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Heavy metals recovery from industrial wastewater using Taguchi method

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Abstract

The aim of this work is to study an electrochemical reactor 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 reactor performance was evaluated considering the system efficiency and energy consumption. Taguchi method was selected as the statistical technique since it allows the main effects to be estimated with a minimum number of experimental runs. Moreover, it makes use of fractional factorial and orthogonal arrays to identify the factors, which present the greatest influence on the system, and the optimum factor setting for each experiment run. The highest current efficiency obtained were 75.8%, 89.9% and 30.3% for lead, copper and nickel, respectively.

Keywords: Heavy metals recovery; Electrochemical reactor; Taguchi method

1. Introduction

Metals contamination in waste water is a serious problem for several industrial sectors such as metal finishing and the electronics industry. The outlet wastewater from these industrial processes normally contains metal concentration higher than the acceptable limits settled by law [1]. Metal removal or recovery from aqueous waste streams is becoming an increasingly important issue because of growing economic and environmental concerns. Electrodeposition is an interesting method to recover metals such as copper, lead, zinc, silver, among other metals. This method has a high efficiency for the copper case because of its high reduction potential [2].

Nowadays, this wastewater is discharged within the permitted concentrations limits of suspended solids and dissolved salts. Demanding excessive chemicals, this process results in large volumes of waste for disposal with no recovering process fesability.

Electrodeposition is a clean technology, offering an efficient way 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", [3,4]. The literature on electrolytic metal ion removal from aqueous solutions using porous electrode cells is extensive [5–10]. By flowing simulated effluents containing metal ions through three-dimensional porous cathodes, it is possible to achieve both high mass transfer rates and large surface areas for the electrochemical reaction.

Fluidized-bed electrolytic cell was developed by Backhurst and co-workers [11] and applied originally to electrochemical synthesis and fuel cell [12]. It consists of a steel particles bed, 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 electrode in two main aspects. Firstly, as the cathode is a bed of particles, it has a larger relation surface-area per volume. Thus, for any given cell current, the current density at the cathode surface is very low [13,14]. Secondly, a very high degree of agitation exists within the bed, which reduces the Nernst 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 significant loss of current efficiency.

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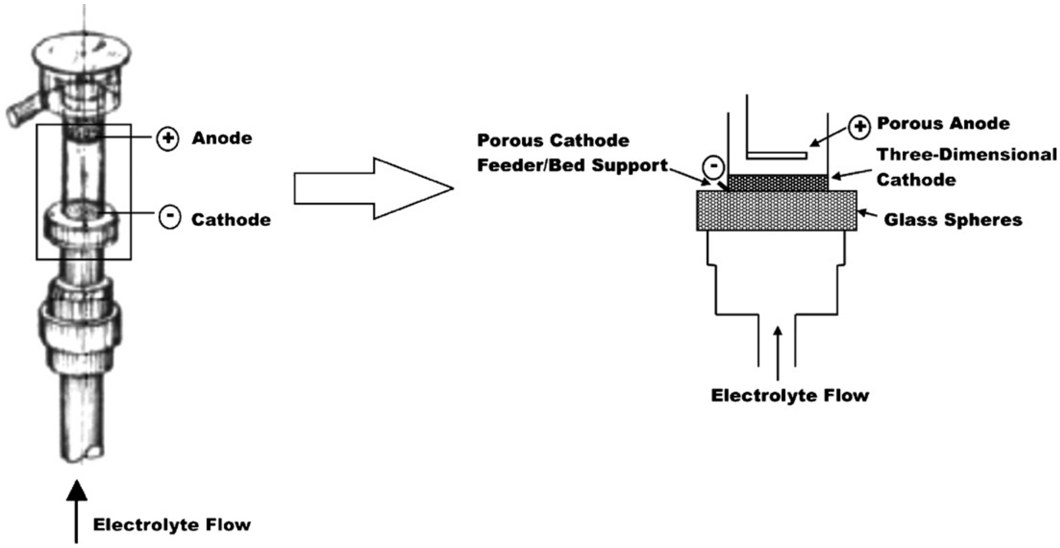

Fig. 1. Electrochemical reactor (flow-through cell) and detailed view of the reactor.

