

Determination of Lead in Waste Water Using Cyclic Voltammetry by Platinum Wire Electrode

Riyanto*

*Department of Chemistry, Universitas Islam Indonesia,
Jalan Kaliurang KM 14,5 Sleman Yogyakarta Indonesia 55584
Corresponding author: Tel: (0274) 896439 ext 3012; Fax: (0274) 896439
E-mail: riyanto@uui.ac.id

ABSTRAK

Telah dilakukan penentuan Pb pada air limbah menggunakan metode siklik voltammetri dengan elektroda batang Pt. Metode siklik voltammetri dilakukan dengan tiga elektroda yaitu elektroda batang Pt sebagai elektroda kerja, elektroda lempeng Pt sebagai elektroda pembanding dan Ag/AgCl (KCl jenuh) sebagai elektroda rujukan. Instrumen yang digunakan yaitu PGSTAT 100 N 100 V/250 mA type (Metrohm Autolab). Elektroanalisis dilakukan dalam larutan elektrolit 0.1 M KCl. Hasil penelitian menunjukkan bahwa analisis Pb dengan metode siklik voltammetri menghasilkan parameter analisis seperti koefisien korelasi $R^2 = 0.999$, LOD = 0.9029 mg/L, LOQ = 3.0098 mg/L dan recovery = 100,67%. Metode ini sangat sesuai untuk analisis Pb karena mempunyai parameter analisis yang sangat baik, selain itu metode ini sangat sederhana dan sedikit penggunaan bahan kimia.

Kata-kata kunci: Pb, air limbah, siklik voltammetri, batang platinum.

ABSTRACT

Determination of lead in waste water using cyclic voltammetry by platinum wire electrode has been carried out. The cyclic voltammetry method was performed in a three electrodes system using platinum wire as a working electrode, an Ag/AgCl (saturated KCl) as reference electrode and platinum plate as the counter electrode. PGSTAT 100 N 100 V/250 mA type (Metrohm Autolab) was used for electroanalysis measurements. Electroanalysis of lead in waste water was performed in 0.1 M KCl as an electrolyte. From this research showed that the developed electroanalysis lead in waste water using platinum wire electrode are accurate, precise, reproducible and inexpensive with acceptable correlation of determination ($R^2 = 0.999$), LOD = 0.9029 mg/L, LOQ = 3.0098 mg/L and recovery = 100,67%. The methods can be used for the analysis of lead in waste water. This method is simplicity of sample preparation and use of low cost reagents are the additional benefit.

Keywords: lead, wastewater, cyclic voltammetry, platinum wire

Introduction

Heavy metals such as lead, cadmium and mercury are rapidly increasing continuously to an alarming level, particularly in rivers and near shore waters where industrial wastes are being discharged. They tend to concentrate in all matrices in the

environment (Srivastav et al. 1994). Lead is one of the very toxic heavy metals that not only accumulate in individual but also have the ability to affect the entire food chain and disrupt the health system of human beings, animals and phytoplanktons (Singh et al. 2012). In human, it is absorbed directly into

the blood stream and is stored in soft tissues, bones and teeth (95% in bones and teeth) (David et al. 2003). It can also affect the kidney and most importantly the nervous system and brain. Thus, lead can accumulate over a lifetime and it causes diseases such as anemia, encephalopathy, hepatitis and nephritic syndrome. It exceeds the WHO (2004) allowable standard 0.15 mg/L and constant exposure may lead to delay in physical or mental development in infants and children while adults may have kidney problems and high blood pressure. Lead contaminates water by the corrosion of household plumbing system and erosion of natural deposits (US EPA 2005).

Lead is a cumulative poison that enters the body from lead water pipes, lead-based paints and leaded petrol. Presence of even traces of Pb(II) in environmental samples leads to environmental pollution and many fatal diseases including dysfunction of renal blood and neurological systems. Pb (II) easily deposits in blood, kidney, reproductive system, nervous system and brain, and acute lead poisoning can result in colic shock, severe anemia and irreversible brain damage. Lead compounds as antiknocking agents in automobile fuels cause air pollution.

