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Chemical Engineering Journal 105 (2005) 111–115

Chemical Engineering Journal
www.elsevier.com/locate/cej

# Study of the operational parameters involved in designing a particle bed reactor for the removal of lead from industrial wastewater — central composite design methodology

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Received 29 October 2003; received in revised form 16 July 2004; accepted 21 July 2004

## Abstract

The objective of this work was to study the recovery of lead ion using a fluidized bed electrode to simulate an industrial effluent. The reactor's performance was evaluated based on dimensionless variables: voidage of the bed ($\varepsilon$), current density ($i$)/limiting currents density ($I_{\mathrm{lim}}$), transport number of lead ($t_{\mathrm{Pb}}$) and transport number of support electrolyte ($t_{\mathrm{Na}}$), and their influence on current efficiency (EC) and power consumption (CE). Due to the almost total absence of mathematical models that fit the system and also due to the complexity of such models, the choice fell upon a statistical technique, the central composite design (CCD), to obtain the desired responses as empirical functions. Response surfaces were then plotted to identify the behavior of current efficiency and power consumption when the values of variables dimensionless were changed.

*Keywords:* Recovery of lead ion; Fluidized bed electrode; Central composite design; Response surfaces

## 1. Introduction

Uncountable tons of precious or toxic metals are discarded each year in the form of industrial wastewater, usually directly into natural environments. The recovery of metals (Fe, Cu, Al, Sn, Ni, Cd, Cr, Mg, Va, B, Hg and Pb) in diluted solutions is an everyday problem associated with ecological and economic aspects [1–4].

Ultimately, this wastewater is discharged in permitted concentrations of suspended solids and dissolved salts. This approach uses excessive chemicals, producing large volumes of waste for disposal with no solution in the form of a recovery process [5–7].

Electrochemical cleaning technology offers an efficient means of controlling pollution through the removal of transition and heavy metals by redox reactions, without the disadvantages of conventional treatments. The inherent advantage of this technology is its environmental compatibility due to the fact that the main reagent, the electron, is a 'clean reagent' [8,9].

The fluidized-bed electrolytic cell was developed by Backhurst and co-workers (1969), originally for application in electrochemical synthesis and fuel cells [10], and consisted of a bed of steel particles fluidized by an upward electrolytic flow. The whole bed is rendered 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, because 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 [11,12]. Secondly,

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doi:10.1016/j.cej.2004.07.011

a very high degree of agitation exists within the bed, which reduces the Nernst diffusion layer and increases the limiting diffusion currents. These two effects reduce the concentration polarization, and under favorable conditions, allow for the recovery of metals in concentrations of parts-per-million without significant loss of current efficiency [13,14].

Fluidized-bed electrochemical reactors (FBE) are, therefore, attractive for their capacity and operability in many fields of electrochemical technology, especially in the treatment of diluted or complex solutions [15]. Several applications have been considered, e.g. fuel cells, hydrogen peroxide synthesis, ore flotation and organic electrosynthesis, but good applications are expected, especially in extraction metallurgy [16,17].

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 solutions. The effect of the following variables was investigated: fluid outflow ($Q$), current ($I$) and lead and support electrolyte concentrations. The central composite design was used to study the main effects and the interactions of these variables. The response surface methodology (RSM) was used to describe the individual and interactive effects of 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 (Fig. 1). In its simplest form, the cell contains two electrodes (the anode and the cathode) and an electrolyte, which is necessarily conductive.

The direction of the electric current and electrolytic flows can be configured into two possible main arrangements called flow-through and flow-by arrangements. Fig. 1 (flow-through) shows the case in which the electrolytic flow and the electric current run in the same direction. This configuration is the one commonly adopted for small-scale work.

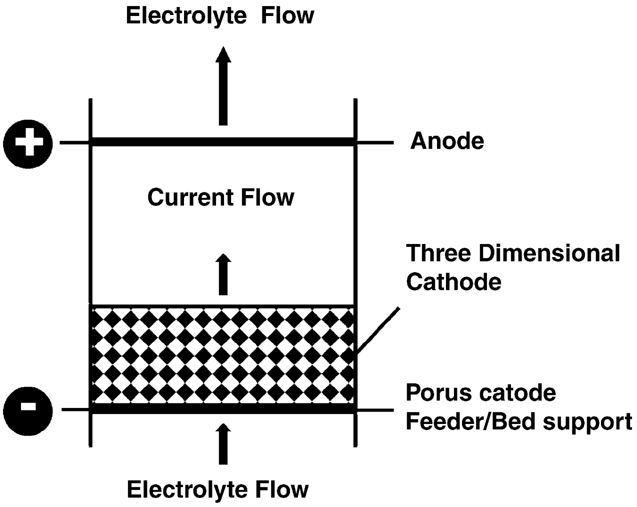

Fig. 1. Schematic representation of the electrolytic cell.

