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Adsorption Enhancement of Pb(II) ion in the Presence of Nicotinic Acid during Cyclic Voltammetry

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The solution phase voltammetry employed in the study of metal ion interaction with a selected ligand. Voltammetry behaviours of lead (II) ion in the presence of ligand with N-heterocycle compounds, such as nicotinic acid (pyridine-3-carboxylic acid) were being studied using cyclic voltammetry (CV) on a hanging dropping mercury electrode (HDME). Assessment of the chemical and physical conditions that may favour optimum current enhancement was done by studying the effect of varying pH, concentration of metal ion and scan rate. It was found that in presence nicotinic acid (NA) result in a shift in peak potential (E_p) and peak current (I_p) in the determination of Pb(II). The addition of 1 x 10^{-2} M nicotinic acid in 0.1 M potassium chloride at pH 4.0 and scan rate of 100 mV/s in CV was required for optimum current enhancement to be observed by about 4.9 fold and 1.6 fold in oxidation and reduction current of Pb(II) respectively. Based on chronocoulometry and chronoamperometry technique the diffusion for Pb(II) were estimated by 9.18 x 10^{-6} cm^2/s and 5.0 μc/cm^2 respectively. The procedure was successfully applied to the simultaneous determination of Pb(II) ion in some real samples.

Keywords: Lead (II) ion, nicotinic acid, cyclic voltammetry, hanging dropping mercury electrode.

1. INTRODUCTION

N-heterocycle compounds are organic compounds that contain a ring structure containing atoms in addition to carbon which is nitrogen and carboxyl, as part of the ring. This types of ligand is also known to form stable chelates with metal ions and oxometal cations and can display widely varying coordination demeanor functioning as a bidentate, tridentate, meridian or bridging ligand [1,2]. It is a versatile N,O-chelating agent with limited stearic hindrance and can further provide possibility to form polymeric complexes through bridging coordination of carboxylates under suitable conditions [3]. The nitrogen heterocyclic ligands selected for this study is pyridine-3-carboxylic acid (nicotinic acid). Nicotinic acid is an organic compound with the molecular formula $C_6H_5NO_2$. It is a derivative of pyridine, with a carboxyl group (COOH) at the 3-position. Nicotinic acid plays interesting roles in biology and in the metabolism reactions of body. Nicotinic acid is used as an intermediate for agrochemicals, feed additives, pharmaceuticals and animal food enrichments. Nicotinic acid has been described as versatile ligand which forms metal complexes useful in medicine, due to their physiological properties [4]. Transition metal complexes such as lead have been the subject of thorough investigation because of their extensive applications in wide ranging areas from material sciences to biological sciences [5]. Because of the increased industrial use of the lead and its serious hazardous effect to human health [6], the development of sensitive methods for the determination of lead ions is required. By using proper electrochemical techniques, such as cathodic stripping voltammetry and pulse voltammetry [7] enhancement was observed for the electrochemical reduction of metal ion. In previous works the determination of heavy metal ions were mostly carried out at mercury electrodes [8-11]. Mercury electrode provides not only good adsorption of the analyte but also a stable and reproducible electrode surface. The advantages of this hanging mercury drop electrode (HMDE) also include renewable surface and high hydrogen overpotential [12]. An electrochemical method is one of the most favorable techniques, because of its low cost, high sensitivity, easy operation and ability of analyzing element speciation [13-15]. Because of there is no report on the use of current enhancement on the electrode surface of nicotinic acid as ligands with lead ions, it is therefore our interest here to report on the work done of electroanalytical study of Pb(II)-nicotinic acid using square wave voltammetry and cyclic voltammetry onto the controlled growth mercury electrode (CGME). This method provides low detection limit with good accuracy and precision and excellent selectivity against the other co-existing ionic species [16].

