HEAVY METALS RECOVERY FROM INDUSTRIAL WASTEWATER USING FLUIDIZED BED ELECTROCHEMICAL REACTOR

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Abstract. *The aim of this work is to study an electrochemical reactor by using metallic particles as cathode for lead, copper and nickel ions recovery from acidified aqueous solutions for different process parameters as metallic ion concentration, current density and bed expansion. The objective is the evaluation of reactor performance related to system efficiency and energy consumption. Taguchi Method was the selected statistical technique once it allows the main effects to be estimated with a minimum number of runs in the experiment. Moreover, it makes use of fractional factorial and orthogonal arrays to identify the factors having greater influence and the optimum setting for each factor. The highest current efficiency obtained in this work was 75,8%, 89,9% and 30,3% for lead, copper and nickel, respectively.*

Keywords*: Heavy metals recovery, electrochemical reactor, Taguchi method.*

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”, (Juttner *et al*., 2000; Walker and Wragg, 1980).

The fluidized-bed electrolytic cell was developed by Backhurst and co-workers (1969) and applied originally to electrochemical synthesis and fuel cell (Monhemius and Costa, 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 (Cognet, Berlan and Lacoste, 1995; Marracino, Coeuret and Langlois, 1987). 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, (Kazdobin, Shvab and Tsapakh, 2000). 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, (Kaminari *et al, 2005)*.

Two main arrangements with respect to the direction of the electric current and electrolyte flows are possible. They are denoted as flow-through (Figure 1 a) and flow-by arrangements (Figure 1 b). In this work was used the flow-through electrodes configuration, which has been commonly adopted for work on a small scale.

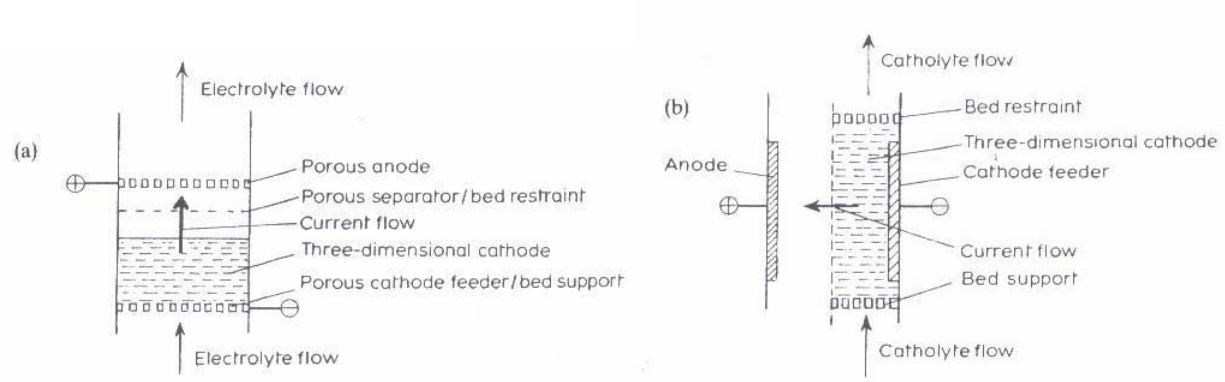

Figure 1. Configurations for three-dimensional electrodes. (a) Flow-through electrodes (b) Flow-by electrodes (Pletcher and Walsh, 1990)

2. Materials and Methods

2.1. Materials

An experimental unit was projected to study the recovery of lead, copper and nickel ions (Figure 2).

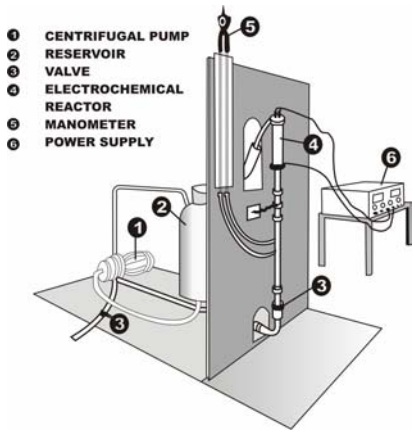

Figure 2. Schematic representation of the experimental unit.

The electrochemical reactor, illustrated in Figure 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.

