

Electrolytic Removal of Zinc Using A Flow-Through Cell With Amalgamated Copper Screen Cathode

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Received on:19/3/2008

Accepted on:7/8/2008

Abstract

The aim of this work was to establish an electrolytic method for the removal of zinc from waste water using a flow-through cell with amalgamated copper screen cathode. The performance of the electrolytic reactor were investigated by using different of electrolyte flow rates (60, 120, 180, 240, 320L/h) and different initial concentration of zinc solutions (48, 96, 150mg/L). A synthetic solution was processed using boric acid (0.1M) plus potassium chloride (0.1M) as the supporting electrolyte. The electrolytic cell employed a constant potential of -1.4V vs. SCE in the controlled potential mode.

Dimensionless Sherwood and Reynolds numbers were correlated to characterize the mass transport properties of the reactor, and they were fitted to the equation:

$$Sh = 0.6835 Re^{0.3895} Sc^{1/3} \quad \text{For } 1 < Re < 6.5, \quad 700 < Sc < 1390$$

Keywords: removal of heavy metal, a flow-through cell, screen cathode.

الازالة الالكتروليتيية للزنك باستخدام خلية من نوع flow-through مع قطب الكاثود من النحاس المملغم من نوع الغربان

الخلاصة

ان الهدف من هذا العمل هو تحقيق عمل الطريقة الالكتروليتيية لازالة الزنك من الماء المهدور باستخدام خلية من نوع (flow-through) يستخدم فيها قطب الكاثود من النحاس المملغم من نوع الغربان. تم البحث باستخدام معدلات جريان مختلفه للالكتروليت (60, 120, 180, 240, 320) لتراساعه وتراكيز ابتدائية مختلفه للزنك (48, 96, 150) ملغم لتر واستخدم في الخلية الالكتروليتيية فرق جهد ثابت (-1.4V) نسبة الى قطب الكالوميل القياسي بطريقة فرق الجهد هو المسيطر. وتم التعامل مع محلول أصطناعي باستخدام حامض البوريك (0.1M) مع كلوريد البوتاسيوم (0.1M) كالكتروليت مساعد. وتم أيجاد معادله لتميز خواص انتقال الكتلة للمفاعل باستخدام رقم رينولد ورقم شيروود، للمديات التاليه:

$$Sh = 0.6835 Re^{0.3895} Sc^{1/3} \quad \text{For } 1 < Re < 6.5, \quad 700 < Sc < 1390$$

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1.Introduction

The quality of water resources and of the environment in general is a permanent concern and has resulted in new solutions for old problems in the field of wastewater treatment. In particular, new efforts have been made at reducing the sources of pollutants and at improving the efficiency of waste treatments.

The ecological and economic problem caused by heavy metals (Cu, Pb, Zn, Ni and Cr) necessitates their recovery from dilute aqueous solutions. Electrochemical technology offers an efficient means of controlling pollution as it provides removal of heavy metals via redox reaction. The literature on application of flow-through porous electrodes in metal ion removal from aqueous solutions is extensive [1-8]. Zinc is one of the heavy metals, which is widely employed as a protective coating on to ferrous material, and electrolytic deposition from an acidic plating bath is the most

The system consisted of an electrochemical cell, two Perspex reservoirs of five liters capacity for catholyte and anolyte, two recirculation pumps, and two sets of flowmeters for controlling the catholyte and anolyte flow rates. These components were connected together by polyvinylchloride and polyethylene tubes. The electrochemical cell was made from six discs of Perspex (each 15cm diameter) joined together with four screws. Silicon rubber gaskets with (1mm) thickness were placed between each of the cell compartments to prevent electrolyte leakage. The cell was divided into cathodic compartment which contains amalgamated copper screen cathode and anodic compartment which contains a graphite anode, separated by anionic ion-exchange membrane. The electrochemical cell is described in detail elsewhere [9].

In this system, the electrolytes flow separately through the catholyte and anolyte compartments. The anolyte composition was the same as that of the

common process. As the main consumer of metallic zinc and its compounds, the electroplating industry is a source of Zn (II) containing aqueous waste.

