JIMMA UNIVERSITY

COLLEGE OF NATURAL SCIENCES

DEPARTMENT OF CHEMISTRY

POLY (AMINO-NAPHTHALENE SULFONIC ACID) AS A LOW COST ELECTRODE MODIFIER FOR ELECTROCHEMICAL SENSING, REACTION KINETICS AND RATE CONSTANT STUDY OF DOPAMINE.

A THESIS SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES, JIMMA UNIVERSITY, DEPARTMENT OF CHEMISTRY, IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTERS OF SCIENCE IN CHEMISTRY (PHYSICAL)

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AUGUST, 2024

JIMMA, ETHIOPIA

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MSc THESIS APPROVAL SHEET

We, the undersigned, member of the Board of Examiners of the final open defense by **Muluken Ayele** have read and evaluated his/her thesis entitled "**Poly (Amino-Naphthalene Sulfonic Acid) as a Low Cost Electrode Modifier for Electrochemical Sensing, Reaction Kinetics and Rate Constant Study of Dopamine**" 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 **PHYSICAL CHEMISTRY.**

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List of abbreviations and acronyms

AMP: Amperiometry

ANSA: Aminonaphtalene Sulfonic acid

ASDPV: Adsorptive stripping differential pulse voltammetry

CA: Chronoamperiometry

CV: Cyclic voltammetry

CE$_S$: Capillary electrophoresis

DA: Dopamine

DPV: Differential pulse voltammetry

EOPGE: Electro chemical over oxidized pencil graphite electrode

FSCV: Fast scan cyclic voltammetry

GC: Gas chromatography

GCE: Glass carbon electrode

HPLC: High performance liquid chromatography

LOD: Limit of detection

LSV: Linear sweep voltammetry

MS: Mass spectrometry

OQ: Oxyquinoline

PANE Au NPS: Poly aniline gold nanoparticle

PBS: Phosphate buffer solution

PIGE: Paraffin wax ipregnated graphite electrode

RSD: Relative stanard deviation

2, 4-DPA: 2, 4-Dichlorophenoxyacetic acid

4-AP: 4-Amino antipyrine

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ABSTRACT

Electrochemical methods are a class of techniques in chemistry which study an analyte by measuring the potential and/or current in an electrochemical cell containing the analyte. It is an attractive alternative for sensing owing to its advantages of sensitivity, simplicity, low cost, and easy miniaturization. Various materials for modification on the electrode surfaces have been widely utilized to enhance sensitivity and chemical specificity of electrochemical sensors. The aim of this work is to develop a sensitive analytical method for determination of Dopamine (DA) at poly amino-naphthalene sulfonic acid modified glassy carbon electrode (poly (ANSA)/GCE). Poly(ANSA)/GCE is prepared by electrochemical polymerization of amino-naphthalene sulfonic acid (ANSA) by successive potential scanning between -0.8 and +1.8 V at 0.1 Vs^{-1} for 12 scans in 0.1 M HNO_3 solution at GCE using cyclic voltammetry (CV). The electrochemical active surface areas of bare and modified electrode in $[Fe(CN)_6]^{-3/-4}$ were 0.07cm^2 and 0.11cm^2, respectively. These results indicated that the modification of GCE with poly (ANSA) results high surface area. The oxidation of DA was examined at both bare GCE and poly (ANSA)/GCE. Poly (ANSA)/GCE exhibited higher oxidation current than bare GCE. The higher oxidation current at poly (ANSA)/GCE attributed to the higher electroactive surface area and the presence of amino and sulfonic groups in its structure that can facilitate electron transfer processes. Common electrochemical parameters have been optimized for better electroanalytical performance of poly-ANSA/GCE. It was calculated that the rate constant (K) and diffusion coefficient (D) of DA were $4.4\times10^3\ M^{-1}s^{-1}$ and 8.7×10^{-6} $cm^2\ s^{-1}$*, respectively, at poly (ANSA)/GCE. A detection limit and a dynamic working linear range of DA at poly-ANSA/GCE were 0.089 μM and 0.5 μM - 100 μM, respectively which was studied using linear sweep voltammetry (LSV). For practical applicability poly (ANSA)/GCE was evaluated by detecting DA in DA injection sample. Hence, a percentage recovery in the range of 94.1 - 102.4% was obtained which it can be a good candidate for the practical useability of the proposed electrochemical sensor for DA detection. The poly (ANSA)/GCE additionally displays good repeatability and reproducibility and satisfactory selectivity.*

Keyword: *- Dopamine, electrochemical determination, electropolymerization, Aminonaphthalene-sulfonic acid.*

1. INTRODUCTION

1.1 Background of the study

Dopamine (DA) is a highly significant catecholamine that is a member of the excitatory chemical neurotransmitter family [1]. It is crucial for the proper functioning of the central neurological, renal, and cardiovascular systems [2]. It is commonly known as 3, 4-dihydroxyphenylethylamine. The brain's caudate nucleus contains high levels of (DA), whereas extracellular fluids have relatively low levels of the neurotransmitter (0.01 – 1 μM) [3]. Accordingly, elevated DA levels signify cardiotoxicity, which causes fast heartbeats, anxiety, sleeplessness, delusions, hypertension, and heart failure [4]. Conversely, a number of neurological conditions, including stress, depression, schizophrenia, Parkinson's disease, and Alzheimer's disease, are linked to low DA levels in the central nervous system [5]. Therefore, it is obvious that DA measurements are required to understand its biological functions and related biological processes and mechanisms.

Due to this, numerous analytical methods have recently been proposed for determining the amount of DA. These methods include gas chromatography (GC) [6], capillary electrophoresis (CE_S) [7], fluorescence [8] , colorimeter method [9] and High performance liquid chromatography (HPLC) [10]. However, the GC can complicate the process, increase analysis time [11] and make samples unstable for larger or thermal labile molecules [12] , the other (CE_S) can struggle with the analysis of complex mixtures [11] and limited sample volume [12] , also fluorescence can complicate sample preparation, and Colorimetric methods have lower sensitivity. While a technique such as high (HPLC) with tandem mass spectrometry (MS) detection is a powerful technique for the quantitative determination of DA [13]. However, its cost is high and consumes more time [11] .Therefore, electrochemical detection methods could be applied for the determination of this compound. Due to high sensitivity, low detection limit, cost effectiveness, versatility in analytical detection, and fast response [14]. However, the direct electrochemical oxidation of DA has poor selectivity towards DA in the presence of common interfering compounds, These interfering species can be oxidized at similar potentials as DA, resulting in overlapping voltammetric responses [15]. Also, DA can be electropolymerized on the electrode surface, leading to electrode fouling and degradation of the response over time [16]. To overcome these limitations, various electrode modification strategies have been explored, such as using conductive polymers, carbon nanomaterials, metal nanoparticles, and other nanomaterial's to improve the selectivity, sensitivity, and stability of DA

detection [17]. Among these, the methods using conductive polymers have gained great influence due to the high sensitivity and selectivity as well as the modest and rapid response [18]. Moreover, the conductive polymers biosensors provide quick and sensitive responses, enabling real-time monitoring.

The most popular strategies used for the modification of electrodes are: the deposition of polymers film acting as redox mediators. The deposition of a polymer material on the substrate provide specific functional groups to facilitate the charge transfer and a high specific surface area to increase the sensitivity of the electrode. Therefore; highly sensitive conducting polymers (CPs) are the most widely studied classes of materials due to the incredibly attractive chemical and electrochemical properties, together with their relatively low cost, easy processing, and their application as sustainable materials. These materials and their composite play different roles in chemical sensors besides providing mechanical stability and improving the Nano filler dispersion, leading to enhanced sensitivity and selectivity [19]. Although a number of recent research reports related to the use of conducting polymers in chemical sensors development [19] and there are certain conducting polymers based sensors applied for determination of DA .

The properties of Poly (ANSA), an aniline derivative polymer material synthesized by electrochemical means, have been thoroughly examined [20] and well characterized [21]. Its structure consists functional group such as amino ($-NH_2$), hydroxyl (-OH), and sulfonic acid ($-SO_3H$). The functional groups present in monomers and their incorporation into the polymer backbone significantly impact a variety of applications [22]. To enhance the solubility of polymers in common polar solvents, for example, the presence of sulfonic acid groups in polymer chains is beneficial [23] . Further, the polymers develop an inherent proton doping capacity, which results in the production of highly soluble homo- and co-polymers that are self-doped [22]. Quite the opposite when compared to their substituted benzene counterparts, the additional benzene ring on substituted naphthalene molecules would increase the hydrophobicity of the films made from these materials. Moreover, it might lead to less solvation, tighter polymer chain packing, and less solvated species diffusing through the film [24]. Additionally, free -OH and $-NH_2$ in the polymer chain aid in the promotion of attachment to other functional groups, which can provide the polymer film with good compatibility and strong binding qualities with other polymer layers and surfaces underneath [25]. Hence, poly (ANSA) enhances the electrochemical performance of GCE through improved sensitivity,

electrocatalytic activity, stability, versatility, and cost-effectiveness, making it a valuable material in electrochemical sensing applications [26].

To the best of our knowledge, there is no report devoted to poly (ANSA) based for specific application, i.e. electoanalytical determination of selective DA sensor based on GCE as recognition element is presented. In this research electropolymerization is selected as a good approach to prepare polymer-modified electrodes in which the electrochemical parameters like film thickness, and charge transport can controlled and characterized. Generally, poly (ANSA) can be used for the selective determination of DA even in the presence of high concentrations of interfering materials such as 4-Aminoantipyrine (4-AP), 2, 4-Dichlorophenoxyacetic acid (2, 4-DPA), Oxyquinoline (OQ), and uric acid (UA). The present work aims to provide a comprehensive overview of the latest research on polymerized modified electrodes, which have demonstrated efficacy in the highly sensitive and selective electrochemical detection of DA. Of the various polymers available, we focused on CPs, which can all improve the electrocatalytic oxidation of DA.

1.2 Statement of Problem

Enhancement of life quality has recently drawn significant research attention. The regulation of food safety and quality as well as drinking water directly affects people's life. In all these fields continuous, fast and sensitive monitoring of various chemical and biological materials are required. Certain electrochemical techniques modified electrodes solved some of the analytical problems such as selectivity, sensitivity and catalytic activities [27]. Unmodified (bare) electrodes are poor in their analytical performance, hence modification of bare electrodes by electro active material allow for an increase in the electro analytical activities [28]. For this reason the analytical applicability of carbon-based electrodes can be greatly enhanced by highly ordered mono- or multi-layer deposition modification [29] . Mostly this deposition performed either chemically or electrochemically, in such case chemically modified electrode may of lack limited control over film thickness , whereas electrochemical deposition (electropolymerization) has great influence for control film thickness, leading to high sensitivity and selectivity [30].

The chemical functionality of carbon surfaces can be enhanced by electrochemically oxidizing amine-containing compounds, aliphatic alcohols, and aryl acetates have been applied [31] . However,

Since they have similar oxidation potentials, it is always difficult to detect DA when other interferences such as uric acid and others are present [32]. Moreover the lower detection limit is essential for determination of lower amount of DA in high concentration of interference. Various modified electrodes have been fabricated to overcome this problem.

In this work ANSA is used for modification of glassy carbon and provide several advantages such as, enhanced electron transfer due to the presence of the aromatic naphthalene structure, increased surface area and stability for long-term use because the sulfonic acid group can facilitate the formation of a stable and uniform film on the electrode surface, increasing the effective surface area for electrochemical reactions and suitable for repeated use.

In this regard, this research is going to give answers for the following questions.

- How polymer based sensor is advantageous for qualitative and quantitative analysis of DA?
- Why DA detection is important and challenging (mention interference issues, low detection limits, etc.)**?**
- Why bare electrodes are inadequate and require modification**?**
- Why ANSA is a suitable material for electrode modification**?**

1.3. Objective of the study

1.3.1. General objective

The general aim of this research work

- To study the electrochemical sensing and kinetics of poly (amino-naphthalene sulfonic acid) as a low-cost electrode modifier for DA detection.

1.3.2. Specific objectives

- To synthesize poly (ANSA)/GCE by electro-polymerization under optimized conditions for enhanced electrochemical sensing.
- To optimize experimental parameters for poly (ANSA)/GCE for its electrochemical performance.
- To evaluate the electrochemical activities of the modified electrodes.
- To investigate the electrochemical sensing, electrokinetics properties and rate constant of DA at poly (ANSA)/GCE.
- To apply the method for the quantification of DA in a real sample.

1.3. Significance of the study

A number of modified electrode materials have been reported for the electrochemical determination dopamine. This paper presents an efficient, and simple approach for the detection of dopamine using electrochemical polymerized polyanilne derivative conducting polymer. Moreover; the electrochemical method has more sensitivity, selectivity, rapid and cost effective approach. Hence, this study will have the following significances

- It helps to provide a possible alternative for electrochemical determination of dopamine in terms of performance, cost and time.
- It serves as a base for further research for electrochemical determination of DA at polymer modified electrodes.