The current efficiency was determined by spectrophotometer analysis of lead, copper and nickel concentration at samples of electrolyte withdrawn from the system at the beginning and ending of the runs. Each experiment was run for 180 minutes.

All the chemicals used in this study were of analytical grade and deionized water was used to prepare all the solutions: (1) Pb(NO3)2, H3BO3 and NaNO3 for lead; (2) CuSO4.5H2O and H2SO4 for copper and (3) NiSO4.6H2O and H2SO4 for nickel. The Table 1 below illustrates the composition of the each work solutions.

Table 1. Composition of the solutions

Solutions	Initial concentration	H_3BO_3 Concentration	$NaNO_3$ Concentration	H_2SO_4 Concentration
1	500 ppm de Pb (II)	0,5 M	0,044 M	-
2	750 ppm de Pb (II)	0,5 M	0,040 M	-
3	500 ppm de Cu (II)	-	-	0,4 M
4	750 ppm de Cu (II)	-	-	0,4 M
5	500 ppm de Ni (II)	-	-	0,02 M
6	750 ppm de Ni (II)	-	-	0,02 M

2.2. Taguchi Method

The Taguchi method is a powerful problem solving technique for improving process performance, yield and productivity. It reduces scrap rates, rework costs and manufacturing costs due to excessive variability in processes (Antony and Antony, 2001).

The techniques for laying out experiments when multiple factors are involved, has been known for a long time and is popularly known as the factorial design of experiments. This method helps researchers to determine the possible combinations of factors and to indentify the best combination. However, in industrial settings, it is extremely costly to run a number of experiments to test all combinations. The Taguchi approach developed rules to carry out the experiments, which further simplified and standardized the design of experiments (DOE), along with minimizing the number of factor combinations that would be required to test for the factor effects. So Taguchi method has been chosen for this study.

Different steps of Taguchi approch to experimental design are (Mohammadi *et al.*, 2005):

- **Determine the quality characteristic** (output or the response) **to be otimized**. In this study, the quality characteristic is the system current efficiency (EC) and energy consumption (CE).
  The current efficiency (EC) is the yield based on the electric charge that reacted during electrolysis, from Faraday's law:

$$EC = \frac{100.z_i.F.\Delta m}{M_i.I.\Delta t} \tag{1}$$

  where: EC is the current efficiency (%); z_i is the number of electrons; F is the Faraday constant (96487 A.s.mol^{-1}); Δm is the mass deposited in the interval of time Δt (g); M_i is the molar mass (g/mol), I is the applied current (A) and Δt is 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.

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

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

- **Identify the noise factors and test conditions.** Noise factors are those parameters which are either uncontrollable or are too expensive to control. In this study, the noise factors include room temperature, pH variation in cell, conductivity, flow velocity, bulk reactant, etc.
- **Identify the control parameters and their alternative levels.** Control parameters are those design factors that can be set and maintaned. The number of levels for each test parameter defines the experimental region. Table 2 represents the control parameters and their levels for this study.

Table 2.Controllable factors and their levels

Mettalic ion concentration	Controllable factors	1 Level	2 Level
Lead	A – Concentration (ppm)	500	750
	B – Current density (A/cm^2)	0,04	0,06
	C – Bed porosity	0,36	0,40
Copper	A – Concentration (ppm)	500	750
	B – Current density (A/cm^2)	0,09	0,14
	C – Bed porosity	0,36	0,40
Nickel	A – Concentration (ppm)	500	750
	B – Current density (A/cm^2)	0,09	0,14
	C – Bed porosity	0,36	0,40

- **Design the matrix experiment.** Taguchi provides many standard orthogonal arrays and corresponding linear graphs for the control parameters to fit a specific study. For this study, an L_4 orthogonal array (Table 3) has been chosen based on the number of factors and levels mentioned in Table 2.

