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Full Paper

Electrochemical Determination of Riboflavin by an Ionic Liquid Modified Carbon Paste Electrode as a Sensitive Sensor

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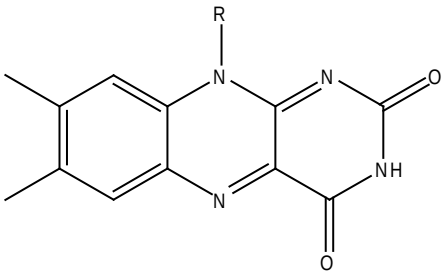
Abstract- In this research, an ionic liquid modified carbon paste electrode was prepared by incorporating 1-hexyl-3-methylimidazolium hexafluorophosphate (HMHP) to a carbon paste. The preconcentration and electroanalysis of riboflavin were employed using the HMHP modified carbon paste electrode (HMHP/CPE). The overall analysis involved a two-step procedure: an accumulation step at open circuit, followed by medium exchange to a pure electrolyte solution for the voltammetric measurement. During the preconcentration step, riboflavin was adsorbed onto HMHP surface. The influence of various experimental parameters on the HMHP/CPE response was investigated (i.e. pH, accumulation time, pulse time and pulse amplitude). Under the optimized conditions, the reduction peak showed that the peak height was found to be directly proportional to riboflavin concentration in the range comprised between 3.5×10^{-8} M and 1.5×10^{-6} M. With this, it was possible to determine limit of detection, which resulted in 11 nM. Common interfering species did not interfere in the determination. The method was successfully applied to the measurement of riboflavin in pharmaceutical formulations.

Keywords- Ionic liquid, Carbon paste electrode, Riboflavin, Electrochemical determination

1. INTRODUCTION

Riboflavin (vitamin B_2) (Scheme 1) is B-group water soluble vitamin and stable in acidic aqueous solution. Human being as well as all animals needs a constant supply of riboflavin

[1]. Its insufficiency is associated with eye lesions and skin disorders [2]. Riboflavin cannot be formed in human body, thus has to be obtained from food (such as liver, cheese, fruit and vegetables) and pharmaceutical products [3]. Recently, several methods have been employed to determine concentration of riboflavin, including chemiluminescence [4], high performance liquid chromatography [5], fluorescence [6] and capillary electrophoresis [7]. Voltammetric determination of riboflavin provides an alternative method, considering rapid response time, the low cost of the analysis, simple instrumentation required and high sensitivity [8]. Glassy carbon electrodes modified with double-stranded DNA [9], flowers-like Fe_3O_4/rGO [10], ordered mesoporous carbon [11], high-density arrays of polythiophene nanotubes [12], poly (3-methylthiophene) [13], graphene [14], nanocrystalline metallosilicate [15], and electropolymerized film of 3-amino-5-mercapto-1,2,4-triazole [16] have been applied to determine of riboflavin. Recently, Gribat et al. have measured riboflavin using hematite (α-Fe_2O_3) film modified rotating disk glassy carbon electrode [17]. Also, bismuth-film modified copper substrate electrode [18] and homoadenine single-stranded DNA/molybdenum disulfide-graphene nanocomposite modified gold electrode [19] have been employed as new electrochemical methodology for vitamin B2 determination. Furthermore, electrically heated graphite cylindrical electrodes made from ground pencil leads have been used to perform adsorptive stripping square wave voltammetry (SWV) measurements of riboflavin [20]. On the other hand, the carbon paste electrode (CPE) and chemically modified carbon paste electrodes are widely applied in several fields of electrochemistry [21]. The application of carbon-paste matrix, besides renewability by simple polishing, presents several other advantages are including uniform distribution of the catalyst into the paste, very low Ohmic resistance, better reproducibility and stability, easy preparation and adequate robustness in aqueous solutions [22]. CPEs have been utilized for potentiometric and voltammetric quantification of various cations, anions, organic and pharmaceutical materials [23]. Only in few articles, application of carbon paste electrode for riboflavin measurement has been published [24,25].



R=$C_5H_{11}O_4$

Scheme 1. Chemical structure of riboflavin

Ionic liquids are ionic materials containing organic cations and various types of anions, which are liquids at temperatures around 298 K and below. Ionic liquids have various

important properties, for example, electrochemical thermal stability, wider electrochemical windows, high ionic conductivity, negligible vapor pressure and so forth [26,27]. Because of their nature, ionic liquids are non-flammable, non-volatile and non-hazardous, which makes them attractive as "green" solvents for many chemical processes on both the industrial and laboratory scale.