2. MATERIAL AND METHODS

2.1. Instrument and apparatus

Voltammetric measurements were measured using a Bioanalytical System BAS CV-100 W Voltammetric Analyzer using a conventional three-electrode electrochemical cell to perform cyclic voltammetry (CV), chronocoulometry (CC) and chronoamperometry (CA). Measurements were using Controlled Growth Mercury Electrode (CGME) as working electrode, the capillary used is the standard capillary having beveled tip with a 100-µM ID. It was used together with a silver/silver chloride serves as reference electrode and a platinum wire serves as counter electrode. The cell was completely shielded from electrical interferences by a faraday cage. The pH was measured using Mettler Toledo pH Meter Model Seven Easy^{TM} S20 equipped with a combined glass electrode.

2.2. Reagents and materials

All reagents and materials of analytical reagent grade purity were used without further purification. All chemical operations and preparations of the electrolyte solutions were carried out using deionised reversed osmosis (RO) water. A lead ion was prepared as a stock solution from lead (II) nitrate salts by diluting it with 0.1M potassium chloride (KCl) as supporting electrolyte. A stock solution of nicotinic acid was prepared fresh in deionised RO water. 0.5M acetate buffer was used, with adjustment to pH 4-6 by either an addition of acetic acid or NaOH. Unbuffered solution of pH < 4 was used with the addition of sulphuric acid.

3. RESULTS AND DISCUSSION

3.1. Electrochemical characterization

Figures 1 show that the presence of suitable ligand such as nicotinic acid which is able to cause a significant increase in the redox peak current of Pb(II) during cyclic voltammetry at the mercury electrode. It was especially for the current obtained during reoxidation process as the oxidation peak of Pb(II) was found to increase by about 4.9 folds in the presence of nicotinic acid during cyclic voltammetry.