2. REVIEW OF LITERATURE

2.1 Dopamine

DA is a neurotransmitter and hormone that plays a crucial role in the brain and body. Neurotransmitters are categorized as excitatory or inhibitory based on their capacity to either stimulate or block the formation of a nerve impulse in the receiving neuron; dopamine is a member of both types and plays important roles in various bodily regions [17]. It is mostly produced in the brain system and adrenal medulla [33]. Tyrosine is hydrolyzed by tyrosine hydroxylase to 3,4-dihydroxyphenylalanine (DA), which is then further decarboxylated to dopamine by aromatic l-amino acid decarboxylase as part of its production. Additionally, dopamine is a precursor of noradrenalin and adrenaline; in fact, dopamine is hydrolyzed to noradrenalin by dopamine β-hydroxylase, and noradrenalin is converted to adrenaline by phenylethanolamine N-methyltransferase [34]. It is clearly involved in motor control, learning, and cognition in the central nervous system; however, it also affects blood pressure, gastrointestinal motility, salt levels, and hormone release in peripheral organs [35]. Many studies conducted over the last few decades have shown that dopamine has a major effect on immune cell function in both the peripheral and central nervous systems; this is crucial because dopaminergic immunoregulation may be a target for drug discovery and disease surveillance [36].

2.1.1 Effect of DA

Numerous disorders in humans can result from abnormal dopamine levels in the body. As an illustration, cardiotoxicity is a symptom of elevated dopamine levels, which can progress to tachycardia, hypertension, and cardiac decompensation [37]. Excessive dopamine levels can also indicate an overactive sympathetic nervous system, which can be brought on by a variety of conditions, including chronic stress, post-traumatic stress disorder, anxiety, and fatigue/e. It can also be linked to conditions like neuroblastoma, pheochromocytoma, neuroendocrine disorders, and neurodegenerative diseases [38]. Conversely, a variety of pathological illnesses, including depression, senile dementia, Parkinson's, and Alzheimer's diseases, have been linked to low dopamine levels [39]. Owing to the numerous physiological and pathological effects of dopamine, clinical diagnosis and medication treatment monitoring depend heavily on its detection.

2.2. Chemical, Physical and electrochemical Properties of dopamine.

2.2.1. Chemical and Proprietary Names

The free base (dopamine) has also been known in the chemical literature as 3-hydroxytyramine and 3,4 dihydroxyphenethylamine, and mostly in commercial exist in the form of dopamine hydrochloride with non-proprietary name of 4-(2-aminoethyl) -1,2-benzenediol hydrochloride. The drug is available generically for the correction of ham dynamic imbalances present in the shock syndrome due to myocardial infarction, tram, endotoxic septicemia, open heart surgery, renal failure and chronic cardiac decanpensation as in congestive heart failure [40]. Proprietary names include Cardiosteril, Docard, Dopamine Fabre, Dopamine Gullini, Dopastat, Dynatra, Intropin, Intropinject, Intropine and Orion. Its Empirical Formula ($C_8H_{11}NO_2$), molecular weight (153.18 g/mol) [41] , and the structural formula in Figure 1 below.

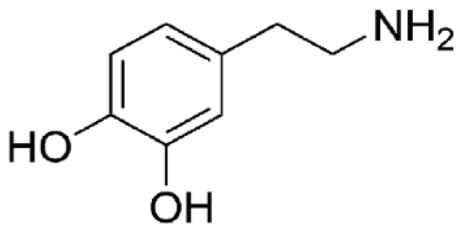


Figure 1. Molecular structure of dopamine

Dopamine (pKa 8.9) has a positive charge at pH 7.0 [42]. Numerous electrochemical techniques have been developed due to the ease with which dopamine can be oxidized [43]. Brown coloration results from self-oxidation and polymerization, which are processes that can be used to prepare polydopamine in an alkaline environment. In order to investigate the initial phases of dopamine oxidation, peroxidase (H_2O_2) and peroxidase mimics were employed as biomimetic oxidizing agents [44]. Furthermore, because of their oxidation susceptibility, uric acid (UA) and ascorbic acid (AA) typically obstructed the detection of dopamine. As a result, in order to effectively discern dopamine from its analogs and interferes, particular ligands are required.

2.2.2. Physical Properties

Dopamine is practically insoluble in ether, chloroform, benzene, and toluene, but freely soluble in water, methanol, and heated ethanol. Dopamine's UV-Vis absorption peak is located at 300 nm, and when it was oxidized, a new peak appeared at about 350 nm [45].

Dopamine fluorescence was examined between pH 2.0 and pH 12.0, with a greater emission seen at pH values of less than 6-7 [46]. At the ideal pH of 3.6, the fluorescence emission was observed at 315 nm with excitation at 279 nm. Recently, dopamine was imaged using multiphoton microscopy with an excitation wavelength of 540 nm [47] .

2.2.3. Electrochemical behaviors of dopamine

A reversible redox process with an oxidation peak was clearly defined by the electrochemical behavior of DA in cyclic voltammogram. The obtained oxidation peak for DA is electrochemically active, which gives dopamine-o-quinone as oxidation product through a two-electron process [48]. In Figure 2 displays the CV for DA oxidation at the poly (ANSA)/GCE in 0.1 M of PBS. According to the ECE mechanism shown in Scheme, the electrochemical oxidation of DA in aqueous solution proceeds in three steps, with E denoting the electrochemical step and C the chemical step. DA undergoes oxidation to dopaquinone and partial reduction to dopamine in the first scan (Figure 3, curve 1). Leucodopaminechrome, which is formed when part of dopaquinone undergoes a cyclization reaction, is instantly oxidized to dopaminechrome. This dopaminechrome is then reduced back to leucodopaminechrome [49].

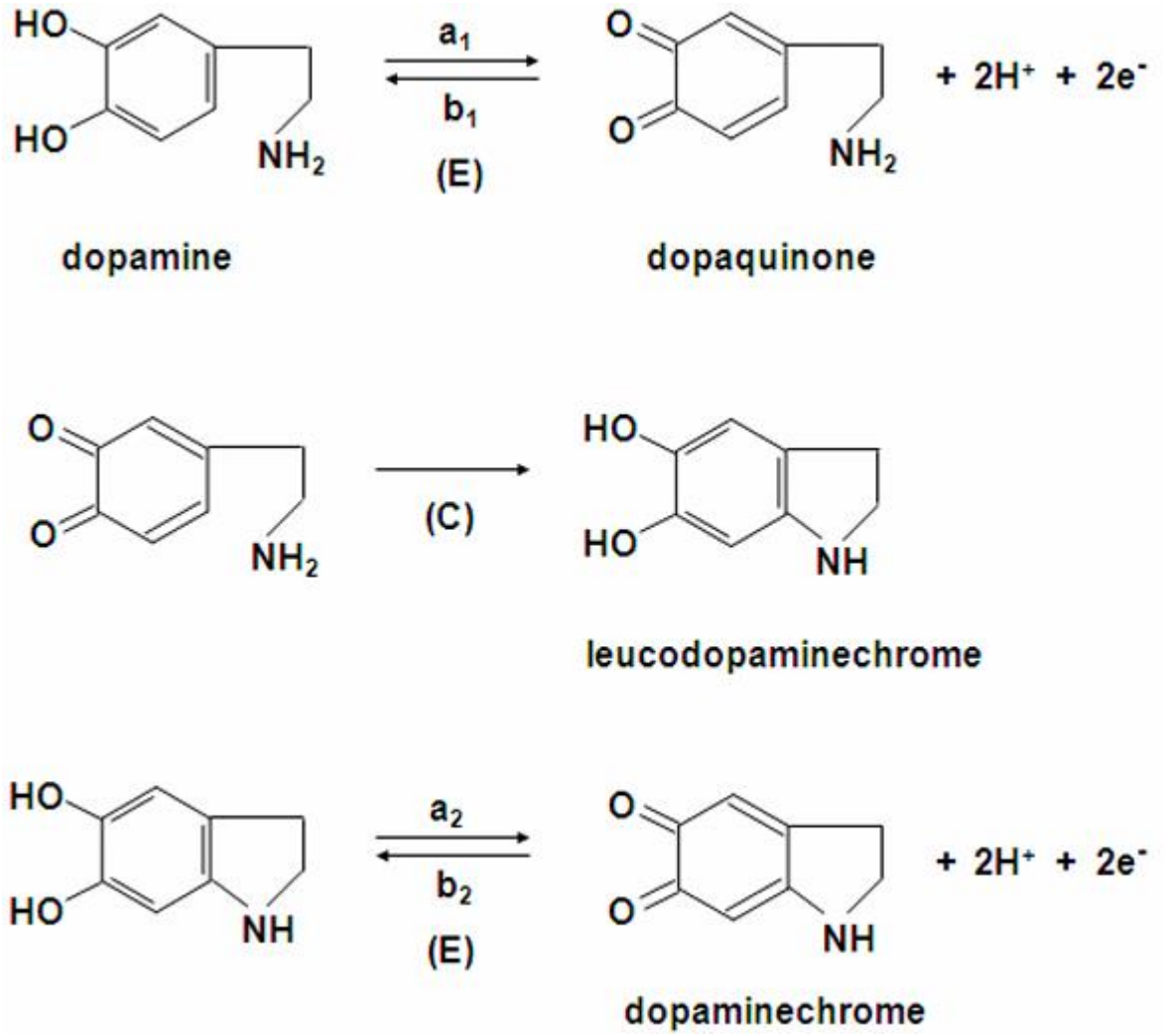


Figure 2. Schematic representation for electrochemical oxidation of DA.

However, electrochemical irreversibility in which the cyclization reaction exerts a profound influence on the Tafel slopes. Moreover, the oxidation product dopaminechrome show some slow kinetic liability on the voltammetric timescale [50].

2.3. Electrochemical methods

There are so many group of electrochemical methods, voltammetry techniques are one of them in which information about the analyte is derived from the measurement of current as a function of applied potential, the measurements being obtained under conditions that encourage polarization of an indicator, or working electrode. There are different types of voltammetry depending on

potential wave supplied for the analysis. Among these cyclic voltammetry, amperiometry, linear sweep voltammetry, and differential pulse voltammetry are most commonly used in different electroanalytical experiments [51].

2.3.1. Cyclic Voltammetry (CV)

A current is created in cyclic voltammetry experiments by sweeping the potential between two electrodes over a range that is connected to the analyte's redox reaction. This redox reaction produces a change in peak current that can be used to determine the analyte concentration and provide precise quantitative analytical data [52]. The benefit of this approach is that it can yield quantitative data from the peak current's intensity as well as qualitative data derived from the current peak's possible location.

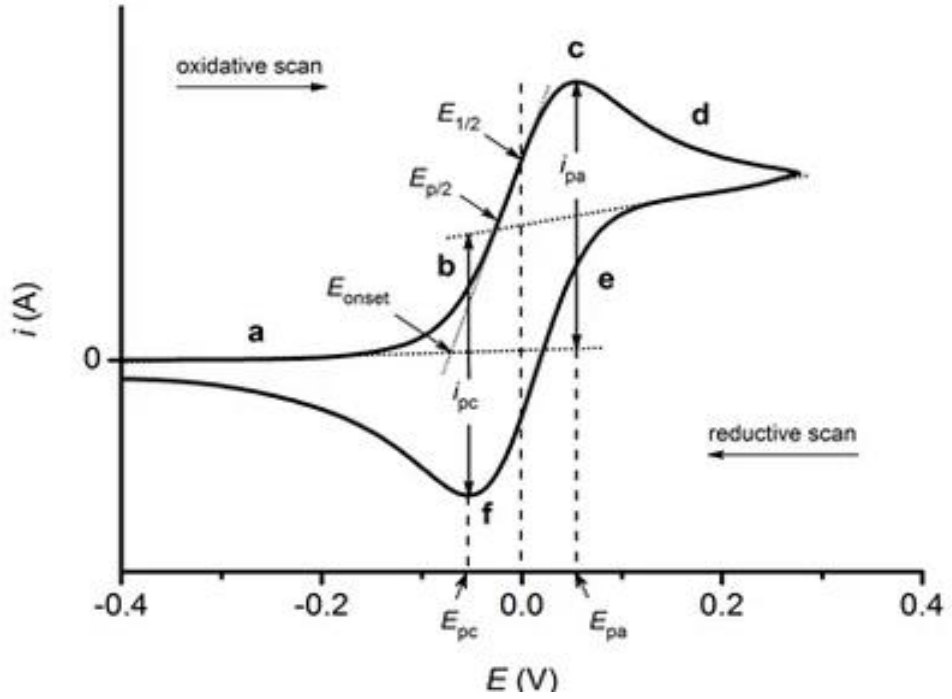


Figure 3. Cyclic voltammogram for reversible redox probe.

