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Synthesis of graphene oxide electrode for lead analysis in enamel paint by cyclic voltammetry

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Abstract
In this study, graphene oxide was synthesized using the Improved Graphene Oxide (IGO) method to be used as an work electrode in lead analysis by cyclic voltammetry. Graphene oxide used due to its good electron conductivity and transportation properties. Graphene oxide has a higher sensitivity than carbon paste. Lead analysis with graphene oxide is influenced by several factors, namely pH, deposition time and scan rate. The 8 : 2 ratio is known as the best composition of the graphene oxide electrode : paraffin. Lead analysis with graphene oxide electrodes reaches optimum condition at pH 5, optimum deposition time at 5 seconds and a scan rate of 100 mV/s. Graphene oxide electrode has a limit detection up to 0.733 ppm or 0.0048 mM and 99.662% recovery data. These results indicate that the electrode has good selectivity, sensitivity, and effectiveness.
Keywords*: Graphene oxide, cyclic voltammetry, lead metal*

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I. Introduction

Lead (PB) is one of the heavy metals that have high toxicity that adversely affects the soft tissues and organs of the human body. The adverse effects are kidney, lung and brain cancer. This heavy metal is also dangerous if it joins the other carcinogens.[1] The sources of Pb exposure include mining, smelting, gasoline-containing Pb, and Pb in paints.[2] Lead in paint known as the main source of lead exposure that mainly affects children.[3] Lead exposure is more harmful to children than adults, and the effect on health is generally irreversible and can have a lifetime impact.[4] Many industrialized countries have imposed laws, regulations or requiring standards that prohibit the manufacturing, import or use of lead in paints for interiors or exteriors homes, schools and commercial buildings. The standard limit that many countries have for lead in paint is at a range of 90 to 600 ppm for total lead (dry weight).[5] So far, conventional methods used for the determination of lead levels using atomic absorption spectroscopy (AAS)[6] and inductively coupled plasma mass spectrometry (ICPMS) .[7]

Analytical techniques with low detection limits are useful for determining the lead rate in a sample that have small amounts of number up to 600 ppm.[8] Cyclic voltammetry as one voltammetry technique has been widely used to determine the electrochemical properties present in metal material.[9] Voltammetry is one of the preferred techniques due to its high level of sensitivity, ease, and environment-friendly. The voltammetry instrument has 3 electrodes namely auxiliary electrode, working electrode, and reference electrode. The working electrode is where the analytes react. The reaction is in the form of reduction and oxidation reactions. Electrodes in the form of solids are more widely used because they are easier to use and have a wide range of anode than liquid electrodes such as DMG. Another advantage is the working electrode properties in voltammetry are easy to develop with simple modifications in material or surface of the electrodes to achieve a better selectivity and sensitivity.[10] One of the commonly used working electrodes is carbon paste.[11]

The Carbon pasta electrode is a low cost, has a renewable electrode surface, is easy to modify and used in electroanalytical and electrocatalytic applications.[12] Generally, the carbon paste electrode is composed of powdered graphite, conductors, and binders such as silicon and mineral oils, which do not affect the current. To enhance the conductivity properties of this electrode can be done by synthesizing graphite (allotropes of carbon) into graphene oxide (GO). [13]

GO is a new form of graphite that has been synthesized, have multilayer oxidized due to chemical reactions involving the use of oxidizing agents, potassium permanganate (KMnO4).[14] GO as a derivative product of graphite has very broad benefits in its application. One of the applications related to this research is the use of GO as a working electrode.[15] GO has a conductivity value of 5000W/mK[16] with a surface area of 2630 m2/g .[17]

Graphene oxide obtained through the synthesis method has powder form. When used as a working electrode should be added adhesive material to avoid easy release. Paraffin is considered to have a suitable trait

as an adhesive material for GO. It has a good composite mixture due to its low vapor pressure, nucleation behavior, and low cost.[18]

In this research, the GO electrode showed a good lead reduction peak response and showed a good detection limit in detecting lead in commercial samples.

