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Removal of cadmium from simulated wastewater by using stainless steel concentric tubes electrochemical reactor

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ABSTRACT

Performance of a pilot scale, flow-through electrochemical reactor with stainless steel concentric tubes electrode was investigated for the removal of cadmium from simulated waste-water in batch-circulation mode. Cathodic reduction of Cd^{2+} was conducted in a 0.5 M Na_2SO_4 supporting electrolyte solution. Effect of pH, initial cadmium concentration, and electrolyte flow rate were studied. Figures of merit were introduced in order to show the reactor's performance. Results were correlated in the following dimensionless correlation $Sh = 0.016Re^{1.126}Sc^{1/3}$:

Keywords: Electrodeposition; Cadmium; Concentric tubes cathode; Flow-through cell; Mass transfer control

1. Introduction

Heavy metal species in wastewater form a serious environmental problem since they are not biodegradable, and they may cause a serious human and environmental impact when they are released to environment as a result of bioaccumulation. They are extremely toxic even in trace amount [1]. One of the most toxic non-essential heavy metals is cadmium. The main source for cadmium is the wastewater from different 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].

Electrochemical deposition was found to be a good alternative to other conventional methods for cadmium removal [5]. Electrochemical reactors could be well designed in order to have high efficiency in removal process. Electrochemical reactor performance could be analyzed and compared by introducing "figures of merit" [6–9]. There are several ways to define figures of merit depending upon its relationship to processing time and reactor space. Batch-recycle reactor could be simply treated and modeled as a simple batch reactor. Concentration decay for such a system could be expressed as:

$$\ln\left(\frac{C_{(t)}}{C_o}\right) = -\frac{V_e k_m A_e t}{V_T} \tag{1}$$

Fractional conversion for reactants in batch recycle reactor is given by the following equation: [10–13]

$$X_{(t)} = 1 - \exp\left(-k_m A_e t\right) \tag{2}$$

Current efficiency could be expressed as:

$$\beta_{(t)} = \frac{nFVC_{(o)}X_{(t)}}{\int_0^t I_{(t)}dt} \tag{3}$$

Mass transfer in electrochemical reactors could be correlated with the following generalized mass transfer dimensionless correlation: [14]

$$Sh = m\mathrm{Re}^n Sc^{1/3} \tag{4}$$

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2. Experimental work

2.1. Apparatus

In the present work, electrodeposition was conducted in a pilot scale flow-through reactor working in batch-recycle mode. Schematic diagram of the pilot plant illustrated in Fig. 1.

Electrolytic cell container and piping system were constructed from Teflon material. Two glass reservoirs with 10 l capacity were used as a catholyte and anolyte reservoirs. Pumps with 700 l/h discharge capacity, with Teflon impeller were used to pump the electrolytic solutions from reservoirs to the cell.

Electrolytic solutions flow rates were controlled by means of variation of the feed and recycle valves, and they were recorded via flow meters.

Electrolytic cell consists of a Teflon box with (25 × 25 × 19 cm) dimensions, and this in turn divided into two compartments; catholyte chamber and anolyte chamber. Catholyte chamber was with (25 × 25 × 17 cm) dimensions, and it was constructed from three Teflon plates. The terminal plate is solid, while the two other plates contain a central hole with 20 cm internal diameter, and rubber gasket separators to prevent solution leakage. Cationic membrane (Product No. MA-3475, Syborn Chemicals Inc., Brimming, NJ), was used to separate between catholyte and anolyte chambers. Anode chamber was constructed from a (25 × 25 × 5 cm) Teflonplate with central hole of 20 cm internal diameter.

Stainless steel (316L) concentric tubes cathode was installed inside the catholyte chamber with a distributer at the catholyte entrance to distribute the inlet solution. Cathode consisted of eight concentric stainless steel tubes with the dimensions listed in Table 1.