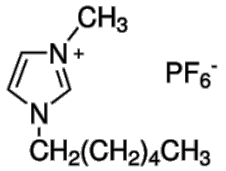
Ionic liquid modified carbon paste electrodes have been fabricated using hydrophobic and highly viscous ionic liquids as binders [28]. In spite of classical binders, for example, paraffin and silicon oil, which are chemically inert and electrochemically inactive, ionic liquids are made out of highly conductive ions. Relating to general properties of the ionic liquids, the most as often as utilized as binders are those with alkyl substituted imidazolium and pyrrolidinium cations in combination with hexafluorophosphate or bis(trifluoromethylsulfonyl)imide anions [29]. Carbon paste electrodes modified with the ionic liquids show many advantages over the classical devices, for example, the increasing rates of increased sensitivity, reduced volatility, high conductivity, and electron transfer [30]. They have been applied for the detection of biologically active substances that include morphine, ascorbic acid, nitrites, and DNA [31-33]. Although electroanalytical quantification of some analytes at unmodified and modified carbon paste electrodes has been well demonstrated in literature [34-36], the use of ionic liquid modified carbon paste electrodes for detection of riboflavin has been less commonly investigated [7,37]. Also, based on our knowledge, the 1-hexyl-3-methylimidazolium hexafluorophosphate as an ionic liquid was used for the modification of some few electrodes such as Pt [38]. On the other hand, this ionic liquid was applied only for one case of carbon paste electrode modification in order to H_2O_2 determination, which was used along with hemoglobin entrapped in dextran film as other modifiers [39], but, in this work, no further modification was applied. Thus, this report describes the adsorption and electroanalytical behaviors of riboflavin on the ionic liquid bulk-modified carbon paste electrode surface, as well as the application of this modified electrode for simple and selective determination of riboflavin in multivitamin preparations.

2. EXPERIMENTAL

2.1. Reagents and chemicals

The 1-hexyl-3-methylimidazolium hexafluorophosphate (Scheme 2) (HMHP, purity 99%) was purchased from Ionic Liquids Technology Company and used as received. Riboflavin came from Merck. Graphite powder and high-purity paraffin oil from Fluka were used for fabrication the carbon paste electrode. All solutions were freshly prepared with double distilled water. All other reagents were of analytical grade. Stock standard solution of riboflavin (0.01 M) was prepared from the dry substances in double distilled water. The stock solutions were protected from light with aluminum foil, kept in a refrigerator, and used within

2 day. Sulfuric acid (pH 1.0) and phosphate buffer (pH 2-8) was used as supporting electrolyte and adjusting pH.



Scheme 2. Chemical structure of 1-hexyl-3-methylimidazolium hexafluorophosphate (HMHP)

2.2. Apparatus

Electrochemical studies were performed at a Metrohm Computrace Voltammetric Analyzer Model 797 VA with a conventional three-electrode cell. The working electrode was a bare or HMHP-modified CPE, the auxiliary electrode was a platinum rode, and an Ag/AgCl/KCl (3 M) was used as a reference electrode. During the measurements, the solution in the cell was neither stirred nor aerated. Measurements of pH were made with a Denver Instrument Model 827 pH meter equipped with a Metrohm glass electrode.

2.3. Procedure

The modified carbon paste electrode was immersed in a cell containing 20 mL of the riboflavin sample solution adjusted to a pH value, to get the chemical deposition. Meanwhile the solution was stirred by a 1.5-cm magnetic stirrer bar (rotating about 200 rpm) at open circuit. After a preconcentration step, the electrode was removed from the preconcentration cell, rinsed with water and placed in the measurement cell containing the supporting electrolyte (sulfuric acid with pH 1). The differential pulse voltammetry (DPV) was applied from -800 mV to 200 mV *vs*. Ag/AgCl/KCl (3 M) with a scan rate of 50 mV s^{-1} and pulse amplitude of 0.05 V and pulse time of 0.04 s. The difference between oxidation peak currents and residual (background) current lines was used as the method of measuring the magnitude of the analytical signals. Also, experimental procedure voltammetric measurements were conducted as cyclic voltammetry (CV) with a scan rate of 50 mV s^{-1} (if not stated otherwise) for characterizing the electrochemical behavior of the analyte at the unmodified and modified electrode surface. All experiments were performed at room temperature.

2.4. Preparation of working electrode

The HMHP/CPE was prepared by thoroughly mixing 1.0 g of graphite powder with 0.65 g of HMHP in a mortar to form a homogeneous carbon paste. A portion of the carbon paste

was filled firmly into one end of a glass tube (internal radius 3 mm), and a copper wire was inserted through the opposite end to establish an electrical contact. The surface of the HMHP/CPE was polished on a piece of weighing paper to obtain a smooth surface just before use. The bare CPE was fabricated according to same procedure, with adding paraffin oil (0.40 g) to graphite powder (1.0 g) instead of HMHP for comparison purpose.