In this paper an electrolytic cell with a porous cathode of amalgamated copper screen designed to remove Zinc from aqueous streams. By flowing simulated effluents Zinc ion containing through copper screen cathode, it is possible to achieve both high mass transfer rates and large surface areas for the electrochemical reaction.

2.Experimental Work

A synthetic effluent was used as catholyte solution which was, prepared from $ZnCl_2$ in such away that Zn (II) concentration were (48,96.150mg/L), using 0.1mole/L of boric acid and 0.1mole/L of potassium chloride as the supporting electrolyte. The resulting solution was presented at pH of 5.5. The flow system is shown schematically in Fig. (1)

catholyte, but without Zn (II).The flow rates of both electrolytes were adjusted to the same values (60,120,180,240,320 L/h).Then a constant potential of -1.4V vs. SCE was applied to the cell from a potentiostat system, in the controlled-potential mode. The reduction of Zinc at this potential is mass transport controlled [9]. At predetermined intervals, the solution leaving the cathodic compartment was sampled, and the remaining metal concentration was quantified by atomic absorption spectrometry. This procedure was used for different initial concentration of Zinc solution (48, 96. 150 mg/L).

3.Results and Discussion

Figure (2) shows the decrease in normalized Zn (II) concentration ($c(t)/c_0$) with the time of electrolysis, using different catholyte flow rates (60,120,160,240,320 L/h)with solution of 48 mg/L of Zn (II).

All these curves had the same profile in which the zinc ion concentration decreases exponentially with the time. Exponential decay of metal concentration is only observed if the reduction reaction occurred at limiting current [10]. Therefore potentials used in the experiments apparently cause the Zn (II) reduction reaction to be mass transfer limited. It can

Figure (3) shows plot of $\ln(c(t)/c_0)$ against time of electrolysis, using data shown in Fig. (2). Expectation of linearity is confirmed and the slopes from straight lines give an indication of the cell performance, since they are related to the mass transfer coefficient. A controlled potential electrolysis at cathode, carried out under mass transfer controlled in a recycle mode is described by [11]:-

The values obtained for k_m are plotted vs. electrolyte velocity (log-log) in Fig. (4). It can be seen from the Fig. (4) that the higher flow rates enhance the mass transfer coefficient, k_m , therefore increasing the reduction rate of Zn (II). The results are correlated by the empirical expression:-

Figure (5) shows zinc mass deposition versus time, calculated by mass balance for different initial concentration of Zn Figure (6) and figure (7) show the curves of normalized concentration as a function of time, using different flow rates of electrolyte (60.160.320L/h) with initial

Figure (8) and figure (9) show the $\ln(c(t)/c_0)$ against time plot. As mentioned before values of k_m were calculated from

Figure (10) shows the variation in k_m with the mean linear flow rate for different initial concentration of Zn (II) solution (48,

It can be seen from Fig. (10) that the mass transfer coefficient decreases with increasing of initial concentration of Zn(II) solution for a given velocity of electrolyte because the electrolysis demands a greater time for higher initial concentrations of Zn(II) solution as shown in Fig. (5). The mass transfer coefficients from Fig. (10) are used to calculate the dimensionless

be seen from Fig. (2) that as the flow rate increases the reduction of Zn (II) becomes more effective [9]. This behavior is attributed to greater rate of mass transport of Zn (II) due to an increase in the electrolyte flow rate which reduces the thickness of the boundary layer for mass transfer [4].

$$\ln\left(\frac{c(t)}{c_0}\right) = -\frac{V_e k_m A_e}{V_T} t \quad \dots\dots\dots (1)$$

Since V_e/V_T ratio is 0.000908 for the cell and A_e has been calculated and is equal to $53.4 \text{ cm}^2/\text{cm}^3$ [9] values of k_m can be estimated from the slopes of $\ln(c(t)/c_0)$ vs. time plots for each flow rate considered.

$$k_m = 0.0066 u^{0.364} \quad \dots\dots\dots(2)$$

With CR=0.956 and ER=0.0003, where k_m and u have the units cm/sec.