An experimental unit was designed to study the recovery of lead ions (Fig. 2).

The electrochemical reactor illustrated in Fig. 2 was made from an acrylic cylinder having an internal diameter of 44.4 mm and a length of 200 mm. The three-dimensional cathode was composed of 1 mm diameter-high carbon steel particles filling the bed up to 200 mm height. A distributor consisting of a packed bed of glass spheres (diameter = 1 mm, height = 15 mm) was used to distribute the fluid uniformly in the bed. The electrical contact with the fluidized bed consisted of a stainless steel feeder electrode (cathode). The anode was a drilled stainless steel disc located 20 mm from (above) the surface of the particle bed.

All the chemicals used in this study were of analytical grade and deionized water was used to prepare all the $Pb(NO_3)_2$ and boric acid ($H_3BO_3$, 0.5 M) solutions, with sodium nitrate ($NaNO_3$) as the supporting electrolyte.

The current efficiency was determined based on a spectrophotometric analysis of the concentration of lead in electrolyte samples taken from the system at the beginning and end of each run. Each experiment lasted for 120 min.

### 2.2. Methods

#### 2.2.1. Experimental design

Prior knowledge of the procedure is generally required to produce a statistical model [18–20]. The three steps used in the experimental design included statistical design experiments, estimation of coefficients through a mathematical model with response prediction, and analysis of the model's applicability. The experiment was conducted with two response variables in central composite design (CCD). Current efficiency and power consumption were selected as dependent variables in the experiment (CCD). Four dimensionless independent parameters were chosen as variables. The $t_{Pb}$

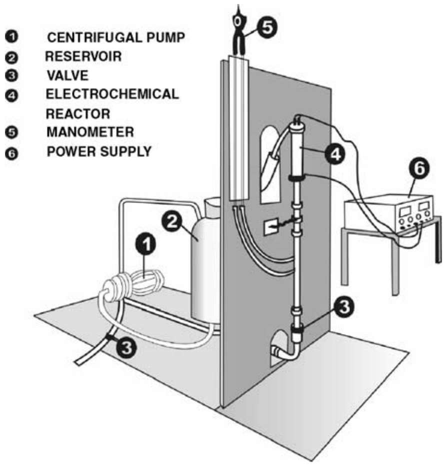

Fig. 2. Schematic representation of the experimental unit.

Table 1
Values of coded levels

| Variable | −2 | −1 | 0 | 1 | 2 |
|---|---|---|---|---|---|
| $t_{\mathrm{Pb}}$ | $5.52 \times 10^{-5}$ | $5.51 \times 10^{-4}$ | $1.05 \times 10^{-3}$ | $1.55 \times 10^{-3}$ | $2.04 \times 10^{-3}$ |
| $t_{\mathrm{Na}}$ | $4.03 \times 10^{-3}$ | $3.51 \times 10^{-3}$ | $2.99 \times 10^{-3}$ | $2.45 \times 10^{-3}$ | $1.93 \times 10^{-3}$ |
| $\varepsilon$ | 0.36 | 0.40 | 0.44 | 0.48 | 0.53 |
| $I/i_{\mathrm{lim}}$ | 65.19 | 62.19 | 54.95 | 51.27 | 42.32 |

and $t_{\mathrm{Na}}$ were calculated according to Ref. [21]. The coded factors, coded levels and their corresponding operating parameters and values are summarized in Table 1.

The correlation of the independent variables and the response was calculated by a second-order polynomial Eq. (1), using the least squares method, as shown below:

$$Y = b_0 + \sum_{i=1}^{4} b_i X_i + \sum_{i=1}^{4} b_{ii} X_1{}^2 + \sum_{i=1}^{4} \sum_{j=1\, i<j}^{4} b_{ij} X_i X_j + \xi \quad i \neq j \tag{1}$$

where $Y$ is the predicted response (EC and CE), $X_i$ the variables in the coded forms of the input variables, $b_0$ the model's intercept (constant), $b_{ii}$ the regression quadratic coefficients, $b_{ij}$ a cross-product coefficient and $\xi$ the stochastic term that is supposed to have Gaussian distribution [$\xi \sim N(0,\sigma^2)$] and is estimated by the difference between the predicted (by model) $\hat{Y}$ and observed value $Y$.

### *2.2.2. Data analysis*

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

$$\mathrm{EC} = \frac{\text{charge used in forming product}}{\text{total charge}} \tag{2}$$

From Faraday's law:

$$\mathrm{EC} = \frac{100\, z_i\, F\, \Delta m}{m_i\, I\, \Delta t} \tag{3}$$

where EC is the current efficiency (%), $Z_i$ the number of electrons, $F$ the Faraday constant (96487 A s mol$^{-1}$), $\Delta m$ the mass deposited in the interval of time $\Delta t$ (g), $m_i$ the molar mass (g/mol) and $\Delta t$ the interval of time (s).

