



Recovery of lead from simulated wastewater by using stainless steel rotating cylinder electrode electrochemical reactor

Raid Tariq Hadi^a, Anas Bdiwi Salman^{b,*}, Safa Nabeel^b, Soud Ali Soud^b

^aChemical Engineering Department, University of Al-Muthanna, Baghdad, Iraq, email: dr.raidt@yahoo.com

^bChemical Engineering Department, University of Baghdad, Baghdad, Iraq, emails: anas1982_engineer@yahoo.com (A.B. Salman), safa1nabeel@yahoo.com (S. Nabeel), soudali2010@gmail.com (S.A. Soud)

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ABSTRACT

Recovery of lead from simulated wastewater was investigated in a batch mode rotating cylinder electrode reactor. Lead ions were cathodically reduced in a 0.5 M sodium chloride solution at a 316L stainless steel rotating cylinder electrode. These experiments were conducted for different Pb²⁺ concentrations (50, 100, 150 and 200 ppm), different values of solution pH (2, 3, 5 and 6.5) and different rotation rates (100, 150, 200 and 250 rpm). The potential under which the process is mass transfer control was found to be -1 V vs. standard calomel electrode, which is a reference electrode. Diffusion coefficient and diffusion layer thickness for this process was found experimentally. A dimensionless empirical correlation was constructed according to the experimental results among the Sherwood number, Reynolds number and Schmidt number.

Keywords: Electrodeposition; Lead; Rotating cylinder electrode; Mass transfer control

1. Introduction

Heavy metals represent serious environmental pollutants when discharged with effluents, due to their high toxicity and ability to accumulate in the human body and due to their non-degradability [1]. Lead is one of the most hazardous heavy metals and forms a basic reason of kidney, brain, reproductive system and liver damage [2].

Several methods for heavy metals removal have been used such as chemical precipitation [3], membrane separation [4,5], adsorption [6], ion exchange [7], electrochemical methods, coagulation and floatation [8]. In comparison with other treatment methods, electrochemical removal methods have the advantages of low cost, efficiency [9], versatility [10], recovery of the metal in its most valuable form of zero oxidation state, and avoiding generation of byproducts those need further treatment before discharging to environment [11].

Several industrial processes bring Pb(II) to environment in association with wastewater such as lead-acid batteries industries, fertilizers industries, paints industries, fuel combustion, vehicles emissions, lead-containing pipes [12].

As an electrochemical heavy metal removal process, rotating cylinder electrode reactor represents an efficient heavy metal removal process in high mass transfer turbulent flow regime [13], and good geometry to attain a high fractional conversion [14]. In addition to electrochemical recovery of heavy metals, rotating cylinder electrode is suitable for different studies such as alloy formation, Hull cell, corrosion and effluent treatment [15].

In the present work, removal of lead ions from dilute solution was investigated using a smooth stainless steel rotating cylinder electrode since turbulent convection could be attained at low rotation rates, uniform reaction rate at the cathode surface with well established mass transfer equations.

* Corresponding author.

2. Methodology

2.1. Experimental setup

The system used in this work consists of 1 L capacity electrochemical reactor configured as a three electrodes cell. The cathode (working electrode) is stainless steel (316L) cylinder with 3 cm diameter and 9 cm length. Four graphite plates (6.5 × 4 × 0.5 cm) arranged symmetrically around the cathode acted as the counter electrode (anode). A standard calomel electrode (SCE) was used as the third electrode, which is used to measure the cathode potential recorded during the experiments. The working electrode was rotated at different rotation rates using variable velocity electrical motor.

A DC power supply in association with multi-turn resistance and two multi-meters to monitor the current vs. potential during the linear cathodic sweep was utilized to construct the polarization curves. Schematic diagram of the system is shown in Fig. 1.

2.2. Solutions

Distilled water with sodium chloride salt with (99.99% purity) was used to prepare the supporting electrolyte, and lead chloride salt was used to obtain the required lead concentrations (50–200 ppm) in the supporting electrolyte.