As shown figure 3, initially the potential is not sufficient to oxidize the analyte (a).As the potential approaches several gas constant and temperature of the standard potential, the onset (E_{onset}) of oxidation is reached. Following this, the current exponentially increases (b) as the analyte begins its oxidation at the working electrode surface. For a reversible process, here the current rises initially as if there is no change in the concentration of oxidant. The current is dictated by the rate of diffusion of the oxidant to the electrode, as well as the proportion converted to the reduced form. This can be understood according to the Nernst equation. Gradually, as the scan continues, more oxidant is

depleted. The concentration gradient adjusts to this. It is this change which causes a peak in the voltammogram. The decrease in current from depletion of the oxidant outweighs the increase from changing the proportion of oxidant oxidized at the electrode.

The current reaches peak maximum at point c (anodic peak current (i_{pa}) for oxidation at the anodic peak potential (E_{pa}). Here, more positive potentials cause an increase in current that is offset by a decreasing flux of analyte from further and further distance from the electrode surface. From this point the current is limited by the mass transport of analyte from the bulk to the double layer diffusion interface, which is slow on the electrochemical timescale. This results in a decrease in current (d), as the potentials are scanned more positive. This occurs until a steady-state is reached where further increases in potential no longer has an effect.

Scan reversal to negative potentials (reductive scan) continues to oxidize the analyte. This continues until the applied potential reaches the value where the oxidized analyte (which has accumulated at the electrode surface) can be re-reduced (e).

The process for reduction mirrors that for the oxidation. The only difference is that it occurs with an opposite scan direction and a cathodic peak (i_{pc}) at the cathodic peak potential (E_{pc}) (f). The anodic and cathodic peak currents should be of equal magnitude but with opposite sign. This is only provided that the process is reversible (and if the cathodic peak is measured relative to the base line after the anodic peak) [51].

2.3.2. Amperiometry (AMP)

AMP for analyte detection involves applying a constant oxidising or reducing potential over a defined period to the working electrode and recording the resulting steady-state current as the detection signal [53]. In AMP, as the capacitance current decays quickly, sensitive analyte detection can be achieved with detection limits comparable to sensors using differential pulse voltammetry and square wave voltammetry. Additionally, the simple instrumentation required for amperometric experiments makes these sensors easy to program, while allowing them to be fabricated into compact sizes at relatively low costs that on-site detection desires. A constant potential that is sufficient to oxidize dopamine to dopamine-o-quinone through a two-electron process is applied in the case of dopamine biosensors. The quantification of dopamine concentration in the sample is made possible by the current's proportionality to dopamine concentration over a relatively wide concentration range [54]. However, amperometric sensors usually suffer from poor cross-selectivity

arising from the oxidation/reduction reactions of electrochemically active species in the electrolyte with a lower standard potential than the applied potential. In this way, these species will also contribute to the Faradaic current detected in the amperometric profile, leading to interference in the detection process.

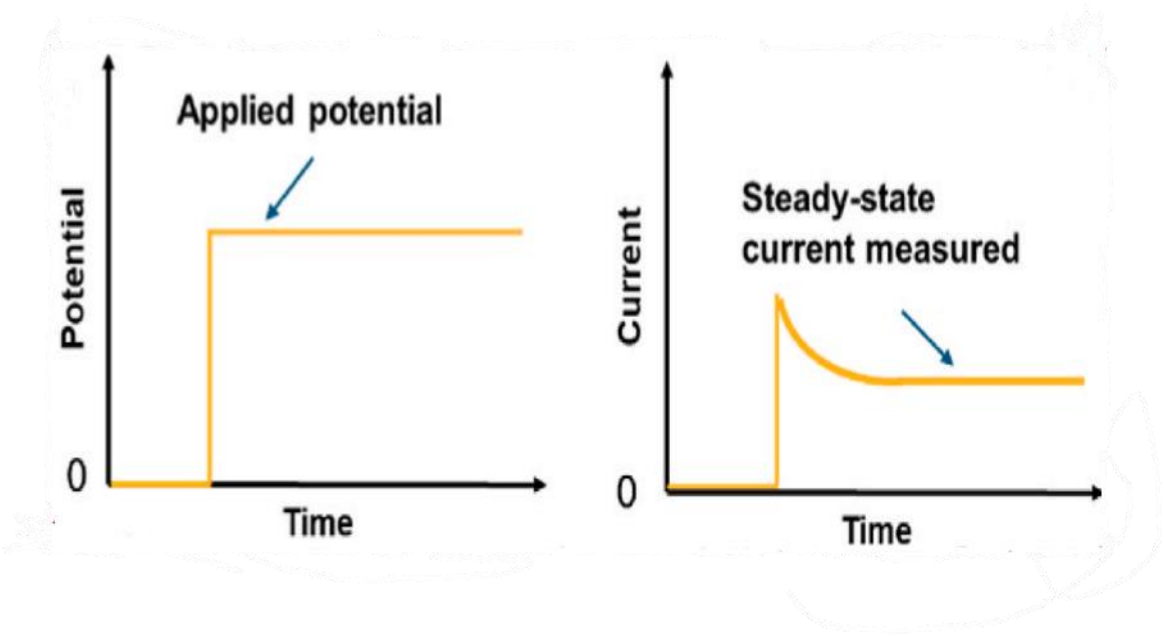


Figure 4. Amperiometry.

2.3.3. Linear Sweep Voltammetry (LSV)

In linear sweep voltammetry, the potential between a working electrode and a reference electrode is swept linearly in time as the current at the working electrode is measured. At the potential where a species starts to be oxidized or reduced, oxidation or reduction of that species is recorded as a peak or through in the current signal [55].

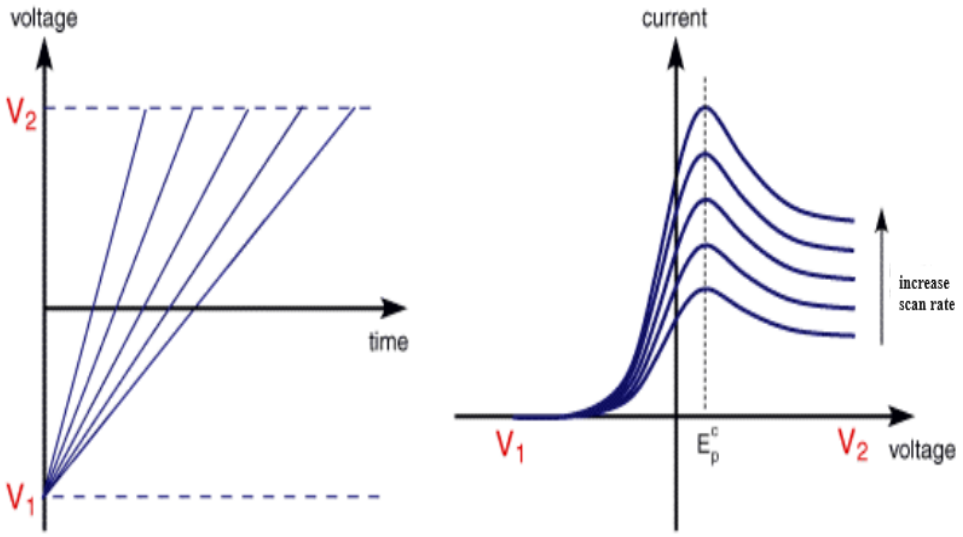


Figure 5. Linear sweep voltammogram.

2.3.4. Differential Pulse Voltammetry (DPV)

Differential pulse voltammetry is a method that can effectively mitigate background (non-Faradaic) current interference and selectively isolate Faradaic current (i.e. oxidation and reduction current) to enhance analyte detection. In a typical potential waveform used in differential pulse voltammetry (Figure. 6), an initial potential is applied for a predetermined duration. This potential is then incrementally raised by several hundred millivolts and maintained at this level for a brief duration before gradually decreasing to a level slightly higher than the initial baseline, resulting in a potential pulse. Such a process is iterated to generate a waveform resembling a staircase (Figure. 6). To minimize the influence of capacitive current, the current in differential pulse voltammetry is sampled twice in each step, (1) just before the pulse, and then again (2) at the end of the pulse ((s1 and s2, respectively, Figure. 6). The difference between these two current samples is plotted against the potential to obtain the voltammogram. By using differential pulse voltammetry, detection limits for common volatile organic compounds such as formaldehyde were reported as low as 10 nM in some studies, depending on the sensor design and conditions [53].

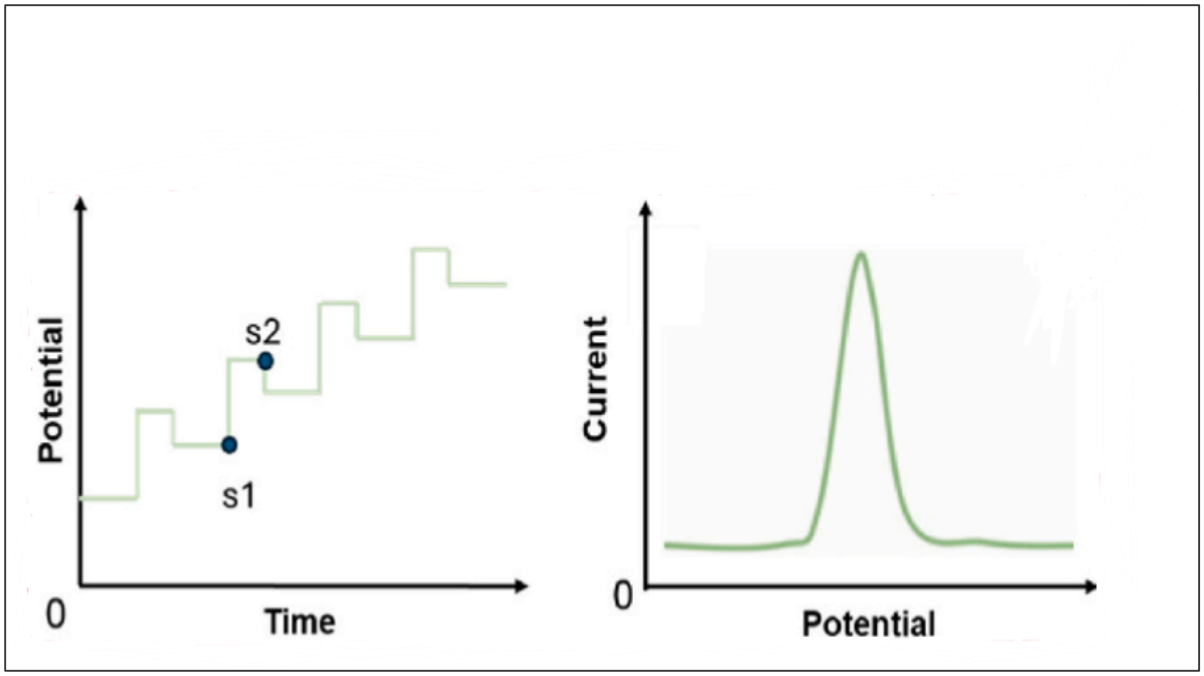


Figure 6. Differential Pulse Voltammetry.

2.3.5. Square Wave Voltammetry (SWV)

Square wave voltammetry represents another promising electroanalytical sensing method based on pulse voltammetric principles. In this technique, a series of forward and backward pulses (e.g., oxidation and reduction) from an initial potential to a final potential is applied to the working electrode. Electrical currents are recorded twice in each forward-reverse scan cycle. By subtracting the reverse current from the forward current, the capacitive current is significantly minimized. In comparing the two pulse techniques, square wave voltammetry offers several advantages for electroanalytical compound sensing. Notably, due to the reduction of capacitive current, it readily allows much faster volatile organic compound detection at high scan rates (e.g., 1V s^{-1}) than differential pulse voltammetry (e.g., 0.05V s^{-1}) [53] . Square wave voltammetry also ensures high detection resolution even at low concentrations (e.g., at parts per billion level). With these merits, square wave voltammetry is often considered a preferred technique for current research and development of electroanalytical sensing [53].

