

Fabrication of Poly (Evans blue) Modified Graphite Paste Electrode as an Electrochemical Sensor for Sensitive and Instant Riboflavin Detection

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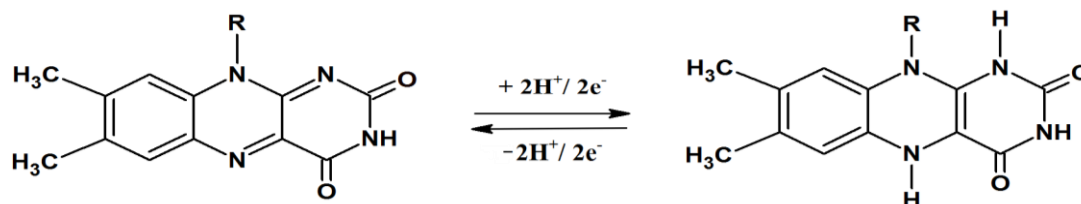
Abstract

Electro-analysis of Riboflavin (RN) consumed as vitamin has been delved by constructing the poly (Evans Blue) modified graphite paste electrode (PEBMGPE) as an electrochemical detector. Voltammetric determination of RN in 0.2 M PBS (pH 7.0) at the electro-active layer of the PEBMGPE was conducted. The PEBMGPE plays a crucial role as sensing tool towards the detection of RN compared to the BGPE. The topographical features of the bare graphite paste electrode (BGPE) and PEBMGPE was acquired by the Field émission scanning electron microscope (FE-SEM) surface analysis. All experimental factors such as applied potential, the effect of scan rate, impact of the pH were optimized. Employing the Differential pulse voltammetry (DPV) approaches using the optimized experimental circumstances, the analytical curve was linear in the range of 6×10^{-6} - 1.5×10^{-4} M. The detection limit and limit of quantification gained as 2.1×10^{-7} M and 7.1×10^{-7} M, respectively. Subsequently, good repeatability, excellent reproducibility, and adequate stability, high sensitivity were achieved for the PEBMGPE sensor. In addition, the PEBMGPE sensor was applied for the interference study of RN with Dopamine (DA) and Paracetamol (PR). Besides, the practicability of the projected sensor was successfully utilized for the detection of the RN in pharmaceutical formulations.

Keywords: Voltammetric study, Electropolymerisation, Electrochemical sensor, detection limit, Dopamine, Paracetamol.

1. Introduction

RN is one amongst the types of vitamin B, which is also referred to as vitamin B₂. RN exists as a fundamental component of the flavoenzymes [1-3]. The supply of RN to humans and all animals must be constant, and it is commonly present extensively in the food products such as green vegetables, nuts, meat, eggs, milk, and supplemented flour [4-6]. Its inadequate supplements arises the diseases such as sores at the corners of the mouth, eye syndromes, and skin slashes, and immature growth have been recorded. Burning feet may also indicate a lack of RN [7-10]. To escape from all these mentioned problems the detection of RN is essential. The reviewed literature exposes that, at present numerous methods were established for the detection of RN they are Spectrophotometry [11-12], fluorescence [13-14], high performance liquid chromatography [15-20], chemiluminescence [21], and capillary electrophoresis [22]. Some of these mentioned methods have good sensitivity but also have some deficiency such as sophisticated procedure, expensive, unattractive due to their importable sensing approaches. Therefore, to overcome all these limitations the development of an electroanalytical method is mandatory. Electroanalytical methods with electrochemical sensor have the benefits such as minimal cost, quick preparation, and the brief assessment time [23-24]. Graphite paste electrode used as an electrochemical sensor owing to their favourable chemical and physical properties of graphite paste for its modification with various electro active molecules [25-28]. One of the feasible pathways for electrode surface modification is the electrochemically regulated formation of thin polymer film on electrode surfaces known as electro-polymerization [29-30]. In this current article, the fabrication and electro-catalytic efficiency of PEBMGPE was investigated and implemented as an electrochemical sensor for the electrochemical study of RN through the cyclic voltammetry (CV) and DPV approaches. The electro-oxidation mechanism of RN was exposed in the scheme 1. As recorded in the reviewed literature, the RN detection based on the PEBMGPE as the sensor has not yet been performed. Besides, selectivity of the projected sensor was achieved in the existence of DA and PR along with RN. The designed sensor has also been efficiently utilized to monitor the RN in the pharmaceutical product.



Scheme 1. Redox reaction of RN.

