A NOVEL METHOD FOR ELECTROCHEMICAL REMOVAL OF CADMIUM FROM SIMULATED WASTE-WATER BY USING STAINLESS STEEL MESH CONCENTRIC TUBES CATHODE

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ABSTRACT

Performance of a novel pilot scale, flow-through electrochemical reactor, with a stainless steel mesh 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 to represent the reactor performance. Results were correlated in a dimensionless correlation:

$Sh = 99.6836Re^{0.505}Sc^{1/3}$

Keywords: Electro deposition, Cadmium, Mesh Concentric tubes cathode, flow-through cell, mass transfer control.

INTRODUCTION

I 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 a high efficiency in removal process.

Electrochemical reactor performance could be analyzed and compared by introducing "figures of merit" [6, 7, 8, and 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:

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

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

$$X_{(t)} = 1 - exp(-k_m A_e t) \qquad (2)$$

Current efficiency could be expressed as :

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

Specific energy consumption could be calculated by the following equation:

$$E_{(s)} = \frac{z.F.E_{cell}}{\zeta.M} \qquad (4)$$

Space time yield could be determined via the following equation:

$$\rho_m = \frac{C_o x_{(t)}}{t} \qquad (5)$$

And the space velocity could be calculated by the following equation:

$$S_N = -\frac{\ln(1-x_{(t)})}{t.ln(10)} \qquad (6)$$

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

$$(7)\ Sh = mRe^n Sc^{1/3}$$

EXPERIMENTAL WORK

Apparatus

In the present work, electro deposition was conducted in a pilot scale flow-through reactor working in batch-recycle mode with stainless steel mesh concentric tubes as a cathode. Schematic diagram of the pilot plant is shown in figure (1):

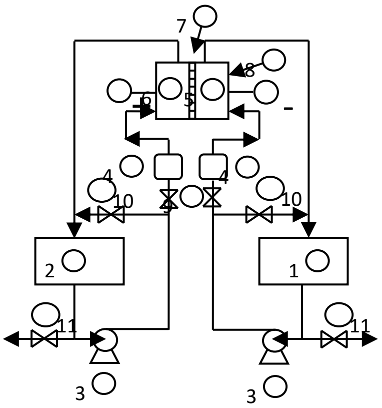

Figure 1. Schematic diagram of the pilot plant batch-recycle system.
(1)
(1) Anolyte reservoir, (2) Catholyte reservoir (3) Pumps, (4) Flow meters, (5) Catholyte chamber, (6) Anolyte chamber, (7) Cationic membrane, (8) Electrolytic cell, (9) Inlet valves, (10) Recycle valves, (11) Drain valves

Electrolytic cell container and piping system were constructed from Teflon material. Two glass reservoirs with 10 liters 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 (25x25x19) cm dimensions, and this in turn divided into two compartments; catholyte chamber and anolyte chamber. Catholyte chamber was with (25x25x17 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 (25x25x5 cm) Teflon plate with central hole of 20 cm internal diameter.

Stainless steel mesh concentric tubes cathode was installed inside the catholyte chamber with a distributer at the catholyte entrance to distribute the inlet solution. These cylinders were constructed with (316L) stainless steel 45 in^{-1} mesh, and 0.2 mm wire diameter plane weave metallic wire mesh screen.

Cathode consisted of 8 mesh concentric stainless steel tubes with the dimensions listed in table (1):

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

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).

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 was used to obtain the desired concentration. Solution pH was adjusted by means of sulfuric acid and sodium hydroxide. Table (2) lists the physical properties of the electrolyte

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

RESULTS AND DISCUSSION

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 figure (2):

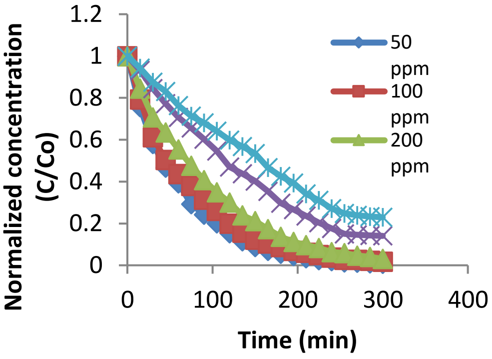

Figure 2. Normalized concentration (C / C$_o$) as a function of time for cadmium removal at different initial cadmium concentration