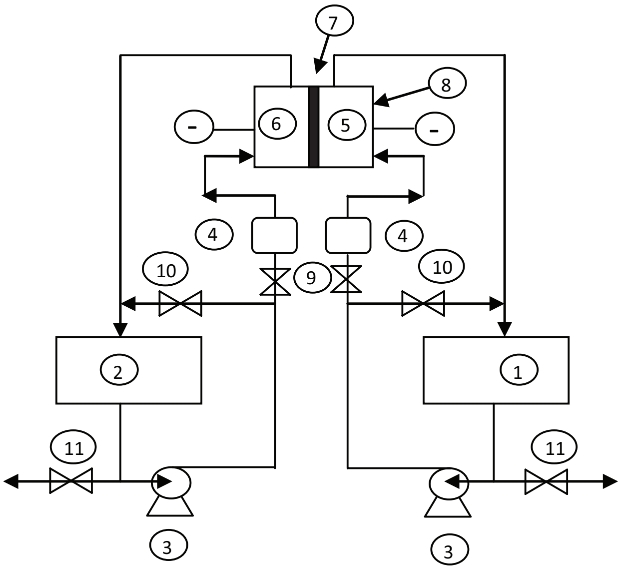

Fig. 1. Schematic diagram of the pilot plant batch-recycle system. (1) Anolyte reservoir, (2) Catholyte reservoir (3) Pumps, (4) Flow meters, (5) Catholyte chamber, (6) Anolyte chamber, (7) Cationic membrane, (8) Electrolytic cell, (9) Inlet valves, (10) Recycle valves, (11) Drain valves.

A carbon disk with 14 cm diameter and 1 cm thickness was used as an anode. Cathode potential was measured against SCE by a voltmeter (Kyoritsu model 1009).

2.2. Materials

Electrolytic solution used in the present work was a 0.5 M sodium sulphate solution with different initial cadmium concentrations of (50, 100, 200, 300, and 400 ppm) as a catholyte. Anolyte solution was 0.5 M Na_2SO_4 solution. The solutions were prepared by using analytical Na_2SO_4 reagent and distilled water. Analytical cadmium sulphate salt has been used to obtain the desired concentration.

Solution pH has been adjusted by means of sulphuric acid and sodium hydroxide. Table 2 lists the physical properties of the electrolyte.

3. Results and discussion

3.1. Effect on initial concentration

Effect of initial cadmium concentration was studied by conducting experiments at 200 l/h, and pH = 7 for different initial cadmium concentrations (50, 100, 200, 300, and 400 ppm).

A normalized concentration (C/C_o) was plotted as a function of time, and this plot is shown in Fig. 2.

This figure shows that the cadmium concentration decays exponentially with time. This decay is steeper for low concentrations, and this is thought to be caused by hydrogen evolution reaction. At low concentrations, the area available for hydrogen evolution reaction will be

Table 1
Geometric dimensions of the cathode

Tube number	Inner diameter (mm)	Outer diameter (mm)
1	39.23	40.95
2	62.93	64.65
3	82.08	83.8
4	101.6	103.32
5	125.71	127.43
6	147.74	149.46
7	168	169.72
8	191	192.72

Table 2
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

higher, and this will promote hydrogen evolution reaction to be the predominant reaction, and this in turn will promote mass transfer coefficient via bubbles turbulency, and hence increase the rate of cadmium reduction leading to a deeper decay for low concentrations.

Standard cadmium discharge limit (less than 2 ppm), could be attained in 225 min for 50 ppm initial cadmium concentration, while for higher cadmium initial concentrations; the allowable discharge limit needs a high relative time to be attained. To realize the allowed discharge limits in case of high initial concentrations, cascaded electrodes could be used.

In order to calculate mass transfer coefficient k_m, the plot of ln (C/C_o) vs. time could be utilized, and this plot will give a straight line with a slope equals to $(k_m A/V_T)$. This plot is shown in Fig. 3.

