Addis Ababa University

College of Natural and Computational Sciences

Department Of Chemistry

Water Hyacinth-Derived Activated Carbon Paste Electrode for the Electrochemical Determination of Dopamine

By

Gashaw Girma

Advisor

Dr. Solomon Mehretie

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Declaration

I hereby declare that this research study is my own original work and that all references have been correctly indicated and acknowledged, and it has been submitted to Analytical Chemistry, Addis Ababa University.

The thesis “water hyacinth-derived activated carbon paste electrode for electrochemical determination of dopamine” is conducted under the supervision of Dr. Solomon Mehretie, Department of Chemistry, Addis Ababa University, Ethiopia.

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Name: Gashaw Girma Bekalo

Signature: _____

This thesis has been submitted for examination with my approval as university advisor.

Advisor’s Name

_____

Signature_____

Place and date of submission: Natural and computational sciences

Addis Ababa University, August 2024

ADDIS ABABA UNIVERSITY

NATURAL AND COMPUTATIONAL SCIENCES

DEPARTMENT OF CHEMISTRY

APPROVAL OF THE THESIS

Approved by the examining committee

Signature

Dr. Solomon Mehretie ……...……. Date……

(Advisor)

Prof. B.S. Chandravanshi ……..… Date……

(Examiner)

Dr. Merid Tessema…… Date……

(Examiner)

Abbreviations

CV	cyclic voltammetry
DPV	differential pulse voltammetry
DA	3,4-Dihydroxyphenyl ethylamine (dopamine)
AA	ascorbic acid
UA	uric acid
ADHD	hyperactivity disorder
CPE	carbon paste electrodes

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Abstract

The electrochemical determination of dopamine gains great interest due to its important role in the central nervous system (CNS) in various neurological disorders. This study explores the development of a non-toxic and cheap activated carbon paste electrode made from water hyacinth. The activated carbon was synthesized from water hyacinth through a carbonization process followed by chemical activation with phosphoric acid, yielding a material with good electrochemical activity. The synthesized activated carbon was then used to fabricate a carbon paste electrode, which was characterized using cyclic voltammetry (CV). The capacity of the water hyacinth-derived carbon paste electrode to quantify dopamine using differential pulse voltammetry (DPV) in phosphate buffer electrolyte solution. The electrode works with a linear range of 1.0–100 µM and a detection limit of 0.1 µM. The electrochemical sensor was applied to urine sample with a recovery range of 97.1-104.0 % result shown that this electrode could serve as an alternative for dopamine sensing to urine samples. It has different applications, including organic fertilizer, mulching, biofuel, and to clean the sewage. Moreover, this study provides a new application that contributes to the development of green technologies in sensors.

1. Introduction

3,4-Dihydroxyphenyl ethylamine, known as dopamine (DA), is an important neurotransmitter in the mammalian central nervous system [1]. DA presents as a cation in an acidic solution (pKa 8.87) [2].

Dopamine is an important endogenous catecholamine acting as a neurotransmitter in the brain. Its essential role lies in regulating attention, movement, cognition, pleasure and hormonal processes. In addition, it is extensively distributed in the renal, central nervous, cardiovascular and hormonal systems. A significant reduction of DA has been mainly associated with illnesses such as schizophrenia, restless leg syndrome, HIV infection, attention deficit hyperactivity disorder (ADHD), and Parkinson's disease [4, 5, 6]. DA is an electrochemically active molecule that gives dopamine-ortho-quinone (DOQ) as an oxidation product [7].

The main problem electrochemical determination of DA is the interferences of uric acid (UA), and ascorbic acid (AA) and, which have nearly similar oxidation potential in real systems and physiological samples and it needs to fabricate simple and rapid methods for their determination. Commonly, the concentration of DA is 0.01 to 1 μM while AA is as high as 100 μM in biological systems [3].

Electrochemical techniques are promising for detecting dopamine (DA), but DA, uric acid (UA), and ascorbic acid (AA) often produce similar electrochemical signals, making it difficult to isolate DA [6].

To overcome this interference, researchers have developed modified electrodes that selectively detect DA, minimizing interference from UA and AA.[8]

Common modifiers used for DA detection include, metal complexes[10,11], enzymes[12], organic polymers[9], nanoparticles, surfactants[15], carbon nanotubes[13,14],and organic molecules[16].

These modifiers are integrated into electrodes in different techniques like self-assembly[17,18], covalent attachment, coating with polymeric films[19], adsorption[20], or embedding in conductive matrices.

Adsorbed layers have limited functional groups and poor stability. While more stable, polymeric films can suffer from memory effects, unbalanced thickness, and poor reproducibility due to the solvent evaporation method.

Self-Assembly & Covalent Attachment ,While offering excellent stability, these methods make it hard to renew the electrode surface if contamination or inactive.

Carbon paste electrodes (CPEs) offer advantages such as ease of preparation, a porous surface, reproducibility, and affordability. These features make CPEs a suitable platform for modified electrodes.

A key limitation of CPEs is the loose association of modifiers, leading to degradation over time. To address this, researchers immobilize modifiers onto high surface area supports before embedding them into the carbon paste, preserving the sensor's functionality despite modifier diffusion or solubility.

Water hyacinth, an invasive aquatic species, offers a sustainable source of activated carbon due to its high carbon content and rapid growth. By converting water hyacinth into activated carbon through pyrolysis and chemical activation, it is possible to produce a material with a high surface area and excellent conductivity. These properties make water hyacinth-derived activated carbon good for constructing paste electrodes, which can be used in electrochemical sensors.

The activated carbon paste electrodes derived from water hyacinth exhibit superior electrocatalytic properties, making them effective for the sensitive and selective detection of dopamine. This approach also the environmental issue of water hyacinth proliferation but also contributes to the development of low-cost, green electrochemical sensors for biomedical applications, and developing environmentally friendly, highly sensitive electrodes for DA detection is essential for advancing diagnostics, and therapeutic technologies.

The interface between an electrode and the electrolyte is critical for determining the overall performance of an electrochemical sensor. In the case of water hyacinth-derived activated carbon paste electrodes (CPEs), the interface plays a significant role in enhancing the sensitivity and selectivity of the sensor, particularly for applications such as the electrochemical determination of dopamine. This study investigates the interfacial properties of water hyacinth-derived

activated carbon paste electrodes and explores how these characteristics influence electrochemical performance.

The surface morphology of the activated carbon paste electrode directly affects the interface between the electrode and the electrolyte. The water hyacinth-derived activated carbon exhibits a high surface area due to its extensive porosity, which is enhanced through the activation process. This porous structure increases the available active sites for electrochemical reactions, facilitating electron transfer at the interface.

