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Graphene Oxide-Paraffin-Nanobentonite as Working Electrode for Cyclic Voltammetry Analysis for Nicotinic Acid

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The composition of graphene oxide (GO):paraffin:nanobentonite electrode was optimized to acquire the optimal working electrode to analyze nicotinic acid under the optimum conditions through cyclic voltammetry. Graphene oxide was synthesized from graphite by employing the improved Hummer method. Bentonite was synthesized using the sonothermal method. The ratio of GO:paraffin:nanobentonite electrodes of 3:3:4 provided the optimal voltammogram. The results indicated that the composition of the comparative working electrodes of GO-modified nanobentonite was best 3:3:4 with a good peak recovery averaged value of 96.16%.

Keywords: Graphene oxide, Cyclic voltammetry, Nicotinic acid, Paraffin, Nanobentonite.

INTRODUCTION

Niacin or nicotinic acid is a B-complex vitamin (vitamin B_3) having cholesterol-reducing activity. Studies have reported that the therapeutic doses of nicotinic acid can lead to changes in lipoproteins and some lipid plasma, thereby enhancing the capacity of increasing high-density lipoprotein (HDL) cholesterol [1]. Vitamin B_3 is produced through food consumption and processed using amino acid tryptophans. These foods include fish, meat, nuts, *etc.* whereas niacin is available as a supplement. Similarly, in the deficiency of other vitamins, human bodies undergo certain variations while fixing the niacin deficiency [2]. Vitamin B_3 or niacin deficiency leads to some problems, such as headaches, depression, diarrhoea and skin problems [3]. Vitamin B_3 must be acquire from the aforementioned healthy food sources to prevent deficiency. Taking the supplements of vitamin B_3 requires supervision because some known drug interactions and side effects can occur. The most common side effects include nausea (4-9%), flushing (88%), and vomiting (2-9%). Other less common but serious side effects are hepatotoxicity, liver necrosis and rhabdomyolysis. The simultaneous utilization of statins, mostly simvastatin and nicotinic acid can lead to an increase in rhabdomyolysis or myopathy risks [4].

Precise equipments and techniques are required for the analysis of nicotinic acid in medicines to obtain the correct dosage. Several techniques have been used for nicotinic acid detection, which include ion chromatography (IC), high performance liquid chromatography (HPLC) and voltammetry [2]. The waste produced from HPLC is hazardous since the employed mobile phase has volatile and also the interference of contaminants affects the sample readings [3]. In case of ion chromatography, the main disadvantages is the longer time required to analyzed nicotinic acid sample (17.2 min) [4].

Voltammetry is an analytical method, which is based on the measurement of current as the potential function. This method can be used to detect the peak currents for quantitative and qualitative analysis and can be employed to investigate electron transfer reversibility [5]. In the electroanalysis field, carbon based electrodes widely developed because they present several advantages, such as low background currents, wide potential ranges, low cost, inert nature and are also suitable for different sensors [6]. During voltammetric measurements, cells employ three electrodes *viz.* working, comparison and assistive electrodes. The quality of working electrodes is dependent on two factors: (i) the oxidation-reduction reaction of analytes and (ii) the background current required in the potential range for measurements. A working electrode must have

good electrical conductivity and a wide potential range, and the resulting voltammogram must provide clearly visible reduction or oxidation peak having high current.

Although as an electrode, carbon materials provide good stability, their capacitive value is limited to approximately 60 F/g and that of GO reaches to approximately 244 F/g. GO is a derivative sheet of allotropic carbon having 2630 m^2/g surface area [7] and the thermal conductivity of GO is 5000 W/mK [8]. The conductivity of carbon is 25-470 W/mK for 1000-2000 m^2/g area surface [9]. Graphite was selected as the starting material to produce graphene oxide (GO) since the electrical conductivity of graphite is 3.4×10^3 S m^{-1}, which is better than charcoal of 1.11 S m^{-1} [10]. Studies have reported that GO has a limitation of edge density and with electron transfer, transfer may slow down [11]. Thus, GO requires modification to increase its effectiveness and sensitivity. In this study, GO was modified using a modifier material *viz*. bentonite. The electrode was modified to expedite electron transfer.

