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Experimental design for copper cementation process in fixed bed reactor using two-level factorial design

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Abstract This work deals with cementation of copper onto iron grid in a fixed bed reactor. The influence of several parameters is studied, namely: initial concentration of copper $[Cu^{2+}]_0$, temperature and flow rate. Moreover, their influence on the copper cementation reaction is investigated statistically by the experimental design in view of industrial application. The estimation and the comparison of the parameter's effects are realized by using two-level factorial design. The analysis of these effects permits to state that the most influential factor is initial concentration of copper $[Cu^{2+}]_0$ with an effect of (+2.4566), the second in the order is the temperature with an effect of (+0.18959), the third is the flow rate of the electrolytic solution with an effect of (−0.4226). The significance interactions found by the design of experiments are between initial concentrations of copper ions–flow rate (x_1x_3) with an effect ($b_{13} = +0.6965$).

1. Introduction

Uncountable tons of precious or toxic metals are discharged each year in the form of industrial waste water, 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 a problem associated with ecological and economical aspects. Ultimately, this wastewater is discharged in permitted concentrations of suspended solids and dissolved salts. This approach uses excessive chemicals, producing large volumes of disposals with no solution in the form of a recovery process (Nosier and Sallam, 2000).

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 consists in its environmental compatibility due to the fact that the main reagent, the electron, is the 'clean reagent' (Nosier and Sallam, 2000). The cementation process is one of the electrochemical techniques very often used in the removal of toxic or precious metals.

The cementation process was already known from the ancient times of human culture but the early knowledge about the process was spread in Europe at the beginning of the

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middle Ages. At that time, the process was used by alchemist mainly for performing of the miracle of metals transmutation. For several decades, cementation is commonly used in industry for recovery of metals, removal of metal ions from dilute wastes and for purification of solutions (Sulka and Jaskula, 2005). The advantage of the cementation process includes its relative simplicity, ease of control, and the possible of recovery valuable metals (Nosier and Sallam, 2000).

This technique consists of a heterogeneous and spontaneous reduction of a noble or toxic metal ion, contained in a liquid phase, with a sacrificial solid metal (Boyanov et al., 2004). The cementation reactions is clearly composed of two redox half reaction involving, on the one hand, the reduction of the more noble metal ions and on the other hand, the oxidation of a sacrificial solid metal (El Batouti, 2005).

This article concerns about the study of copper cementation by iron in a fixed bed reactor. Copper has been selected for a double interest: treatment and recycling of toxic metals whose effects on the environment have been clearly proven and whose raw matter cost is still increasing. Iron has been chosen as a sacrificial metal because of its availability, its low cost and its possible re-use in hydrometallurgical processes. The corresponding global cementation reaction of copper ions by iron can be presented as follows:

$$Cu^{2+} + Fe \rightleftharpoons \underline{Cu}\downarrow + Fe^{2+} \quad (1)$$

The technique of statistical design for the experiments can be used for process characterization, optimization and modelling. It is widely accepted in the manufacturing industry for improving the product performance and reliability, the process capability and yield. In the statistical design of the experiments, the factors involved in an experiment at their respective levels, can be simultaneously varied. Thus, a lot of information can be taken with a minimum number of experiment trials.

Basically, the classical parameter design is complicated and not easy to use, especially: a large number of experiments must be conducted when the number of the process parameters increased. For this reason, the design of experiments is a useful tool to study the interactions between two or more variables at reduced number of experimental trials. It is a collection of mathematical and statistical techniques useful for modelling and analysis in complex process optimization (Moghaddam et al., 2006; Guerra and Dreisinger, 1999).

Although the optimization of experimental conditions using design of experiments are widely applied in a large area of chemical processes, but its application in the cementation reaction is a very rare exception of some works (Moghaddam et al., 2006; Guerra and Dreisinger, 1999; Djoudi et al., 2007). In fact, there are no reports about cementation of copper onto iron using this statistical approach. The main objectives of this work are to investigate the individual and the interactive effects of three operating parameters, mainly: initial concentration of copper ions, temperature and flow rate cementation reaction of copper by iron in a fixed bed reactor by using a full factorial design (FFD).