This figure shows that the cadmium concentration decays exponentially with time. The same behavior was followed all over the range of initial concentration used in this set of experiments. Steeper decay was noticed at lower initial cadmium concentration, and the could be attributed to the fact that the mass transfer coefficient is inversely proportional to the concentration difference (i.e., inversely proportional to the driving force) according to the relation:[Henley et al.]

$$k_m = \frac{molar\ flux}{\Delta C_A} \tag{8}$$

Molar flux in this equation could be considered as a constant since amount of flux depends on the current passed, and since the effect of hydrogen evolution eliminated by working in medium with pH=7.

In order to calculate mass transfer coefficient k_m, the plot on {ln (C / C_o)} versus time could be utilized, and this plot will give a straight line with a slope equals to (k_mA / V_T). This plot is shown in figure (3):

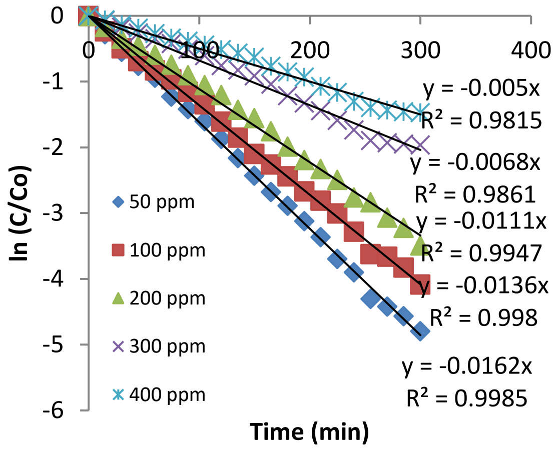

Figure 3. Linearization of normalized concentration (C / C_o) as a function of time for different initial cadmium concentration and 200 l/h

From this figure, mass transfer coefficient could be predicted for different values of initial cadmium concentration. These values are listed in table (3).

Table (3). Mass transfer coefficient for different initial cadmium

Initial cadmium concentration ppm	Km (m / s)
50	2.83 E-4
100	2.299 E-4
200	1.945 E-4
300	1.0612 E-4
500	8.844 E-4

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 figure (4). From this plot, data was correlated with (CR=0.97) in the following form:

$$km = 7x10^{-10}C^2 - 9x10^{-7}C \qquad (9)$$

As mentioned before, mass transfer coefficient will increase with the decrease in initial cadmium concentration due to the nature of inverse proportionality between the mass transfer coefficient and the concentration difference.

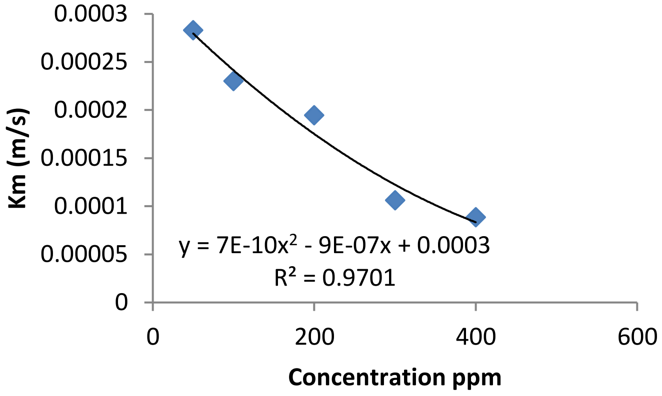

Figure 4. Mass transfer coefficient as a function of initial concentration

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 figure (5):

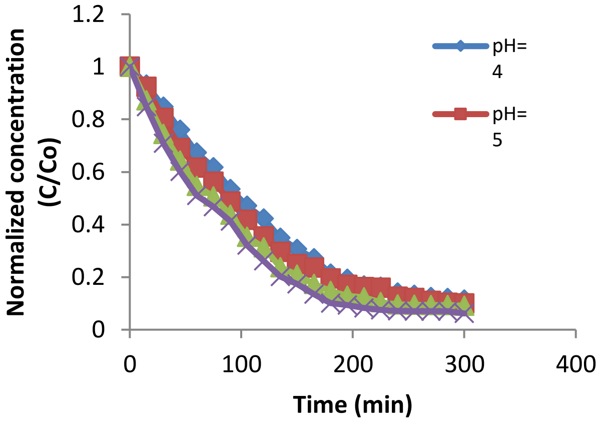

Figure 5. Normalized concentration as a function of time for different pH values at 200 ppm cadmium initial concentration and 200 l/h flow rate