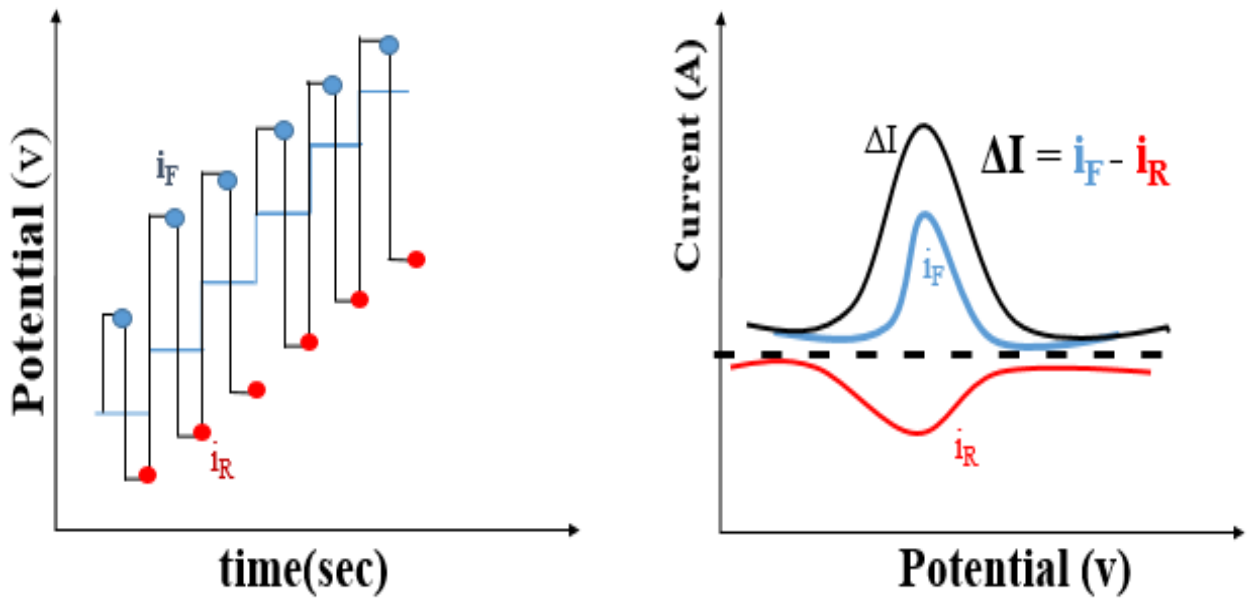


Figure 7. Square wave Voltammetry.

2.4. Three-electrode system electrochemical setup

An electrochemical cell is considered to be a sample holder, where the analyte dissolved in an appropriate solvent (and supporting electrolyte) which electrodes are immersed. Figure 8 represent a typical three electrodes system named as working electrode, counter electrode, and reference electrode. The current flows between the working and counter electrodes, the reference electrode is used to accurately measure the applied potential relative to a stable reference reaction. The reduction or oxidation of a substance at the surface of a working electrode, at the appropriately applied potential, results in the mass transport of new material to the electrode surface and the generation of a current. Even though the various types of voltammetric techniques may appear to be very different at first glance, their fundamental principles and applications derive from the same electrochemical theory [56].

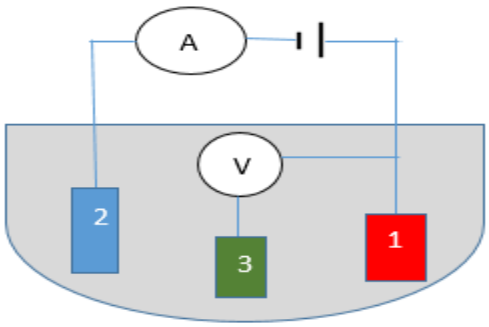


Figure 8. Three-electrode set-up: (1) working electrode, (2) auxiliary electrode, (3) reference electrode

2.4.1. Working Electrode

The interesting electrochemical event is carried out by the working electrode. The applied potential of the working electrode can be adjusted as a function of the reference electrode potential using a potentiostat. Being made of redox inert material within the potential range of interest is the most significant feature of the working electrode. To provide distinct potential windows or to lessen or increase the species of interest's surface adsorption, the working electrode type can be changed from experiment to experiment. Common working electrodes can be made of inert materials such as Au, Ag, Pt, glassy carbon (GC), Hg drop, film electrodes [57] .

2.4.2. Reference electrode

A reference electrode's equilibrium potential is steady and well-defined. In an electrochemical cell, it serves as a benchmark for measuring the potential of other electrodes. Standard hydrogen electrode (SHE), AgCl/Ag electrode, and saturated calomel electrode (SCE) are a few examples of reference electrodes that are frequently used in aqueous media. In the three-electrode technique, the reference electrode's general function is to serve as a reference for measuring and controlling the working electrode's potential in the absence of a current flow [58].

2.4.3. Counter Electrode

Current starts to flow when the working electrode is potentialized to allow for the reduction (or oxidation) of the analyte. Completing the electrical circuit is the goal of the counter electrode. Electrons moving between the working electrode and counter electrode are recorded as current. The surface area of the counter electrode is larger than that of the working electrode in order to guarantee that the kinetics of the reaction taking place there do not impede those taking place there.

A counter electrode is usually a platinum wire or disk, although carbon-based counter electrodes are also available [59].

2.5. Modification of working electrode.

Electrode surface modification is a widely used technique in electrochemistry that enhances the performance of electrodes for various applications. It also advantageous for improved Selectivity, Versatility, sensitivity , Faster Response Times and Stability [60]. The most common techniques used for modifying electrode surfaces like Chemical Modification, Electroadsorption, Deposition Techniques, Electrochemical Polymerization, and Enzyme Immobilization which is listed.

1. Chemical Modification

Chemical modification involves altering the electrode surface through chemical reactions to improve its properties. This can include Covalent bonding and Self-Assembled Monolayers. Attaching organic groups to the electrode surface have formed by Covalent bonding, which can enhance selectivity and sensitivity for specific analytes. For example, gold electrodes can be modified using thiolic compounds to create stable surfaces for further applications like enzyme immobilization [61]. Whereas Formation of organized molecular layers on the electrode surface that can enhance electron transfer and provide specific binding sites for biomolecules have been Self-Assembled Monolayers.

2. Electro-adsorption

Electro-adsorption is the process where charged species are adsorbed onto the electrode surface under an electric field. This technique can significantly increase the concentration of reactants at the electrode interface, enhancing electrochemical responses. It is particularly useful in sensor applications where rapid detection is required.

3. Deposition Techniques

Deposition techniques involve applying materials on to the electrode surface to modify its characteristics. Electrodeposition is one of deposition method that allows for the deposition of metals or nanoparticles on to the electrode through electrochemical reactions. For instance, gold electrodes can be modified by electrodeposition of diazonium compounds, resulting in stable and functionalized surface [61]. Physical and Chemical Vapor Deposition, also deposition methods

create thin films on electrodes through physical or chemical processes, enhancing their properties for specific applications.

4. Electrochemical Polymerization

Electrochemical polymerization involves forming polymer films on the electrode surface through electrochemical reactions. This technique is beneficial for creating conductive polymer coatings that improve electron transfer rates. Conductive polymers like polypyrrole or polyaniline are commonly used to enhance the electrochemical properties of electrodes.

5. Enzyme Immobilization

Enzyme immobilization is a critical technique for developing biosensors. It involves attaching enzymes to the electrode surface to facilitate specific biochemical reactions. Enzymes can be immobilized through covalent bonding, adsorption, or entrapment within polymer matrices. This enhances the stability and reusability of enzymes in electrochemical sensors. Applications Enzyme Immobilization electrodes with immobilized enzymes are widely used in biosensors for detecting glucose, lactate, and other biomolecules due to their high specificity and sensitivity.

Table 1. Summarize the possible techniques used for modifying electrode surfaces.

Techniques	Modification	Ref
Chemical Modification	Attaching specific chemical groups or compounds to the electrode surface.	62
Electroadsorption	The electrostatic attraction between charged species in solution and the electrode surface	62
Deposition Techniques	Depositing materials onto the electrode surface to create thin films or coatings.	63
Electrochemical Polymerization	The formation of polymer films on the electrode surface, which can enhance the electrode's electrochemical properties	64
Enzyme Immobilization	Attaching enzymes to the electrode surface creates biosensors that can selectively detect specific analytes through biochemical reactions	65

2.6. Conducting polymers (CPs)

CPs are widely used modifiers that can be deposited over bare electrodes by chemical or electrochemical means from their monomer solutions. Their exceptional electrical and optical properties stem from their extended π-conjugated structure. The conjugated double bonds across the polymeric chain and delocalization of π - electrons in the polymeric backbone is a common feature. As the π - electrons delocalization increase resulting in the decrease in energy band gap between valence band and conduction band. CPs, in particular, are capable of achieving excellent electrical conductivity. Due to such excellent electrical property, CPs have benefits for various electrochemical sensing the application. A number of CPs like Polypyrrole [66], Poly (3,4-ethylenedioxythiophene) [67] have been used for modification and fabrication of working electrode for electrochemical sensing of DA

Modification with a particular functional groups or nanoparticles, like conducting polymer, metal oxide nanoparticles [68] and metal or carbon nanostructures [69], form analytical advantage on the surface of substrate by form a protective layer to prevent surface fouling, high biocompatibility, and the ability to be selective towards the target bioanalytes. Such modification avoid the effect of interfering species through hydrophobic, hydrophilic, ion-exchange, or electrostatic interactions. All of these allow conducting polymers and their nanocomposites to be more popular in the biomedical field [70] , especially for electrochemical biomolecule sensing [71], which includes the detection of neurotransmitters like dopamine [72]. In conductive polymer, like ANSA can be used as a reagent for the detection and quantification of certain substances due to its unique property and interaction with various analyte. The oxidation of dopamine was demonstrated to be facilitated by the electrostatically attractive interactions between positively charged amino groups of dopamine and negatively charged sulfonate groups of the polymer as well as by the hydrogen bond formation between hydroxyl groups of dopamine and the polymer's sulfonate groups [73].

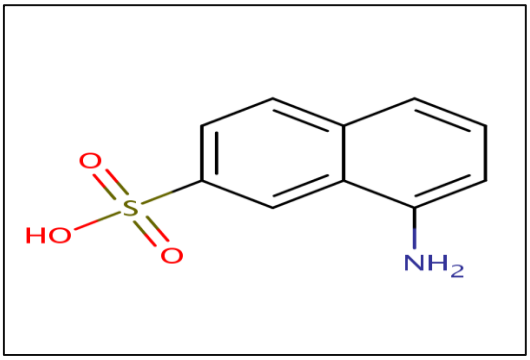
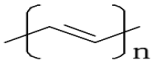
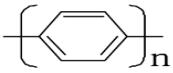
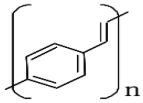
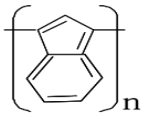
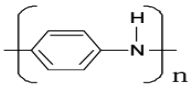
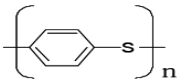
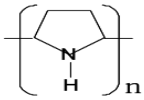
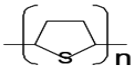
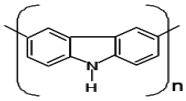
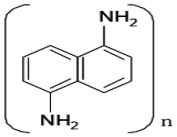


Figure 9. Schematic representation for ANSA.

Table 2 : Names, structures, and conductivities of some common conducting polymers [19]

Conducting Polymer	Structure	Conductivity (S/cm)
Polyacetylene		~ 1000
Polyparaphenylene		100 ~ 500
Polyparaphenylene vinylene		~ 3
Polyazulene		~ 0.1
Polyaniline		1 ~ 100
Polyparaphenylene sulfide		1 ~ 100
Polypyrrole		40 ~ 100
Polythiophene		10 ~ 100
Polycarbazole		10 ~ 100
Polydiaminonaphthalene		10^{-3}

3. MATERIAL AND METHODS

3.1. Chemicals and Materials

3.1.1. Chemicals

All of the chemicals used in this study were of the reagent grade, including: aminonaphtaline-sulfonic acid (ANSA) (Sigma-Aldrich); dopamine (FINKE, India); alumina slurries (Sancial, China); Hexacyano-ferrate (BDH); disodium hydrogen phosphate (FINKE, India); sodium dihydrogen phosphate (Nice, India); potassium chloride (FINKE, India); hydroquinone (BCH, Germany); uric acid (FINKE, India); hydrochloric acid (37%) (Riedel-de Haen, Germany); and sulfuric acid (98%) (Shanghai, China).

3.1.2. Material and instruments

All the electrochemical measurements was performed with Epsilion EC-Ver 1.40.67, voltammetric analyzer (Bioanalytical Systems, USA) using three-electrode system consisting of glassy carbon (GCE) working electrode, a platinum wire counter electrode, and an Ag/AgCl/Cl (3.0 M) reference electrode. pH meter (pH -016 pH METER, China), analytical balance (WANT Balance Instrument Co., Ltd, China), ultrasonic washer (Elma-78224 singen/l, made in Germany), Micro pipette (BS-220x300T, made in china) and Magnetic stirrers were used whenever necessary.