3. RESULTS AND DISCUSSION

3.1. Characterization of the HMHP/CPE

Cyclic voltammetry was first used for investigation of electrochemical properties of the unmodified CPE and HMHP/CPE in $K_4Fe(CN)_6$ solution. Fig. 1 illustrates the cyclic voltammograms of the electrochemical oxidation of $K_4Fe(CN)_6$ at the surface of the bare CPE (a) and HMHP/CPE (b) in the 10 mM of $K_4Fe(CN)_6$ solution. As can be seen in Fig. 1, the anodic and cathodic peak currents for the HMHP/CPE are higher than that at the unmodified CPE. The experimental results show reproducible anodic and cathodic peaks ascribed to $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox couple at slow scan rates at the surface of HMHP/CPE. This is a quasi-reversible system because the peak separation potential, ΔE_p (E_{pa}-E_{pc}), is equal to 178.6 mV (250-71.4) and is greater than 59 mV that expected for a reversible system. The ΔE_p at the surface of the bare CPE was obtained to be 345.1 mV and is greater than that at the HMHP/CPE.

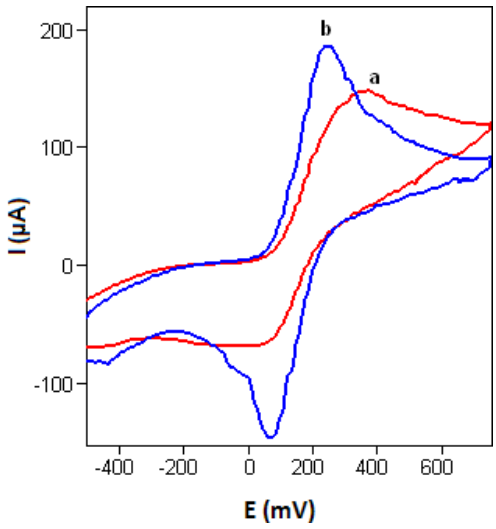


Fig. 1. The cyclic voltammograms of 10 mM $K_4Fe(CN)_6$ at the surface of (a) bare CPE and (b) HMHP/CPE in the phosphate buffer solution (pH 7.0) at a scan rate of 20 mV s^{-1}

Electrochemical impedance spectroscopy was widely applied to characterize the interface properties of the electrode [40]. Electrochemical impedance spectroscopy was employed in order to discriminate between the unmodified and modified electrodes. Fig. 2 showed the

typical Nyquist plots for the unmodified CPE (a) and HMHP/CPE (b) in phosphate buffer solution (pH 7.0) consisting of redox probe $[Fe(CN)_6]^{3-/4-}$ (2.0×10^{-3} M). It is clear, considerable differences in the electrochemical impedance spectroscopy were observed for these two electrodes. The unmodified CPE presented a large semicircle in the high frequencies range with a large resistance of electron transference, showing a low electrochemical activity of $[Fe(CN)_6]^{3-/4-}$ on the unmodified CPE. This may be due to the presence of oil as an insulating material, which it decreases the electron transfer rate of the $[Fe(CN)_6]^{3-/4-}$ redox couple at the electrode surfaces. Notwithstanding, the HMHP/CPE showed a quasi-semicircle section of much smaller diameter in the high frequencies range, which was is related to the suitable ionic conductivity of HMHP and the lower resistance to electron transfer of the HMHP/CPE. The obtained results about the HMHP/CPE exhibited that the Nyquist plot is a straight line with a larger slope compared to the unmodified CPE, at low frequencies, which is related to a diffusion-limited electrochemical process. Based on the results, it was proved that the HMHP/CPE could successfully increase the electron transference rate of $[Fe(CN)_6]^{3-/4-}$and obtained very varied features from those of the unmodified CPE.

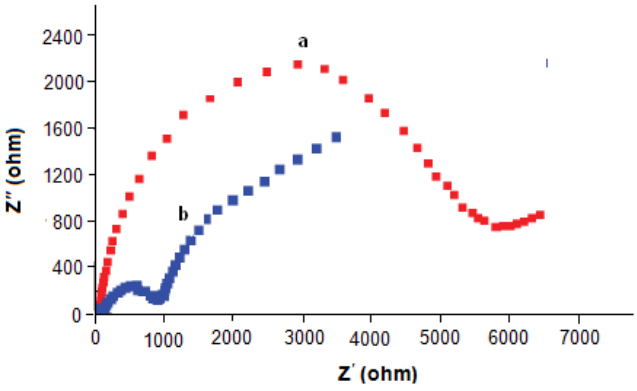


Fig. 2. Electrochemical impedance spectroscopy for the unmodified CPE (a) and the HMHP/CPE (b) in phosphate buffer solution (pH 7.0) containing 2.0×10^{-3} M $[Fe(CN)6]^{3-/4-}$ at the frequency range from 1 Hz to 100 kHz