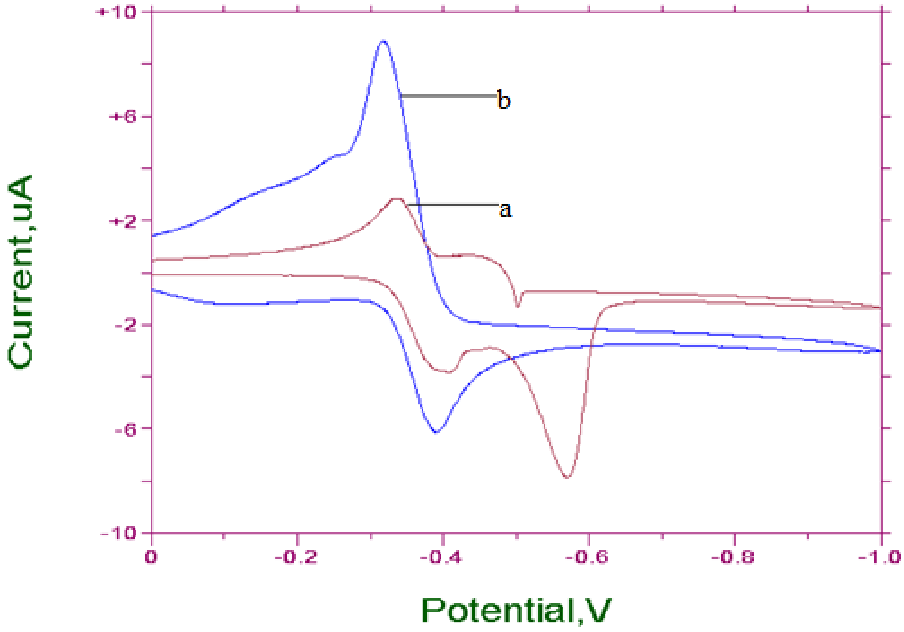


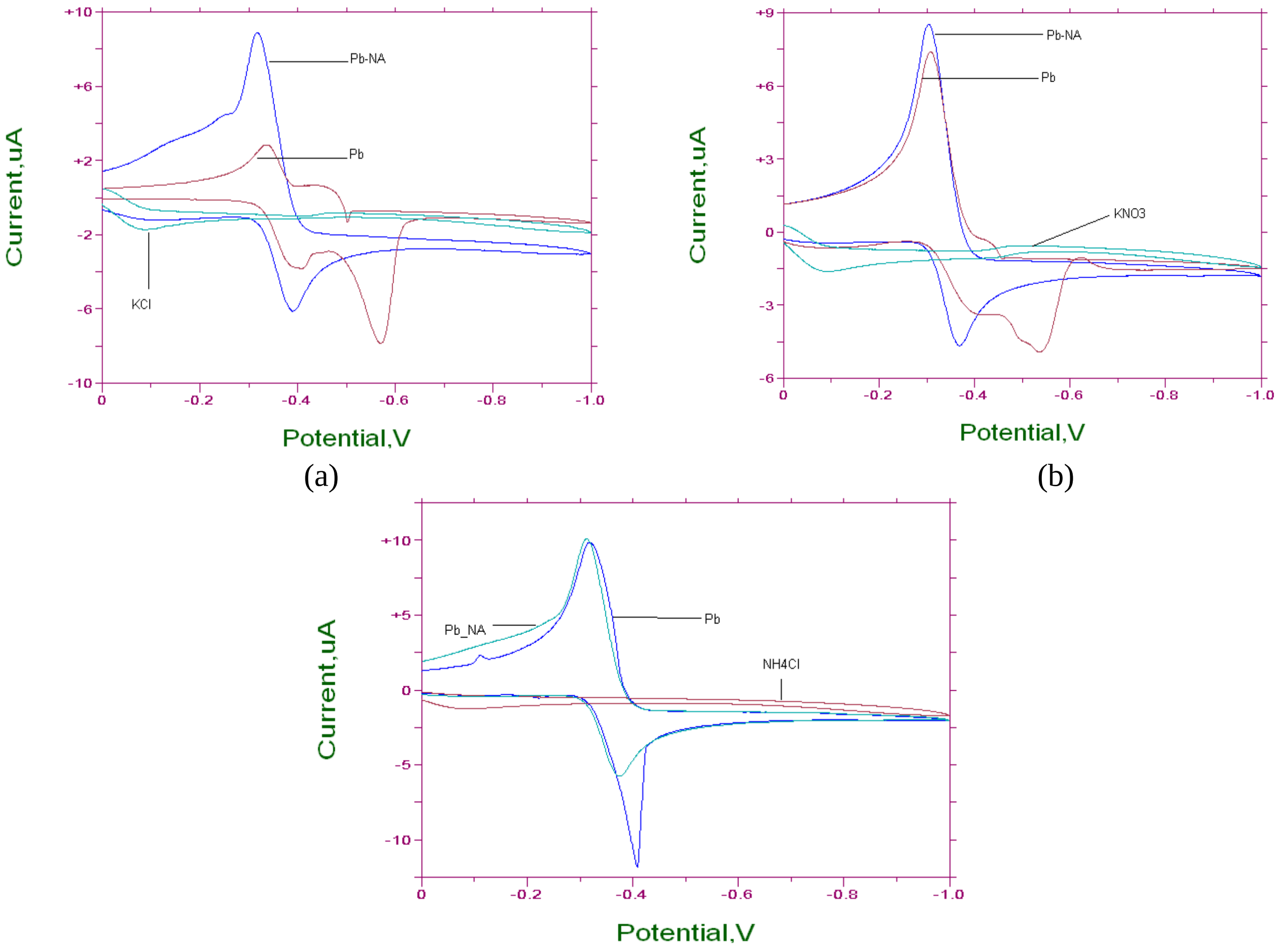
Figure 1. Cyclic voltammetry of 1.0 mM Pb(II), 0.1M KCl, 0.05M sodium acetate buffer pH 4.0 (a) without nicotinic acid (b) with 1 x 10^{-2}M nicotinic acid; 100mV/s.