2. Experimental

All reagents used in this study were analytically graded and distilled water was used. The experimental tests were carried out by using the experimental device schematized in Fig. 1. The device is mainly composed of the following parts: electrochemical reactor (1) made from a pyrex glass cylinder having an internal diameter of 20 mm and a length of 155 mm, a storage tank (2) made of pyrex glass, containing 1 L of copper solution. The copper solution was prepared from the dissolution of pentahydrated copper sulphate ($CuSO_4 \cdot 5H_2O$, 99% purity).

The temperature of the electrolyte was maintained with a thermostated bath (3) in which a storage tank is placed. A centrifugal pump (4) was used to assure the copper solution circulation and the flow rate was measured by a flow meter (5) regulated through a plastic by-pass (6). The sacrificial metal used was an iron electrode shown in Fig. 1 and for each run, a fresh electrode and a fresh solution of copper sulphate were used.

The cementation process of copper onto iron was investigated by varying initial concentration of copper ions, temperature and flow rate parameters. The kinetic study has allowed to fix the pH as well as the time of experiment at their optimal values, respectively, pH 3 and 180 min. pH solution was controlled by adding concentrated sulfuric acid (H_2SO_4; 96% purity). Samples (5 mL) are withdrawn in the storage tank at regular intervals during 180 min. They are dosed via atomic absorption spectrophotometry (SCHIMADZU AA6500) at 324.8 nm wavelength.

3. Statistical design of experiments

3.1. Full factorial design

Factorial designs allow the simultaneous study of the effects that several factors may have on the optimization of a particular process. It determines which factors have the important effects on the response as well as how the effect of one factor varies with the level of the other factors. The effects are the differential quantities expressing how a response changes as the levels of one or more factors are changed. Also, factorial designs allow measuring the interaction between each different group of factors.

The interactions are the driving force in many optimizations of the processes. Without the use of factorial experiments, some important interactions may remain undetected, and the overall optimization may not be attained. One of the simplest types of factorial designs used in experimental work is one having two levels (2^k). In a 2^k factorial design experiment, each factor may be assigned two levels: low (−1) and high (+1). If k factors are considered, then 2^k measurements are required to perform a factorial design analysis (Kaminari et al., 2005; Klimova et al., 2006).

In this investigation, three operating factors were chosen as independent variables, namely: initial concentration of copper ions (x_1), temperature (x_2) and flow rate (x_3). Other variables such as a time of experiments and pH are fixed at 180 min and 3, respectively. The natural values of each factor and their respective levels are presented in Table 1. The selection of levels of different factors is carried out on the basis of the preliminary trials and previous publishing results (Hedayata and Pesotanb, 2007; Pavan et al., 2007): Initial copper concentration $[Cu^{2+}]_0$ ranging from 10 to 300 mg/L, flow rate from 0.238 to 1.548 mL/s and temperature from 25 to 60 °C. The design performed according to Table 2 was composed of 2^3 factorial designs.

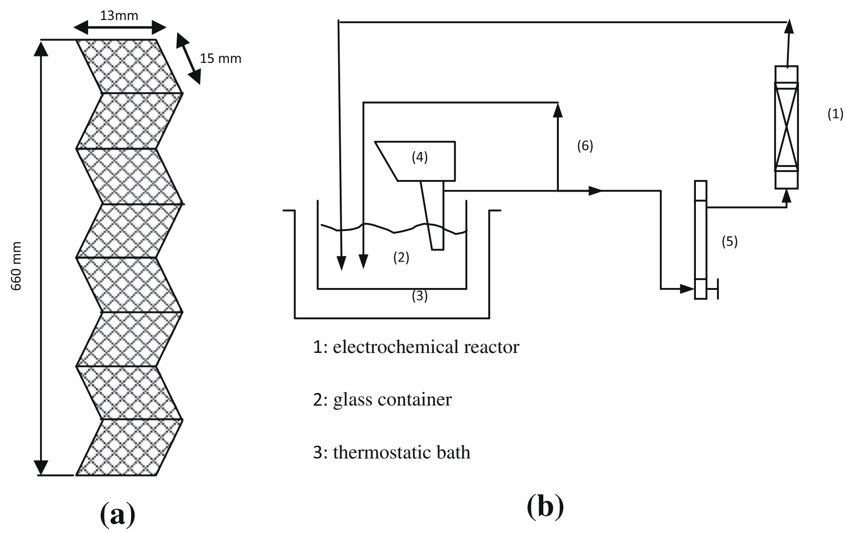

Figure 1 (a) Schematic representation of the experimental set-up. (b) Iron electrode.

