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Electrolytic removal of zinc from simulated chloride wastewaters using a novel flow-by fixed bed electrochemical reactor

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Abstract

The cathodic deposition of zinc from simulated chloride wastewater was used to characterize the mass transport properties of a flow-by fixed bed electrochemical reactor composed of vertical stack of stainless steel nets, operated in batch-recycle mode. The electrochemical reactor employed potential value in such a way that the zinc reduction occurred under mass transport control. This potential was determined by hydrodynamic voltammetry using a borate/chloride solution as supporting electrolyte on stainless steel rotating disc electrode. The results indicate that mass transfer coefficient (K_m) increases with increasing of flow rate (Q) where $K_m \propto Q^{0.402}$.The electrochemical reactor proved to be efficient in removing zinc and was able to reduce the levels of this metal to lower than 0.7 ppm starting from initial concentration of 48.4 mg dm^{-3} ppm in 120 minutes using ratio of cathode volume/catholyte volume equal to 0.0075. Sherwood and Reynolds numbers were correlated to characterize the mass transport properties of the reactor as follows: $Sh = 0.0644 Re^{0.3686} Sc^{1/3}$

Key Words: Heavy metals, Electrochemical reactor, Zinc, Flow-by electrode, Mass transfer

Introduction

Preventing of pollution and environmental damage by industrial waste causes governments to implement stricter environmental legislation. Industrial wastewater containing toxic ions represents a challenging case owing to the difficulty of removing these ions by biodegradation [1]. Pollution by toxic metals including Cu, Cd, Cr, Pb, Hg and Zn is generated by a wide range of manufacturing industries such as mining, metal finishing, electroplating, photographic development, printed circuit board production and battery [2]. Several methods have been used to remove toxic metals from wastewater effluents; including chemical precipitation [3], electrodialysis [4], ion exchange process [5,6], adsorption onto activated carbon [7, 8], low cost adsorbents such as kaolin, bentonite, blast furnace slag and fly ash [9], ion imprinted polymer [10], organic-based ligand precipitation [11], membrane and reverse osmosis processes [12]. The industrial utilization of these methods has been found to be limited, because of the high capital and operating costs and/or the ineffectiveness in meeting stringent effluent standards [13].

Electrochemical removal technology by cathodic deposition gives an efficient mean of controlling pollution through the removal of transition and heavy metals by redox reactions, without the shortcomings of conventional treatments. The main advantage of this technology is its environmental compatibility due to the fact that the main reagent, the electron, is a ‘clean reagent’ [14].

The using of porous materials as three dimensional electrodes in the design of electrochemical reactors led to increase the use of electrochemical technologies in the environmental treatment [15]. The main advantages of this kind of electrode are having high specific surface area as well as high mass transfer rate. Two principal configurations for the three dimensional electrodes have been developed: the flow-through configuration in which the fluid flows parallel to the current; and the flow-by configuration, where the fluid flows perpendicularly to the current[16]. Unfortunately the flow- through porous electrode does not prove its efficiency on the industrial scale because of the non-uniform current and potential distribution, poor selectivity and low conversion per pass [17]. To avoid these shortcomings attention has been directed to the flow-by electrode [18-20].

Several types of flow-by electrode have been used industrially in removing of heavy metals, for example, carbon or metal particles [21,22], metallic or metal plated foams and felts [23,24] ,and reticulated vitreous carbon (RVC) [25]. However, these electrodes suffer from many problems like the clogging of the pores due to the continuous metal deposition and high pressure drop. Besides, metal felt and metal foam fixed bed electrodes may entrap gas bubbles (H_2) which are likely to evolve simultaneously with the main reaction from dilute solutions with a consequent increase in cell resistance and electrical energy consumption [26]. The use of screens as three dimensional electrodes offers many advantages, such as high specific area, high turbulence-promoting ability, high porosity and relatively low pressure drop, ease of coating with a catalyst, and ready availability at modest cost [27-31]. In addition, they present a rigid structure and are relatively easy to construct.