Therefore, 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 [15]. Several applications have been considered, e.g., fuel cells, hydrogen peroxide synthesis, ore flotation and organic electrosynthesis, but the best applications are expected especially in extraction metallurgy [16,17].

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

To evaluate the current efficiency and the energy consumption the Taguchi method was selected as a statistical technique once it allows the main effects to be estimated with a minimum number of experiment runs. A design plan is based on the use of orthogonal arrays introduced by Taguchi. Through the application of Taguchi's S/N ratio, the optimal operational condition from an experiment can be determined. It leads to several implications: (1) reduced experimental time, (2) identification of a fractional design containing the best operational condition that can be studied for full experimentation, (3) within a subset of a fractional design plan, the best operational condition can be found, and (4) significantly reduces of experimental cost since a minimal number of simulation runs is required to identify the best operational condition [18].

2. Experimental

2.1. Materials

The experimental apparatus consisted of an electrochemical reactor, a centrifugal pump to recirculate the solution, a manometer and a reservoir. The experiments were been conducted at ambient temperature and under galvanostatic conditions. The current control was achieved by using a constant current source (Power Supply—model EMG 18134).

The electrochemical reactor, illustrated in Fig. 1, was made from a cylinder of acrylic with an internal diameter of 4.44 cm and 20 cm length. The bed was composed by carbon steel particles with 1 mm diameter and 20 mm bed height. In order to obtain a uniform fluid distribution inside the bed, it was used a distributor composed by a packed glass spheres ($d = 1$ mm) and 15 mm height bed. The electrical contact with the fluidised-bed was obtained through a steel feeder electrode (cathode). The anode was a stainless steel disc, located at 2 cm 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 runs. The spectrophotometer used was the UV-vis—model FEMTO 600 Plus. The time spent for run was about 180 min.

Table 1
Composition of the solutions

Solutions	Initial concentration	H_3BO_3 concentration (M)	$NaNO_3$ concentration (M)	H_2SO_4 concentration (M)	$E_{standard}$ *vs.* NHE (mV)
1	500 ppm [Pb (2+)]	0.5	0.044	–	−126
2	750 ppm [Pb (2+)]	0.5	0.040	–	
3	500 ppm [Cu (2+)]	–	–	0.4	340
4	750 ppm [Cu (2+)]	–	–	0.4	
5	500 ppm [Ni (2+)]	–	–	0.02	−230
6	750 ppm [Ni (2+)]	–	–	0.02	

All the chemicals used in this study were of analytical grade. Deionized water was used to prepare all the solutions: (1) $Pb(NO_3)_2$, H_3BO_3 and $NaNO_3$ for lead, (2) $CuSO_4{\cdot}5H_2O$ and H_2SO_4 for copper and (3) $NiSO_4{\cdot}6H_2O$ and H_2SO_4 for nickel. Table 1 below displays the composition of the each working solution.

The voltammetric experiments were carried out in a conventional three-electrode cell. The small steel (1020) working electrode was cylinder shaped, with a cross-sectional area of $0.196\,\text{cm}^2$ glued inside a PirexTM glass tube with AralditeTM epoxy resin, with a pre-soldered copper wire for electrical contact. The working copper electrode was built by the same procedure as that used for the steel electrode, with a cross-sectional area of $0.156\,\text{cm}^2$. The counter-electrode was 1 mm diameter spiral platinum wire and the reference electrode was Ag/AgCl (KCl sat). The equipment used in this work was a potentiostat/galvanostat – Voltalab PGZ 301 from Radiommeter Analytical coupled to a computer through the Voltamester 4 software program.

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 [19].

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 identify 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 the factor effects. So Taguchi method has been chosen for this study.