3.2. Methods

3.2.1 Preparation of standard solutions

0.1 M standard DA stock solution in 100 mL volumetric flask was prepared by dissolving an accurately weighed amount of DA in deionized water. The 0.1 M phosphate buffer solutions with various pH values were prepared by mixing the stock solutions of 0.1 M NaH_2PO_4 and Na_2HPO_4. The working solutions of 0.1 M HNO_3, 0.5 M H_2SO_4, 0.1 M UA, 0.1 M 2,4-DPA, 0.1 M OQ and 0.1 M 4AP were prepared just prior to use. Other chemicals used were of analytical grade. All solutions were prepared with doubly distilled water. All experiments were carried out at room temperature.

3.2.2. Preparation of polymer-modified/GCE

The poly (ANSA)/GCE was prepared based on the previous report [20]. Prior to electrochemical modification, GCE was polished up to the mirror finish using 0.05 μM alumina slurries on a polishing pad, then sonicated successively with distilled water. Then the electrode was treated by potential scanning between -0.8 and +1.8 V at 0.1 Vs^{-1} for 12 cycle in 0.1M HNO_3 solution

containing 2 mM monomer. The polymer films on the electrodes was then stabilized in monomer free 0.5 M H_2SO_4 solution by scanning the potential between -0.8 and +0.8 V until the voltammogram become stable. Then the modified electrode poly (ANSA)/GCE was obtained.

3.3. Electrochemical characterization of the working electrode

The redox behavior of poly (ANSA)/GCE was studied in the redox probe $[Fe_2(CN)_6]^{3-/-4}$ system. To evaluate the electroactivity of the modified electrode toward 1 mM $[Fe(CN)_6]^{3-}$ prepared in 0.1 M KCl was selected as probe and cyclic voltammetry was performed at a scan rate 100 mVs^{-1} .

3.4. Real sample analysis

For the practical application of the developed modified electrode DA hydrochloride injection was used as real sample. Standard addition method was used for LSV determination of DA at poly (ANSA)/GCE. 1.00 mL of dopamine hydrochloride injection (specified content of DA is 10.00 mg mL^{-1}) was diluted to 50 mL with distilled water. The LSV response of 5 µM of the DA injection sample solution spiked in 0.1 M PBS (pH 7) was measured. For every successive 20 s intervals, the standard DA solution was added into the cell as internal standards.

4. RESULT AND DISCUSSION

4.1 Electropolymerization of the poly (ANSA) on modified GCE.

The poly (ANSA)/GCE was prepared potentiodynamically from 2 mM monomer solution prepared in 0.1 M HNO_3. Electropolymerization was carried out for 12 cycles, at a scan rate of 100 mV/s, over the potential range of -0.8 V to +1.8 V, as shown in Figure 10. Initially all the peak current gradually rose at -0.48 V in the cathodic sweep and peaks of 0.2 V and 1.47 V in the anodic sweep with increasing number of cycles which indicate the growth of polymer film on the surface of GCE. After a few consecutive sweeps, a steady state voltammogram was seen during the cyclic scanning process. It suggests that the GCE surface was covered with a polymerization coating that eventually developed [20] .

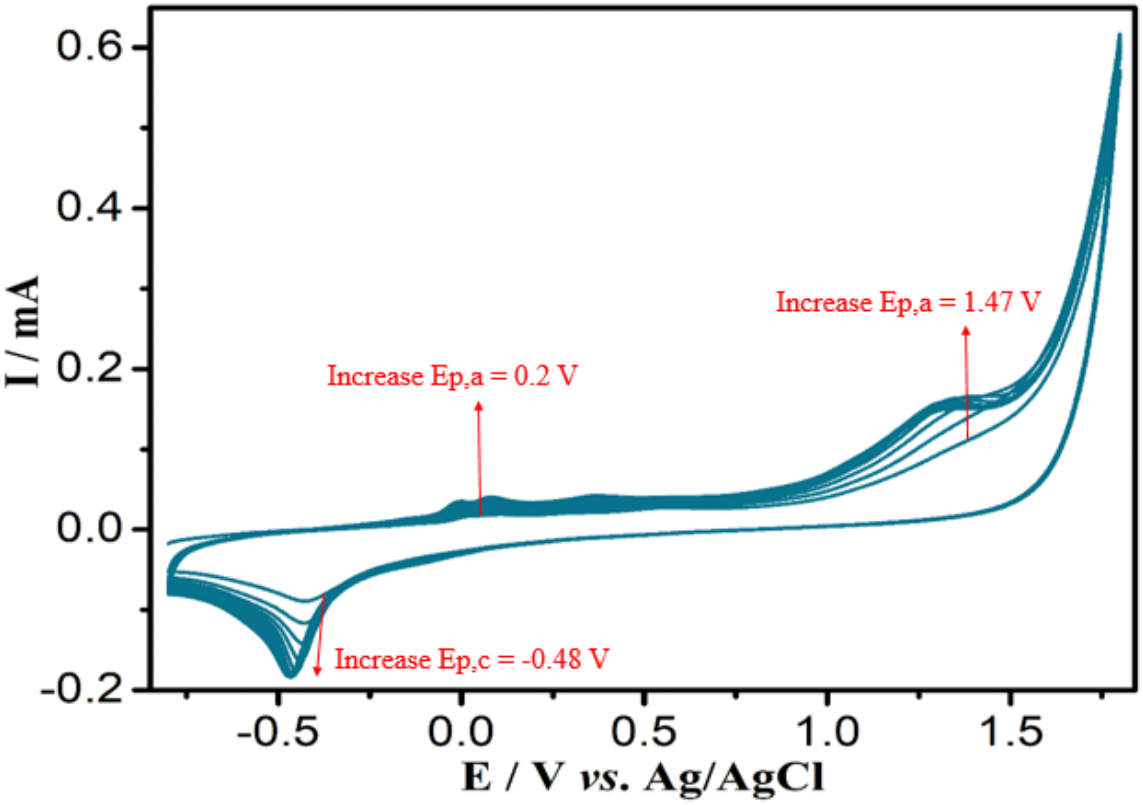


Figure 10. CVs of 2mM developed poly (ANSA) in 0.1M HNO_3 at 12 cycles with a scan rate of 100mV/S.

4.2 Optimization of film thickness

The polymer film thickness was controlled by controlling the number of polymerization cycle. The number of polymerization cycles was varied from 5 to 20 cycles, which was directly connected

with the electrocatalytic activity of poly (ANSA)/GCE. The optimal polymeric film thickness was obtained in 12 cycles, as shown in Figure 11, due to the observed significant increase in sensitivity. A further increase in scan cycles to 16 was linked to a dramatic fall in sensitivity. The observed phenomenon can be explained by the excess polymer building up on the GCE surface, which prevents the electron transfer required for the DA oxidation process [74]. Because of their enhanced conductivity and convenience of analyte access which can be deduced from the increased charge transferred during polymerization thin polymer films are generally superior in sensing investigations. Hence, twelve polymerization cycles were employed as optimal film thickness for proceeding studies.

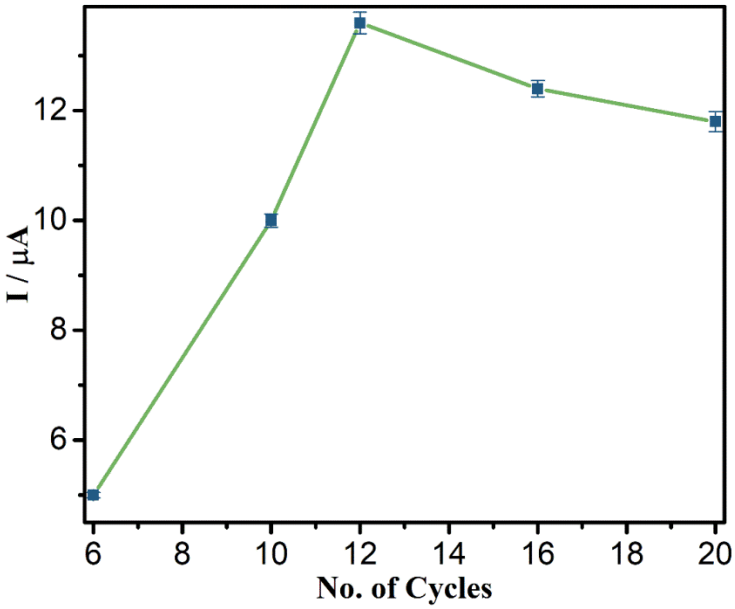


Figure 11. Effect of film thickness on the linear sweep voltammetry response of 10 µM DA at poly (ANSA)/GCE.

4.3. Electrochemical Characteristics of bare GCE, and poly (ANSA)/GCE

The bare GCE and poly (ANSA)/GCE electrochemical behaviors were examined in 1 mM $[Fe(CN)_6]^{3-/4-}$ redox probe prepared in 0.1 M KCI supporting solution. The CV responses of bare GCE and poly (ANSA)/GCE in $[Fe(CN)_6]^{3-/4-}$ demonstrates the redox reaction of $[Fe(CN)_6]^{3-/4-}$ has two distinct redox peaks. Nonetheless, in comparison to the bare GCE, the poly (ANSA)/GCE showed enhanced redox peak current and a smaller peak-to-peak potential separation. This is may be the presence of –OH and $–NH_2$ functional cites give rise to ANSA to provide higher active surface area and conductivity, which facilitates fast electron transfer at the interface [25 75]. Both -

NH_2 and -OH groups appear to be involved in the electropolymerization process, and the film's conductivity is 4.9×10^{-7} S cm^{-1} [75] .

Moreover, CVs of $[Fe(CN)_6]^{3-/4-}$ were recorded at various scan rates ranging from 10 to 300 mV/s on bare GCE and poly (ANSA)/GCE to determine electrochemical active surface area (Figure 12). The Randles–Sevcik equation was used to determine the electrochemical active surface area of bare GCE and poly (ANSA)/GCE [76].

$$I_p = 2.69 * 10^5 n^{3/2} A \upsilon^{1/2} D^{1/2} C \quad \ldots\ldots (1)$$

Where, I_p is the peak current, D is the diffusion coefficient (7.6×10^{-6} cm^2s^{-1}), C is the concentration of the $[Fe(CN)_6]^{3-/4-}$ molecules (mol L^{-1}), A is the electrochemical active area (cm^2), n is the number of electron transfer and υ is the scan rate (V s^{-1}). From the slopes of the I_{pa} versus $\upsilon^{1/2}$ (Figure 12B and 12D) the electro active surface areas were calculated to be 0.07 cm^2 and 0.11cm^2 for the bare GCE and poly (ANSA)/GCE, respectively. These results indicated that the poly (8-AN2SA)/GCE has a high electroactive surface area, due to the presence of amino and sulfonic groups in the structure of ANSA that can facilitate electron transfer processes, making the modified surface more reactive. This reactivity can lead to higher current responses in electrochemical measurements, which is indicative of a larger active surface area [77]. Additionally the structure of the modified surface often exhibits a more porous morphology due to the polymerization process. This porosity allows for better penetration of electrolytes and increased interaction with analyte during electrochemical processes, further enhancing the effective surface area available for reactions [77].

