

Full Paper

Determination of Nicotinic Acid by Square Wave Voltammetry on a Carbon Paste Electrode: the Crucial Effect of Electrode Composition and Analytical Conditions

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Abstract- The foregone studies have shown that nicotinic acid cannot produce noticeable reductive signal at carbon-based electrodes without appropriate modification of the electrode. This is an obvious reason that mercury is known as the main electrode material for electroreduction of nicotinic acid. In this study, it has been shown that it is possible to create a remarkable reduction signal for NA at a carbon paste electrode (CPE) without any modification. This achieved by precisely adjustment of electroanalysis pH, appropriately choosing of binder kind, precisely controlling of the percentage of the binder in the electrode composition and utilizing of an effective voltammetric technique. A carbon paste electrode, containing 30% of n-eicosane (as binder) was shown to be the best electrode for NA determination. It was also shown that utilizing of square wave voltammetry in place of differential pulse voltammetry led to remarkably improvement in the analytical signal of NA. The pH value of the electroanalysis solution was shown to be a crucially effective factor for creating of NA signal and an optimum value of pH equal to 2.2 was chosen as the best pH condition. The optimized method exhibited a dynamic concentration linear range of 3.0×10^{-6} - 3.0×10^{-3} molL⁻¹ with a detection limit of 5.63×10^{-7} molL⁻¹. As an analytical application, the proposed sensor was successfully used for determination of nicotinic acid in the urine, serum and pharmaceutical samples.

Keywords- Nicotinic acid, Carbon paste electrode, Square wave voltammetry, n-Eicosane

1. INTRODUCTION

Nicotinic acid (niacin or pyridine-3-carboxylic acid, NA) plays important biological roles in the human body. It enters the body through eating foods and fruits (including yeast, fish, milk, eggs, green vegetables and cereal grains) and also is produced in the body from its precursor called tryptophan [1]. The shortage of NA results in pellagra, as well as causes adverse effects in the central nervous system, gastrointestinal tract, and skin (It is a well-known skin-lightening compound). High amount of NA may beget life-threatening poisonous reactions, thickening of the retina and raise the level of uric acid in the blood [2,3]. Nicotinic acid has been widely used in medicine and food additives. Its derivatives have been investigated in clinical trials for treating diabetes [4,5] and for antitumor properties [6]. The detection of NA is important in diagnoses and treatments of several diseases [7]. Nicotinic acid is one of the water-soluble vitamins, it is destroyed when boiled in water, and it can't be reserved in the human body for a long time and is usually found in urine [8].

The determination of NA in biological samples, food, nutrient materials and pharmaceutical preparations has been a subject of growing interest due to the effect on human health. Different and many analytical methods have been developed for NA determination, including various chromatography methods [2,6,9-27], capillary electrophoresis [24,28] drop-to-drop solvent microextraction coupled to matrix-assisted laser desorption/ionization mass spectrometry [3], and enzyme sensor [29]. Most of the above mentioned methods need complicated and expensive instruments and usually trained operators are required to execute the determination method.

The electrochemical methods can be a good alternative to be used instead of the spectroscopic and chromatographic methods, utilized traditionally for NA determination. There are only a few electrochemical methodologies for the analysis of NA using the different working electrodes including mercury electrode [30], polycrystalline gold electrode [31], mercapto acetic acid-coated gold electrode [32], carbon paste electrode modified by carbon nanotube/La-doped TiO₂ nanocomposite [8], molecularly imprinted polymer membrane-modified glassy carbon electrode [33] and multiwall carbon nanotubes modified glassy carbon electrode [34]. The electrochemical reaction mechanism of NA is complex and the highly divergent results were reported in these articles [30].

