



Graphene Oxide-Paraffin as Working Electrode for Cyclic Voltammetry Analysis for Cadmium(II)

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In this work, the composition ratio of graphene oxide-paraffin as the best working electrode for analysis of cadmium solution at optimum conditions using cyclic voltammetry is reported. Graphene oxide from graphite was synthesized and characterized using the improved Hummer method. Testing the composition and condition of graphene oxide:paraffin electrode is best done by manipulating the graphene oxide:paraffin ratio, pH, deposition time and scan rate. The composition with a ratio of 8:2 % of graphene oxide:paraffin electrode produces the best of voltammogram. Recovery analysis is also performed with the results of linear curves in cadmium(II) solution with linearity 0.98992. Cyclic voltammetry analysis using graphene oxide:paraffin electrodes at optimum pH resulted an average recovery of 97.64 %.

Keywords: Graphene oxide, Cyclic voltammetry, Cadmium, Paraffin.

INTRODUCTION

Some heavy metal elements, including arsenic, lead, mercury, cadmium and chromium are included in the top-20 hazardous and toxic materials [1]. Heavy metals can cause harmful effects on the environment even present in very small amounts, so it is necessary to detect them effectively and accurately. In practice, it is difficult to be able to detect heavy metal elements at the ppb level, so techniques and equipment are needed to monitor the levels of toxic heavy metals in the water [2]. Therefore, an alternative method is needed that can overcome the limitations of the two methods [3]. Voltammetry was chosen as an alternative method of analysis because it has high sensitivity or low detection limits to concentrations reach 10^{-10} M [4].

Cyclic voltammetry is one of the voltammetry methods that is widely used compared to other voltammetry techniques in heavy metal analysis because it has good analytical sensitivity so that metals with very small concentrations can be analyzed. In addition, cyclic voltammetry techniques are reversible so they do not change the concentration of the sample solution and the electrode can be used repeatedly. In this method, metal ions are reduced on the surface of the electrode to form

amalgams. The amount of metal accumulated is directly proportional to the given deposition time [5].

The performance of the voltammetry method is strongly influenced by the working electrode material. Mercury electrodes also have a limited range of potential anodes, so that they cannot be used for the measurement of oxidized compounds. Alternative electrodes commonly used are solid electrodes, which are modified with complexing compounds [6]. Solid electrodes have a wider range of potential anodes. From various solid materials that can be used as working electrodes, the most commonly used are carbon, platinum and gold. Carbon-based electrodes are now highly developed in the field of electroanalysis compared to precious metals because they have several advantages, namely a wide potential range, low background current, low-cost, inert and suitable for various sensors [7].

Several combinations of materials such as graphene oxide are used to improve electrode performance. Graphene oxide is expected to help load storage using an electric double layer capacitance. The advantages of graphene oxide properties towards electricity are expected to be used or used as good electrodes [8]. Graphene oxide can be synthesized from graphite with the Improved Hummer method then characterization is carried out to ensure that graphene oxide is formed as desired.

As a graphene oxide electrode requires a binder so as not to decompose when put in solution. Paraffin is selected in the manufacture of electrodes as graphene oxide binders, besides that graphene oxide is non-polar so it is not soluble in water-based (aqueous) solutions. Comparison of the composition of graphene oxide with paraffin produces a different voltammogram.

EXPERIMENTAL

Zinc powder, potassium permanganate, hydrochloric acid 37 % p.a, hydrogen peroxide 30 %, sulfuric acid 96 % v/v p.a, phosphate acid 85 % v/v p.a, demineralized water, ethanol 96 % v/v p.a, disodium hydrogen phosphate p.a (Na_2HPO_4), sodium dihydrogen phosphate dehydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$), potassium chloride were of analytical grades (Merck), $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ crystal, graphite and paraffin oil (Merck).

Preparation of graphene oxide: Making graphene from graphite using modified improved graphene-oxide method. The initial process of weighing 300 mesh graphite as much as 1 g and put into a beaker. The weighed graphite is 97 % (v/v) and 85 % pa phosphoric acid (v/v) with 9:1 ratio of 100 % sulfuric acid solvent. The solution is stirred with a magnetic stirrer at room temperature for 6 h. Then add 6 g of potassium permanganate. After that the solution was stirred again with a magnetic stirrer for 18 h at 50 °C. The solution was originally greenish black turned into a thick dark brown colour. Then add 1 mL of 30 % hydrogen peroxide. Next, the solution is stirred again and 400 mL of demineralized water is added. The solution is precipitated and decanted. The precipitate is then centrifuged at 4000 rpm. The precipitate was washed repeatedly using demineralized water, 1 M HCl and ethanol pa to reduce the concentration of acid, bind existing metal ions and dehydrate the water in graphite oxide. Then the sediment is ovenized at 70 °C for 24 h.

