A STUDY OF OPERATIONAL PARAMETERS INVOLVED IN THE PROJECT OF A PARTICULED BED REACTOR FOR LEAD REMOVAL OF INDUSTRIAL WASTEWATER

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Abstract. *The objective of this work was to study the recovery of lead ion using an fluidized bed electrode simulating an industrial effluent. The reactor performance was evaluated by the following variables: fluid outflow (Q), current (I), lead (C_{Pb}) and support electrolyte (C_{NaNO3}) concentrations, and their influence on current efficiency (EC) and power consumption (CE). Due to the almost total lack of mathematical models fitting the system and also due their complexity, it was decided to use a statistical technique, the Central Composite Design (CCD), for the attainment of the desired responses as empirical functions. Then, response surfaces were plotted in order to get the current efficiency and power consumption behavior when values of outflow, current, concentration of sodium nitrate and lead ion were changed..*

Keywords *.recovery of lead ion, fluidized bed electrode, central composite design and response surfaces.*

1. Introduction

Many tons of precious or toxic metals are thrown away each year as industrial wastewater and most frequently directly in natural environment. The metals recovery (Fe, Cu, Al, Sn, Ni Cd, Cr, Mg, Va, B, Hg and Pb) in dilute solutions is an everyday problem associated to ecology and economy aspects. [Ponce de Leon and Pletcher (1996)].

Ultimately, this wastewater is discharged within permitted concentrations of suspended solids and dissolved salts. This approach uses excessive chemicals producing large volumes of waste for disposal with no recovering process solution.

Electrochemical cleaning technology offers an efficient means of controlling pollution as it provides removal of transition and heavy metals by redox reactions without the disadvantages of conventional treatment. The inherent advantage is its environmental compatibility, due to the fact that the main reagent, the electron, is a “clean reagent”.

The fluidized-bed electrolytic cell was developed by Backhurst and co-workers (1969) and applied originally to electrochemical synthesis and fuel cell [Monhemius (1975)] consisting of a bed of steel particles, which is fluidized by an upward flow of electrolyte. The whole bed is made cathodic by a “feeder” electrode inserted into the bed with an inert anode immersed in the electrolyte. The fluidized-bed cathode differs from the conventional planar one in two main aspects. Firstly, as the cathode is a bed of particles, it has a very large surface-area to volume ratio. Thus, for any given cell current, the current density at the cathode surface is very low. Secondly, a very high degree of agitation exists within the bed, which reduces the Nerst diffusion layer increasing the limiting diffusion currents. Both these effects reduce the concentration polarization and, under favorable conditions, make it possible to electrowin metals down to parts-per-million concentrations without loss of current efficiency.

This way, fluidized-bed electrochemical reactors (FBE) are attractive for their capacity and operability in many fields of electrochemical technology, especially in the treatment of dilute or complex solutions. Several applications have been considered, for example fuel cells, hydrogen peroxide synthesis, ore flotation and organic electrosynthesis, but it is especially in extraction metallurgy that good applications are expected.

The object of this work was to study the changes in the current efficiency (EC) and power consumption (CE) of a laboratory scale fluidized–bed cell during the treatment of lead solution. The effect of the following variables was investigated: fluid outflow (Q), current (I), lead (C_{Pb}) and support electrolyte (C_{Na}) concentration. In order to study both the main effects and also the interactions of these variables, the Central Composite Design was used. The response surface methodology (RSM) was used to describe the individual and interactive effects of the four variables at five levels, combined according to a Central Composite Design.

2. Materials and Methods

2.1. Materials

The basic unit is the electrolytic cell (Figure 1). In its simplest form the cell contains two electrodes (the anode and the cathode) and an electrolyte, which is necessarily conductive.

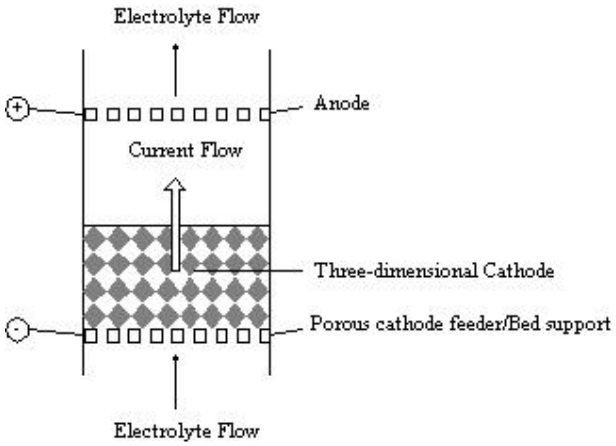

Figure 1. Schematic representation of the electrolytic cell

Two main arrangements with respect to the direction of the electric current and electrolyte flows are possible. They are denoted as flow-through and flow-by arrangements. The Figure 1(flow-through) shows the case where the electrolyte flow and the electric current run in the same direction. This situation is the one, which has been commonly adopted for work on a small scale.