Most of electrochemical reactors are operated via two modes of operation, namely batch recirculation and once-through flow. In the former mode product from cell is mixed with the feed and the liquor concentration gradually decreases in value during operation until the required terminal concentration is achieved. In the latter the inlet and outlet cell concentration remain constant with time and process is ended when all the liquor is passed through the cell [32].To maintain a high recovery or removal efficiency in once through systems, the electrolyte has to pumped very slowly through the electrode. Sioda [33] gave an equation for calculation of this critical velocity corresponding to complete reaction controlled by diffusion. Too low flow rate, however, is also not practical when thousands of gallons of effluents have to be treated. A recirculation operation is thus more adapted for industrial application and its behavior has been investigated theoretically by considering the porous electrode as the analog of a chemical reactor [34-36].

Most of previous works on the removal of heavy metals using a flow-by electrochemical cell composed of stack of nets were carried out using once through or single –pass flow mode of operation where mass transfer correlations that describe this system have been determined [37-40].

However no previous work was conducted to removal of zinc using screens as a flow-by fixed bed electrochemical reactor operated at either single–pass flow or batch recirculation mode. The purpose of this work was to develop an improved reactor design that is easy to fabricated and operated at batch recycle model where the mass transfer correlation was determined and compared with previous works. The choice of stainless steel as cathode material in this study is based on the observation of previous works that stainless steel has been proved to be very effective as a cathode for metal removal from wastewaters [41-43]. This material showed a good stability as cathode and could also be anodically polarized during its regeneration process without damage. Furthermore, stainless steel is an inexpensive material when compared with graphite felt or reticulated vitreous carbon which has been extensively used in wastewaters treatment.

Experimental Work

The development of the electrolytic cell for zinc removal was carried out in two stages. Initially, a voltammetric study of the Zn(II) reduction on a stainless steel rotating disc electrode was performed in order to determine the potential over which this reaction is controlled by mass-transfer. Subsequently, the selected potential was applied to a flow-by electrolytic cell containing a stack of stainless steel screens cathode. All reagents were of analytical grade and did not undergo further purification. Distilled water was used to prepare all solutions. Metallic ion solutions were prepared in such a way that the metallic concentration was around 50 mg/L. zinc solution was prepared from $ZnCl_2$ plus 0.5M NaCl and 0.1 M H_3BO_3 with a final pH of 5. Solution viscosity and density were determined by an Ostwald viscometer and density bottle, respectively [44].Table 1 represents the physical properties of electrolytic solution.

Table 1, Physical properties of the solution at 25°C

Property	value
Concentration(ppm)	50
Density(g/cm^3)	1.0471
Kinematic viscosity(cm^2/s)	0.00915

Electrochemical experiments were controlled with an electric circuit consisting of power supply (model UNI-T: UTP3315TF-L), resistance boxes, ammeter and voltmeter. All experiment were performed at 25±1°C.The hydrodynamic voltammetric experiments were carried out in a conventional three-electrode cell with separated compartments for each electrode. A stainless steel (316-AISL) rotating disc electrode as a working electrode with an active cross sectional area of 0.0314 cm^2, a large-surface platinum counter-electrode, and a saturated calomel reference electrode (SCE) within a Luggin capillary, were used. The stainless steel electrode was polished to a mirror-like surface, using emery paper of grade 600 (3M). The current-voltage curves were obtained for several rotation speeds (400, 800, 1200, 1600, and 2000 rpm) by linear sweep of the working electrode potential starting from open circuit potential to the more cathodic potential up to -1600 mV vs. SCE.

The dual continuous-flow cell design is shown schematically in Fig.(1).It consists of an electrochemical cell, two 5-L capacity Perspex reservoirs for the catholyte and the anolyte, two magnetic recirculation pumps(EHEIM kerisel), and two sets of flowmeters, with a flow range from 60 to 480 l/h, for controlling the catholyte and anolyte flow rates. These components were connected together by polyvinylchloride tubes.