The formed graphite oxide was taken as much as 50 mg and homogenized with 50 mL of demineralized water with ultrasonic bath instrument into graphene oxide sheet. The sonication process of graphite oxide into graphene oxide was carried out for 120 min. The graphene oxide is further reduced by a Zn metal powder reducing agent. Zinc metal powder was weighed as much as 0.8 g. Graphene oxide solution is put into 10 mL of 37 % HCl as an acid and stirred atmosphere maker. Then put Zn metal powder, which has been weighed and stirred for 30 min. Then again add 10 mL HCl 37 % pa into the solution. The precipitate phase formed after the reduction process is washed repeatedly with demineralized water to reduce acid concentration and ethanol pa to dehydrate the remaining water. Then the sediment was kept in an oven at 100 °C for 24 h.

Characterization: The resulting graphene oxide is characterized to ensure that the graphene oxide is formed as desired. Graphene oxide carried out two types of characterization including physical and chemical characterization. Physical characterization using particle size analyzer to determine the particle size, using XRD to determine its crystallinity and chemical characterization using FTIR to determine its functional group. All the electrochemical measurements were performed using a 797 VA Computrace. A three-electrode cell was used at 25 ± 1 °C. An Ag/AgCl (KCl, Sat.) electrode, a platinum wire and

a carbon paste modified by graphene oxide electrodes were used as reference, auxiliary and working electrodes respectively. Fisherbrand accumet AE150 pH Benchtop Meter was used for pH measurements.

Preparation of graphene oxide:paraffin electrode: The manufacture of graphene oxide paste electrodes is carried out with a single 10 cm copper cable. Carbon paste is made by mixing graphene oxide and paraffin at different comparisons, graphene oxide:paraffin 5:5, 6:4, 7:3 and 8:2. The graphene oxide paste mixture is then inserted in an insulator (plastic) pipe with the same diameter as a single copper cable. The length of carbon paste inserted in the insulator pipe is about 0.5 cm, copper wire is peeled around 0.2-0.3 cm to get contact on the carbon paste. By peeling the top of the copper wire cable it can be used as a working electrode on a voltammetric instrument.

RESULTS AND DISCUSSION

Fourier-transform infrared spectroscopy (FTIR): Chemical characterization is needed to determine the functional groups that are formed, change or eliminated from the process of making or synthesizing graphene oxide. In this study FTIR was used for the functional group analysis of the starting material (graphite) and synthesis results (graphene oxide). The FTIR spectrum of graphite Fig. 1(a) and graphene oxide Fig. 1(b) resulting from the synthesis shows significant differences. At first glance the spectrum Fig. 1(a) is the spectrum produced from graphite. It can be seen that in spectrum Fig. 1(a) there are almost no peaks, which show that there is a functional group that represents the structure of graphite, which has only carbon atoms. A significant change occurred in spectrum Fig. 1(b) at a wave number of $\sim 3447 \text{ cm}^{-1}$ indicating the formation of a phenolic -OH group after the synthesis process. In addition, it can be seen in spectrum Fig. 1(b) there is also a peak in the wave number $\sim 1632 \text{ cm}^{-1}$ which indicates that the previous graphite changes without the double bond $\text{C}=\text{C}$ formed in graphene oxide due to the release of bonds between layers of graphite. Another functional group that shows graphite Fig. 1(a) to graphene oxide Fig. 1(b) oxidation process is also confirmed by the presence of CO (carboxy) at wave numbers $\sim 1383 \text{ cm}^{-1}$ and C-O in $1300\text{-}1000 \text{ cm}^{-1}$ region. Fig. 1(b) spectrum shows the formation of $\text{C}=\text{C}$ and CO bonds.