An experimental unit was projected to study the recovery of lead ion (Figure 2).

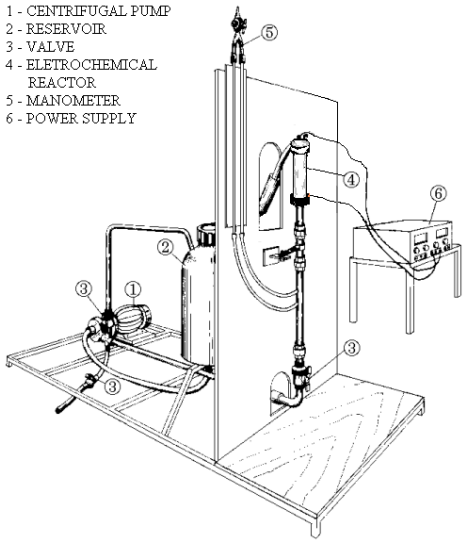

Figure 2. Schematic representation of the experimental unit

The electrochemical reactor, illustrated in Fig. 2, was made from a cylinder of acrylic with an internal diameter of 4,44 cm and a 20 cm length. The bed was composed by carbon steel particles with 1 mm diameter and 20 mm height. In order to obtain a uniform distribution of the fluid inside the bed, it was used a distributor composed by a packed bed with glass spheres (d = 1mm) and 15 mm height. The electrical contact with the fluidized bed was made by of steel feeder electrode (cathode). The anode was a disc of stainless steel, located at 2cm from the top of the particles bed.

All used chemicals were of analytical grad. Deionized water was used to prepare all solutions from $Pb(NO_3)_2$,boric acid (0.5 M) with sodium nitrate as the supporting electrolyte.

The current efficiency was determined by spectrophotometer analysis of lead concentration at samples of electrolyte withdrawn from the system at the beginning and ending of the runs. Each experiment was run for 120 minutes.

2.2. Methods

2.2.1. Experimental Design

Generally, a prior knowledge of the procedure is needed to achieve a statistical model [Techapun et al. (2002)]. The three steps of this experimental design included statistical design experiments, coefficients estimation in a mathematical model with response prediction, and applicability analysis of the model. The current efficiency and power consumption were chosen as independent variables in central composite design (CCD).

The coded values of the variables are given in Table 1.

Table 1. Values of coded levels

VARIABLE	-2	-1	0	1	2
Lead Conc. (ppm)	50	500	950	1400	1850
$NaNO_3$ Conc.(g/l)	4,25	3,69	3,14	2,58	2,03
Current (A)	0,2	0,5	0,7	0,9	1,0
Outflow (m^3/s)	$78,83.10^{-6}$	$86,69.10^{-6}$	$94,61.10^{-6}$	$102,52.10^{-6}$	$110,39.10^{-6}$

The relationship of the independent variables and the response was calculated by the second order polynomial equation (1) by using the method of least squares as follows:

$$Y = b_0 + \sum_{i=1}^{4} b_i X_i + \sum_{i=1}^{4} b_{ii1} X_1^{\,2} + \sum_{i\neq 1}^{4}\sum_{j=1}^{4} b_{ij} X_i X_j + \varepsilon \qquad i\neq j \qquad (1)$$

Where Y is the predicted response (EC and CE); X_i the coded forms of the input variables; b_0 a constant; b_{ii} the quadratic coefficients, b_{ij} a cross-product coefficient and ε is the error term, the difference between the predicted and observed value.

2.2.2. Analysis of data

The current efficiency (EC) is the yield based on the electric charge reacted during electrolysis:

EC = (charge used in forming product)/(total charge) (2)

From Faraday's law:

$$EC = \frac{100.z_i.F.\Delta m}{M_i.I.\Delta t} \qquad (3)$$

where:
EC = Current efficiency (%);
z_i = Number of electrons;
F = Faraday constant (96487 $A.s.mol^{-1}$);
Δm = Mass deposited in the interval of time Δt (g);
M_i = Molar mass (g/mol);
Δt = Interval of time (s).

