



VOTAMMETRIC DETERMINATION OF DOPAMINE AT COBALT OXIDE NANOPARTICLES MODIFIED GLASSY CARBON ELECTRODE

Dr (Ms) Phebe Kingsley Mal* and Ms Archita Guddu Rajbhar¹

^{*,1}Department of Chemistry,

N.E.S Ratnam College of Arts, Science and Commerce, (Autonomous)

Bhandup 400 078

Abstract

In this present study, a glassy carbon electrode was modified with cobalt oxide nanoparticles to determine voltammetric determination of Dopamine using Differential pulse voltammetry. The reference and counter electrode used were Ag/AgCl and Pt wire, respectively and the working electrode was cobalt oxide nanoparticles modified glassy carbon (CoGCE). pH optimization revealed pH 7 in Britton-Robinson buffer as the most suitable, yielding maximum peak current and minimal background noise. The results with the CoGCE demonstrated high electrocatalytic activity toward Dopamine with increase in surface area compared to glassy carbon electrode. Under optimized conditions, the calibration curve for Dopamine concentration was linear in $1.2 \times 10^{-8} M$ to $3.5 \times 10^{-3} M$ with a low Limit of Quantification of $8.50 \times 10^{-10} M$ and a Limit of detection of $2.80 \times 10^{-10} M$. The prepared sensor provides a sensitive and rapid strategy for the detection of Dopamine.

Keywords: Cobalt oxide nanoparticles, Glassy carbon electrode, Dopamine, cyclic voltammetry, Differential pulse voltammetry

1. INTRODUCTION:

Dopamine is a catecholamine hormone and a monoamine neurotransmitter (or chemical messenger) found in diverse organisms ranging from vertebrates to humans. It is also a required intermediate in the formation of neurotransmitters adrenaline and noradrenaline. Dopamine signaling affects a wide variety of physiological functions, from gastrointestinal motility, pituitary hormone release to voluntary movements and higher cognitive processes. Thus determination of accurate estimation of dopamine in biological fluids is very necessary[1]. Although, dopamine neurotransmission is normally a highly regulated process, drugs have been developed to modify its signalling. Some commonly used drugs affect dopamine neurotransmission indirectly (by changing its synthesis, storage, release, reuptake or inactivation), whereas other drugs more directly mimic or block the actions of dopamine at its biological targets (i.e. multiple cell surface dopamine-responsive receptors). A broad range of central nervous system disorders (including Parkinson disease, schizophrenia, attention deficit hyperactivity disorder and sleep disorder), other medical conditions (such as nausea, excessive pituitary hormones, gastrointestinal disorders and cardiovascular shock) are currently treated using such dopamine[2].

Various techniques have been employed to quantify the levels of dopamine, such as high-performance liquid chromatography [3], mass spectrometry [4], colorimetry [5], fluorescent spectroscopy [6], and electrochemical techniques [7-13]. Electrochemical methods are very interesting and promising because they have benefits like high sensitivity, low cost, and very simple compared to other time consuming traditional methods. However, the bare GCE has poor sensitivity and selectivity for determining drugs, such as dopamine. To overcome these disadvantages, chemically modified electrodes were used with various materials, such as nanostructure material [14], nanoparticles [15,16], Ionic liquids (ILs) [17], metal nonmaterial [18], and nanocomposites [19-21].

In this study, for enhancing the electrical characteristics and improve the efficiency the glassy carbon electrode was modified with cobalt oxide nanoparticles was used to detect dopamine voltammetrically using Cyclic Voltammetry and differential pulse voltammetry.

2. MATERIAL AND METHODS

2.1 Chemicals:

All chemicals were of Analytical grade and were used as received without further purification. Dopamine Boric Acid, o-Phosphoric Acid, Glacial Acetic Acid, NaOH, Conc. HCl, Sodium Citrate, Citric Acid anhydrous, Disodium Hydrogen Phosphate, Potassium Dihydrogen Phosphate, Sodium acetate, Acetone and cobalt oxide nano powder were purchased from S.D. fine Chemicals, India. Double distilled water was used for the preparation of aqueous solutions having a specific conductivity 0.4 - 0.9 μ S.