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II. EXPERIMENTAL

Material and Methods:

Graphite pencil faber-castell 2B, sulfuric acid 96% v/v p.a, phosphoric acid 85% v/v p.a, potassium permanganate, hydrogen peroxide p.a 30%, hydrochloric acid p.a 37%, ethanol 96% v/v p.a, zinc powder, sodium citrate dihydrate p.a ($Na.C_6H_8O_7.2H_2O$), citric acid dihydrate p.a ($C_6H_8O_7.2H_2O$), aqudemineral water, potassium chloride, paraffin oil, lead(II) nitrate p.a ($Pb(NO_3)_2$), enamel paint yellow color.

Synthesis of graphene oxide

Graphene oxide was prepared using Improved Graphene Oxide (IGO) which inspired by Hummer method. For chemical characterization of graphene oxide was analyzed by fourier transform infra red (FTIR) and physical characterization analyzed by XRD and PSA.

The IGO method was inspired from hummer method and then improved by increasing the amount of potassium permanganate. Graphene oxide reduced by adding 0,8 g zinc powder to the graphite oxide in mixed of hydrochloric acid p.a 37% and deionized water then stirred about 30 minutes. The mixtured then measure to reach neutral pH 7 by Fisherbrand accumet AE150 pH Benchtop meter. The precipitates then dried at 100°C for 24 hours.

All the electrochemical measurements were performed using a 797 VA Computrace. A three-electrode cell were use at 25 ± 1 °C. An Ag/AgCl (KCl sat.) electrode, platinum wire and graphene oxide electrode were used respectively as reference, auxiliary and working electrode.

Preparation of electrode

To obtained the best condition for graphene oxide-paraffin electrode, we used 4 various composition (5:5; 6:4; 7:3; 8:2). The optimum condition of lead metal measurements was shown by maximum peak current intensity. The graphene oxide electrode was prepared by mixing graphene oxide powder with paraffin oil together using spatula until it formed a unity paste. This paste then packed into the ependorf tube (about 15 cm long and 2.5 mm i.d.). A copper wire then insert into the graphene oxide paste to provide an electrical contact.

III. RESULTS AND DISCUSSION

Graphene oxide best composition

The electrode was prepared by various composition to find out which composition give the best result for lead analysis. The voltammetry method used in determining the best working electrode is cyclic voltammetry. The results obtained are voltammograms with the peak current cathode (reduction) and peak current anode (oxidation). The peak current of each composition is compared to knowing which is the best. The best electrode composition is demonstrated by the high value of the oxidation peak and the narrow reduction peak.

Lead measurements with concentration of 50 ppm and pH 5 were performed at potential difference range -2 to 1 Volt, 5-second deposition time and scan rate 100mV/s. The results of the Ip_a and Ip_c obtained by each composition indicate the increased peak current value of the oxidation which is directly proportional to the increasing number of graphene oxide from each composition. These results correspond to the nature of graphene oxide as conductors.

In this case, the results of the best graphene oxide: paraffin composition is 8:2. The results were shown by the largest Ipc from 8:2 composition compared to other composition variations (Fig. 1). Graphene oxide electrode has a peak value of lead reduction at a potential difference of -0.52963. Result of Voltammogram of lead measurements with graphene oxide electrodes of various compositions can be seen in Fig. 1

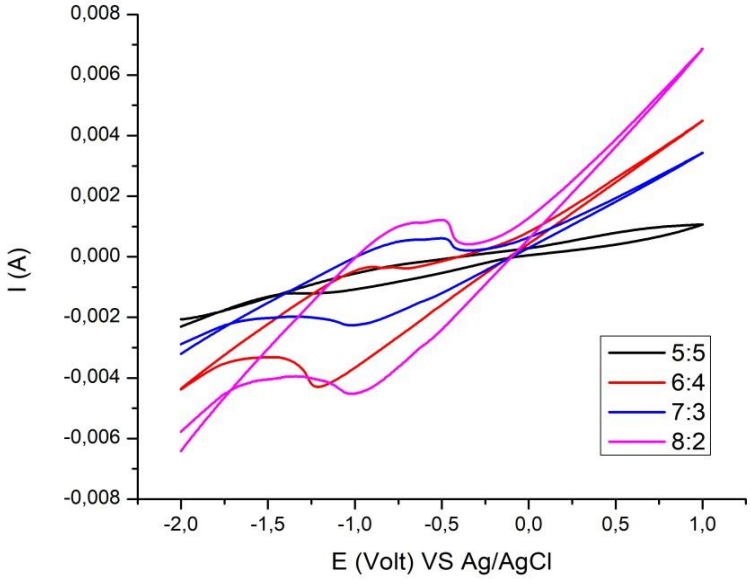

Fig. 1 Cyclic voltammogram of lead with concentration 50 ppm, containing 0.1 M citrate buffer solution (pH = 5) and 5000 ppm potassium chloride at various composition of graphene oxide:paraffin

