JIMMA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

DEPARTMENT OF CHEMISTRY

ELECTROCHEMICAL DETERMINATION OF HYDROQUINONE BY USING POLY MALACHITE GREEN MODIFIED CARBON PASTE ELECTRODE PREPARED FROM ACTIVATED CARBON FROM *AFRAMOMUM CORORIMA* HUSK AND GRAPHITE POWDER

APRIL, 2023

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A THESIS SUBMITTED TO SCHOOL OF GRADUATE STUDIES JIMMA UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

BY: ALEMAYEHU AMBISA

ADVISOR: SHIMELES ADDISU (PhD)

Co-ADVISOR: GETU SISAY (MSc)

APRIL, 2023
JIMMA, ETHIOPIA

Declaration

I declared that Electrochemical determination of HQ by using poly malachite green modified carbon paste electrode prepared from activated carbon from *Aframomum cororrima* husk is my original work, except where reference is made, and has never been submitted anywhere for award any degree or diploma in any university.

ALEMAYEHU AMBISA

This M.Sc. Thesis has been submitted with our approval as supervisors

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Shimeles Addisu (PhD)

Chemistry Department

Jimma University

SCHOOL OF GRADUATE STUDIES

JIMMA UNIVERSITY

COLLEGE OF NATURAL SCIENCES

MSc THESIS APPROVAL SHEET

We, the undersigned, member of the Board of Examiners of the final open defense by **Mr. Alemayehu Ambisa** have read and evaluated his/her thesis entitled "**Electrochemical Determination of Hydroquinone by Using Poly-malachite Green Modified Carbon Paste Electrode Prepared from Activated Carbon from *aframomum cororrima* Husk and Graphite Powder**" and examined the candidate. This is therefore to certify that the thesis has been accepted in partial fulfillment of the requirements for the degree Master of Science in Analytical Chemistry.

Dr. Tsegaye Girma	_____	_____
Name of the Chairperson	Signature	Date
Dr. Shimeles Addisu	_____	_____
Name of Major Advisor	Signature	Date
Dr. Tamene Tadesse	_____	_____
Name of the Internal Examiner	Signature	Date
Prof. Dejene Ayele	_____	_____
Name of the External Examiner	Signature	Date

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Abbreviations

BE Bare Electrode

CE Counter Electrode

CPE Carbon Paste Electrode

CV Cyclic voltammetry

HQ Hydroquinone

LOD Limit of detection

LSV Linear sweep voltammetry

MCPE Modified carbon paste electrode

PBS Phosphate buffer solution

PMG-CPE Poly malachite green modified carbon paste electrode

RE Reference Electrodes

WE Working Electrodes

UCPE Unmodified carbon paste electrode

Abstract

Hydroquinone (HQ) is the oxidation product of some aromatic compounds. HQ is widely found in cigarette smoke, diesel engine lubricant and the chemical industry. Industrial development has caused a huge increase in the release of potentially toxic compounds into the atmosphere, water bodies and soils. Therefore, a simple, cheap and sensitive determination method of HQ is highly desired. In this work, the electrochemical determination of HQ was reported. The oxidation current response of HQ at the poly malachite green modified carbon paste electrode (PMG-CPE) was investigated using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) methods. The performance between unmodified carbon paste electrode (UCPE) and PMG-CPE was made toward the determination of HQ. Due to the different interactions of the HQ at the electrode surface, the PMG-CPE electrode signal intensity of the developed method gives much higher than UCPE in phosphate buffer solution (PBS). Under the optimized experimental conditions, the electrode oxidation peak current was a direct relationship with the concentration of HQ in the range of 1 μM to 75 μM and a limit of detection (LOD) of 0.82 μM (3σ/m). The reported PMG-CPE was further applied for the determination of HQ in waste water with acceptable recoveries.

Keywords: Hydroquinone, Poly malachite green-modified carbon paste electrode, electrochemical determination, waste water.

CHAPTER ONE

1. Introduction

Hydroquinone (benzene 1,4-diol, HQ) is a positional isomer of a phenolic compound. HQ is widely found in cigarette smoke, diesel engine lubricant and the chemical industry [1]. Moreover, HQ has been used in bleaching creams, pesticides, medicines, cosmetics, secondary colouring materials, photography, chemicals and flavoring compounds [2]. It is also used as a topical application for skin whitening for reducing the colour of skin [3]. HQ is difficult to degrade in the ecological environment and highly toxic to human health even at low concentration [4]. High concentration of HQ can lead to acute myeloid leukemia, tinnitus, headache, fatigue, dizziness, nausea, edema of internal organs, skin irritation and cause kidney damage in humans [5].

Industrial development has caused a huge increase in the release of potentially toxic compounds into the atmosphere, water bodies and soils. However, HQ is still found in the waste water at present [6]; therefore, the HQ sensor is pivotal , primarily waste water As for today, there are some methods for the HQ analysis, such as potentiometric titration, oxidometric titration, iodometric titration, calorimetric titration, paper chromatography, spectrophotometer [7,8], high performance liquid chromatography (HPLC) [9,10], and chemiluminescence [11]. All of these methods are complicated in the sample pre-treatment stage, expensive in terms of the instruments and time consuming in the analysis [12]. In contrast, electrochemical methods that lead to an electrochemical sensor for HQ have gained attention due to their quick results, cheap, simple operation, and high sensitivity [12].

Electrochemical techniques are known to offer some benefits such as fast analysis, low in cost, higher sensitivity and accuracy [13]. However, the major problem frequently encountered in the electroanalysis of HQ is the effect of interferents caused the substances with similar redox potential at conventional electrodes which results in poor selectrivity, the tendency of the organic liquid binder to dissolve in solution containing appreciable fraction of organic solvents and fouling effect due to surface accumulation of the oxidizing products, and because of similar structure and properties the oxidation of dihydroxy benzene isomers at bare electrode was indistinguishable [14,15,16]. Thus its difficult to detect specifically one substance in the presence of others substances in real environmental sample at carbon paste electrode. Based on

its properties different techniques were developed to detect HQ selectively. Modification of electrode with the development of electrochemical sensor is conducted through the electropolymerization of the surface electrodes. Modification of working electrode with modifiers like polymer based methylene blue [17], Prussian blue [18], neutral red [19] and aniline [20] showed promising applications in the fabrication of sensors for sensitive and selective detection of HQ. The most distinguishing feature of chemically modified electrodes is their modification by a selected substance that is coated onto the electrode surface which provides the electrode certain desirable properties. The use of nano materials for nano structuring of electrode surface has aroused the interest of analysts. Because nanostructure materials can be tailored to improve selectivity and sensitivity of the sensors.

Activated carbon can be produced from several kinds of carbon-rich raw materials such as coal, Kororima husk,rice husks and wood [21,22]. Kororima husk contains more than 37% elemental carbon by weight, [23] thus making it a potential raw material for the production of activated carbon. The activated carbon or carbon based materials are considered as promising electrode modifiers for the development of new electrodes for electrochemical quantitation [24].

In this study, carbon paste electrode was prepared from mixture of graphite and activated carbon prepared from kororima husk (*Aframomum cororrima*) and then electropolymerized with MG. We have demonstrated the improvement in selectivity and sensitivity for determination of HQ using the electrode surface modification method we have developed. MG is also dye that has an open but ionized structure hence the conducting polymers of malachite green have been electrochemically synthesized for chemical and biochemical sensors application [25,26]. MG has been found important modifying agent for the preparation of modified carbon paste electrode. Therefore, in this study, we demonstrated electroanalytical techniques using PMG-CPE for electroanalysis of HQ. The electrochemical to determination of HQ is possible due to its oxidation-reduction at the electrode. In general, it is believed that oxidation -reduction of HQ is a reversible process involving two electrons and two protons. The synthesized electrode was used to for determination of HQ.The proposed electrode exhibits a low limit of detection and good sensitivity, stability, and reproducibility towards the HQ determination.

