Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.903520

54 (2015) 2557–2563
May

Taylor & Francis
Taylor & Francis Group

Electrochemical removal of cadmium from simulated wastewater using a smooth rotating cylinder electrode

Abbas Hamid Sulaymon, Basma A. Abdulmajeed, Anas B. Salman*

Chemical Engineering Department, University of Baghdad, Baghdad, Iraq, Email: anas1982_engineer@yahoo.com

Received 2 June 2013; Accepted 26 February 2014

ABSTRACT

Rate of mass transfer to a smooth stainless-steel rotating cylinder electrode was found by measuring the limiting current for the cathodic reduction of Cd^{2+} in 0.5 M sodium sulfate supporting electrolyte in hydrodynamic voltammetry mode. The studied parameters were electrolyte pH (4, 5, 6, and 7), initial Cd^{2+} concentrations (50, 100, 200, 300, and 400 ppm), and rotation rates (100, 150, 200, and 250 rpm). Reduction potential for mass transfer control conditions was found to be –0.13 V. Diffusion coefficient was determined and correlated with the bulk concentration of Cd^{2+} in sodium sulfate solution. The experimental data were well fitted by an empirical dimensionless correlation among the Sherwood number, Reynolds number, and Schmidt number.

Keywords: Hydrodynamic voltammetry; Cadmium; Electrodeposition; Rotating cylinder electrode

1. Introduction

Heavy metals in wastewaters form a serious environmental problem, since these are not biodegradable, and may cause a serious human and environmental impact when they are released into the environment as a result of bioaccumulation, and extremely toxic even in trace amounts [1].

One of the most toxic non-essential heavy metals is cadmium. The main source for cadmium is the wastewater from industries; such as plating, rechargeable batteries (Ni–Cd batteries), alloy, pigments, phosphate fertilizers, solar energy capture devices, stabilizers, petroleum refining, welding, and pulp industries [2–4].

Cadmium human impacts include; kidney damage [5], cancer, lung problems, changing the composition of bones, liver, and blood problems [6]. World Health Organization recommended that cadmium quantity in drinking water should not exceed 0.005 mg/L [7].

Different methods were modified for cadmium removal from wastewater. Conventional methods include; ion exchange, reverse osmosis, co-precipitation, coagulation, solvent extraction, adsorption, and electrochemical treatment [7–9]. Ion exchange and reverse osmosis were proven to be either too expensive or inefficient to remove cadmium from wastewater. Chemical treatment is inefficient due to several disadvantages like, high cost maintenance, problem of sludge handling, and its disposal. Adsorption by different materials was proven to have low efficiency and high cost [7]. Electrochemical deposition was found to be an alternative to the above conventional methods for cadmium removal [10].

---

*Corresponding author.

In the present work, electrochemical removal of cadmium in hydrodynamic mode with rotating cylinder electrode was utilized. The main features of rotating cylinder electrode include: [11]

- It provides a simulation conditions for turbulent convection at low rotation rates since it can attain turbulent convection at Re < 100.
- It promotes a uniform reaction rate over the cathode due to uniform potential and current distribution.
- Ability to enhance mass transfer using rough electrodes.
- Mass-transfer equations are well established.

2. Experimental work and materials

2.1. Apparatus

An 800 mL electrochemical cell with three electrodes configuration was used in this work. A stainless-steel (316 L) cylinder of diameter 3.39 cm and length 8 cm was used as a working electrode. The anodes were constructed using four carbon plates, each of length 5 cm, width 5 cm, and thickness 0.3 cm. These plates were distributed symmetrically around the rotating cylinder. Cathode potential was measured vs. standard calomel electrode. Electrical motor with digital tachometer (Heidolph Company Germany) was used to rotate the working electrode at different rotation rates.

A DC power supply with two resistance boxes were used for the linear cathodic sweep for the construction of polarization curves. Current and cathode potential were measured using two digital multi-meters (Kyoritsu 1,009). Negative terminal of the power supply was connected to the working electrode via aluminum plate as a current feeder, while the positive terminal of the power supply was connected to the counter electrode. The schematic diagram of the rotating cylinder electrochemical cell is shown in Fig. 1.