Optimization of pH

pH is one of the factors that can affect the measurement of an analyte. Analytical measurements with optimum pH can increase the peak oxidation and reduction values. In this case, the lead measurement of concentrations of 50 ppm in pH variations (pH 3; 4; 5; 6) using graphene oxide 8:2 electrodes was carried out at a potential difference range of-2 to 1 Volt, a 5-second deposition time and a scan rate of 100 mV/s.

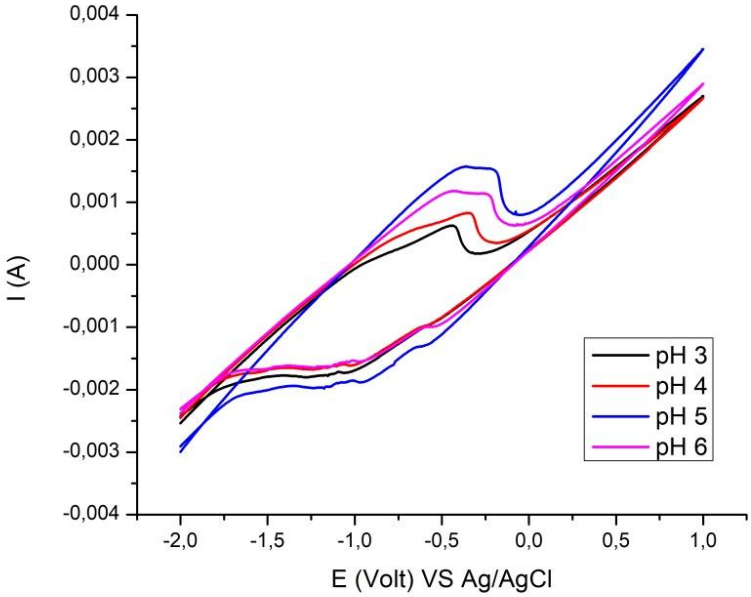

Fig. 2 Cyclic voltammogram of lead with concentration 50 ppm, 5 second deposition time, and scan rate 100 mV/s at various range pH from 3 – 6

Voltamogram in Fig. 2 shows that graphene oxide electrodes can oxidize Pb to Pb^{2+} and reduce Pb^{2+} to Pb being reviewed from the peak oxidation and reduction. In this case, the peak currents of cathode (Ip_c) increased from pH 3 to pH 5. At pH 6 there is a decrease in the peak current because at pH 6 ions Pb^{2+} not stable so that the ions weren't detected maximal.

Optimization of deposition time

Deposition time is the time it takes to collect analytes on the electrode surface during cyclic voltammetry test. Determination of optimum deposition time performed by measure lead 50 ppm in pH 5 and carried out at a potential difference range of -2 to 1 volt with 5 second deposition time and scan rate 100 mV/s. Fig. 3 shows a voltammogram for lead measurements with various deposition time.