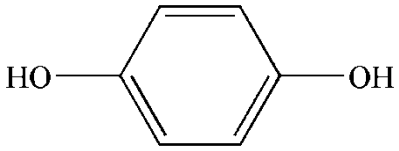


Figure 1. Structure of HQ

1.1. Statement of the Problem

Environmental analyses by electro analytical methods play an important role in determination of compounds influencing the environment and the health of population. Industries release toxic potential compound to water bodies. Environmental pollutants have been directly connected to the increase in human diseases, particularly those involved with the immune system. The contribution of hydroquinone and its metabolites to this issue making a public health problem. The main aim of the analysis is to serve the human to make them free from potential illness. Determination of HQ is important in various field of research, particularly in the soil, air and waste water. Therefore, it becomes essential to detect the trace of HQ in waste water. Previousily, various analytical methods have been developed using different type of modified electrode to detect HQ.

It is still difficult to determine HQ directly at unmodified electrode due to the slowness of the redox process leads to high potential at the electrode. Therefore, this problem is solved by modifying the electrodes suitable materials using various modification methods.

In this study, we tried to develop a simple voltammetric method for the determination of HQ at MCPE electrodes. The oxidation of HQ was studied at different electrodes. Hence, this study may answer the following questions;

i. Which electrode can give higher sensitivity for the determination of HQ?

ii. What will be the responsible reason for having a different response of electrodes?

1.2. Objective of the study

1.2.1. General Objective

- ✓ To develop an effective voltammetric method for the determination of HQ at PMG-CPE from graphite and activated carbon from kororima husk.

1.2.2. Specific objectives

❖ To investigate the electrochemical behavior of HQ at UCPE and PMG-CPE electrodes

❖ To optimize analytical parameters for the determination of HQ.

❖ To determine HQ under optimized conditions at the PMG-CPE electrode.

1.3. Significance of the study

The previous analytical techniques for the determination of HQ were relatively time consuming, lack sensitivity and require expensive instruments. Developing a less expensive analytical method is important. Hence this work has the following significance;

- To develop a simple electrochemical determination method for HQ using poly (malachite green) modified carbon paste electrode prepared from graphite and activated carbon from kororima husk.
- It serves as baseline information and as reference materials for those who want to study HQ.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Dye Electro polymerization

Dyes electro polymerization is used for electro analytical and energy conversion purposes over carbon materials **[**27]. Their polymerization potential and the electro analytical affinity of their polymers will strongly depends on their chemical composition. The majority of dye polymers assist proton transference in electro analytic, their efficacy for this purpose will be different [28].

2.1.1. Poly (neutral red)

Poly neutral red is a polyaniline derivative. Polyaniline and its derivatives have attracted much attention for both the theoretical reasons and potential application in sensors, reachargable batteries and potential applications in electronic devices. Due to its conjugative ring structure, phenazine may be a promising block for building high quality conducting polymer. In fact, the electrochemical oxidation of phenazine neutral red, an aniline derivative, has been studied extensively in weak acidic, neutral and basic solutions. The poly (neutral red) film produces useful electrode transfer mediators and it is immobilization of enzymes. This polymer also exhibits electrocatalytic activity, for example Electro-oxidation of NADH [29], and electro-reduction of NO_2^-, IO_3^- and BrO_3^-, and also for the development of new biosensors for glucose and pyruvates [30].

2.1.2. Poly (aniline)

Polyaniline has been known and studied extensively since the 1980s [31], Polyaniline is synthesized by electrochemical polymerization in a medium of proton acid of small molecular size,such as HCl or H_2SO_4 via a radical cation Mechanism [31] from its monomer aniline. The interest of this material and its derivatives is mainly due to its interesting electrical and optical properties together with its chemical tenability, ease of derivatization, solubility in a variety of solvents, processability into fibers and films, and its stability [32].

2.1.4. 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, has been under study

of nearly 60 years. Karaykinet al.found that an electro active surface layer was formed at high positive potentials only in neutral and basic solution [33]. This is in contrast with the electro polymerization 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 [34]. These unique properties of methylene blue electro polymerization and the structure of the monomer molecule allowed one to expect poly (methylene blue) as one of representative of a new group of electro active polymer [35].

2.1.5. Prussian blue

Prussian blue is the historical name of an ancient pigment that today is recognized as belonging to a very important family of functional inorganic materials: the transition metal hexacynoferrates. Prussian blue 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 method introduced by Neff and co-workers allowed the first straight forward formation of Prussian blue films [36]. There exist two well-known forms of the PB crystal: the so called"insoluble" Prussian blue with the formula $FeIII_4[FeII(CN)_6]_3$ and the "soluble" $KFeIII[FeII(II(CN)_6]$. In truth, both forms are completely insoluble in water and most common solvents [37]. Prussian blue has been used in the electro catalytic 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 process that can or cannot be electrocatalysed by an electrode modified by Prussian blue [38].

2.1.6. Poly(malachite green)

MG 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 [39]. Poly (malachite green) can be generated by electrochemical polymerization of malachite green, the chemical structure of

which is illustrated in Figure-2. Malachite green has an open 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 [40].

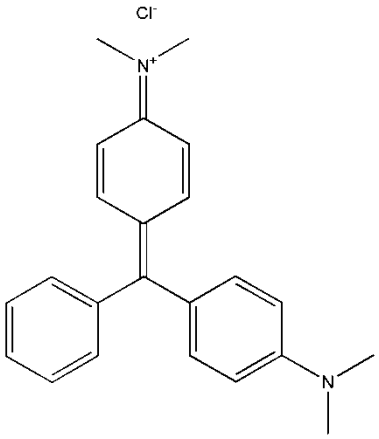


Figure 2. Chemical structure of MG

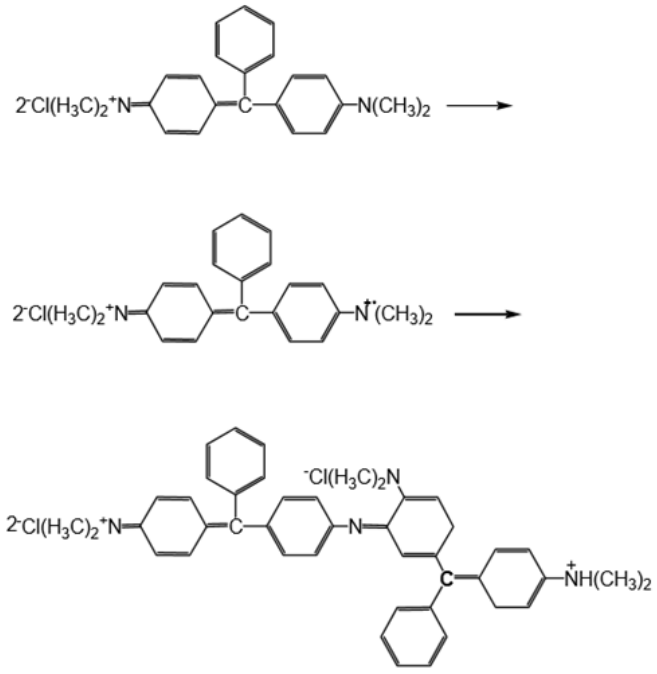


Figure 3. Possible formation of poly(malachite green)

2.2. Method of Analysis of HQ

For determining the concentration of HQ in a system, a number of analytical ways are being applied. These are potentiometric titration, oxidometric titration, iodometric titration,

Calorimetric titration, Paper Chromatography, High liquid performance Chromatography, Spectrophotometric method, Chemilunescene method and Electrochemical method.