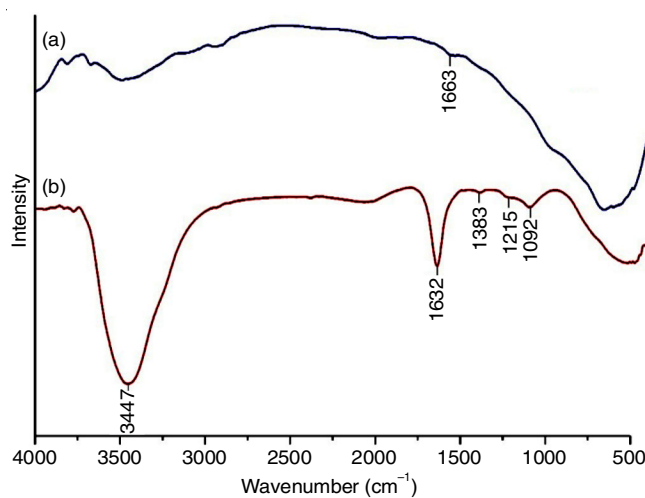


Fig. 1. FTIR spectra of (a) graphite and (b) graphene oxide

X-ray diffraction (XRD): The XRD of graphite and graphene oxide is done on scan range 5° - 80° and the wavelength of 1.540598 \AA . As a reference for the data published by JCPDS through the International Center for Diffraction Data (ICDD), 2013, it was reported that on the graphene oxide there were 2 θ diffraction peaks between ~ 7 - 12° and a widening peak around $\sim 19^{\circ}$ which represented components due to the chemical process of graphite to make graphene oxide [9]. At the same source it is also shown that the 2 θ diffraction peaks in graphite are around $\sim 26^{\circ}$. X-ray diffraction results in this study is shown in Fig. 2. Seen in Fig. 2 that in graphite (red spectrum) there are 2 θ diffraction peaks at 26.44° which correspond to the reference source of ICDD. Similarly in the spectrum produced by graphene oxide (blue spectrum) there are 2 θ diffraction peaks at 11.53° which is also in line with the reference. So that it can be confirmed through XRD analysis that the starting material in the form of graphite is formed graphene oxide based on the position of the diffraction peaks of the 2 θ produced.

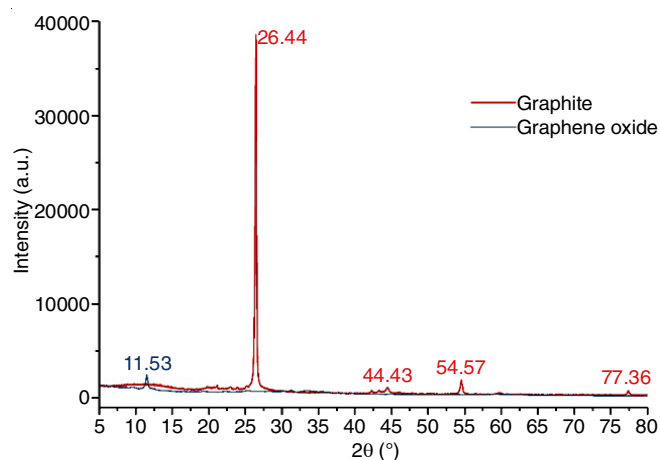


Fig. 2. XRD spectra of graphite and graphene oxide

Particle size analysis: The particle size and distribution of graphite and graphene oxide are carried out through particle size analyzer. Particle size is possible to change from graphite to graphene oxide due to changes in chemical structure. So it is necessary to analyze the graphite and graphene oxide so that the potential changes can be known. Data that can be collected from the PSA instrument are presented in Table-1. As seen in Table-1 that in all distributions 10, 50 and 90 % showed that there was a decrease in the particle diameter from graphite to graphene oxide. A decrease in diameter means that the graphene oxide particle size is smaller than the graphite. This is because there are structural changes that involve breaking the bonds between layers from one graphite particle to several graphene oxide particles. So the particle size in all distributions has a breakdown or decrease.