The energy costs of the applied electrochemical process are related closely to the energy efficiency. The power consumption may be referred as the amount of substance on a molar, mass or volume basis.

$$CE = \frac{2,778.10^{-4}.V.I.\Delta t}{\Delta m} \qquad (4)$$

where:
CE = Power consumption ($kW.h.kg^{-1}$);
V = Cell potential (V);

3. Results and Discussion

As a result of the applied model to the experiments the following equations were obtained:

$$EC = 57,72 + 4,86C_{Pb} - 1,51C_{Na} - 1,53Q + 4,23I^2 - 4,80C_{Pb}C_{Na} + 4,80C_{Pb}Q + 2,24C_{Na}Q - 5,86C_{Na}I - 2,09QI \quad (5)$$

$$CE = 5,18 + 0,47C_{Na} - 0,95I + 0,34C_{Pb}^2 + 0,41C_{Pb}C_{Na} - 0,31C_{Pb}Q + 0,54C_{Pb}I - 0,39C_{Na}Q + 0,26C_{Na}I + 0,21QI \quad (6)$$

The computed F-value obtained for EC and CE were greater than the F-value in statistic table, indicating that the model were significant at a high confidence level (99,9%). The probability P-value was also relatively low ($P<0,05$), indicating the significance of the model. The coefficient of variation for EC ($R^2 = 0,9057$) and CE ($R^2 = 0,9095$) indicates a high correlation between experimental and predicted observed values (Fig. 3 and Fig 4).

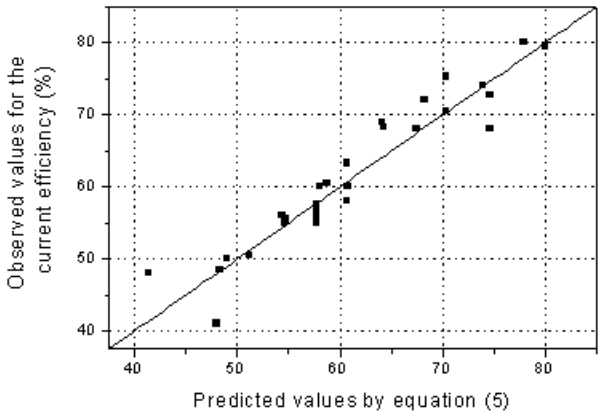

Figure 3. Experimental and predicted values by equation (5)

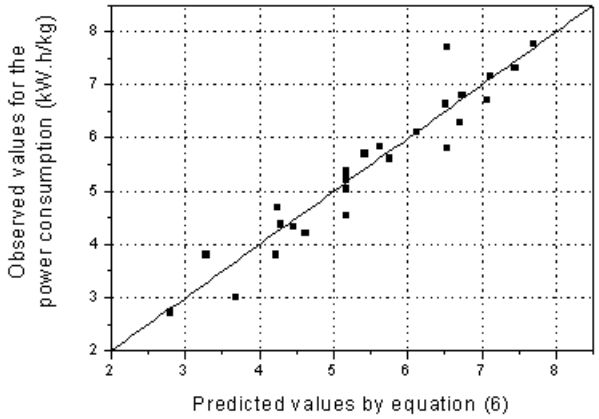

Figure 4. Experimental and predicted values by equation (6)

The Response Surface Methodology (RMS) is an statistical modeling technique employed for multiple regression analysis using quantitative data obtained from properly designed experiments to solve multivariable equations simultaneously. RSM is used to determine the optimum response (EC e CE). Response Surfaces can be visualized as three-dimensional plots by presenting the response as a function of two factors by keeping the other constant.

The largest EC is obtained for the largest fluid outflow and lead concentration [Fig 5 (a) e (b)], due to the increase of mass transfer rate followed by a larger renewal of reacting species.