3.2. Electrochemical response of riboflavin at the HMHP/CPE surface

The ability of the HMHP/CPE to accumulate riboflavin was investigated. Fig. 3A and B indicate the cyclic voltammograms obtained for unmodified electrode and modified electrode before (a) and after (b) accumulation in 0.1 μM riboflavin, respectively. But, when the HMHP/CPE was dipped into the accumulation solution containing 0.1 μM riboflavin for 5 min and then to place in the detection medium, well-defined anodic and cathodic peaks with peak potentials of 331 mV and -521 mV were presented, respectively (Fig. 3B(b)). However,

the unmodified electrode no distinct redox peak was observed (Fig. 3A(a)). Therefore, these results provided suitable evidences for the accumulation of riboflavin at the HMHP/CPE.

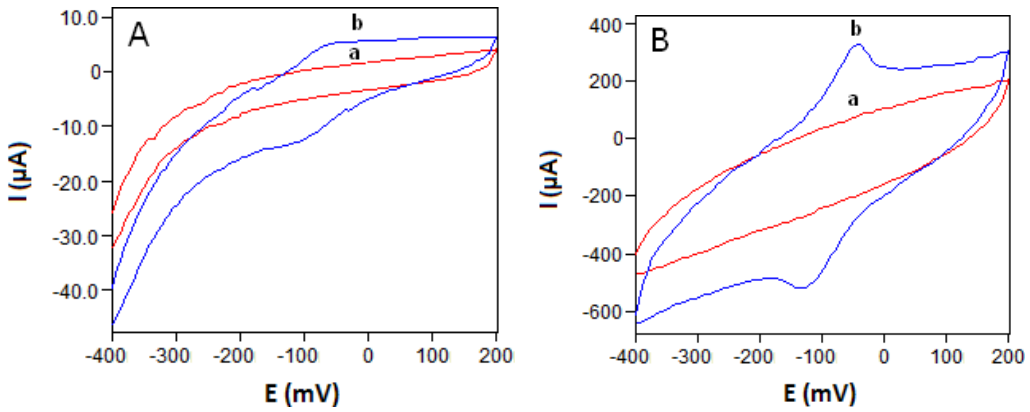


Fig. 3. Cyclic voltammograms of bare CPE (A) and HMHP/CPE (B) in sulfuric acid solution pH 1.0, before (a) and after (b) accumulation in 0.1 μM riboflavin, respectively, at scan rate of 50 mV s^{-1}

3.3. Effect of scan rate

In order to investigate the behavior of the electrochemical reaction of riboflavin on HMHP/CPE, the influence of the scan rate on the anodic peak potential and anodic peak current at HMHP/CPE with was studied using 0.1 μM riboflavin in buffer solution at pH 1. The scan rate was changed in the range of 10-1000 mV s^{-1}. The peak potential shifted to more anodic values with increasing scan rate (Fig. 4A). This behavior indicates that the oxidation process is quasi-reversible. As can be seen, the anodic and cathodic currents were enhanced with increasing of scan rate and a potential moved to positive values. The positive shift may be due to the kinetic limitation in diffusion layer which created at high current density. Obviously, the anodic and cathodic peak currents are linearly proportional to the potential sweep rate at low values from 10 to 50 mV s^{-1} (Fig. 4B). At scan rates larger than 50 mV s^{-1}, the plot of I_{pa} *vs* $\upsilon^{1/2}$ was found to be linear (Fig. 4C). This result confirmed that the oxidation and reduction process on the electrode surface is controlled by diffusion rather than by adsorption. Also, increase of the scan rate causes significant increase of ΔE_p. These results indicate quasi reversible process for the nature of electrochemical reaction [41].