The flow-by reactor design in this study was based on the criteria established by Risch and Newman [45]. According to Risch and Newman criteria, a flow-by reactor with an aspect ratio of the electrode length to thickness, *L/t* > 5, will produce a higher maximum processing rate than a flow-through configuration. The aspect ratio of present cell is 33.33. The electrolysis cell, which is shown in Fig.(2), was basically a rectangular flow channel constructed from two machined blocks of poly tetrafluoroethylene(PTFE).The first is the cathodic chamber having external dimensions(30x14x2.5cm) while the second is the anodic chamber with dimensions (30 x14 x 3.5 cm).The anodic chamber has two cavities; internal (10 x10 x2.2 cm)in which graphite block (10 x10 x2 cm) working as anode was fixed ,and external (24 x10 x0.5 cm)in which the anolyte is flowing over anode upward. The anode was grooved lengthwise to increase its surface area. The cathode chamber has also two cavities; internal (10x10x0.6cm) in which copper plate (10x10x0.5cm) working as current feeder was fixed, and external (24x10x0.3cm) in which the catholyte passes through two stacks of screens: the first consisted seven polypropylene meshes with mesh number (30wire/inch) working as calming zone.

The second consisted five stainless steel screens (316-AISI) of mesh number (30 wire/inch) working as flow-by. The Current feed to the electrodes was provided by screw connectors through the walls of the cell. A saturated calomel reference electrode within a teflon Luggin capillary entered the cathode chamber through a 3mm-hole drilled from the back near the copper plate. The anodic and cathodic chambers were separated from each other by a cationic membrane (IONIC-64LMR) which was supported on both sides with 2mm thickness PTFE perforated plates. The cell was held vertically and the electrolytes were circulated upwards. The flow system was loaded with 4.0 liters of catholyte and anolyte, each in a separate reservoir.

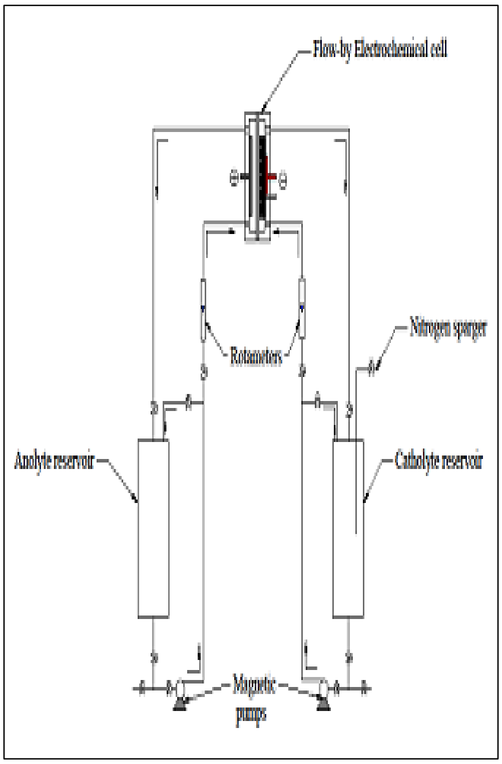


Fig.1, Schematic view of the batch recirculation electrochemical system

The catholyte was composed of 0.5M NaCl and 0.1 M H_3BO_3 with zinc concentration of 50 ppm at final pH of 5. The anolyte composition was the same as the catholyte, with the exception of the metal ions, and the flow rates of both electrolytes were adjusted to the same value.