2.2 Methods:

i) Preparation of Standard Dopamine Solution (1×10^{-4} M) :

Standard solution was prepared by dissolving 0.00153g of dopamine in distilled water and made the volume upto 100ml with the distilled water

ii) Preparation of Buffer Solution:

1. BR Buffer (0.04M) : Prepare buffer solution by adding 4.948g boric acid, 4.56ml glacial acetic acid and 5.84ml of o-phosphoric acid in distilled water
2. Phosphate Buffer (0.1M): Prepare buffer solution in 500ml by adding 14.1g disodium hydrogen phosphate and 11.45g of potassium dihydrogen phosphate.
3. McIlvaine buffer (0.1 M): 0.2M Disodium hydrogen phosphate (Na_2HPO_4) and 0.1 M Citric acid.

iii) Preparation of different pH solution of BR buffer from BR buffer of pH 2:

Take 100ml buffer solution and then adjust at different pH from 2 to 8 with NaOH or HCl. Dilute 10ml standard solution with adjusted pH solution.

iv) Preparation of Different concentration solution:

Perform serial dilutions of the stock solution to prepare lower concentration solutions from 1×10^{-4} M diluted with BR buffer solution (0.1M) for concentration study of Dopamine.

v) Preparation of modified Glassy carbon electrode:

Polish the GCE using alumina slurry on a polishing cloth to remove any surface impurities and create a smooth surface. Allow it to dry at room temperature. Perform electrochemical tests (e.g., CV and DPV) to evaluate the performance of the modified electrode and ensure that the nanoparticles are effectively enhancing the electrode's properties. Take 1g of cobalt oxide nano powder (Sigma Aldrich company) in beaker, add 4-5 ml of beaker of ethanol mix well. Then sonicate the solution in sonicator for 30 min for evenly mixing of the solution. Apply the paste with the help of capillary tube on to the GCE.

2.3. Instrumentation:

All voltammetric measurements study has been performed on PhadkeSTAT 20 potentiostat. A three electrode system employing an Ag/AgCl (3M KCl) as reference electrode, platinum electrode as counter electrode and glassy carbon as working electrode was used. The pH measurements were performed using an ELICO LI 120 pH meter.

2.4. Determination of Dopamine

Cyclic Voltammetric (CV) and Differential pulse voltammetric (DPV) studies were carried out with appropriate quantity of the analyte (Dopamine) in 50mL standard volumetric flask and then making up to the mark with 0.04M BR buffer pH 7.0. The solution was then transferred into an electrochemical cell and the measurements were carried out at $25 \pm 0.2^\circ\text{C}$. N_2 gas purging was not required as oxygen did not interfere in the measurements.

Glassy carbon electrode (GCE) was polished with the alumina gel for 5-8 minutes to clean its surface then washed with the distilled water to remove any leftover material. A solution of $\text{K}_3\text{Fe}(\text{CN})_6$ was tested using cyclic voltammetry (cv) from -0.2V to 1.8V, at scan rate 50mV per second and run for 10 cycles and subjected to cyclic voltammetry under same parameters, the peak separation was noted to be around 56mV. If the observed peak separation was outside the acceptable range the electrode was re-polished and the entire process was repeated until the desired electrochemical response was obtained.

3. RESULTS AND DISCUSSION:

3.1. Effect of pH:

The effect of change in pH on peak potential for Dopamine was investigated by different pulse voltammetry from pH 2 to 9 employing Britton-Robinson (BR) buffer (0.04M) by DPV. Standard solution of Dopamine ($1 \times 10^{-4}\text{M}$) was used to find the optimum pH of the supporting electrolyte at GCE. Fig. 1 represents the graph of I_p vs E_p for various pH of BR buffer.