These techniques provide insight into the surface roughness, pore distribution, and particle size, all of which influence the electrochemical behavior. A rougher surface with uniform porosity typically enhances the adsorption of dopamine, leading to improved sensor performance.

The electrochemical behavior of water hyacinth-derived activated carbon paste electrodes is heavily dependent on the quality of the interface between the electrode and the electrolyte. The activation process introduces functional groups such as hydroxyl, carboxyl, and carbonyl on the carbon surface, which facilitate better electron transfer and enhance the adsorption of dopamine.

Cyclic voltammetry (CV) is used techniques to study the electrode-electrolyte interface. CV can help determine the redox properties of dopamine at the electrode surface. Lower charge transfer resistance indicates a more efficient electron exchange between the electrode and the dopamine. which is desirable for sensitive detection.

The detection of dopamine relies on the strong interaction between the dopamine and the surface of the activated carbon electrode. The porous nature of the water hyacinth-derived activated carbon enhances the adsorption of dopamine molecules, while the functional groups introduced during activation improve the electron transfer kinetics.

The interface's ability to effectively adsorb and oxidize dopamine is crucial for the electrode's performance. The oxidation of dopamine at the electrode surface generates an electrochemical signal, which can be measured and correlated with the concentration of dopamine in the sample. The higher the surface area and the better the functionalization of the activated carbon, the more sensitive and selective the electrode will be for dopamine detection.

The binder used in the carbon paste electrode, typically paraffin oil or mineral oil, also affects the interface properties. The binder acts as a medium that holds the carbon particles together but can also influence the electrode's hydrophobicity and overall conductivity. The type and amount of binder must be optimized to ensure a stable interface without obstructing electron transfer or reducing the active surface area of the carbon particles.

1.3. Objectives

1.3.1. General objective

The main objective of this research is to study electrochemical determination of dopamine with water hyacinth-derived activated carbon paste electrodes

1.3.2. Specific objectives

The specific objectives of this study include

1. To study the effect of the effect of pH, scan rate, effect of modifier on the sensitivity of "carbon paste electrode".

2. To study electrochemical determination of dopamine with water hyacinth-derived activated carbon paste electrode.

3. To study the quantification of dopamine in biological samples with water hyacinth-derived activated carbon paste electrodes.

2. Literature Review

2.1 Catecholamine

Catecholamines are a group of neurotransmitters and hormones that play critical roles in the body, especially in the nervous system. They are derived from the amino acid tyrosine and share a common core structure.

Dopamine: Primarily associated with pleasure, motivation, reward, and movement. It's involved in conditions like Parkinson's disease and addiction. Norepinephrine (Noradrenaline): Plays a key role in the "fight or flight" response, alertness, and attention. It's also important for regulating mood, sleep, and appetite. Epinephrine (Adrenaline): A potent hormone released during stress, increasing heart rate, blood pressure, and energy mobilization. It's also involved in the "fight or flight" response. They act as chemical messengers within the nervous system, transmitting signals between neurons. Some catecholamines, like epinephrine, act as hormones released into the bloodstream, influencing a wide range of physiological processes. Physiological Effects: They regulate heart rate, blood pressure, breathing, energy metabolism, mood, attention, sleep, and the "fight or flight" response.

2.2 Health Implications:

Neurological Disorders: Imbalances in catecholamine levels can contribute to conditions like Parkinson's disease (low dopamine), depression (low norepinephrine), and anxiety (high norepinephrine).Cardiovascular Diseases: Excessive levels of epinephrine can contribute to high blood pressure and heart problems. Stress Response: Catecholamines play a central role in the body's response to stress, both physically and mentally.The process of creating catecholamines from tyrosine involves a series of enzymatic steps. Catecholamine Metabolism: The breakdown of catecholamines is regulated by specific enzymes. Catecholamine Receptors: These are specialized proteins that bind to catecholamines and trigger cellular responses.

2.3. Water hyacinth electrochemical material

Water hyacinth (Eichhornia crassipes) is the most rapidly growing, very productive free-floating aquatic plant, and widely distributed species that originated in the Amazon, South America [15]. The entry of water hyacinths into Africa, Asia, Australia, and North America was facilitated by human activities [16]. Specifically, Africa has been affected by the introduction and widespread of water hyacinth, facilitated in part due to a lack of controlling and removal mechanisms.

Water hyacinth reproduces itself very quickly by short runner stems (stolons) that radiate from the base of the plant to form daughter plants, and also reproduces by seed and it has the ability to covers large water bodies in different countries within a short period of time. Lake Tana, Amhara region in Ethiopia is the one which is covered by water hyacinth as shown in Figure 2.

Water hyacinth has the potential to degrade water quality, water volume, aquatic organisms, and biological diversity by blocking photosynthesis, which greatly reduces oxygen levels in the water [17]. Water hyacinth affects biodiversity, ecosystem, human and animal health, and socioeconomic development significantly [18]. Till now a lot of money and resources have been spent in order to destroy the water hyacinth to prevent the water body from drying. Nowadays, it has different applications, including organic fertilizer, mulching, biofuel, and cleaning sewage.

As reported in the literature [21], titanium phosphate silica gel modified carbon paste electrode prevent the oxidation of ascorbic acid by repulsion, and also improving the oxidation signal of dopamine by attraction.

The main concern of the this method is based on the opposite ion forms of DA, UA, and AA at pH of 6. AA and UA exist in the anionic form (pKa= 4.10 and 5.75, respectively) while DA is in the cationic form (pKa= 8.87).

Similarly, the carbon paste electrode modified with water hyacinth- derived activated carbon paste electrode (CPE)), which acts as a cation exchanger [22], repels the negatively charged AA and UA and selective sensing of DA can be achieved. This suggested the potential usefulness of the modified electrode for the selective determination of DA in the presence of AA and UA.

Major advantages of the this modified electrode such as good stability (because of the low solubility of water hyacinth-derived activated carbon paste electrode (CPE), ease of preparation and surface regeneration by simple polishing, and very good selectivity toward DA, make it very suitable for the selective and sensitive determination of DA in the presence of AA and UA.

In other studies, $Fe(CN)_6^{3-}$ has been proposed as an electrochemical probe. Typically altering electrodes with charged species significantly influences the electrochemical charcteristics of redox reactions. These influences are contingent on the charges of both the electrode surface and the redox probe. When the charges are opposite, the redox reactions of the charged probe exhibit more reversible behavior at the modified electrodes. Conversely, when the charges are similar, the redox reactions show less reversibility.

