

MASS TRANSFER CORRELATION FOR THE REMOVAL OF COPPER IONS FROM WASTEWATER

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ABSTRACT

One of the biggest problems with ore processing in extractive metallurgical industries is the high toxicity of the heavy metals waste content (e.g., copper, lead, nickel and chrome). This work investigates the copper (II) ions removal from aqueous solutions in concentrations up to 1000 ppm. Therefore, a fluidized bed electrolytic reactor was used with flow-by configuration considered as a hopeful method due to the large specific surface area and the high mass transfer rate. The performance of the electrochemical reactor was investigated by using different porosities. Dimensionless Sherwood and Reynolds numbers were correlated to characterize the mass transport properties of the reactor, and they were fitted to the equation $Sh = a.Re^b.Sc^{1/3}$.

Keywords: Fluidized bed reactor; Effluent treatments; Copper recovery; Dimensionless correlation

NOMENCLATURE

A	electrode surface, m ²
a	constant
b	constant
C	concentration, ppm
C _{lim}	limit concentration, ppm
C ₀	initial concentration, ppm
D	diffusion coefficient, m ² /s
dh	hydraulic diameter, m
dp	particle diameter, m
I _{lim}	limit current, A
k _m	mass transport coefficient, m/s
k ₁	constant 1, s ⁻¹
k ₂	constant 2, s ⁻¹
L	characteristic length, m
Re	Reynolds number
Re _p	Reynolds number based on particle diameter
Sh	Sherwood number
Sc	Schmidt number
t	time, s
t _{lim}	limit time, s
v	velocity of electrolyte, m/s
V _R	reactor volume, m ³

Greek symbols

μ	absolute viscosity, kg/m.s
ε	porosity
ν	fluid kinematic viscosity, m ² /s
ρ	electrolyte density, kg/m ³
δ	diffusive layer thickness, m

INTRODUCTION

Copper is a metal of great industrial importance, widely used in electronic industries (Fornari and Abbruzzese, 1999), electroplating and mining. The effluents containing metal ions, even at low concentrations (0.009 mg/L for copper, Resolution 357/2005), are very toxic effluents. The disposal of untreated effluents can cause various types of pollution such as: extermination of aquatic life and human health related problems.

The most commonly used methods for the removal of metal ions are: precipitation with hydroxides, sulphites or oxalates; chemical or electrochemical ion exchange, reverse osmosis, chemical or physical adsorption, stabilization or solidification, chemical reduction, biochemical remediation and more recently, electrochemical deposition (Rajeshwar and Ibanez, 1997). Precisely effluents with low metal concentrations form toxic effluents. An ideal solution to this problem could be a process to recover and recycle the metal and the water. The classic methods have become unviable due to the large amount of material to be recovered, including the high cost to many companies due the use of chemical reagents and the need to store the large quantities of sludge (environmental liabilities) formed (Bertazzoli et al., 1998).

An alternative potential method is the recovery of metals from dilute solutions using the fluidized bed reactor (Sioda and Piotrowska, 1980; Simonsson, 1984; Langlois and Coeuret, 1989; Widner et al.,

1998; Ruotolo and Gubulin, 2002; Kaminari et al. 2005; Kaminari et al. 2007). The fluidized bed or three-dimensional reactor has been considered promising due to the high specific surface area and high mass transfer coefficients, making the system attractive for various electrochemical processes (Wilkinson, 1971).

However, the electrochemical process has several technological challenges, such as: 1) The decrease of concentrations with time causing low current efficiency, 2) The need for a support electrolyte to be added when the ion concentration is very low 3) interference of the hydrogen evolution and/or oxygen reaction that must be prevented or minimized, 4) The deposition rate and composition of the solution in some cases may promote the production of dendrites or spongy deposits and 5) The need for high flow rates that favor increasing the limit current, and reduce the residence time, providing small removal rates (Rajeshwar and Ibanez, 1997; Ponte, 1998).