Solution pH was adjusted using sodium hydroxide and hydrochloric acid.

3. Results and discussion

3.1. Reduction potential

Voltammograms for lead ions reduction were constructed by rotating cylinder electrode in hydrodynamic voltammetry mode. Potential was swept vs. an SCE at a scan rate of 50 mV s⁻¹ and recorded against current on the stainless steel rotating cylinder electrode for different Pb²⁺ concentrations (50, 100, 150 and 200 ppm) at different rotation rates (100, 150, 200 and 250 rpm) and pH equals to 6.5.

Voltammograms for these conditions are shown in Fig. 2.

This figure shows that the reduction potential for lead ions in 0.5 M sodium chloride solution is -1 V and this was

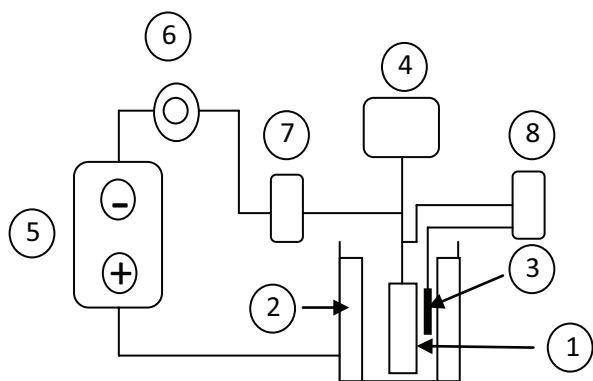


Fig. 1. Schematic diagram of the rotating cylinder electrode electrochemical reactor. (1) Rotating cylinder electrode, (2) graphite counter electrode, (3) SCE, (4) electrical motor, (5) DC power supply, (6) resistance, (7) multi-meter, (8) multi-meter.

determined at the centre point of the plateau of the polarization curves. This figure shows a wider plateau at lower rotation rates, and this is the behavior of mass transfer control electrochemical processes [16].

Table 1 shows the values of the limiting current for the present conditions.

This table shows that the limiting current increases when the lead ions concentration increases and this confirms the proportionality between the limiting current and the bulk concentration at mass transfer control conditions as supposed by Nernst equation. At lower rotation rates, the process is under mass transfer control conditions, and the proportionality between the limiting current and bulk concentration of electro-active species and the chemical polarization is nearly negligible. At higher rotation rates, chemical polarization becomes more significant and this will deviate the process from mass transfer control conditions and hence deviate the proportionality between the limiting current and bulk concentration.

The increase in rotation rate will reduce the diffusion layer thickness and this will enhance the mass transfer coefficient, which in turn enhances the step of mass transfer of the electro-active species to the electrode surface.

3.2. Initial lead ions concentration effect

Effect of lead ions concentration was studied for different lead ions concentrations (50, 100, 150 and 200 ppm) at constant cathode rotation rate of 150 rpm and pH of 6.5. Fig. 3 illustrates effect of concentration.

This figure shows that the limiting current increases with the increase in the lead ions concentration, and this effect becomes nearly negligible at concentrations higher than 150 ppm.

3.3. Effect of pH

To study effect of pH, four solutions were prepared at different pH values (2, 3, 5 and 6.5) with 50 ppm Pb²⁺, and the experiments were conducted at 150 rpm cathode rotation rate. Voltammograms for pH effect experiments are illustrated in Fig. 4.

This figure shows that the decrease in pH value will increase the limiting current value and reduce the plateau of the voltammograms, and for pH values lower than 3, no plateau will be defined. At lower pH values, hydrogen evolution reaction will be promoted, and this in turn will interrupt the mass transfer control process, and this is why the polarization curve plateau becomes smaller at lower pH.