EXPERIMENTAL

Graphite powder 300 mesh, zinc powder, potassium permanganate, hydrochloric acid 37% p.a, hydrogen peroxide 30%, sulfuric acid 98% p.a, phosphoric acid 85% p.a, ethanol 96% p.a, potassium chloride, nicotinic acid grade and bentonite were procured from Sigma-Aldrich Co. Equipment that used were glassware, electrolyzing circuit, pH meter, oven, set of voltammetry instrument VA737, XRD, FTIR. Instrumental analysis was analyzed at The State University of Surabaya, Institute Technology of Sepuluh November, and Universitas Airlangga, Indonesia.

Synthesis of graphene oxide: Graphene oxide (GO) was synthesized using the improved Hummer method and characterized through XRD and FTIR. Initially, 1 g of graphite was weighed and placed in a 1000 mL beaker. This 1 g of graphite was treated with 98% H_2SO_4 and 85% H_3PO_4 in the ratio of 9:1. The solution was stirred for 6 h at room temperature by using the VWR IKA VMS-C7 S1 stirrer hotplate. After 6 h, 6 g of $KMnO_4$ (oxidation level regulator) was added to the solution to oxidize graphite. The more $KMnO_4$ employed leads to the higher oxidation levels and an increase in GO crystallinity. Subsequently, the solution again was stirred for 18 h at 50 ºC. After 18 h, 1 mL of 30% H_2O_2 was added and then the solution was again stirred and 400 mL of distilled water was added. Finally, H_2O_2 was added to terminate oxidation. The solution was then deposited and decanted. Subsequently, the precipitate was centrifuged at 4000 rpm and the obtained precipitate was repeatedly washed using distilled water, 1 M HCl and ethanol. Afterwards, the precipitate heated at 70 ºC for 24 h.

Graphite oxide (0.1 g) was homogenized with 100 mL of distilled water in an ultrasonic bath to obtain GO sheets. The sonication of graphite oxide into GO was conducted for 120 min. After sonification, GO was reduced using 1.6 g of Zn metal powder as a reducing agent followed by the addtion of 20 mL of 37% HCl and the resulting mixture was sterilized for 30 min. The precipitate was obtained through repeated reduction reactions by using distilled water to reduce the ethanol concentration. The precipitate was heated for 24 h at 100 ºC for the removal of the air remaining in GO and residual ethanol.

Synthesis of nanobentonite: Nanobentonite was prepared using bentonite as the starting material by employing the sonochemical method. Initially, bentonite was activated by mixing 20 g of bentonite with 50 mL of 2 M sulphuric acid. The mixture was stirred for 6 h by using a magnetic stirrer and then allowed to stand for 24 h. Subsequently, the mixture was filtered and washed using a hot distilled water to separate bentonite and sulphate ions. After the removal of sulphate ions, bentonite was filtered and dried at 100 ºC for 3 h in an oven. Afterwards, dry activated bentonite was mashed and sieved through a 300-mesh sieve. To obtain nanobentonite, 50 mL of 96% ethanol was added to 0.18 g of activated bentonite in a beaker. This mixture was then sonicated for 2 h and subsequently was heated at 60 ºC for 30 min in the oven. Bentonite was heated to at 800 ºC for 4 h in a furnace.

Preparation of graphene oxide-nanobentonite modified electrode: The working electrodes of modified-nanobentonite GO were prepared using a 10 cm long copper wire. Modified nanobentonite-GO electrodes were fabricated by mixing GO: paraffin:nanobentonite with various compositions *viz*. 3:3:4; 3:2:5; 3:4:3 and 3:5:2. A mixture of GO:paraffin:nanobentonite was placed in an insulated (plastic) pipe having a diameter the same as that of a copper wire. The length of GO:paraffin: nanobentonite placed in the insulator pipe was approximately 0.5 cm, and 0.2 to 0.3 cm of copper wire was peeled in order to made it in contact with graphene oxide:paraffin:nanobentonite. By removing the top of the copper wire, the wire was used as the electrode functioning on voltammetry equipment.