The work herein investigates the deposition of copper ion on the particles of particulated reactor, for different porosities (ϵ). This parameter is one of the most important of this system, directly related to the charge transfer, and the amount of available charge in the reactor is responsible for the reduction reaction of copper ion. The properties of mass transport from the reactor were characterized by a dimensionless correlation

MATERIALS AND METHODS

MATERIALS

The fluidized-bed electrochemical reactor (FBE) was made from acrylic, enabling a better visualization of the process. The rectangular geometry is 180 mm in length, 370 mm in height and a thickness of 24 mm. A distributor, consisting of a packed bed of cylindrical polyethylene particles (diameter = 2.5 mm and height = 1.5 mm), was used to distribute the fluid uniformly in the bed. The electrical contact with the fluidized bed consisted of a copper plate (cathode) and the anode was a Pb/Sb alloy plate. The reactor consisted of copper particles, 1 mm in diameter, which served as an electrically conductive bed in direct contact with the plate current feeder (cathode). Is the surface of these particles occurring electrochemical reactions of reduction of copper ion in the solution through the voltage applied to the cell.

An experimental unit was designed to study the recovery of copper ions (Fig. 1).

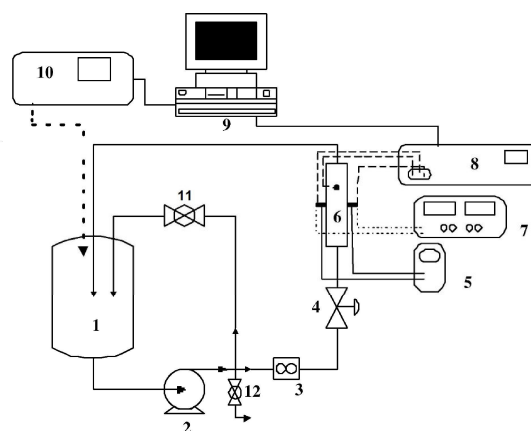


Figure 1. Schematic representation of the experimental units: (1) electrolyte reservoir; (2) centrifugal pump; (3) flow rate digital meter; (4) diaphragm valve; (5) voltmeter; (6) electrochemical reactor; (7) power supply; (8) potentiostat; (9) computer; (10) UV-Vis spectrophotometer; (11) ball valve (by-pass); (12) ball valve (for electrolyte exhaustion).

The fluidized bed electrodes can have two configurations, according to the direction of the current and electrolytic flows, called flow-through and flow-by configuration. In this work it was used the flow-by configuration which the electrolytic flow and the electric current run in perpendicular directions.

All the chemicals used in this study were of analytical grade and deionized water was used to prepare all the CuSO_4 (0.016 mol/L approximately 1000 ppm Cu ions) solution and H_2SO_4 (0.4 mol/L) as the supporting electrolyte. The electrolyte flow was obtained by means of a centrifugal pump, thus achieving a continuous flow, and the flow control was done through valves. Samples were collected at the beginning and end of each experimental run at predetermined intervals and the concentrations were measured in the spectrophotometer (UV-VIS model FEMTO 600 Plus).

METHODS

To achieve the objectives of this work the following steps were performed:

- Experimental Design - to specify the variables to be studied and set the variables values in the experimental runs. The variables used were: porosities (ϵ) (0.40, 0.43 and 0.47) and current (I) (4.9A, 6.5A and 8.0A). In all experiments the temperature was maintained at around 25° C.
- Preparation and execution of experiments - the following steps were used: preparation and storage of electrolyte, filling the bed with the particles to a height of pre-determined bed according to the porosity; adjustment of the current source so that the determined electrical current was known, admission of electrolyte in a

pre-established flow, setting the electric current source; coupling of the electrical contacts. The experimental runs were designed for the reactor to remain in operation for about 3 hours, during which samples were collected in regular time intervals, in order to monitor the variation of the copper concentration in the electrolyte. At the same time that the samples were withdrawn, the instantaneous potential difference was determined (provided by source).

- c) Data treatment - According to Pletcher and Walsh (1990), the system can be modeled satisfactorily as a simple batch reactor. Based on the data of changes in concentrations over time and obtaining the figures of merit, it is possible to determine the conditions for the limit current for each case, and thus develop a correlation between dimensionless groups such as:

$$Sh = a \cdot Re^b \cdot Sc^{1/3} \quad (1)$$

where a and b are constant, Sherwood (Sh), Reynolds (Re) and Schmidt (Sc) defined as:

$$Sh = \frac{k_m \cdot L}{D} \quad (2)$$

$$Re = \frac{\rho \cdot v \cdot L}{\mu} \quad (3)$$

$$Sc = \frac{\mu}{\rho \cdot D} \quad (4)$$

where:

k_m = mass transport coefficient ($m \cdot s^{-1}$)

L = characteristic length (m) or hydraulic diameter (dh) $dh = \frac{\varepsilon}{(1 - \varepsilon)} dp$