2.2.1. Potentiometric titration

Since potentiometric titration simplifies and speeds up routine analyses and minimizes the human error involved in judging color changes at the end of titration, it has been used to analyze photographic developer solution [41,42] and rubber antioxidant [43] for HQ. Two extractions with ethyl acetate are necessary to obtain the maximum amount (99.4%) of HQ from the developer solution [44]. The analysis requires a minimum amount of equipment, but the determination of HQ in the organic solvent after extraction is difficult and time consuming.

2.2.2. Oxidimetric titration

Kolthoff and Lee [45] analyzed pure hydroquinone solution, and Brunner et al [46] determined the HQ content in color film developers, by oxidimetric titration. They used sulfate in the presence of ortho-phenanthroline-ferrous sulfate complex (ferroin) as an indicator. This indicator made the titration simpler and faster than the potentiometric titration procedure described by Stott [47] because the color change was easily discernible. The determination of HQ in color film developers was 99.5 ± 1.5% accurate [48]. Oxidimetric titration of HQ was 99.98% accurate [49].

2.2.3. Iodometric titration

Baumbach [50] reported a single methyl acetate extraction method involving potentiometric titration of Metol (methyl-para-aminophenol sulfate) followed by oxidation of both Metol and HQ with iodine. Molecular HQ and Metol were extracted from the photographic developer solution at pH 8.0-8.5 with methyl acetate. The extract was dissolved directly in water; then it was titrated, first with hydrochloric acid to determine Metol and then with iodine at pH 6.5- 7.0, to determine the sum of Metol and HQ. This procedure produced high extraction coefficients for both HQ and Metol, but quantitative measurements were not presented. This method is time consuming and, in some cases, not sufficiently accurate [51]. Shaner and Sparks [52] modified Baumbach's [51] procedure by using a U-tube extractor and methyl ethyl ketone as a solvent. For HQ analysis, the reproducibility (95.4-97.8%) and error (1.6-4.0%) of this method were quite adequate. However, it was difficult to determine the end point of titration when using these methods [51,53].

2.2.4. Calorimetric determination

Oglesby et al [51] analyzed airborne quinone and HQ samples by a colorimetric procedure based on comparing, at 520 nm, the yellow color developed by mixing the sample with phloroglucinol in potassium hydroxide with that of standards. Concentrations of airborne quinone vapor measured by this method ranged from 0.01 to 3.2 ppm (about 0.04-12.8 mg/cu m), and those of hydroquinone dust ranged from less than 1.0 to 35 mg/cu m. The sensitivity of this method is as low as 0.1 /ug/ml of solution, with good reproducibility between 0.1 and 2.0 mg/cu m, but it cannot distinguish quinone from HQ. Whettem [54] used sodium tungstate as the reagent for colorimetric determination of HQ in 1 ml of styrene. Two milliliters of a sodium phosphotungstate solution and 4 ml of a sodium carbonate solution were added to the sample and standards, and the solutions were mixed well after each reagent was added. After 15 minutes, the color of the sample was compared with that of the standards. This method is sensitive to 0.01 mg of HQ in 1 ml of styrene, or to 10 mg/liter. It can be made to detect 1 mg/liter by extracting 10 ml of styrene instead of 1 ml with water [55].

2.2.5. Paper chromatography

Woodard [15] analyzed HQ by measuring absorption at 294 nm. Quantities of HQ as low as 0.005 mg/ml of solution were determined easily by this method. Borecky [56] reported a paper chromatographic method for separating and identifying 16 substances, including HQ, that are used as developing agents in various commercial photographic developing mixtures. The substances were separated by paper chromatography using various solvent systems. This method [57] had several disadvantages. The separation of the individual substances was indistinct. Occasionally, some decomposed during the chromatographic procedure. The working range over which this method is valid and its specificity and sensitivity for detecting HQ at the environmental limit were not stated. National Institute for Occupational Safety and Health recently validated an analytical method that can be used to measure hydroquinone aerosol [58].

2.2.6. High-pressure liquid chromatography method

Hydroquinone be sampled by collection through a mixed cellulose ester membrane filter and analyzed by high pressure liquid chromatography. Sampling involves the collection of personal samples of hydroquinone aerosol on mixed cellulose ester membrane filters. Analysis involves

extraction with 1% acetic acid and measurement with a high pressure liquid chromatography equipped with a variable wavelength UV detector set at 290 nm [59].

This chromatographic method is complicated and generally takes quite a long time for a single analysis because of extra steps for pretreatment and separation before the signal detection [9]. Optical methods usually require an additional reagent for the signal generation. Therefore, it is not preferable for simultaneous detection of such reagent, even though they are generally very sensitive for an individual detection. However, gas chromatography and high performance liquid chromatography involve costly, sophisticated instruments and skilled staff alongside the usage of extra-pure and large volume of organic solvents; hence ,they are inappropriate for routine field analysis [9, 60-62] .

2.2.7. Spectrophotometric determination

The spectrophotometric determinations of HQ in cosmetic products were based on direct measurement of UV absorbance of HQ, UV derivative spectrometry, spectrometric ratio difference method, the successive ratio subtraction coupled with constant multiplication UV spectrometry, Fluorescence spectroscopy, or the absorbance measurements after its oxidation to p-benzoquinone(BQ) by oxygen in presence of ammonium meta-vanadate as an oxidizing catalyst [6]. The catalytic oxidation of HQ to BQ by $KMnO_4$ was also used for the spectrometric determination of HQ [7]. Ammoniummolybdate (Mo(VI) was used to oxidize HQ in acidic medium and the resulting molybdenum(V) was spectrometrically monitorized [63]. The inhibitor effect of HQ on oxidation of an organic reagent (RhodamineB) was used for HQ determination by a kinetic spectrophotometric method. UV spectrophotometric investigation of the HQ polymerization in the presence of Cr(VI) were also recently reported [63]. In the determination of HQ via spectrophotometric technique, the presence of correlated compound interferes the result.

2.2.8. Chemilunescene method

Is analytical technique that can be used in the determination of different compound in various fields. In recent years, it has received much attention, especially with flow injection (FIA), due to its high sensitivity, wide linear range and simple instrumentation. And some Chemiluminscene method have been developed for the detection of HQ and Catechol. He et al.[11] have proposed a Chemiluminescene method based on enhancing effect of polyhydroxy phenol on Fe^{3+},H_2 O_2,

Rh_6G system. Du et al [64] have developed another method for determination of pyrogallol, phloglucinol, HQ and resorcinol based ferricyanide-enhanced luminopolphenol.

2.2.9. Electrochemical method

The development of electrochemical sensors is conducted through the surface of working electrode [12]. Electrochemical method is preffered due to for both organic and inorganic species, a large numbers of useful solvents and electrolytes, wide range of temperature, rapid analysis time, simultaneous determination of several analytes, the ability to determine kinetics and mechanistic parameters, a well developed theory and the ability to reasonably estimate the value of unknown parameters and the case with which different potential unknown form can be generated and small currents measured. Low cost of the method is another benefit. Eelectrochemical methods that lead to an electrochemical sensor for HQ have gained attention due to their cost effectiveness, easy handling, rapid response, stability, high sensitivity, high selectivity, a wider detection range, and a lower limit of detection (LOD) makes the electrochemical method a promising analytical approach for the detection of pollutants [65,66].