3.2. Effect of varying supporting electrolyte

Table 1 and Figure 2 represent the effect of supporting electrolyte on Pb(II) oxidation in the absence and presence of NA. The results show that the type of supporting electrolyte plays an important role in influencing E_{pa} and i_{pa} of Pb(II) ions. In the presence of NA, current enhancement varies in different electrolyte in accordance to the following order: KCl < KNO_3 < NH_4Cl. The range of current enhancement is 1.1 to 4.9 µA.

Table 1. Effect of 0.1M various supporting electrolyte on I_p and E_p of 1.0mM of Pb(II) with and without 1x 10^{-2}M nicotinic acid (NA) during CV using mercury electrode.

Supporting electrolyte	Ipa(uA)		Epa(mV)		Enhancement Factor
	Without NA	With NA	Without NA	With NA	
0.1M KCl	2.2	10.8	-336	-317	4.9
0.1M KNO_3	8.0	9.5	-320	-305	1.2
0.1M NH_4Cl	11.3	11.9	-335	-322	1.1
0.1 M Na_2SO_4	5.5	4.1	-347	-346	-0.7
0.1 M K_2SO_4	10.4	6.2	-346	-349	-1.7



(a) (b)

(c)

Figure 2. CV voltammograms for 1.0mM of Pb(II) ion with 1 x 10^{-2} M nicotinic acid in various supporting electrolyte : (a) KCl, (b)KNO_3 and (c) NH_4Cl using mercury as working electrode; scan rate 100mV/s.

The highest value of i_{pa} was attained in KCl for Pb-NA complexes. It is therefore, regard as the best supporting electrolyte to be used in this study. However, Na_2SO_4 and K_2SO_4 seems to have a lesser effect on the enhancement of peak current due to the precipitation formed in the solution.

3.3. Effect of varying pH

The solution pH was varied from 1.5 to 7.0 to determine its effect on the reduction of Pb(II) with 1 x 10^{-2} M nicotinic acid at the mercury electrode. The effect of pH on enhancement was studied in 0.1M KCl electrolyte. From figure 3 it shown that the optimum pH range for greater current output was between pH 3 to 5. The maximum current enhancement was at pH 4.0. However, at pH 6 onwards current gradually decreased due to the precipitation process.