TABLE-1
PARTICLE DIAMETER OF GRAPHITE AND GRAPHENE OXIDE FROM PSA

Distribution (%)	Particle diameter (μm)	
	Graphite	Graphene oxide
10	28.00	1.50
50	101.26	29.96
90	189.85	117.73

Analysis of condition of cadmium(II) using graphene oxide:paraffin electrode: To determine the best graphene oxide paste composition, graphene oxide:paraffin electrode with various comparisons was included in 10 mL of 10 ppm cadmium(II) standard solution mixed with 10 mL of KCl solution with a concentration of 50-100 times greater than the standard concentration and then measured the current potential -2 V to 1 V. The resulting cyclic voltammogram results are shown in Fig. 3. It is clearly seen that the electrode composition between graphene oxide:paraffin greatly influences the cyclic voltammogram produced in a 10 ppm cadmium(II) solution. In the ratio of 5:5 and 6:4 there is only a peak of cathodic current (I_{pc}) whereas in the ratio of 7:3 and 8:2 it produces a better cyclic voltammogram with the presence of both anodic current peaks (I_{pa}) and cathodic current peaks (I_{pc}). Both the anodic and cathodic current peaks of each comparison also have significant differences with each other. The peak of anodic and cathodic currents resulting from various electrode composition comparisons as presented in Table-2. A clear difference is shown at the peak of the current produced in each comparison of graphene oxide electrode composition:paraffin. The more graphene oxide used, the higher the peak current as shown in Fig. 3 and the values shown in Table-2. This is due to the nature of graphene oxide which tends to be conductor and paraffin which tend to be insulator in accordance with the theory mentioned by Huang *et al.* [10]. The better the conductivity of an electrode, the greater the maximum current peak generated due to the ease of electron transfer for the process of reduction and oxidation reactions. A good electrode is that which produces a high and clear peak current, so that the graphene oxide:paraffin electrode with a ratio of 8:2 is the best electrode ratio.

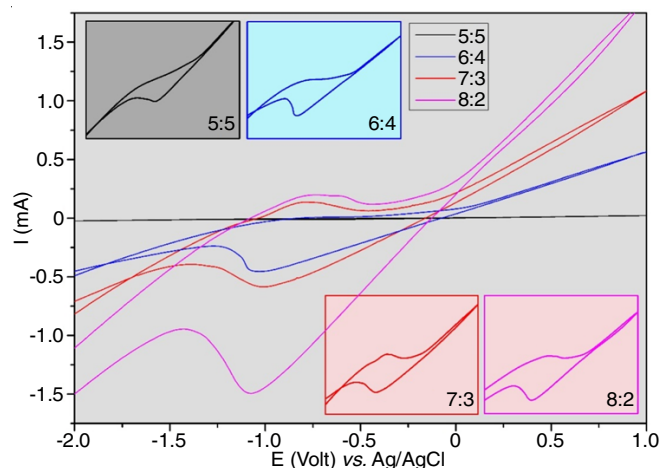


Fig. 3. Voltammogram of cadmium(II) solution 10 ppm using graphene oxide:paraffin electrode with different composition

TABLE-2
MAXIMUM CURRENT PEAK OF CADMIUM(II) SOLUTION 10 ppm AT DIFFERENT GRAPHENE OXIDE:PARAFFIN COMPOSITION RATIO

Composition of electrode (graphene oxide:paraffin)	Maximum current peak (mA)	
	I_{pa}	I_{pc}
5:5	-	-0.01100
6:4	-	-0.58535
7:3	0.01303	-0.45403
8:2	0.19893	-1.49280

Nuryono and Suyanta [11] explained that cadmium has a distribution of species that change depending on the pH of the solution, including Cd^{2+} , CdOH^+ , $\text{Cd}(\text{OH})_2$, $\text{Cd}(\text{OH})_3^-$ and $\text{Cd}(\text{OH})_4^{2-}$. The distribution of metal ions of cadmium(II) in pH 4-8 range so that pH variations are carried out in such a range so that the optimum pH is found [11]. This study uses a more specific pH variation at pH 5; 5.5; 6; 6.5; 7; 7.5 and 8 using a phosphate buffer in a cadmium solution with a concentration of 10 ppm. The resulting voltammogram using the graphene oxide:paraffin 8:2 electrode ratio is presented is shown in Fig. 4. As seen in Fig. 4, the pH affects the voltammogram produced. The peak of anodic and cathodic currents each comparison also has differences with each other. The peak of anodic and cathodic currents resulting from variations in pH as presented in Table-3. Based on Table-3, although the pH affects the maximum peak current obtained but not very different, it is very significant. The highest maximum current peak can still be seen at pH 6.5 (a negative sign indicates the direction of the current). This shows that the process of oxidation reaction and reduction of cadmium(II) at pH 6.5 can run optimally due to the maximum distribution of cadmium(II) species. So that it can facilitate the oxidation reaction process and the reduction that occurs at the surface of the electrode.