2.3 .Types of electrochemical sensors

Electrochemical sensors can be divided into three types based on their nature and working principle. These are potentiometric, conductometric and amperometric sensors. Here we briefly discuss all types but will focus more on amperometric sensors as this study is related to the amperometric sensing of HQ.

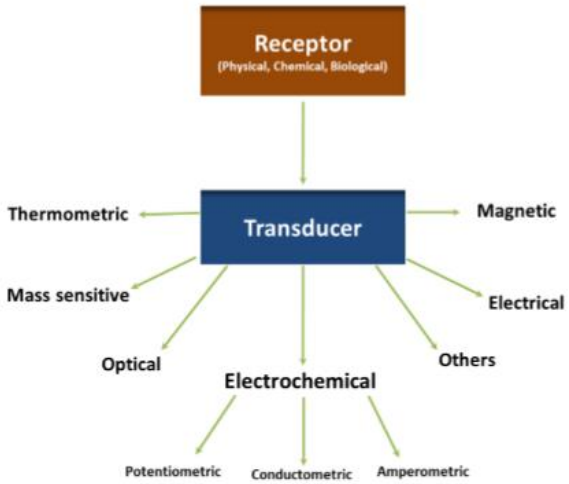


Figure 4. Different class of chemical sensor

2.3.1. Potentiometric sensors

As the name suggests, potentiometric sensors measure the potential difference between a sample solution and a reference solution with the help of a reference electrode and an indicator electrode. The two solutions are separated by a membrane m which contains an ionophore that is selective to target ion. The Nernst equation provides the relationship between potential difference and target ion activity.

$$E = E_0 + \frac{RT}{ZF}\ln \frac{a^s}{a^m} \quad \ldots\ldots\ldots\ldots\ldots\ldots \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ldots.. \; 1$$

Where E_0 is the standard potential of sensor electrode, F is Faraday's constant, T is absolute temperature, R is universal gas constant, z is valency of ion and a is the target ion activity **[**67**].** Potentiometric sensors have been widely used since 1930's due to their simplicity and ease of use. There are three main types of potentiometric devices used which include ion- selective electrodes (ISE), coated wire electrodes (CWES) and field effect transistors (FETS) **[**68]. The ion-selective electrode measures the activity of particular ionic species in the surrounding solution. The principle of ISE devices is based on permselective, ion conducting membrane which separates the electrode from outside solution. The composition of membrane is very important for producing the ISE for particular ionic species. In working principle of ISE, the reference electrode potential is kept constant while the potential of working electrode is determined by the surrounding environment. The change in working electrode potential or potential difference is considered as the concentration of the target ion [69**]** pH electrode is the best and most widely used example of potentiometric sensor, the success of this electrode lays in its robust nature, easy handling, reproducibility, wide range of application and cost effectiveness [68**].** Bakker and Pretsch discussed in detail the breakthrough developments in nanoscale potentiometry, limit of detection and sensor stability [70].

2.3.2. Conductometric sensors

Conductometric sensors are based on the principle of providing sensory information as a result of changes in the electrical conductivity of material (used in construction of sensing device) which is in contact with the analyte. Conductometric sensors are basically non selective but as a result of more precise miniaturization and surface modification, selectivity can be improved. Conductometric sensors do not require reference electrode for functioning and hence reduce the

cost as well as make these sensors simpler for use. Reports for different kind of thin films modifications are available in literature mainly for the detection of gases. Examples of these thin film modified conductometric sensors include, Copper doped oxides are used for the detection of H_2S,[70] CH4 detection done by using Ga_2O_3 semiconductor films,[71] Modification by conductive polymers such as polypyrole for volatile amine detection,[72]**.** CdS films modification for the detection of oxygen [73]**.** and modification by $MnWO_4$ films to be used as humidity sensors [74].

2.3.3. Amperometric sensors

In amperometric sensing, the current is measured as a result of an electron transfer reaction while the potential is controlled with a potentiostat. The potential can be kept constant (potentiostatic detection) or it can be scanned between two values (potentiodynamic detection). The principle is based on the electron transfer between the analyte and working electrode. The basic instrumentation for amperometric sensing includes a potentiostat and three electrodes (working, reference and counter) dipped in a suitable electrolyte to form an electrochemical cell. The auxiliary or counter electrode is made up of an inert conducting material such as graphite, platinum, stainless steel etc. In amperometric sensing the electron transfer reaction takes place at the surface of working electrode. The reference electrode provides a reference potential to working and counter electrode [68**].**

2.4. Electrochemical techniques

2.4.1. Cyclic Voltammetry

Cyclic Voltammetry (CV) is a reversal technique and is a potential scan equivalent of double potential step chronoamperometry. CV has become a very popular technique for initial electrochemical studies of new systems and has proved very useful in obtaining information about fairly complicated electrode reaction [9]. CV was used both to polymerize the monomer and to characterize the resultant polymer electrochemically. The method consists basically of measuring the current resulting from an applied triangular potential wave form.

The potential is cycled within a given potential range at constant rate and the current is measured as a function of the potential. The rate can vary from less than 1mV/s to several hundred V/s. When high potential is applied at an electrode surface to cause oxidation and

reduction of species in solution, a current rises due to the depletion of the species in the vicinity of the electrode surface. As a consequence, a concentration gradient appears in the solution [74]. The current I is proportional to the gradient slope imposed ($i \propto dc/dx$). In the case of CV, however, the potential does not stay constant. It rises at a constant rate until it reaches a chosen maximum immediately after imposition of the potential, as the potential is not immediately great enough to give rise to any reaction. It then continues to rise rapidly as the surface concentration of the species become smaller and smaller (the concentration gradient increases) [75].

2.4.1. Linear Swept Voltammetry

LSV is the simplest voltammetric technique [76]. In LSV the current at a working electrode is measured while the potential between the working electrode and a reference electrode is scanned from a lower limit to an upper limit linearly in time [77]. Oxidation or reduction of species is registered as a peak or trough in the current signal at the potential at which the species begins to be oxidized or reduced. The characteristics of the linear sweep voltammogram recorded depend on several factors including the rate of the electron transfer reaction(s), chemical reactivity of the electro active species, and voltage scan rate [75].

2.5. Working electrodes

The working electrode carries out the electrochemical event of interest. The most important aspect of the working electrode is that it is composed of redox-inert material in the potential range of interest. It is the place where oxidation or reduction of analytes occurs. The working electrode is the electrode where the potential is controlled and where the current is measured. Depending on whether the reaction on the electrode is a reduction or an oxidation, the working electrode is called cathode or anode, respectively. It is an inert material such as gold, platinum or inert carbon such as glassy carbon and mercury drop and film electrodes. Chemically modified electrodes are also used for the analysis of both organic and inorganic samples [75].

2.5 .1.Types of working electrodes

Working electrode is an important entity in electrochemical device, as the reaction of interest takes place on working electrode. As a general rule there are some characteristics which a working electrode should possess for its consideration as a suitable candidate in electrochemical analysis, these include inert nature, low background current over a wide potential window, cost and high rate of reproducibility. In addition to these properties composition and geometry of

working electrode also play a major role in electro analytical applications. There are many types of working electrodes available and this list is continuously increasing. Commonly used working electrodes are made from conducting materials such as platinum, silver, gold, carbon and mercury. Size and shape of working electrode also varies depending on application. Here we will discuss major types of electrodes which are or were important for environmental analysis by electro analytical techniques.