So it is very important to find a very sensitive and selective method for the

determination of trace levels of lead in the environment. Various methods have been reported for the determination of lead in environmental samples. These methods include resonance light scattering technique (Cui et al. 2012) and spectrophotometric methods (Naeem et al. 2012). Different techniques were used for trace lead analysis such as spectroscopic methods especially graphite furnace atomic adsorption spectroscopy (GF-AAS) (Duran et al. 2009), and inductively coupled plasma mass spectroscopy (ICP-MS) (Voica et al. 2012). These methods have excellent sensitivity and good selectivity, but have different drawbacks such as time consuming used for analysis and very expensive instruments are required.

Electrochemical methods including cyclic voltammetry have recognized powerful tools for measuring trace analysis. It have shown different advantages such as speed of analysis, higher selectivity and sensitivity, low cost, easy operation and the ability of analyzing element speciation. Different working electrodes were used for the voltammetric determination of lead such as hanging mercury drop electrode (HMDE) (Raj et al. 2013), mercury film electrode (Carapuc et al. 2004), graphite electrode (Marichamy and Ramalakshmi 2013), silver

electrode (Zen et al. 2002) and gold electrode (Laschi et al. 2006).

Chemically modified electrodes have been developed in the recent years for the electrochemical determination of heavy metals due to different advantages such as easy manufacture, no poison, renewable, fast response, high selectivity, low detection limit, stable in various solvent, longer life time and low cost.

In the present work a new, simple and precise method is proposed for the determination of lead in environmental samples. The method is based on electrochemical analysis in KCl solution at room temperature using platinum wire electrode. Platinum wire electrode is the simple and low cost electrode fabrication, high speed, reproducibility, high stability, wide linear dynamic range and high sensitivity.

Experimental Section

Materials

All solutions were prepared by dissolving their analytical grade reagent (Merck) in deionised distilled water. Pt wire and plate (Metrohm Autolab) was used for anode and cathode electrodes. KCl 0,1 M was prepared using KCl (Merck) and aquabidest. Pb solutions were prepared by

dilution of absolute Pb with Certified Reference Material (CRM) from Merck with deionised distilled water. The calibration curve was made by using Pb concentration of 10-100 mg/L.

Waste Water Samples

Samples of waste water were collected from Center Laboratory, Islamic University of Indonesia, Yogyakarta, Indonesia.

Instrumentation

PGSTAT 100 N 100 V/250 mA (Metrohm Autolab) was used for electroanalysis measurements while data acquisition was accomplished by using the Nova software. Instrument is equipped with three electrodes system using Pt wire as a working electrode, an Ag/AgCl (saturated KCl) as reference electrode and platinum plate as the counter electrode.

Procedure

Electroanalysis of Pb

The electrochemical process of Pb was performed in 0.1 M KCl solution at room temperature. The electrochemical studies by cyclic voltammetry (CV) were performed in 50 mL capacity glass electrochemical cell. The cyclic voltammetry experiments were performed in a three electrodes system using Pt wire as a working electrode, an Ag/AgCl

(saturated KCl) as reference electrode and platinum plate as the counter electrode. All potentials given are with respect to the Ag/AgCl reference electrode.

Calibration and validation method

Calibration curves were obtained by plotting anodic peak height (current) versus

Pb concentration. Validation parameters including linearity, limit of detection (LOD), limit of quantification (LOQ), precision and accuracy were assessed. Cyclic voltammograms (CVs) of Pb solutions were recorded in a wide range of concentrations (10-100 mg/L) in 0.1 M KCl solution at room temperature.