From this figure, mass transfer coefficient could be predicted for different values of initial cadmium concentration (50, 100, 200, 300, and 400 ppm). These values are 5.45 E-4, 4.431 E-4, 3.749 E-4, 2.045 E-4, and 1.363 E-4 respectively.

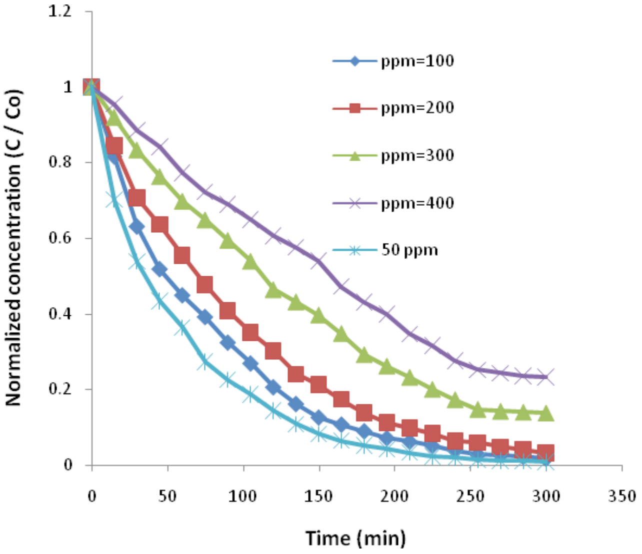

Fig. 2. Normalized concentration (C/C_o) as a function of time for cadmium removal at different initial cadmium concentration.

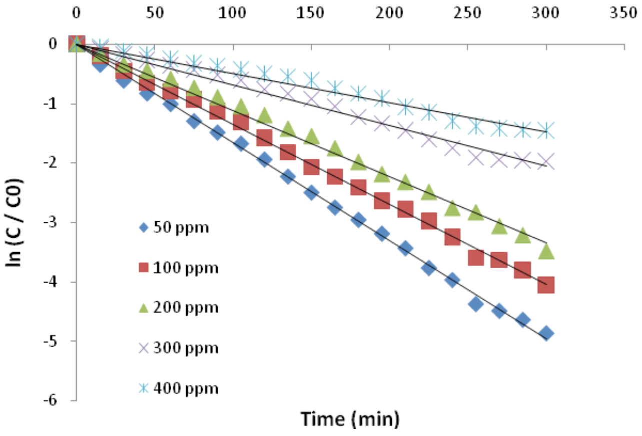

Fig. 3. Linearization of normalized concentration (C/C_o) as a function of time for different initial cadmium concentration and 200 l/h.

To correlate mass transfer coefficient with initial cadmium concentration, the predicted values of mass transfer coefficient were plotted versus initial cadmium concentration as shown in Fig. 4.

From this plot, data was correlated with (CR = 0.98) in the following form:

$$k_m = 6\times10^{-10}C^2 - 1\times10^{-6}C \tag{5}$$

3.2. Effect of pH

Experiments were conducted at 200 ppm initial cadmium concentration and 200 l/h flow rate for different pH values of (4, 5, 6, and 7).

Normalized concentration as a function of time is shown in Fig. 5.

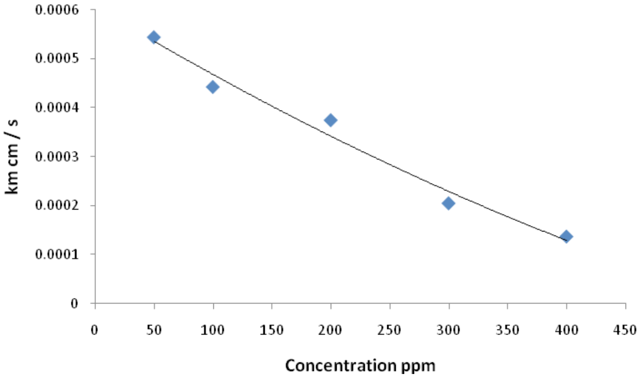

Fig. 4. Mass transfer coefficient as a function of initial concentration.