2. Materials and methods

2.1. Reagents and Solutions

The standard RN, EB, Monosodium dihydrogen phosphate (NaH₂PO₄), and Disodium hydrogen phosphate (Na₂HPO₄) were procured from Molychem, India. Silicone oil and graphite powder were purchased from Nice Chemicals, India. All of the chemicals essential in this work were pure analytical quality and were used without additional purification. By using 0.1 M NaOH, stock solution of RN (25×10⁻⁴ M) was prepared. By using the distilled water 25×10⁻⁴ M EB stock solution was made. Phosphate buffer solution (PBS) was prepared by mixing proper quantity of 0.2 M NaH₂PO₄ and Na₂HPO₄. All voltammetric measurements were done at the laboratory temperature (25±1°C).

2.2 Instrumentation

The voltammetric experiments were conducted with CHI-6038E (CH-Instruments-USA) electrochemical working station linked to the personal computer for the extraction of data. The electrochemical analyser was furnished with an

electrochemical cell comprised of tri-electrode compartment. This encompassed with a BGPE or PEBMGPE as a working electrode, Hg/HgCl₂ electrode works as a reference electrode and a platinum wire supports as auxiliary electrode. In order to supply the solution with the desired pH for the experiment the EQ-610 digital pH meter model was employed.

2.3 Fabrication of the PEBMGPE

Proceeding to the fabrication of the PEBMGPE, BGPE was synthesized first by blending the reliable mixture of the graphite powder and silicone oil with the support of pestle in an agate mortar up to a homogenous graphite paste was attained. The obtained homogenous graphite paste was loaded into the hole of the teflon tube. It was then polished on a weighing paper to obtain a uniform surface. A copper wire offers electrical contact, which was introduced into the teflon tube. The PEBMGPE was fabricated by the EB electro-deposition on the exterior of the prepared BGPE. After the electro-polymerisation, surface of the electrode was thoroughly rinsed with the distilled water and it is used for the further electrochemical analysis. Thus, PEBMGPE was fabricated.

3. Results and Interpretation

3.1. Electrochemical polymerization of EB on the surface of BGPE

Electro-polymerization of 1×10^{-4} M EB in 0.2 M PBS of pH 7.0 was performed on the surface of the BGPE between the potential ranges from 0 to 1.4 V for 10 sequential cycles at a sweep rate 0.1 Vs^{-1} . Cyclic voltammograms (CVs) recorded during the electro-polymerisation of the EB on the surface of the BGPE are represented in Fig.1 which designates the satisfactory development of the polymer layer on the surface of the BGPE. A sufficient polymer growth was attained by using electropolymerization technique. This result provides that the electro-deposition of EB on the surface of the BGPE was successfully achieved. The electro-polymerisation of the EB on the surface of the BGPE has already been reported [31-32].

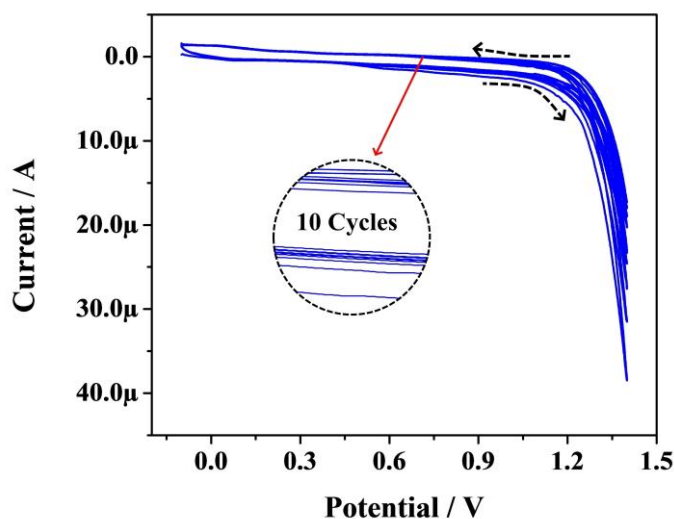


Figure 1. CVs of EB electropolymerisation on BGPE.

3.2 Surface Morphological analysis of BGPE and PEBMGPE

Surface morphological feature of the prepared BGPE and PEBMGPE was investigated with the microscopic imaging surface analysis. FE-SEM is one of the microscopic imaging surface analysis technique in which thin film surface morphology was analysed. Fig.2 (a) and (b) depicts the FESEM magnified image of the BGPE and PEBMGPE respectively. The FE-SEM magnified image of the BGPE that indicates the flakes of the graphite and the rough

surface morphology. However, the FE-SEM image of PEBMGPE shows the uniformly deposited poly EB on the surface of the unmodified GPE. Therefore, this confirms that poly EB film was effectively electrodeposited on the BGPE.