3.4. Diffusivity

Eisenberg equation for rotating cylinder electrode was adopted to predict the diffusivity of Pb²⁺ ions in the simulated water solution [17]. This equation states that:

$$I_L = 0.0791nFC_0 u^{0.7} d^{-0.3} \nu^{-0.344} D^{0.644} \quad (1)$$

Fig. 5 shows the plot of the limiting current density I_L vs. $u^{0.7}$ from which the diffusion coefficient could be predicted.

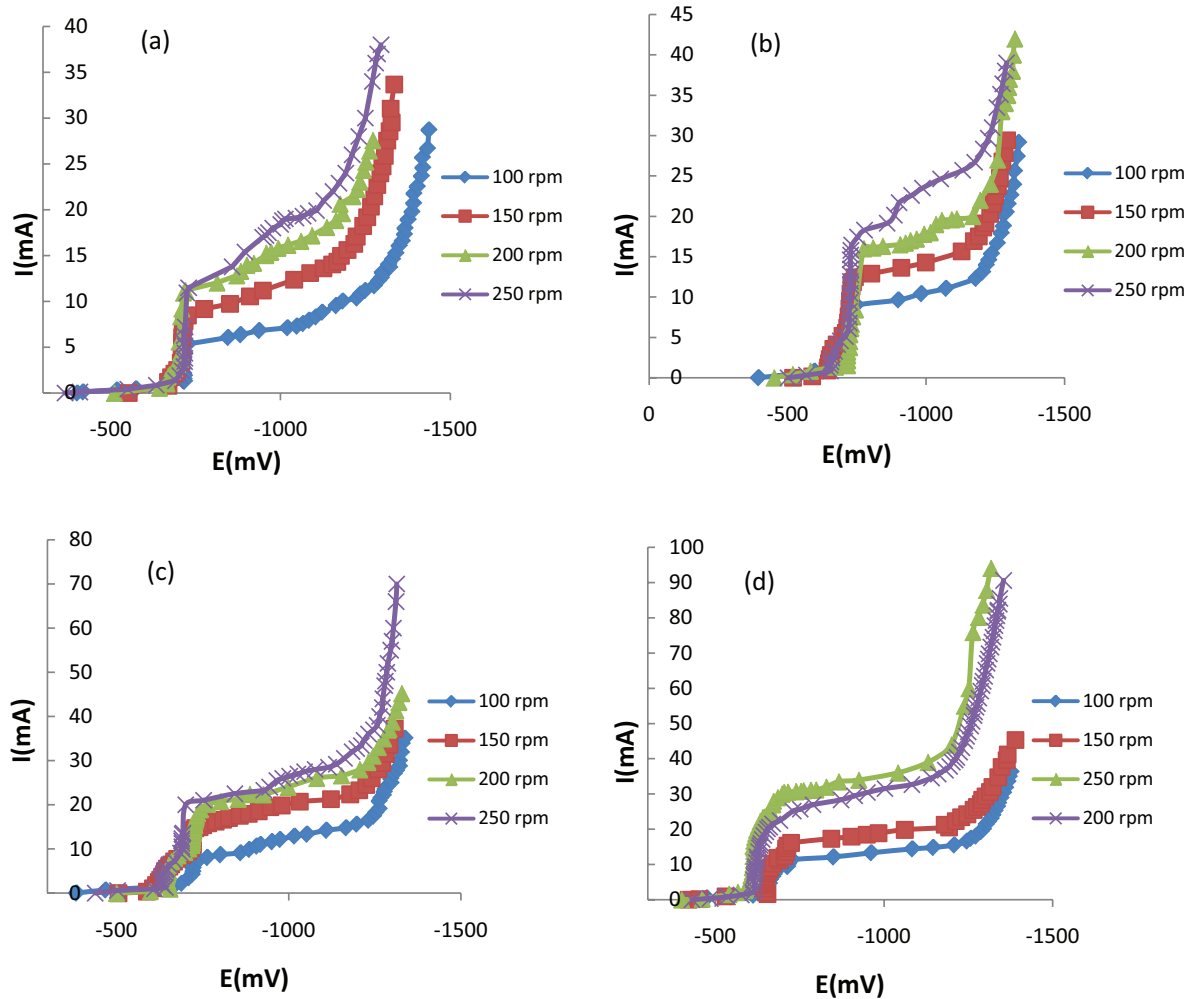


Fig. 2. Polarization curves for (a) 50, (b) 100, (c) 150 and (d) 200 ppm Pb²⁺.