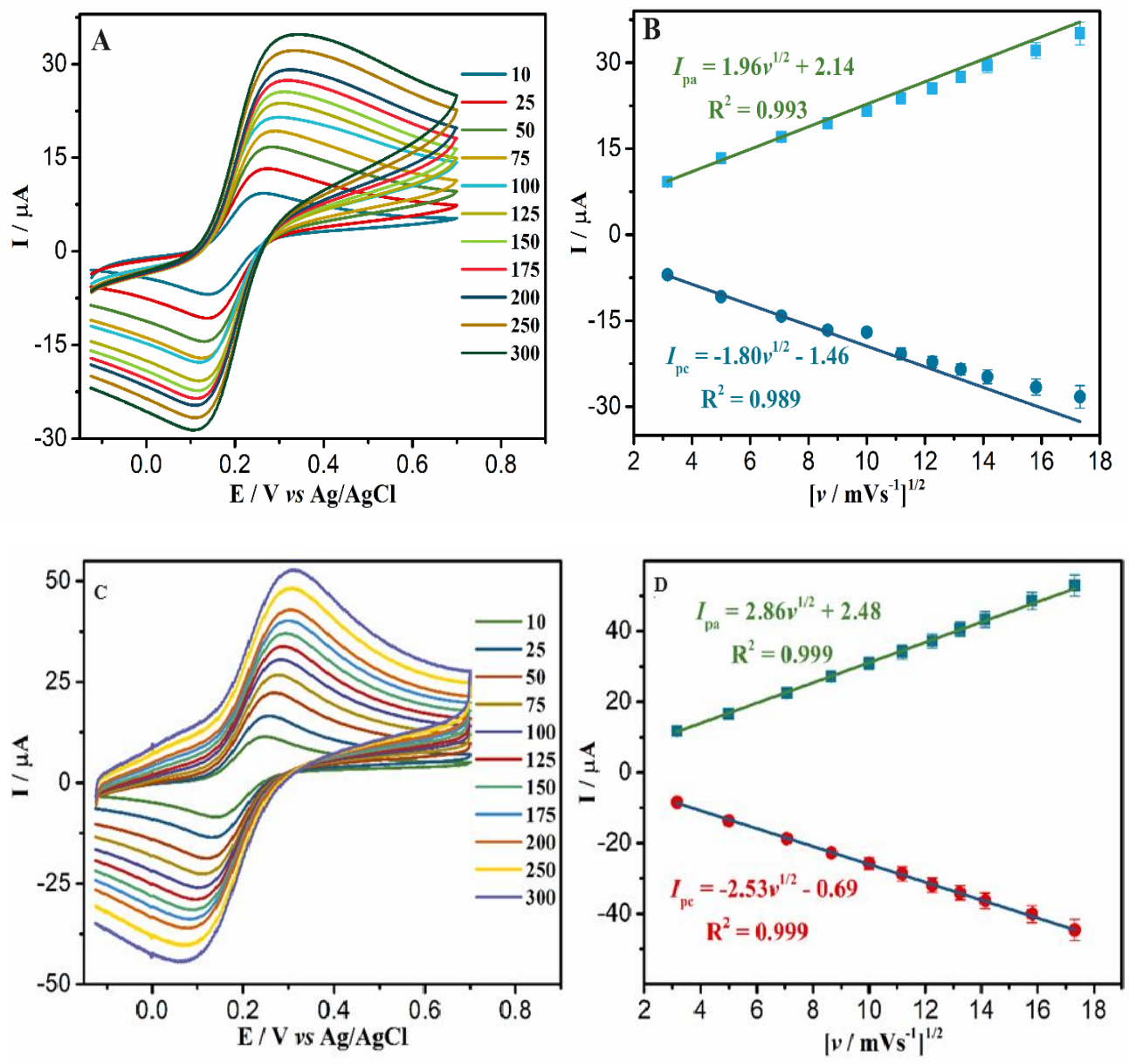


Figure 12. (A) CVs of the bare GCE and (C) poly (ANSA)/GCE in 1 mM $[Fe(CN)6]^{3-/4-}$ in 0.1 M KCl at various scan rates for ECSA calculation and (B) and (D) shows the plot of I vs.$v^{1/2}$ for bare CGE and ANSA respectively.

4.4 Electrochemical Behavior of DA at bare GCE and poly (ANSA)/GCE.

Figure 13 depicts the CVs of bare GCE and poly (ANSA)/GCE in blank PBS (0.1 M pH 7.0) and in the presence of 10 µM DA (0.1 M pH 7.0 PBS). Bare GCE shows no redox peaks in blank PBS. But a greater background current was observed for the poly (ANSA)/GCE, which is the result of analyte ions interacting with the poly (ANSA)/GCE surface interlayer. On the other hand with the

presence of DA, bare GCE shows very weak anodic and cathodic currents. The redox current response of DA at poly (ANSA)/GCE increased considerably, demonstrating that ANSA is used for modification of glassy carbon and provide enhanced electron transfer due to the presence of the aromatic naphthalene structure and also increased electrochemical active surface area because the sulfonic acid group increasing the effective surface area for electrochemical reactions. Our results are clearly in line with the results of the electrochemical active surface area [77].

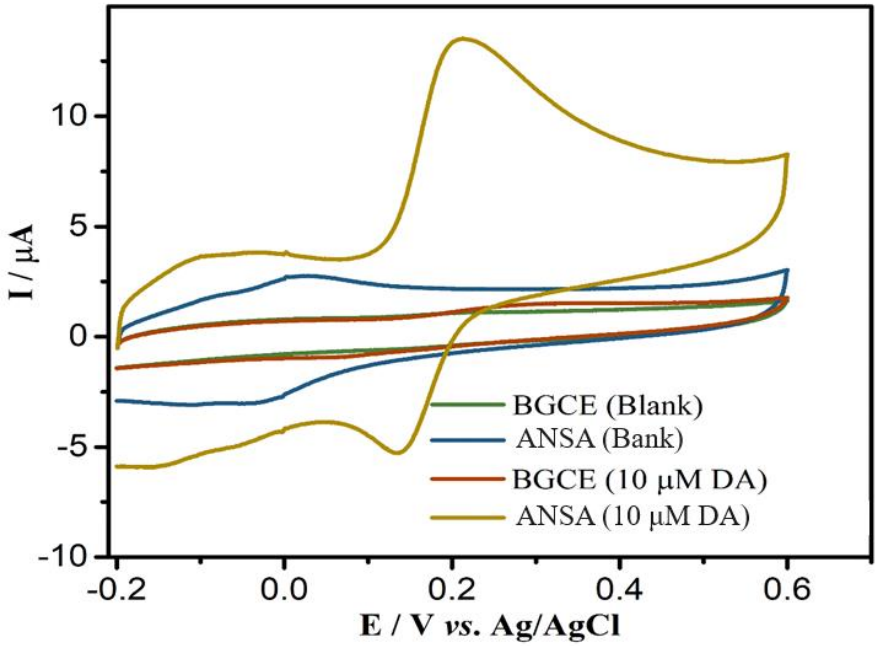


Figure 13. Cyclic voltammogram for response of bare GCE and poly (ANSA/GCE) in the absence and presence of 10 µM DA in 0.1M of PBS at 100 mV/s scan rate.

4.5. Effect of pH

The effect of buffer pH on DA oxidation at poly (ANSA)/GCE was studied by recording CVs of 10 µM DA in 0.1 M PBS in the pH range of 3.0 to 8.3, as shown in Figure 14A and 14B. The greatest DA oxidation current (I_{pa}) was recorded at pH 5.5. But, the pH of human blood and urine were quite near to 7.0, the PBS of pH 7.0 was chosen as the ideal threshold for detection of DA. As a result, pH 7.0 was selected as optimal condition to determine DA [78] . Moreover, the anodic peak potentials (E_{pa}) values of DA shifted to less potential as the pH value increases. This observation suggested that in the oxidation reaction of DA at poly (ANSA)/GCE proton transfer is involved. A linear relationship with a slope of about -0.063 V/pH was found.

$$E_p = \frac{-0.0591\, m}{n} pH + b \text{.....(3)}$$

Where m and n are the protons' and electrons' numbers, respectively.

The slope of -0.063 V/pH is in close proximity to the theoretical value of -0.0591 V/pH, suggesting that the oxidation process involves two protons and two electrons [79]. It is estimated that two protons and two electrons are involved in the electrochemical process of DA.

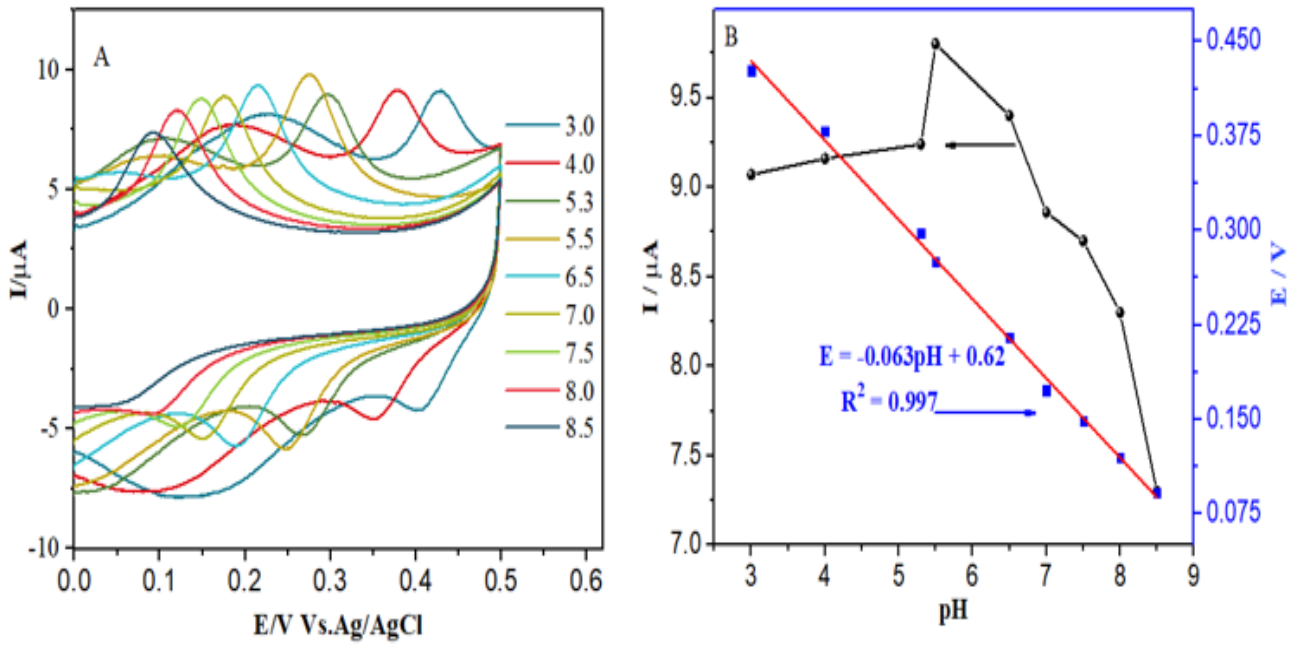
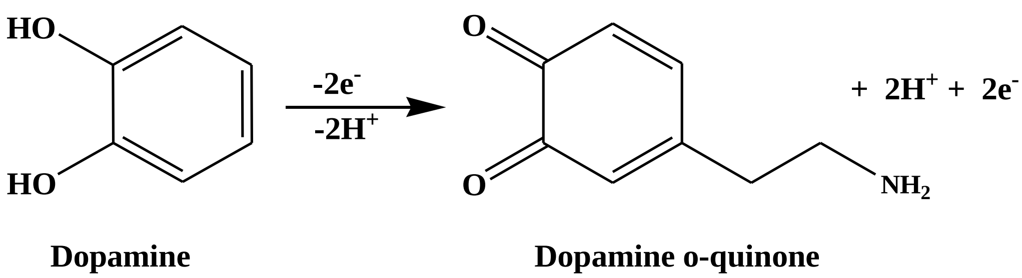


Figure 14. (A) Effect of pH on oxidation of 10 μM DA at 100 mV/S by poly (ANSA)/GCE in 0.1M PBS. (B) Plot of oxidation current and potential of DA as a function of pH.

4.5.1. Mechanism Behaviors of DA at poly (ANSA)/GCE

According to the mechanism shown in Scheme 1, the electrochemical oxidation of DA in aqueous solution proceeds in to dopamine o-quinone and also Leucodopaminechrome, which could be formed when part of dopamine o-quinone undergoes a cyclization reaction, is instantly oxidized to dopaminechrome. However the oxidation of DA to dopamine o-quinone would be drawn, due to the oxidation product dopaminechrome show some slow kinetic liability on the voltammetric timescale [50].



Scheme 1. Mechanism of Electrochemical Oxidation of DA at the poly (ANSA)/GCE.

4.6. Effects of Scan Rate

Cyclic voltammograms of DA at the poly (ANSA/GCE) in 0.1 M buffer solutions (pH = 7) were studied at various scan rates are shown in Figure 15. When the scan rate was increased from 10 to 200 mV/s, the anodic peak currents (I_{pa}) and cathodic peack currents (I_{pc}) also increased (Figure 15A). Plots of the I_{pa}, I_{pc} vs. square root of the scan rate ($\upsilon^{1/2}$) and the I_{pa}, I_{pc} vs. scan rate (υ) are displayed in Figures 15C and 15B, respectively. The I_{pa} and I_{pc} were linearly related with υ in the range of 10 mV/s to 200 mV/s than $\upsilon^{1/2}$, with the correlation coefficients shown in Figure 15B and 15C. The I_{pa} were linearly related with the (υ) in the range of 10 mV/s to 200 mV/s, with correlation coefficients of 0.991. Nonetheless, the correlation coefficient value suggests that the redox reaction of DA at poly (ANSA)/GCE is an adsorption-controlled mechanism. As shown in Figure 15B, from the slope of the linear plot of I versus υ, the surface coverage of the electroactive species (Γ) can be estimated to be approximately 0.43 nmol/cm^2 according to the following equation [80].

$$I_p = \frac{n^2F^2\upsilon A\Gamma}{4RT} \qquad (3)$$

Where n is the number of electrons, F (96500 C/mol) is the Faraday's constant, R (8.31 J/mol) is the gas constant, T is the temperature (K) (298.15), A is the area of the electrode (0.07cm^2)