Different steps of Taguchi approach to experimental design are [20]:

- Determining the quality characteristic (output or the response) to be optimized. In this study, the quality characteristic is the system current efficiency (CE) and energy consumption (EC).

  The current efficiency (CE) is the yield based on the electric charge that reacted during electrolysis, from Faraday's law:

  $$\text{CE} = \frac{100 z_i \cdot F\Delta m}{M_i I \Delta t} \tag{1}$$

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

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

  $$\text{EC} = \frac{2.778 \times 10^{-4}\, VI\Delta t}{\Delta m} \tag{2}$$

  where EC is the energy consumption (kWh kg^{-1}) and V is the cell potential (V).
- Identification the noise factors and test conditions. Noise factors are those parameters which are either uncontrollable or are too expensive to be controlled. In this study, the noise factors include room temperature, pH variation in cell, conductivity, flow velocity, bulk reactant, etc.
- Identification the control parameters and their alternative levels. Control parameters are those design factors that can be set and maintained. The number of levels for each test parameter defines the experimental region. Table 2 represents the control parameters and their levels for this study.
- Designing 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 L4 orthogonal array (Table 3) has been chosen based on the number of factors and levels mentioned in Table 2.
- Conducting the matrix experiment. A matrix experiment consisting of a set of experiments, where the setting of the various parameters, is studied need to study from one experiment to another, is changed.
- Analyzing the data and determining the optimum levels. To analyze the results, the Taguchi method uses a statistical measurement of performance called signal-to-noise (S/N) ratio. The S/N equation depends on the criterion for the quality characteristic to be optimized. 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

Table 2
Controllable factors and their levels

Mettalic ion concentration	Controllable factors	First level	Second level
Lead	*A*, concentration (ppm)	500	750
	B, current density (A/cm^2)	0.04	0.06
	C, bed porosity (ε)	0.36	0.40
Copper	*A*, concentration (ppm)	500	750
	B, current density (A/cm^2)	0.09	0.14
	C, bed porosity (ε)	0.36	0.40
Nickel	*A*, concentration (ppm)	500	750
	B, current density (A/cm^2)	0.09	0.14
	C, bed porosity (ε)	0.36	0.40

Table 3
Orthogonal array L4

Experiments	*A* factor	*B* factor	*C* factor
1	1	1	1
2	1	2	2
3	2	1	2
4	2	2	1

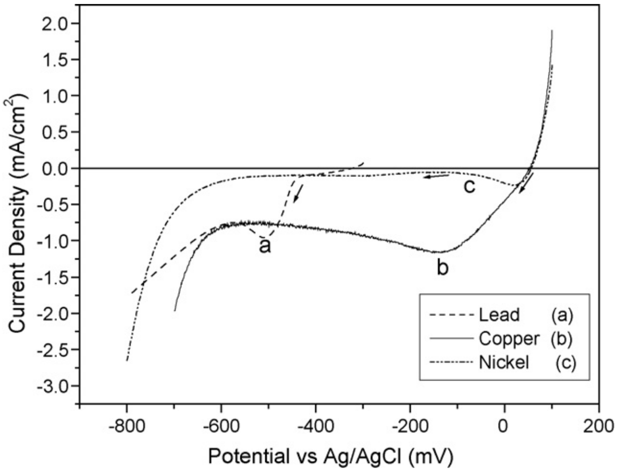

Fig. 2. Voltammograms for lead (working electrode: steel 1020), copper (working electrode: copper) and nickel (working electrode: copper), concentration utilized 750 ppm. The scan rate is 10 mV s^{-1}.

study, the biggest-is-best (CE) [Eq. (3)] and the smallest-is-best (EC) ratio [Eq. (4)] were used, following relation is used for S/N calculation:

$$\frac{\mathrm{S}}{\mathrm{N_{LTB}}} = -10\log\left[\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right] \qquad (3)$$

$$\frac{\mathrm{S}}{\mathrm{N_{STB}}} = -10\log\left[\frac{1}{n}\sum_{i=1}^{n}y_i^2\right] \qquad (4)$$

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

3.1. Voltammetric analysis

The voltammetric analysis was necessary to know the reactions that are involved in each system and also to the solution characterization. Through of the voltammetric profiles (Fig. 2) the equilibrium potential values gotten were of approximately −323, 54 and 60 mV for the systems Pb, Cu and, Ni, respectively.