2.2. Materials

Electrolytic solution used in the present work was a 0.5 M sodium sulfate solution with concentrations of cadmium ion prepared in the range (50–400 ppm). The solution was prepared using analytical grade Na_2SO_4 reagent and distilled water. Analytical grade cadmium sulfate salt was used to obtain the desired concentration.

Solution pH was adjusted by means of sulfuric acid and sodium hydroxide. Table 1 lists the physical properties of the electrolyte at pH = 7.

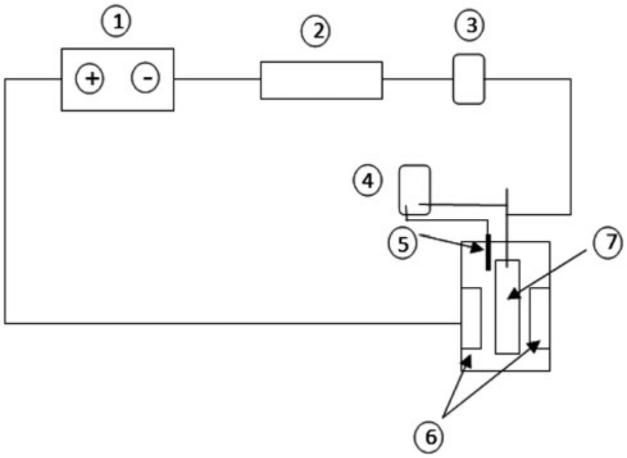

Fig. 1. Schematic diagram of the rotating cylinder electrochemical cell. (1) DC power supply, (2) resistance box, (3) ammeter, (4) voltmeter, (5) standard calomel electrode, (6) counter electrode, and (7) rotating cylinder working electrode.

Table 1
Physical properties of the electrolyte

Concentration (ppm)	Density (g/cm^3)	Viscosity (cst)
50	1.057	0.715
100	1.056	0.724
200	1.053	0.731
300	1.052	0.735
400	1.05	0.745

3. Results and discussion

3.1. Reduction potential

Reduction reaction was carried out at mass transfer control conditions. Reduction potential was determined via a series of voltammograms those were obtained from a rotating cylinder electrode in hydrodynamic voltammetry mode. Potential was swept on a stainless-steel rotating cylinder electrode at rotation rates, (100, 150, 200, and 250 rpm) and initial concentrations of Cd^{2+} solutions, (50, 100, 200, 300, and 400 ppm), respectively.

Fig. 2(a)–(e) shows a series of voltammograms for cadmium ion concentrations (50, 100, 200, 300, and 400 ppm), respectively, at different rotation rates.

Reduction potential was determined as the midpoint of the plateau in the polarization curves. These were found to be (–1,000 to –1,600 mV). The midpoint of this range is –1,300 mV and this is the appropriate potential for Cd^{2+} reduction for the used solution.

These figures also show that the plateau of polarization curves are wider at lower rotation rates, this is