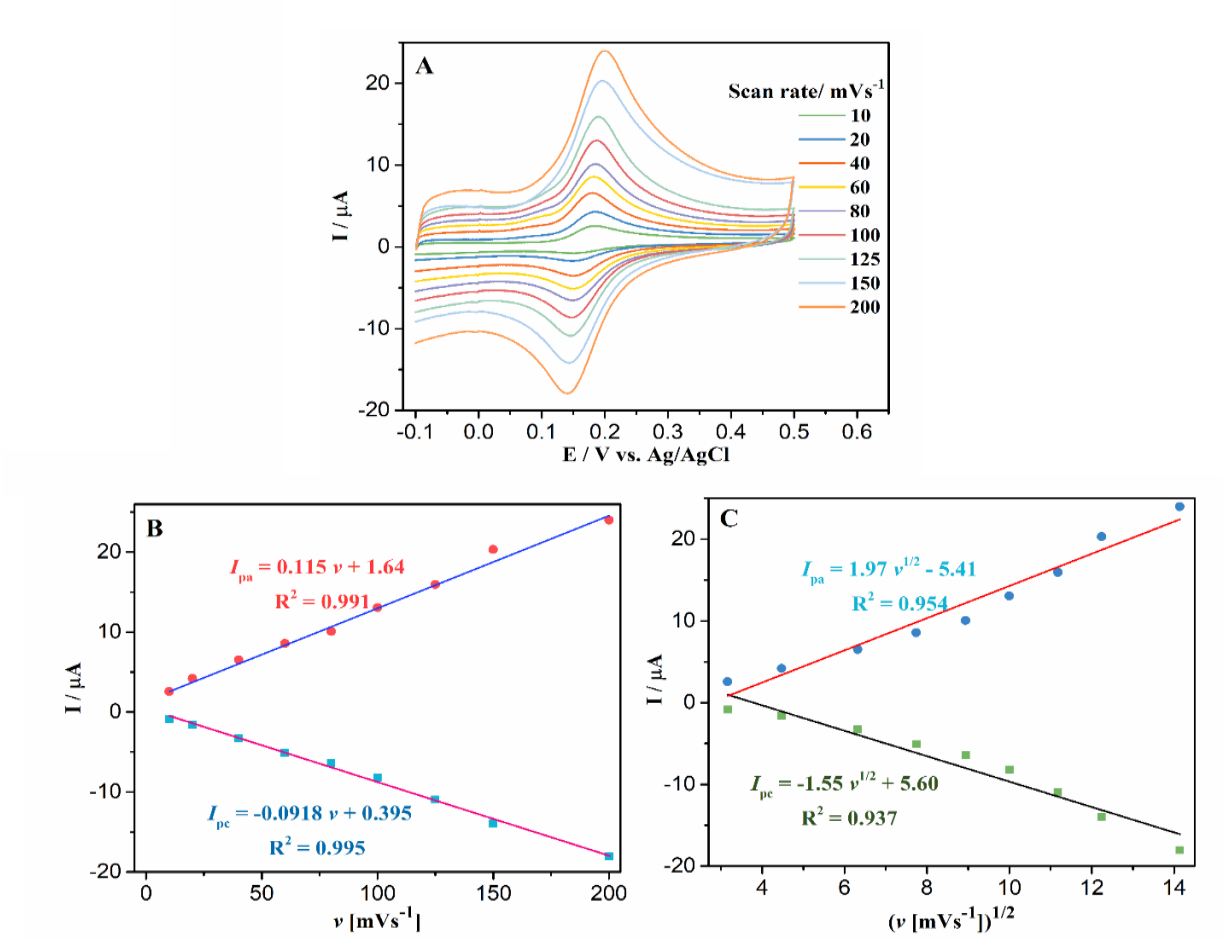


Figure 15. (A) CVs at various scan rates for 10 µM DA in PBS (pH = 7) at poly (ANSA)/GCE: 10, 20, 40, 60, 80, 100, 125, 150, and 200 mV s −1. (B) Plots of the linear relationship between peak currents vs. scan rate and (C) peak currents vs square root of scan rate.

4.7. Reaction kinetics for oxidation of DA at poly (ANSA)

Using chronoamperometry (CA) in 0.1 M of PBS (pH 7.0) at a voltage of 0.6 V, the electrochemical kinetic rate of poly (ANSA) was examined. The Cottrell equation, which is stated in equation 4, can be used to calculate the diffusion coefficient (D) of DA [81].

$$I_p = \frac{nFAC\sqrt{D}}{\sqrt{\pi t}} \quad \text{.....(4)}$$

Where Ip stands for peak current (A), n is the number of electrons, F is the Faraday constant (96,500 C mol^{-1}), A is the electrode surface area (cm^2), C is the bulk concentration of the analyte (mol cm^{-3}), and t is the time (seconds). A linear relationship was obtained from the plot of Ip *vs*

$t^{-1/2}$ of the CA measurements for different concentrations of DA (Figure 16 B). Next, the concentration of DA was plotted against the slopes of Ip vs $t^{-1/2}$ of each individual curve from Figure 16 B (Figure 16 C). As a result, the estimated value of D for DA was 8.7×10^{-6} cm^2 s^{-1}.

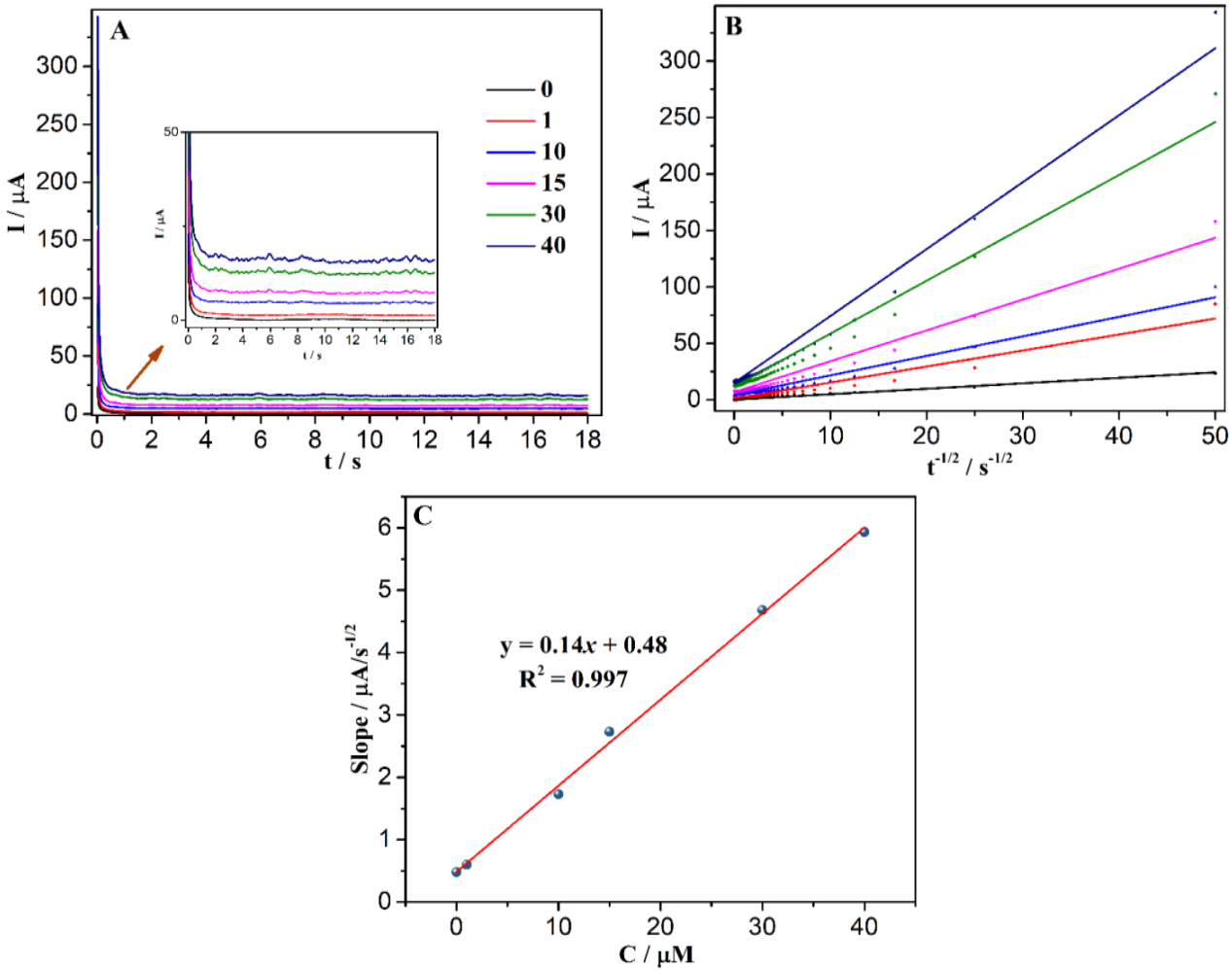


Figure 16. (A) CA obtained at poly (ANSA)/GCE with the addition of different concentrations of DA. (B) Plot Ip vs $t^{-1/2}$, (C) plot of the slopes from (i) vs concentration of DA.

The poly (ANSA)/GCE's CA response with and without the addition of DA is displayed in (Figure 17). A more current response was noted in the absence of DA addition, which may have resulted from their surface imperfections. But when 40 µM of DA was gradually injected at the poly (ANSA)/GCE in 0.1M PBS (pH 7.0), the current response grew significantly and exceeded that of bare. The kinetic rate constant (K) can be determined based on equation (5) [82] .

$$\frac{I_p}{I_b} = (\pi KCt)^{1/2} \quad \text{.....(5)}$$

Where I_p and I_b are the obtained current in with and without the addition of the DA, K is the catalytic rate constant, C is the substrate concentration (mol cm^{-3}) and t is the time (s). From the slope of I_p/I_b *vs.* $t^{1/2}$ (Figure 17B), the calculated value of *K* was about $4.4\times10^3\ M^{-1}s^{-1}$.

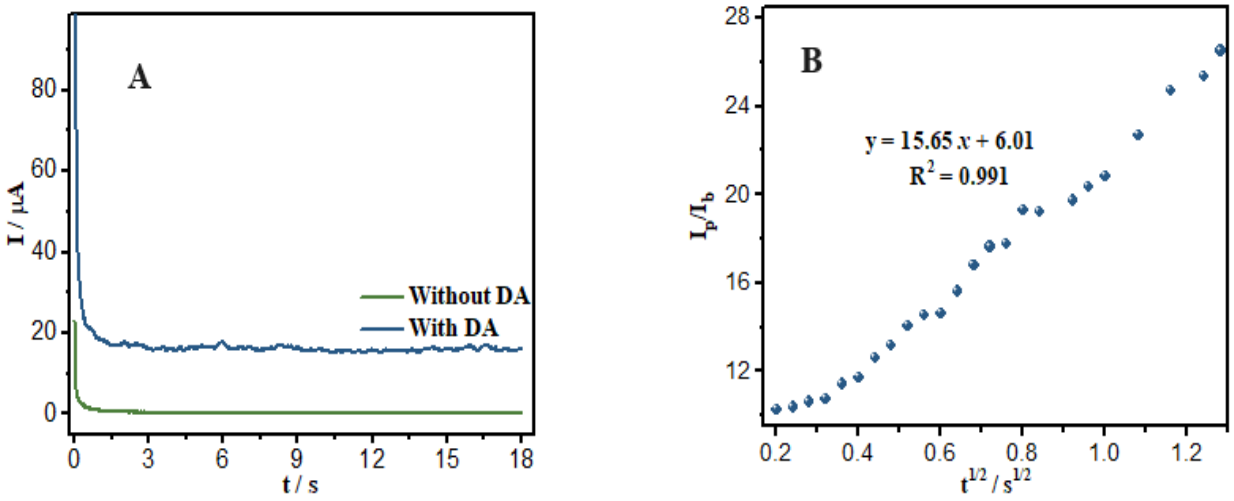


Figure 17. (A) Chronoamperometric (CA) response of poly (ANSA)/GCE in with (40 µM) and without addition of DA; (B) I_p/I_b vs. $t^{-1/2}$.

4.8. Performance of the Developed Electrochemical Sensor for DA Detection in Analytical Tests.

The linear range and limit of detection (LOD) of DA were investigated by using the LSV technique. As shown in Figure 18 LSVs of varied DA concentrations at the poly (ANSA)/GCE recorded under optimal experimental conditions. The anodic current response of DA was rises with increasing the concentration of DA (Figure. 18A). The anodic current of DA at poly (ANSA)/GCE is proportional to DA concentrations ranging from 0.50 - 100 µM (Figure 18B), with the regression equation: *I* (µA) = 1.28 C (µM) + 0.63, R^2 = 0.998. The LOD was calculated to be 0.089 µM ($3\sigma/m$) [83]. Where σ is the standard deviation of the blank and *m* is the slope of the calibration equation. The dynamic linear range, modifier type, and LOD of the current work were compared with other related voltammetric techniques reported previously for the detection of DA and

summarized in Table 3. We can confirm that the poly (ANSA)/GCE attained a comparable linear range, the type of modifier used and LOD with the previously reported electrochemical methods.