The electrochemical reactions are:

$\mathrm{Pb}^{2+} + 2\mathrm{e}^- \to \mathrm{Pb}$ (profile a)

$\mathrm{Cu}^{2+} + 2\mathrm{e}^- \to \mathrm{Cu}$ (profile b)

$\mathrm{Ni}^{2+} + 2\mathrm{e}^- \to \mathrm{Ni}$ (profile c)

The voltammograms gotten in this work are according to the literature [8,21,22] for these metals.

Fig. 3 shows the concentration decay profiles for Pb ion. It can be noted that the curves are linear up to the moment when they become exponential in time. Thus, the recover level of these ions after 180 min was approximately 70%. Standing out that this behavior was similar for the Cu and Ni ions [22].

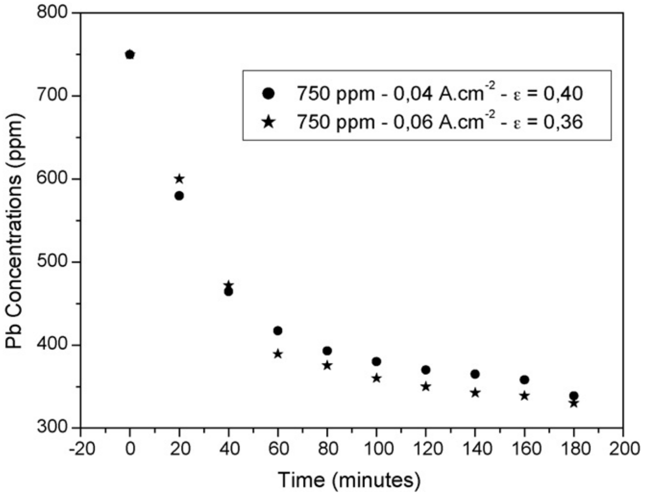

Fig. 3. Pb ions concentration *vs*. time in fluidized reactor.

3.2. Current efficiency (CE)

The results of the current efficiency is show at Table 4, obtained after 3 h of continuous experiment for lead, copper and nickel ions recovery process, respectively. The obtained values are represented in Figs. 4–6. It was observed that the current efficiency values obtained experimentally compared to those obtained by replications were very similar values indicating good reproducibility of the experimental values.

The low current efficiencies values for Ni ion recovery can be explained, by the hydrogen evolution reaction that occurs at lower current densities values [22]. This reaction favors parallel reactions decreasing the efficiency of the system. Moreover, the process of Ni ion reduction is not reversible. As the particles covered by nickel reach the dissolution zone, which exists in flow-through electrodes configuration, and a passivated layer is formed at their surface. When these particles return back to the reduction zone, they stay inactive. This phenomenon does not occur with the copper case, i.e., the dissolution reaction proceeds with no passivation process maintaining the particle active. This behavior explains the high values of current efficiencies obtained for copper experiments. Although the current efficiency of Ni

Table 4
Current efficiency (CE) for each run

Metallic ion concentration	Run	Current efficiency (%)
Lead	1	27.1
	2	50.4
	3	75.8
	4	49.1
Copper	1	75.3
	2	65.5
	3	89.9
	4	73.9
Nickel	1	12.1
	2	8.1
	3	30.3
	4	12.1