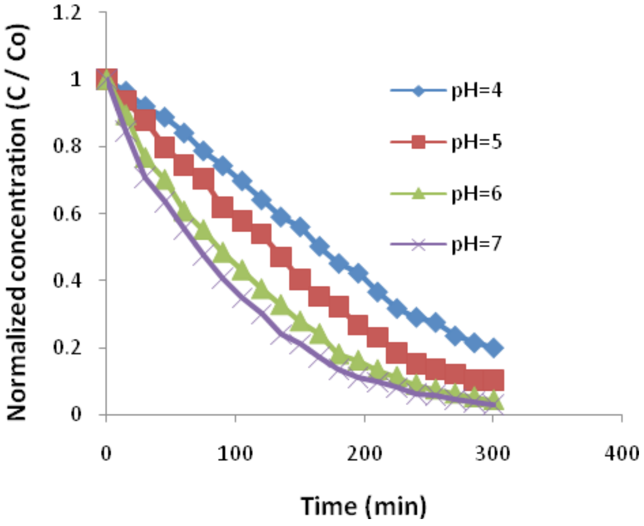

Fig. 5. Normalized concentration as a function of time for different pH values at 200 ppm cadmium initial concentration and 200 l/h flow rate.

Normalized concentration shows an exponential decay with time, and the increase in pH promotes the deposition, and this effect will be nearly negligible at pH values above 7.

This behavior could be attributed to the fact that the hydrogen evolution reaction will be inhibited by increasing pH, and hence increasing pH will increase the electrochemical reactor performance by supplying a higher electrode area for the main electrodeposition reaction, since the hydrogen evolution reaction will consume a part of the current supplied to the reactor and uses a part from the active electrode's area.

Effect of pH on mass transfer coefficient values could be obtained by plotting ln (C/C_o) vs. time to obtain a straight line with a slope equal to $(k_m A/V_R)$, and this plot is shown in Fig. 6.

Mass transfer coefficient for different pH values (4, 5, 6, and 7), 200 ppm initial cadmium concentration, and 200 l/flow rate are 1.36E-4, 2.386E-4, 3.068E-4, and 3.749E-4 cm/s respectively.

3.3. Effect of electrolyte flow rate

Effect of electrolyte flow rate was studied by conducting the experiments at pH = 7, initial cadmium concentration of 200 ppm, and at different flow rates (100, 200, 300, and 400 l/h).

Normalized concentration as a function of time at different flow rates is shown in Fig. 7.

The plot shows exponential concentration decay with time. It is obvious that the increase in flow rate will promote the deposition rate, and this behavior attributed to the fact that the increase in flow rate leads to increase the turbulency, and hence promoting convective mass transfer rate.

As shown in Fig. 7, the effect of flow rate diminishes gradually to have a clear gab between 100 and 200 l/h, and this gab will be lessened gradually with continuous increase in flow rate.

In order to find the effect of flow rate on mass transfer coefficient, values of $\ln(C/C_o)$ at different flow rates were plotted as a function of time to give a straight line with a slope equal to $(k_m A/V_R)$. This plot is shown in Fig. 8.

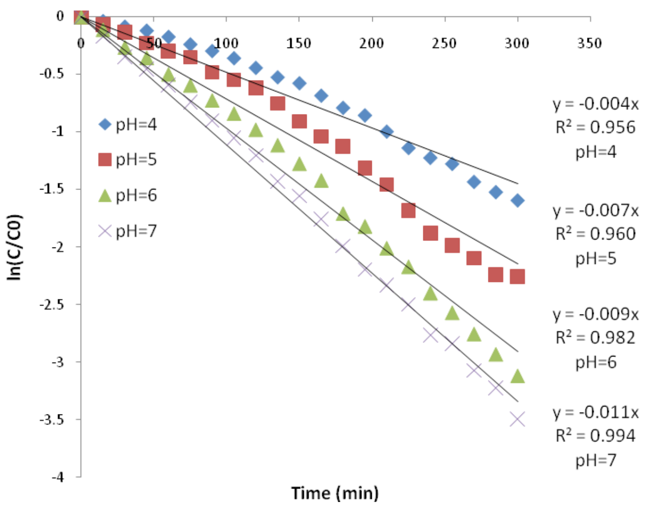

Fig. 6. Linearization of normalized concentration as a function of time for different pH values, and at 200 ppm initial cadmium concentration and 200 l/h flow rate.