2.5.1.1. Mercury electrodes

Mercury electrodes have attractive electrochemical properties which make them a good choice for use in electroanalytical applications (yielding low limits of detection and high selectivity). However the use of mercury electrodes has become obsolete due to many disadvantages attributed mainly to Hg toxicity. They are also unsuitable for on-site and flowing applications, for the study of oxidation of organic compounds [78]. There are three main types of mercury electrodes with wide spread use in previous years for electro analytical applications which include dropping mercury electrode, hanging mercury drop electrode and mercury film electrodes. Dropping mercury electrode was the first mercury electrode developed for environmental and electro analytical applications, in particular for reduction studies of organic compounds.

2.5.1.2. Solid electrodes

Concerns regarding the toxicity of mercury and limited anodic potential range led to increased use of solid electrodes for electroanalytical applications. Solid electrodes advantageous in different analytical applications which were not possible with mercury electrodes.[79]. The most important is their non-toxic nature and ease of handling, on-site electroanalytical applications and possibility of surface modifications. The behaviour of voltammetric device is strongly influenced by the nature of working electrode.

2.5.1.3. Metal and metal oxides based electrodes

Metal based electrodes have widespread use in electroanalytical applications, such as gold, silver, platinum, palladium, copper and metal oxides films such as Indium tin oxide (ITO), Fluorine-doped tin oxide (FTO). Advantages associated with metal electrodes are their inert nature, good conductivity, fairly broad potential window, low background current, reproducibility and suitability for sensing applications. Few disadvantages include low

overvoltage for hydrogen evolution, limited range in cathodic potential domain as compared to mercury and dissolution of metals to form metal oxide layers during aqueous reactions. The formation of oxide layers during an analysis can seriously hamper the validity of analysis, also it is difficult to explain how these electrode materials will interact with the analyte during preconcentration for stripping analysis [80]. ITO and FTO are made up of transparent metal oxide films and have applications in sensing and optical measurements. Platinum and gold are among the most widely used metal electrodes; both these electrodes provide fairly broad potential range, although in cathodic domain they are much inferior than mercury electrodes while at high anodic potential values they undergo oxide formation in aqueous solutions resulting in poor reproducibility as well as slow electron transfer reactions [81].

2.5.1.4. Carbon based electrodes

Carbon based electrodes have been extensively used in electrochemical applications including sensing and electroanalysis. Characteristics such as inert nature, large potential window, rich surface chemistry and resistance to corrosion make carbon based electrodes a superior choice for electrochemists [82]. However a disadvantage which is usually associated to carbon based electrodes is slow electron transfer reactions as compared to the metallic counterparts.

There are few basic electrochemical characteristics attributed to carbon based electrodes, which depend on the composition of electrodes as well as procedure used to make them. These include background current, electron transfer rates, reproducibility and adsorption [83]. Adsorption can sometimes be beneficial or it can seriously hamper the output of analysis, for desired applications adsorption can greatly enhance the response of target analyte, whereas unwanted analytes can also adsorb on electrode leading to behaviour which is not in accordance with diffusion controlled processes and cause of electrode surface fouling as well [77]. On the basis of structure and composition, carbon based electrodes can be divided into two categories (i) Homogenous and (ii) Heterogeneous. Homogenous electrodes are composed of solely single carbon compound e.g. glassy carbon, carbon nanotubes, graphite while heterogeneous have another substance incorporated with carbon compound e.g. carbon paste and screen printed electrodes [80].

In this study we used carbon paste electrode as working electrode due to its rich surface chemistry, inert nature and resistance to chemicals, hardness and compact nature, possibility of

modifications, surface renewal, sensitivity and applicability for sensing applications as compared to other electrode materials.

2.6. Modified electrodes

Chemically modified electrodes (CMEs) found their applications in different electrochemical applications such as sensing, energy conversion, optical and electronics. Modification of electrode materials is carried out usually by adsorption or covalent attachment to form a layer of modifier which imparts properties of interest to the underlying electrode surface [84]. Different approaches used for chemical modification of electrode surfaces include:

2.6.1. Chemisorptions

These modifications are based on adsorption process on the electrode surface. Self-assembled monolayers (SAMs) are formed by this method.

2.6.2. Covalent bonding

Organosilane are covalently attached to electrode surface to form a strong interaction, these modifications can also be performed by electrografting. In next step, these covalently bonded silane molecules can be used as linking agent for strong adhesion of modifier having properties of interest to form a thin film.

2.6.3. Composite

Chemical modifier is directly incorporated in electrode matrix to give it properties of interest, such as modified carbon paste electrodes in which a modifier is also used in addition to graphite and binder for formation of electrode.

2.6.4. Polymer films

Organic, organometallic or inorganic polymer films are deposited at electrode surface by having chemical interaction or physical attachment. Polymer films can be conductive or non-conductive in nature, these films deposited at electrode surface may have chemical modifier already incorporated inside them or may be introduced later by technique known as functionalization [85]. Polymer films can be formed by dip coating with film thickness of 0.1 - 10 µm, spin coating, electrochemical deposition and polymerization [86].

2.7. Methods of Modification

One of the merits of chemically modified carbon paste electrodes is their ability to be easily fabricated. Some of principal routes to modify carbon paste electrodes include:

2.7.1. Direct Mixing

This method is most commonly used for preparing chemically modified carbon paste electrodes. The unique advantage of this approach is pronounced ease of modification, most simply done by admixing of a reagent (modifier) to the paste [87]. In order to obtain reproducible and comparable results, the concentration of the modifier on the electrode surface must be similar in analogous experiments. For this reason thorough mixing of the two solid phases is essential to ensure that the same amount of modifier is always exposed to the analyte solution.

2.7.2. Electrode Coating

The basal plane of the carbon electrode is cleaned and polished. Then, the electrode coating modifier dissolved in a suitable solvent is transferred on the exposed area of the electrode and allowed to dry [88]. While this method is simple, it is difficult to control the amount of material that ends up on the electrode surface. Hence, spin coating is mostly used to yield uniform film thickness [89].

CHAPTER THREE

3.1. MATERIALS AND METHODS

3.1.1. Apparatus /Instrument

A three-electrode, consisting of unmodified carbon paste and modified carbon paste as the working electrode, a platinum wire as a counter electrode, and Ag/AgCl electrode as a reference electrode. Electrochemical techniques were performed using Epsilon EC-Ver 1.40.67 voltammetry analyzer (Bioanalytical Systems, USA). pH meter (pH -016 pH METER, China), analytical balance (WANT Balance Instrument Co., Ltd, China), and magnetic stirrer were also used.

3.1.2. Chemicals

Malachite green ($C_{23}H_{25}ClN_2$,99%(UK) , Hydroquinone ($C_6H_4(OH)_2$, 99%(UK)), Sodium Nitrate ($NaNO_3$, 99.5%, Germany), potassium hydrogen phosphate (K_2HPO4 98% ,Finkem, India), Potassium dihydrogen phosphate (KH_2PO4, 98%, Finkem, India), Sodium hydroxide (NaOH, 90% BDH, England), Hydrochloric acid (HCl, 37% Riedel-deHaen, Germany) were used. Distilled water was used during experimental work.

3.1.3. Preparation of the carbon paste electrodes

The carbon paste electrode was prepared from activated carbon prepared from kororima husk and graphite powder by the following composition.

Graphite powder, activated carbon paste prepared from kororima husk and paraffin oil was homogeneously mixed for 20 min until a uniform paste was formed.