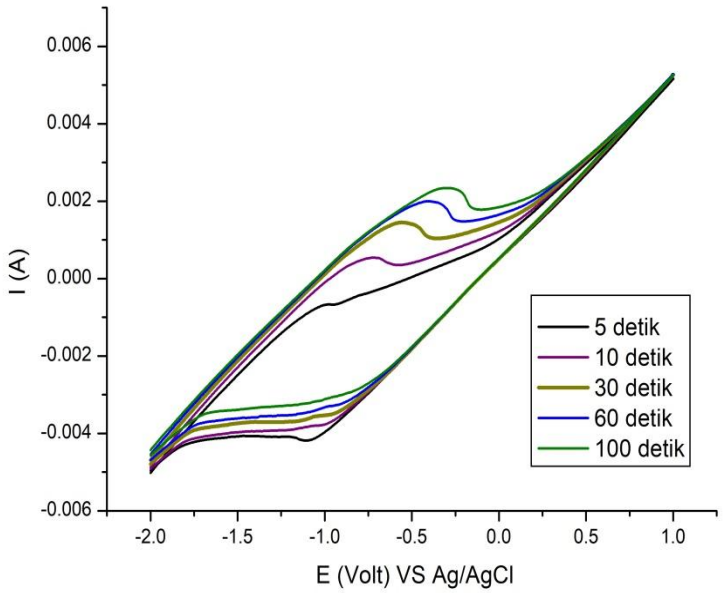

Fig. 3 Cyclic voltammogram of lead 50 ppm in pH 5 and scan rate 100 mV/s with various deposition time

The result show a decreasing value of Ip_c along the longer deposition time. The highest peak of reduction shown at 5 second. These results indicate the optimum deposition time of lead measurements is 5 seconds. The lowest peak at 100 second caused by lead that already accumulated at the surface of electrode.

Optimization of scan rate

The scan rate of the experiment controls how fast the applied potential is scanned. Faster scan rates lead to a decrease in the size of the diffusion layer; as a consequence, higher currents are observed. Determination of the optimum scan rate in lead analysis of 50 ppm was performed using graphene oxide electrode 8:2 and carried out at a potential difference ranger of -2 to 1 volt, with citrate buffer pH 5, 5 second deposition time and various scan rate (100; 200; 300; 400; 500 mV/S). Voltammogram for optimum scan rate is shown in Fig. 4.

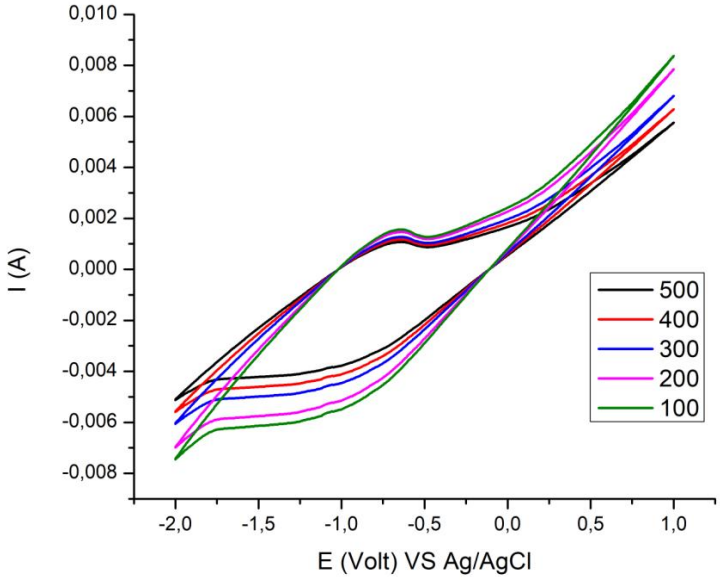

Fig. 4 Cyclic voltammogram of lead 50 ppm in pH 5 with 5 second deposition time and various scan rate (100; 200; 300; 400; 500 mV/s)

Voltamogram in Figure 4 shows there is a decrease in the peak current as the scan rate increases. The scan rate optimization is obtained at 100 mV/s as it generates the highest oxidation and reduction current. The presence of a significant distance range between 100 mV/s – 200 mV/s also supports the optimum scan rate measurement conditions at 100 mV/S.

Lead determination with graphene oxide electrode

This study aims to identify the sensitivity of graphene oxide electrodes in lead analysis. The determination of the lead content has been done by measuring the lead concentration (10; 20; 30; 40; and 50 ppm) and carried out at the potential difference range -2 to 1 volt with citrate buffer pH 5, 5 sec deposition time and scan rate 100 mV/s. The result of voltammogram from this experimental is processed with Origin Pro 8.5 as shown in Figure 5