Result and Discussion

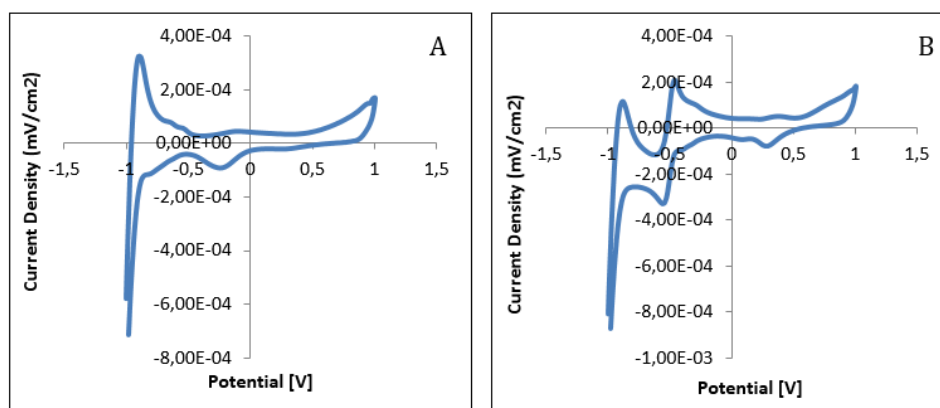


Figure 1. Cyclic voltammograms using Pt wire electrode in (A) KCl 0.1 M and (B) KCl 0.1 M + 10µL Pb(NO₃)₂ 1000 mg/L with scan rate 50 mV/sec.

Figure 1 shows cyclic voltammograms using Pt wire electrode in (A) KCl 0.1 M and (B) KCl 0,1 M + 10µL Pb(NO₃)₂ 1000 mg/L with scan rate 50 mV/sec. Figure 1A shows the cyclic voltammogram in KCl 0.1 M. Figure 1B shows the cyclic voltammogram of KCl 0,1 M + 10µL Pb(NO₃)₂ 1000 mg/L. For a reversible system (Figure 1B), the separation of anodic peak potential and

cathodic peak potentials of the couple is $57/n$ mV and the formal electrode potential is the average of the two peak potentials to a good approximation. If electron transfer reaction is irreversible system, then peak to peak distance is large whereas in reversible system, the peak to peak distance is short (Mehta and Sindal 2010).