Nowadays, carbon paste electrodes (CPEs) are the most popular electrochemical or bioelectrochemical sensors in wide applications. The CPE was invented by Ralph Norman Adams from the University of Kansas in 1958. Due to its unique properties including a large potential window on both anode and the cathode region, the simplicity of its preparation, low cost, a simple modification of them, and low capacitive currents, leading to high signal to noise ratio, CPEs represent one of the most frequent types of working electrodes [35-39].

The foregone studies have showed that NA could not produce remarkable signal at CPE without modification of CPE. In the recent study that has been reported by our group, as the

first time, a remarkable signal was created for NA at unmodified CPE [40]. This achieved by precisely adjustment of electroanalysis pH as well as the percentage of the binder in the electrode composition. However, the main disadvantage of the as described method is its high limit of detection for NA. Therefore, further study was performed to increase the analytical performance of the method. The studies showed that when the square wave voltammetry was used instead of differential pulse voltammetry, the observed flow intensity of reduction of nicotinic acid increased considerably. The effects of some other parameters including type of the binder material, used for the carbon paste electrode fabrication, and potential scan rate were investigated and optimized. Also in this work, studies have been performed on the reduction mechanism of nicotinic acid in detail. As a result of this study, the detection limit of the method was decreased considerably, compared to the previous method. Finally, the developed method was successfully used for determination of nicotinic acid in the urine, serum and pharmaceutical samples.

2. EXPERIMENTAL

2.1. Instruments and reagents

Electrochemical data were obtained with a three-electrode system using a potentiostat/galvanostat model PGSTAT302, Metrohm. The CPE was used as a working electrode. A platinum wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Nicotinic acid (NA) and n-eicosane were supplied by Sigma–Aldrich (Munich, Germany), and used as received. Graphite powder was purchased from Fluka (Buchs, Switzerland). Other chemicals were of analytical grade and were purchased from Merck (Darmstadt, Germany).

2.2. Preparation of the sensors

The certain amounts of graphite and binder were mixed with a stainless steel spatula. In case binder of n-eicosane, it is noteworthy that before mixing, n-eicosane was melted in a dish at 45–50 °C. The procured paste was utilized to fill a hole (2.00 mm in diameter, 3 mm in depth) at the end of a Teflon body, the excess of solidified material was removed with the assistance of a paper sheet. The electrode can be reused after each experiment by moving the electrode surface on a paper sheet in order to extrude a thin layer of the electrode surface.

2.3. Nicotinic acid measurement in pharmaceutical Samples

Five nicotinic acid tablets were weighed and eroded by mortar. An accurate weight of the powder containing 25 mg (and 100 mg) of NA was dissolved in 50 mL of distilled water in the ultrasonic bath (35 °C) for 10 min. The solution was filtered through a filter paper. The sample solution (having the concentration lied in the calibration curve of the method) was prepared

from the stock sample solution by dilution of the sample solution using a required volume of electrolyte solution (containing KCl (0.1 M) and HCl (0.01 M)). The solution prepared was then applied for NA analysis by the optimized method. The determination of NA content of the samples was based on a well-known standard addition method.

2.4. Nicotinic acid measurement in urine and serum samples

The urine and serum samples were obtained from the Iran Health Centre and were stored in a refrigerator immediately after collection. Ten milliliters of the samples were centrifuged for 20 min at 2500 rpm. The supernatant of the urine sample was diluted 5 times and the supernatant of serum sample was diluted 10 times with electrolyte solution. The solution was transferred into the voltammetric cell to be analyzed without any further pretreatment under optimum conditions. The standard addition method was then used for the determination of NA in the real samples.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behavior of nicotinic acid by cyclic voltammetry

The cyclic voltammetry behavior of nicotinic acid at various potential scan rates at CPE is shown in Fig. 1I.