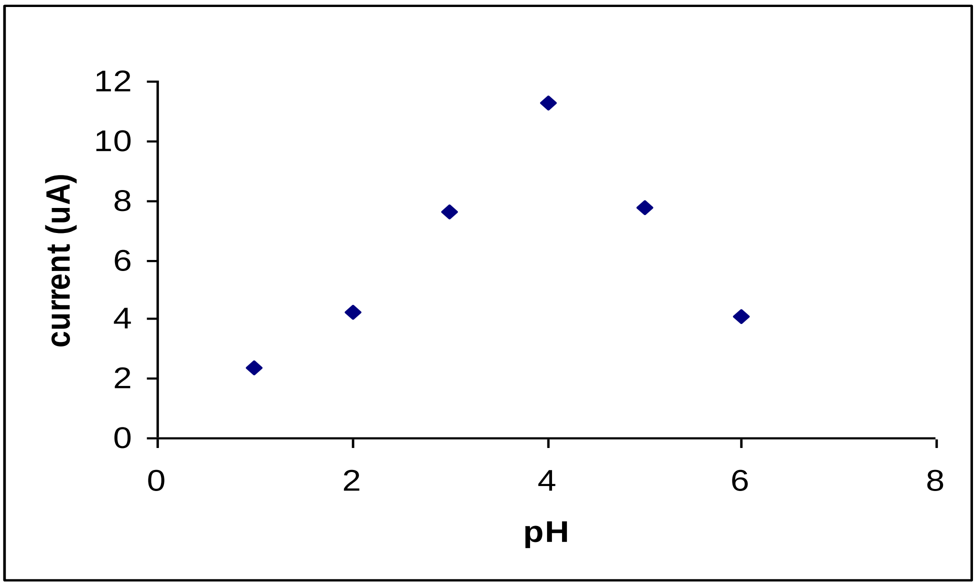
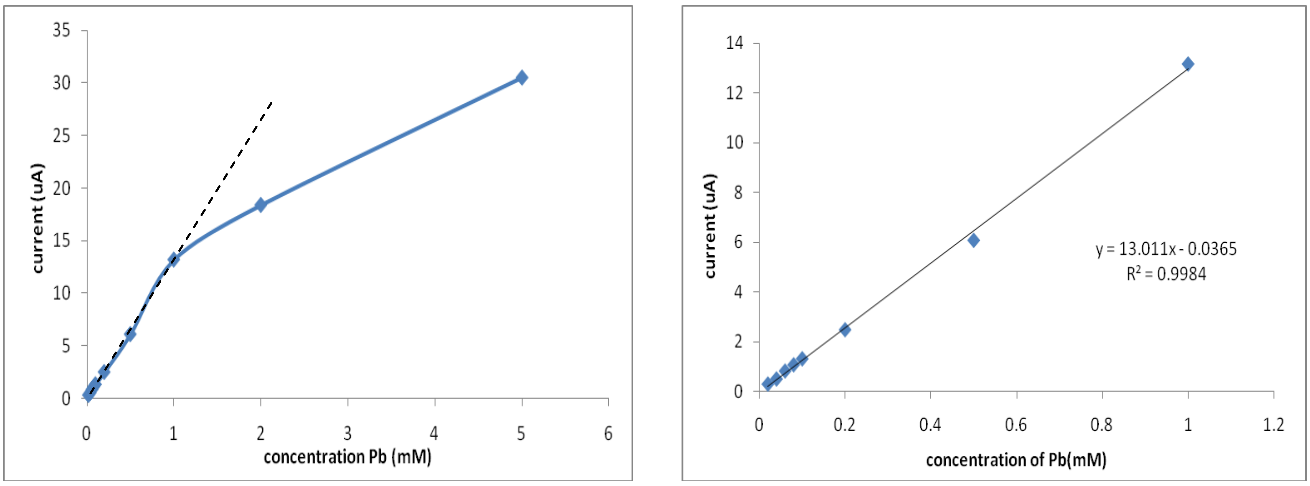


Figure 3. Graph of current against pH for Pb(II) peak with 0.1M KCl, 0.05M sodium acetate buffer,1.0mM Pb(II), 1 x 10^{-2}M nicotinic acid using mercury as working electrode during CV with potential scanning in a positive direction from 0 to -1000 mV at a scan rate of 100 mV/s.

3.4. Effect of varying Pb(II) concentration

Figure 4(a) representative of the studies done on the effect of varying Pb(II) ion concentration in the presence of 1 x 10^{-2}M nicotinic acid at pH 4. Ip value for reduction of nicotinic acid increased gradually with increasing amount of Pb(II). The dependence of the reduction current on Pb(II) concentration was shown in figure 4(b).

A linear relationship graph was observed for the concentration range of 0.02 to 1.0 mM. The sensitivity, expressed as the slope of the linear region of the calibration curve was 13.01 uA/mM and detection limit of 3.55 µM.



a) b)

Figure 4. a) Graph Ip versus [Pb] on effect of varying Pb(II) concentration at constant nicotinic acid concentration of 1 x 10^{-2}M in 0.1M KCl during CV at pH 4.0; 100mV/s. b) Linear region of the calibration plot.

3.5. Scan rate study

Figure 5 shows the Pb(II) oxidative current demonstrated the dependence of log oxidative current, I on log scan rate, υ of 1.0mM Pb(II) with 1 x 10^{-2}M NA at pH 4.0 at various scan rates (10 – 1000 mV/s) in aqueous solution containing 0.1 M KCl using mercury electrode. The result shows that the current increased with an increasing scan rate. The slope of graph log I versus log υ was 0.6 indicating the Pb(II)-nicotinic acid complex species is not very strongly adsorbed on to the Hg electrode surface. This value is far from 1, this is due to the change in chemical properties of Pb(II) ion.