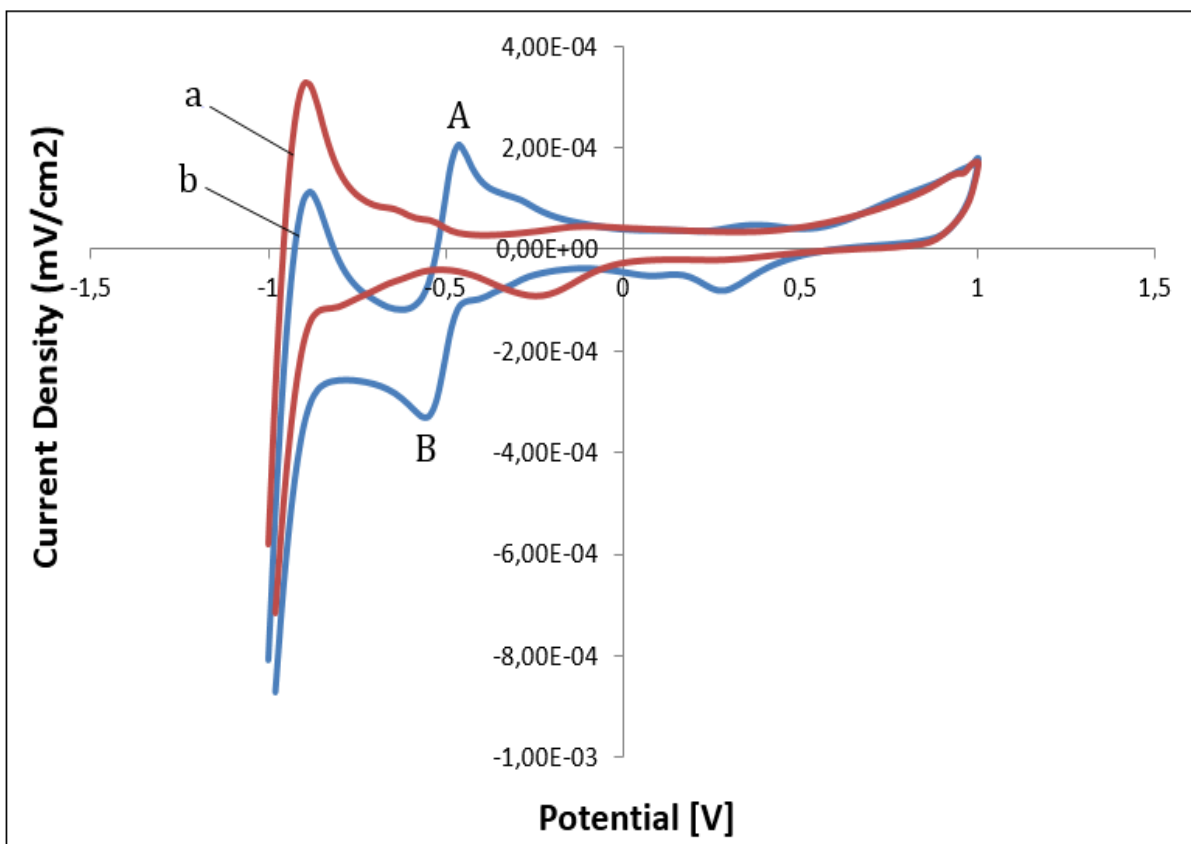


Figure 2. Cyclic voltammograms using Pt wire electrode for (a) KCl 0.1 M without $\text{Pb}(\text{NO}_3)_2$ and (b) KCl 0.1 M + $10\mu\text{L Pb}(\text{NO}_3)_2$ 1000 mg/L with scan rate 50 mV/sec.

Figure 2 shows overlay of the cyclic voltammograms using Pt wire electrode for (a) KCl 0,1 M without $\text{Pb}(\text{NO}_3)_2$ and (b) KCl 0.1 M + $10\mu\text{L Pb}(\text{NO}_3)_2$ 1000 mg/L. The A peak at Figure 2b shows the oxidization peak of Pb, when added Pb^{2+} increasing current density at A peak was observed. The B peak at Figure 2b shows the reduction process of Pb (II) to Pb (0). Cyclic voltammetry measurements were performed in an electrochemical cell with a volumetric capacity of 50 mL containing a Pt wire electrode working electrode (Metrohm

Autolab), a Pt plate counter electrode, and an Ag/AgCl reference electrode (saturated with KCl). The potential was swept in inverse scanning mode starting from -1.0 to 1.0 V with a scanning rate of 50 mV/s. Figure 2 shows the anodic peak potential (E_{pa}) and peak current (i_{pa}) (peak A), from peak B are cathodic peak potential (E_{pc}) and peak current (i_{pc}).