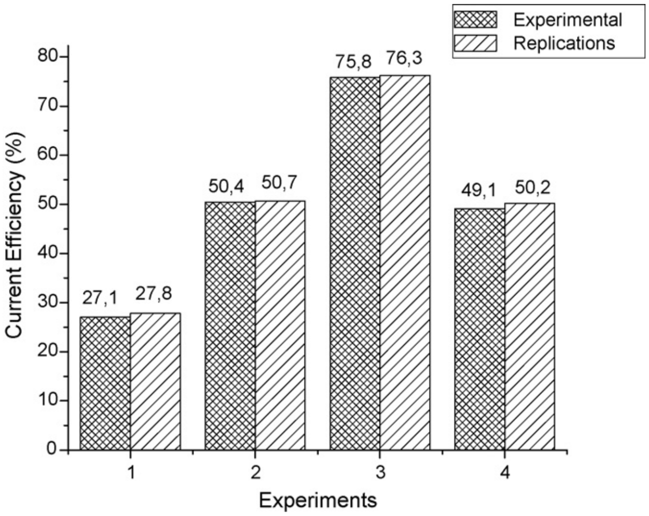

Fig. 4. Current efficiency for Pb ion recovery.

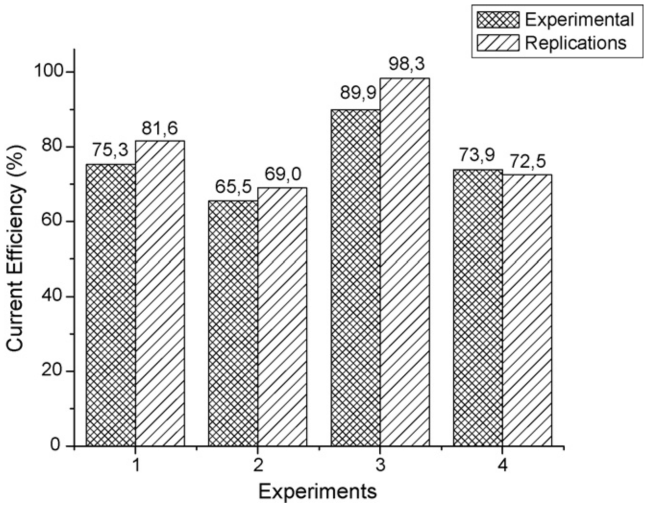

Fig. 5. Current efficiency for Cu ion recovery.

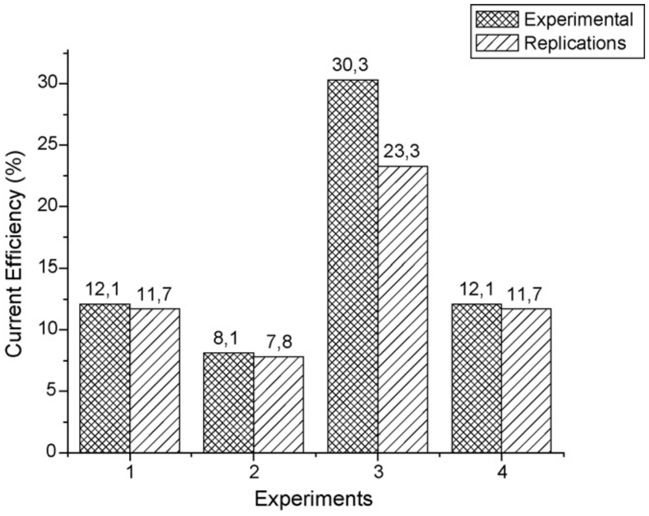

Fig. 6. Current efficiency for Ni ion recovery.

Table 5
Average of S/N ratio for current efficiency

Mettalic ion concentration	Controllable factors	Current efficiency (%)	
		First level	Second level
Lead	*A*, concentration (ppm)	31.42	35.77
	B, current density (A/cm^2)	33.19	33.99
	C, bed porosity	31.34	35.84
Copper	*A*, concentration (ppm)	37.10	38.38
	B, current density (A/cm^2)	38.67	36.81
	C, bed porosity	37.59	37.89
Nickel	*A*, concentration (ppm)	19.76	25.00
	B, current density (A/cm^2)	25.00	19.76
	C, bed porosity	21.51	23.25