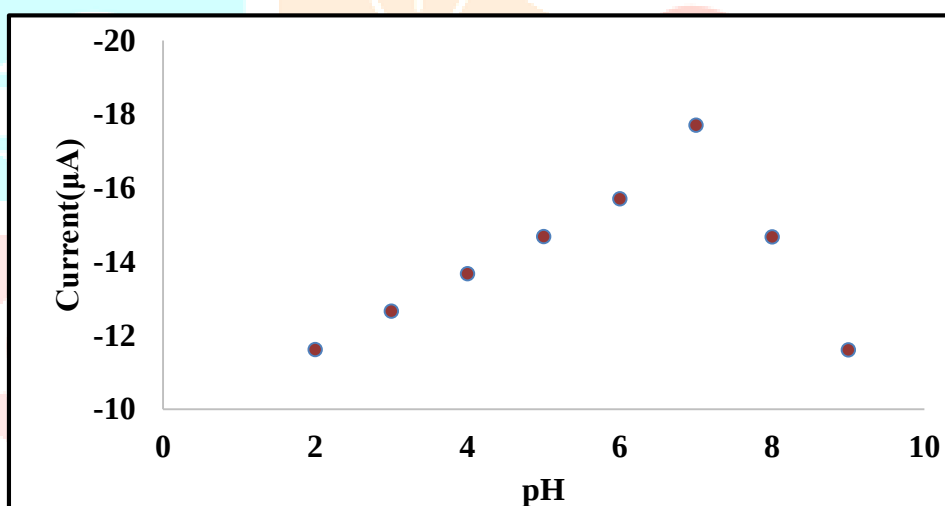


Fig. 1: Plot I_p vs pH of $1 \times 10^{-4}\text{M}$ Dopamine at; glassy carbon vs. Ag/AgCl; in 0.04M BR buffer ; scan rate 50mV/s at 25°C

The peak currents were found to increase in the beginning with the increase in pH showing maximum at pH 7.0 and decrease thereafter. The plot of E_p vs pH shows a negative shift of E_p values (Fig 2) with increasing pH suggest the involvement of protons for the electro-reduction of Dopamine.

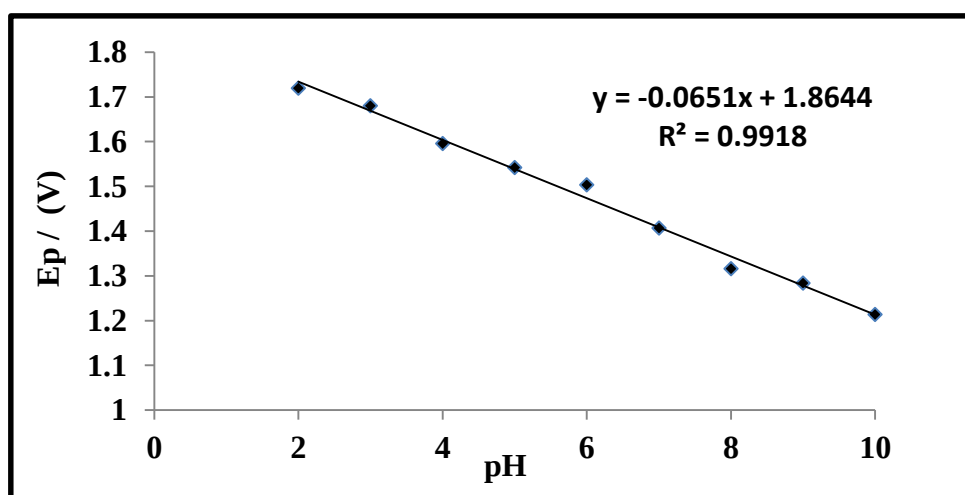


Fig. 2: Plot of E_p vs pH by Differential pulse voltammetry for reduction of $1 \times 10^{-4}\text{M}$ Dopamine at; glassy carbon vs. Ag/AgCl; in 0.04M BR buffer ; scan rate 50mV/s at 25°C .

The reduction became kinetically less favorable due to repulsive electrostatic interactions with the surface of the electrode. Therefore this pH (pH 7) was selected as the optimum pH for further studies

3.2 Effect of supporting electrolyte

The effects of several supporting electrolytes viz. phosphate buffer(0.1M), BR buffer (0.04M) and