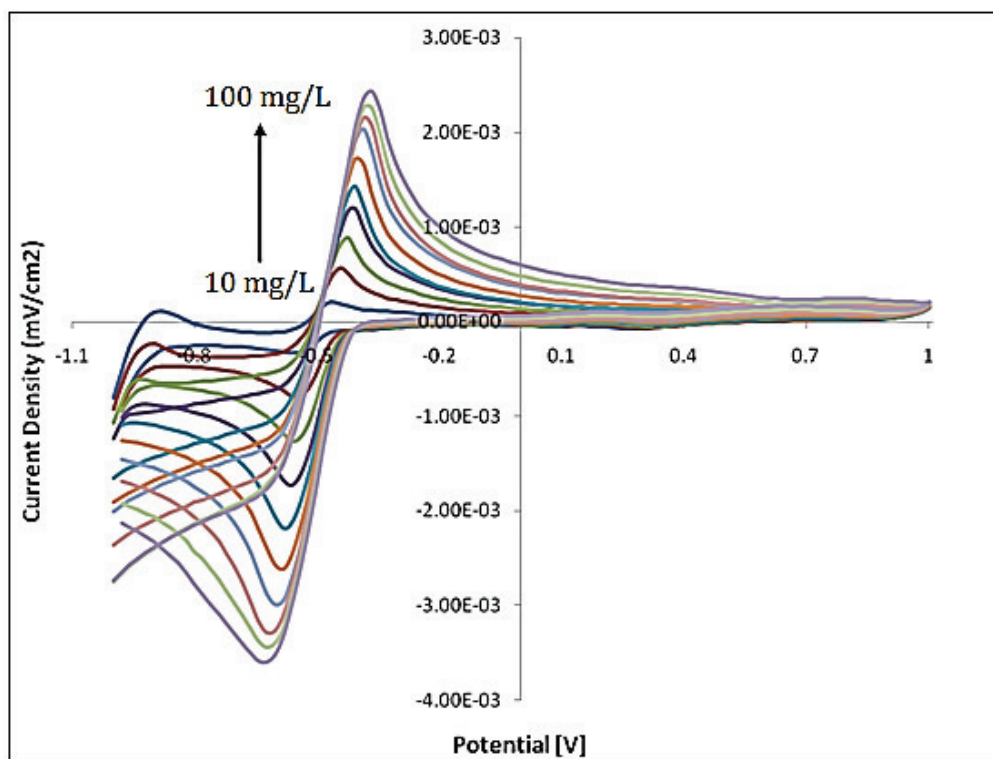


Figure 3. Cyclic voltammograms using Pt wire electrode for KCl 0,1 M + 10 μ L Pb(NO₃)₂ with different concentration 10-100 mg/L with scan rate 50 mV/sec.

Calibration curve form oxidation peak

Figure 3 shows the effect of Pb²⁺ concentration to current density. Figure 3 shows the peak current density increased with increasing of Pb²⁺ concentration. As it can be seen from Figure 3 there is an increase in oxidation peaks current with the increase in lead concentrations which leads to a linear relation between these two parameters. Figure 3 shows the effect of Pb²⁺ concentration can be shown by recording the CV at each concentration (10-100 mg/L) and plotting current density versus concentration for either the anodic peak or the cathodic

peak (Figure 4B and 4C). The equation obtained from the linear calibration graph in the studied concentration range for Pb (II) in aqueous KCl is (where represents the value of oxidation current and, the value of lead (II) concentrations, expressed as mg/L with a correlation coefficient of $R^2=0.997$. Results obtained are shown in (Figure 4C). The effect of concentration on the peak current of Pb was examined from 10 mg/L to 100 mg/L, the resulted calibration curve showed a linear range from 10 mg/L to 70 mg/L with a correlation coefficient of $R^2 = 0.997$. The limit of detection (LOD) and limit of

quantification (LOQ) for Pb(II) was (oxidation peaks) and it was found to be calculated based on calibration curve 3.4039 and 11.3463 mg/L, respectively.