(II) solution (48, 96,150mg/L).It can be noticed that the curves are exponential with time.

concentration of 96mg/L of Zn (II) and 150mg/L of Zn (II) respectively. As expected, an exponential decay of zinc concentration is observed.

the slopes of the $\ln(c(t)/c_0)$ against time plot for each flow rate considered.

96, 150 mg/L) combined together for comparison.

Sherwood number and j_D - factor for the three concentration of Zn (II) solution (48, 96,150mg/L). Figure (11) shows a $Sh/Sc^{0.33}$ versus Re (log-log) plot and Figure (12) shows j_D -factor versus Re (log-log) plot for three different concentration of Zn (II) solution (48, 96,150 mg/L). The data for all three concentration of Zn (II) solution have been fitted to a single correlation as

follows:-

$$Sh = 0.6835 Re^{0.3895} Sc^{1/3} \quad \text{--- (3)}$$

With CR=0.896 and ER=0.097

$$j_D = 0.6818 Re^{-0.6104} \quad \text{---- (4)}$$

With CR=0.895 and ER=0.081

For $1 < Re < 6.5$, $700 < Sc < 1390$

Conclusions

This research has demonstrated that a flow-through porous electrode made of amalgamated copper screen can be an effective device in removing Zinc from simulated effluents, and the

concentration of Zn (II) was reduced to 5mgL^{-1} (allowable of Zn (II) containing solution for final discharge of the aqueous waste stream as in the literature) during recirculation times ranging from 100 to 190min, depending on the flow rate. The best rates of Zinc

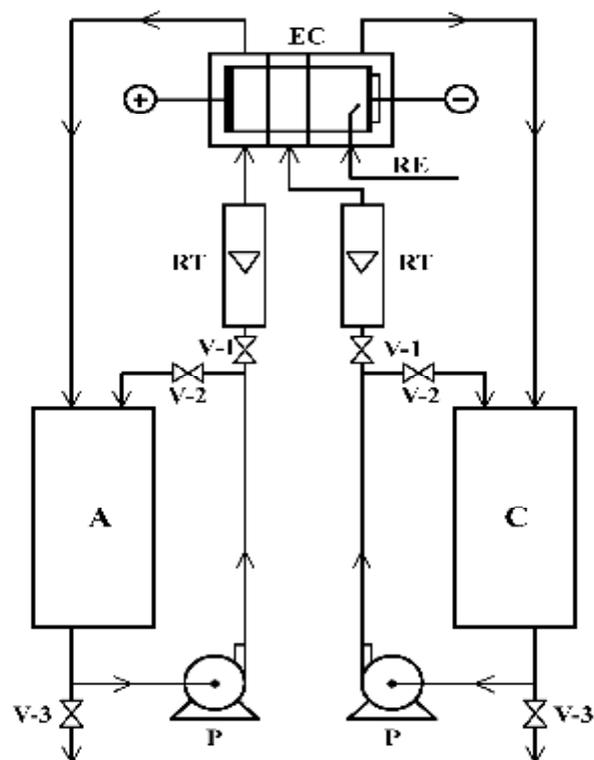
removal and the highest values for the mass transfer coefficient were obtained at the higher flow rates and higher initial concentration of Zn (II) solution. An empirical correlation was obtained for the effect of electrolyte velocity on the mass transfer coefficient in the electrode. Mass transfer coefficients and hydrodynamic data were correlated through equation (3) and equation(4) as follow:

$$Sh = 0.6835 Re^{0.3895} Sc^{1/3} \quad \text{----(3)}$$

$$j_D = 0.6818 Re^{-0.6104} \quad \text{----(4)}$$

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EC: Electrolytic Cell.
 RE: Reference Electrode.
 RT: Rotameter.
 P: Pump.
 A: Analyte Reservoir.