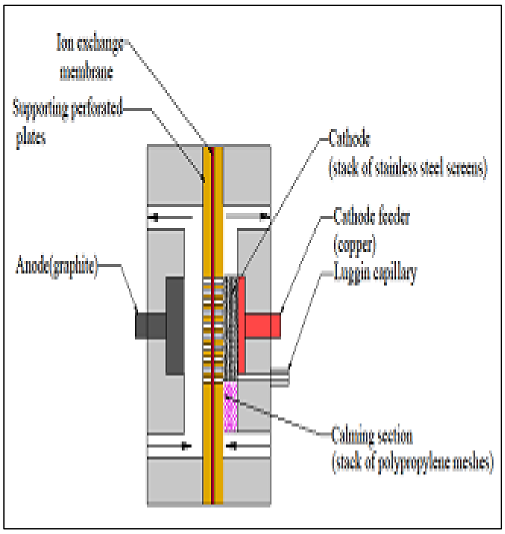


Fig. 2, the flow-by electrochemical cell

The catholyte was purged with high purity nitrogen (99.999%) for 30 min to prevent contamination with oxygen. A constant potential (determined from voltammetry experiment) for reduction of zinc at the limiting conditions was applied to the cell from the power supply, in the controlled-potential mode, for two hours. At predetermined intervals, the solution leaving the cathodic compartment was sampled, and the remaining metal concentration was quantified by atomic absorption spectrometry (Varian SpectrAA 200 spectrometer), in order to monitor the effectiveness of electrolysis. The properties of this screen{ opening size of screen(D) cm , porosity(ε) and specific surface area(a) cm^{-1}} were calculated using equations of Armour and Cannon[46].The properties of this screen are shown in Table 2.

Table 2, Screen parameters

Mesh number wire/inch	30
Woven type	Plain square
Wire diameter(cm),d	0.03
Opening size(cm),D	0.0547
Screen porosity, ε	0.7048
Specific area (cm^{-1}),a	39.366

Discussion

1- Hydrodynamic Voltammetric Experiments

Fig.(3)shows polarization curves corresponding to zinc electrodeposited on stainless steel rotating disc electrode for several rotation speeds (400, 800, 1200, 1600, and 2000 rpm). The voltammograms show a limiting current zone in the potential range from -1160 to -1350 mV vs. SCE. Under such conditions, the reaction rate is limited by the mass transport rate and the limiting current at the smooth rotating disc in laminar flow can be predicted by the Levich equation [47]:

$$I_L = 0.62\, z\, F A D^{2/3} \omega^{1/2} \nu^{-1/6} c_b \; \ldots (1)$$

where I_L is the limiting current mA, A is the area of electrode cm^2, D is the diffusion coefficient cm^2/s, ω is the rotation rate rad/ s, ν is the kinematic viscosity of the electrolyte cm^2/s and c_b is the bulk concentration(mol/ cm^3).

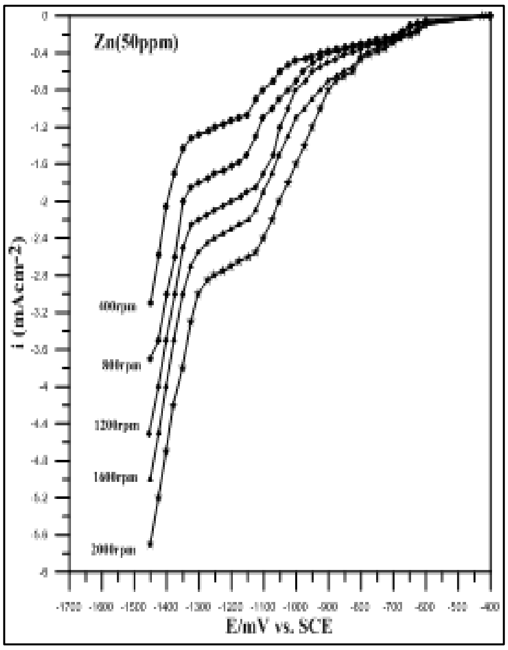
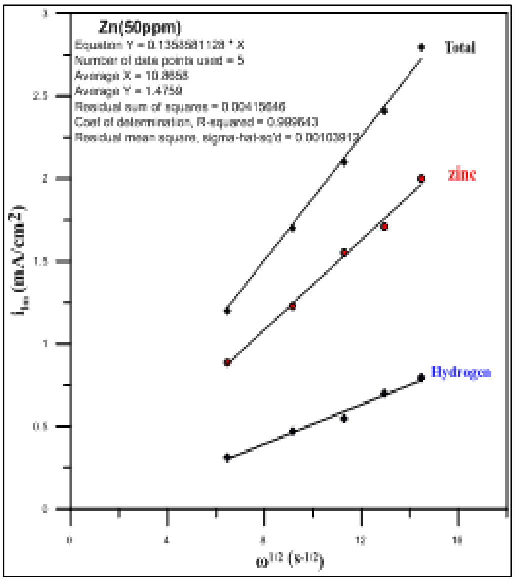
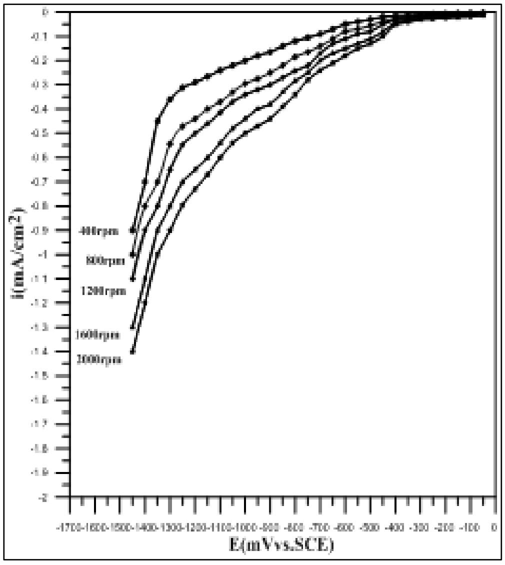