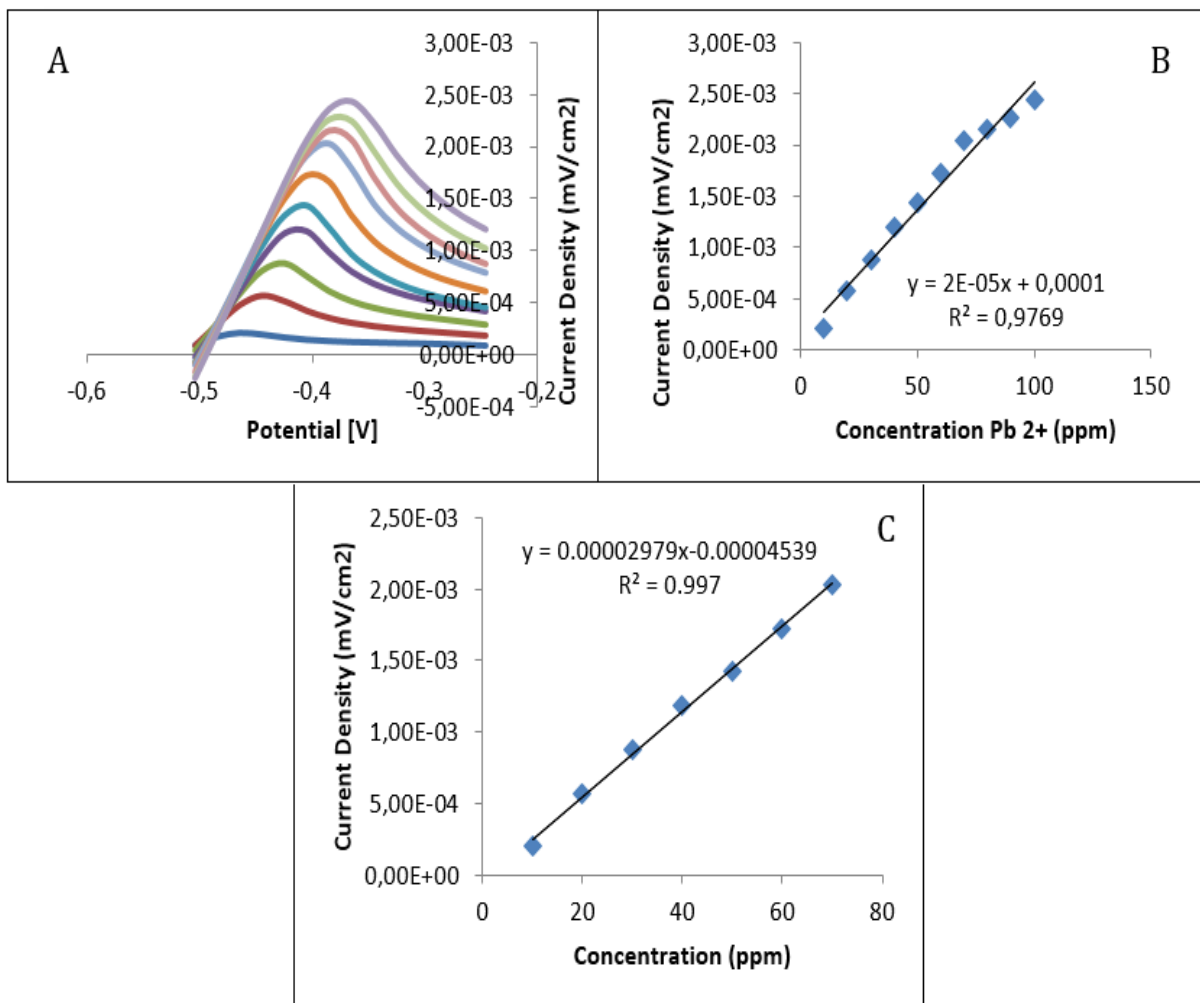


Figure 4. Voltammograms from oxidation peak with different Pb²⁺ concentrations from Figure 3 (A), the calibration curve from oxidation peaks, without selected data (B) and the calibration curve from oxidation peaks with selected data (C)

Calibration curve form reduction peak

Figure 4. Voltammograms from reduction peak (Figure 4A), calibration curve from reduction peaks, without selected data

(Figure 4B) and calibration curve from reduction peaks with selected data (Figure 4C). The relationship between concentration and peak height anodic current was linear

from 10 to 60mg/L of Pb^{2+} . A concentration range of 10 to 60 mg/L of Pb^{2+} was chosen for calibration curve preparation because in this range the correlation coefficient was almost unity ($R^2 = 0.999$). Base on the calibration curve form reduction peak, the

limit of detection (LOD) and limit of quantification (LOQ) for $Pb(II)$ was calculated based on calibration curve (reduction peaks) and it was found to be 0.9029 and 3.0098 mg/L, respectively.