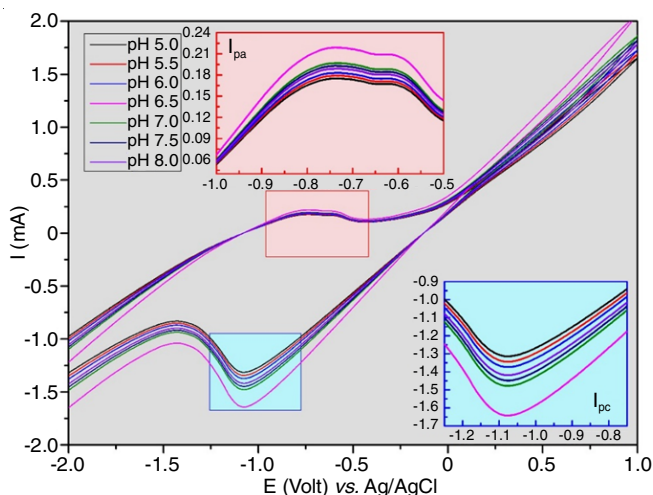


Fig. 4. Voltammogram of cadmium(II) solution 10 ppm using graphene oxide:paraffin electrode 8:2 with different pH

TABLE-3

MAXIMUM CURRENT PEAK OF CADMIUM(II) SOLUTION 10 ppm AT BEST GRAPHENE OXIDE:PARAFFIN COMPOSITION RATIO WITH DIFFERENT pH

pH	Maximum current peak (mA)	
	I_{pa}	I_{pc}
5.0	0.175058	-1.313664
5.5	0.179037	-1.343520
6.0	0.183016	-1.373376
6.5	0.218823	-1.642080
7.0	0.196941	-1.477872
7.5	0.192962	-1.448016
8.0	0.188983	-1.418160

Deposition time affects the deposition (pre-concentration) stage. Deposition time serves to increase sensitivity and reduce detection limits during the pre-concentration stage [7]. The

duration of deposition of cadmium(II) will affect the stability of species formed on the surface of the electrode. To study the effect of deposition time can be done by comparing the voltammogram of the measurement results of 10 ppm cadmium(II) solution in phosphate buffer solution pH 6.5 with the deposition time varied. The measured voltammogram is shown in Fig. 5 and measurement data is shown in Table-4. As seen in Fig. 5 the deposition time affects the voltammogram produced but not too significant because the voltammogram is almost coincident. The peak of the anodic and cathodic currents of each scan rate variation also has differences with each other. The peak of anodic and cathodic currents resulting from variations in deposition time are presented in Table-4. Based on Table-4, even though the deposition time affects the maximum peak current obtained but not very significantly different. The highest maximum current peak can still be seen at 80 s deposition time (negative sign indicates the direction of current). The longer the deposition time the maximum peak current produced is higher. This shows that the longer the deposition time given when preconcentration will increase the stability of the species, which is collided on the surface of the electrode.

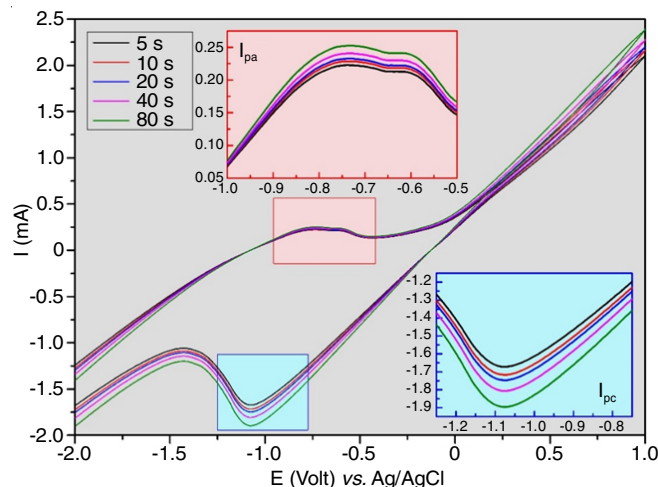


Fig. 5. Voltammogram of cadmium(II) solution 10 ppm using graphene oxide:paraffin 8:2 electrode at pH 6.5 with different deposition time