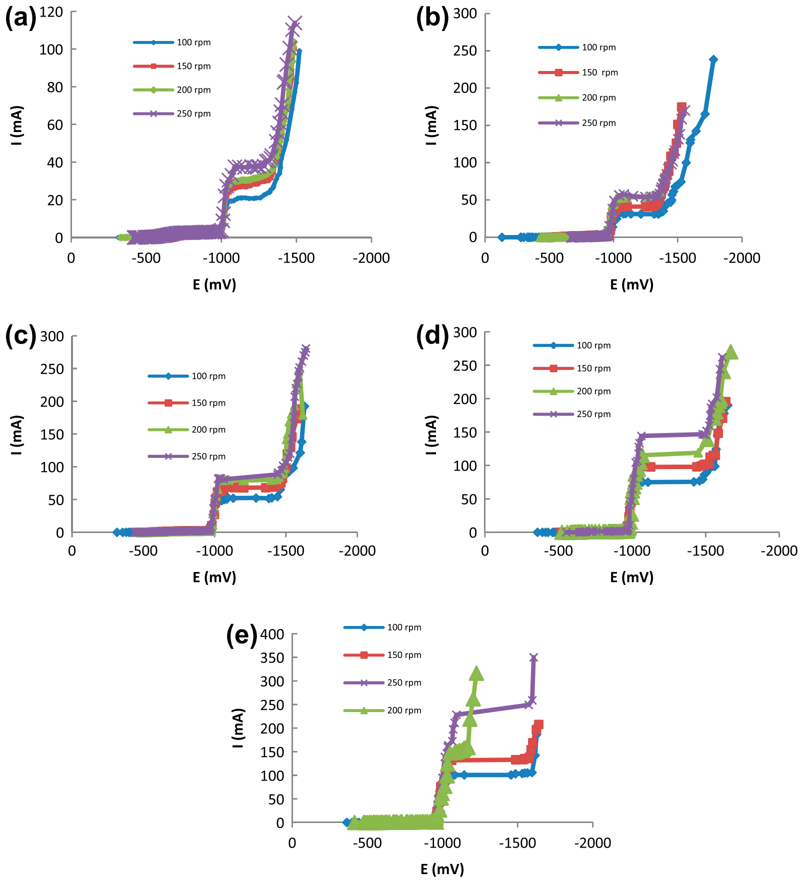

Fig. 2. Voltammograms for reduction (a) 50, (b) 100, (c) 200, (d) 300, and (e) 400 ppm Cd^{2+}.

the characteristic behavior of mass transfer controlled electrochemical process [12].

Values of limiting current for different concentrations and rotation rates were determined from these voltammograms. These values are listed in Table 2.

It is obvious from this table that the limiting current increased with increase in the initial cadmium concentration. This behavior was expected since the limiting current was proportional to the bulk concentration under mass transfer control conditions, and this proportionality was expressed by the Nernst equation. Limiting current increased with increase in the rotation rate, since the increase in rotation rate will increase the mass transfer coefficient due to the decreasing boundary layer thickness [13].

Table 2
Limiting current for different concentrations and rotation rates

	Limiting current (mA)			
Concentration (ppm)	100 rpm	150 rpm	200 rpm	250 rpm
50	16.5	24	28.2	33.7
100	27	39	50	57
200	50	64	77	86
300	75	97.5	112	130
400	80	120	147	181

3.2. *Effect of initial cadmium concentration*

Initial concentration effect was studied by conducting hydrodynamic voltammetry experiments at 200 rpm for five different initial concentrations (50, 100, 200, 300, and 400 ppm). Increasing the initial concentration was found to increase the limiting current. This effect is shown in Fig. 3.

3.3. *Effect of pH*

Effect of pH was obtained by conducting hydrodynamic voltammetry experiments at pH (4, 5, 6, and 7); 200 rpm rotation rate, and 100 ppm Cd^{2+} initial concentration. This effect is shown in Fig. 4.

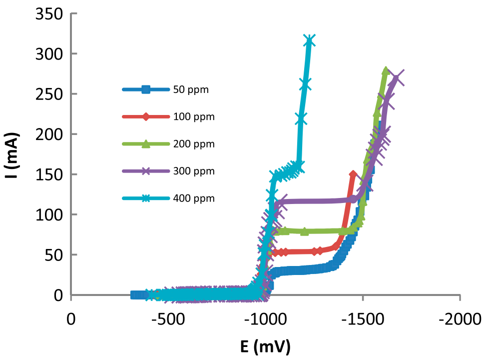

Fig. 3. Effect of initial Cd^{2+} concentration at rotation rate of 200 rpm.

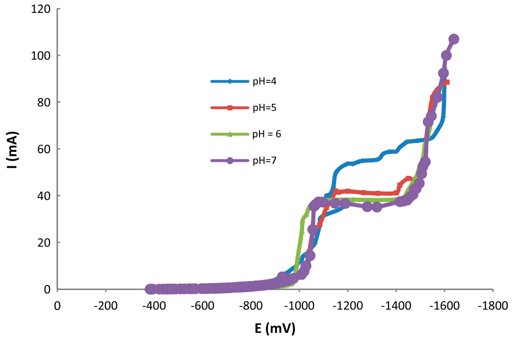

Fig. 4. Effect of initial pH value at 100 ppm initial concentration and 200 rpm rotation rate.