Table 1 The experimental ranges and levels of independent variables.

Levels	$[Cu^{2+}]_0$ (mg/L)	T (°C)	Qv (mL/s)
−1	10	25	0.238
+1	300	60	1.548

Table 2 2^3 full factorial design.

Runs No.	$[Cu^{2+}]_0$ (mg/L)	Qv (mL/s)	T (°C)	y (residual concentrations of Cu^{2+})
1	−1	−1	−1	2.654
2	−1	−1	−1	0.437
3	−1	−1	1	2.434
4	−1	−1	1	0.174
5	−1	1	−1	5.458
6	−1	1	−1	7.735
7	−1	1	1	6.670
8	−1	1	1	5.489

The coded values of x_j were obtained from the following relationship (Berkani, 1992; Sulka, 2002):

$$x_j = \frac{Z_j - Z_j^0}{\Delta Z_j}, \quad j = 1, 2, \ldots, k \tag{2}$$

$$\text{With}: Z_j^0 = \frac{Z_{j\,\max} + Z_{j\,\min}}{2} \text{ and } \Delta Z_j = \frac{Z_{j\max} - Z_{j\min}}{2}$$

where x_j is the coded value of jth variable, Z_j is the encoded value of jth variable, Z_j^0 is the value of Z^j at the centre point of the investigation domain and ΔZ_j is the step size. Here, $Z_{j\ \max}$ and $Z_{j\ \min}$ represent the maximum and the minimum level of factor j in natural unit, respectively. The experimental data are analyzed by full factorial design to fit the following first order polynomial equation:

$$y = b_0 + \varepsilon + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3 \tag{3}$$

where y the estimated residual concentration of copper ions; b_0 is the value of fitted response at the centre point of design; b_j and b_{ji} are the linear and interaction terms, respectively (Goupy, 2001; Box et al., 1978).

When the response data are obtained from the test work, a regression analysis is carried out to determine the coefficients of the response model $(b_1, b_2, \ldots b_n)$, as well as their standard errors and their significance. In addition to the constant (b_0) and error (ε) terms, the response model incorporates (Pavan et al., 2007).

- Linear terms in each of the variables $(x_1, x_2, \ldots, x_n)$.
- First-order interaction terms for each paired combination $(x_1x_2, x_1x_3, \ldots, x_{n-i}x_n)$

In general Eq. (3) can be written in matrix form:

$$Y = BX + \varepsilon \tag{4}$$

The b coefficients, which should be determined in the second-order model, are obtained by (Goupy, 2001):

$$B = [X^T \cdot X]^{-1} \cdot [X]^T \cdot Y \tag{5}$$

where B is the column matrix of estimated coefficients; $[X^T \cdot X]^{-1}$ the dispersion matrix; $[X]^T$ the transpose matrix of experiments matrix $[X]$ and Y is the column matrix of observations.

4. Results and discussion

The model equation for copper cementation by grid iron was obtained after performing eight experiments and discarding the insignificant effect (b_{12}) is as follows using some statistical tests (Cochran, Student and Fischer) (Goupy, 2001; Box et al., 1978):

$$\hat{y} = 3.8813 + 2.4566 \cdot x_1 + 0.1895 \cdot x_2 - 0.4226 \cdot x_3 + 0.6965 \cdot x_1 \cdot x_3 + 0.4375 \cdot x_2 \cdot x_3 - 0.4269 \cdot x_1 \cdot x_2 \cdot x_3 \tag{6}$$

The model's coefficients were estimated by standard lest square regression techniques using an EXCEL software. A good adjustment of the (Eq. (6)) to the experimental data