Consequently, at the carbon paste electrodes modified to be negatively charged probe $Fe(CN)_6^{3-}$ displays broader redox peaks with reduced reversibility, indicated by a ΔEp that is greater than that unmodified CPE. This is attributed to the electrostatic repulsion between negatively charged electrode and the $Fe(CN)_6^{3-}$ probe.

As the pH decreases, the protonation of phosphate groups of the modifier reduces the negative charge on the electrode surface, leading to more reversible behavior of the probe at the modified CPE . In contrast, the positively charged dopamine (DAH+) exhibits the opposite behavior at the modified electrode.

3. Experimental

3.1. Reagents and solutions

All reagents used were of analytical grade from Fluka or Merck and were utilized without any additional purification. Solutions were made using distilled water.

The necessary pH levels were achieved by adjusting appropriate volumes of the solution with sodium hydroxide. Fresh stock solutions of ascorbic acid(AA),dopamine(DA),and uric acid(UA) were prepared in distilled water as needed. Voltammetric experiments conducted in the Phosphate buffer solution (PBS, 0.1 M, pH=6) which was made using monobasic sodium phosphate (NaH_2PO_4) and dibasic sodium phosphate (Na_2HPO_4). Pure water was used for all solutions preparations, including the 0.1 M phosphate buffer at pH 6 for, UA, AA ,and DA.

3.2. Apparatus

All voltammetric measurements were performed using a water hyacinth derived activated carbon-paste working electrode, platinum wire as the auxiliary electrode, and saturated Ag/AgCl as reference electrode

Differential pulse voltammetry (DPV) experiments were conducted with a pulse interval of 0.3 s, scan rate of 20 mV/s, and a pulse amplitude of 50 mV, using an Autolab PGSTAT 30 Potentiostat Galvanostat (EcoChemie, The Netherlands) connected to a 663 VA stand (Metrohm, Switzerland). pH measurements were taken with a Metrohm 744 pH meter.

3.3 Synthesis of Activated Carbon from Water Hyacinth

Freshwater hyacinth plants are collected from aquatic environments. The plants are thoroughly washed with distilled water to remove any dirt and impurities. After washing, the plants are cut into smaller pieces and air-dried for several days. The dried plant material is then further dried in an oven at around 105°C to remove moisture completely. The dried water hyacinth is subjected to pyrolysis in a furnace at a temperature ranging from 400°C to 600°C under an inert atmosphere, such as nitrogen gas, to prevent oxidation. This process decomposes the organic matter, leaving behind carbon-rich material. The carbonization step typically lasts for 1-2 hours, depending on the desired properties

The carbonized material is chemically activated to enhance its porosity and surface area. This can be done by treating the carbon with chemical agents such as potassium hydroxide (KOH), phosphoric acid (H_3PO_4), or zinc chloride ($ZnCl_2$). The mixture is stirred thoroughly to ensure even impregnation of the chemical agent. The impregnated carbon is heated again at higher temperatures (700°C to 900°C) in an inert atmosphere. This step activates the carbon, opening up the pores and increasing the surface area, which enhances its adsorptive and electrochemical properties. The heating is typically maintained for 1-3 hours**.**

After activation, the material is cooled and washed thoroughly with distilled water to remove any residual chemicals. The washing continues until the pH of the rinse water is neutral. The activated carbon is then dried in an oven at 105°C for several hours. The dried activated carbon is ground into a fine powder and sieved to obtain uniform particle sizes suitable for making paste electrodes or other applications. This activated carbon can then be used to prepare paste electrodes for various electrochemical applications, including the detection of dopamine. The high surface area and enhanced porosity of the activated carbon provide better sensitivity and selectivity in sensor applications.

The modified carbon paste was created a previously established method found in the literature [21,22]. This process involves two main steps. First, approximately 50 g of water hyacinth , which had been dried in an oven at 150 °C, under vacuum, was soaked in a solution containing 11.6 g dissolved in 300 ml of dry ethanol. This mixture was refluxed for 8 hours at 80 °C after which the resulting material was decanted, washed, and then heated at 150 °C for 4 h.

Next, the material under went hydrolysis by being immersed in distilled water. The solid was then washed with water to eliminate all chloride ions and dried in an oven at 120 °C for 5 hours. Subsequently, about 25 g of this material was combined with 200 mL of a 0.1 M H3PO4 solution and shaken for 10 h at 90 °C. Finally, the solid was washed with distilled water and dried in an oven at 100 °C for 4 hours.

3.4. Preparation of modified carbon paste electrodes

The initial carbon paste was made by mixing 600 milligrams of graphite powder with 337 microliters of paraffin oil, which was thoroughly blended using a mortar and pestle. A portion of this mixture was then inserted into the end of an insulin syringe (with an inner diameter of 2 mm) and connected to a copper wire for external electrical contact.

The surface was smoothed using a piece of paper. A new surface can be created by extruding excess paste from the tube, removing the surplus, and then mechanically polishing the electrode surface again. The impact of the carbon paste composition on the voltammetric response of dopamine oxidation at the modified electrode was assessed using differential pulse voltammetry. As anticipated, the amount of water hyacinth-derived activated carbon in the electrode significantly affected its response, with the peak current increasing as the concentration of the modifier in the carbon paste electrode rose.

4. Results and discussion

4.1. Voltammetric Properties of Dopamine with Activated Carbon-Paste Modified Carbon Paste Electrode

Initial experiments were conducted to determine the general characteristics of dopamine (DA) behavior on a carbon paste electrode. Figure 1 displays cyclic voltammograms of 10 µM DA in 0.1 M phosphate buffer (pH 6) for both unmodified and modified carbon paste electrodes. A minor peak was detected in the potential range of 0 to 400 mV (relative to Ag/AgCl) at the bare carbon paste electrode (CPE). The cyclic voltammograms for DA using the water hyacinth-derived activated carbon paste are also presented. The increase in anodic current observed with the water hyacinth-derived activated carbon paste indicates that the sodium phosphate carbon paste significantly contributes to the accumulation of DA on the electrode surface.

The influence of accumulation time on the peak current of DA was examined, revealing that the peak current increased with longer accumulation times. After immersing the water hyacinth-derived activated carbon paste in a 50 µM DA solution for 2 minutes and subsequently rinsing it with distilled water, a response to DA was detected on the modified electrode in a blank solution. These findings confirmed that DA was adsorbed onto the surface of the modified electrode. Figure 1a illustrates the cyclic voltammogram of DA at an unmodified CPE, where the anodic peak for DA was noted at 0.043 V versus the Ag/AgCl (3 M KCl) reference electrode. Figure 1b shows the cyclic voltammogram for a similar solution at the water hyacinth-derived activated carbon-paste electrode, which exhibited an 80% increase in peak current due to the use of this modified electrode.