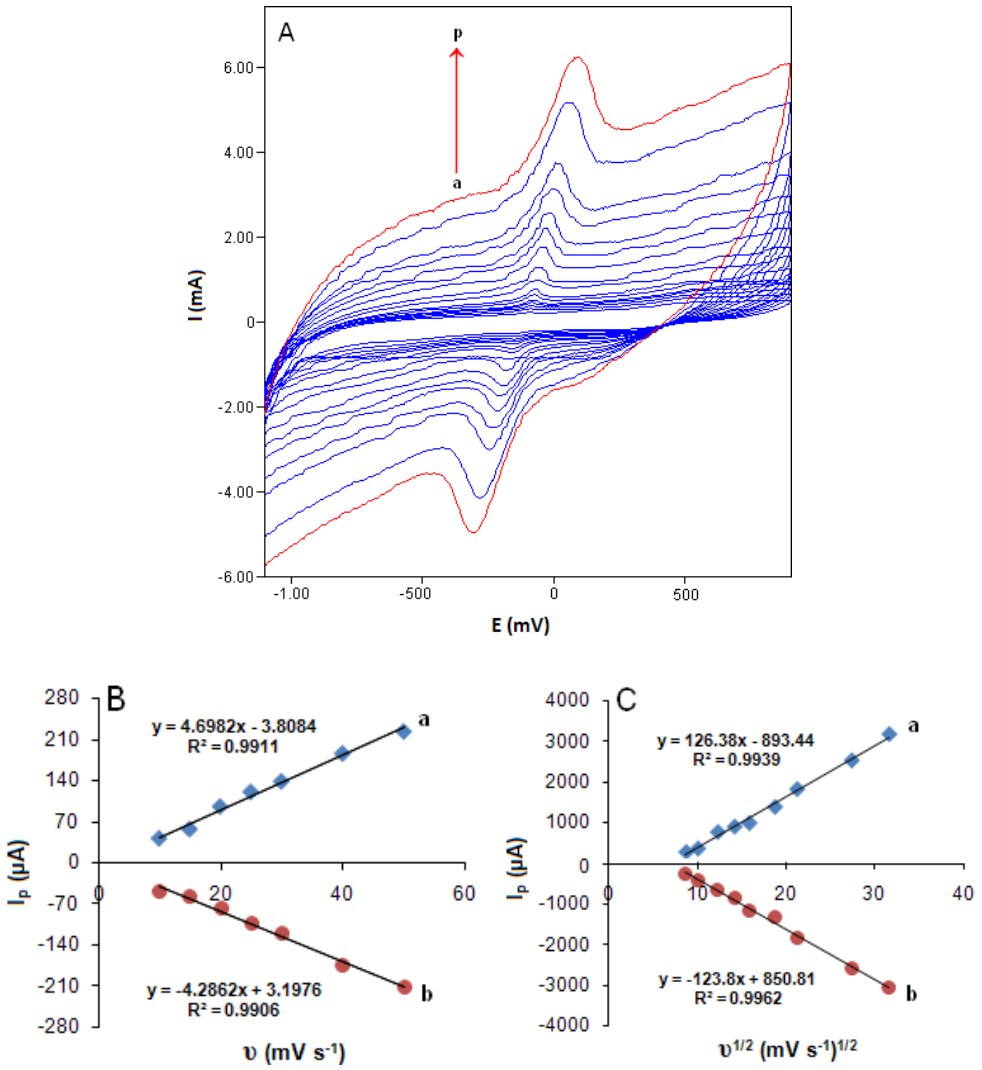


Fig. 4. (A) The cyclic voltammograms of HMHP/CPE in sulfuric acid solution pH 1.0, after accumulation in 0.1 µM riboflavin, at some scan rates from (a) to (p): 10, 15, 20, 25, 30, 40, 50, 75, 100, 150, 200, 250, 350, 450, 750 and 1000 mV s^{-1}; (B) The dependency of I_{pa} (a) and I_{pc} (b) on υ at lower values of υ (10-50 mV s^{-1}), and (C) the plot of I_{pa} (a) and I_{pc} (b) on $υ^{1/2}$ at higher values of υ (υ>50 mV s^{-1})

3.4. Influence of the medium pH

The mechanisms of many organic reactions are known to involve a pH dependent process. In this case, acidity of electrolyte affected the electrooxidation behavior of riboflavin because proton participated in the electrode reaction. Thus, the effect of pH on riboflavin oxidation was studied at the HMHP/CPE surface using CV and DPV at accumulation time 5 min. In the preliminary experimental studies, nine individual pH values in the range 1.0-8.0 were tested to identify the scale of the pH factor in the experimental domain. As can be seen in Fig. 5A, the peak potential of riboflavin at the surface of HMHP/CPE is shifted to the less positive values by increasing the solution pH. Also, DPV technique was applied with pulse

amplitude of 0.05 V and pulse time of 0.04 s in order to find the optimum pH. Similar to the obtained results in CV, the peak current decreased considerably beyond pH 1.0 (Fig. 5B). Also, the peak potential of riboflavin was shifted to more negative potentials with increasing of the pH of buffers. Based on these results, pH 1.0 was chosen for further tests. When considering pH from 1 to 8 the peak potential shift to the more negative values occurs with the corresponding equation E_p=-55.329×pH-53.554. The slope of 55.329 mV per pH unit is close to the ideal value of 59 mV which might indicate that the number of protons and electrons involved in the electrochemical reaction is in the ratio 1:1. Resulted proton/electron ratio is in accordance with the oxidation reaction of riboflavin where two electrons and two protons are involved.