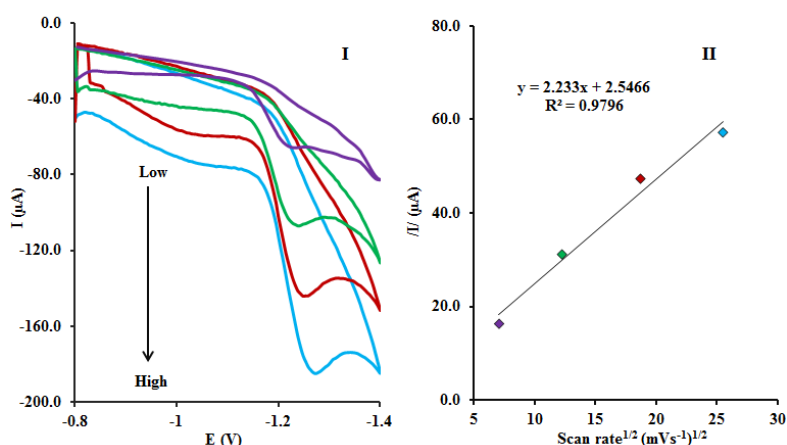


Fig. 1. Cyclic voltammograms for 1 mM of nicotinic acid in 10 ml electrolyte solution containing of KCl (0.1 M) and HCl (0.01 M) in different scan rates (In order from top to bottom 50, 150, 350 and 650 mVs⁻¹) with step potential=5 mV (I); A Linear relation between peak current and the square root of the scan rate (II); The composition of electrode: graphite and n-eicosane (80/20)

As seen, when the scan rate is increased the current response magnitude increases correspondingly. Moreover, increasing of scan rate leads to significant shift of potential of current peak to more negative values. These proofs suggest an irreversible redox mechanism for electrochemical reaction of NA. Fig. 1II shows that the reduction current peak of NA versus the square root of scan rate ($v^{1/2}$) is linear. This finding shows that the reduction current of NA is a diffusion-controlled process.

3.2. Comparison of differential pulse voltammetry and square wave voltammetry to determine nicotinic acid

The NA electrochemical behavior also was also studied by DPV and SWV under the same experimental conditions of the electrode composition, supporting electrolyte and NA concentration in order to compare the effectiveness of these techniques for NA determination. As can be seen in Fig. 2, the peak current intensity of NA obtained when using SWV is significantly higher than that recorded using DPV. This is reasonable, since SWV technique is inherently sensitive than DPV. The fact that using of SWV technique instead of DPV do not lead to broaden and distort of NA reduction peak indicates that the charge transfer rate of NA at CPE electrode is fast enough to accord itself to relatively fast scan rate of SWV technique. Moreover, it is clear that the peak potential of NA in the case of using SWV shifts slightly towards negative potential value. This is because of SWV related potential scan rate which is fast inherently, compared to DPV. Based on the described result, SWV was chosen as the main electrochemical technique for nicotinic acid determination.

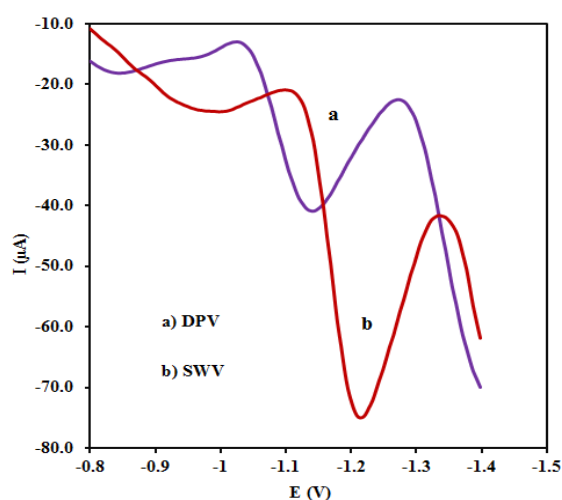


Fig. 2. Comparison of differential pulse voltammetry and square wave voltammetry for nicotinic acid (5×10^{-4} M) in 10 ml electrolyte solution containing of KCl (0.1 M) and HCl (0.01 M). DPV conditions: step potential=5 mV, modulation amplitude=100 mV, modulation time=0.05 s, interval time=0.1 s. SWV conditions: Frequency=50Hz, step potential=5mV, amplitude=50 mV. Composition of electrode: graphite and n-eicosane (80/20)