RESULTS AND DISCUSSION

FT-IR studies: The chemical properties of graphene oxide (GO) and GO-nanobentonite were studied using FTIR to determine the groups present in the GO and GO-nanobentonite. The peaks appearing at 3444.80, 1621.57 and 1041.51 cm^{-1} corresponding to the hydroxyl (OH), carbonyl (C=O) and epoxy (CO) groups, respectively. The FTIR spectra indicated the formation of C-O and C=C bonds, thereby confirming the GO formation (Fig. 1a). The FTIR spectra of GO-nanobentonite exhibits the peaks at 1624.87, 1018.05, and 790.28 cm^{-1} correspond to the carbonyl (C=O) groups, epoxy (C-O) groups and SiO_2, respectively (Fig. 1b).

XRD studies: The X-ray diffraction (XRD) was used to investigate the nanostructure morphology of nanobentonite and GO obtained after the structural treatment of the analyzed sample [12]. Fig. 2 illustrates the XRD results of GO obtained at the scanning range of 5º-80º. The characteristic peaks appeared at the 2θ of 11.22288º with a distance (d) 7.88014 Å between lattice planes. For nanobentonite, the characteristic peaks appeared at the 2θ of 27.3499º with a distance (d) of 3.26097 Å between lattice planes [12].

Optimum compositions of the electrode: To estimate the composition of modified-nanobentonite GO, various ratio of GO:paraffin:nanobentonite electrodes were analyzed in the 10 mL of the 50 ppm standard solution of nicotinic acid which was mixed with 10 mL of KCl solution having a 50-100 times