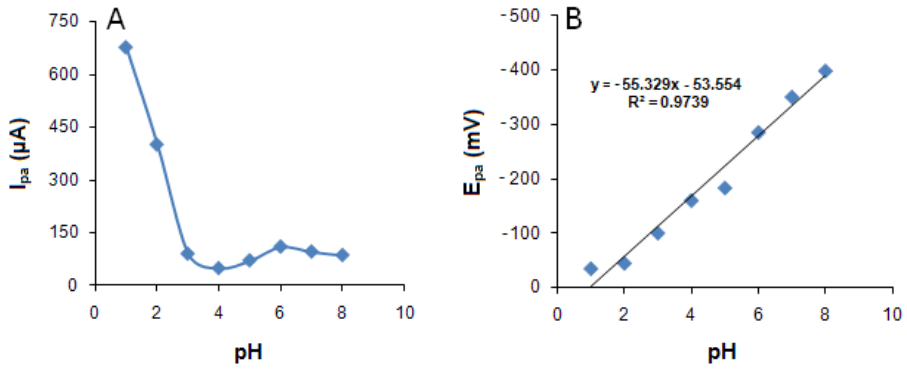


Fig. 5. Effect of pH on (A) the peak current and (B) the peak potential of the HMHP/CPE in sulfuric acid solution pH 1.0 after accumulation in 0.1 μM riboflavin, using DPV at pulse time 0.04 s and pulse amplitude 0.05 V at scan rate of 50 mV s^{-1}

3.5. Optimization of DPV parameters

Differential pulse voltammetry is a powerful method for the quantitative determination of analytes due to the low background currents and low detection limits and has been used in the present study for the detection of riboflavin. Pulse amplitude and pulse time as important parameters for DPV were optimized to obtain the best experimental setup for the determination of riboflavin. The optimization was performed in previously selected buffer at pH 1.0 with the concentration of 0.1 μM riboflavin at accumulation time 5 min. During this optimization procedure one investigated parameter was varied while the others were kept fixed. When the pulse amplitude was changed from 0.01 to 0.30 V, the peak current sharply increased up to value of 0.20 V and with further increase of the pulse amplitude obtained current was slightly decreasing (Fig. 6A). Therefore, the most suitable peak current was observed at 0.20 V. Also, varying the pulse time in the range of 0.01-0.10 s, the peak currents increased up to 0.07 s; after which, it decreased (Fig. 6B). Consequently, a value of 0.07 s of pulse time was selected as an optimum parameter.

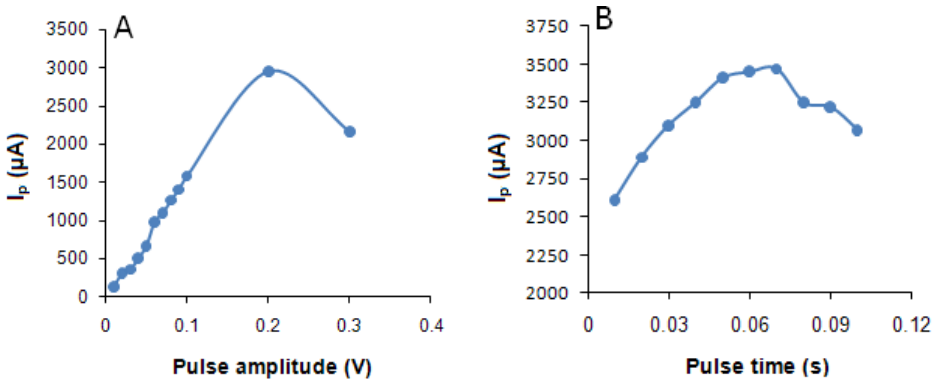


Fig. 6. Influence of pulse amplitude (A) and pulse time (B) on the peak current of the HMHP/CPE in sulfuric acid solution pH 1.0 after accumulation in 0.1 µM riboflavin, using DPV with pulse time 0.04 s (A) and pulse amplitude 0.05 V (B) at scan rate of 50 mV s^{-1}

3.6. Influence of accumulation time

Fig. 7 shows the plots of anodic peak current of the HMHP/CPE versus the accumulation time for H_2SO_4 solution (pH 1.0) containing 0.1 µM riboflavin at the seven different accumulation times 2.5, 5.0, 7.5, 10.0, 12.5, 15.0 and 17.5 min by DPV technique (with pulse amplitude 0.2 V and pulse time 0.07 s). At first, the peak current increased with accumulation time, indicating a case before achieve the adsorptive equilibrium so that at longer accumulation time, the more riboflavin was adsorbed and thus the peak current became larger. However, after a specific accumulation period, the peak current tended to level off; illustrating that adsorptive equilibrium was achieved. An accumulation time of 12.5 min was chosen for further experiments. All other tests such as calibration curve, interference investigations, and real sample analysis were performed under these optimized factors: pH 1.0, accumulation time 12.5 min, pulse amplitude 0.20 V and pulse time 0.07 s.