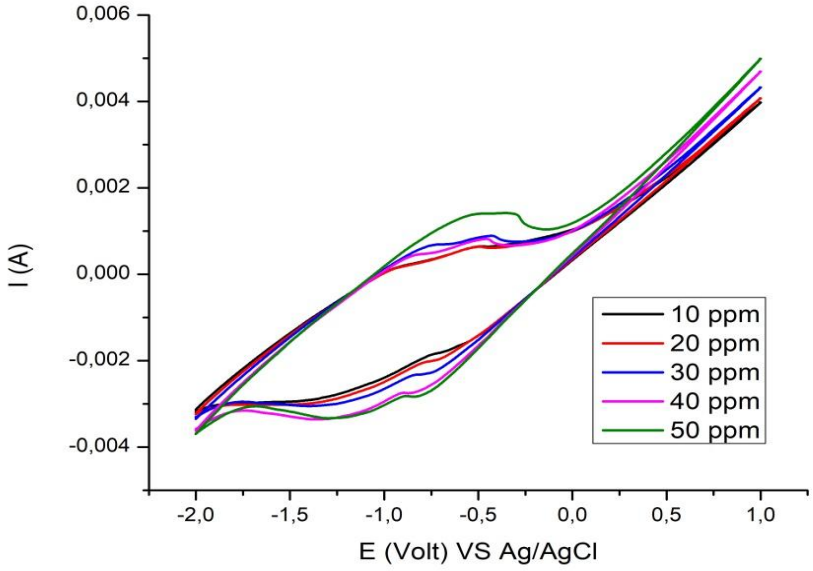

Fig. 5 Lead voltammogram with a concentration of 10 – 50 ppm in citrate buffer solution pH 5 with 5 s deposition time and scan rate 100 mV/s

From fig. 5 the graph relationship between the concentration of the lead standard solution with the cathodic peak give equation 1 with regression $R^2 = 0.99158$

$$y = -2{,}05714 \times 10^{-5} - 0{,}00188 \qquad (1)$$

The linear equatisons 1 is used to determine the lead concentrations in industrial product.

Recovery data and limit of detection

Determination of percent recovery data aims to determine the accuracy of graphene oxide electrodes in lead analysis. Determination of percent recovery done by re-measuring the lead standard solution, then the measured peak current is included in Equation 1. The concentration gained through the calculation then compared with the actual Pb concentration. Percent recovery is calculated using Equation 2

$$\textbf{Recovery}\ (\%) = \frac{\textbf{concentration obtained}}{\textbf{real concentration}}\ \textbf{x100} \qquad (2)$$

Percent recovery data obtained from lead analysis using graphene oxide electrode 8:2 is 99.6620%. The recovery data shows good sensitivity and accuracy of graphene oxide electrodes.

A Limit of detection is used to detect how far the electrode is capable of detecting analytes. The detection limit is the lowest limit of Pb that can be detected by graphene oxide. The detection limit indicates the sensitivity of graphene oxide as an electrode. In this study, the electrode that has been made has sensitivity to detect Pb to a concentration of 0.733 ppm (0.0048 mM or 4.8 µM)

Application to real sample

Determination of feasibility and selectivity of the graphene oxide electrode in analyzing the lead on Indutrsi products is necessary. Industrial products used as samples are enamel paints. The lead content in paint samples tested using the graphene oxide electrode and then validated with AAS. The results of both measurements are shown in table 1. Good recovery data results show that GO electrodes are well used in measuring industrial products.

Table 1. Lead in industrial samples

Sample	Detected at electrode	Detected at AAS
Sample 1	48,656	44,01
Sample 2	48,207	44,79
Sample 3	47,335	48,56

Based on the data from the table 1, it shows that the lead analysis using graphene oxide electrodes is voltammetrically compared to atomic absorption spectrometry. There is no statistical difference.

IV. CONCLUSIONS

Graphene oxide electrodes show a good detection limit to determine lead in paint at 0.733 ppm. It shows that graphene oxide electrodes has good sensitivity and high selectivity in cyclic voltammetry. Validation of lead analysis results with graphene oxide electrodes done by AAS and showing good recovery data.