Table 1
Limiting current at different conditions

Concentration ppm	<i>I_L</i> (mA)			
	100 rpm	150 rpm	200 rpm	250 rpm
50	6.8	12	17	19
100	10.5	14.32	18	23.5
150	12.8	20	22	24
200	14	19	30	35

Straight line behavior adopted by these figures indicates that the recovery process is mass transfer control process [16].

Values of diffusivity at different Pb²⁺ ions concentrations in 0.5 M NaCl solution are listed in Table 2.

3.5. Diffusion layer

Diffusion layer thickness was calculated according to the following equation [17]:

$$\delta = 99.62 \frac{d^{-0.4} v^{0.344} D^{0.356}}{S^{0.70}} \quad (2)$$

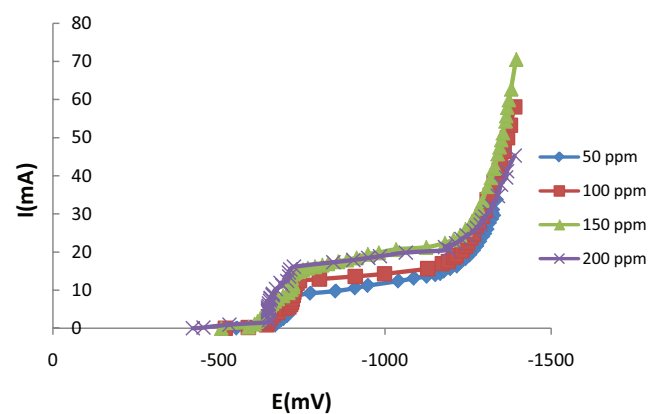


Fig. 3. Effect of Pb²⁺ ions concentration at 150 rpm rotation rate and pH = 6.5.

Values of diffusion layer thickness are listed in Table 3.

This table shows that the increase in lead ions concentration reduces the diffusion layer thickness and this effect becomes negligible above 150 ppm Pb²⁺ concentration which makes the electrodeposition recovery method more effective

at higher lead ions concentration since lower mass transfer resistance will be available at higher concentrations. On the other hand, the increase in rotation rate will significantly reduce the diffusion layer thickness and hence reduce the mass transfer resistance generated around the working electrode.

3.6. Mass transfer correlation

For rotating cylinder electrode working in turbulent flow region, the experimental results could be well expressed by

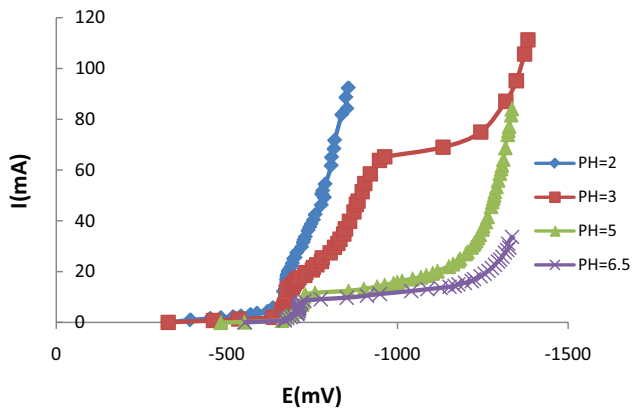


Fig. 4. Effect of pH at 50 ppm Pb²⁺ and 150 rpm rotation rate.

an empirical dimensionless groups correlation in the following form [18,19]:

$$Sh = k Re^a Sc^b \tag{3}$$

where *k*, *a* and *b* are constants.