Figure (1) Schematic Diagram of the Flow System
 V-1 Inlet valve, V-2 Recycle valve, V-3 Drain valve
 M- Membrane

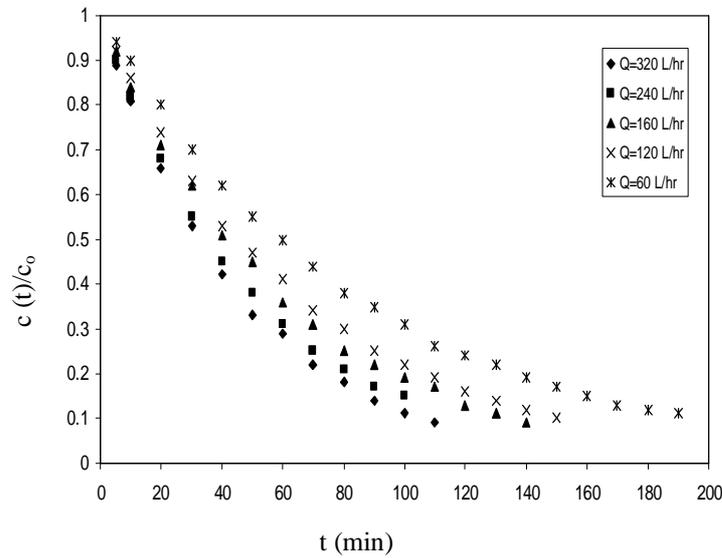


Figure (2) Normalized concentration ($c(t)/c_0$) against time curves for Zn (II) removal for different flow rate and Zn (II) concentration of 48 mg/L

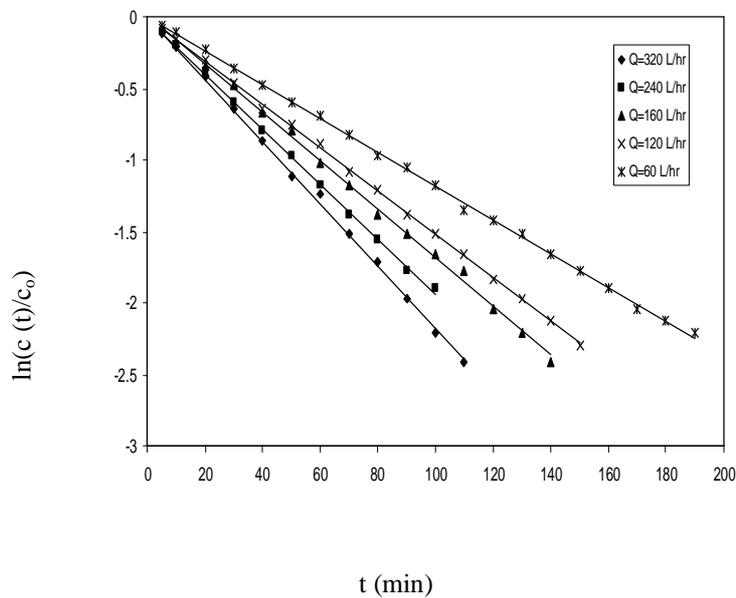


Figure (3) Linearization of normalized Zn (II) concentration against time for different flow rate and Zn (II) concentration of 48 mg/L

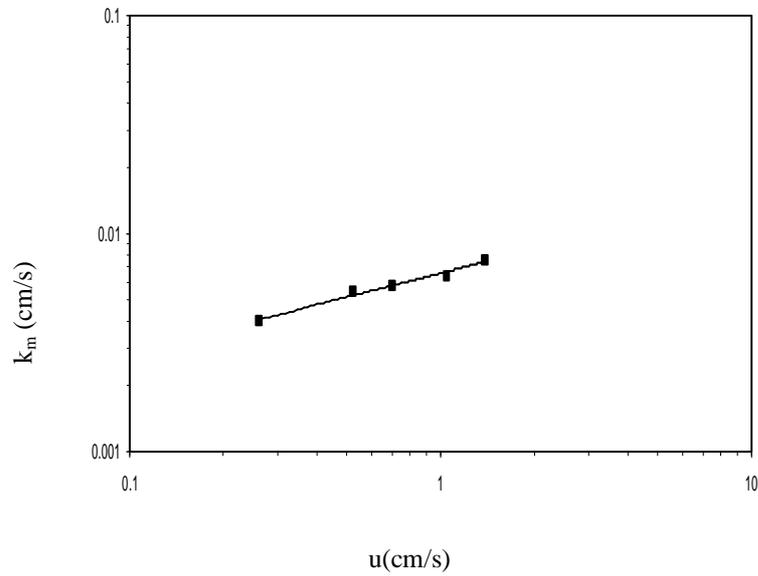


Figure (4) Variation of k_m with electrolyte velocity for Zn (II) concentration of 48 mg/L