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Figure Captions

Fig. 1 Cyclic voltammogram of lead with concentration 50 ppm, containing 0.1 M citrate buffer solution (pH = 5) and 5000 ppm potassium chloride at various composition of graphene oxide:paraffin

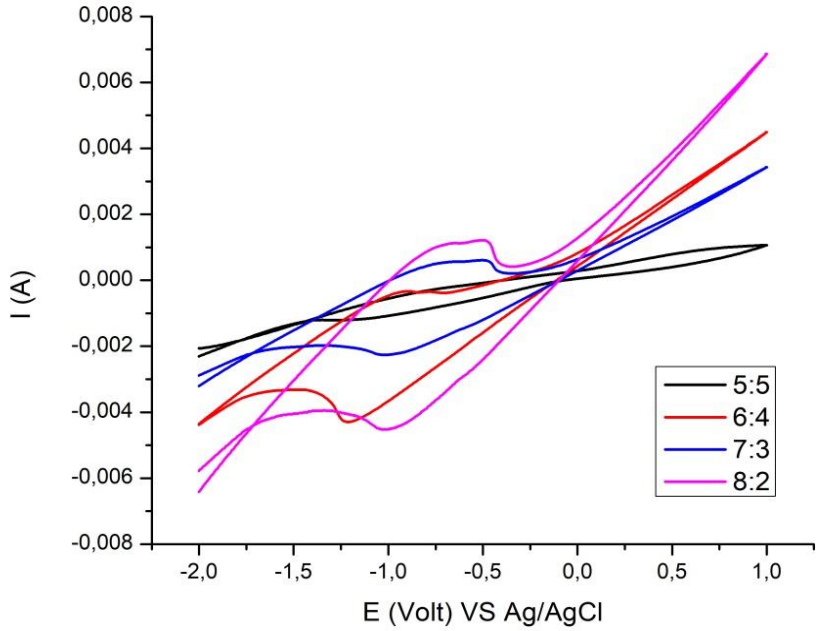


Fig. 2 Cyclic voltammogram of lead with concentration 50 ppm, 5 second deposition time, and scan rate 100 mV/s at various range pH from 3 - 6

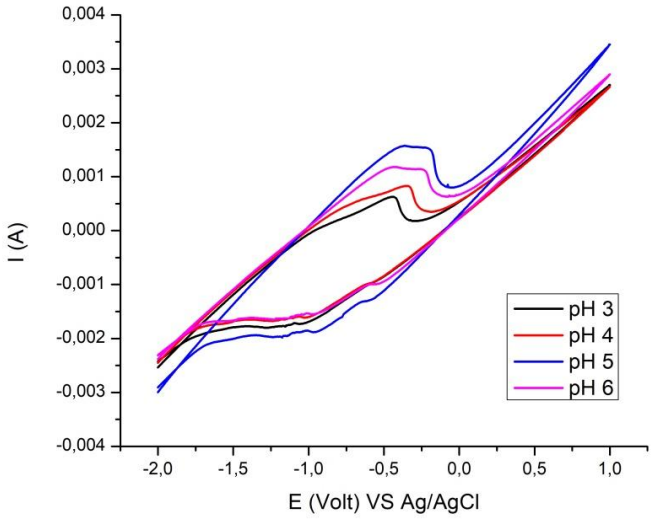
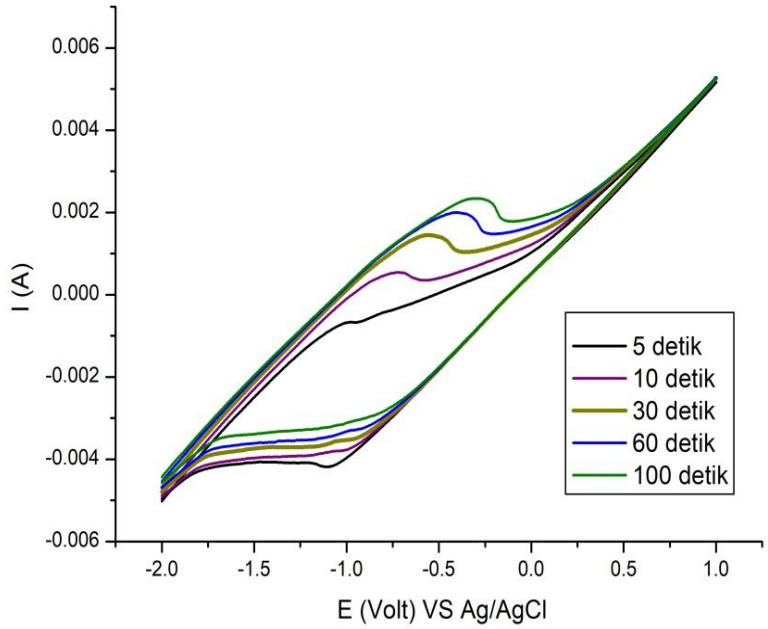