Fig. 3, Linear voltammetric curves for reduction of Zinc on stainless steel rotating disc electrode at different rotation speeds: [Zn] =50 ppm supporting electrolyte (0.5 M NaCl +0.1 M H_3BO_3), pH=5

To investigate whether the reduction of zinc occurred under mass transfer condition, the limiting currents were calculated from the polarization curves and plotted against $\omega^{1/2}$ as shown in Fig.(4-a) .The limiting current is found at the middle point of a straight line that follows the plateau region and is limited by E_{max} and E_{min} [48].



(a)



(b)

Fig. 4, (a) Levich plots for the limiting currents taken at potentials of -1260 mV for total reduction (zinc and hydrogen) and zinc reduction (b) Linear voltammetric curves without zinc on stainless steel rotating disc electrode at different rotation speeds

These values are the points at which the straight line departs from the I vs. E curve. The results indicate that the reduction of zinc is under mass transfer control. During the zinc metals electrodeposition, hydrogen evolution is always a competitive parallel process.In this case hydrogen evolution amplifiers the response without apparently changing its shape. Thus, in order to correctly determine the Zn^{+2} diffusion coefficients in the supporting electrolyte, it was necessary to bubble N_2 in the solution to eliminate dissolved O_2 and to discount the hydrogen contributions to the total current density. Fig.(4-b) shows the voltammogrames recorded using the supporting electrolyte(0.5 M NaCl + 0.1M H_3BO_3) and pH=5 without zinc under the same rotations as those employed to obtain the data shown in Figure (3), so that the current densities recorded under the potentials of mass transfer of this metal resulted exclusively from the reduction of hydrogen. Data of the best fit of the limiting current of zinc only from Fig.(4-a) were used to estimate the diffusion coefficient of zinc at 50 ppm, using the Levich equation. Taking the value of the electrolyte kinematic viscosity from Table (1),the value of diffusion coefficient of zinc in the present work was estimated to be 17.7 x 10^{-6} cm^2/s which is slightly higher than those obtained at the previous works [49, 50].The reason may be the effect of boric acid used in the present work.

2- Cell Performance For Electrolytic Copper Removal

The use of the batch recirculation (or batch recycle) mode is a versatile strategy that allows the operator to adjust the volume of the system, monitoring and controlling the concentration of ions and pH [51]. Modelling of the batch recirculation plug flow reactor is more complex than that of the single pass plug flow reactor as both the reactor and reservoir have time dependent concentrations associated with them. A rigorous model of concentration-time relationships in recirculating electrochemical reactor system has been proposed by Walker and Wragg[35], However, it is possible to simplify this model by manipulating the setup such that pseudo-steady state, isothermal conditions are achieved. A pseudo-steady state system is approached by the use of a reservoir with a far greater volume than that of the reactor, such that the change in concentration with time at any given point in the reactor is insignificant in comparison to the change in concentration with distance through the reactor. Consequently the change in concentration as a function of time can be described by the following equation [52]:

$$C(t) = C(0)\exp\left\{-\frac{tQ}{V_r}\left[1-\exp\left(-\frac{K_m aL}{u}\right)\right]\right\} \quad \text{... (2)}$$