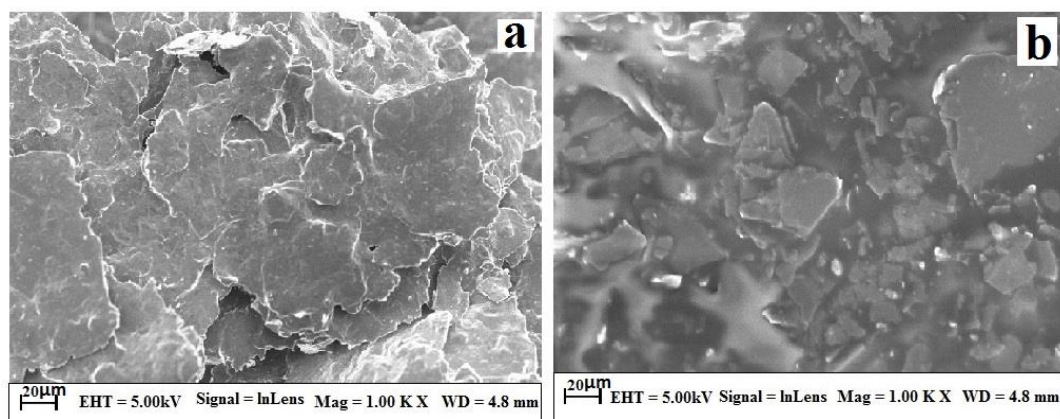


Figure 2. FE-SEM magnified image of BGPE (a), PEBMGPE (b).

3.3 Evaluation of the voltammetric behaviour of the RN at the PEBMGPE by CV and DPV method

The electrochemical behaviour of the RN molecule was exposed on the proposed electrode via CV technique. The reported CVs in Fig.3 were obtained for the 1×10^{-4} M RN in 0.2 M PBS of pH 7.0 at the PEBMGPE (dashed line) and BGPE (solid line). In both cases a well-defined reduction peak occurred. However, at BGPE a low response oxidation peak can be seen. At PEBMGPE, a well-precise oxidation peak of the RN appeared with E_{pa} and I_{pa} 0.410 V and 4.41 μ A correspondingly. The reduction peak of the RN at the PEBMGPE obtained with E_{pc} 0.485 V and I_{pc} 0.14 μ A. The anodic and cathodic potential difference (ΔE_p) is 0.075 V, which confirms that the redox behaviour of the RN on the surface of the PEBMGPE is quasi-reversible process [33]. As predicted the voltammetric response of the RN at PEBMGPE was relatively high, specifies that PEBMGPE has enriched electro-catalytic activity towards the detection of RN.

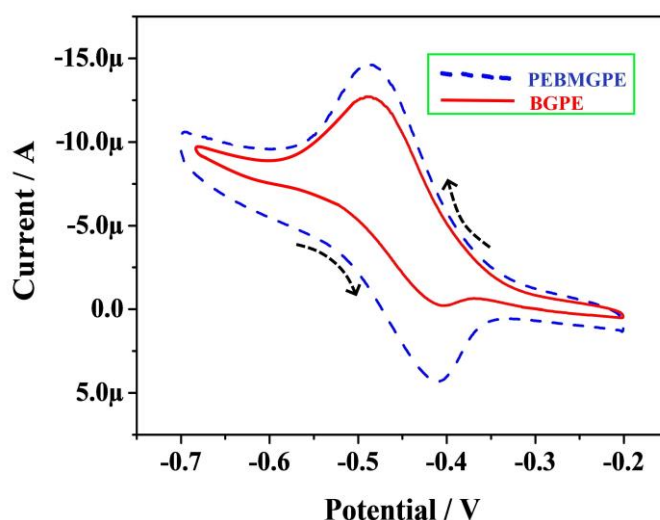


Figure 3. CVs obtained to the voltammetric response of RN (1×10^{-4} M) at BGPE (solid line), and PEBMGPE (dashed line) in 0.2 M PBS (pH 7.0), at the sweep rate 0.1 Vs^{-1} .

The electrochemical behaviour of the 1×10^{-4} M RN in 0.2 M PBS (pH 7.0) was evaluated at PEBMGPE by means of a DPV technique. Fig.4 deduces the Differential pulse voltammograms (DPVs) acquired for the voltammetric response

of the RN, which discloses that RN at BGPE has a least significant signal with the I_{pa} 8.6 μA , while at the PEBMGPE Produces enhanced peak signal for RN with I_{pa} 23.7 μA . This inferences indicates that the electrochemical response of RN was boosted by PEBMGPE using DPV approach.