3.3. Electrochemical reduction of nicotinic acid on carbon paste electrode by square wave voltammetry

The reaction mechanism of NA is somewhat complex; this may be a reason that different results about the electrochemical reduction of NA were reported by several papers [8,30-34]. Rodriguez-Amar and et al [30] performed a detailed study on the oxidation and reduction mechanism of NA on a mercury electrode in acidic, alkaline and neutral environments. The results of their studies showed that NA has one or two reduction peaks depending on the pH of the medium. Below pH of 0.5, they observed only one peak for NA. It was very close to the discharge of the dissolved H^+ ions. Above this pH value, however they observed that the peak split into two peaks that the appeared. The new pek was corresponded to the dimerization of radicals produced in the first electron transfer via a radical-radical coupling in the reaction layer. However, the peaks overlaped above pH=4.5. At further pH values the overlapped peal decreases, disappearing completely at pH=10. Such a described mechanism has been confirmed by Yao and et al. [33] who performed NA reduction at modified-glassy carbon electrode. In order to uncover the mechanism of creation of electrochemical signal of NA at CPE, in this research, we SWV response of NA was recorded at various pH values. The results are represented in Fig. 3. As expected, the results of this experiment show that not only the current peak intensity of NA is seriously affected by electroanalysis pH condition but also the peak potential influenced considerably by the pH.

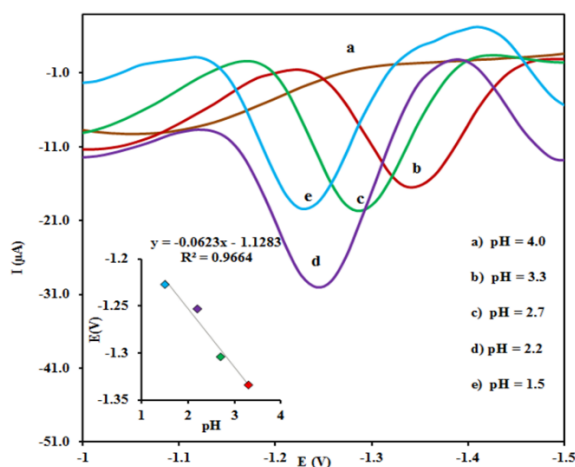
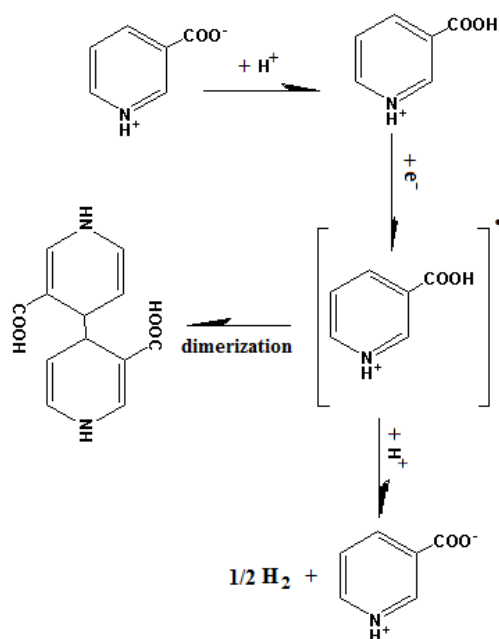


Fig. 3. Square wave voltammograms for nicotinic acid (2.5×10^{-4} M) in different pHs of the electrolyte. SWV conditions: Frequency=50 Hz, step potential=5 mV, amplitude=50 mV. Composition of electrode: graphite and n-eicosane (80/20)