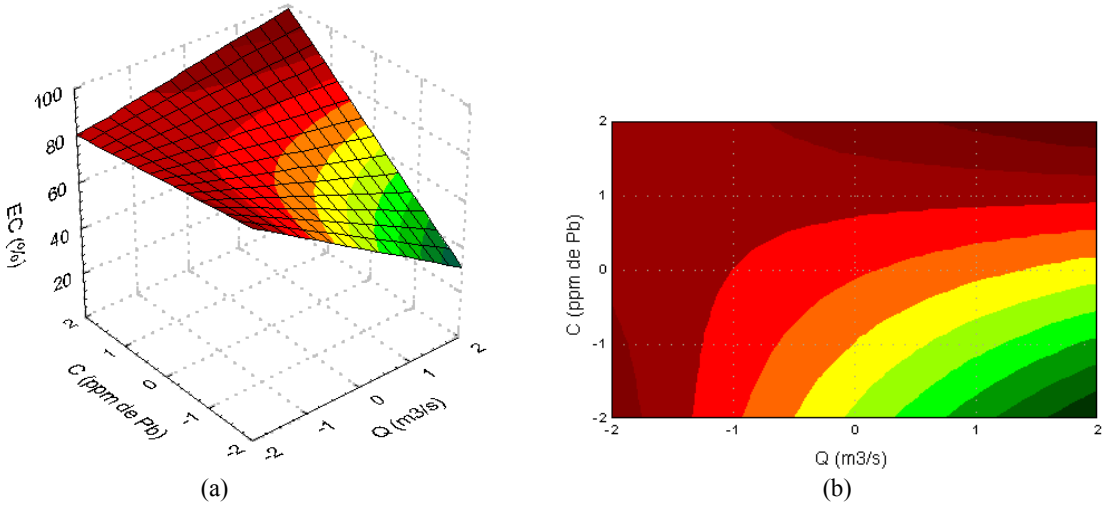

Figure 5. (a) Current Efficiency for I = 2 and C_{NaNO3} = -2
(b) Contour plot of the current efficiency: effect of lead concentrations (C_{Pb}) and fluid outflow (Q)

The smallest values of CE are observed with decreasing the fluid outflow and increasing the support electrolyte concentration [Figure 6 (a) and (b)], due to a better particles electric contact caused lower expansion.

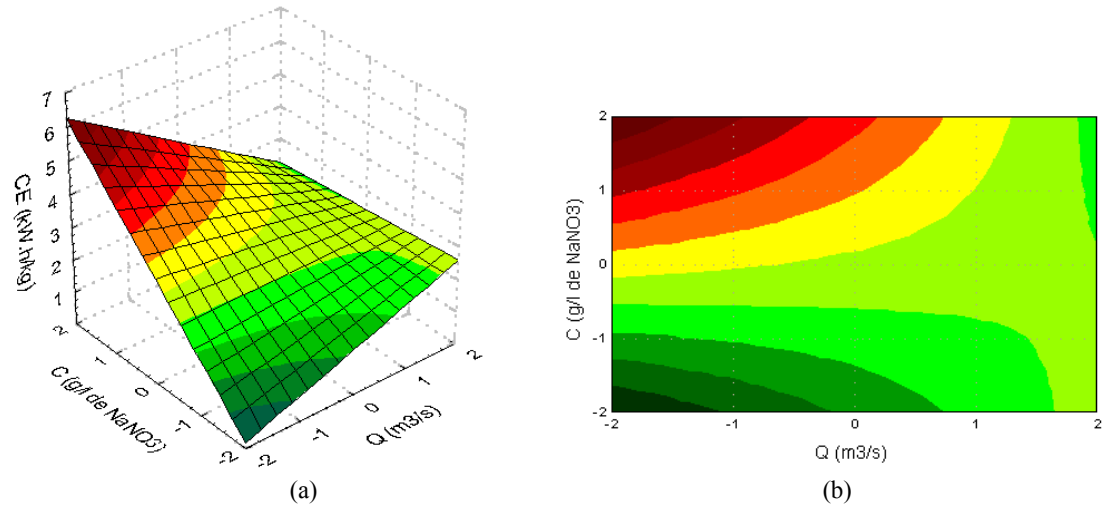

Figure 6. (a) Power Consumption for C_{Pb} = 2 and I = 2
(b) Contour plot of the power consumption: effect of support electrolyte concentrations (C_{NaNO3}) and fluid outflow (Q)

4. Conclusion

The process parameters applied in this study showed a good performance in removing lead from simulated effluents. The CCD, regression analysis and Response Surface Method was effective to find the optimum conditions of EC and CE. Through the RSM several important information were obtained. The good fittings obtained for EC and CE were highly significant. It was also concluded that reduction reaction of lead ions, in the electrochemical reactor, was controlled by a mixed process, that is, mass transport and charge transfer controls, subjects to parallel reactions. It was verified that actually, as mentioned in the literature, the particulate bed could present a great current efficiency, for reduction reactions of the lead ion in diluted solutions, when operated in some particular conditions The optimum condition was estimated to be EC = 80% and CE = 4,37 kW.h/kg, for a experimental run with the concentration of 1400 ppm of C_{Pb}.

It may be concluded that the system of particuled bed reactor can be effectively optimized using RSM with a a minimum number of experiments.