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

$$\mathrm{CE} = \frac{2.778 \times 10^{-4}\, V\, I\, \Delta t}{\Delta m} \tag{4}$$

where CE is the power consumption (kW h kg$^{-1}$) and $V$ the cell potential (V).

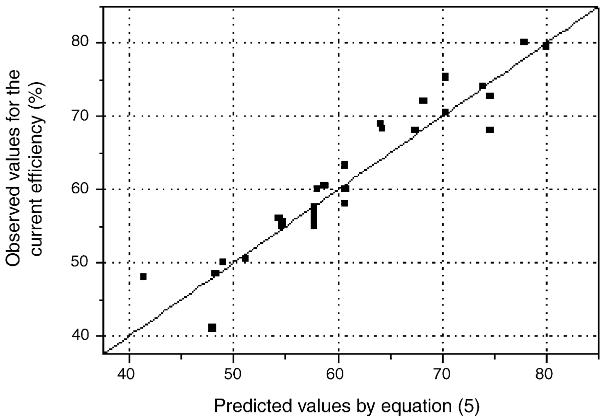

Fig. 3. Experimental values and values predicted by Eq. (5).

## 3. Results and discussion

The model applied to the experiments resulted in the following equations:

$$\mathrm{EC} = 57.72 + 4.86 t_{\mathrm{Pb}} - 1.51 t_{\mathrm{Na}} - 1.53\varepsilon + 4.23\left(\frac{i}{i_{\mathrm{lim}}}\right)^2 - 4.80 t_{\mathrm{Pb}} t_{\mathrm{Na}} + 4.80 t_{\mathrm{Pb}}\varepsilon + 2.24 t_{\mathrm{Na}}\varepsilon - 5.86 t_{\mathrm{Na}}\left(\frac{i}{i_{\mathrm{lim}}}\right) - 2.09\varepsilon\left(\frac{i}{i_{\mathrm{lim}}}\right) \tag{5}$$

$$\mathrm{CE} = 5.18 + 0.47 t_{\mathrm{Na}} - 0.95\left(\frac{i}{i_{\mathrm{lim}}}\right) + 0.34 t_{\mathrm{Pb}}{}^2$$

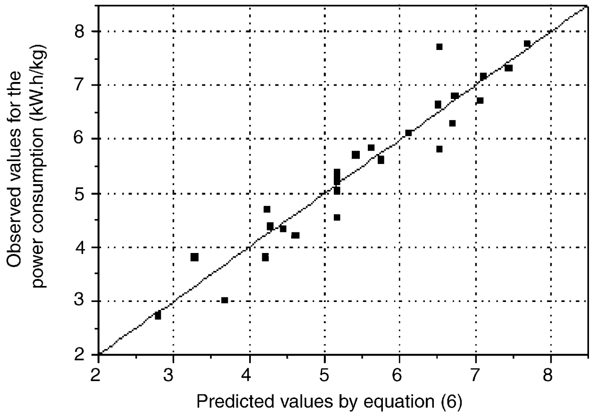

Fig. 4. Experimental values and values predicted by Eq. (6).

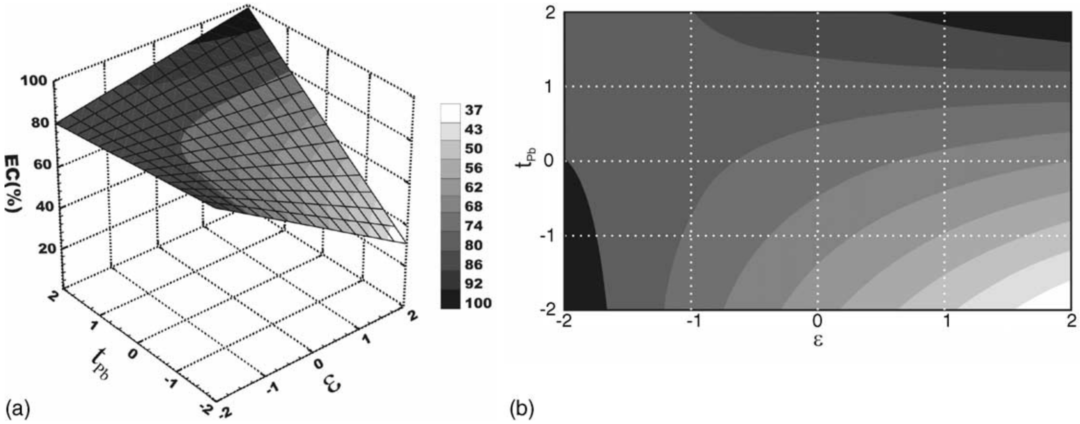

Fig. 5. (a) Current efficiency for $i/i_{\lim} = 2$ and $t_{Na} = -2$. (b) Contour plot of the current efficiency: effect of $t_{Pb}$ and $\varepsilon$.