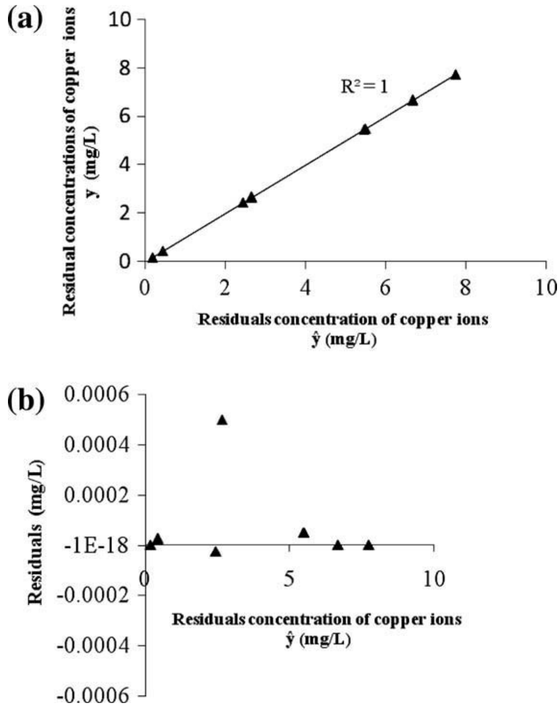

Figure 2 Analysis of quality of model (a) Comparison of experimental and predicted responses. (b) Residual analysis for estimated model.

Table 3 Comparison between observed and predicted residuals concentration.

Runs	y (mg/L)	$\hat{y}$ (mg/L)	Residuals e_i (mg/L)	Error (%)
1	2.654	2.653	−1E−08	3.76818 E−05
2	0.437	0.437	2.501E−05	5.72868E−03
3	2.434	2.434	2.501E−05	1.02755E−03
4	0.174	0.174	1E−08	5.73970E−05
5	5.458	5.458	4.999E−05	9.15861E−04
6	7.735	7.735	−3E−08	3.8784E−07
7	6.670	6.670	−1E−08	1.4992E−07
8	5.489	5.489	5.001E−05	9.1113E−04

was verified through the high correlation coefficient value obtained $R^2 = 1$ (Fig. 2). The random distribution of the residuals (Fig. 2) shows the absence of a trend, indicating that the mathematical model is adequate and that there is no inconsistency between the experimental and calculated values of the response. Table 3 shows that the difference between the measured and the predicted values do not exceed 1%. Therefore, all those results indicate that the model can adequately represent the data.

Initial copper concentration $[Cu^{2+}]_0$ (x_1) has the strongest effect on the response since coefficient of x_1 ($b_1 = +2.4566$) is large than the coefficients of the other investigated factors, the positive sign indicate that there is a direct relation between Initial copper concentration $[Cu^{2+}]_0$ and response (residual concentration of copper ions).

According the regression equation, temperature (x_2) has a positive effect on the response ($b_2 = +0.1895$) which has been explained (Djoudi et al., 2007) by the decrease in solution viscosity with the consequence increases of the bulk diffusivity of copper ions and so of the mass transfer coefficient. Flow rate (x_3) has a negative effect on the response ($b_3 = -0.4226$) which has been explained by reduction in residence time. The significance interactions found by the design of experiments are between initial concentrations of copper ions–flow rate (x_1x_3) with effect ($b_{13} = +0.6965$).

5. Conclusion

The first order model was developed according to the two levels factorial design to determine the main effects and the first interactions of initial concentration of copper ions, temperature and flow rate, on the reaction of copper cementation. However, factorial experimental designs at two levels did not provide the optimal conditions; it represented an understanding on the influence of several variables on the copper cementation and their trends and behaviour. The regression equation obtained above (Eq. (6)), shows that initial copper concentration, temperature and flow rate have an individual influence on the reaction of copper cementation. The significance interactions found by the design of experiments are between initial concentration of copper ions–flow rate (x_1x_3), between temperature–flow rate (x_2x_3) and between initial concentrations of copper ions–temperature–flow rate ($x_1x_2x_2$).

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