Mass transfer coefficients for different electrolyte flow rates (100, 200, 300, and 400 l/h), at 200 ppm initial cadmium concentration, and pH = 7 are 1.363E-4, 3.749E-4, 3.749E-4, and 6.477E-4 cm/s respectively.

4. Reactor performance

4.1. Fractional conversion

Fractional conversion for cadmium deposition reaction was calculated by using Eq. (2) for the variables used in this work.

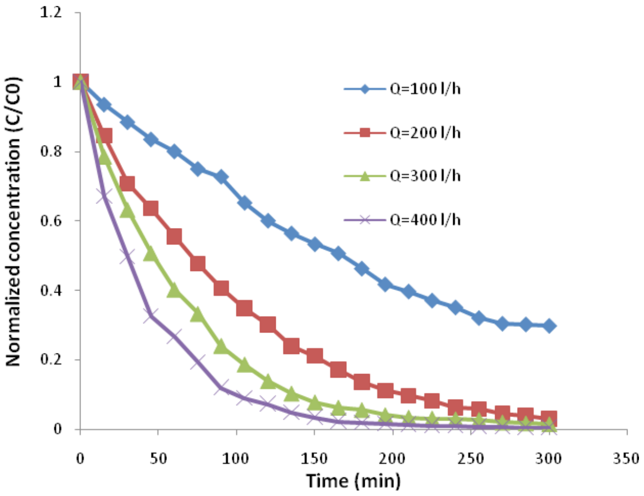

Fig. 7. Normalized concentration as a function of time for different electrolyte flow rates at 200 ppm initial cadmium concentration and pH = 7.

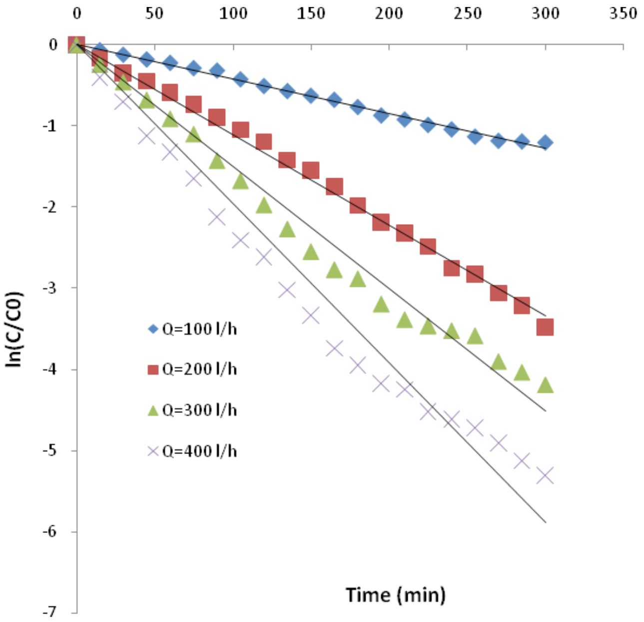

Fig. 8. Linearization of normalized concentration as a function of time for different electrolyte flow rates at 200 ppm initial cadmium concentration and pH = 7.

To find the effect of initial cadmium concentration, pH values, and electrolyte flow rate on the reactor performance, fractional conversion was plotted as a function of time for different initial cadmium concentrations (50, 100, 200, 300, and 400 ppm), and different electrolyte flow rates. This plot is shown in Fig. 9a, b.