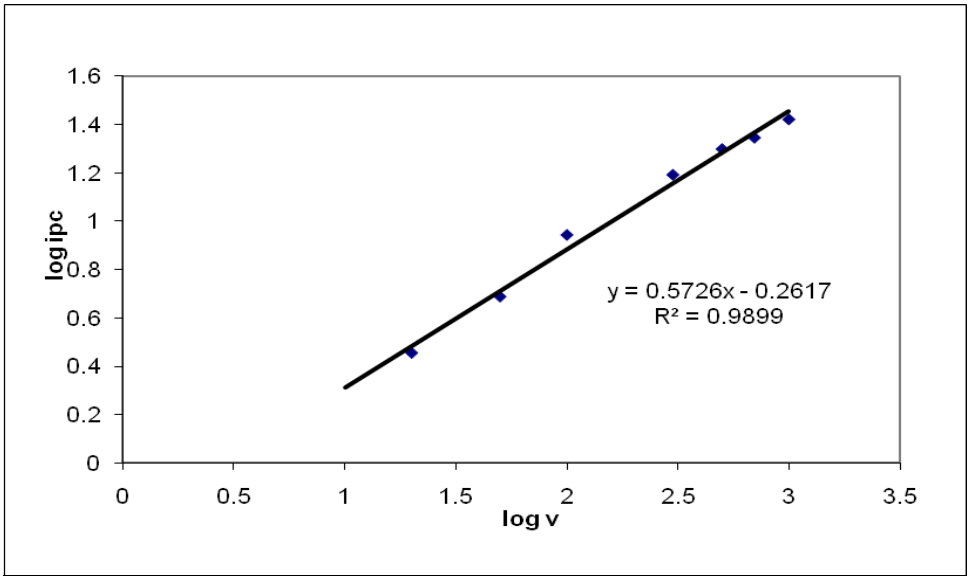


Figure 5. Graph of log I against log v of 1.0mM Pb(II) with 1 x 10^{-2}M nicotinic acid in 0.1M KCl using mercury as working electrode during CV with scan rate 10 mV/s to 1000 mV/s. Potential scanning in positive direction from 0 to -1000 mV.

3.6. Chronocoulometry

Chronocoulometry (CC) is the integral analogs of the corresponding chronoamperometry approaches. A double step chronocoulometric experiment for 1.0 mM Pb(II) ion with 1 x 10^{-2}M nicotinic acid onto mercury electrode was carried out in contact with 0.1 M KCl consists of an initial potential step from 0 to -1000 mV with 250 msec pulse width values, the out-put voltammograms is shown in Figure 6. The integral of the Cottrell equation gives the cumulative charge passed in reducing or oxidizing the diffused component [17]:

$$Q = 2nFAD^{1/2}C_o t^{1/2} / \pi^{1/2} \qquad (1)$$

where Q = Charge and the other parameters have its usual meanings

The diffusion coefficient, D of Pb-NA complex species is estimated to be equal to 9.18 x 10^{-6} cm^2/s, as compared with D of Pb(II) in KCl = 3.71 x 10^{-6} cm^2/s. Surface charge coverage of 1.0mM Pb(II) – 1 x 10^{-2}M nicotinic acid at a mercury electrode of 0.0304 cm^2 is estimated to be 5.0 μc/cm^2.