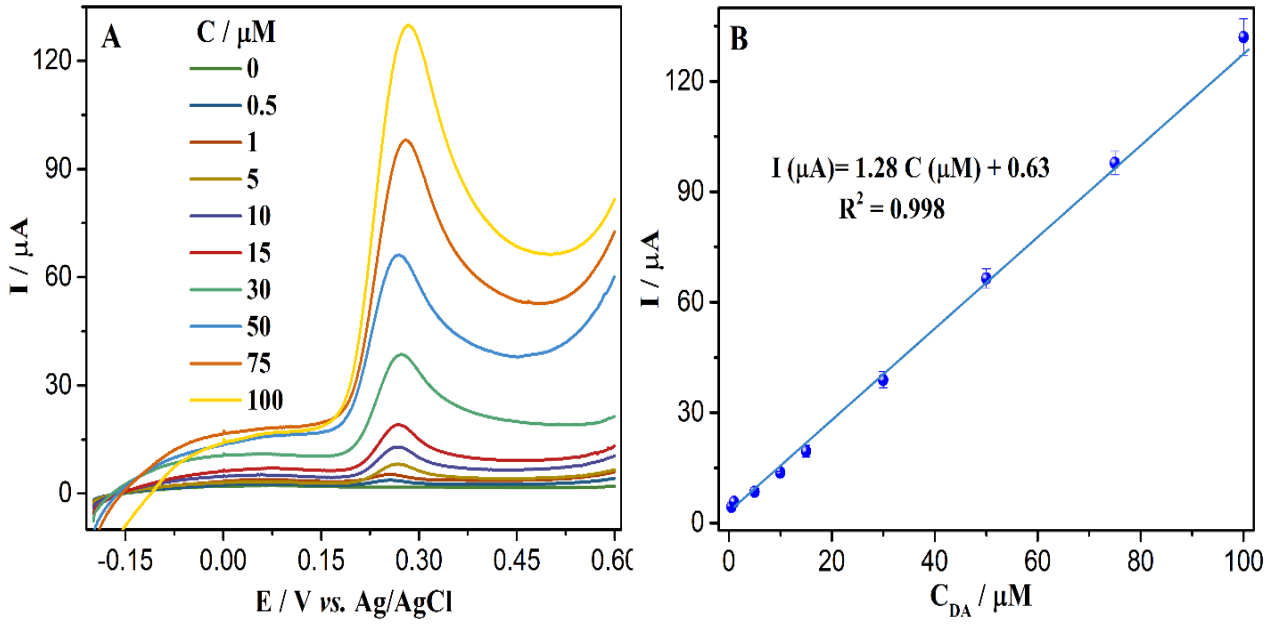


Figure 18. (A) LSV response of poly (ANSA/GCE) in the presence of DA a range of DA in concentrations ranging from 0.5 to 100 µM. (B) Calibration curve of DA at poly (ANSA)/GCE at a pH of 7.0.

Table 3. A comparison of the performances of electrochemical dopamine biosensors based on different conducting polymers and electrochemical method

Active Layer	Electro chemical method	Working electrode	Linear range(µg/L)	LOD(µM)	Ref
Poly(pyrrole-3-carboxylic acid)	ASDPVs	EOPGE	0.025–7.5 µM	2.5 nM	[84]
Polypyrrole	DPV	PGE	1–1000 µM	7 nM	[85]
Polycystine–Carbon Nanotube	CV	GCE	10–200 µM	2.8 µM	[86]
Poly(2-naphtol)	DPV	PIGE	0.6–250 µM	95 nM	[87]
Polypyrrole–Graphene	DPV	GCE	0.8–10 µM	4 nM	[88]
Poly(eriochrome black T)	DPV	GCE	0.1–200 µM	20 nM	[89]
PANI–Au NPs	DPV	PANI/GCE	20–100 µM	16 µM	[90]
Poly (ANSA)	LSV	ANSA/GCE	0.5-100 Mm	0.089 µM	This work

4.9. Repeatability and reproducibility

The oxidation current response for 10 µM DA were recorded for 12 repeated tests to determine the repeatability of poly (ANSA)/GCE. As a result, the RSD was determined to be 3.3% (Figure 19A). A reproducibility test was conducted using three distinct poly (ANSA)/GCE assemblies that were assembled independently using the same assembly technique. The results showed an RSD of 4.03% for the measurement of 10 µM DA (Figure 19B).

Therefore, we can conclude that the DA at poly (ANSA)/GCE was determined with extremely good repeatability and reproducibility. Furthermore, following at the same condition reserve for the electrode, the stability of the anodic current response of 10 µM DA was examined at poly (ANSA)/GCE. Excellent stability was demonstrated by the observed result, which shows that 87% of the initial oxidation current value was obtained.

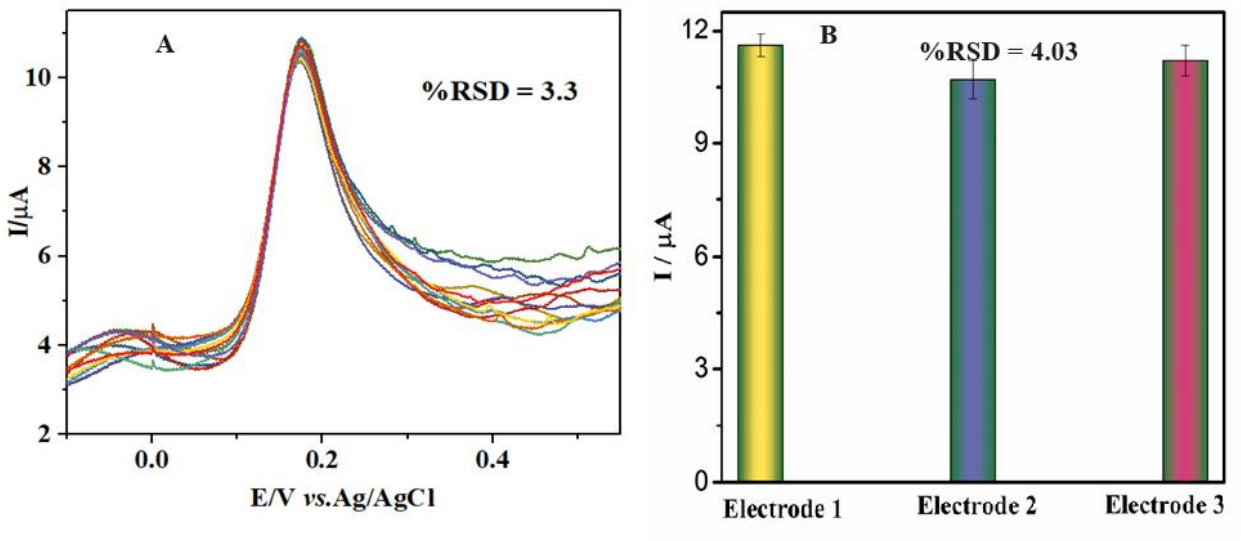


Figure 19. (A) LSV recorded for 12 successive measurements at poly (ANSA)/GCE using 10μM DA in 0.1M PBS (PH = 7.0); (B) Reproducibility study of the poly (ANSA)/GCE for the detection of 10 μM DA at three different modified electrodes.

4.10. Recovery test

It was possible to detect DA in DA hydrochloride injection by using the prepared modified GCE's to observe the practical applicability for sensing DA. Utilizing the LSV approach, it was completed. According to the injection parameters, the average determination result of DA in the injections closely matched the prescribed value. With regard to DA, the anodic peak current was measured and the LSV was noted. Ultimately, dopamine injection detection was achieved with the application of the designed poly (ANSA)/GCE. As shown in Table 4, the recovery of the tested samples were within the range of 94.1to 102.4%, which indicating that our method is sufficiently effective to detect DA in real samples.

Table 4. Determination of DA by poly (ANSA)/GCE in real sample

Real sample	**Addition amount (μM)**	**Measurements (μM)**	**Recovers (%)**	**RSD (%)**
DA injection	**-**	**5**	**-**	**3.2**
	2	**7.12**	**101.7**	**2.8**
	4	**8.47**	**94.1**	**4.6**
	8	**13.31**	**102.4**	**3.8**

4.11. Interference study

As shown in Figure 20 LSV recordings of DA with interference such as UA, 2,4-DPA, OQ and 4AP at modified electrode in PBS. The line (A) corresponds to 10µM DA, line (B) corresponds to (10µM DA + 100µM OQ), line (C) corresponds to (10µM DA + 100µM UA) and line (D) corresponding to (10µM DA + 100µM 4AP) at modified electrode in PBS. At the modified electrode, it is evident that the electrochemical signals of DA and interference (UA, 2,4-DPA, OQ, and 4AP) are separable. The anodic peak potentials signal for DA, UA, 2,4-DPA, OQ, and 4AP were occurred at +0.229, +0.433, +0.332, +0.542, and +0.412 V, respectively. The result showed that the LSV response of DA did not interfered due to the presences of UA, 2,4-DPA, OQ, or 4AP. Hence, a LSV response of poly (ANSA)/GCE could detect DA with high selectivity and sensitivity even in the presence of UA, 2,4-DPA, OQ, and 4AP: Different current responses or unique stimulated potentials for their oxidation was result from variations in current intensities [91].

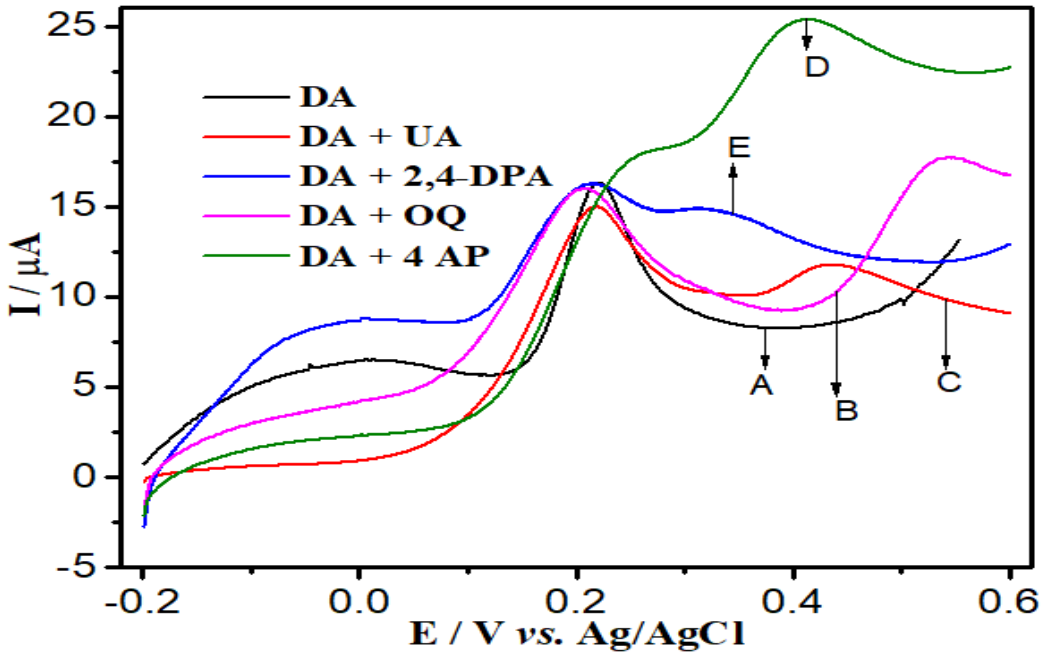


Figure 20. (A) LSV recorded for 12 successive measurements at poly (ANSA)/GCE using 10µM DA in 0.1M PBS (PH = 7.0); (B) Reproducibility study of the poly (ANSA)/GCE for the detection of 10 µM DA at three different modified electrodes.

5. Conclusion

The development of Poly (ANSA)/GCE for the sensitive determination of DA is described in the current work. Electropolymerization of the poly (ANSA) on modified GCE was optimized on film thickness in order to enhance conductivity and convenience of analyte. The created sensor demonstrated strong catalytic activity in the process of determining DA. The electrochemical oxidation mechanism was observed based on the DA redox process. The qualitative and quantitative performance of the sensor was well characterized by CV, LSV and CA. Diffusion coefficient and kinetic rate constant values were assessed as examples of kinetic parameters. The values of LOD was computed based on the influence of concentration. It was successful to determine the DA in the presence of UA, 2,4-DPA, OQ, and 4AP. Good stability, reproducibility, and repeatability have been demonstrated by the designed sensor. Ultimately, the created sensor underwent successful testing to recover DA in a pharmaceutical formulation.

Recommendation

Simultaneous determination of DA with other compound like ascorbic acid, UA, OQ and others by using poly (ANSA) on glass carbon electrode has forward to the future. In order to improve sensitivity during determination of DA on polymer modified electrode, using other voltammetry techniques that have best sensitivity than LSV to be suggested as suitable.

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