In this work, voltammetry studies were performed in a solution of KCl (0.1 M), adjusted to various pH in the range of 1.5 to 5, by HCl solution. The results are shown in the Fig. 3. The results represented in the figure are compatible with the reported results in our previous article

[36] and suggest that the sensor response to nicotinic acid is very sensitive to pH value. It can be seen that the only a reduction peak with the considerable flow intensity has been observed in acidic pHs and it disappeared fully in pH 4. Fig. 3, also displays the potential shifts towards low negative values by reducing pH and it is varied linearly with the pH with a slope of -62.3mV, which indicated that H^+ ions took part in the reduction process. According to previous reports [30,33], NA can cause the catalytic discharge of hydrogen, proposed mechanism is brought in Scheme 1.



Scheme 1. Reduction mechanism of nicotinic acid

3.3. Study of composition of electrode on sensor response

One of the effective and important parameters in determination of NA was found to be type of electrode composition. To achieve the best combination of the electrode, types of binders (glycerin, nujol, paraffin and n-eicosane) were tested under identical conditions. Also, the glassy carbon electrode was investigated under the similar conditions. The results are shown in Fig. 4. As it is seen, when glycerin was used as a binder in the composition of electrode, no peak was observed and of among the rest of binders, n-eicosane had the best response. Also, the observed response with glass carbon electrode than CPE with a binder of n-eicosane was very low. In the next stage, in order to find the best composition for CPE, the amount of binder percent was changed in the fixed conditions of voltammetric determination and then the obtained responses were used for the conclusion. The results are shown in the Fig. 5I. It can be seen that 30% of the binder is an optimum amount in electrode composition.

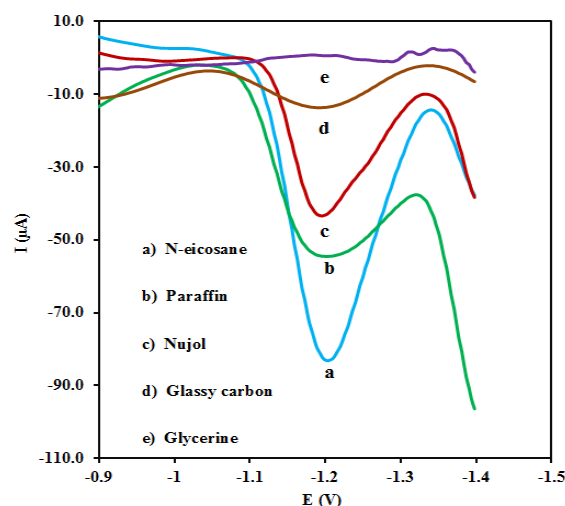


Fig. 4. Square wave voltammograms for nicotinic acid (5×10^{-4} M) in 10 ml electrolyte solution containing KCl (0.1 M) and HCl (0.01 M) with different electrodes (glassy carbon and carbon paste with different binders (80/20)). SWV conditions: frequency=50 Hz, step potential=5 mV, amplitude=50 mV