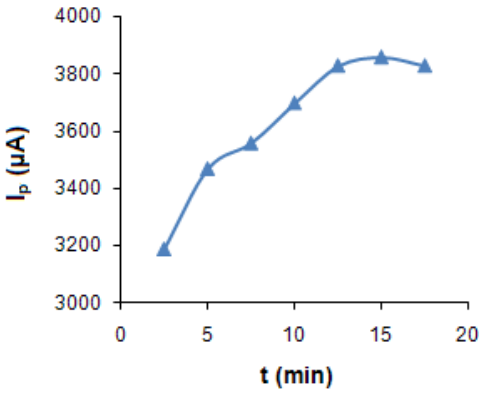


Fig. 7. Effect of accumulation time on peak current of the HMHP/CPE in sulfuric acid solution pH 1.0 after accumulation in 0.1 µM riboflavin, using DPV with pulse time 0.07 s and pulse amplitude 0.20 V at scan rate of 50 mV s^{-1}

3.7. Calibration graph

The optimal parameters selected from the above experiments have been applied to build a calibration curve (Fig. 8). The accumulation was performed for 12.5 min in a solution containing various riboflavin concentrations in distilled water pH 7.0. The detection was carried out in pH 1.0. The inset of Fig. 8 is a diagram of I_{pa} versus riboflavin concentration that shows the linear region usable for determination of riboflavin. A linear response in the 3.5×10^{-8}-1.5×10^{-6} M concentration range was observed, which was followed by a decrease in sensitivity at higher concentrations. A limit of detection of 11 nM was calculated for a signal-to-noise ratio of 3.

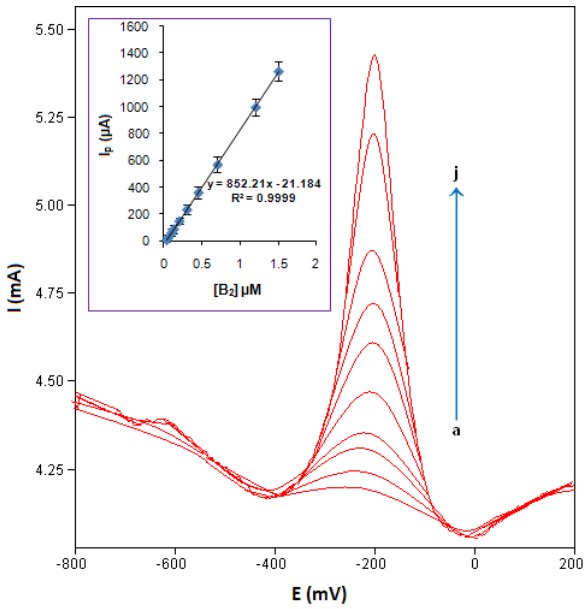


Fig. 8. The cyclic voltammograms of the HMHP/CPE in sulfuric acid solution pH 1.0 after accumulation in different concentrations of riboflavin: (a) 0.035, (b) 0.055, (c) 0.10, (d) 0.13, (e) 0.20, (f) 0.030, (g) 0.45, (h) 0.70, (i) 1.20 and (j) 1.50 μM at scan rate of 50 mV s^{-1}. Inset: calibration curve for the determination of riboflavin

The comparison of several parameters of riboflavin at some modified electrodes is summarized in Table 1 [9-20,24,25]. It can be seen in this Table, this sensor offers low detection limit, wide linear range with a good sensitivity and reproducibility and in comparison with previously reported data this sensor possess comparable or better characteristics for the quantification of riboflavin