TABLE-4

MAXIMUM CURRENT PEAK OF CADMIUM(II) SOLUTION 10 ppm AT BEST GRAPHENE OXIDE:PARAFFIN COMPOSITION RATIO AND pH WITH DIFFERENT DEPOSITION TIME

Deposition time (s)	Maximum current peak (mA)	
	I_{pa}	I_{pc}
5	0.222802	-1.671936
10	0.228770	-1.716720
20	0.232748	-1.746576
40	0.240705	-1.806288
80	0.252641	-1.895856

At the time of high voltammetry analysis, the peak current is also affected by scan rate. To study the effect of scan rate, it can be done by comparing the voltammogram measured by a 10 ppm cadmium(II) solution in a phosphate buffer solution pH 6.5 with the scan rate varied. The measured voltammogram shown in Fig. 6 and the measurement data are shown in Table-5. As shown in Fig. 6, the scan rate has an effect on the voltammogram produced but not too significant because the voltammo-

gram is almost coincident. The peak of the anodic and cathodic currents of each scan rate variation also has differences with each other. The peak of anodic and cathodic currents resulting from variations in scan rates as presented in Table-5. Based on Table-5, even though the scan rate affects the maximum peak current obtained but not significantly different. The highest maximum current peak can still be seen at the scan rate of 50 mV s^{-1} (negative sign indicates the direction of current). The faster the rate, the higher peak current produced. This is caused by the higher the scan rate, the speed of the oxidation reaction and the reduction is faster, so that the height of the peak current increases [5]. The current is proportional to the speed of the reaction that occurs on the surface of the electrode. The reaction takes place on the surface of the electrode in response to potential.

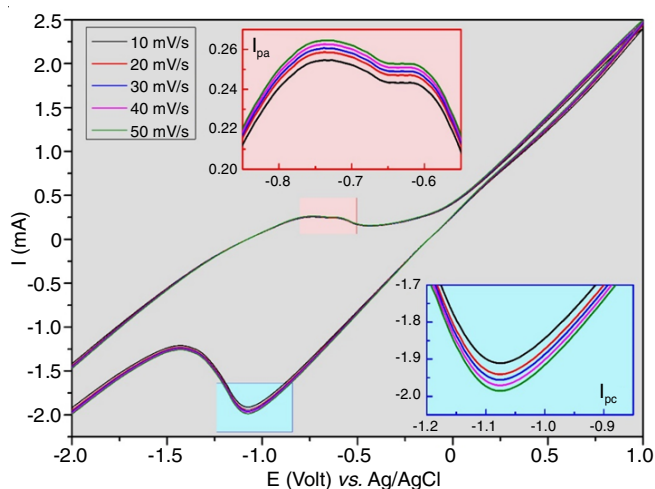


Fig. 6. Voltammogram of cadmium(II) solution 10 ppm using graphene oxide:paraffin 8:2 electrode at pH 6.5 and deposition time 80 s with different scan rate

Scan rate (mV s^{-1})	Maximum current peak (mA)	
	I_{pa}	I_{pc}
10	0.254630	-1.910784
20	0.258609	-1.940640
30	0.260598	-1.955568
40	0.262588	-1.970496
50	0.264577	-1.985424

Recovery analysis of cadmium(II) using graphene oxide:paraffin electrode: After obtaining the optimum variable in the voltammetry analysis of cadmium(II) solution, the cadmium(II) metal analysis is performed on the optimum conditions. The analysis was performed using a graphene oxide:paraffin 8:2 electrode ratio, 80 seconds deposition time, at pH 6.5 and a scan rate of 50 mV s^{-1} . The analysis begins by measuring the standard solution of cadmium(II) 5 ppm, 10 ppm, 15 ppm, 20 ppm and 25 ppm. The resulting voltammogram is shown in Fig. 7. As shown in Fig. 7, the higher the concentration of cadmium(II) solution, the higher the maximum current produced. The maximum peak current increase is clearly seen at the peak of the cathodic current. The value of

the maximum peak current generated is presented in Table-6. The relationship between the maximum current peak with concentration will produce a linear curve with the equation $y = ax + b$. Because of the significant differences, the peak data of cathodic currents is used to form a linear curve. The resulting curve is like in Fig. 8. Based on the linear curve, regression is 0.98992 which shows that the curve is good (close to 1). The linear equation obtained is $y = -0.13316x - 0.32244$. This linear equation can be used to determine the concentration of cadmium(II) solution to determine % recovery. The results of voltammetry analysis on cadmium(II) solution in Table-7 were obtained. Based on Table-7 an average value of % recovery of Cd(II) data using a cyclic voltammetry of 97.64 %. This shows that the graphene oxide:paraffin electrode with a ratio of 8:2 with optimum analysis conditions is a good electrode to be used as a cadmium(II) metal analysis using cyclic voltammetry.