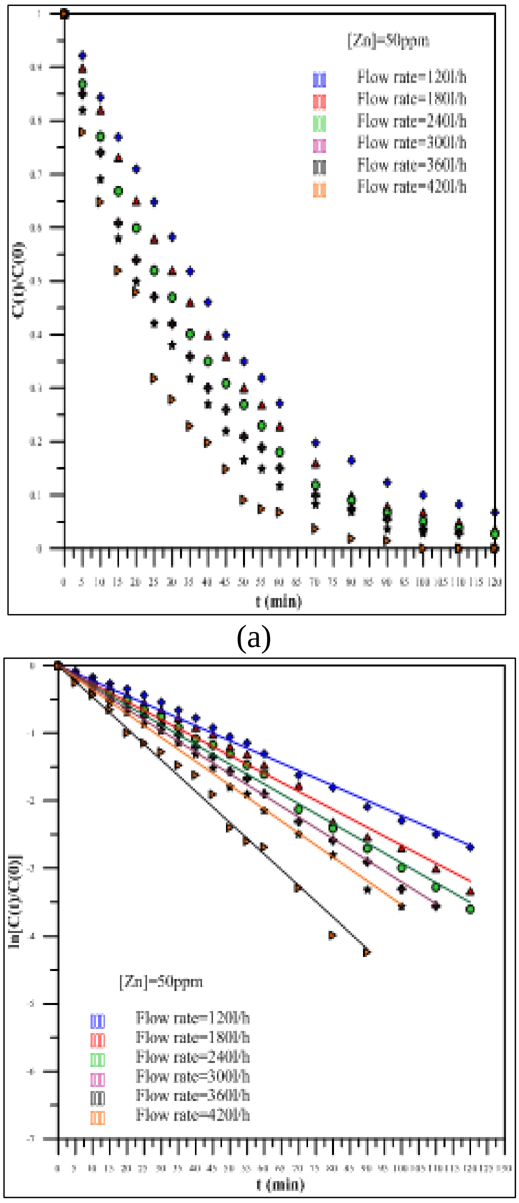
Where C(t) is the concentration at time t (mole/cm^3), C(0) is the initial concentration(mole/cm^3), Q is catholyte flow rate (cm^3 /s), V_r is catholyte volume (cm^3), k_m is mass transfer coefficient(cm/s), a is specific surface area (cm^{-1}),L is cathode length(cm) and u is superficial velocity (cm/s). Eq. (2) can be written as follows:

$$\ln\frac{C(t)}{C(0)} = st \quad \text{... (3)}$$

Where s is the slope of logarithmic concentration against time, from which mass transfer coefficient can be calculated as follows:

$$k_m a = -\frac{Q}{V_c}\ln\left(1+\frac{V_r s}{Q}\right) \quad \text{... (4)}$$

Where V_c is the cathode volume (cm^3).



(a)

(b)

Fig. 5, (a) Normalized concentration [C(t) /C(0)] against time curves for zinc removal experiments at different flow rate, (b) Plots of ln[C(t) /C(0)] against time.

Walker and Wragg[35] found that this approximated model can be applied for a reactor: reservoir volume ratio of higher than1:100.In the present work the ratio is 30cm^3:4000cm^3 (1:133.333) which is in agreement with the assumption of the approximated model. Fig. (5-a and b) shows the plot of normalized concentration (C(t) /C(0)) as a function of time and the linearized concentration profile for different flow rates.

The data show that as the flow rate increases, the removal of zinc become more effective, this behavior was attributed to a greater rate of mass transport of zinc ions due to an increase in the electrolyte flow rate. Although the plots of C(t) /C(0) as a function of electrolysis time were apparently exponential. Table (3) shows values of initial concentrations, C (0), the times for 90% and 99% removal, and values of k_m as a function of flow rate. Also Fig. (6) depicted the relation between of k_m and Q. It is clear that K_m increases with Q raised to the power of 0.402.