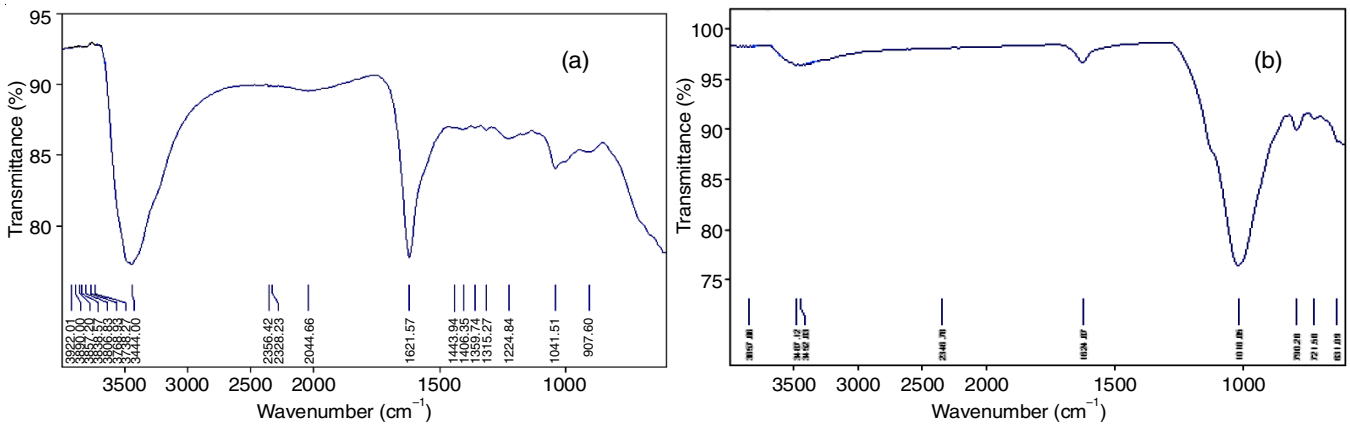

Fig. 1. FTIR spectra of (a) graphene oxide and (b) graphene oxide-nano bentonite

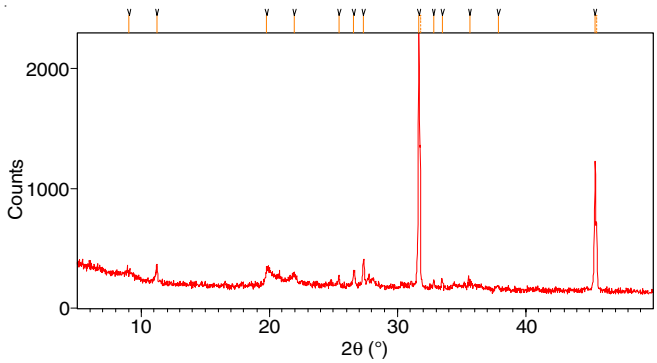

Fig. 2. XRD spectrum of graphene oxide-nanobentonite

higher concentration than the standard concentration. Subsequently, 5 mL of pH 5 buffer citrate was used to measure the current at a potential from –2 V to 1 V.

The composition of GO:paraffin:nanobentonite electrodes strongly influences the cyclic voltammogram obtained in the 50 ppm nicotinic acid. The cathodic and anodic peaks of each comparison are considerably different. Fig. 3 presents the cathodic and anodic current peaks obtained from different ratio of the electrode composition. A difference was evidenced in peak currents obtained for each ratio of GO:paraffin:nanobentonite electrodes. The better was the electrode conductivity, the higher was the peak of the maximum current generated because of easy transfer of electrons for reduction and oxidation reactions [13]. Hence, the graphene oxide:paraffin:nanobentonite electrode having the 3:3:4 ratio is the optimal (Table-1).

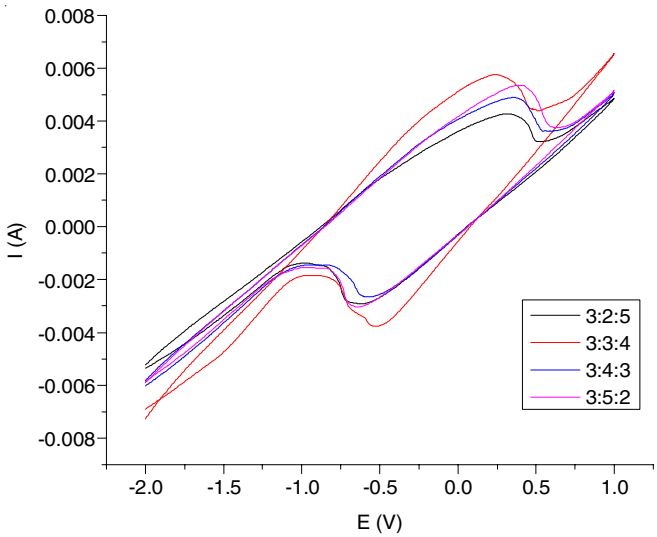

Fig. 3. Voltammogram of nicotinic acid solution using prepared electrode with different compositions

TABLE-1
MAXIMUM CURRENT PEAK OF NICOTINIC ACID SOLUTION AT DIFFERENT GRAPHENE OXIDE:PARAFFIN: NANOBENTONITE COMPOSITION RATIO

Composition of electrode (graphene oxide:paraffin: nano bentonite)	Ip_c	Ip_a
3:2:5	-0.00289	0.00426
3:3:4	-0.00375	0.00574
3:4:3	-0.00265	0.00488
3:5:2	-0.00302	0.00535

Effect of pH: pH influences the reaction during analyte voltammetric measurements. The oxidation of nicotinic acid on the electrode surface that involved hydrogen ions can lead to a change in solution pH. The optimum pH is the state in which an analyte gives the highest reduction and oxidation currents on the voltammetry instrument. The modified nanobentonite GO working electrode having the composition of 3:3:4 was used for the working electrode.