The homogenized paste was packed at the tip of Teflon tube and kept at room temperature for the 24 hrs. For electrical contact a copper wire was placed in the tip of the Teflon tube. Finally, the surface of the assembled CPE was smoothed on a clean smooth weighing paper.

Table 1. The composition of CPE tested

No	Composition (%w/w)		
	Kororima husk activated carbon	**Graphite powder**	**Paraffin oil**
1	0	80	20
2	10	70	20
3	15	65	20
4	20	60	20
5	25	55	20
6	30	50	20

3.1.4. Preparation of Poly (malachite green) modified carbon paste electrode.

Poly (malachite green) modified carbon paste electrode was prepared as follows. The carbon paste electrode was immersed in a cell containing 10.0 mM MG aqueous solution containing 0.5 M $NaNO_3$ and 0.025 M PBS (pH 6) and scanning the potential in the range of -1.4 V to 1.8 V scan cycles at scan rate of 100 mVs^{-1} using the CV technique.

Then the electrode was removed from the monomer solution and rinsed with distilled water. The electrode was then dipped in 0.1 M PBS at optimum pH for hydroquinone detection.

3.1.5. Standard Solution Preparation

A stock solution of 100 µM was prepared by dissolving 1.101 g of HQ in 100 mL of 0.1 M PBS at an optimum pH solution. From the stock solution, working solutions of various concentrations were prepared through serial dilution using PBS at optimum pH each day.

Stock solution of 0.1 M MG was prepared by dissolving 4.64 g of MG in 50 mL of a solution containing 0.5 M $NaNO_3$ and 0.025 M PBS (pH 6) buffer solution. From this stock solution working solution was prepared.

3.1.6. Buffer preparation

Supporting electrolyte of 0.1 M of PBS in pH range 2.0 – 8.0 was prepared from 0.1 M KH_2PO_4 and 0.1 M K_2HPO_4 in distilled water in 100 mL volumetric flask. 0.1 M NaOH and 0.1 M HCl

Solutions were used to adjust the pH of the buffer solution. Distilled water was used to prepare all aqueous electrolyte solutions throughout the analysis.

3.1.7. Procedure of Repeatability of PMG-CPE

For the repeatability study, the PMG-CPE was prepared and the concentration of HQ was measured three times in one day at PMG-CPE. Then, the %RSD of the readings was calculated to evaluate the repeatability of the measurements.

3.1.8. Procedures of Real Sample Preparation

Waste water was taken from Main campus of Jimma University. The waste water was filtered and the pH was adjusted at pH 5. Finally, 5 µL of waste water sample solutions was prepared. Triplicate of LSV was measured and the mean values was recorded. Also two different solutions of HQ was prepared by mixing 5 µL of waste water sample solution with 0 µM, 10 µM and 20 µM standards of HQ and the % recovery was calculated. Then electrochemical measurements was performed at the PMG-CPE. The recovery was also studied based on the formula in (equation). All samples and experiments was conducted at room temperature.

$$\%\text{Recovery} = \frac{Concentration\ of\ spiked - concentration\ of\ unspiked}{Concentration\ of\ added\ amount}\ X\ 100 \ldots\ldots\ldots\ldots\ldots\ldots.2$$

3.1.9. Optimization of pH

The effect of pH on the voltammetric determination HQ at the PMG-CPE electrode was studied. 100 µM of HQ was prepared in 0.1 M PBS with different pH values using CV with a scan rate of 100 mVs^{-1} and the oxidation currents of HQ were measured. The pH with the highest oxidation peak current was chosen for the subsequent electrochemical measurements.

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1. Electro polymerization of Malachite Green

As seen from Figure 5, one anodic peak at 1.5 V and cathodic peak at -0.4 V were noticed. The peak currents of this wave enlarged with increase cycling numbers although with a little shift of peak potentials. From the CVs of electro polymerization of MG solution, the peak at around -0.65 V indicates the reduction of the poly MG film formed at the surface of the carbon paste electrode. Similarly the peak at around 1.15 V is responsible for the oxidation of MG monomer. The increase in both peak 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 electro polymerization of MG is most probably due to two superposition processes. This was oxidation reaction of the monomer and poly MG film.

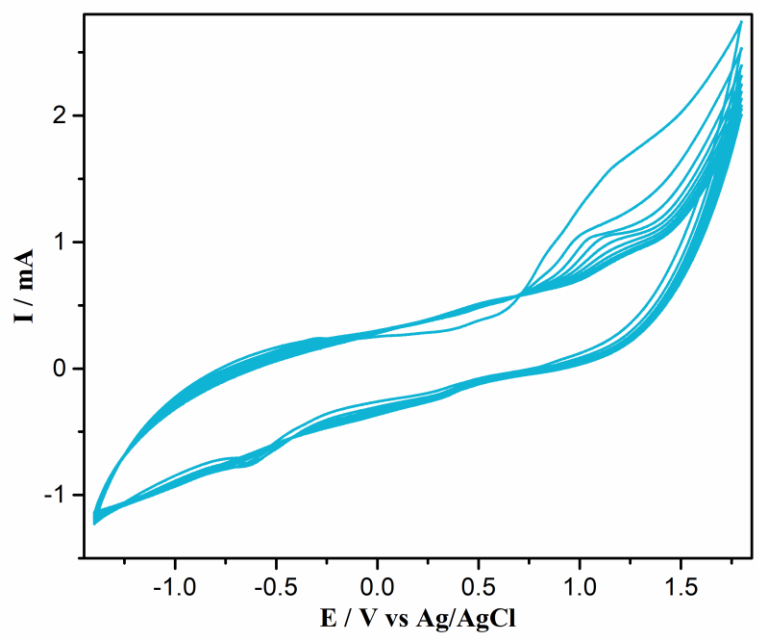


Figure 5. Cyclic voltammograms of the electro polymerization of 10 mM MG (scan rate: 0.1 Vs^{-1}; number of scans: 20).

4.2. Electrochemical Behavior of HQ, Blank buffer at UCPE and PMG-CPE

CV was used to examine the electrochemical properties of the UCPE and PMG-CPE in the presence and absence of HQ using CV in PBS pH 5. As shown in Figure 6, there was no redox

peak observed at UCPE and PMG-CPE in the absence of HQ also there was no redox peak observed at UCPE in the presence of HQ. Whereas the CV recorded at PMG-CPE in HQ showed two peaks at potential of about 0.35 V and 0.15 V. This was corresponding to its oxidation and reduction respectively. The presence of Poly(MG) modified electrochemical sensors have been reported to exhibit interesting enhancement in the electro catalytic activity towards the oxidation and reduction of selected electro active species, which caused an increase in response to HQ [*25*].

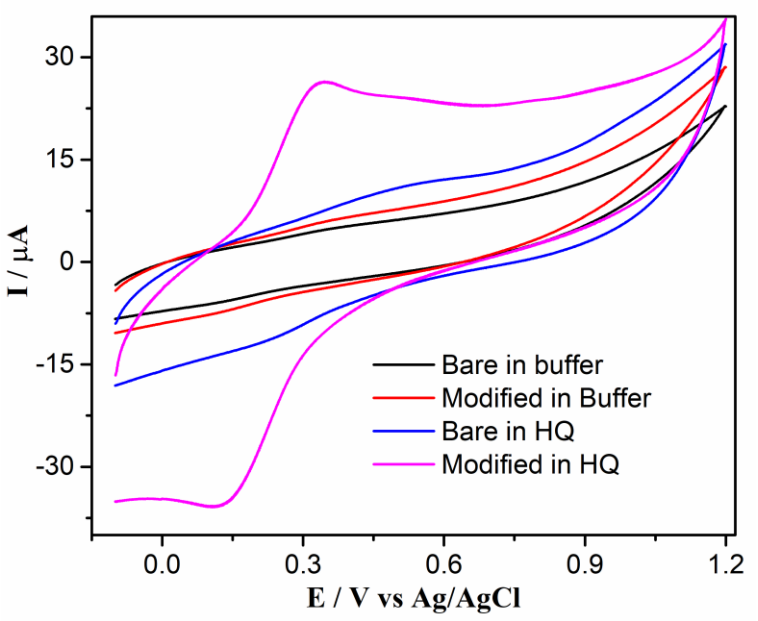


Figure 6. Cyclic voltammograms of UCPE and modified CPE in pH 5 PBS in the absence and presence of 10 µM Hydroquinone at a scan rate of 100 mV s^{-1}.