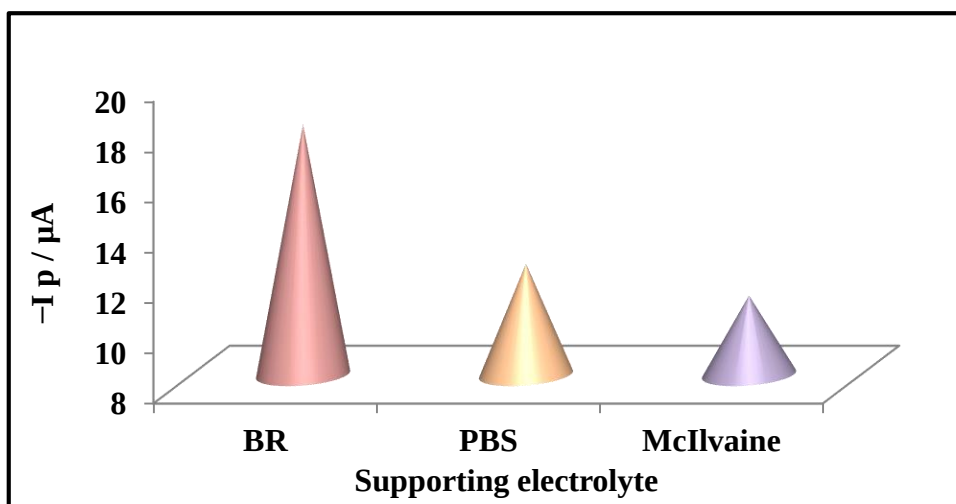


Fig. 3: Plot of I_p vs supporting electrolyte by Differential pulse voltammetry for $1 \times 10^{-4}\text{M}$ Dopamine at; glassy carbon vs. Ag/AgCl;; scan rate 50mV/s at 25°C

McIlvaine buffer (0.1M) at pH 7 for $1 \times 10^{-4}\text{M}$ Dopamine on peak current is shown in Fig.3. Amongst all the buffers used, BR buffer at pH 7 gave the best response in terms of peak current and peak shape for Dopamine. Thus, BR buffer was chosen for further studies.

3.3. Effect of modifier

The effective surface areas of the glassy carbon electrode (GCE) and cobalt oxide nanoparticles modified glassy carbon electrode (CoGCE) of the same bore size were

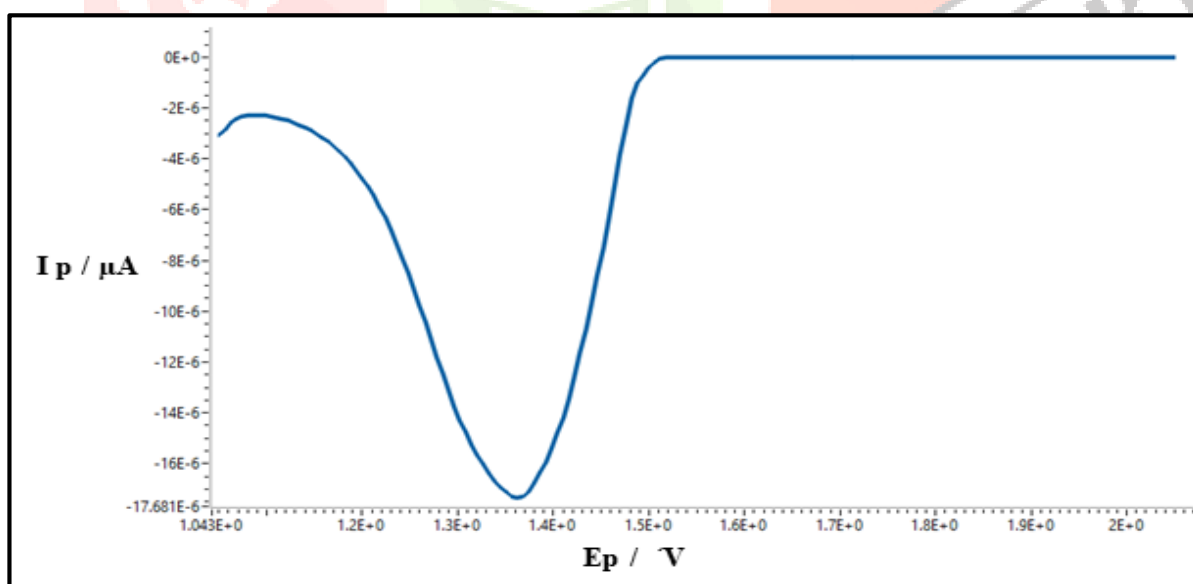


Fig. 4: DPV of $1 \times 10^{-4}\text{M}$ Dopamine at;GCE vs. Ag/AgCl;; scan rate 50mV/s at 25°C

determined through cyclic voltammetry (CV) using 6 mM of mixture of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ system in 0.1 N KNO_3 . The surface area of both the electrodes