The pH varied specifically in the range of 2-5 by using the citrate buffer in 50 ppm nicotinic acid solution. Table-2 presents the peak cathodic and anodic currents acquired from the pH variations [14]. Fig. 4 illustrates the voltammogram of the GO:paraffin:nanobentonite electrode employed in nicotinic acid solution, which shows that pH 5 provides the highest peak among the other studied pH (2, 3 and 4).

TABLE-2
MAXIMUM CURRENT PEAK OF NICOTINIC ACID SOLUTION USING PREPARED ELECTRODE AT DIFFERENT pHs

pH	Ip_c	Ip_a
2	-0.00290	0.00360
3	-0.00326	0.00283
4	-0.00262	0.00263
5	-0.00337	0.00608

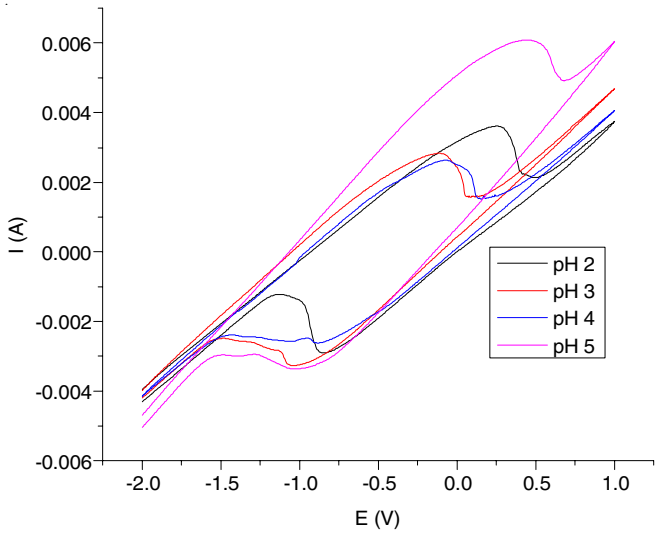

Fig. 4. Voltammogram of nicotinic acid solution using prepared electrode at different pHs

Effect of deposition time: The deposition time reduces the detection limit and increases the sensitivity in the preconcentration stage. The time of nicotinic acid deposition affects the stability of the species produced on the electrode surface. The deposition time can investigated by comparing the voltammogram obtained from 50 ppm nicotinic acid solution in the buffer solution of pH 5 at various deposition times. The deposition time influences the voltammogram obtained however, this effect is insignificant because the voltammogram remains almost the same (Fig. 5). Table-3 presents the cathodic currents and anodic peaks acquired from changes in the deposition time. The deposition time influences the highest peak current produced but does not cause the substantial difference. The longer is the deposition time, the higher is the maximum peak current. The longer the deposition time is provided when preconcentration enhances species stability. The optimal deposition time determined during the analysis of the nicotinic acid samples in the citrate buffer of pH 5 with GO:paraffin:nanobentonite

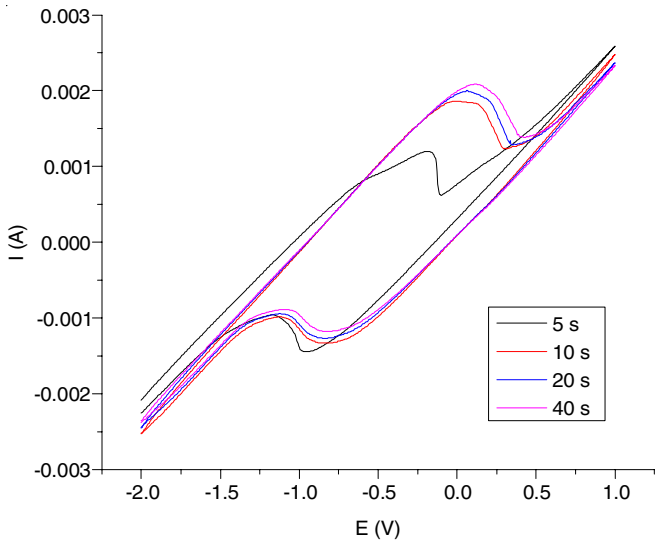

Fig. 5. Voltammogram of nicotinic acid solution using prepared electrode at different deposition time