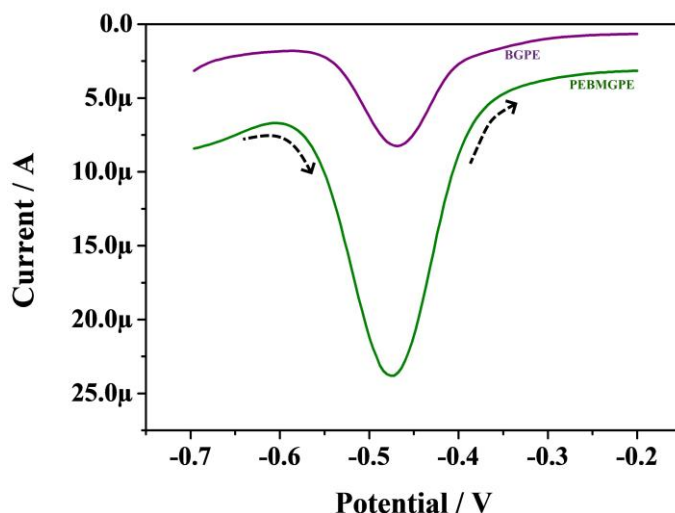


Figure 4. DPVs achieved for the electrochemical response of 1×10^{-4} M RN at PEBMGPE in 0.2 M PBS (pH 7.0), at the scan rate 0.1 Vs^{-1} .

3.4 Investigation of the electrochemical behaviour of the RN

The electrochemical response of the RN was investigated at the PEBMGPE through the CV technique in the presence and absence of the RN. Fig.5 describes the CVs for the electrochemical response of the 1×10^{-4} M RN in 0.2 M PBS of pH 7.0 on the surface of the PEBMGPE with the existence (dotted line) and absence (solid line) of the RN. As can be seen in the Fig.5, a well-distinct redox peak was attained in the presence of RN but the redox peak without RN was not obtained. This indicates that the PEBMGPE detects the RN by using the CV approaches.

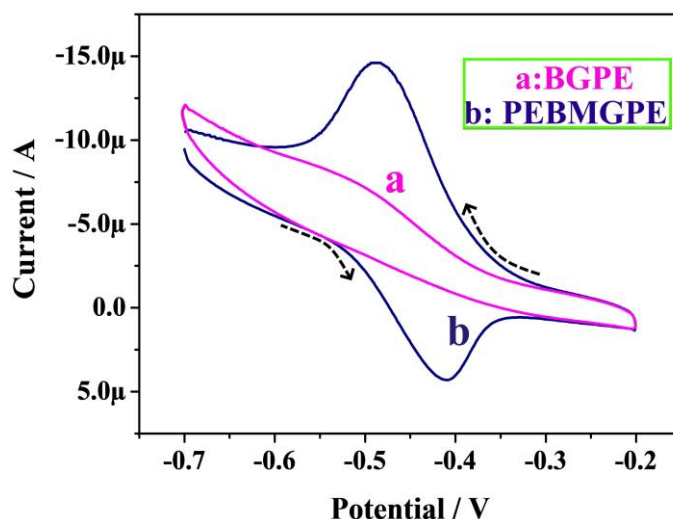


Figure 5. CVs acquired for PEBMGPE of 1×10^{-4} M RN (dotted line) and absence of RN (solid line) in 0.2 M PBS of pH 7.0, sweep rate 0.1 Vs^{-1} .

3.5 Evaluation of the pH impact on the redox behaviour of RN at PEBMGPE

The voltammetric response of the RN changes by varying the pH of the supporting electrolyte. As pH changes from 6.0 -7.5 corresponding potential shift towards more negative side. Fig.6a depicts the CVs documented for the 1×10^{-4}

M RN in 0.2 M PBS of different pH at a sweep rate 0.1 Vs^{-1} . From the acquired data, the graph of E_{pa} vs. pH (Fig.6b) was constructed, the linear relationship was obtained between the potential and the pH and linear regression equation represented as $E_{\text{pa}} (\text{V}) = -0.0464 - 0.0522 \text{ pH}$ ($R^2 = 0.9968$). The slope 0.052 occurred from the graph is near to the speculative value 0.059 V/pH , which clearly indicates that in the RN electro-oxidation both the proton and electron involved in the same quantity [34]. From the data collected, the plot of the pH vs. I_{pa} (Fig.6c) displays that at 7.0 pH, an emphasized output of RN was observed and thus 7.0 pH opted for further analysis.