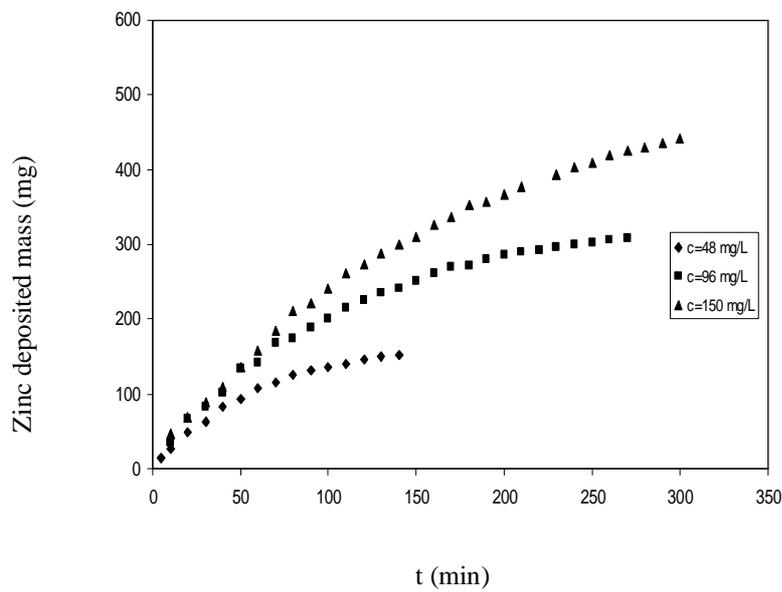


Figure (5) Zinc deposited mass versus time curves at flow rate of 160 L/h for different initial concentrations of Zn (II) solution.

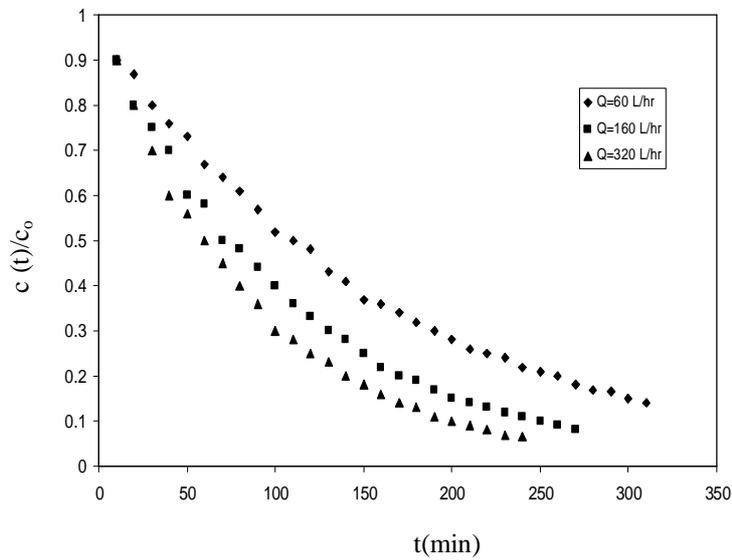


Figure (6) Normalized concentration decay as a function of time for Zn (II) removal experiments for different flow rates with solution of 96 mg/L of Zn (II).