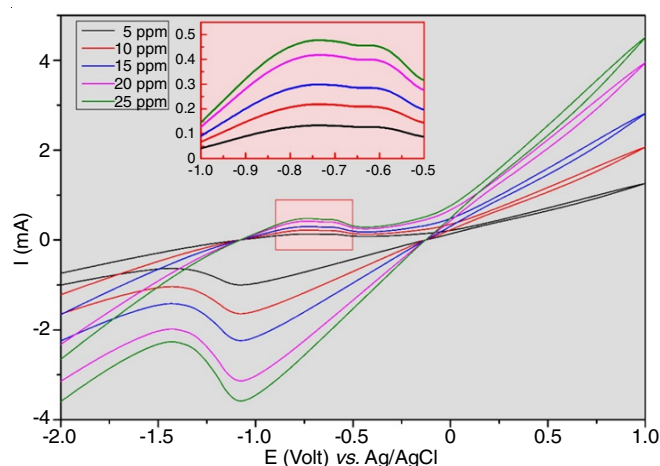


Fig. 7. Voltammogram of cadmium(II) standard solution using graphene oxide:paraffin 8:2 electrode in optimum condition

Concentration (ppm)	Maximum current peak (mA)	
	I_{pa}	I_{pc}
5	0.133283	-1.000176
10	0.218823	-1.642080
15	0.298395	-2.239200
20	0.417753	-3.134880
25	0.477432	-3.582720

Theoretical conc. (ppm)	I_{pc} (mA)	Experimental conc. (ppm)	Recovery (%)
15	-2.263270	14.571096	97.14
20	-2.919860	19.500450	97.50
25	-3.594640	24.566370	98.27

Conclusion

Graphene oxide synthesis characterization results show that the results are in accordance with the reference data

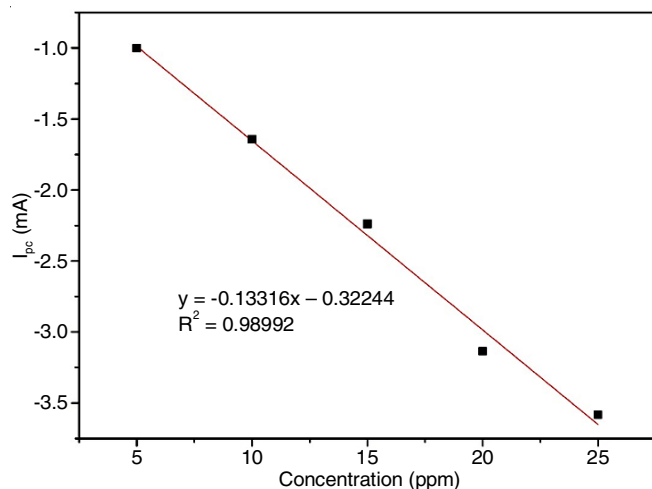


Fig. 8. Linear curve between I_{pc} and concentration of cadmium(II) standard solution in cyclic voltammetry analysis

using the FTIR spectrum which confirms the formation of CO groups, XRD graphene oxide spectra which have 2θ diffraction peaks at 11.53° and particle size analysis results indicate a decrease in particle size. The composition of the graphene oxide:paraffin electrode that produces the best voltammogram is the composition with a ratio of 8:2. The optimum condition for cadmium(II) analysis using graphene oxide:paraffin electrodes is at pH 6.5; 80 s deposition time and 50 mV s^{-1} scan rate. Graphene oxide:paraffin electrodes produce linear curves in cadmium(II) solution with linearity of 0.98992. Cyclic voltammetry analysis using graphene oxide:paraffin elec-

trodes at optimum conditions resulted in an average recovery of 97.64 %.

CONFLICT OF INTEREST

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

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