$dp = 1 \cdot 10^{-3} m$ = particle diameter

$D = 6 \cdot 10^{-10} m^2/s$ = diffusion coefficient

$\rho = 1005.6 kg/m^3$ = electrolyte density

$\mu = 9.29 \cdot 10^{-4} kg/m \cdot s$ = absolute viscosity

v = velocity of electrolyte (m/s)

RESULTS

Following the aforementioned experimental procedures, the limit conditions were obtained by analyzing the graphs of concentration versus time. The curve represents a variable-order reaction, i.e., the data fit a particular reaction order at high concentrations and by another order at low concentrations. Based on this study, the limit condition that is the point when the reaction is zero order, the changes for a first-order reaction can be obtained (Figure 2) (Levenspiel, 2000). The zero-order reaction system is controlled by the current and the first-order reaction system is controlled by mass transport.

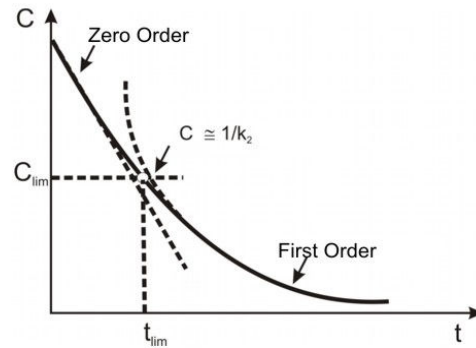


Figure 2. Behavior of a variable-order reaction (Levenspiel, 2000).

In the experiments, the three currents were analyzed (4.9 A, 6.5 A and 8.0 A) for a period of 3 hours. To calculate the C_{lim} it was necessary to obtain the value of k_2 , because $C_{lim} = 1/k_2$ via linear regression, thus obtaining the value of t_{lim} . Linear regression was performed according to equation (5).

$$\frac{C_0 - C}{\ln(C_0/C)} = \frac{1}{k_2} + \frac{k_1}{k_2} \left[\frac{t}{\ln(C_0/C)} \right] \quad (5)$$

where:

C_0 = initial concentration (ppm)

C = concentration (ppm)

k_1 = constant 1 (s^{-1})

k_2 = constant 2 (s^{-1})

t = time (s)

Figure 3 shows the linear regression curves using equation (5), hence obtaining the results presented in Table 1. The limit condition chosen for this porosity was equal to the current 6.5 A, because for this condition there is a greater predominance of mass transport, the process that starts 1.68 h after the experiment begins. The same procedures were performed for other porosities, obtaining the results presented in Table 1 and the final limit conditions are in Table 2.

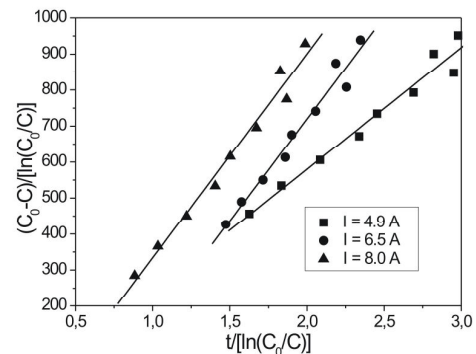


Figure 3. Calculation of C_{lim} for $\varepsilon = 0.40$ and $I = 4.9 A, 6.5 A$ and $8.0 A$.

Table 1. Values obtained for the limit condition.

Porosity	I (A)	4.9	6.5	8.0
0.40	k_1 (s ⁻¹)	3.50	1.37	2.44
	k_2 (s ⁻¹)	10.30E-3	2.43E-3	4.31E-3
	C_{lim} (ppm)	97	400	232
	t_{lim} (h)	3.33	1.68	1.95
0.43	k_1 (s ⁻¹)	39.18	6.85	5.24
	k_2 (s ⁻¹)	161E-3	18.8E-3	12.93E-3
	C_{lim} (ppm)	6	53	78
	t_{lim} (h)	4.21	3.05	2.50
0.47	k_1 (s ⁻¹)	32.06	10.47	9.87
	k_2 (s ⁻¹)	133E-3	29.6E-3	22.9E-3
	C_{lim} (ppm)	7.5	34	44
	t_{lim} (h)	4.27	3.06	2.50

Table 2. Limit condition selected.

