MODELING A PROCESS FOR THE REMOVAL OF CADMIUM FROM SIMULATED WASTEWATERS BY ELECTRO-DEPOSITION ON STAINLESS STEEEL TUBES BUNDLE

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ABSTRACT

Electrochemical processes can provide valuable contributions to the protection of the environment through implementation of effluent treatment and production-integrated processes for the minimization of waste and toxic compounds.

The performance of a novel pilot scale, batch re-cycled, flow-through cell, with stainless steel tubes bundle cathode in the removal of cadmium was investigated utilizing the potential results obtained from a batch mode. The studied electrochemical reaction was the cathodic reduction of Cd^{+2} using 0.5 M sodium sulphate as supporting electrolyte. The analyzed parameters were different initial Cd^{+2} concentrations (50, 100, 200, 300, 400 ppm) and different electrolyte flow-rates (100, 200, 250, 300, 350 L/hr), the tubes number was 920 of 0.6 cm diameters.

The overall empirical mass transfer correlation was found to be:

$$Sh = 0.051\ \mathrm{Re}^{0.859}\ Sc^{1/3}$$

For $5 < Re < 20$ and $Sc = 649$

Experimental results, analysis and correlations showed good performance of the cell and proved its adequacy in the removal of Cd^{+2} from simulated effluents.

الخلاصـــــــــة

تحقق العمليات الكهروكيميائية مشاركة فاعلة في الحفاظ على البيئة من خلال معالجة المياه العادمة و عمليات الانتاج المتكاملة الهادفة الى تقليل المخلفات و المركبات السامة.

تمت دراسة كفاءة اداء منظومة ريادية مستحدثة، تعمل بنظام شبه الدفعات المستمر وخلية جريان متوازية، قطبها السالب عبارة عن حزمة من الانابيب الفولاذية، في ازالة الكادميوم، وباستخدام الجهد الكهربائي الذي تم الحصول عليه من نظام الدفعات.

التفاعل الكهروكيميائي الذي تمت دراسته هو الاختزال الكاثودي لايونات الكادميوم الثنائية باستخدام محلول سلفات الصوديوم (0.5 مولار) كألكتروليت مساعد. المؤشرات التي تم اعتمادها للتحليل هي تراكيز مختلفة لايونات الكادميوم (50، 100، 200، 300، 400 جزء في المليون) و محاليل بمعدلات جريان مختلفة (100، 200، 250، 300، 350 لتر/ساعة)، انابيب الكاثود كانت بعدد 920 و باقطار 0.6 سم.

تم ايجاد علاقة ارتباط تجريبية لخواص انتقال الكتلة للخلية الكهروكيميائية و كما يلي:

$$Sh = 0.051\ \mathrm{Re}^{0.859}\ Sc^{1/3}$$

للمدى التالي: $5 < Re < 20$ و $Sc = 649$

اظهرت نتائج التجارب والتحليل المختبرية، اضافة الى علاقات الارتباط التجريبية، اداء جيد للخلية المستخدمة وملاءمتها لازالة الكادميوم من المياه العادمة المختلقة.

KEYWORDS: **Electrochemical, Flow-through cell, Cadmium, Tubes bundle.**

INTRODUCTION

With a rapidly growing world population and an increasing number of reports on detrimental effects on the environment, its protection has become a major issue and a crucial factor for future technological progress, which will have to meet the requirements for sustainable development. The strategies for environmental protection in industry generally include processes or products which have no or less harmful effects on the environment. Electrochemistry has important roles to play in these strategies; industrial electrochemistry has undergone developments towards cleaner processes and more environmentally friendly products. [*Simonsson, (1997)*].

Cadmium is a toxic and bio-persistent element and, once absorbed by an organism, remains resident for many years although it is eventually excreted. In humans, long-term exposure is associated with renal dysfunctions. High exposure can lead to obstructive lung disease and has been linked to lung cancer. [*Lenntech, (2009)*].

The electrolytic method for the removal of heavy metals from aqueous media by using porous electrodes of various geometric shapes and materials, with flowing solutions, represents a successful reactor which presents high mass-transfer conditions. [*Tramontina, (2002)*].