Table 3. Orthogonal array L_4

Experiments	A Factor	B Factor	C Factor
1	1	1	1
2	1	2	2
3	2	1	2
4	2	2	1

- **Conduct the matrix experiment.** A matrix experiment consists of a set of experiments where the setting of the various parameters which need to study from one experiment to another is changed.
- **Analyze the data and determine the optimum levels.** To analyse the results, the Taguchi method uses a statistical measure of performance called signal-to-noise (S/N) ratio. The S/N ratio, the ratio of the mean (signal) to the standard deviation (noise), is a performance measure to choose control levels that best cope with noise. The S/N equation depends on the criterion for the quality characteristic to be otimized. While there are many different possible S/N ratios, three of them are considered standard and are generally applicable in the most situations: larger the best (LTB), small the best (STB), nominal the best (NTB). In this study, the biggest-is-best (EC) and the smallest-is-best (CE) ratio were used, following relation is used for S/N calculation:

$$S/N_{STB} = -10.\log\left[\frac{1}{n}\sum_{i=1}^{n} y_i^2\right] \tag{3}$$

$$S/N_{LTB} = -10.\log\left[\frac{1}{n}\sum_{i=1}^{n} \frac{1}{y_i^2}\right] \tag{4}$$

where n is the number of experiments and y_i is the response of each experiment. S/N ratio is expresses in decibel (dB) scale.

3. Results and Discussion

For each run the EC and the CE had been calculated, the table below illustrates the results.

Table 4 – Current efficiency (EC) and energy consumption (CE) for each run

Mettalic ion	Run	Current Efficiency (%)	Energy Consumption (kWh/kg)
LEAD	1	27,1	7,26
	2	50,4	5,37
	3	75,8	2,23
	4	49,1	5,24
COPPER	1	75,3	1,16
	2	65,5	1,62
	3	89,9	0,96
	4	73,9	1,38
NÍCKEL	1	12,1	62,91
	2	8,1	147,60
	3	30,3	20,93
	4	12,1	78,32

The S/N ratio for each level of process parameters is computed based on the S/N analysis. Regardless of the category of the quality characteristic (EC and CE), a greater S/N ratio corresponds to better quality characteristic (EC and CE). Therefore, the optimal level of the process parameters is the level with the greatest S/N ratio, as show in Figures 3 – 8 and Table 5.