TABLE-3
MAXIMUM CURRENT PEAK OF NICOTINIC ACID SOLUTION USING PREPARED ELECTRODE AT DIFFERENT DEPOSITION TIME

Deposition time (s)	Ip_c	Ip_a
5	-0.00144	0.00119
10	-0.00133	0.00185
20	-0.00126	0.00199
40	-0.00118	0.00208

with the optimal composition of 3:3:4 is 5 s, since the settling time is not too long but produces the highest and lowest cathodic and the anodic current peak, respectively, compared with other settling times.

Effect of scan rate: During the voltammetry analysis, the scan rate affected the peak current, which can be achieved by comparing the voltammogram obtained using the 50 ppm nicotinic acid solution in the buffered citrate solution of pH 5 at different scan rates. The scan rate affects the produced voltammogram; however, the change is insignificant since the voltammogram remains almost the same (Fig. 6). Table-4 presents the cathodic and anodic current peaks acquired from changes in the scan rate. The scan rate influences the highest peak current obtained; however, it does not significantly change it. The higher is the scan rate, the higher is the generated peak current. This phenomenon occurred because of faster oxidation, higher scanning rate and higher reduction reaction rates to increase the peak current height. The optimal scanning rate of 100 mV/s was measured during the analysis of nicotinic acid samples in a citrate buffer of pH 5 with nanobentonite-modified GO

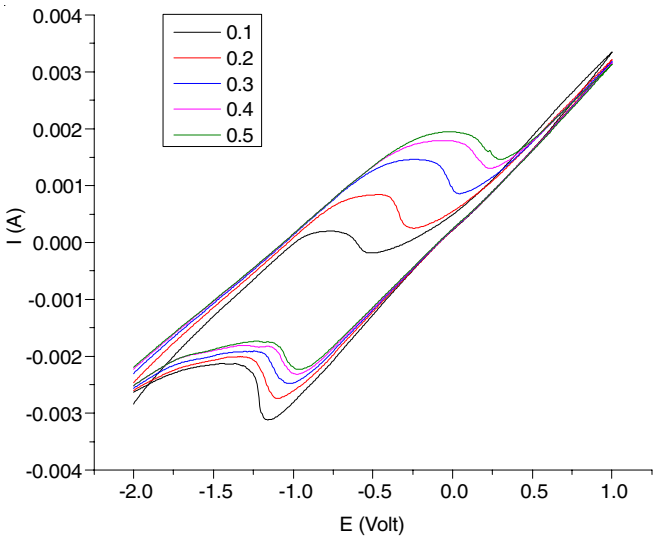

Fig. 6. Voltammogram of nicotinic acid solution using prepared electrode at pH 5 and deposition time 5 s at different scan rate

TABLE-4
MAXIMUM CURRENT PEAK OF NICOTINIC ACID SOLUTION AT DIFFERENT SCAN RATE

Scan rate (mV/s^{-1})	Ip_c	Ip_a
100	-0.00272	0.000190
200	-0.00310	0.000830
300	-0.00247	0.001420
400	-0.00230	0.001750
500	-0.00310	0.000197

electrodes having the optimal composition of 3:3:4. The scanning rate measurement did not require considerable time; however, it produced the highest and lowest cathodic and peak current, respectively, compared with other scanning rates.