EXPERIMENTAL WORK

The performance of a novel pilot scale flow-through cell, with stainless steel tubes bundle cathode was studied. Potential values over which cadmium is controlled by mass transfer, was obtained from a rotating disc electrode from previous experiments [*Al-Shalchi, (2010)*], a value of -1 V was applied for the removal of cadmium from a synthetic solution in the batch re-circulation mode.

The catholyte solution used was a 0.5 M sodium sulphate with different concentrations of cadmium sulphate. Electrolytes with cadmium concentrations of (50, 100, 200, 300 and 400 mg/L) were prepared in the 0.5 M sodium sulphate used as supporting electrolyte. The bulk pH was adjusted to a value of 4.8. The anolyte used had the same composition as the catholyte, but without the presence of cadmium.

The catholyte and anolyte flow-rates used were (100, 200, 250, 300, 350 L/hr).

The novel pilot scale electrochemical reactor used had an overall dimension of (25×25×17) cm; it was made from four Teflon discs. A silicon rubber layer of (1 mm) thickness was placed between each two disks to prevent the electrolyte leakage. The main cell compartments are the cathode chamber and the anode chamber.

The cathode was a configuration of tubes bundle consisting of 920 stainless steel tubes of 0.6 cm outer diameters and 0.4 cm inner diameters arranged on a fixed perforated stainless steel plate inside a disc of 20 cm diameter in triangular pitch arrangement; and the anode was made of a graphite disc of 14 cm diameter and 2 cm thickness. **Figure (1)** illustrates a sectional sketch of the tubes bundle electrode.

The pilot flow system used, operating under batch re-circulating conditions, consisted in addition to the electrochemical cell, the catholyte and anolyte porcelain reservoirs, two recirculation pumps, and two sets of flow meters for measuring the catholyte and anolyte flow rates. **Figure (2)** illustrates the schematic diagram of the pilot plant flow system.

At time intervals of 15 minutes, catholyte samples were taken from the catholyte reservoir in order to be analyzed for Cd^{+2} concentrations by using Atomic Absorption.

RESULTS AND DISCUSSION

The performance of a novel pilot scale, batch re-cycled, flow-through cell, with stainless steel tubes bundle cathode in the removal of cadmium was examined by utilizing the potential results obtained from previous batch mode experiments, it was equal to -1 V.

Effect of Initial Concentration

Experiments were carried out to study the removal rate of Cd^{+2} from solutions of different Cd^{+2} initial concentrations with catholyte and anolyte flow rate of 250 L/hr.

Figure (3) shows the curves of normalized Cd^{+2} concentration ($c(t)/c_o$) as a function of time for different cadmium initial concentrations (50, 100, 200, 300, 400 ppm). As expected, cadmium concentration decays exponentially with time. It can be seen the trends and behaviors of the curves for the different Cd^{+2} concentrations are the same.

Plotting the logarithmic normalized concentration $\ln(c(t)/c_o)$ as a function of time, **Figure (4)**, gives linear relationships; the slopes of the straight lines were used to estimate the mass transfer coefficients by using eq. (1). This

equation is for a batch-recycle mode electrolysis process carried out under mass transfer control: [*Bertazzoli, (1998)*].

$$\ln(\frac{c(t)}{c_0}) = -\frac{V_e k_m A_e}{V_T} t \qquad (1)$$

Where:

k_m = mass transport coefficient cm s^{-1}
V_T = volume of electrolyte cm^3
V_e = overall electrode volume cm^3
A_e = electrode area per unit electrode volume cm^{-1}
t = time s
c_0 = initial concentration ppm
$c_{(t)}$ = concentration at time (t) ppm

Since (V_e) and (V_T) are known parameters and (A_e) is calculated; then (k_m) can be estimated from the above equation.

The estimated values of (k_m) were plotted against the bulk Cd^{+2} concentrations; **Figure (5)**. It can be seen that the mass transfer coefficient is inversely proportional to the Cd^{+2} concentrations.

Figure (5) shows higher values of mass transfer coefficient with lower values of bulk Cd^{+2} concentrations, this is attributed to the hydrogen evolution, which is the predominant cathodic reaction at low values of the inlet cadmium concentration.

In order to find the mass of Cd^{+2} deposited with time, a mass balance was conducted on three different initial concentrations of cadmium solutions (50, 200, 400 ppm). **Figure (6)** illustrates the mass deposition of cadmium as a function of time. The resulted curves are also exponential with time.