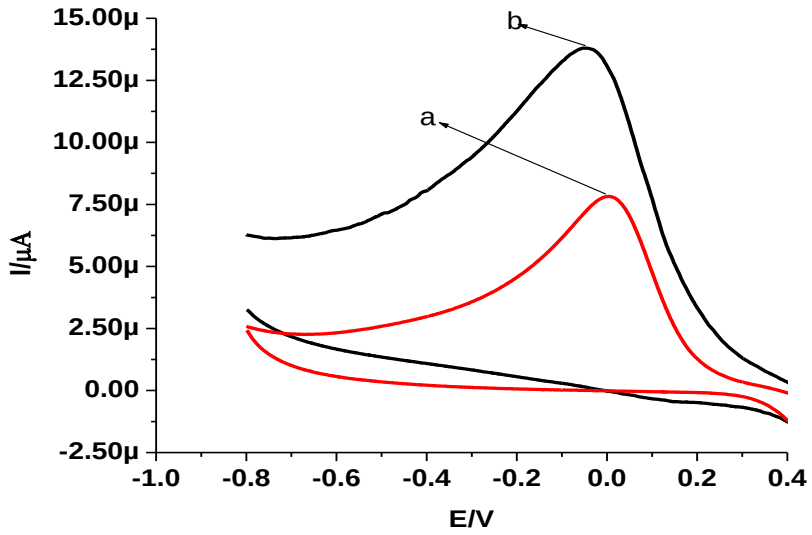


Fig. 1 cyclic voltammogram of a 10 µM DA In 0.1M PBS (pH=6) at the scan rate 50 mV/s at (a) bare electrode and (b) water hyacinth derived activated carbon-paste electrode

4.2 effect of scan rate

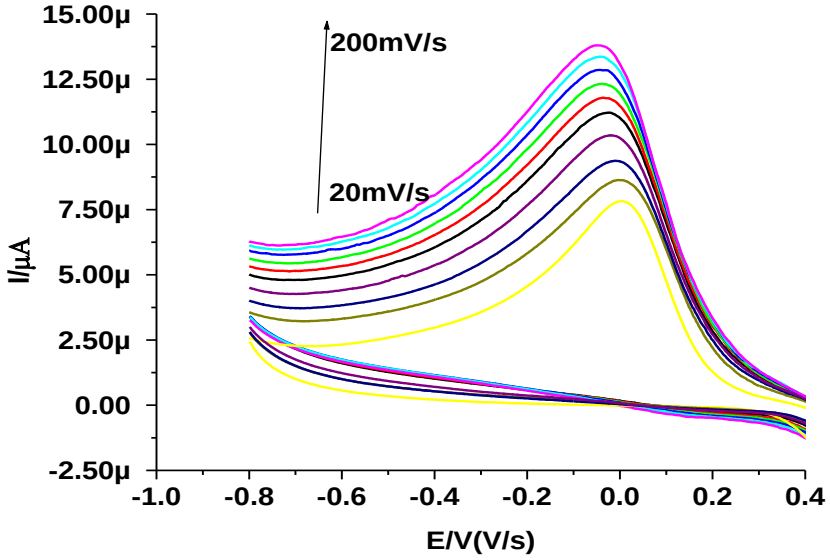


Figure 2 shows cyclic voltammograms recorded at a scan rate of 100 mV/s for a 50 µM dopamine solution buffered at pH 6, using an activated carbon-paste electrode .

The anodic peak was observed to shift to a less positive potential of -0.12 V. At pH 6, the potential difference between the anodic and cathodic peaks (ΔEp) for dopamine (DA) was measured at 180 mV for the carbon paste electrode (CPE) modified with water hyacinth, compared to 340 mV for the unmodified CPE. The modifier does not possess any electroactive sites, and the cyclic voltammogram of the water hyacinth-derived activated carbon-paste electrode in a buffer solution did not reveal any significant peaks. Consequently, the variations in the voltammetric behavior of DA in the presence and absence of the water hyacinth-derived activated carbon-paste electrode can be attributed to the electrocatalytic effect of the modified electrode on DA oxidation.

The impact of the potential scan rate on the peak current of DA oxidation at the water hyacinth-derived activated carbon-paste electrode was examined, revealing a linear increase in the anodic peak current (in microamperes) with rising scan rates (in mV),

described by the equation: $Ip = 0.000336\nu + 0.0074$.

Thus, it can be concluded that the differences in the electrochemical behavior of DA at bare and modified CPEs stem from changes in the mass transfer dynamics of DA. Specifically, DA reaches the surface of the bare CPE solely through diffusion, while it adsorbs onto the surface of the modified electrode. At pH 6, DA exists in its cationic form (pKa = 8.87), and since the water hyacinth-derived activated carbon-paste electrode acts as a cation exchanger, it is suggested that the adsorption of DA on its surface is due to electrostatic interactions.

The effect of the scan rate on the anodic peak current of DA was analyzed using cyclic voltammetry, and the results indicated that the peak current increased with the scan rate. A strong linear correlation between $\nu 1/2$ and IPa within the scan rate range of 10 to 140 mV/s supports the notion of a diffusion-controlled process occurring on the modified electrode.

4.3 The influence of pH and electrode composition on dopamine peak current

Figure 3 illustrates how the peak current in the differential pulse voltammetric oxidation of dopamine (DA) varies with the pH of the solution. The anodic peak current increased as the pH rose, reaching a maximum at pH 6. However, beyond this point, the peak current began to decline as the pH continued to increase.This phenomenon can be explained as follows: as the pH of the solution increases, the negative phosphate groups on the surface of the activated carbon-paste electrode derived from water hyacinth also increase, which attracts more positively charged DA molecules to the electrode. Consequently, the anodic peak current rises with pH from 1 to 6. Beyond pH 6, the protonation of DA decreases as pH increases.

When the pH exceeds 6, although the negative phosphate groups on the electrode surface increase, the amount of positively charged DA decreases significantly. This reduction diminishes the electrostatic attraction between DA and the phosphate groups, leading to a decrease in the anodic peak current as pH surpasses 6. Figure 3B depicts how the peak potential changes with solution pH. It is evident that the peak potential for DA oxidation shifts negatively with increasing pH, following the equation Ep(mV) = 521.1 - 56.9pH. The slope of 56.9 mV/pH, which is close to the theoretical value of 59 mV/pH, indicates a 2e−/2H+ process within the examined pH range.