Fig. 9a shows that higher conversion could be obtained at lower concentration and this is attributed to the fact that at lower initial concentration, hydrogen evolution reaction will be predominant, and this in turn will promote mass transfer coefficient.

Fig. 9b shows that the increase in the electrolyte flow rate will increase conversion, i.e., increases the reactor performance, since the increase in electrolyte flow rate increases turbulency and promotes mass transfer coefficient and hence increases the reactor performance.

4.2. Cumulative current efficiency

Cumulative current efficiency was calculated by using Eq. (4) for different initial cadmium concentrations (50, 100, 200, 300, and 400 ppm). Current efficiency was plotted as a function of time for these concentrations, and this plot is shown in Fig. 10.

This figure shows that at the beginning of electrodeposition, the reactor shows a high performance. This performance will be lowered with time as a result of cadmium ions exhaustion, which in turn promotes the oxygen reduction as the cathodic side reaction.

5. Mass transfer correlation

Electrochemical reactor used in this work was correlated with a dimensionless mass transfer correlation [Eq. (4)] depending on the data obtained by the set of experiments at pH = 7, 200 ppm initial cadmium concentration, and for different electrolyte flow rates (100, 200, 300, and 400 l/h).

Starting from the generalized dimensionless mass transfer correlation, the values of m and n were determined by plotting (Sh/Sc1/3) vs. Reynolds number. This plot will give a straight line with a slope equal to n and intercept equal to *n*. This plot is shown in Fig. 11.

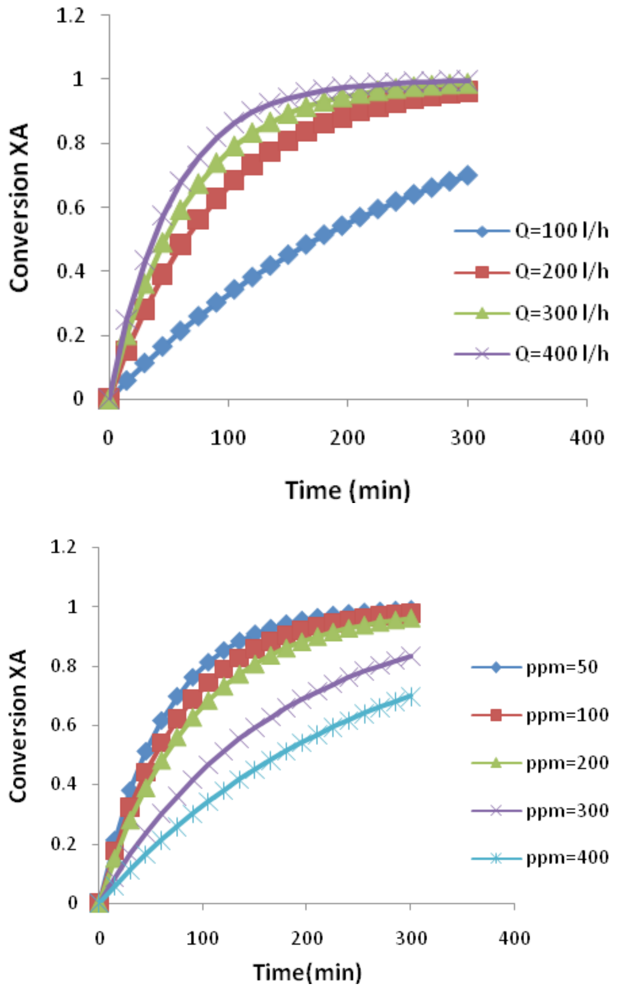

Fig. 9. Fractional conversion of Cd^{+2}. (a) for different initial Cd^{+2} concentration and 200 l/h flow rate and pH = 7. (b) For different electrolyte flow rates at 200 ppm initial Cd^{+2} concentration and pH = 7.