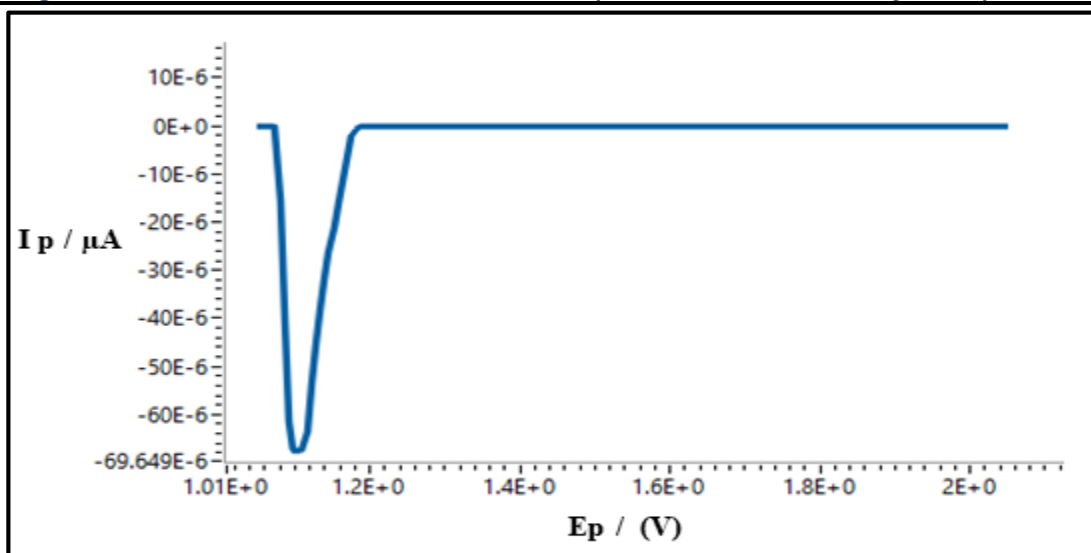


Fig. 5: DPV of 1×10^{-4} M Dopamine at; CoGCE vs. Ag/AgCl;; scan rate 50mV/s at 25°C. GCE and CoGCE were calculated using Randles–Sevcik [22] equation and were found to be 0.105 cm² and 0.662 cm² respectively suggesting an increase in the effective surface area of the CoGCE electrode. Comparing the DPV's of Dopamine at GCE and CoGCE from Fig 4 and Fig 5, it is clearly seen the enhancement in current at CoGCE showing the efficiency for the determination of dopamine at CoGCE.

3.4 Effect of scan rate

The effect of scan rate between 50 and 350 mV/s for Dopamine was studied by cyclic voltammetry in 0.04M BR buffer (pH 7.0) at CoGCE as given in Fig. 6. It is observed from the figure that on increasing the scan rate, the peak current also increased. An excellent linearity between anodic peak current and the square root of scan rate has been indicated ($R^2 = 0.9909$) seen from Fig.6 indicating the electrode reaction to be diffusion controlled.

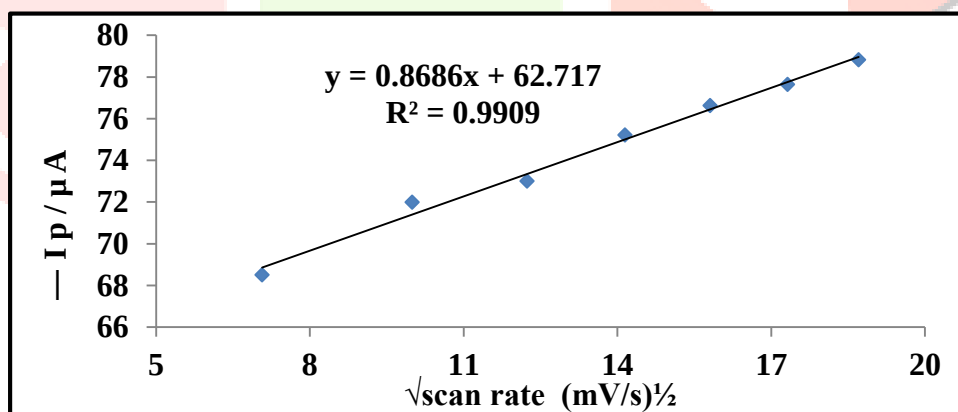


Fig. 6: Plot of I_p (μ A) vs $\sqrt{v}$ for 1×10^{-4} M Dopamine at; CoGCE vs. Ag/AgCl;; scan rate 50mV/s at 25°C.