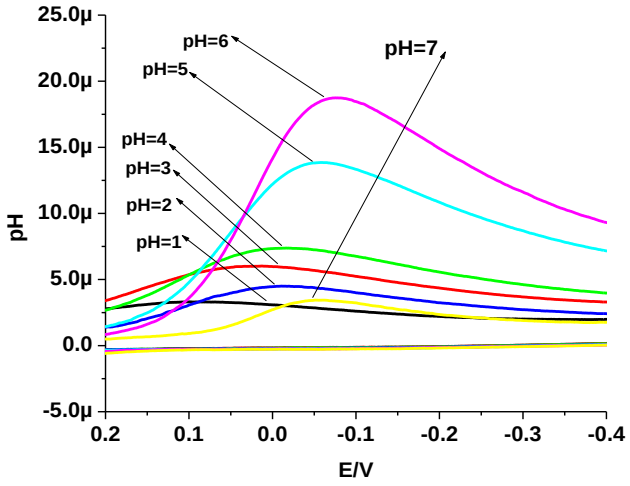


Fig. 2 Effects of pH on peak current

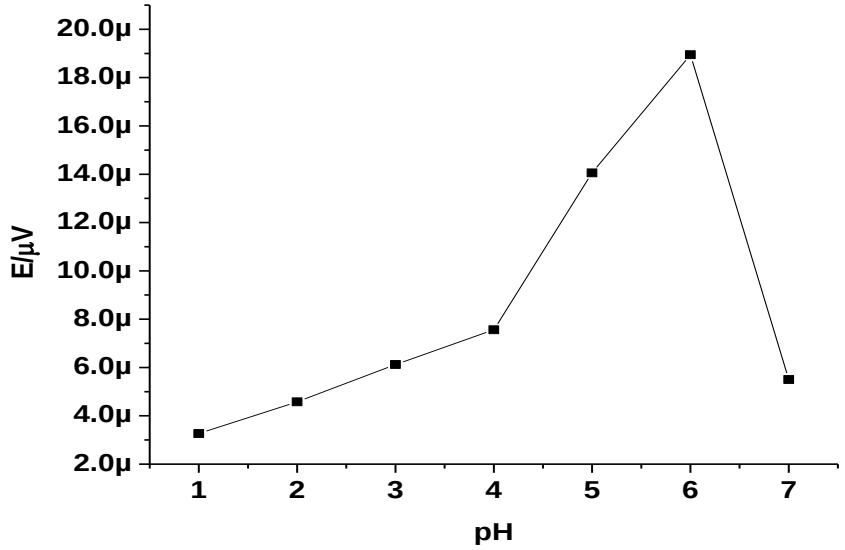


Fig. 3 Effects of pH on peak potential at water hyacinth derived activated carbon-paste electrode modified carbon paste electrodes on differential pulse voltammetric response of 100μM DA.

4.4 Effect of concentration

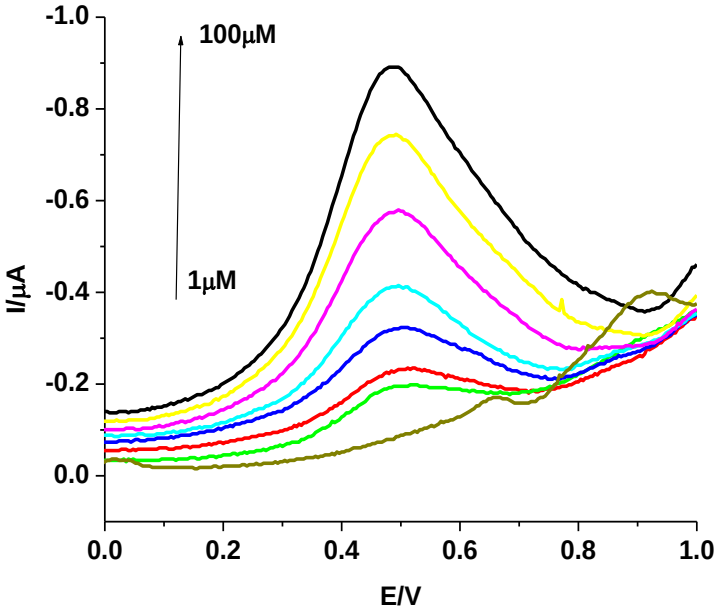


Fig. 4 Differential pulse voltammograms of dopamine (DA) were obtained using a modified carbon paste electrode (CPE) under optimal conditions. The concentrations of DA in micromolar (μM) were as follows: (1) 1.0, (2) 5.0, (3) 20.0, (4) 40.0, (5) 60.0, (6) 80.0, and (7) 100.0.

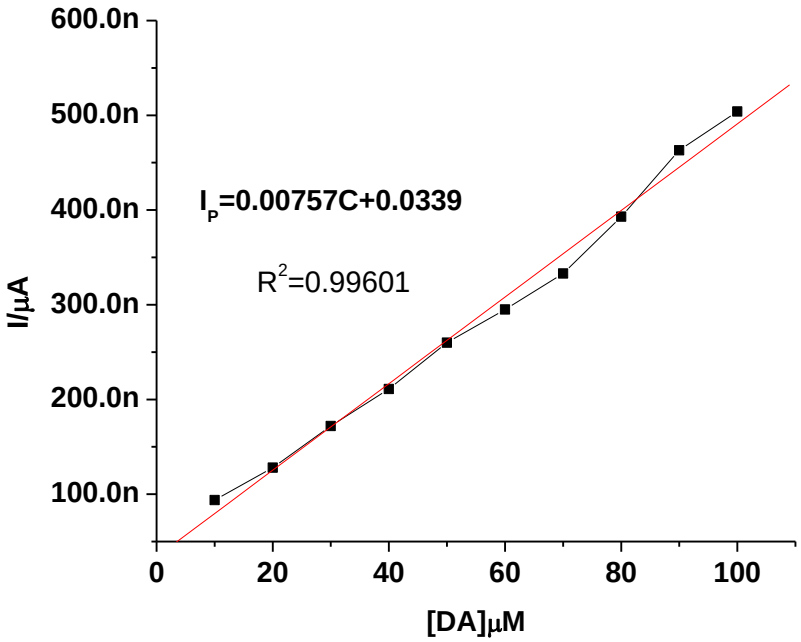


Fig. 5 The change in peak current in relation to DA concentration, within the range of 1.0 to 100 μM, under optimal conditions.

The concentration was increased from 1.0 to 100 µM. As shown in Fig. 5, the height of the DPV peak at the modified electrode exhibits a linear relationship with DA concentration within the range of 1.0 to 100 µM. The linear regression equation is as follows:

I p µA = 0.00757[DA] µM + 0.339; (R2 = 0.99694).