Fig. 4 shows that the limiting current is inversely proportional with pH, i.e. the limiting current decreases with increase in the pH, with a tendency to be nearly constant at pH above 5, but there will be a little change in limiting current value with respect to pH, and this effect will be completely negligible for pH at 7 and above. This could be attributed to the fact that the hydrogen evolution reaction will be negligible at pH 7. This figure also shows that the plateau will

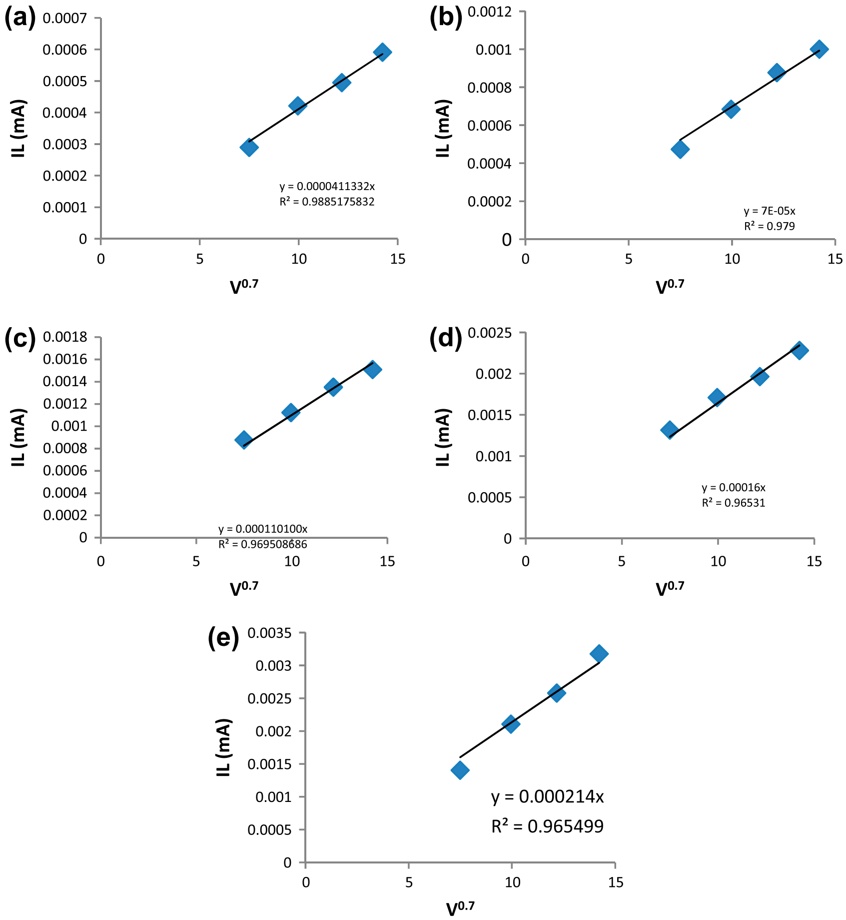

Fig. 5. Eisenberg equation plot for diffusivity determination at (a) 50, (b) 100, (c) 200, (d) 300, and (e) 400 ppm Cd^{2+}.

Table 3
Diffusion coefficient for Cd^{2+} in aqueous solution at 298 K

Initial concentration (ppm)	Diffusion coefficient (cm^2/s)
50	3.77819E−05
100	3.09126E−05
200	2.137E−05
300	2.04292E−05
400	2.00833E−05

be hardly defined for low pH values. This behavior is thought to be resulted from the fact that the decrease in pH value will promote hydrogen evolution reaction at the cathode, and this in turn will interrupt the reduction process under mass transfer conditions, and hence interrupt the limiting current plateau [12].

3.4. Diffusion coefficient

Cadmium diffusion coefficient in the aqueous solution was determined using Eisenberg Eq. (1) for rotating cylinder electrode cell [12]:

$$I_l = 0.0791nFC_oV^{0.7}d^{-0.3}\upsilon^{-0.344}D^{0.644} \quad (1)$$

Diffusion coefficient was calculated by plotting limiting current vs. $V^{0.7}$ as shown in Fig. 5(a)–(e).

These figures have the shape of straight lines, and this confirms that the process was a mass transfer controlled one [12]. Values of diffusion coefficient for different initial concentrations are tabulated in Table 3.