The value of *b* could be assumed as *b* = 0.356 [20], and hence Eq. (4) will be:

$$Sh = k Re^a Sc^{0.356} \tag{4}$$

Experimental data for the present work is represented in Fig. 6.

This figure shows that the values of *k* and *a* for the present work are *k* = 0.0198 and *a* = 0.846 and hence, the empirical equation for the present work could be expressed as:

$$Sh = 0.0198 Re^{0.846} Sc^{0.356} \tag{5}$$

Table 2
Diffusivity of Pb²⁺ in 0.5 M NaCl solution at pH = 6.5

Concentration (ppm)	Diffusion coefficient (cm ² /s)
50	6.58913E-05
100	4.23085E-05
150	2.26156E-05
200	2.26292E-05

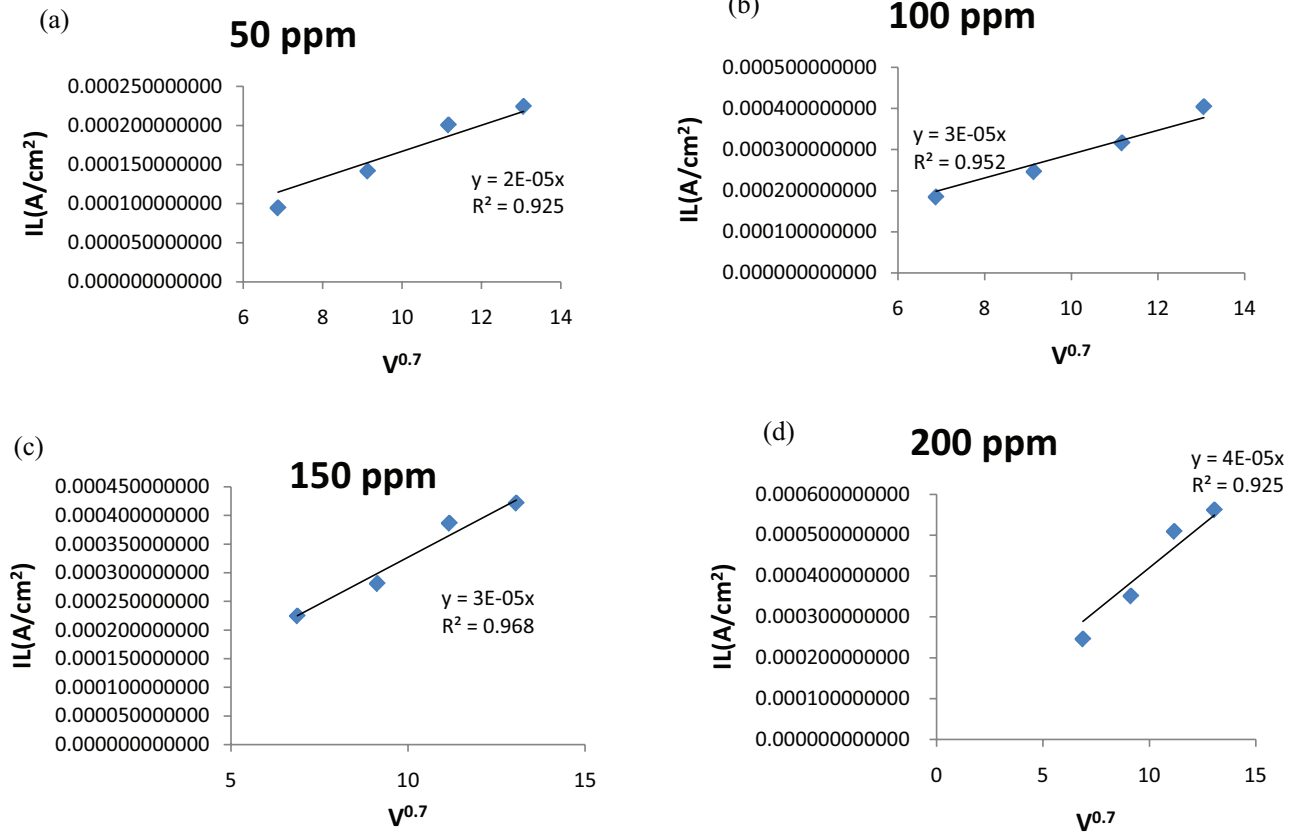


Fig. 5. Determination of diffusivity by Eisenberg equation at (a) 50 ppm, (b) 100 ppm, (c) 150 ppm, (d) 200 ppm.

