in 0.10 molL^{-1} PBS (pH 7.0). The results are given above in table 9 and table 10. When known amount of CC were added to the water control samples containing HQ, quantitative recoveries of 88.85 % - 99.05 % were obtained. When known amount of HQ were added to the water control samples containing CC, quantitative recoveries of 87.45 % -117.5 % were obtained. The feasibility application of the poly-(p-ASA)/MWCNT/GCE for the determination of HQ and CC is evident.

6. CONCLUSION

Electrochemical technique is one of the promising methods for preparation of polymer modified electrodes with varying thickness and functionalities of polymer at the surface.

This study demonstrates an excellent approach for the development of a novel voltammetric sensor for hydroquinone and catechol based on a covalently modified glassy carbon electrode with MWCNT and p-ASA. Fast electron transfer, high selectivity and excellent sensitivity for oxidation of hydroquinone and catechol are achieved at the composite modified electrode. This composite modified glassy carbon electrode showed excellent sensitivity, selectivity and antifouling properties and can separate oxidation peaks towards hydroquinone and catechol, which are indistinguishable at the bare glassy carbon electrode.

As voltammetric signals of hydroquinone and catechol are well separated at the composite modified electrode, the sensitive determination of catechol in the presence of hydroquinone or the reverse can be achieved.

The modification of glassy carbon electrode with MWCNT and p-ASA is a promising approach to the determination of isomers.

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