Determination of nicotinic acid using working electrode: After the optimal variable was obtained from the voltammetric analysis of nicotinic acid solution, nicotinic acid was analyzed under optimum conditions. This analysis was conducted using nanobentonite-modified GO electrode with the composition of 3:3:4 and deposition time of 5 s at the citrate buffer and scan rate of pH 5 and 100 mV/s, respectively. The analysis was commenced by measuring the 10, 20, 30 ppm standard solutions of nicotinic acid. The higher is the nicotinic acid concentration, the higher is the maximum current generated (Fig. 7). The maximum peak current increased at the cathodic peak current. Table-5 presents the produced maximum peak current. The relationship between the maximum peak current and concentration led to the production of a linear curve that followed the equation: $y = ax + b$. Due to the significant differences, the cathodic peak current values were used to create the linear curve. Acceding to linear curves, the obtained regression is 0.99959, indicating that the curve is a linear. The linear equation obtained is as follows: $Y = -7.90285 \times 10^{-6} - 5.96004 \times 10^{-4}$.

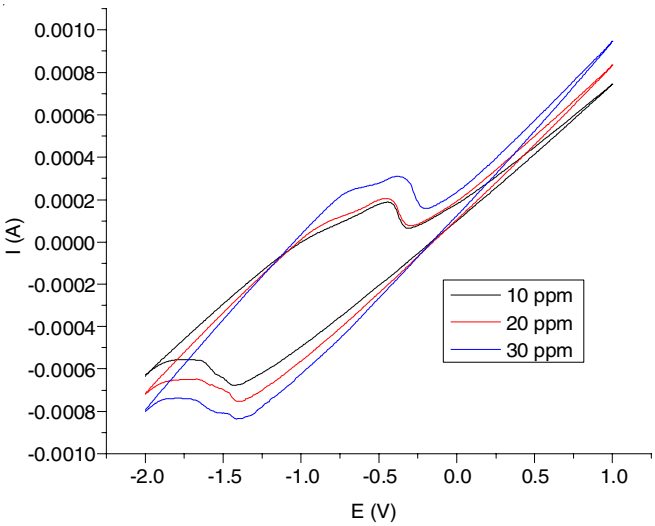

Fig. 7. Voltammogram of nicotinic acid standard solution using graphene oxide: paraffin:nano bentonite 3:3:4 electrode under optimum conditions

TABLE-5
MAXIMUM CURRENT PEAK OF NICOTINIC ACID STANDARD SOLUTION AT OPTIMUM CONDITIONS

Concentration (ppm)	Ip_c	Ip_a
10	-0.00067	0.00018
20	-0.00075	0.00020
30	-0.00083	0.00030

This linear equation was employed to evaluate the nicotinic acid concentration to determine percentage recovery. Table-6 presents the voltammetry analysis results obtained in the nicotinic acid solution. The average recovery value of the nicotinic acid by using the cyclic voltammetry was found to be 96.16% (Table-6). This result showed that GO:paraffin: nanobentonite electrode with the 3:3:4 ratio under the optimal analysis conditions are good for their application in nicotinic acid studies through cyclic voltammetry.

TABLE-6
DETERMINATION OF NICOTINIC ACID STANDARD SOLUTION AT OPTIMUM CONDITIONS

Concentration (ppm)	Ip_c (A)	Experimental conc. (ppm)	Recovery (%)
10	-0.00067	9.36320	93.63204
30	-0.00083	29.60907	98.69688

Conclusion

The FTIR spectra of the synthesized GO and GO-nanobentonite confirmed the formation of the C-O groups. The XRD spectra of GO presented a diffraction peak at 2θ of 11.22º. The GO:paraffin: nano-bentonite electrode with the composition ratio of 3:3:4 produces the optimal voltammogram. The optimal conditions for the analysis of nicotinic acid by using graphene oxide:paraffin:n anobentonite are as follows: deposition time of 5 s, the citrate buffer of pH 5, deposition rate of 5 s and deposition rate is 5 scans 100 mV/s. The nanobentonite-modified GO electrodes generate linear curves in the nicotinic acid solution with a linearity of 0.99959. The cyclic voltammetry analysis conducted using nanobentonite-modified GO under optimal conditions leads to a recovery of 96.16%.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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