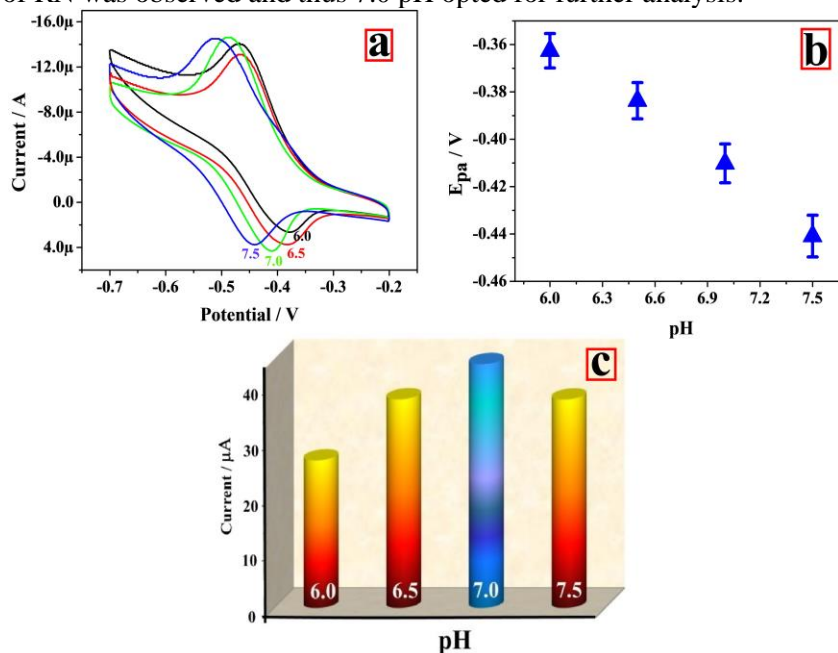


Figure 6. (a) CVs documented for electrochemical response of $1 \times 10^{-4} \text{ M}$ RN at PEBMGPE, changing the pH range from 6.5-7.5, sweep rate 0.1 Vs^{-1} , (b) The graphical plot of pH vs. E_{pa} , (c) The plot of pH vs I_{pa} .

3.6 Evaluation of the scan rate impact on the redox response of RN

An adequate electrochemical attributes of the quasi-reversible redox behaviour of the RN was determined based on the potential scan rate by the aid of CV. Fig. 7a provides the CVs recorded for $1 \times 10^{-4} \text{ M}$ RN in 0.2 M PBS of the pH 7.0 in the potential sweep rate range from 0.1 Vs^{-1} to 0.3 Vs^{-1} . From the CVs obtained, the graph of the scan rate vs. I_{pa} was constructed (Fig.7b). As can be inferred from the graph, rise in the potential scan rate lead to consecutive increments in the peak current. There is a linear relationship between the scan rate and I_{pa} . The fitted regression equation can be expressed as $I_{\text{pa}} (\mu\text{A}) = -3.0590 + 0.9436 (\nu)$ ($R^2 = 0.9988$). This inference indicates that the electro-oxidation of the RN on the surface of the PEBMGPE is an adsorption-controlled process. The graphical plot of \log scan rate vs. $\log I_{\text{pa}}$ was generated (Fig.7c) and the linear fitted equation is represented as $\log I_{\text{pa}} (\mu\text{A}) = -1.705 + 1.2624 \log \nu$ ($R^2 = 0.9980$). The acquired slope from the graph is 1.26, which is near to the theoretical value 1.0 for adsorption-controlled process. Hence, the redox process of the RN at PEBMGPE is adsorption-controlled process [35].

3.7 Calibration Curve and Detection limit

The main intention of this article is to detect the low concentration of the RN at the projected sensor. To detect low concentration, DPV is a suitable voltammetric technique due to its high sensitivity. The electro-oxidation of RN was done at the PEBMGPE in 0.2 M PBS of pH 7.0 by varying the concentration of the RN in the range of $6 \times 10^{-6} - 1.5 \times 10^{-4} \text{ M}$. The oxidation peak current increases linearly while increasing in the