Effect of Electrolytes Flow Rate

Experiments were carried out to study the influence of flow rate of catholyte on the removal rate of Cd^{+2} from solutions with initial concentration of 200 ppm.

Figure (7) shows the curves of normalized Cd^{+2} concentration ($c(t)/c_o$) as a function of time for different catholyte flow rates (100, 200, 250, 300, 350 L/hr). As expected, cadmium concentration decays exponentially with time. It can be seen that higher flow rates enhance the removal of Cd^{+2}. This behavior is attributed to greater rates of mass transport of Cd^{+2} with increased electrolytes flow rates, which reduce the thickness of the boundary layer for mass transfer.

Plotting the logarithmic normalized concentration $\ln(c(t)/c_o)$ as a function of time, **Figure (8)**, gives linear relationships. Following the same previous procedures, values of (k_m) were calculated for each flow rate.

Mass Transfer Correlations

Mass transfer coefficients estimated from the series of experiments on different flow rates were fitted to find an empirical correlation of dimensionless Sherwood number for the tubes bundle cathode under the medium and conditions of the experiments.

Starting from the typical mathematical relationship for dimensionless Sherwood number, which is suitable for electrolytic reactors design:

$$Sh = m\,\mathrm{Re}^{n}\, Sc^{1/3} \qquad (2)$$

And the so called j_D factor correlation:

$$j_D = Sh\,\mathrm{Re}^{-1}\, Sc^{-1/3} \qquad (3)$$

Where:

$Sh = k_m d_e / D$ Sherwood number
$Re = u_\varepsilon d_e / v$ Reynolds number
$Sc = v / D$ Schmidt number
$u_\varepsilon = u / \varepsilon$ characteristic flow velocity
D diffusion coefficient $cm^2\ s^{-1}$
ε porosity
d_e equivalent diameter (a characteristic length)
v kinematic viscosity $m^2\ s^{-1}$
m and n empirical constants dependent on the geometry of the system

[*Pletcher, (1991)*].

The following correlation is obtained:

$$Sh = 0.051\,\mathrm{Re}^{0.859}\, Sc^{1/3} \qquad (4)$$

for $5 < Re < 20$ and $Sc = 649$ (calculated from batch mode)

This obtained correlation is of good agreement with [*Pickett, (1979)*] :

$$Sh_{av} = 0.023\,\mathrm{Re}^{0.8}\, Sc^{1/3}$$

It can be used for different reactor geometries providing that the relevant equivalent diameter is correctly formulated:

Table (1) lists the data used for the analysis.

Figures (9) and (10) summarize the Sherwood – Schmidt – Reynolds and j_D correlations, with (CR=0.996) and (CR=0.95) respectively.

CONCLUSIONS

Conclusions

- The performance of the stainless steel tubes bundle electrode, operating in the batch re-circulated mode, was successful in the removal of Cd^{+2} from simulated wastewater.
- The mass transfer coefficient increased with lower values of bulk Cd^{+2} concentration, due to hydrogen evolution; the mass transfer coefficient was correlated with the bulk concentration of Cd^{+2} in sodium sulphate.
- The mass transfer coefficient increased with higher flow rates, due to the reduction in the boundary layer thickness; the mass transfer coefficient was correlated with the electrolyte velocity.
- The overall empirical mass transfer correlation was found to be:

$$Sh = 0.051\ \mathrm{Re}^{0.859}\ Sc^{1/3}$$

for $5 < Re < 20$ and $Sc = 649$

Which is in good agreement with literature.

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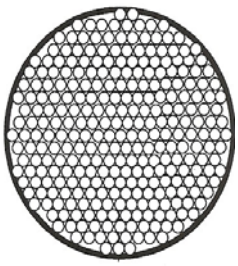