The favorable signal-to-noise ratio of these results indicates a detection limit of 0.1 µM (based on S/N= 3).

4.5. Stability and Reproducibility

One of the benefits of the modified electrode is its operational stability. This was evaluated by observing the reduction in voltammetric currents during repeated DPV measurements of DA. For instance, when the modified electrode was tested every 30 minutes for 10 µM DA in a 0.1 M phosphate buffer solution (pH 6) without refreshing the electrode surface, it maintained 94% of its initial activity after 240 minutes.

The long-term stability of the modified electrodes is excellent. When stored in the open air, the current response remained nearly constant even after two weeks. The high stability of the activated carbon paste derived from water hyacinth may be attributed to the robust nature of the modified carbon paste and the insolubility of the water hyacinth-derived activated carbon paste in water. A key advantage of the modified electrode is that its surface can be refreshed as needed.

The reproducibility of the method was assessed by performing ten repeated measurements of 1 and 10 µM DA under identical conditions. The relative standard deviations of the peak currents were found to be 3.52% and 2.61%, respectively. Thus, the response from the water hyacinth-derived activated carbon paste is both stable and reproducible.

4.6. Interference Studies

It is widely recognized that ascorbic acid (AA) and uric acid (UA) often coexist with dopamine (DA) in biological samples. Therefore, minimizing the interference from AA and UA is crucial for any analytical methods aimed at detecting DA. The interference from AA in DA detection stems from two main factors: the similar oxidation potentials of AA and DA at standard electrodes, and the electrocatalytic oxidation of dopamine by ascorbic acid, where oxidized dopamine (dopamine-o-quinone) is chemically reduced by AA.

Similarly, the interference from UA in DA measurement is attributed to the comparable oxidation potentials of DA and UA. Consequently, it is anticipated that the oxidation wave of DA will be influenced by the presence of both AA and UA. At a pH of 6, the negatively charged activated carbon-paste derived from water hyacinth repels the anions of AA and UA, allowing only the cations of DA to pass through. In a phosphate buffer at this pH, DA exists as a cation (pKa=8.87), while AA (pKa=4.17) and UA (pKa=3.70), along with the phosphate groups of the modifier, exist as anions.

In Figure 7, curve a represents the differential pulse voltammogram of AA at the modified carbon paste electrode (CPE). It is evident that AA does not produce an electrochemical response on the surfaces of the water hyacinth-derived activated carbon paste, effectively avoiding interference from the overlapping oxidation wave of AA. Additionally, curve c in the same figure illustrates the differential pulse voltammogram of a solution containing 100 µM DA and 100 µM AA, which closely resembles the voltammogram of DA in the absence of AA (curve b).

The experiment demonstrated that the electrocatalytic oxidation effect of AA can also be mitigated using the water hyacinth-derived activated carbon paste. Similar investigations were conducted to assess the interference of UA on DA measurement. Figure 8 displays the differential pulse voltammograms for 100 µM UA (curve a), 100 µM DA (curve b), and a mixture of 100 µM DA and 100 µM UA at the modified CPE under comparable conditions. The findings from this study indicate that the interference from UA in DA determination can be effectively eliminated by employing the modified electrode.

To establish the sustainable levels of AA and UA, calibration curves for DA were created while varying the concentrations of AA and UA. It was observed that the detection limit and calibration equation for DA remained consistent with increasing UA and AA concentrations up to 100 µM and 400 µM, respectively. However, at higher levels of AA and UA, both the detection limit and the limit of determination for DA increased as the concentrations of AA and UA rose. This study indicates that the interference caused by UA and AA in the determination of DA can be significantly reduced by using phosphate. Similar interference tests were also conducted with other substances.

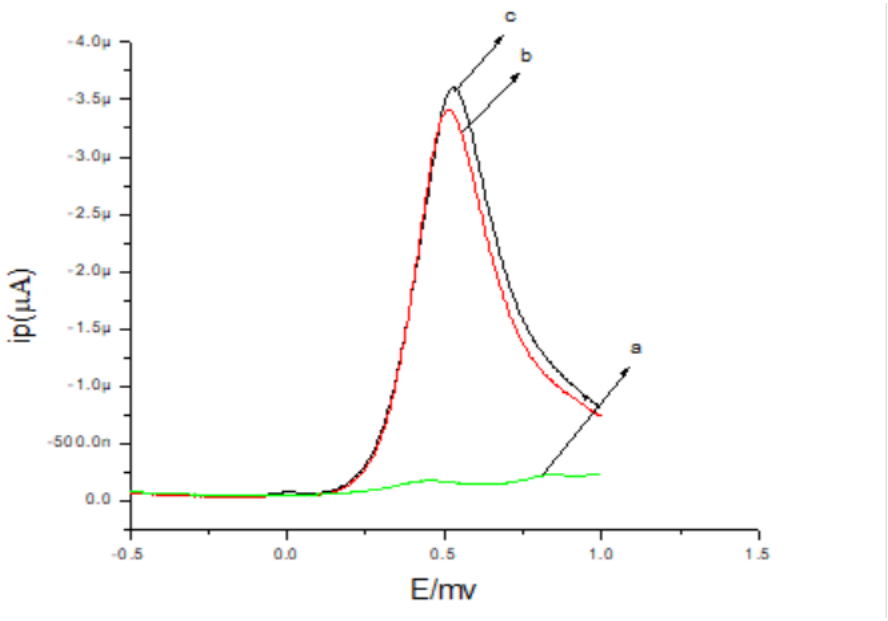


Figure 6 Differential pulse voltammograms for (a) 100 µM ascorbic acid (AA), (b) 100 µM dopamine (DA), and (c) a mixture of 100 µM AA and 100 µM DA.