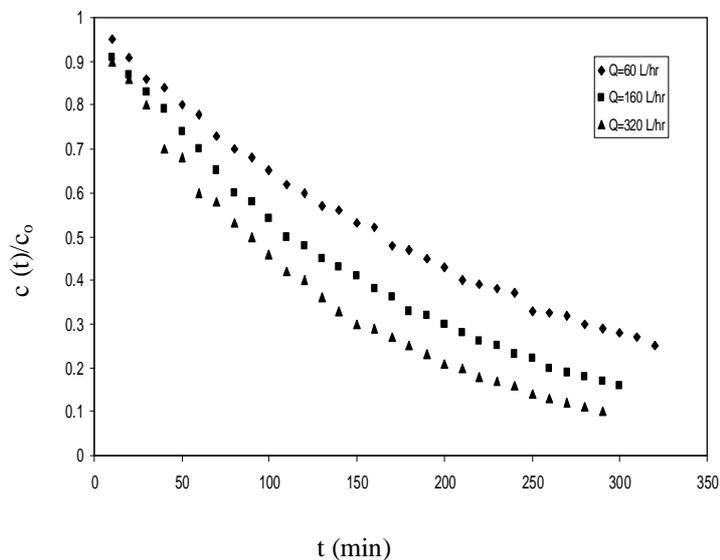


Figure (7) Normalized concentration ($c(t)/c_0$) against time curve for Zn (II) removal for different flow rates, obtained for Zn (II) concentration 150 mg/L.

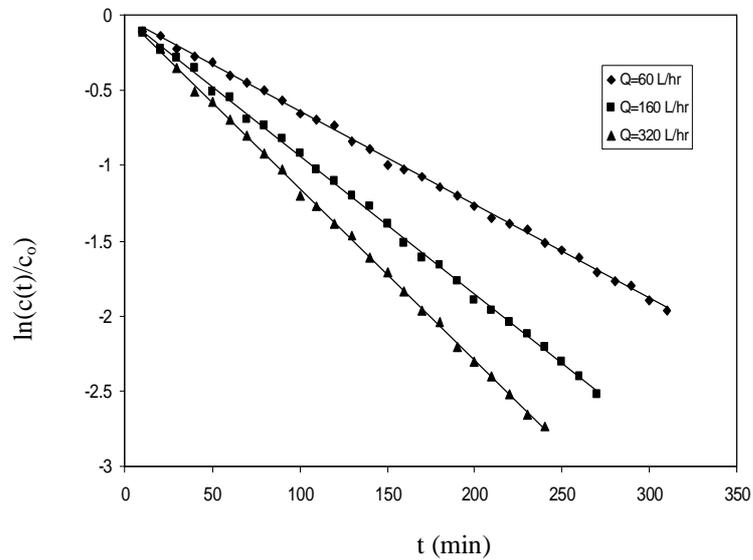


Figure (8) Plots of $\ln[c(t)/c_0]$ vs. time for Zn (II) removal experiments for different flow rates with solution of 96 mg/L of Zn (II).

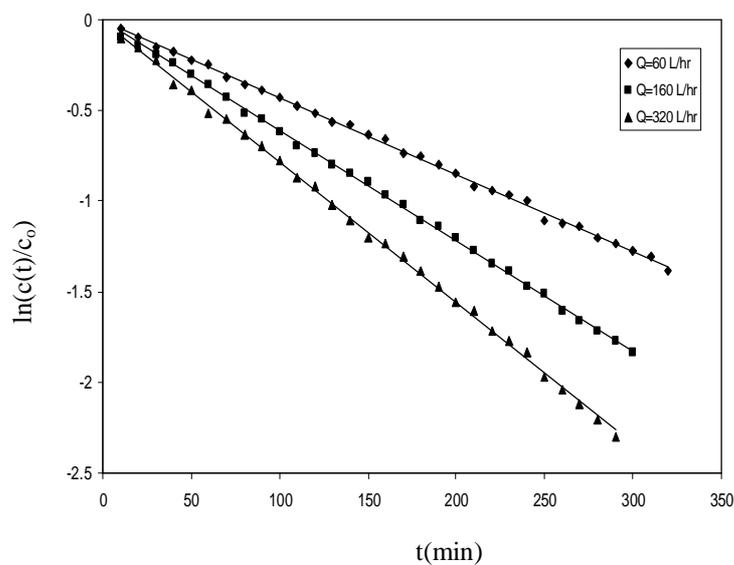


Figure (9) Linearization of normalized Zn (II) concentration against time for different flow rates, obtained for Zn (II) concentration 150 mg/L.