Table 3, Effect of the flow rate on the removal rate of zinc from chloride medium, pH 5.0, five screens, mesh no.30 (wire/inch)

Q (l/h)	C(0) (ppm)	$t_{90\%}$ (s)	$t_{99\%}$ † (s)	K_m(cm/s) x10^{-3}	C‡ (ppm)
120	48.6	6000	9600	1.2819	3.3
180	50.6	4800	8280	1.5284	1.8
240	47.9	4560	8160	1.6741	1.3
300	49.3	3600	6960	1.8319	< 1.4
360	49.7	3390	6780	2.0234	< 1.4
420	48.4	2940	5940	2.6619	< 0.7

†These values were calculated based on linear extrapolation

‡electrolysis time =120 min

Table (4) represents values of Re, K_m, and Sh for zinc deposition reaction and Fig. (7) shows plots of the log ($ShSc^{-1/3}$) against log(Re). A best fit line was used to correlate the data of the power relation as follows:

In terms of Sherwood number

$$Sh = 0.0644Re^{0.3686}Sc^{1/3} \qquad \ldots (4)$$

In terms of j_D

$$j_D = 0.064Re^{-0.6314} \qquad \ldots (5)$$

Where $Re=\rho u d_w/\mu$, $Sh=k_m d/D$, $Sc=\mu/\rho D$, $J_D=Sh/(ReSc^{1/3})$. The linear correlation coefficient is 99.394%. This correlation was established for Reynolds number $52 \leq Re \leq 180$ and Schmidt number (Sc)=2362.5

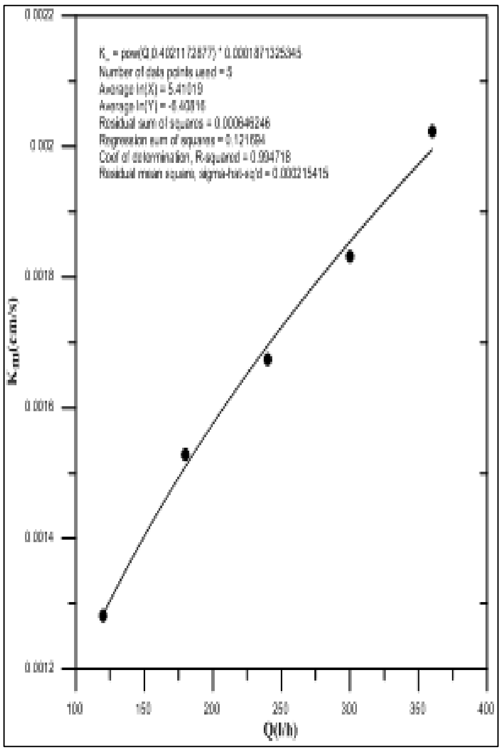


Fig. 6, The relation between mass transfer coefficient and flow rate in zinc removal.

Table, 4, Values of Re and Sh and their respective logarithmic values for the removal rate of zinc, pH 5.0, five screens, mesh no.30 (wire/inch)

Re	Sh	Sh/Sc 1/3	Log(Re)	Log(Sh /$Sc^{1/3}$)
51.6915	2.1728	0.2707	1.7134	-0.5675
77.5372	2.5905	0.3228	1.8895	-0.4911
103.3829	2.8375	0.3536	2.0145	-0.4515
129.2287	3.1049	0.3869	2.1114	-0.4124
155.0744	3.4295	0.4273	2.1905	-0.3693
180.9202	4.5116	0.5621	2.5749	-0.2501

No previous work on removal of zinc using screens electrode has been conducted, only Sabri [53] studied the removal of zinc using flow through electrode operated on batch recycle model. The obtained correlation was as follows:

$$Sh = 0.9089 Re^{0.363} Sc^{1/3} \qquad \text{... (6)}$$

Table 5, Comparison of Sabri results with present work

Author	electrolyte	Q l/h	C(0) ppm	C $_{t=100min}$ (ppm)	RE (%)
Sabri [53]	0.1MKCl ,0.1MH_3BO_3	120	44.16	10.56	76.087
		240	43.2	7.2	83.333
This work	0.5M NaCl , 0.1M H_3BO_3	120	48.6	4.9	89.918
		240	47.9	2.4	94.989