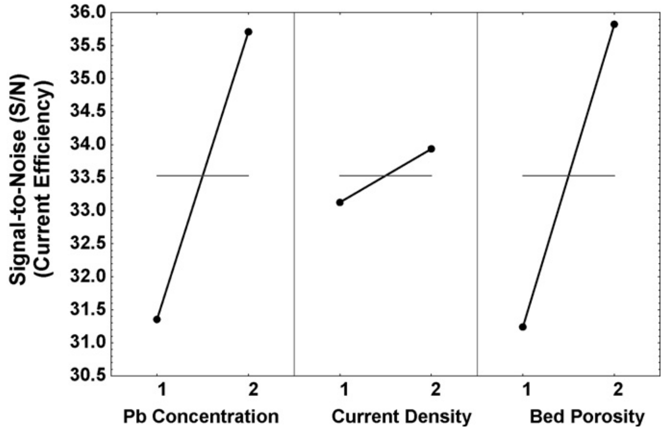

Fig. 7. S/N ratio for CE from Pb ion.

ion recovery has been low (30.3%), compared with the value in literature (40%) [23], it is close to each other. The nickel recovery process is still a technological challenge [24].

A statistic analysis is employed to find the optimum level. By taking the numerical values of current efficiency, the average for each level of the three factors can be obtained as show in the Table 5, Figs. 7–9. An alternative to recover Ni ion could be a perpendicular flow configuration reactor, with no dissolution zone.

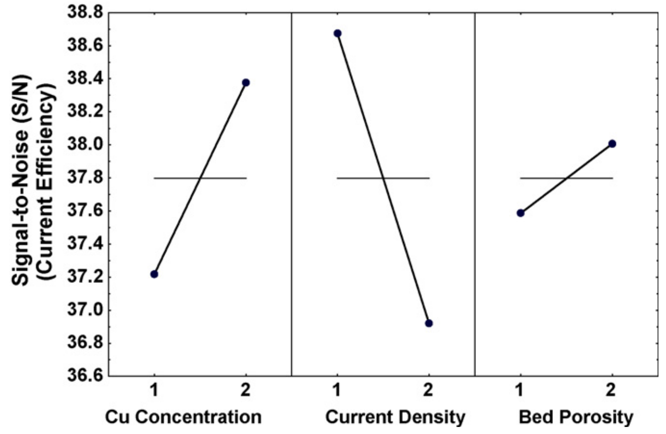

Fig. 8. S/N ratio for CE from Cu ion.

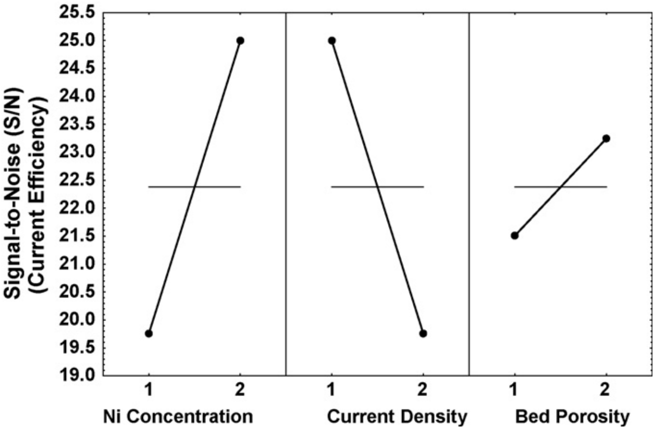

Fig. 9. S/N ratio for CE from Ni ion.

A greater S/N ratio is equivalent the less loss function. Then, the greater value of the average S/N ratio for each factor maximizes this relation. Using the Pb values presented in Table 5, it is observed that the greater value of the average S/N ratio is 35.77 (level 2) of the ion concentration factor; 33.99 (level 2) of the current density factor and 35.84 (level 2) of the bed porosity factor (Table 6). The current efficiency is normally equal or lower with rising current density since side reaction (hydrogen reduction) become more important. This behavior was retrieved for Cu and Ni, but not for Pb. This occurs because the hydrogen evolution potential is more high compared with the ones of the Cu and Ni ions. In the range of the applied current density did not occur significant of the hydrogen evolution reaction.