Figure (1) Sectional sketch of the tubes bundle electrode

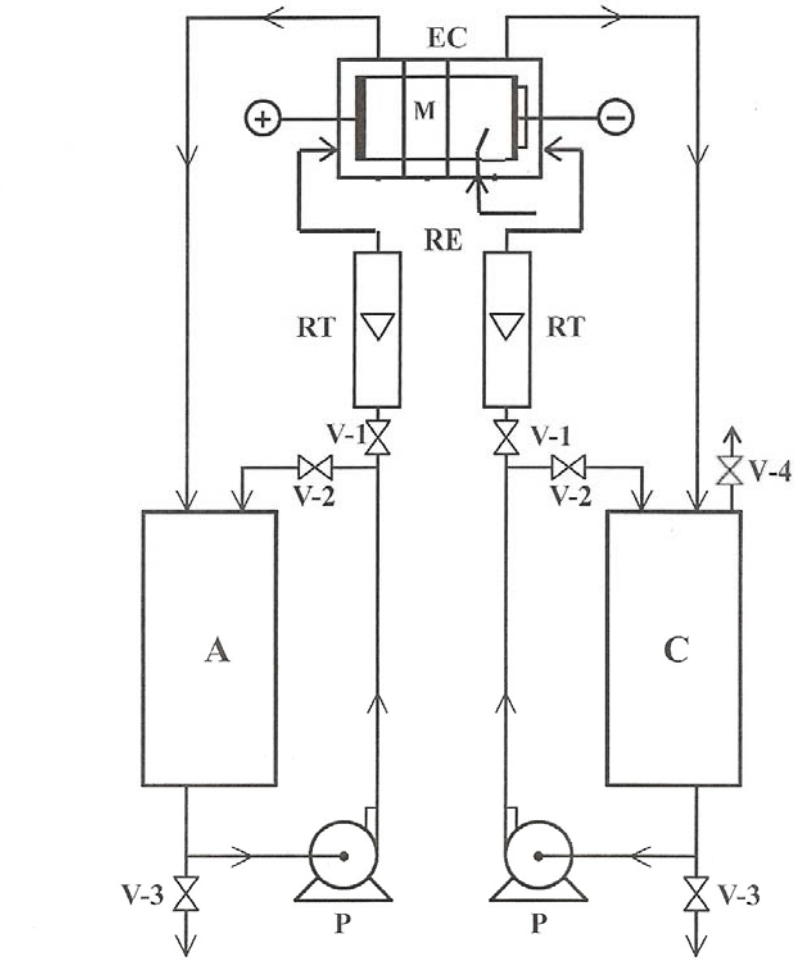

Figure (2) Schematic Diagram of the Pilot Plant Flow System

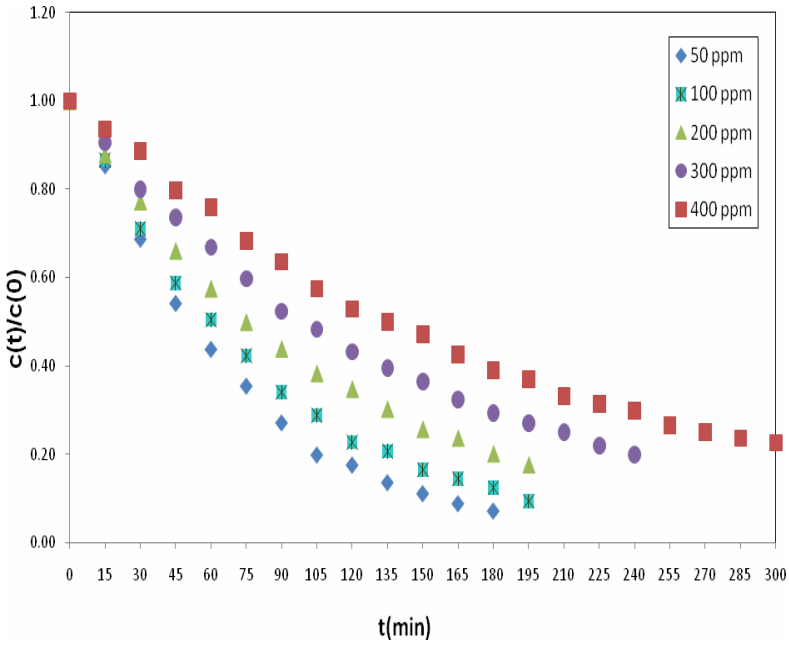

Figure (3) Normalized concentration ($c(t)/c_o$) as a function of time for removal of different Cd^{+2} concentrations and flow rates 250 L/hr