concentration of the RN. There are two linearities were obtained for the variation of RN in the concentration range 6×10^{-6} - 5×10^{-5} M and 6×10^{-5} - 1.5×10^{-4} M respectively, and shown in the graphical plot of the concentration of the RN vs. I_{pa} (Fig.8). The two linear fitted equations corresponding to the two linear ranges is expressed as $I_{pa} (\mu A) = 1.17 \times 10^{-5} + 0.0689 M$ ($R^2 = 0.9964$) and $I_{pa} (\mu A) = 1.26 \times 10^{-5} + 0.0455 M$ ($R^2 = 0.9989$) respectively. By considering the first lower linear range, the detection limit and LOQ were estimated to be 2.1×10^{-7} M and 7.1×10^{-7} M based on the formula $3 \times S/M$, $10 \times S/M$ respectively. Where, S is the standard deviation of the blank and M is the slope of the regression line [36]. The detection limit achieved from the developed method was compared with the detection limit of the reported voltammetric studies on RN detection with an electrode and is presented in Table 1 [37-39]

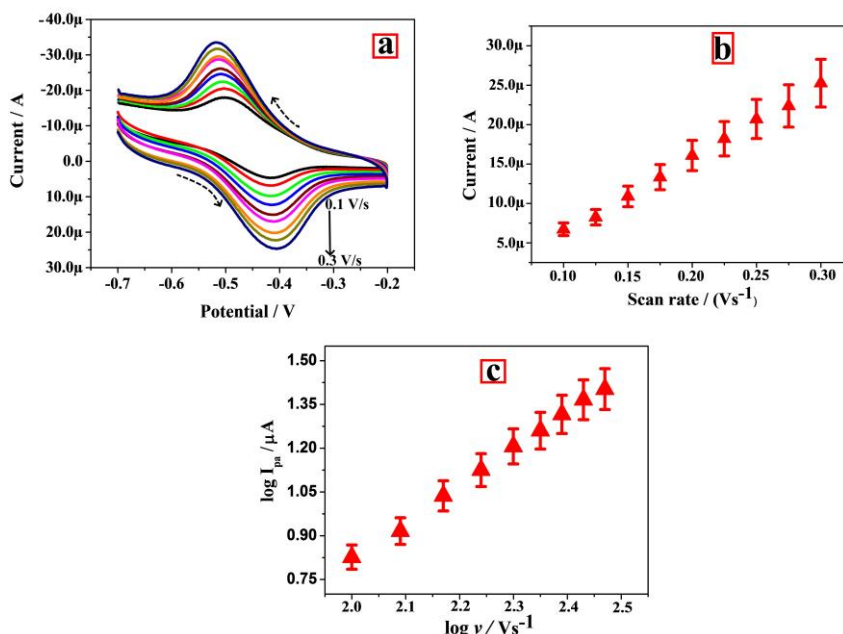


Figure 7. (a) CVs recorded for the voltammetric response of 1×10^{-4} M RN at a various scan rate by using PEBMGPE in 0.2 M PBS of pH 7.0, (b) The graph of scan rate vs. I_{pa} , (c) The plot of log scan rate vs. log I_{pa} .

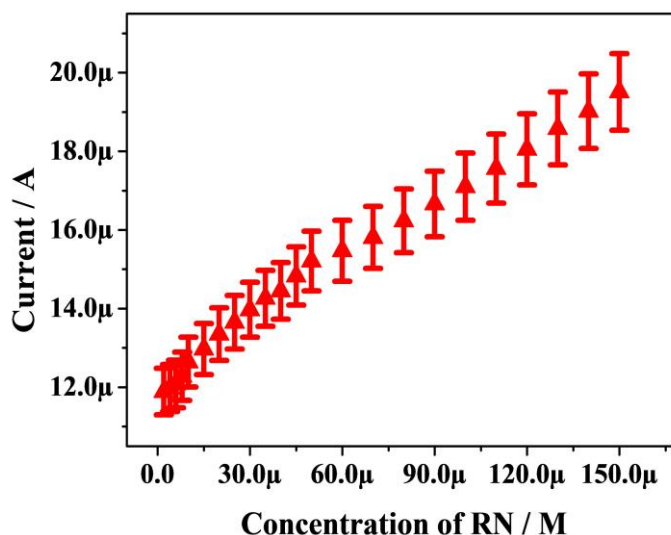


Figure 8. The graphical plot of concentration of RN vs. I_{pa} .