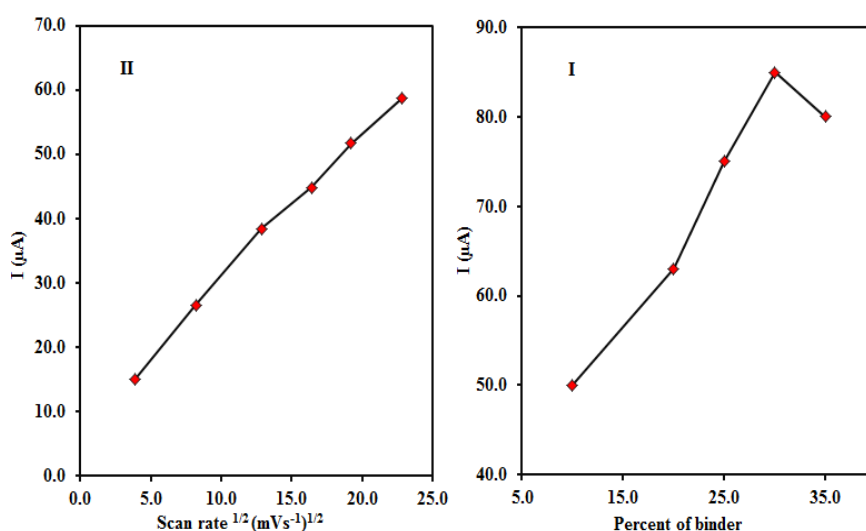


Fig. 5. optimization of percent of binder of n-eicosane in electrode composition for nicotinic acid (5×10^{-4} M) in 10 ml electrolyte solution containing of KCl (0.1 M) and HCl (0.01 M), SWV conditions: Frequency=50 Hz, step potential=5 mV, amplitude=50 mV (I) and linear relation between peak current and the square root of the scan rate in nicotinic acid (2×10^{-4} M) in 10 ml electrolyte solution containing of KCl (0.1 M) and HCl (0.01 M), Composition of electrode: graphite and n-eicosane (70/30)

3.4. Investigation of the effect of scan rate on electrode response using square wave voltammetry

Scan rate is the other important parameter on the electrode response. In low scan rates, the reduction peak current intensity reduced considerably. Similar to the method of cyclic

voltammetry, the reduction peak current varied linearly with the square root of scan rate ($v^{1/2}$). Because the peak shape was flattened in very high scan rate, 270 mVs^{-1} was selected as optimal scan rate.

3.5. Interference studies

After the optimization and establishment of the determination method for the prepared sensor, the effects of some possible interfering substances on the response of sensor have been investigated. The tolerance limit was established as the maximum concentration of foreign species that caused a relative error of 7% in the analytical signal. For this purpose, SWVs were performed in $5 \times 10^{-5} \text{ M}$ NA in the absence and presence of different concentrations of each interfering substances. Owing to the specific potential of NA on CPE, few reagents should interfere with the response of NA by SWV. Experimental results showed 30-fold excess of ascorbic acid, dopamine, VB2 (riboflavin), and uric acid and 10-fold excess VB1 (thiamine) and VB6 (Pyridoxine) don't significantly influence the electrode response.

3.6. Calibration and detection limit

The effect of NA concentration on the electrode response was investigated. The peak current intensity was found to increase with increasing NA concentration. The calibration curve (shown in Fig. 6) of the prepared sensor showed a linear relationship over NA concentration in the range of 3.0×10^{-6} to $3.0 \times 10^{-3} \text{ M}$ with a detection limit of $5.63 \times 10^{-7} \text{ M}$ according to 3δ rule. Each point of the calibration graph is the average of three replications. Moreover, five separate determinations of NA by the same electrode resulted in an $\text{RSD}\% = 1.5$ ($n=5$). This can be an indicative of the repeatability of the method.

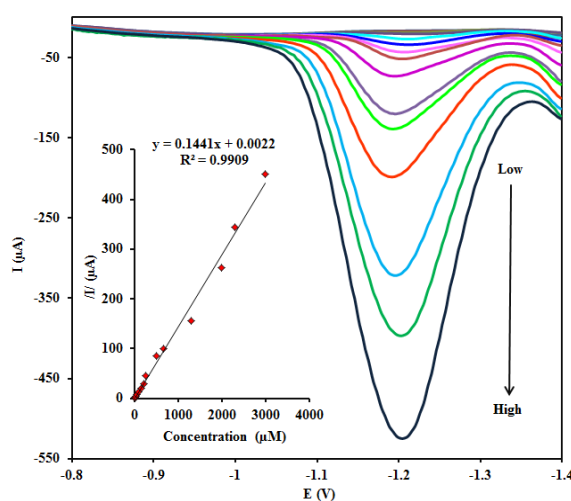


Fig. 6. Square wave voltammograms of nicotinic acid in different concentrations and of the optimized electrode for determination of nicotinic acid