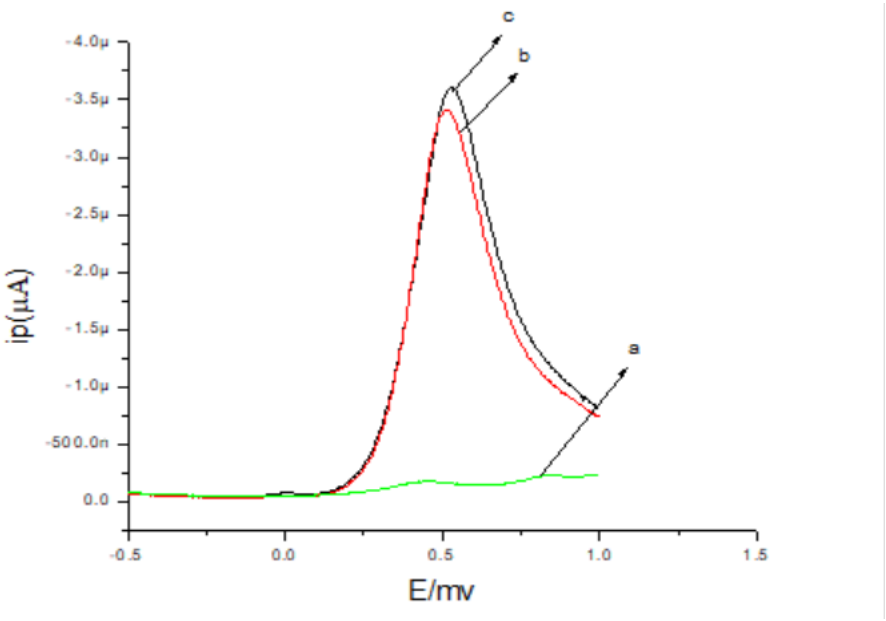


Fig. 7 Differential pulse voltammograms for (a) 100 µM uric acid (UA), (b) 100 µM dopamine (DA), and (c) a mixture of 100 µM UA and 100 µM DA, obtained under optimal conditions.

Table 1

A recovery test was conducted to determine DA levels in a human urine sample, which was filtered and then diluted tenfold with a 0.1 M phosphate buffer solution at pH 6.

DA added(μM)	Total found (μM) (±RSD%)	Recovery%
0	0.0	-
10.0	10.4(±4.0)	104.0
20.0	20.4(±3.5)	102.0
50.0	49.5(±5.3)	99.0
80.0	78.8(±3.4)	98.5
100.0	97.1(±4.2)	97.1

4.7. Analytical Applications

To evaluate the effectiveness of the proposed electrode in real-world analytical scenarios, it was utilized to determine the recovery of dopamine in human urine samples. Fresh urine samples from volunteers were collected, filtered, and diluted with a 0.1 M phosphate buffer solution at pH 6, with a 10.0 ml portion placed into the voltammetric cell. Various concentrations of dopamine were added to the diluted urine sample, and differential pulse voltammetry (DPV) was performed using the modified electrode. After each addition of dopamine, the electrode surface was gently polished. The results for dopamine spiked in the diluted urine samples (10-fold dilution) ranged from 97.1% to 104.0% (see Table 1).

The modified electrode was also used to analyze dopamine spiked to a diluted concentration of 10 µM. The spiking of dopamine was assessed using a calibration plot based on the method described earlier. Additionally, specific amounts of standard solutions were incorporated into the corresponding spiking for recovery testing. The relationship between the experimentally determined dopamine concentration and its expected value (DA experimental) is illustrated in Fig. 9. Data analysis revealed a regression coefficient (R^2) of 0.9996, with an intercept of 0.0541 and confidence limits of -1.814 to +2.895, which includes the ideal value of zero. The slope of the graph was 0.0983, with a 94% confidence interval of 0.907 to 1.059, also encompassing the expected value of 1.0. The research findings indicate that the suggested approach is successful in measuring dopamine levels in fluctuating conditions.

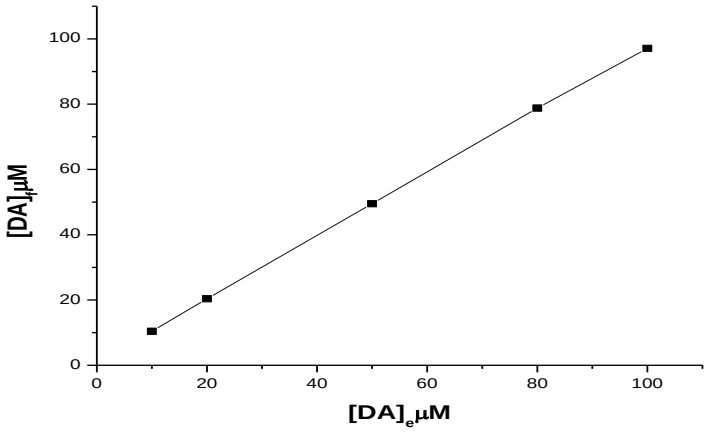


Fig. 8. Variation of the experimentally determined DA concentration compared to its anticipated.

Table 2. Comparison of the developed sensor with previously reported electrochemical sensors

Electrode	Method	Linear range	Limit of detection	Reference
Gold nanoparticles modified screen printed carbon sensor	Square wave voltammetry	0.2–100 µM	0.008 µM	Gupta, Goyal, and Shim (2015)
Graphene nanosheets and nickel oxide nanoparticles modified carbon screen printed electrode	Differential pulse voltammetry	1–500 µM	0.314 µM	ahani and Beitollahi (2016)
CuO-doped multi-wall carbon nanotubes/nafion modified glassy carbon electrode	Differential pulse voltammetry	1–80 µM	0.04-0.03 µM	Yang et al. (2013)
Pretreated/carbon paste Electrode	Differential pulse voltammetry	0.1–100 µM	0.198 µM	Mahanthesha and Swamy (2013)
N,N′-bis(4-{2-[2-(2-methoxyethoxy ethoxy] ethoxy}phenyl)-3,4:9,10-perylene tetracarboxydiimide	Differential pulse voltammetry	1–100 µM	0.011 µM	Tuğba Ören, Özgül Birel & Ülkü Anık(2016)
Water hyacinth derived activated carbon paste electrode	Differential pulse voltammetry	1–100 µM	0.10 µM	This work