To correlate the diffusion coefficient with the bulk Cd^{2+} initial concentration; the diffusion coefficients were plotted against the Cd^{2+} initial bulk concentration as shown in Fig. 6. This figure represents a polynomial relationship which can be expressed by Eq. (2):

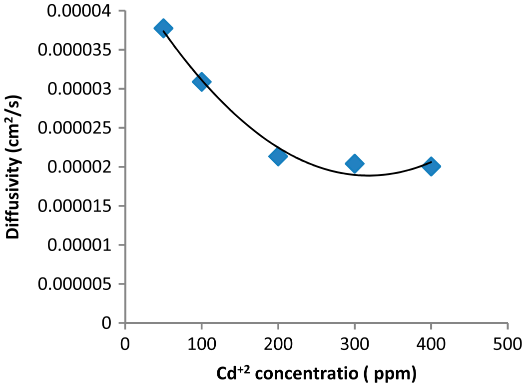

Fig. 6. Variation of diffusivity of Cd^{2+} with initial Cd^{2+} concentration.

$$D = 4 \times 10^{-10}C_o^2 - 2 \times 10^{-7}C_o + 5 \times 10^{-5} \quad (2)$$

3.5. Diffusion layer

Diffusion layer thickness was determined at different rotation rates utilizing Eq. (3): [14]

$$\delta = 99.62\frac{d^{-0.4}\upsilon^{0.344}D^{0.356}}{S^{0.70}} \quad (3)$$

The diffusion layer thickness values are listed in Table 4.

3.6. Mass transfer correlation

It was found that mass transfer to a rotating cylinder electrode in turbulent flow may be expressed by empirical dimensionless correlation: [15]

$$Sh = KRe^aSc^b \quad (4)$$

where Sherwood, Reynolds, and Schmidt numbers represent mass transport, fluid flow, and transport properties of electrolyte.

Some previous works have derived a value of b as $b = 0.356$ [16], and hence Eq. (4) will be:

$$Sh = KRe^aSc^{0.356} \quad (5)$$

Experimental data in the present work was correlated as shown in Fig. 7.

From Fig. 7, values of K and a in Eq. (5) were found to be $a = 0.769$ and $K = 0.047$. Hence, Eq. (5) may be written for the cell used in this work as:

$$Sh = 0.047\,Re^{0.769}Sc^{0.356} \quad (6)$$

Table 4
Diffusion layer thickness for different concentrations and rotation rates

Concentration (ppm)	Diffusion layer thickness (cm)			
	100 rpm	150 rpm	200 rpm	250 rpm
50	0.011848	0.008921	0.007294	0.006239
100	0.011079	0.008341	0.00682	0.005834
200	0.009747	0.007338	0.006	0.005132
300	0.00961	0.007235	0.005916	0.00506
400	0.009596	0.007225	0.005907	0.005053

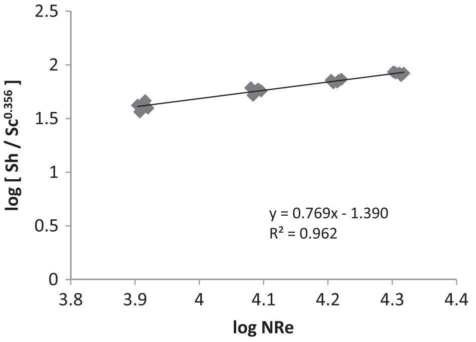

Fig. 7. Empirical correlation for experimental data.

Conclusions

(1) A stainless-steel rotating cylinder electrode operating in batch mode was used to generate the polarization curves for the reduction of Cd^{2+}. From the determined current plateaus, the limiting currents and the potential range under which the reduction reaction is mass-transfer controlled.

(2) The reduction potential of Cd^{2+} ion in 0.5 M Na_2SO_4 electrolyte solution at pH = 7 was found to be –1,300 mV, and this was mounted as the midpoint of voltammograms' plateau.

(3) The limiting current (at which the process was mass-transfer control) was directly proportional with the initial Cd^{2+} concentration, and rotation rate, and inversely proportional to pH with a tendency to be nearly constant at pH above 5, this proportionality with respect to pH values will be completely negligible at pH 7.

(4) The range of potential under which the process is mass-transfer controlled is wider at higher pH values, since the mass-transfer controlled reduction process will be interrupted by hydrogen evolution reaction at lower pH values.