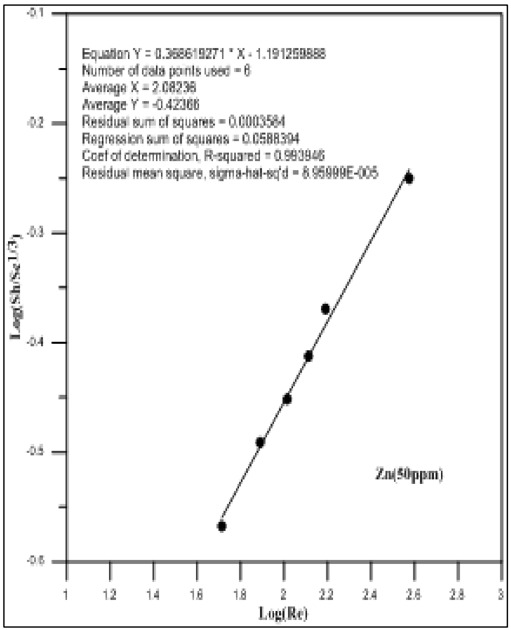


Fig. 7, log ($Sh/Sc^{1/3}$) verses log (Re)

The exponent of Re in the present work is somewhat higher than Sabri, however the correlation constant in Eq.(6) is higher than obtained in the present work leading to a higher mass transfer. This behavior was expected because the system in Sabri work was flow through in which jetting effect is occurred which leads to higher mass transfer as approved by Sedahem [54]. The removal efficiency of present work is much higher than Sabri work as shown in Table (5).This is an indication that hydrogen evolution in Sabri work is higher than the present work.

Lanza and Bertazzoli[55] investigated removal of zinc using RVC electrode and chloride solution at batch recycle mode ,in spite of no mass transfer correlation was determined ,they studied the effect of different variables on mass transfer coefficient. Table (6) shows the comparison between the present work and results of Lanza and Bertazzoli for RVC having specific surface area 37.4cm^{-1} which is closer to the surface area of screens used in this work.

Table 6, Comparison of Lanza and Bertazzoli results with present work

Q	Q l/h	C(0) ppm	$t_{90\%}$ (s)	$t_{99\%}$ (s)	K_m(cm/s) x10^{-3}
Lanza and Bertazzoli [55]	120	54.4	1500	1680	1.83
This work	120	48.6	6000	9600	1.2819

It is clear that $t_{90\%}$ and $t_{99\%}$ is lower in Lanza and Bertazzoli work, this is because the ratio(V_r/V_c) is 37 while in the present work is 133.33 therefore they modeled their system as a simple batch not as batch recycle mode in spite of their working at batch recycle mode. With (V_r/V_c) equal to 133, it was expected that electrolysis time is higher than Lanza and Bertazzoli system if the system operated at higher current efficiency as the case of present work. the increasing of mass transfer in Lanza and Bertazzoli work may be resulted from evolution of hydrogen gas due to decreasing the concentration during the electrolysis which is expected since (V_r/V_c) is lower than 100.

Conclusions

A flow-by vertical stack of nets electrode has been used effectively for the removal of zinc ions from diluted solutions. Hydrodynamic voltammetry proved to be adequate for studying the zinc reduction under mass transport control. The concentration of zinc was reduced from 48.4 ppm to less than 0.7 ppm in batch recirculation mode at flow rate of (420l/h) with electrolysis time 120 minutes operated under constant cathode potential. This behavior cannot be achieved in single pass-flow mode at this initial concentration and flow rate. The ratio between the time of electrolysis for concentration reduction of 99% and that for concentration reduction 90% is about two for most of the experiments. This is an evidence of a mass transport controlled process. Most of previous works on removal of zinc using other electrode materials operated on batch recycle mode used a ratio of catholye volume to cathode volume ≤100, this ratio in the present work higher than (130) leading to less than 2% error in adapting the approximated model Eq. (2) according to Walker and Wragg observations [35].Therefor the present results are more accurate and compatible with the batch –recycle model assumptions.

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