Following the same procedure for Cu and Ni ions recovery the obtained values are presented in Table 6. The levels of each factor are represented by the level that maximize the average of S/N ratio for Pb, Cu and Ni ions and, therefore, being this the optimum setting to get the highest current efficiency.

The lower current efficiency for Ni was because the passivated Ni particles do not react (inactive) after having crossed the dissolution zone. The applied current is constant and will be distributed to fewer particles with progressing passivation. The current density increases and therefore the current efficiency decreases according to Fig. 9.

The most significant parameters for CE of Pb ion recovery are the ion concentration and the bed porosity, as show in Fig. 7. This probably occurs due to the increasing mass transfer rate, promoting a bigger renewal of the species to be deposited.

For Cu ion recovery the most significant parameters according to Fig. 8, are the current density followed by the ion concentration and the bed porosity. The higher current efficiency is obtained for lower current density. This probably occurs due to a competition reaction between the metal deposition and the hydrogen reduction process.

Table 6
The optimum setting for CE

Factors	Pb	Cu	Ni
Ion concentration	2	2	2
Current density	2	1	1
Bed porosity	2	2	2

Table 7
Energy consumption (EC) for each run

Metallic ion concentration	Run	Energy consumption (kWh kg^{-1})
Lead	1	7.26
	2	5.37
	3	2.23
	4	5.24
Copper	1	1.16
	2	1.62
	3	0.96
	4	1.38
Nickel	1	62.91
	2	147.60
	3	20.93
	4	78.32

The recovery of the Ni ion presented the smaller CE compared with the others ions. The parameter that most influences the current efficiency are the ion concentration and the density current, as shows in Fig. 9.

3.3. Energy consumption (EC)

The energy consumption is a linear function of current efficiency and voltage drop [Eq. (2)]. The energy consumption values are representing in Table 7.

A statistic analysis employed to find the optimum level; is obtained by taking the numerical values of energy consumption. The average for each level of the three factors can be obtained as show in Table 8, Figs. 10–12.

The greater S/N ratio corresponds to better quality characteristics (CE or EC). Therefore, the optimal level of the process parameters is the level with the greatest S/N ratio, as represented in Table 9.

The EC from Pb ion recovery is largely influenced by the ion concentration and bed porosity, as shown in Fig. 10. The current density has less influence, i.e., there is not difference in the CE with levels variations, perhaps due to the operating current be lower than the limiting current. The EC from Cu ion recov-

Table 8
Average of S/N ratio for energy consumption (EC)

Mettalic ion concentration	Controllable factors	Energy consumption (kWh kg^{-1})	
		First level	Second level
Lead	*A*, concentration (ppm)	−15.84	−10.61
	B, current density (A/cm^2)	−12.02	−14.43
	C, bed porosity	−15.70	−10.75
Copper	*A*, concentration (ppm)	−2.44	−1.05
	B, current density (A/cm^2)	−0.08	−3.42
	C, bed porosity	−1.91	−1.58
Nickel	*A*, concentration (ppm)	−39.84	−32.80
	B, current density (A/cm^2)	−31.85	−40.79
	C, bed porosity	−37.09	−35.55

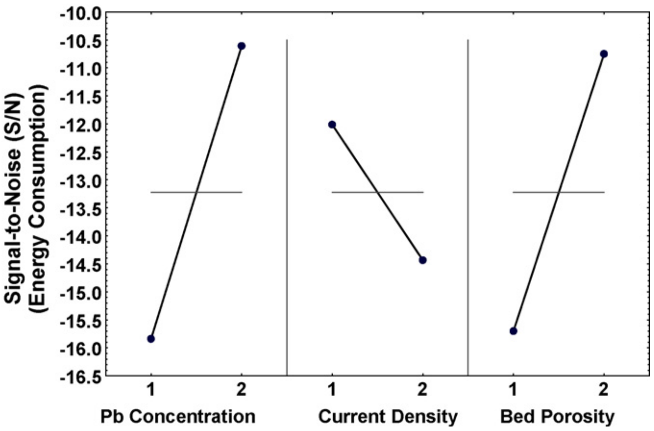

Fig. 10. S/N ratio for EC from Pb ion.