4.3. Optimization of Parameters for Determination of HQ

4.3.1. Effect of pH on determining the HQ

The pH of the supporting electrolyte is an important parameter that could have a significant influence on the response of the electrode in electro-analysis [52]. The influence of the PBS pH value on the HQ response at PMG-CPE was studied in a range of pH of 2.0-8.0. The Variation of pH value influenced the electro catalytic oxidation of HQ (10 µM) at PMG-CPE by influencing both peak current and redox peak potential, which was confirmed in Figure 7. It shows that the oxidation peak current of HQ increase significantly at the varying pH from 2.0 to 5.0. This are

due to protonation phenomena of HQ during oxidation reaction. This is improved with increasing pH until it reaches its maximum at pH 5.0. The peak current gradually decreased from 5.0-8.0. After pH 5.0, the current begins to decrease which may be due to the repulsive interaction between the negatively charged electrode surfaces and HQ. At the higher pH Value, the proton in solution was decreased therefore figuring out the electrochemical reaction was more difficult since it hinders the redox process. The decreasing peak current result from a decrease of the concentration of proton in the solution [3-4, 11, 17-19]. As a result, pH 5.0 was selected to detect the HQ concentration.

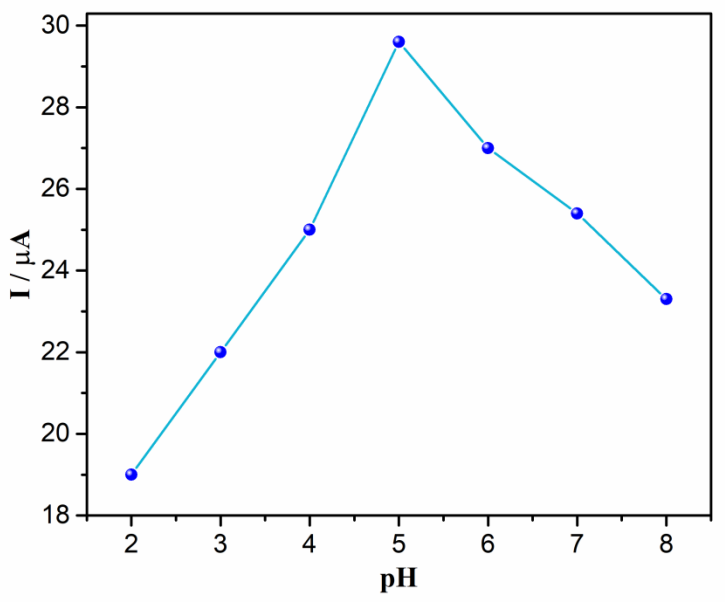
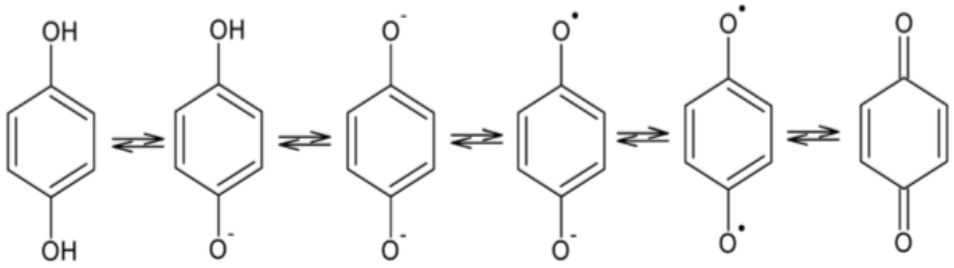


Figure 7. Effect of pH

Hydroquinone was oxidized to 1,4-Benzoquinone by a participation of two electron-two proton process according to the following mechanism.



Hydroquinone 1,4-Benzoquinone

Figure 8. Electrochemical oxidation pathway for HQ

4.3.2. Effect of scan rate on the peak current of HQ

The scan rate of the experiment controls how fast the applied potential is scanned. It shows the reaction process at the electrode surface was either diffusion or not. The effect of scan rate on the electrochemical behavior of HQ was also investigated at different scan rates. A positive shifts of the peak potentials increases as oxidation peak current increases with an increase in scan rate. The interaction between the electrode and the HQ was explored through the influence of the scan rate. The CV of 10 µM HQ at pH 5.0 PBS media using PMG-CPE was evaluated for the variance of the scan rate. Figure -8, displays the effect of the scan rate on the oxidation-reduction current of HQ at PMG-CPE. When the scan rate increased from 10 to 200 mV/s, the oxidation–reduction peak currents gradually increased and the peak currents was shown to rise linearly with the square root of the scan rate implying that the electrochemical process is diffusion controlled process [54].

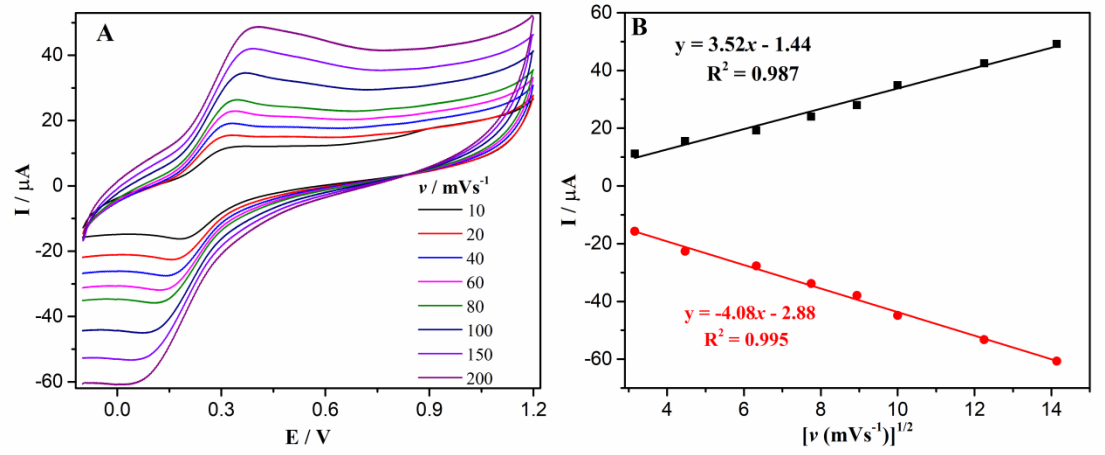


Figure 9. (A) Cyclic voltammograms for HQ in PBS (pH 5) at PMG-CPE with different scan rates: 10, 20, 40, 60, 80, 100, 150, and 200 mVs^{-1}; (B) the plots of the linear relationship between peak currents *vs*. square root of scan rate**.**

4.3.3. Effects of composition of activated carbon from kororima husk and Graphite powder

The amount of graphite powder and the activated carbon from kororima husk in the modified CPE on the voltammetric response of HQ was studied by changing the amount of graphite powder and activated carbon from kororima husk. As presented in Figure 9, the maximum oxidation-reduction peak was observed at 15% (w/w) composition of kororima husk activated carbon in the carbon paste. The peak current decreased when the amount of kororima husk

activated carbon is higher than 15% (w/w). The decrease in peak current of the electrode is because of the reduction of the electric conductivity as a result of decrease in the graphite content in the paste. The best composition for the electrode was found to be 15% (w/w) kororima husk activated carbon, 65% (w/w) graphite powder and 20% (w/w) paraffin oil.