Porosity (ε)	I (A)	I_{lim} (A)	C_{lim} (ppm)
0.40	6.5	6.0	400
0.43	8.0	4.0	78
0.47	8.0	5.6	44

Table 3. Values of mass transport coefficient (k_m).

Porosity	I (A)	k_m (m/s)
0.40	6.0	1.29E-5
		1.26E-5
0.43	4.0	2.50E-5
		2.24E-5
0.47	5.6	2.82E-5
		3.40E-5

Based on the results of Table 2, 3 additional experiments in duplicates were carried out with the new values of C_{lim} and I_{lim} , in order to determine the k_m in the region where the mass transport phenomenon actually predominates. The C_{lim} is now the C_0 and the samples were taken at every 15 minutes, which is the minimum for the solution mixture in the reservoir. The k_m was determined through linear regression in Figure 4, Figure 5 and Figure 6. Table 3 shows the values of k_m calculated using equation (6).

$$\ln[C(t)] = \ln[C(0)] - \left(\frac{k_m \cdot A}{V_R} \cdot t \right) \quad (6)$$

where:

$C(t)$ = concentration at time t (ppm)

$C(0)$ = initial concentration (ppm)

A = electrode surface (m²)

V_R = volume of electrolyte (m³)

The values of k_m in Table 3 increase with increasing porosity, this was expected since the

increase in porosity causes a decrease in the thickness of the diffusive layer and hence the increase in k_m , because the k_m values are inversely proportional to the diffusive layer thickness (δ) ($k_m = D/\delta$).

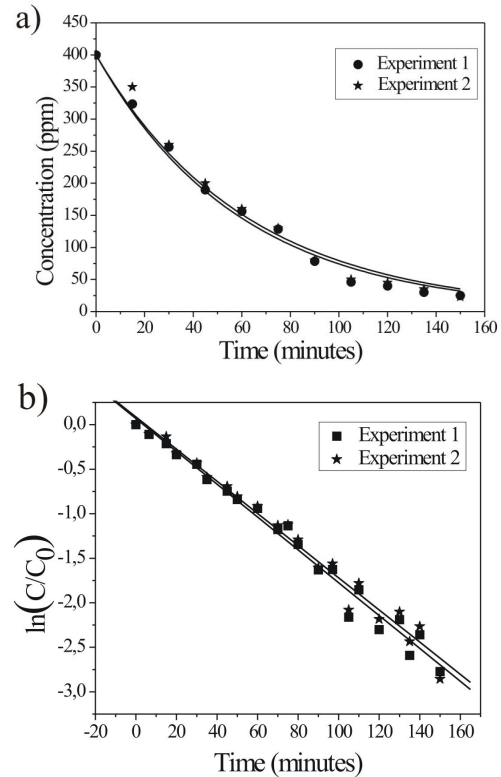
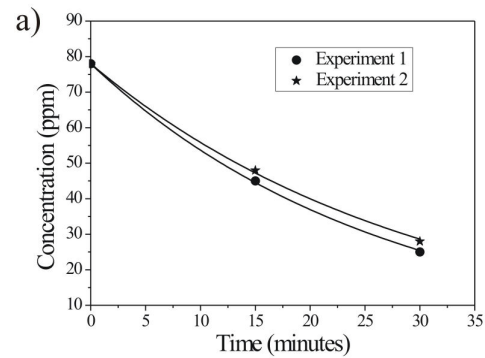


Figure 4. a) Concentration (ppm) versus time (minutes) and b) $\ln(C/C_0)$ versus time (minutes) – porosity 0.40.



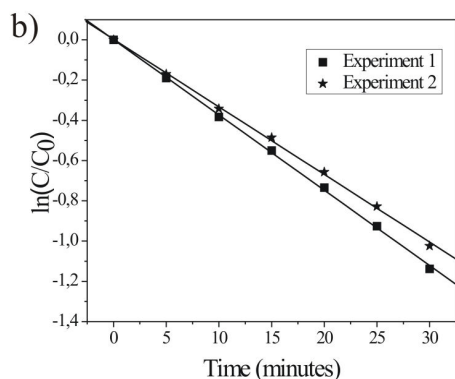


Figure 5. a) Concentration (ppm) versus time (minutes) and b) $\ln(C/C_0)$ versus time (minutes) – porosity 0.43.