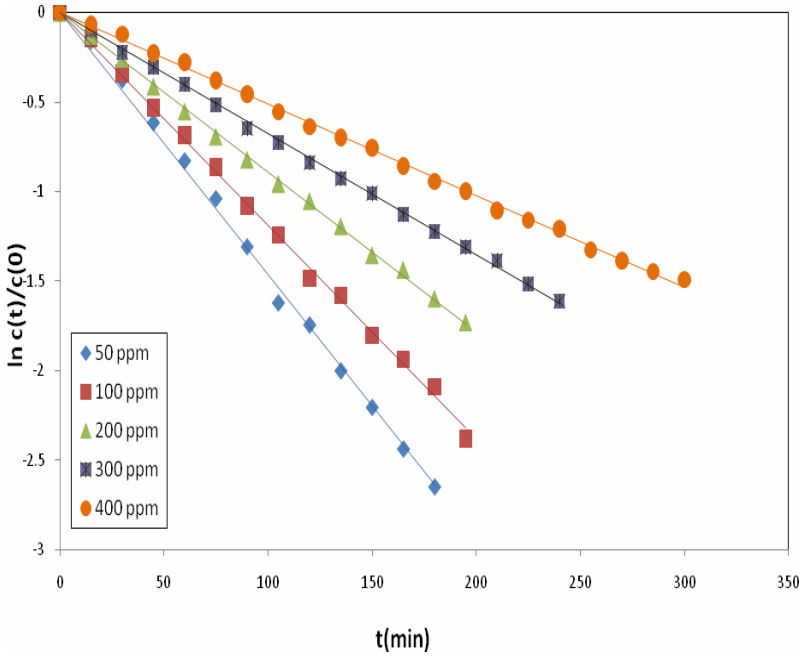

Figure (4) Linearization of normalized concentration as a function of time for different Cd^{+2} concentrations and flow rate of 250 L/hr