5. Acknowledgement

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6. References

Achcar, J.A., 1995, "Planejamento de experimentos em engenharia e indústria", ICMSC-USP, São Carlos, SP., pp.226-238.

Bernardes, A.M., Dalla Costa, R.F., Fallavena, V.L.V., Rodrigues, M.A.S., Trevisan, M.D. and Ferreira, J.Z.,2000, "Electrochemistry as a clean technology for the treatment of effluents: the application of electrodialysis", Metal Finishing, Vol. 98, No. 11, pp.52-58.

Bertazzoli, R., Rodrigues, C.A., Dallan, E.J., Fukunaga, M.T., Lanza, M.R.V., Leme, R.R. and Widner, R.C., 1998, "Mass transport properties of a flow-through electrolytic reactor using a porous electrode: performance and figures of merit for Pb(II) removal", Brazilian Journal of Chemical Engineering, Vol. 15, pp. 396-405.

Box, G. E. P., Hunter, W. G.and HUNTER, J. S., 1978, "Statistics for experimenters – An introduction to design, data analysis and model building", John Wiley & Sons, N.Y.

Box, G. E. P. and DRAPER, N. R., 1987, "Empirical Model – Builiding and Response Surfaces",USA.

Coeuret, F., 1980, "The fluidized bed electrode for the continuous recovery of metals", Journal of Applied Electrochemistry, Vol. 10, pp.687-696.

Juttner, K., Galla, U. and Schmieder, H., 2000, "Eletrochemical approaches to enviromental problems in the process industry.", Eletrochimica Acta, Vol. 45, pp. 2575-2594.

Kazdobin, K., Shvab, N. and Tsapakh, S., 2000, "Scaling -up of fluidized-bed electrochemical reactors", Chemical Engineering Journal, Vol 79, pp.203-209.

Kreysa, G., Pionteck, S. and Heitz, E.,1975, "Comparative investigations of packed and fluidized bed electrodes with non-conducting particles", J. Appl. Electrochem., Vol. 5, pp. 305-312.

Monhemius, A.J.and Costa, P.L.N.,1975, "Interactions of variables in the fluidised-bed electrowinning of cooper", Hydrometallurgy, Vol 1, pp. 183-203.

Naidu, G.S.N.and Panda, T., 1998, "Application of response surface methodology to evaluate some aspects on stability of pectolytic enzymes from Aspergillus niger", Biochemical Engineering Journal, Vol. 2, pp. 71-77.

Pletcher, D.and Walsh, F.C., 1990, "Industrial Electrochemistry", Second edition, Chapman and Hall, Londres.

Ponce de Leon C. and Pletcher D.,1996, "The removal of Pb(II) from aqueous solutions using a reticulated vitreous carbon cathode cell – the influence of the electrolyte medium",Electrochimica Acta, Vol 41, pp 533-541.

Ponte, M.J.J.S.,1998, "Estudo da remoção do íon cobre de solução aquosa diluída e eletrodos de leito particulado", São Carlos, UFSCar, pp 218. (Tese).

Ponte, M.J.J.S., and Gubulin, J.C.,1992, "Eletrodeposição de metais pesados em sistemas particulados: Uma revisão bibliográfica", XX Encontro sobre escoamento em meios porosos, Anais. São Carlos, UFSCar, pp.669-678.

Rao, K.J.,Kim, C.H. and Rhee S.K., 2000, "Statistical optimization of medium for the production of recombinant hirudin from saccharomyces cerevisiae using response ssurface methodology", Process Biochemistry, Vol 35, pp. 639-647.

Ragnini, C.A.R., Di Iglia, R.A.,Bizzo, W. and Bertazzoli, R.,2000, "Recycled niobium felt as an efficient three dimensional electrode for electrolytic metal ion removal", Water Research, Vol. 34, No. 13, pp.3269-3486.

Rambali, B., Baert, L.and Massart, D.L., 2001, "Using experimental design to optimize the process parameters em fluidized bed granulation on a semi-full scale", International Journal of Pharmaceutics, Vol. 220, 149-160.

Safarazi, F. and Ghoroghchian, J.,1994, "Electrochemical copper removal from dilute solutions by packed bed electrodes", Microchemical Journal, Vol. 50, pp.33-43.

Techapun, C., Charoenrat, T., Watanabe, M., Sasaki, K.and Poosaran, N., 2002, "Optimization of thermostable and alkaline -tolerant cellulase-free xylanase production from agricultural waste by thermotolerant Streptomyces sp. Ab 106, using central composite experimental design", Biochemical Engineering Journal, Vol 12, pp 99-105.