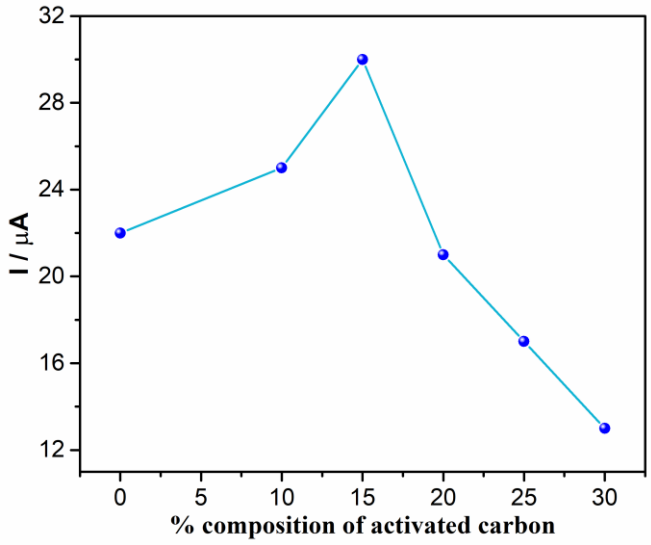


Figure 10. Effects of composition

4.3.4. Effect of analytes vs response relationship

The PMG-CPE electrode exhibited a well-defined peak with reproducible peak current values for repetitive measurements using varying the concentration of HQ. As the concentration of HQ increased, the obtained oxidation peak of current was also increased. The effect of HQ concentration at various HQ concentrations from 1 μM to 75 μM was studied using the LSV technique. The result shows that the oxidation peak current (I) was proportional to the HQ concentration. The obtained linear regression equation for HQ was $I = 2.30C + 0.76$ ($R^2 = 0.996$) . The detection limit was found to be 0.82 μM (3σ/m).

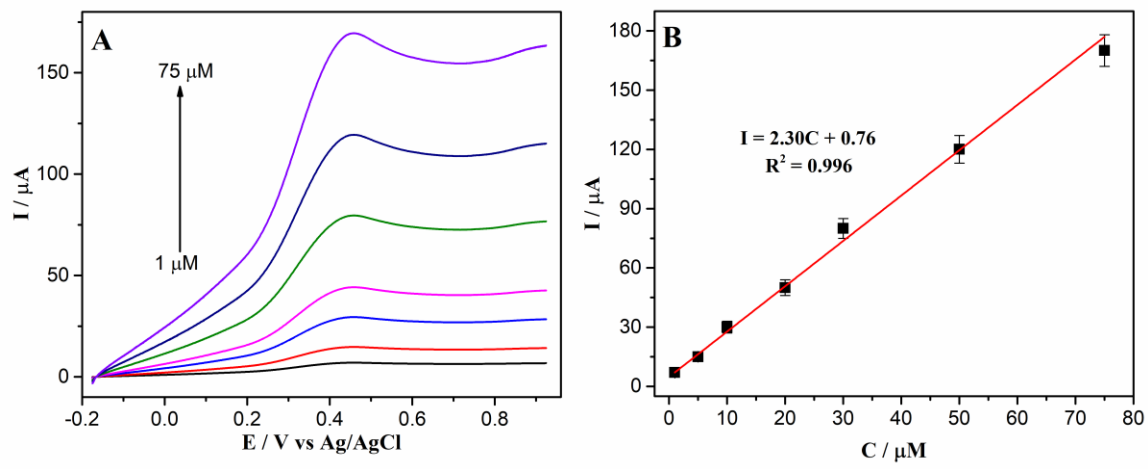


Figure 11. (A) The LSV response for different concentration of HQ at PMG-CPE; (B) Plot of linear calibration curve of HQ at PMG-CPE at a pH 5 (Concentration range: 1 – 75 µM).

4.4. Repeatability of PMG-CPE

The repeatability of PMG-CPE was obtained by estimating the percent relative standard deviation (%RSD) of triplicate determination of a solution of 10 µM HQ. The %RSD were obtained to be 2.4%. This result showed that the repeatability of the PMG-CPE was satisfactory.

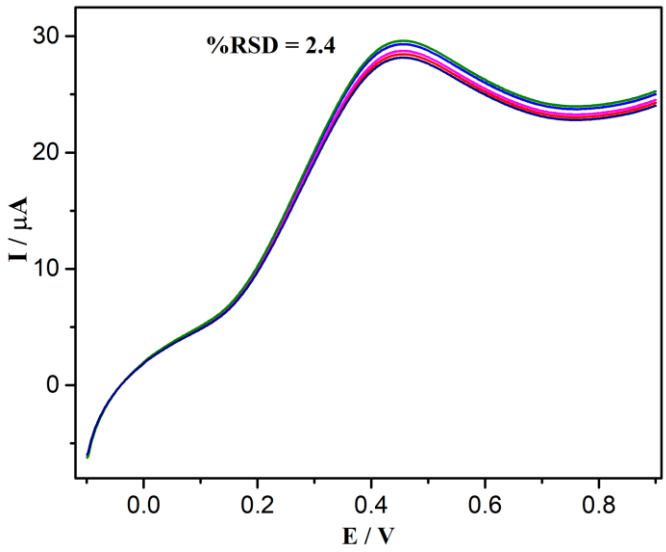


Figure 12. LSV response seven repeated measurement of 10 µM HQ at PMG-CPE.

4.5. Real sample Analysis

For the recovery studies, 5 µL of waste water real samples were transferred into the electrochemical cell. The recovery was performed by spiking two different concentrations of HQ

(0, 10, and 20 μM) to each sample. The resultant current peak of LSV was obtained using the PMG-CPE electrode. Table 2, shows the respective good recovery percentage for the determination of HQ in Waste water sample was in the range of 89 - 111% demonstrating the sensitivity for the detection of HQ from complex sample matrices using an PMG-CPE electrode.

Table 2. The application of CV PMG- CPE for determination of HQ in waste water

Sample	**Spiked (μM)**	**Found (μM)**	**Recovery %**
Waste water	0	ND	-
	10	11.1	111
	20	17.8	89

CHAPTER FIVE

5. Conclusion

In this work, the electrochemical determination of HQ was studied at the PMG-CPE for the first time. Under the optimized experimental conditions, the oxidation peak current of HQ at the PMG-CPE shows a good relationship with the concentration of HQ in the range of 1 μM to 75 μM and a limit of detection of 0.82 μM . The electrode process is diffusion-controlled (hence, the square root of the scan rate has a linear relationship with the current). The method has exhibited very good electro-analytical properties such as high sensitivity, and a lower limit of detection. It was shown that the PMG-CPE enhanced the oxidation peak current of HQ compared with the UCPE. This method was successfully applied to the determination of HQ in Waste water samples. Furthermore, the detection of HQ in waste water was accomplished with acceptable recoveries.

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