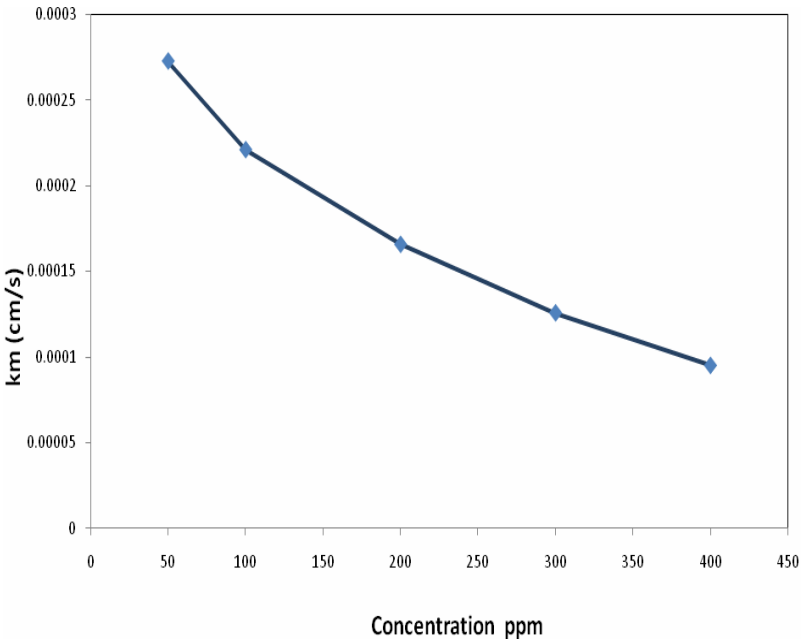

Figure (5) Variation of mass transfer with bulk Cd^{+2} concentrations

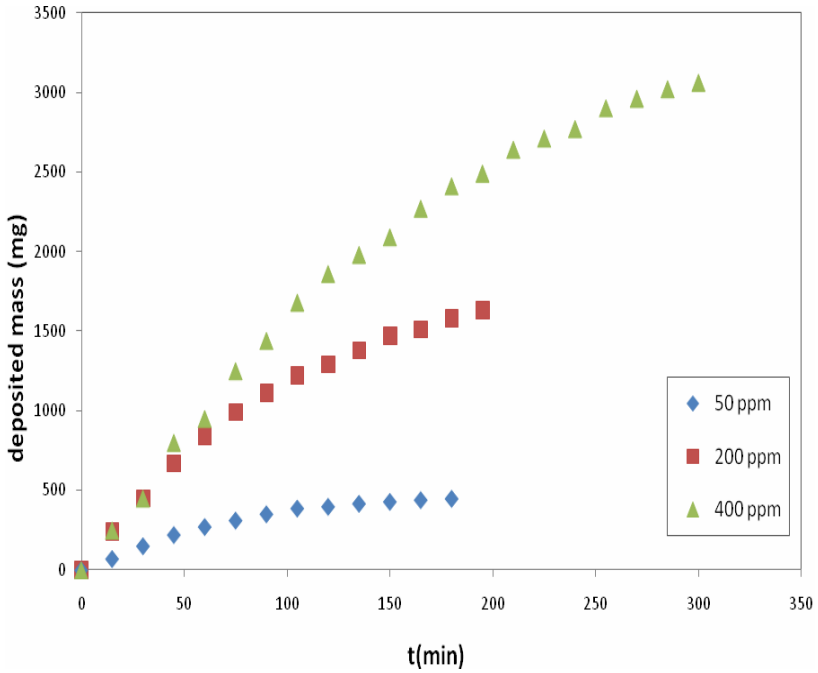

Figure (6) Mass deposited of cadmium with time for different Cd^{+2} concentrations and at flow rate of 250 L/hr

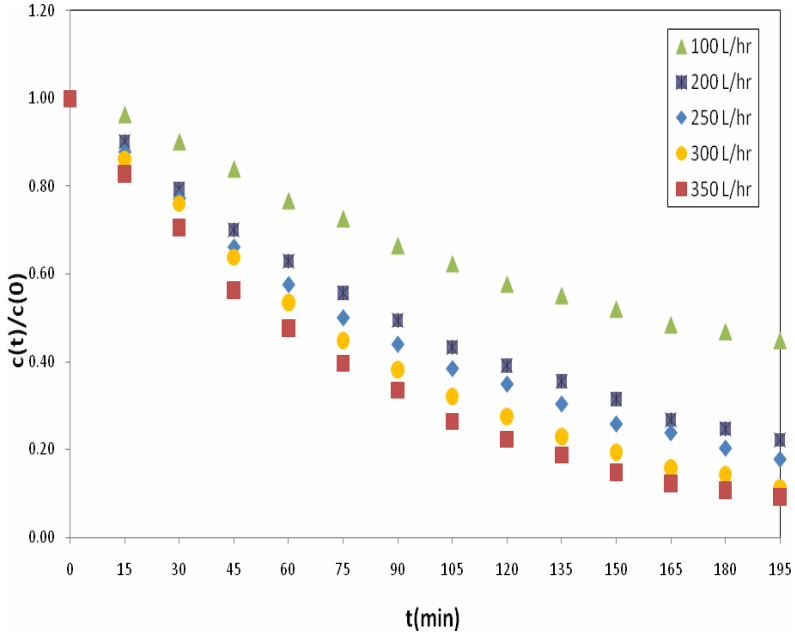

Figure (7) Normalized concentration ($c(t)/c_o$) as a function of time for Cd^{+2} removal for different flow rates and Cd^{+2} concentration of 200 ppm

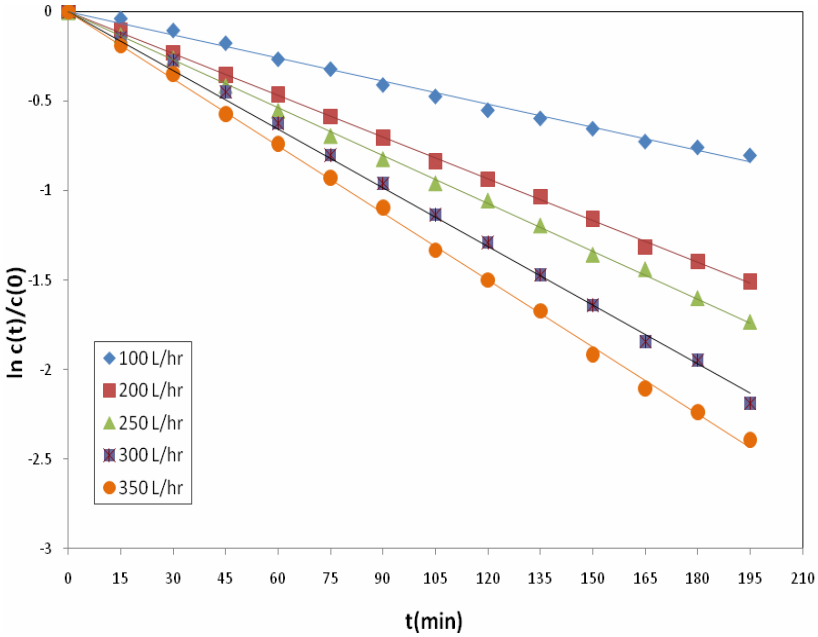

Figure (8) Linearization of normalized concentration as a function of time for different flow rates and Cd^{+2} concentration of 200 ppm