Table 1. Comparison of the detection limit of the reported voltammetric studies of RN

Technique	Electrode	Linear working range (mol/L)	Detection limit (mol/L)	References
CV	Zeolite/CPE	1.7×10^{-6} - 3.4×10^{-5}	7.0×10^{-7}	[37]
DPV	DNA-modified PGE	5.0×10^{-7} - 7.0×10^{-8}	3.0×10^{-7}	[38]
SWV	C18-modified gold electrode	-	2.3×10^{-6}	[39]
DPV	PEBMGPE	6×10^{-6} - 5×10^{-5} M	2.1×10^{-7}	Present work

SWV: square wave voltammetry, PGE: pencil graphite paste electrode, C18: di-n-octadecyldisulfide

3.8 Repeatability, stability, reproducibility of the PEBMGPE

The efficiency of the proposed sensor was evaluated by checking the stability, repeatability, and reproducibility through the CV approaches. The repeatability of the PEBMGPE was executed by the continuous four measurements in the identical experimental conditions of the same electrode by changing the analyte solution and generates the relative standard deviation (RSD) 2.6%. By measuring the response of four separately prepared PEBMGPE with the constant RN concentration, the reproducibility of the sensor PEBMGPE has been assessed and the RSD was attained to be 3.6%. For both reproducibility and repeatability of the sensor have RSD below 4%. This suggests that the developed sensor has an acceptable repeatability and an adequate reproducibility. Stability of the fabricated PEBMGPE was examined by sweeping the electrode for 30 consecutive cycles. The percentage degradation was estimated by using the formula percentage degradation = $100 \times I_{pn} / I_{p1}$, where I_{pn} and I_{p1} are the n^{th} and first anodic peak current respectively [40]. The calculated percentage degradation conveys that the modified electrode sustained 96% of its functions even after 30cycles. Excellent stability, adequate repeatability, acceptable reproducibility proves that the projected sensor has outstanding efficiency.

3.9 Interference study

The selectivity of the developed sensor was explored by conducting the detection of RN with DA and PR by utilizing the CV and DPV technique. Fig.9 deduces the CVs of the simultaneous determination of the RN (1×10^{-4} M), DA (1×10^{-4} M), and PR (1×10^{-4} M) in 0.2 M PBS of pH 7.0 with the potential window -1.0 – 1.0 V at a scan rate 0.1 Vs^{-1} . A well-separated peak was obtained for RN, DA, and PR with E_{pa} -0.409 V, 0.228 V, and 0.501 V respectively. This indicates that the selectivity of PEBMGPE, that detects the RN in the presence of DA and PR via CV method.

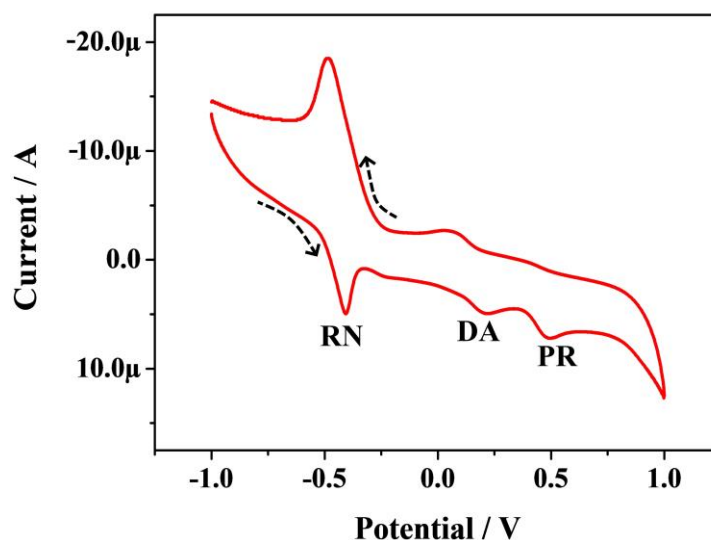


Figure 9. CVs of voltammetric response of RN (1×10^{-4} M), DA (1×10^{-4} M), and PR (1×10^{-4} M) at PEBMGPE in 0.2 M PBS of pH 7.0, at the scan rate 0.1 Vs^{-1} .

The selectivity of the proposed sensor was examined through the DPV technique. Fig.10a denote the DPVs of the instantaneous detection of RN (1×10^{-4} M), DA (1×10^{-4} M), and PR (1×10^{-4} M) in 0.2 M PBS of pH 7.0 with the potential window $-1.0 - 0.8 \text{ V}$ at a scan rate 0.1 Vs^{-1} . A well-resolved peak was observed for RN, DA, and PR with E_{pa} are -0.461 V , 0.130 V , and 0.428 V respectively. Fig.10b depicts the DPVs of the simultaneous detection of varying the concentration of the RN in the range of $1 \times 10^{-4} - 3.5 \times 10^{-4} \text{ M}$ by maintaining the concentration of DA and PR as $1 \times 10^{-4} \text{ M}$ in 0.2 M PBS of pH 7.0 at the scan rate 0.1 Vs^{-1} . By increasing the concentration of the RN, peak current also raised (Fig.10c) and the DA and PR shows the constant current response. These outcome confirm that the constructed sensor has a good selectivity.