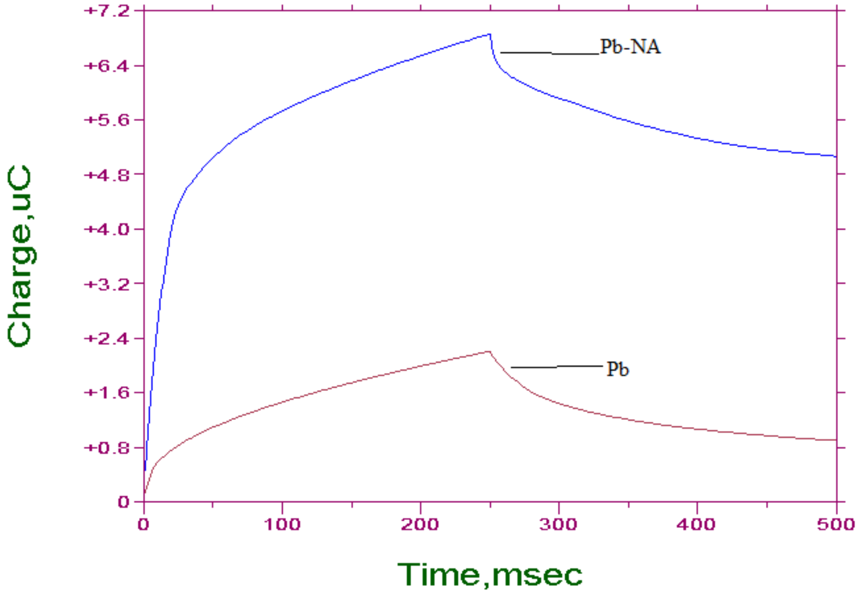


Figure 6. Chronocoulograms of 1.0 mM Pb(II), 0.1M KCl, 0.5M sodium acetate buffer pH 4.0 (a) without nicotinic acid (b) with 1 x 10^{-2}M nicotinic acid.

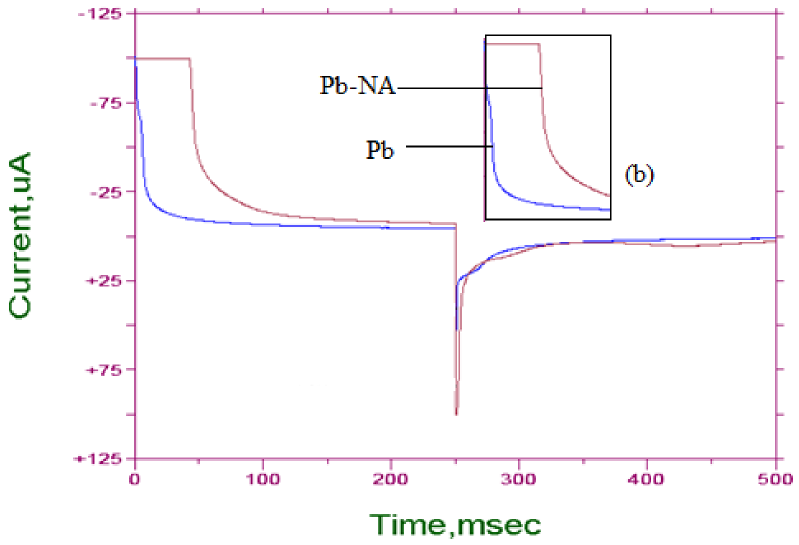
3.7. Chronoamperometry

Figure 7 shows the double step chronoamperomograms of 1.0 mM Pb(II) ion with 1x10^{-2} M nicotinic acid onto mercury electrode, reduced in 0.1 M KCl. The experiment is carried out with an potential step 0 to -1000 mV and reverse potential step from -1000 to 0 mV (versus Ag/AgCl, determined from usual run of CV). In Chronoamperometry (CA) the potential is stepped from an individual value E_i to E_t and the accompany current is recorded as a function of time for an electrode in unstirred solution [17]. The current decays as the electrolysis proceeds to deplete the solution near the electrode of electroinactive species. The current response is described by the Cottrell equation:

$$I = nFAC(D/\pi t)^{1/2} \qquad (2)$$

where I = Current
n = Number of electron per molecule
F = Faraday constant
A = Electrode area
D = Diffusion coefficient of electroactive species
C = Concentration of electroactive species
T = Time

Figure 7(b) shows the evidence of a surface process as the process of non-monotonic current transience observed by chronoamperomogram (Figure 7a) of Pb^{2+} solution.