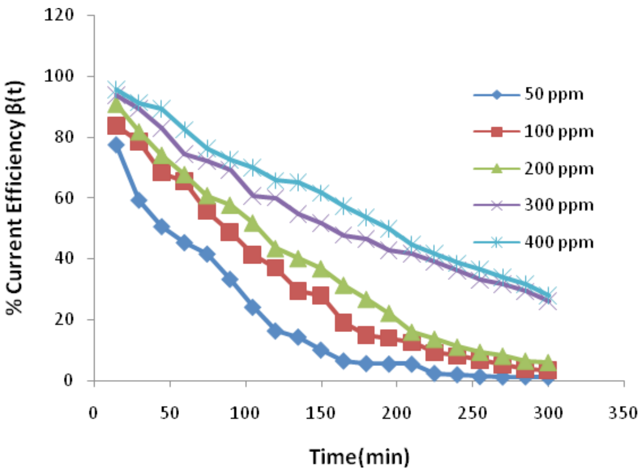

Fig. 10. Cumulative current efficiency for different initial Cd^{+2} concentration at 200 l/h electrolyte flow rate and pH = 7.

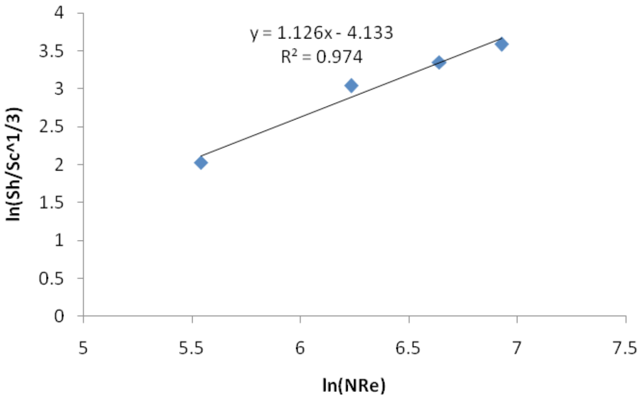

Fig. 11. Sherwood-Reynolds overall correlation at 200 ppm initial cadmium concentration.

From this figure, values of m and n which are function of electrode geometry were found to have the following values: $m = 0.016$ and $n = 1.126$ and the dimensionless correlation is:

$$Sh = 0.016\,\mathrm{Re}^{1.126}\,Sc^{1/3} \tag{6}$$

6. Conclusion

1. The performance of the stainless steel concentric tubes cathode electrode operating in batch recirculation mode was successful for the removal of cadmium from simulated wastewater.
2. Higher mass transfer coefficient is obtainable at lower cadmium concentration due to the impact of hydrogen evolution side reaction.
3. Effect of pH was nearly negligible at pH = 7, and this could be considered as the best pH value for higher performance since this value will suppress the side reactions effects.
4. Higher flow rates enhance cadmium removal rate via the promotion of convective mass transfer rate and reduction of boundary layer thickness for mass transfer.
5. Experimental results were correlated in the dimensionless correlation as:
6. The reactor performance was analyzed by introducing figures of merit, and for 200 ppm initial cadmium concentration, pH = 7, and 200 l/h flow rate, conversion was 87.

Symbols

A — Electrode surface area (cm^2)
A_e — Specific surface area (cm^{-1})
C_o — Cadmium initial concentration (mol/m^3 or ppm)
C(t) — Cadmium concentration at time t (mol/m^3)
CR — Correlation coefficient
D — Diffusion coefficient of cadmium (cm^2/s)
d — Diameters (cm)
F — Faraday constant = 96485 coulomb mol^{-1}
I — Current (A)
I_L — Limiting current (mA)
k_m — Mass transfer coefficient (cm s^{-1})
n — Charge number of electrode reaction
Re — Reynolds number = ud/ν
Sc — Schmidt number = ν/D
SCE — Standard Calomel Electrode
Sh — Sherwood number = $k_m d/D$
t — Time (s)
ν — Kinematic viscosity (cm^2 s^{-1})
V_T — Reactor volume (m^3)
$X_{(t)}$ — Fractional conversion at time t
β(t) — Cumulative current efficiency %

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