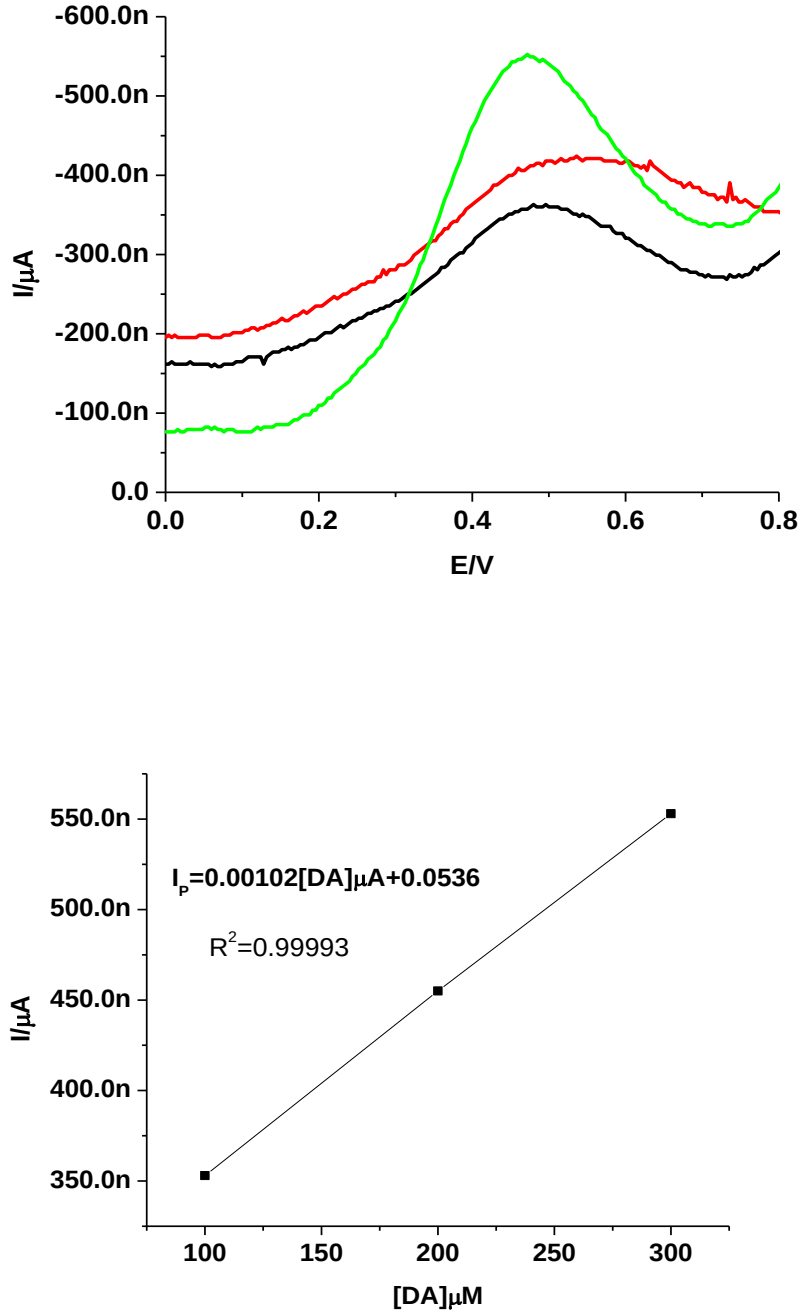
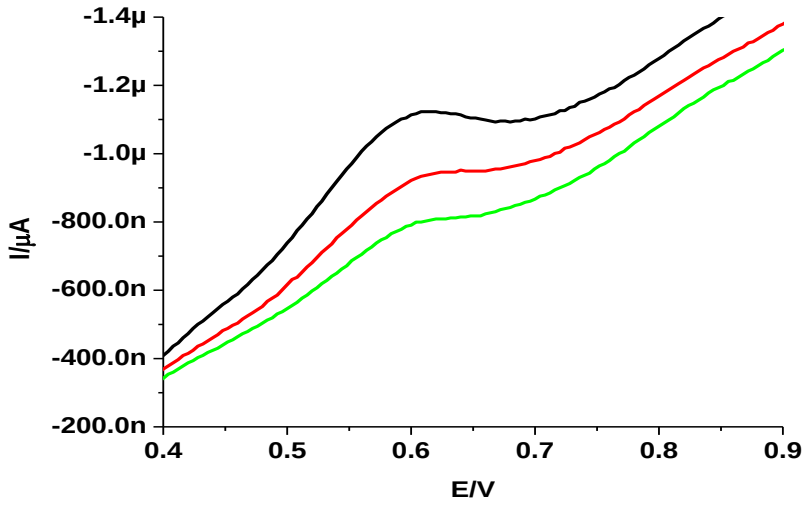


Fig. 9 Anodic stripping voltammetric responses for dopamine in 25mL of phosphate buffer solution and (DA), (a)100 μM (DA) (b)200 μM (DA) and (c)300 μM (DA).



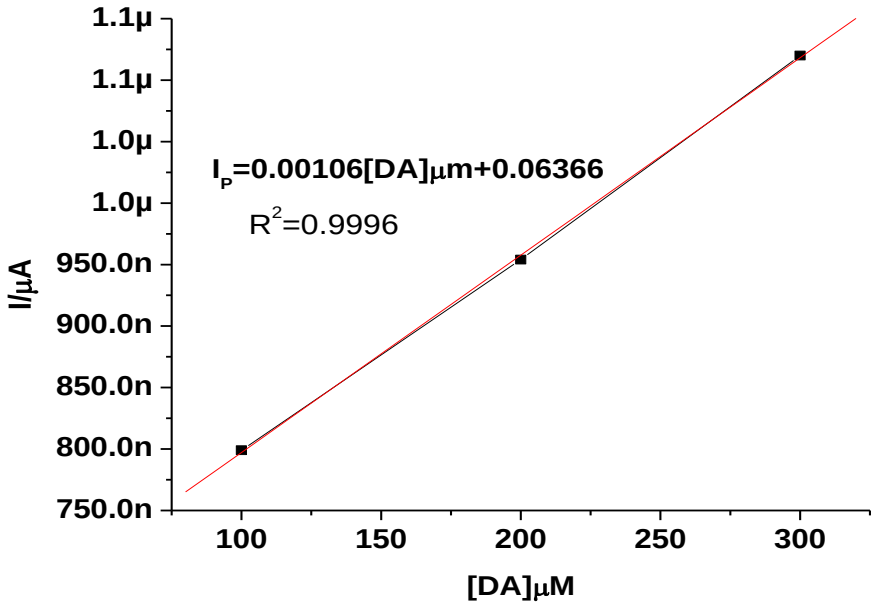


Fig. 10 urine sample ; spiked with (a)0 µM(DA), (b) 100 µM (DA),(c) 200 µM (DA) ,and (d)300 µM (DA)

From the above two figures the slop value is almost the same this shows that there is no matrix effect in the measurements of dopamine in biological samples.

5. Conclusion

This study presents a novel and environmentally friendly electrochemical sensor for the sensitive determination of dopamine, utilizing a water hyacinth-derived activated carbon paste electrode. The electrode demonstrates good electrochemical performance, exhibiting moderate sensitivity and 0.1 µM detection limit. This good performance is attributed to the unique properties of the water hyacinth-derived activated carbon, including its high surface area, excellent conductivity, and biocompatibility. Additionally, the use of this readily available and sustainable biomaterial offers an environmentally sound alternative to traditional electrode materials.

The developed sensor exhibits good selectivity towards dopamine in the presence of common interfering species, demonstrating its potential for real-world applications in the monitoring of dopamine levels in biological samples or for the development of diagnostic devices.The properties of water hyacinth-derived activated carbon gives the way for the development of cost-effective, good performance electrochemical sensors for various analytical applications.

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