(a)

Figure 7. Chronoamperograms of 1.0 mM Pb(II), 0.1M KCl, 0.5M sodium acetate buffer pH4.0 without and with 1 x 10^{-2}M nicotinic acid, (b) evidence of a surface process

3.7. Reproducibility

The sensitivity of cyclic voltammetry is accompanied by good reproducibility. This analytical performance was evaluated from five repeated measurement of electrochemical signal of 1 x 10^{-2}M nicotinic acid and 1.0mM lead ion solution with 100mV/s scan rate. From Table 2, the precision of the electrochemical developed method in terms of the relative standard deviation (RSD %) was 2.8%.

Table 2. Reproducibility data for of 1.0mM Pb(II) with 1 x 10^{-2}M nicotinic acid in 0.1M KCl, 0.5M sodium acetate buffer pH 4.0 during cyclic voltammetry

Scan rate, ν	CV of Pb(II)		RSD (%)
	Epa (mV)	Ipa (μA)	
100	-319	9.70	2.8
	-318	10.02	
	-318	10.29	
	-316	10.45	
	-317	10.06	

Table 3. Determination of lead in water samples.

Sample	Pb(II) found (ppm)
Sea water[a]	0.85
Sea water[b]	1.59

[a] Borders of the beach [b] Near the bridge

Table 4. Recovery data for Pb(II) ion spiked at known concentration into electroplating sample prepared in 0.05M KCl at pH 4 with 1 x 10^{-2}M nicotinic acid. Data was obtained using calibration curve. Currrent was obtained at 100 mV.

Sample	Added (ppm)	CV method Found (ppm)	Average deviation	Relative average deviation (%)	Recovery (%)	Mean recovery (%)
Electroplating		6.0			91	
waste	6.6	6.2	0.09	1.8	94	93
		6.2			94	
		15.2			76	
	20.0	14.6	0.4	2.6	73	74
		14.5			73	

3.8. Determination of Pb ions in water samples

In order to demonstrate its application in pratical analysis, this method was employed to detect Pb^{2+} in some water samples. 10 mililiters of water sample was added with 1 x10^{-2} M nicotinic acid at pH 4.0. After that, the square wave voltammetry peak current was measured for Pb^{2+} as analytical procedure. The concentration of Pb^{2+} was obtained by standard addition method and the result was shown at Table 3.

3.9. Recovery study of Pb(II) ion

The determination of Pb(II) ion concentration in 5mL of electroplating waste sample was carried out using mercury electrode (HDME) with 1 x 10^{-2} M nicotinic acid in 0.05M KCl electrolyte at pH 4.0. Recoveries experiments were evaluated using direct calibration based on Table 4. The recovery of 93% was obtained after the addition of 6.6 ppm of lead into electroplating waste while recovery of 74% was obtained after addition of 20.0 ppm of lead into electroplating waste.

4. CONCLUSION

The electrochemical properties of the redox reaction of Pb(II) ion in the presence of a ligand with N-heterocycle compounds, such as nicotinic acid (pyridine-3-carboxylic acid) were being studied using cyclic voltammetry (CV) on a hanging dropping mercury electrode (HDME). The highest enhancement was found to be on KCl with the enhancement factor of 4.9. Based on the scan rate and pH studies, the redox reaction of Pb(II) ion in the presence of nicotinic acid observed is 0.6 indicating complex surface process with optimum response at pH 4.0. The detection limit was 3.55 µM and the sensitivity of cyclic voltammetry is accompanied by good reproducibility. From chronocoulometry and chronoamperometry technique studied the diffusion for Pb(II) were estimated by 9.18 x 10^{-6} cm^2/s and 5.0 µc/cm^2 respectively. This method was successfully applied for determination of Pb(II) ion in some real samples.

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