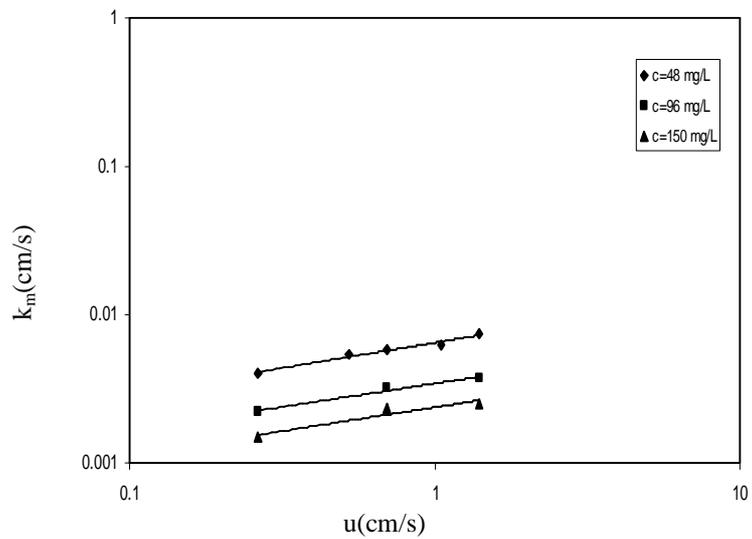


Figure (10) Variation of the mass transfer coefficient with the velocity of electrolyte for different concentrations of Zn (II) solution.

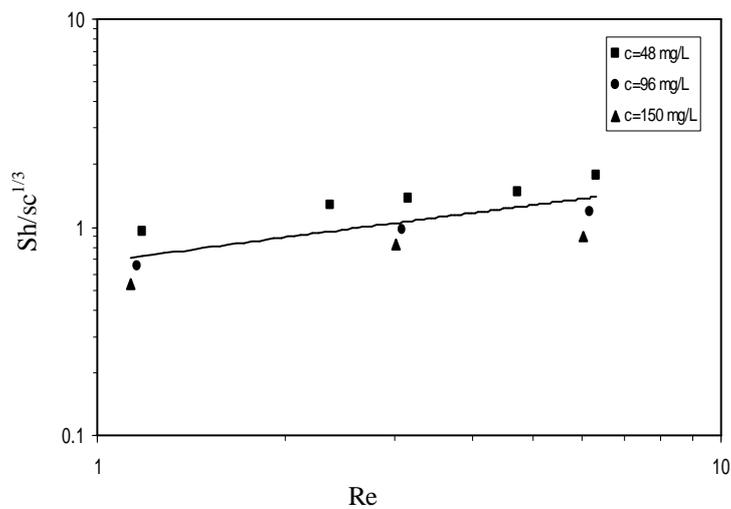


Figure (11) Sherwood-Reynolds correlation for the three initial concentration of Zn (II) solution.

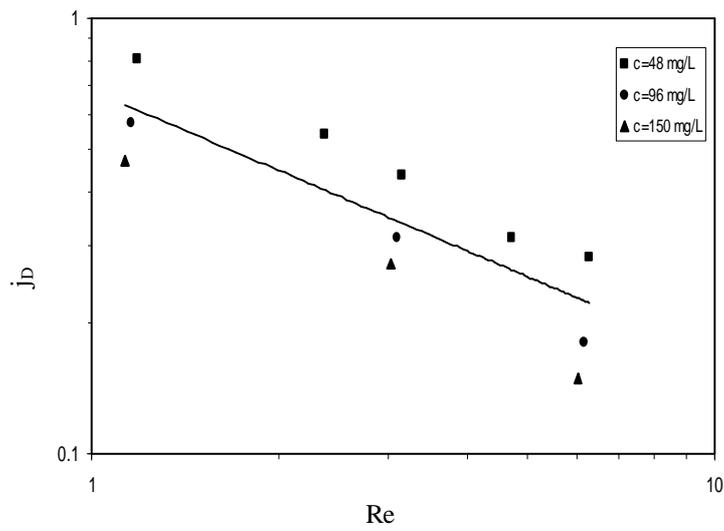


Figure (12) j_D -Reynolds correlation for the three initial concentration of Zn(II) solution.