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 electro deposition reaction, and hence increasing the molar flux of cadmium ions towards the electrode surface, 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) versus time to obtain a straight line with a slope equals to (k_mA / V_R), and this plot is shown in figure (6):

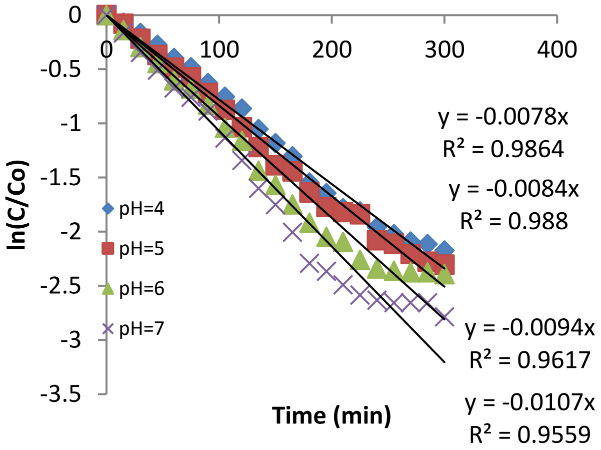

Figure 6. Linearization of normalized concentration as a function of time for different pH values, and at 200 ppm initial cadmium concentration and 200 l/h flow rate

Predicted mass transfer coefficients' values for different pH values are listed in table (4):

Table 4. Mass transfer coefficient for different pH values at 200 ppm initial cadmium concentration ad 200 l/h flow rate

pH	km (cm / s)
4	0.000124
5	0.000142
6	0.000159
7	0.000195

This table shows that higher mass transfer coefficient could be obtained by increasing pH, which will lead to increase the amount of area and current used by the cadmium ions, which in turn increase the molar flux leading to mass transfer coefficient promotion.

Mass transfer coefficient as a function of pH is illustrated in figure (6).

3- Effect of electrolyte flow rate

Effect of electrolyte flow rate was studied by conducting the experiments at pH=7, and cadmium initial concentration equals to 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 figure (7).

The plot shows exponential concentration decay with time. It is obvious that increasing the 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.

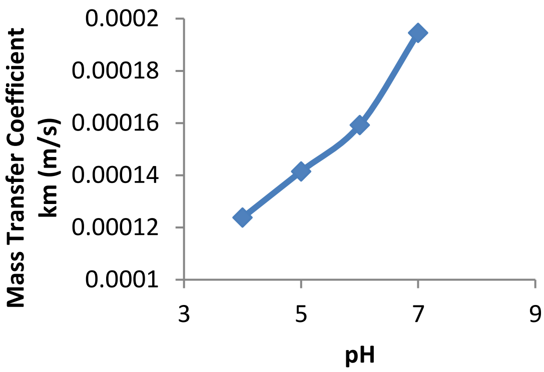

Figure 6. Mass transfer coefficient as a function of pH

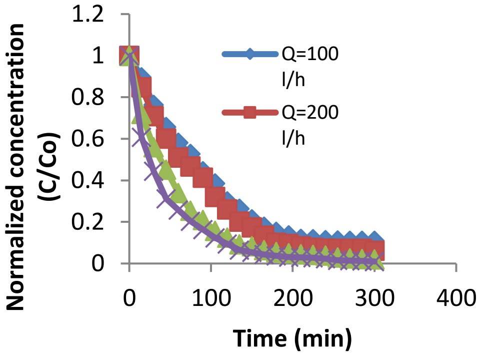

Figure 7. Normalized concentration as a function of time for different electrolyte flow rates at 200 ppm initial cadmium concentration and pH=7

In order to find the effect of flow rate on mass transfer coefficient, values of ln(C/C_0) at different flow rates were plotted as a function of time to give a straight line with a slope equals to (k_mA/V_R). This plot is shown in figure (8):