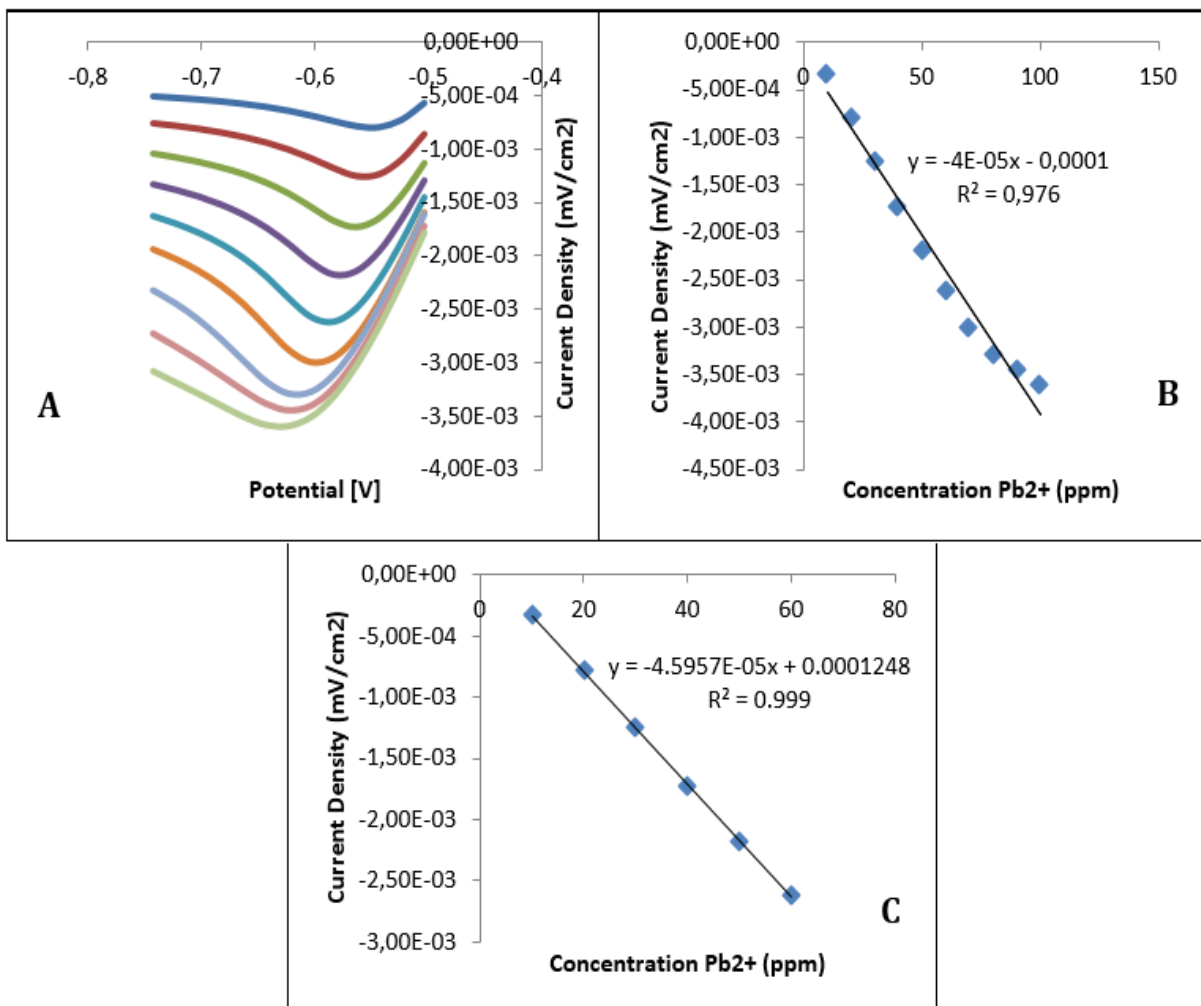


Figure 5. Voltammograms from reduction peak from Figure 3 (A), calibration curve from reduction peaks, without selected data (B) and calibration curve from reduction peaks with selected data (C)