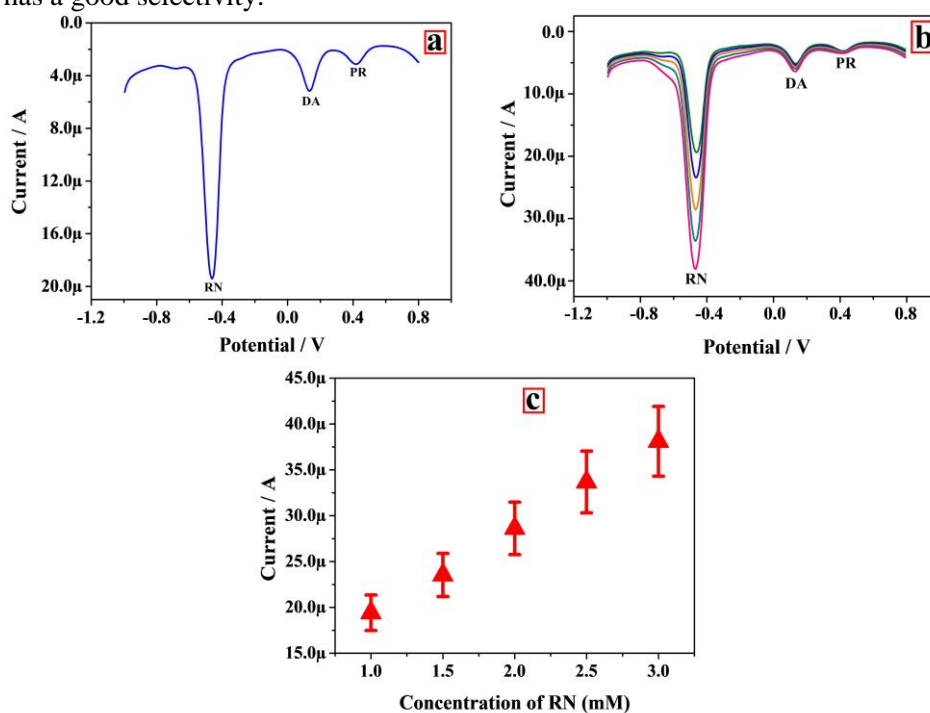


Figure 10. (a) DPVs of electrochemical response of RN (1×10^{-4} M), DA (1×10^{-4} M) and PR (1×10^{-4} M) at PEBMGPE in 0.2 M PBS of pH 7.0, at the scan rate 0.1 Vs^{-1} , (b) DPVs attained for voltammetric response

of RN by changing its concentration from 1×10^{-4} - 3.5×10^{-4} M with constant concentration of DA (1×10^{-4} M) and PR (1×10^{-4} M) at PEBMGPE (c) The plot of concentration of RN vs. I_{pa} .

3.10 Real sample analysis

To monitor the viability of the constructed sensor, the vitamin tablets containing RN were detected through the developed method. The RN tablets were procured from the local drugstore. The purchased tablets were weighed and solution was prepared. The voltammograms were recorded in 0.2 M PBS (pH 7.0) at the sweep rate of 0.1 Vs^{-1} . The percentage recovery was calculated and the recovery obtained in the range of 96% - 100%. The good percentage recovery was acquired from the developed method. Therefore, the developed electrochemical method can be considered for the routine analysis.

4. Conclusion

In this current voltammetric study, an electrochemical sensing device was built using PEBMGPE to determine RN via CV and DPV method. The PEBMGPE act as an electro-catalyst and exhibits an enhanced electro catalyst activity for RN detection. FESEM surface analysis of the proposed electrodes reveals the modification of EB through the electropolymerization technique. The optimization factors such as effect of pH, effect of sweep rate were resolved. The projected sensor provides the detection limit 2.1×10^{-7} M for RN detection. The proposed sensor has an acceptable repeatability, adequate reproducibility and an outstanding stability. Furthermore, the selectivity of the sensor was exposed by the interference studies. Overall, the technique formulated has been effectively implemented in the pharmaceutical formulations to detect the RN.

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