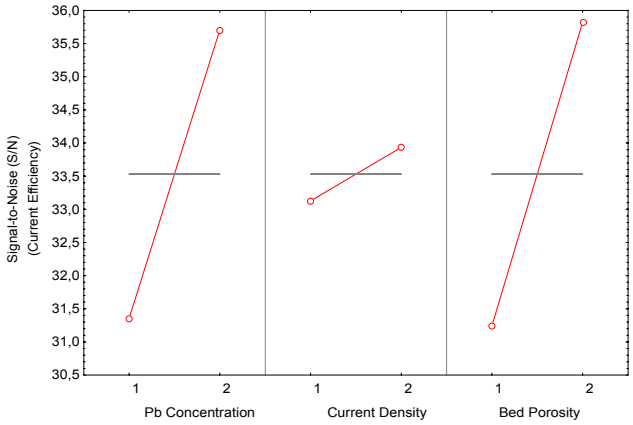

Figure 3. S/N ratio for EC from Pb ion

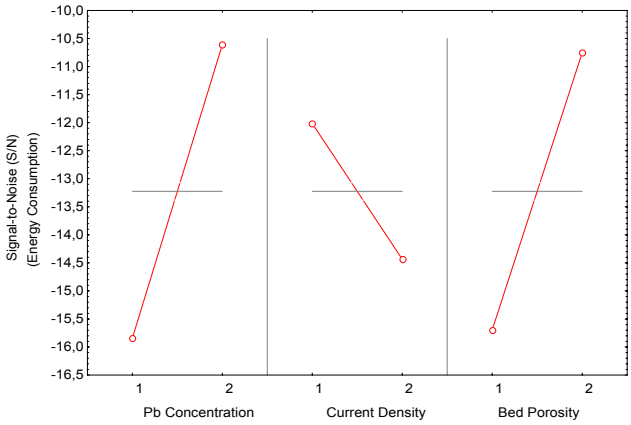

Figure 4. S/N ratio for CE from Pb ion

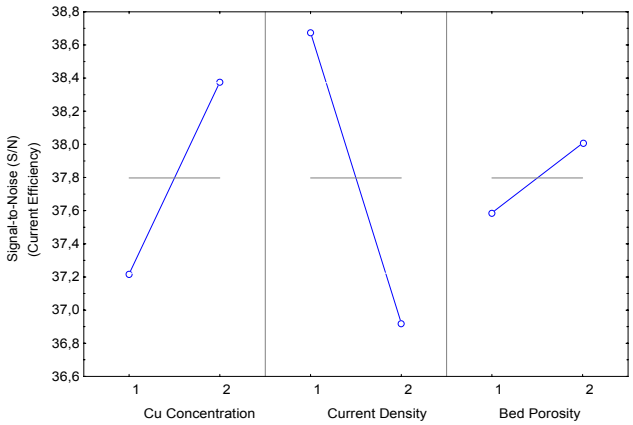

Figure 5. S/N ratio for EC from Cu ion

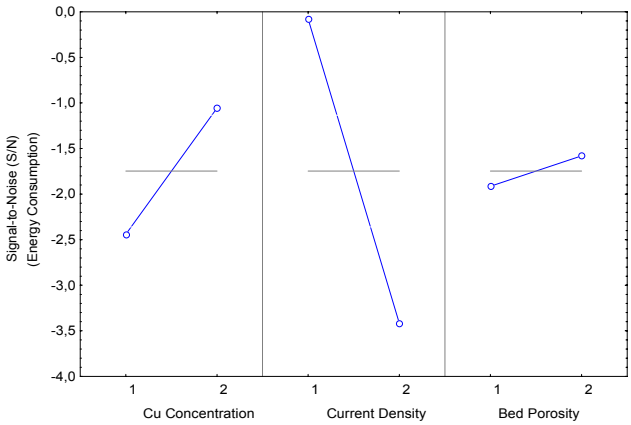

Figure 6. S/N ratio for CE from Cu ion

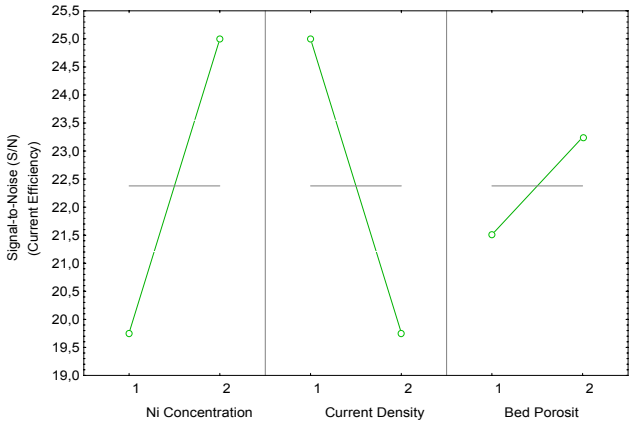

Figure 7. S/N ratio for EC from Ni ion

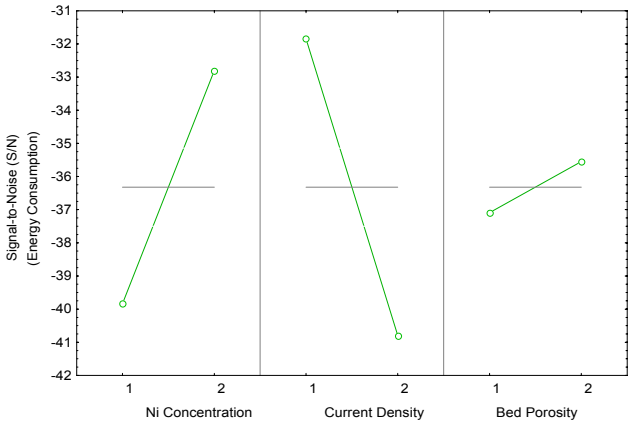

Figure 8. S/N ratio for CE from Ni ion

Table 5 – The optimum setting for each factor

Factors	Pb		Cu		Ni	
	EC	CE	EC	CE	EC	CE
Metallic íon concentration	2	2	2	2	2	2
Current density	2	1	1	1	1	1
Bed porosity	2	2	2	2	2	2

4. Conclusion

- The Taguchi Method allows the maximum number of main effects to be estimated with a minimum number of runs in the experiment and the optimum setting for each factor can be easily identified;
- The highest current efficiencies were obtained for lead and copper ion recovery from diluted solution; 75,8 % and 89,9 %, respectively;
- The main factor for energy consumption was the current density to copper and nickel deposition;
- The main factor for current efficiency was the bed porosity to ion lead, the current density to ion copper, the metallic ion concentration and the current density to ion nickel deposition.

5. Acknowledgements

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