Table 1. shows the analytical parameters of Pb using voltammogram for both E_p anodic and E_p cathodic. From the calibration curve obtained using both anodic and E_p cathodic, the correlation coefficient (r) recorded were 0.9985 and 0.9994, respectively. For the purpose of analysis, the slope and limit of detection were also determined, where the sensitivity of the technique is correctly defined as the slope of the calibration curve.

Table 1. Analytical parameters of Pb using voltammograms from oxidation and reduction peaks

Parameters	Oxidation peaks (E_p anodic)	Reduction Peaks (E_p cathodic)
Equation regression linear	$y = 2.979.10^{-5}x - 4.539.10^{-5}$	$y = -4.596.10^{-5}x + 1.248.10^{-5}$
Slope	$2.979.10^{-5}$	$-4.596.10^{-5}$
Intercept	$-4.539.10^{-5}$	$1.248.10^{-5}$
Correlation coefficient (r)	0.9985	0.9994
Coefficient of determination (R^2)	0.9970	0.9990
Limit of detection (LOD)	3.4039 mg/L	0.9029 mg/L
Limit of quantification (LOQ)	11.3463 mg/L	3.0098 mg/L

The slope for the calibration curve using both E_p anodic and E_p cathodic were $2.979.10^{-5}$ and $-4.596.10^{-5}$, respectively (Table 1). From the analytical parameters, it could be concluded that reduction peaks (E_p cathodic) was more sensitive compared to oxidation peaks (E_p anodic) for the analysis of Pb^{2+} using CV method. Base on LOD and LOQ data the reduction peaks (E_p cathodic) was more sensitive compared to oxidation peaks (E_p anodic).

Table 2. Analytical application of proposed method

No	Wastewater	Pb Concentration in wastewater (mg/L)	Pb Spike (mg/L)	Pb Found (mg/L)	Recovery* (%)
1	Sample 1	12.54	5.0	4.91	98.2
2	Sample 2	12.78	5.0	5.22	104.4
3	Sample 3	11.98	5.0	4.97	99.4

*Average of three determinations

The LOD is defined as the lowest concentration that can be distinguished from the background noise with a certain degree of confidence. Limit of detection (LOD) and

limit of quantification (LOQ) are two important performance characteristics in method validation. LOD and LOQ are terms used to describe the smallest concentration of an analyte that can be reliably measured by an analytical procedure (UNODC, 2009). LOD and LOQ of the Pt wire electrode using Pb^{2+} analysis were found to be 0.9029 mg/L and 3.0098 mg/L, respectively.

Recovery experiments should be performed by comparing the analytical results for extracted samples at three concentrations. Recovery of the analyte need not be 100%, but the extent of recovery of an analyte and of the internal standard should be consistent, precise, and reproducible. Table 2. showed electroanalysis Pb^{2+} in 0.1 M KCl solution using Pt wire electrode have a good recovery is close to 100%.

Conclusions

It was shown that anodic and cathodic peak could be obtained using cyclic voltammetry method for determination of Pb in KCl solution. The oxidation of Pb on Pt wire electrode occurs in a reversible system. Analytical parameters from cathodic peak was a better compared to anodic peak for analyzing of Pb using CV method. As a conclusion, electroanalysis lead in waste water using platinum wire electrode are

accurate, precise, reproducible and inexpensive with acceptable correlation of determination ($R^2 = 0.999$), LOD = 0.9029 mg/L, LOQ = 3.0098 mg/L and recovery = 100,67%. The methods can be used for the analysis of lead in waste water. This method is simplicity of sample preparation and use of low cost reagents are the additional benefit.

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