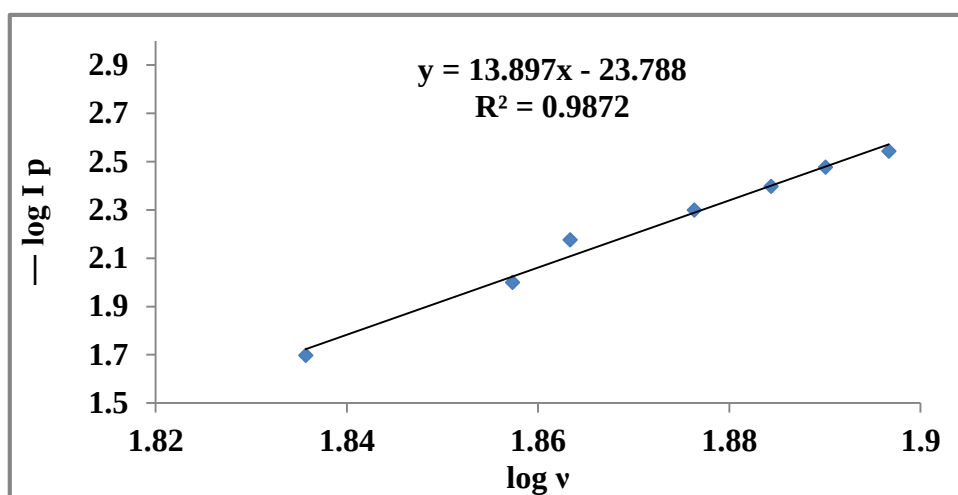


Fig. 7: Plot of $-\log I_p$ vs $\log v$ for 1×10^{-4} M Dopamine at; CoGCE vs. Ag/AgCl; scan rate 50mV/s at 25°C

The slope from the plot of $\log I_p$ and the $\log v$ from Fig 7 is 13.89 suggests that, at lower scan rates, the electrode process is predominantly diffusion-controlled, while at higher scan rates, it is primarily influenced by adsorption makes this electrode nearly ideal for voltammetric analysis of dopamine.

3.5 Number of electrons

The number of electrons (n) involved in the reduction reaction was calculated from the cyclic voltammetry. For a totally irreversible reaction the following equation was used

$$E_p - E_p/2 = 47.7 / n\alpha \text{ mV at } 25^\circ\text{C}$$

$E_p - E_p/2$ value was found to 43 mV for Dopamine whose substitution in the above equation provided the value of $n\alpha$ to be 1.11. If the electron transfer coefficient (α) is assumed to be 0.5 [23]. By substituting the value of α in the above equation above the value of n is calculated to be 2.2 i.e. 2 are electrons involved in electrode reduction reaction of dopamine.

3.4 Determination of Dopamine by Differential Pulse Voltammetry (DPV):

3.4.1 Effect of concentration:

The DPV technique was used for determination of Dopamine at CoGCE the linear working range (LWR), empirical limit of detection (LOD), Limit of quantification (LOQ), Linear regression equation (LRE) and correlation coefficient from Fig 8 were determined and are presented in Table 1.