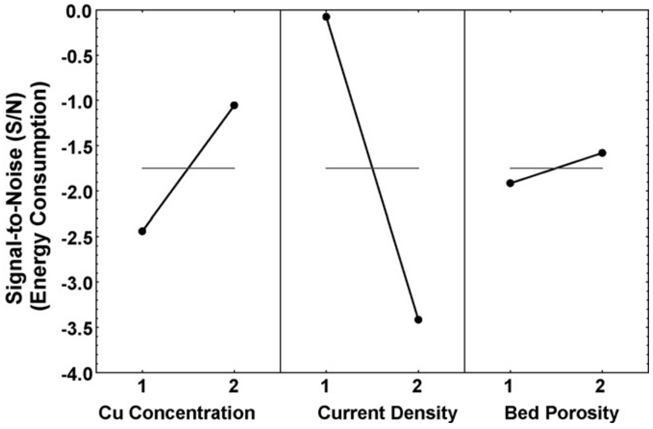

Fig. 11. S/N ratio for EC from Cu ion.

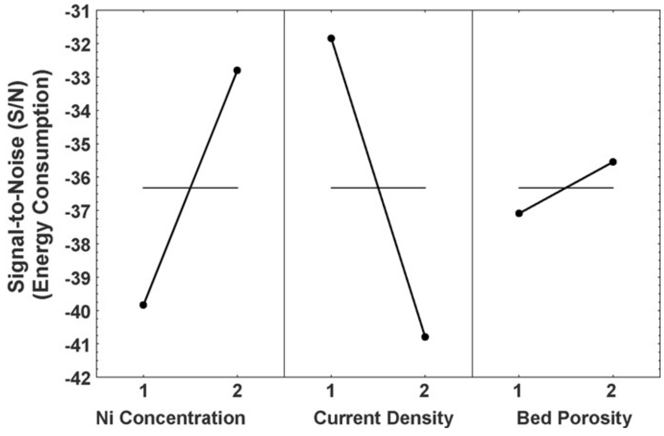

Fig. 12. S/N ratio for EC from Ni ion.

Table 9
The optimum setting for energy consumption (EC)

Factors	Pb	Cu	Ni
Ion concentration	2	2	2
Current density	1	1	1
Bed porosity	2	2	2

ery is influenced by the current density and ion concentration (Fig. 11). The bed porosity has less importance, because it can be working in a situation where the environment favors the mass transport or change transfer. Comparing the three ions studies, the Ni ion recovery represented the greater EC. The parameter with greater influence was the ion concentration and the current density, mainly for Cu and Ni ions. The parameter with lower influence was the bed porosity as shown in Fig. 12.

The experiment with greater current efficiency and less energetic consumption was obtained using: level 2 for initial concentration of metallic ion (750 ppm); level 1 for current density (0.04 A/cm^2 for Pb and 0.09 A/cm^2 for Cu e Ni) and level 2 for bed expansion (10% fluidized).

4. Conclusions

The obtained results allow the following conclusions:

- The Taguchi method allows one to obtain 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 particulate bed can present excellent current efficiency for reduction of some metallic at diluted solutions when operated in particular conditions.
- The highest current efficiencies were obtained for lead and copper ion recovery from diluted solution: 75.8 % and 89.9 %, respectively.
- The low current efficiency (30.3 %) for Ni ions recovery from diluted solutions occurs due to stable oxide formatted at the particle surface when it reaches the reactor dissolution zone.
- The used electrochemical reactor presented economic advantages when comparing the energetic cost of recovering Pb, Cu and Ni ions to other commercial processes.

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