Table 3
Diffusion layer thickness of Pb^{2+} in 0.5 M NaCl solution at pH = 6.5

Concentration ppm	Diffusion layer thickness (cm)				
	50 rpm	100 rpm	150 rpm	200 rpm	250 rpm
50	0.0270	0.0166	0.0125	0.0102	0.0088
100	0.0231	0.0142	0.0107	0.0088	0.0075
150	0.0185	0.0114	0.0086	0.0070	0.0060
200	0.0185	0.0114	0.0086	0.0070	0.0060

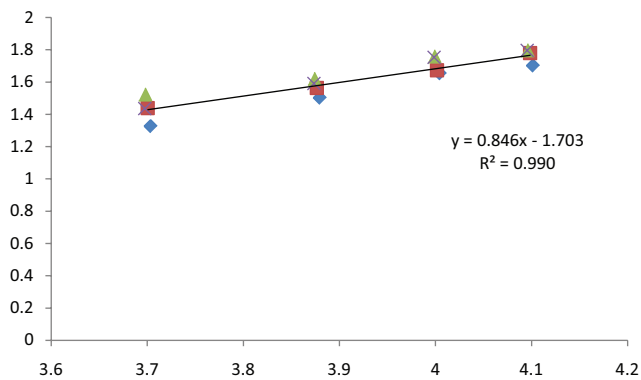


Fig. 6. Mass transfer correlation of experimental data.

4. Conclusions

- Three electrodes configuration electrochemical reactor with stainless steel rotating cylinder electrode was used to construct the polarization curves for lead recovery from simulated wastewater solution in 0.5 M NaCl solution.
- Reduction potential for Pb^{2+} in 0.5 M NaCl solution was found to be -1 V, and this was the reduction potential under which the recovery is mass transfer control process.
- The limiting current for lead recovery in 0.5 M NaCl solution is proportional to Pb^{2+} concentration and this proportionality becomes nearly negligible for concentrations above 150 ppm, and the limiting current is inversely proportional to pH, and this proportionality becomes nearly negligible at pH higher than 5.
- Reduction potential range under which the process is mass transfer control becomes wider at higher pH, since the hydrogen evolution reaction will be inhibited at higher pH, which in turn prevents the mass transfer process interruption.
- The increase in Pb^{2+} concentration reduces the diffusion layer thickness and this effect will be nearly negligible at concentrations higher than 150 ppm, and the increase in the rotation rate will reduce the boundary layer thickness which in turn enhance the mass transfer.
- The experimental data are well correlated by the following empirical correlation:

$$Sh = 0.0198Re^{0.846} Sc^{0.356}$$

Symbols

- A — Electrode surface area, cm^2
 C_o — Lead initial concentration, mol/m^3 or ppm
 CR — Correlation coefficient
 D — Diffusion coefficient of lead, cm^2/s
 d — Electrode diameter, cm
 E — Electrode potential, mV
 F — Faraday constant = 96,485 coulomb
 I — Current, A
 I_L — Limiting current density, mA
 L — Electrode length, cm
 n — Charge number of electrode reaction
 Re — Reynolds number = ud/ν
 S — Rotation rate, rpm
 Sc — Schmidt number = ν/D
 Sh — Sherwood number = $k_m d/D$
 u — Peripheral speed of the rotating cylinder, m/s
 ν — Kinematic viscosity, m^2/s
 δ — Diffusion layer thickness, cm

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