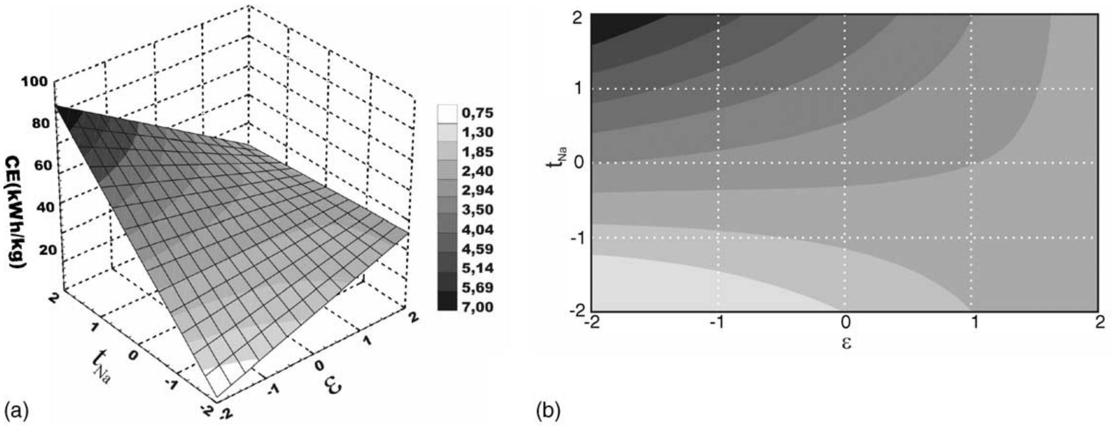

Fig. 6. (a) Power consumption for $t_{Pb} = 2$ and $i/i_{\lim} = 2$. (b) Contour plot of the power consumption: effect of $t_{Na}$ and $\varepsilon$.

$$+0.41 t_{Pb} t_{Na} - 0.31 t_{Pb} \varepsilon + 0.54 t_{Pb} \left(\frac{i}{i_{\lim}}\right) - 0.39 t_{Na} \varepsilon + 0.26 t_{Na} \left(\frac{i}{i_{\lim}}\right) + 0.21 \varepsilon \left(\frac{i}{i_{\lim}}\right) \qquad (6)$$

The *P*-value in the analysis of variance (ANOVA) was less than 0.001 to the computed *F*-values obtained for EC and CE, which were greater than the *F*-value in the statistical table, indicating that the two models (RMS) were significant at a high level of confidence (99.9%). The probability *P*-value was also relatively low ($P < 0.05$), indicating the model's significance. The coefficient of variation $R^2$ for EC was 0.9057, and for CE 0.9095, therefore indicating a high degree of correlation between the response and the independents variables in two responses (experimental and predicted values). The following figures (Figs. 3 and 4) demonstrate the strong correlation between $\hat{Y}$ (predicted values) and $Y$ (experimental values), which is very good for the goodness of fit.

The response surface methodology (RMS) is a statistical modeling technique employed for multiple regression analysis using quantitative data obtained from properly designed experiments to solve multivariable equations simultaneously [21–24]. RSM is used to determine the optimum response (EC and CE). Response surfaces can be visualized as three-dimensional plots that present the response as a function of two factors, while keeping the third one constant.

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

The lowest values of CE are observed with decreasing fluid outflow and increasing concentrations of support electrolyte [Fig. 6 (a) and (b)], due to the improved particles–electricity contact, which causes lower expansion.

## 4. Conclusions

The process parameters applied in this study demonstrated a good performance in removing lead from simulated effluents. The CCD, regression analysis and response surface method were effective in identifying the optimum conditions of EC and CE. Important information was obtained through the RSM. The good fitting obtained for EC and CE was highly significant. It was also concluded that the lead-ion reduction reaction in the electrochemical reactor was controlled by a combined process, i.e., mass transport and charge transfer control, subject to parallel reactions. It was found that, congruent with the literature, particle beds might provide great current efficiency in lead-ion reduction reactions in diluted solutions when operated under specific conditions. The optimum condition was estimated to be EC = 80% and CE = 4.37 kW h $\mathrm{kg}^{-1}$ for an experimental run using a $t_{\mathrm{Na}}$ of $21.07 \times 10^2$. It may be concluded that the particle bed reactor system can be effectively optimized using RSM with a minimal number of experiments.

## Acknowledgement

The authors would like to acknowledge the financial support received from CAPES and the Laboratory of Environmental Technology (UFPR).

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