Fig. 3 Cyclic voltammogram of lead 50 ppm in pH 5 and scan rate 100 mV/s with various deposition time



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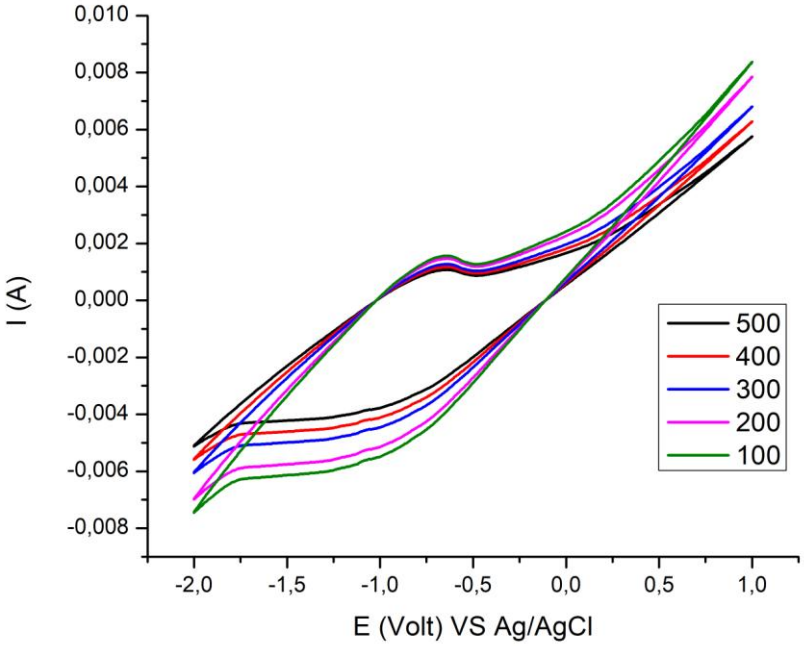
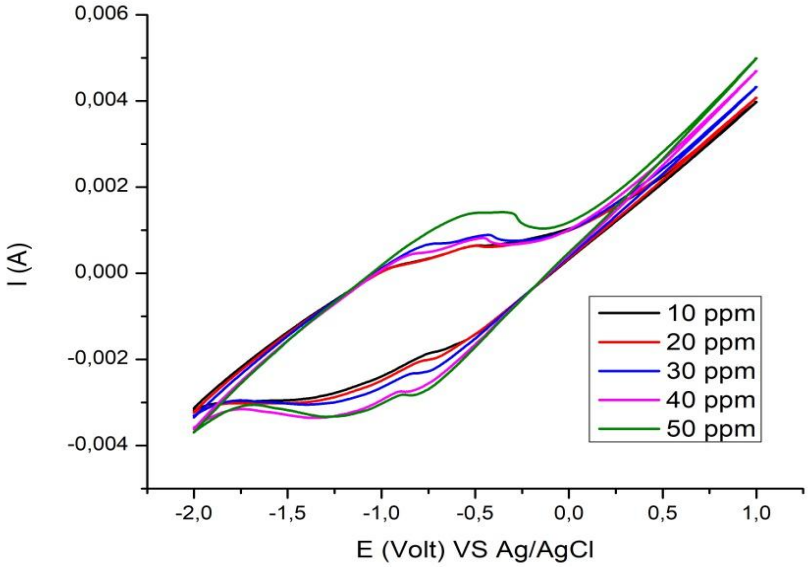


Fig. 5 Lead voltammogram with a concentration of 10 – 50 ppm in citrate buffer solution pH 5 with 5 s deposition time and scan rate 100 mV/s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30 ppm
40 ppm
50 ppm