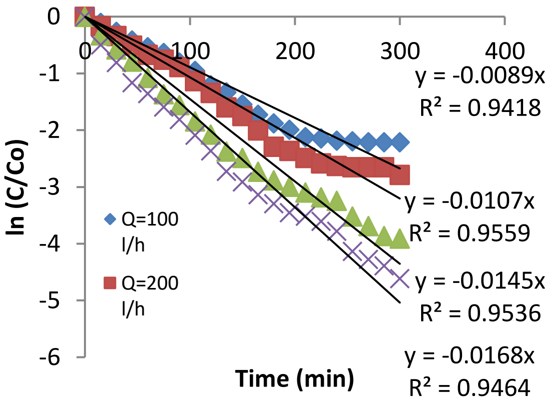

Figure 8. Linearization of normalized concentration as a function of time for different electrolyte flow rates at 200 ppm initial cadmium concentration and pH=7

Mass transfer coefficients for different values of flow rate are listed in table (5):

Table (5) Mass transfer coefficient values for different electrolyte flow rates at 200 ppm initial cadmium concentration and pH=7

Flow rate (l/h)	k_m (m/s)
100	1.415E-4
200	1.945E-4
300	2.476E-4
400	2.83E-4

Mass transfer coefficient increases with the increase in flow rate, since the increase in flow rate will promote the molar flux and hence increases the mass transfer coefficient.

Mass transfer coefficient was correlated with electrolyte flow rate as shown in figure (9):

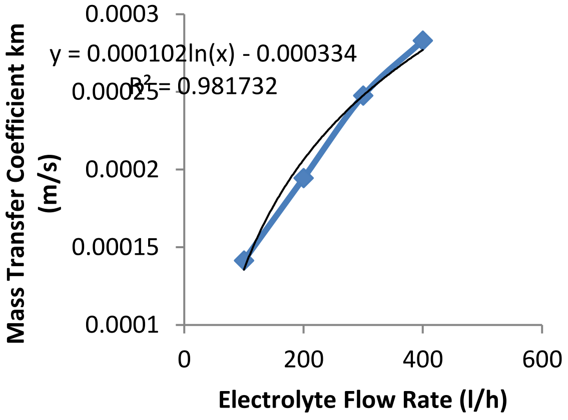

Figure 9. Mass transfer coefficient as a function of initial concentration

So, the mass transfer coefficient could be correlated with electrolyte flow rate as:

$$k_m = 1x10^{-6} \ln(Q) - 3.34x10^{-4} \qquad (10)$$

Reactor performance

1- Fractional conversion

Fractional conversion for cadmium deposition reaction was calculated under the variables used in this work.

To find the effect of initial cadmium concentration, fractional conversion was plotted as a function of time for different initial cadmium concentrations (50, 100, 200, 300, and 400 ppm) in figure (10).

This figure shows that higher conversion could be obtained at lower concentration, and this is attributed to the fact that at lower initial concentration, the mass transfer coefficient will be enhanced, leading to a faster reaction rate.

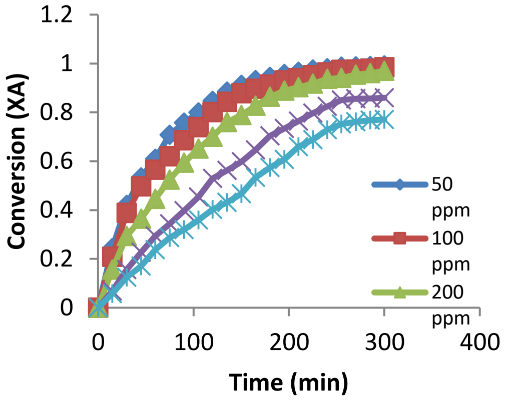

Figure 10. Fractional conversion of cd^{+2} for different initial cd^{+2} concentration and 200 l/h flow rate and pH=7

2-Cumulative current efficiency

Cumulative current efficiency was calculated by 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 figure (11):