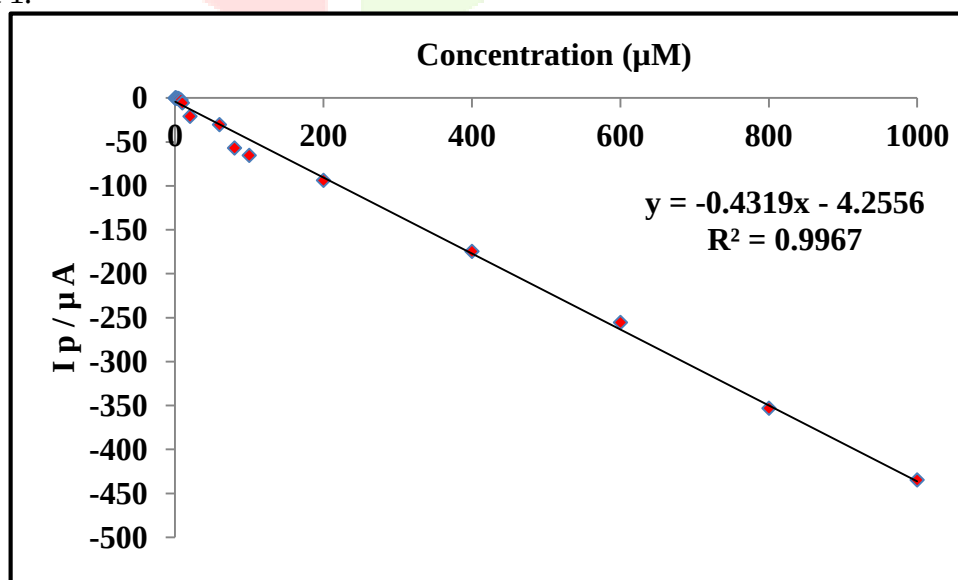


Fig.8. Plot of I_p (μA) vs Concentration (μM) of Dopamine at CoGCE in 0.04M BR buffer (pH 7.0) at; CoGCE vs. Ag/AgCl; scan rate 50mV/s, 0.1sec, 50mV at 25°C

Table 1: Analytical parameters for electrochemical determination of Dopamine at CoGCE in 0.04M BR buffer (pH 7.0) at; CoGCE vs. Ag/AgCl;; scan rate 50mV/s , 0.1sec, 50mV at 25°C

LOD(M)	%RSD	LOQ (M)	LRE	LWR (M)	r
2.80×10^{-10}	± 3.21	8.50×10^{-10}	$I_p(\mu A) = 0.4319(\mu M) - 4.2566$	1.2×10^{-8} to 3.5×10^{-3}	0.9967

3.4.2. Validation studies, interference studies and analytical applications:

For validation of the proposed method, various parameters such as repeatability, reproducibility, precision and accuracy of the analysis were obtained by performing five replicate measurements of 1×10^{-4} M Dopamine over intraday assay (single day, n = 5) and inter-day assay (for a period of 2 week). Satisfactory mean percentage recoveries (%R) and

Table 2: Precision and Bias of assay for standard Dopamine solution by DPV (n =5)

Molecule	Concentration taken (mol L ⁻¹)	Mean concentration found (mol L ⁻¹)	Mean recovery %	Bias	Precision % RSD
Dopamine	Intra day				
	1×10^{-4}	$0.98 \times 10^{-4} M$	98.0	0.02	1.9
	Inter day				
	1×10^{-4}	$0.93 \times 10^{-4} M$	93.0	0.07	2.6

relative standard deviations (% RSD) were obtained and are presented in Table 2. The recoveries obtained confirmed high precision and accuracy of the proposed method In order to further extend the validity of the proposed method and verification of the matrix effect on Dopamine on determinations by DPV was studied. The influences on the peak heights of some commonly interfering molecules present, some of them which form the major components of pharmaceutical preparations were evaluated. Five replicates of each experimental set were performed. The results showed tolerance limit of 150 fold of ascorbic acid, 100 fold for uric acid, 50 fold for fructose and 150 fold for glucose showing that the present modified electrode was highly selective and quantification was feasible towards the determination of Dopamine in the presence of common physiological interfering molecules.

4. CONCLUSION:

A cobalt oxide nanoparticles modified glassy carbon electrode sensor was used for the detection and quantification of Dopamine Under optimized conditions, for Dopamine the concentration was linear in $1.2 \times 10^{-8} M$ to $3.5 \times 10^{-3} M$ with a low Limit of quantification of $8.50 \times 10^{-10} M$ It is shown that the prepared sensor offers rapid analysis, reliable and reproducible and is ideal for on-site or in-situ testing for the detection of Dopamine.

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