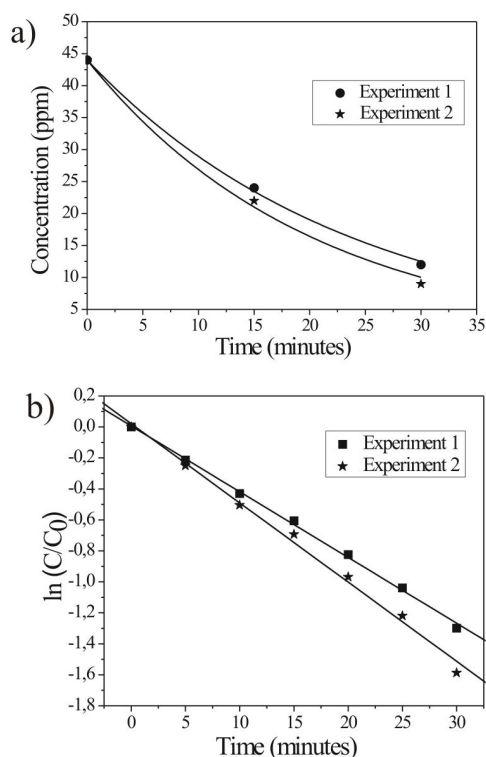


Figure 6. a) Concentration (ppm) versus time (minutes) and b) $\ln(C/C_0)$ versus time (minutes) – porosity 0.47.

The analysis of dimensionless groups is a method to express a correlation when the process of reducing the ion is limited by mass transport in an electrochemical reactor. According to Pletcher and Walsh (1990), the system can be modeled satisfactorily as a simple batch reactor. The correlation was calculated according to equation (1) with the data from Table 4.

Table 4. Parameter values for calculating the correlation.

POROSITY	Sh	Re _p	ln(Re _p)	ln(Sh/Sc ^{1/3})
0.40	14.32	66.67	4.20	15.78 E-2
	14.02			13.60E-2
0.43	31.42	110.05	4.70	94.28E-2
	28.21			83.52E-2
0.47	41.75	145.80	4.98	1.23
	50.31			1.41

The constants a and b were obtained from curve $\ln(Sh/Sc^{1/3}) \times \ln(Re)$ via linear regression.

With the values obtained above, the correlation can be calculated according to equation (1). The constants a and b were obtained from the curve $\ln(Sh/Sc^{1/3})$ vs. $\ln(Re_p)$, Figure 7, via linear regression.

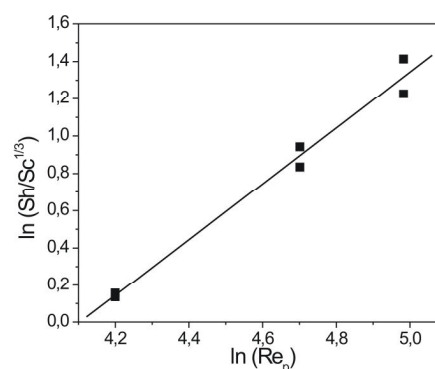


Figure 7. Dimensionless correlation ($R^2 = 98.36\%$).

Equation (1) can be written as:

$$Sh = 2.14 \text{ E-}3 \cdot Re^{1.5} \cdot Sc^{1/3} \quad (7)$$

The result of the adjustment was also evaluated using the parity chart (Figure 8), where the dispersion of residuals is visible.

It can be concluded that the residues are well distributed (Figure 8), which implies that the correlation was able to fit well the experimental data.

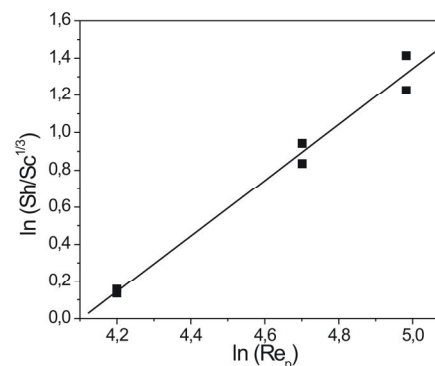


Figure 8. Parity chart.

CONCLUSION

In all cases the system was able to reduce the concentration of copper ions to low levels, confirming that the electrochemical reactor bed particles can be used as a single treatment for dilute aqueous solutions of heavy metals. The reduction reaction of copper ions in the electrochemical reactor, unlike what the literature implies, is a controlled process by mixed process, where parallel reactions occur. The correlation was satisfactory, when compared to those obtained in the literature (Simonsson, 1984; Hunsom et al., 2002), thus successful in representing the properties of mass transport.

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