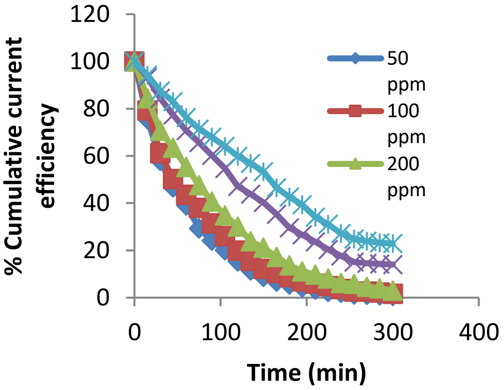

Figure 11. Cumulative current efficiency for different initial cd+2 concentration at 200 l/h electrolyte flow rate and pH=7

This figure tells that at the beginning of electro deposition, 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.

This figure shows that the reactor shows a higher current efficiency for higher concentrations. This behavior could be attributed to the fact that at lower concentrations, high percent of electrode area will be used for hydrogen evolution reaction, which will consume a part of the applied current minimizing the current efficiency.

Specific energy consumption

Specific energy consumption was calculated by equation (4), and to study the behavior of this parameter, energy consumption values were plotted versus time as shown in figure (12):

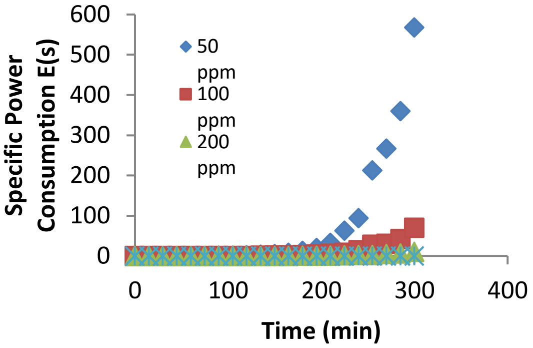

Figure 12. Specific power consumption for different initial cd+2 concentration, 200 l/h, and pH=7.

This figure shows that the specific power consumption increases with time. This behavior could be attributed to the fact that when the solution becomes more dilute, this will decrease the current efficiency as a result of predomination of side hydrogen evolution reaction.
For lower initial cadmium concentration, the efficiency will be lower, and hence the specific power consumption will increase with decrease in initial cadmium concentration.

Space time yield

Mean value of specific time yield for the time intervals utilized in experiments conduction was calculated by equation (5) for different values of initial Cd^{+2} concentration at pH=7 and 200 l/h. Mean value of space time yield as a function of initial Cd^{+2} concentration is shown in figure (13).

This figure shows that the mean value of space time yield increases with the increase in cadmium ions concentration, and this could be attributed to the fact that the space time yield follows the same tendency as the current efficiency at lower concentrations.

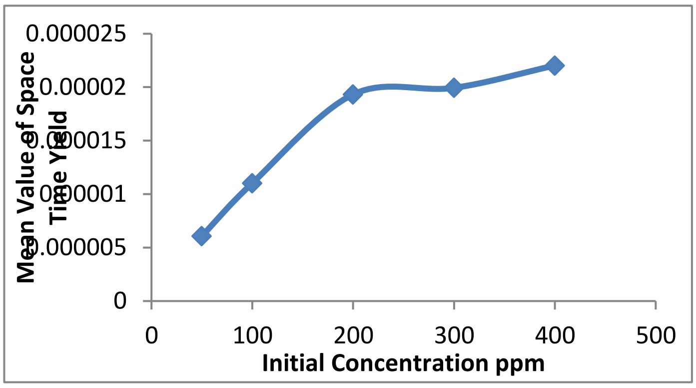

Figure 13. Mean value of space time yield as a function of initial Cd^{+2} concentration at pH=7 and 200 l/h solution flow rate

Normalized space velocity

Normalized space velocity was calculated according to equation (6) for different initial Cd^{+2} concentration at pH=7 and 200 l/h solution flow rate. These values were plotted as a function of Cd^{+2} initial concentration as shown in figure (14):