(5) The diffusion coefficient of cadmium in 0.5 M Na_2SO_4 solution was correlated with initial cadmium concentration to have the following polynomial equation with ($R^2 = 0.979$).

$$D = 4 \times 10^{-10} C_o^2 - 2 \times 10^{-7} C_o + 5 \times 10^{-5}$$

(6) The boundary layer thickness was found to decrease with increase in the rotation rate (i.e. increase in Reynolds number), since the increase in rotation rate will reduce the laminar sub-layer thickness, and this in turn will decrease the boundary layer thickness.

(7) The overall mass transfer correlation that correlates Sherwood, Reynolds, and Schmidt numbers was found:

$$Sh = 0.047\, Re^{0.769} Sc^{0.356}$$

Symbols

A — electrode surface area (cm^2)
C_o — cadmium initial concentration (mol/m^3 or ppm)
CR — correlation coefficient
D — diffusion coefficient of cadmium (cm^2/s)
d — electrode diameter (cm)
E — electrode potential (mV)
F — Faraday constant = 96,485 coulombs
I — current (A)
I_l — limiting current (mA)
L — electrode length (cm)
n — charge number of electrode reaction
Re — Reynolds number = ud/v
S — rotation rate (rpm)
Sc — Schmidt number = v/D
Sh — Sherwood number = $k_m d/D$
U — rotation rate (m/s)
V — kinematic viscosity (m^2/s)

References

[1] V. Hiatt, J.E. Huff, The environmental impact of cadmium: An overview, Int. J. Environ. Stud. 7 (1975) 277–285.

[2] M. Tsezos, Biosorption of metals. The experience accumulated and the outlook for technology development, Hydrometallurgy 59 (2001) 241–243.

[3] Y. Sag, Y. Aktay, Kinetic studies on sorption of Cr(VI) and Cu(II) ions by chitin, chitosan and rhizopus arrhizus, Biochem. Eng. J. 12 (2002) 143–153.

[4] K. Bedoui, Bekri-Abbes, Removal of cadmium (II) from aqueous solution using pure smectite and Lewatite S 100: The effect of time and metal concentration, Desalination 223 (2008) 269–273.

[5] E. Kobayashi, Y. Okubo, Y. Suwazono, Environmental cadmium exposure, adverse effects and preventive measures in Japan, Biometals 17 (2004) 581–587.

[6] L. Friberg, Cadmium, Ann. Rev. Public Health 4 (1983) 367–373.

[7] V. Subramanyan, L. Jothinathan, P. Murthy, Electrocoagulation studies on removal of cadmium using magnesium electrode, J. Appl. Electrochem. 40 (2010) 2023–2032.

[8] L. Jothinathan, Y. Subramanyan, Effects of alternating and direct current in electro-coagulation process on the removal of cadmium from water—A novel approach, Sep. Purif. Technol. 80 (2011) 643–651.

[9] S. Vasudevan, J. Lakshmi, G. Sozhan, Effects of alternating and direct current in electro-coagulation process on the removal of cadmium from water, J. Hazard. Mater. 192 (2011) 26–34.

[10] X. Chen, G. Chen, P.L. Yue, Investigation on the electrolysis voltage of electro-coagulation, Chem. Eng. Sci. 57 (2002) 2449–2455.
[11] D.R. Gabe, G.D. Wilcox, J. Gonzalez-Garcia, F.C. Walsh, The rotating cylinder electrode: Its contiued development and application, J. Appl. Electrochem. 28 (1998) 759–780.
[12] A.H. Sulaymon, A.O. Sharif, T.K. Al-shalchi, Removal of cadmium from simulated wastewater by electrodeposition on stainless steel bundle electrode, Desalin. Water Treat. 29 (2011) 218–226.
[13] J. David Picket, Electrochemical Reactor Design, Elsevier, Manchester, 1977.
[14] M. Eisenberg, C.W. Tobias, Ionic mass transfer and concentration polarization at rotating electrodes, J. Electrochem. Soc. 101 (1954) 306–320.
[15] D.R. Gabe, F.C. Walsh, The rotating cylinder electrode: A review of development, J. Appl. Electrochem. 13 (1983) 3–22.
[16] R.A. Scannell, F.C. Walsh, Comparative mass transfer, and electrode area in electrochemical reactors, Inst. Chem. Eng. Symp. Ser. 112 (1989) 59–71.