3.7. Determination of nicotinic acid in real samples by proposed sensor

The proposed sensor was used to determine NA in serum, urine and pharmaceutical samples. The results showed the urine and serum samples lack any NA in the linear range of our suggested procedure. The standard addition method was used for the determination of NA in real samples. For this purpose, a specific value of NA was spiked to urine samples. The recovery percent was arranged in Table 1. Also in order to verify the efficiency of this technique, we used a medicinal sample containing specified NA. The results obtained are summarized in Table 1. The results clearly show and confirm the ability of the proposed sensor for the voltammetric determination of NA with high selectivity, accuracy, and good reproducibility.

Table 1. Determination of nicotinic acid in the urine, serum and pharmaceutical samples using the proposed sensor

Sample	Labeled value (mg)	Added (μM)	Found (μM)	RSD (%)	Recovery (%)
Urine1	-	10.0	9.75	0.25	97.5
		50.0	48.5	1.20	97.0
		100.0	98.3	2.33	98.3
Urine2	-	10.0	9.54	0.34	95.4
		50.0	47.5	1.23	95.0
		100.0	97.8	3.21	97.8
Plasma	-	10.0	9.25	0.56	92.5
		50.0	46.4	2.31	92.8
		100.0	94.5	3.74	94.5
Nicotinic acid 25^a	25.0	-	24.7 ^b	1.04	98.8
Nicotinic acid 100^a	100.0	-	96.7 ^b	2.32	96.7

^a factory of Sobhan Pharma, Iran

^b mg

3.8. Comparison of proposed electrode with some of the previously reported melatonin voltammetric sensors

The analytical characteristics of the proposed sensor were compared with some previous voltammetric sensors of NA. The comparison results are summarized in Table 2. As it is seen, linear range of proposed sensor is very wider than many of reported articles and its limit of detection is comparable with them. However, the highlighted preference of this sensor than electrodes depicted in the table is its simplicity, fastness, and cheapness. In this work, limit of detection has been decreased 50 times compared with previous work.

Table 2. The comparison of the proposed sensor with some previous reported nicotinic acid voltammetric sensors

Method	Working electrode	Linear range(μM)	LOD (μM)	Investigated real sample	Ref
Linear sweep voltammetry	Mercaptoacetic acid coated gold electrode	0.45-800	0.14	Foods	[32]
Linear sweep voltammetry	Multiwall carbon nanotubes modified glassy carbon Electrode	0.2-40	0.08	Pharmaceutical	[34]
Cyclic voltammetry	Polycrystalline gold electrode	2.7-2400	0.27	Pharmaceutical	[31]
Chronoamperometric	Carbon nanotube/La-doped TiO_2 nanocomposite	1-120	0.27	Urine	[8]
Differential pulse voltammetry	Molecularly imprinted polymer Membrane Modified glassy carbon Electrode	50-5000	-	Wahaha soft drink sample	[33]
Differential pulse voltammetry	Carbon paste electrode	50.0-3000	30.1	Urine	[36]
Square wave voltammetry	Carbon paste electrode	3.0-3000	0.563	Urine, serum pharmaceutical	This work

4. CONCLUSION

In this project, direct electrochemical reduction of nicotinic acid was performed on simple CPE and applying square wave voltammetry. With various investigations including adjusting of electroanalysis pH, the type, and percent of the binder in electrode composition, the effect of scan rate and the selection of appropriate voltammetry techniques, the NA reduction peak was obtained on unmodified CPE. Square wave voltammetry was selected as the best technique to the determination of NA. The effects of some parameters were investigated. The main advantages of the proposed method are its good reproducibility accuracy, selectivity, simplicity, fastness, cheapness and eco-friendliest. The proposed sensor was successfully used for the determination of NA in the urine, serum and pharmaceutical samples.

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