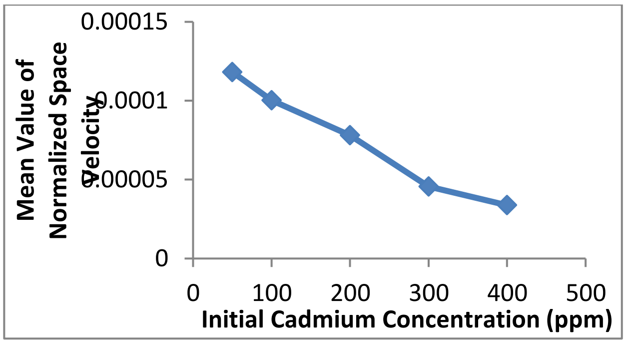

Figure 14. Normalized space velocity as a function of initial Cd+2 concentration at pH=7 and 200 l/h solution flow rate

This behavior is consistent with the definition of normalized space velocity. The increase in initial cadmium concentration will minimize the volume of reactants reduced by 90 %, and hence decrease the normalized space velocity.
Electrochemical reactor used in this work was correlated with a dimensionless mass transfer correlation depending on the data that was 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) versus Reynolds number. This plot will give a straight line with a slope equals to n and intercept equals to n. This plot is shown in figure (15):

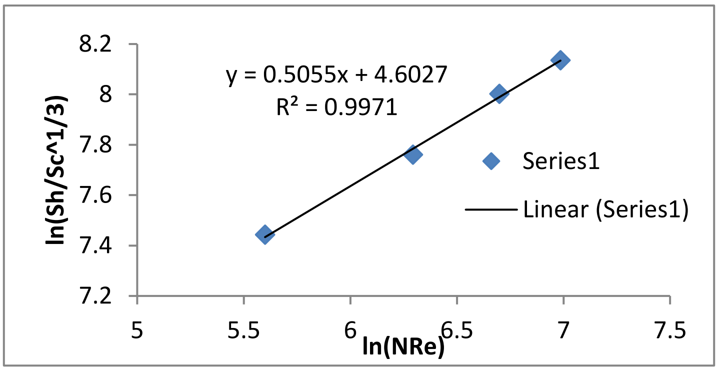

Figure 15. Sherwood-Reynolds overall correlation at 200 ppm initial cadmium concentration

From this figure, values of m & n which are function of electrode geometry were found to have the following values: m=99.683 & n=0.505 and the dimensionless correlation will be:

$$Sh = 99.6836Re^{0.505}Sc^{1/3} \quad (11)$$

For 270 < Re < 1081

CONCLUSIONS

1. The performance of the stainless steel mesh concentric cylinders cathode electrode operating in batch recirculation mode was investigated for the removal of cadmium from simulated wastewater.
2. Mass transfer coefficient was noticeably enhanced by lowering the initial concentration. Mass transfer coefficient was correlated with the concentration according to the following correlation:
   $$km = 7x10^{-10}C^2 - 9x10^{-7}C$$
3. pH effect was negligible at pH=7, where the hydrogen evolution side reaction completely suppressed.
4. Effect of solution flow rate on the mass transfer coefficient was the same as the behavior of the effect acted in the case of smooth cathode. Mass transfer coefficient was correlated with the electrolyte flow rate by the following expression
   $$k_m = 1x10^{-6}\ln(Q) - 3.34x10^{-4}$$
5. Experimental results were correlated in the dimensionless correlation as:
   $$Sh = 99.6836Re^{0.505}Sc^{1/3}$$
   For 270 < Re < 1081
6. The reactor performance was analyzed by introducing figures of merit, and the reactor in the case of concentric mesh cylinders showed better efficiency with enhancement factor reaches to 64.

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NOMENCLATURE

A electrode surface area, cm^2, Ae specific surface area, cm^{-1}, Co 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, E$_{(s)}$ specific energy consumption , J/g, F Faraday constant = 96485, coulomb mol^{-1},I current, A, I$_L$ limiting current mA, km mass transfer coefficient, cms^{-1},n charge number of electrode reaction,Re Reynolds number = ud/ v, Sc Schmidt number = v /D, SCE standard Calomel electrode, S$_N$ Space velocity s^{-1}, Sh Sherwood number = k$_m$d/D, t Time s, v kinematic viscosity cm^{2}s^{-1},V$_T$ reactor volume m^3, X$_{(t)}$ fractional conversion at time t, β(t) cumulative current efficiency %, $\dot{\rho}$m Space time yield (kg / m^3.s)