Table (1) Data used for calculations of dimensionless numbers and Cd^{+2} concentration of 200 ppm

Parameters		Flow Rates (L/hr)
10^5 D ($cm^2\ s^{-1}$)	1.127	100
10^2 ν ($cm^2\ s^{-1}$)	0.731	200
Schmidt number	649	250
Porosity	0.583	300
Equivalent diameter (d_e) (cm)	0.27	350

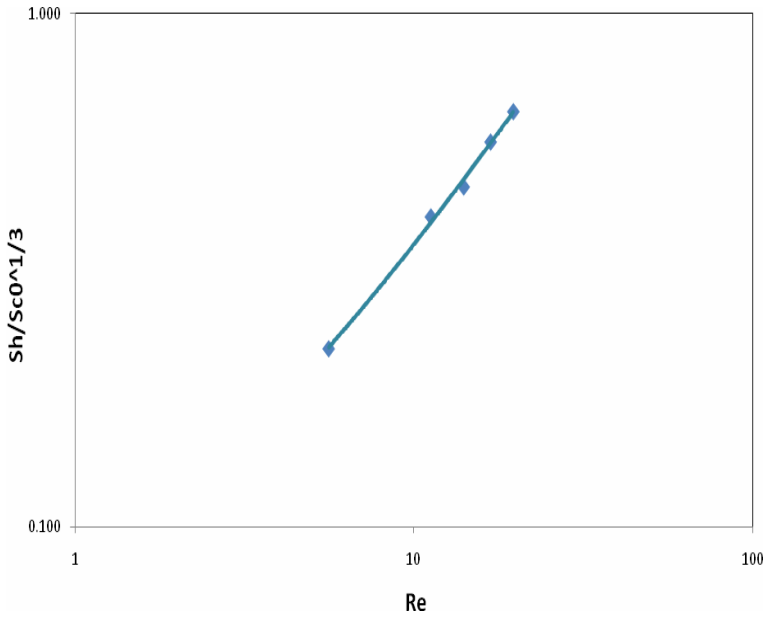

Figure (9) Sherwood-Reynolds correlation for Cd^{+2} concentration of 200 ppm

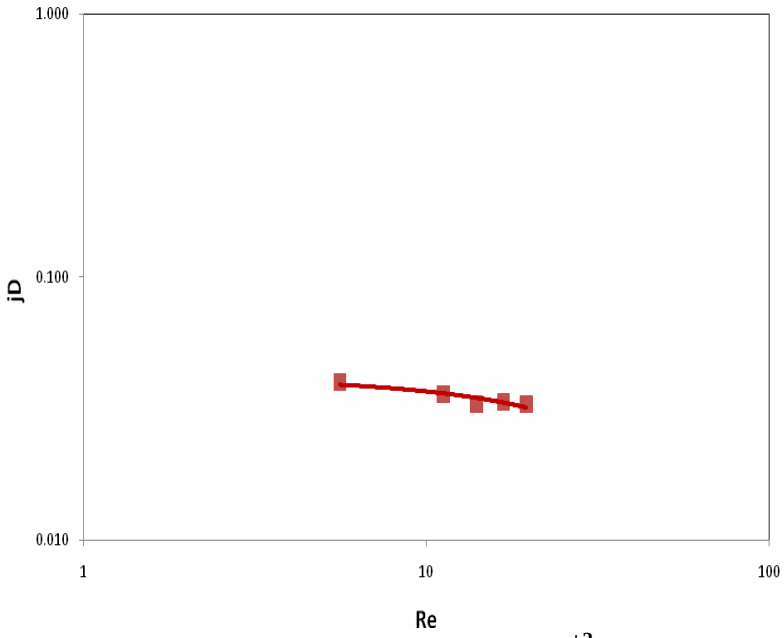

Figure (10) j_D factor-Reynolds correlation for Cd^{+2} concentration of 200 ppm