Table 1. Comparison of some electrochemical sensors for riboflavin determination

Electrode	Modifier	Method	Linear Range	Limit of Detection	Ref.
Glassy carbon disc	Double-stranded DNA	SWV	0.08-1 μM	0.06 μM	[9]
Glassy carbon	Flowers-like Fe_3O_4/rGO	DPV	300 nM-1 μM, 1 μM-100 μM	89 nM	[10]
Copper substrate	Bismuth film	SWAdSV	0.3-0.8 μM, 1.0-9.0 μM	100 nM	[18]
Glassy carbon	Ordered mesoporous carbon	Open circuit accumulation-CV	0.4-1 μM	0.02 μM	[11]
Glassy carbon	High-density arrays of polythiophene nanotubes	DPV	0.01-65 μM	3 nM	[12]
Carbon paste	Manganese dioxide nanoparticles	DPV	0.02-9 μM	15 nM	[24]
Gold	DNA/molybdenum disulfide-graphene nanocomposite	DPV	0.025-2.25 μM	20 nM	[19]
Glassy carbon	Graphene	DPV	1 nM-0.015 μM	0.1 nM	[14]
Glassy carbon	Nanocrystalline metallosilicate	DPV	30 nM-500 mM	5 nM	[15]
Graphite cylindrical	_	SWAdSV	0.01-0.07 μM	5 nM	[20]
Glassy carbon	Poly (3-methylthiophene)	DPV	0.1-200 μM	0.05 μM	[13]
Glassy carbon	Electropolymerized film of 3-amino-5-mercapto-1,2,4-triazole	DPV	10-90 μM	0.0454 μM	[16]
Carbon paste	Co^{2+}-Y zeolite	DPV	1.7-34 μM	0.71 μM	[25]
Rotating disk glassy carbon	Hematite (α-Fe_2O_3)	SWV	1.3-100 μM	8.4 μM	[17]
Carbon paste	Ionic liquid	Open circuit accumulation-DPV	0.035-1.50 μM	11 nM	This study

3.8. Repeatability and stability of the HMHP/CPE

The repeatability of HMHP/CPE was estimated through the relative standard deviation of five replicate determinations of a solution consisting of 0.1 μM riboflavin. The relative standard deviations were obtained to be 4.5%. The reproducibility between electrodes was measured through the similar strategy utilizing three different electrodes. The relative standard deviation was found 7.1% in a solution containing 0.1 μM riboflavin. This result demonstrated that the repeatability and reproducibility of the electrode are suitable. The

stability of the electrode was evaluated by probing of the electrode response to electrocatalytic oxidation of 0.1 μM of riboflavin after being put away at room temperature for 15 days. It was seen that, the current response preserved nearly 94.3% of its initial values.

3.9. Interference studies

An essential factor for a sensor is its ability to discriminate among the interfering species usually present in similar physiological environment and the target analyte. In order to estimate the selectivity of the method toward riboflavin, electrochemical influence of some possible interferences for instance vitamins B_1, B_6 and B_{12}, folic acid, diclofenac sodium, ascorbic acid, diphenhydramine, and ibuprofen were tested in concentrations of 1.0 μM under optimized experimental conditions. It was regarded that tested materials firmly interfere with the determination of riboflavin if gives signal changes more than ±10%. It should be stated that the selected interferences are electroactive, but their oxidation potentials are different from that of riboflavin and in concentration of 1.0 μM, in absence of riboflavin, practically do not provide electrochemical activity in the tested potential range (Table 2). The presence of these interferences in concentration level (1.0 μM) does not causes changes in the peak current found for 0.1 μM riboflavin. Consequently, this method has a good selectivity for the electrochemical quantification of riboflavin.

Table 2. Influence of interferences in concentration of 1.0 μM on the determination of 0.1 μM riboflavin at the optimized DPV parameters

Interfering species	**Signal change (%)**
Vitamin B_6	+1.02
Vitamin B_1	+1.98
Vitamin B_{12}	-0.96
Diclofenac sodium	-0.99
Folic acid	+0.73
Ascorbic acid	+2.67
Ibuprofen	+0.6
Diphenhydramine	-0.4

3.10. Real sample analysis

This strategy was employed to the detection of riboflavin in the B-complex capsules produced by Euro OTC Pharma Company. One B-complex capsule (0.2053 g) containing 9.0 mg vitamin B_2 was dissolved in 150 mL of buffer solution (pH 1.0) and an aliquot (5.0 mL) was added to a 20 mL buffer at pH 1.0 and recorded by DPV under optimized experimental conditions. The riboflavin concentration was determined and a standard addition method was

adopted to evaluate the result. By this method, the obtained riboflavin mean value by the calibration curve 8.65 mg was measured with the mean recovery percent 96.11% (*n*=3). The gained showed that the proposed method was suitable for the determination of the concentration of riboflavin in pharmaceutical formulations. No sample pretreatment was needed for this proposed method.

4. CONCLUSION

Carbon paste electrode was modified with selected ionic liquid. The influence of 1-hexyl-3-methylimidazolium hexafluorophosphate as additive to carbon paste electrode was characterized by cyclic voltammetry of $Fe(CN)_6^{3-/4-}$ and electrochemical impedance spectroscopy. The selective preconcentration and electroanalysis of riboflavin at ionic liquids modified carbon paste electrode has been demonstrated. Sulfuric acid solution pH 1.0 as the electrolyte, an accumulation time of 12.5 min, pulse amplitude 0.20 V and pulse time 0.07 s were optimal for the determination of riboflavin. The developed method provided a low limit of detection, good repeatability and suitable selectivity. This paper showed that the proposed strategy here can be successfully applied for monitoring riboflavin in pharmaceutical formulations.

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