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Review

Optimization of copper cementation process by iron using central composite design experiments

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Abstract

In this study, the effects of various experimental parameters on the cementation yield of copper by iron were investigated statistically. A statistical experimental design based on the second-order central composite rotatable design (CCRD) was planned fixing the cementation period at 2 h. The experimental design was done at five levels of the operating parameters which were the initial copper concentration, temperature, pH and flow rate and their studied ranges are 10–100 mg/L, 20–60 °C, 1–5 and 0.46–4.38 mL/s, respectively. The model equation for copper cementation yield was developed and an optimization study was done.

The optimal conditions determined by using surface contour plots for initial copper cementation, temperature, pH and flow rate were 75.25 mg/L, 60 °C, 2.2 and 3.79 mL/s, respectively. Under these conditions, the copper cementation yield obtained was 99.6%.

Keywords: Copper; Iron; Cementation; Central composite design; Optimization

1. Introduction

Electrochemical cementation is known from a long time to remove noble or toxic metallic ions from solutions and is still used in hydrometallurgy, surface waste treatment and electrolyte purification. It consisted in the spontaneous heterogeneous reduction of a metallic ion present in solution by a more electropositive sacrificial metal. This technique is a type of corrosion reaction in which the anodic half reaction is the dissolution of the less noble metal and the cathodic half reaction is the deposition of the more noble metal [1,2].

The present study concerns the copper–iron system and the corresponding global cementation reaction is

$$Cu^{2+} + Fe \leftrightarrows Cu + Fe^{2+} \quad (1)$$

Removal of heavy metals, especially copper, by cementation has been studied by a number of researches on various substrate materials like Zn, Fe and Al with different type of electrodes, such as rotating disc [3], rotating cylinder [4], powder [5], fixed and fluidized beds [6].

There are a number of variables (temperature, reaction time, agitation, electrode geometry, pH, flow rate, etc.) known to affect cementation reaction and many attempts have been made to optimize them using statistical experiment designs such as TAGUCHI method [7], factorial fractional design (FFD) [8] and central composite design (CCD) [9].

The present study is undertaken to investigate the effectiveness of process variables, namely: initial copper concentration, temperature, pH and flow rate on the copper cementation yield of a laboratory-scale tubular reactor containing volumetric electrode of iron. The experiments are planned using experimental design based on a central composite rotatable design to study the main effects and the interactions of these variables and to found the combination of factors levels that give the optimum operating conditions. Our article has not aspired to bring newness towards the cementation reaction of copper by iron very much investigated but to provide the calculation tool in the field not yet exploited. Indeed, the experimental studies are often carried out by the empirical method, i.e., while varying all parameters at the same time and while seeking to determine the variation domain of the best output. On other side, cause complexity of the electrode as grill in zigzag unfolded into tubular reactor which was used, we think that the experimental designs make it possible to clear the ground in the understanding of the difference influences on the cementation kinetics in this case of figure.

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The main objective in using experimental design is to provide maximum and accurate information from a fewer possible number of runs [9]. Central composite designs are $2k$ factorial treatment designs with $2k$ additional treatment combinations called axial points and n_0 replications at the center of design. The property of rotatability developed for central composite design requires the variance of estimated values to be constant at points equally distant from the center of design [10–12].

The regression equation of fitted model for cementation yield was established and responses surface contour plots were drawn to investigate the interactions of operating parameters. These provide easiness in noticing the change in response when those factors are changed simultaneously.

2. Experimental details

The cementation experiments were carried out in the apparatus shown in Fig. 1. It consisted of an electrochemical reactor (1). Non-corrosive centrifugal pump (2) was used to assure the copper sulphate solution circulation in 1 L cylindrical glass container (3), which was immersed with a thermometer (4) in a thermostatic bath (5). The flow rate was measured by a flowmeter (6), regulated through a plastic by-pass (7) and valve (8). The solutions were deoxygenated using high purity nitrogen gas (99.5% purity) (9) before the beginning of experiments for 20 min and this atmosphere was maintained over the solution during all the experiments. The electrochemical reactor illustrated in Fig. 2 was a glass column having an internal diameter of 20 mm and a length of 290 mm. Its inlet zone which is called quiet zone, was packed with inert rods (diameter = 5 mm, height = 10 mm) to distribute the fluid uniformly in the reaction zone. The sacrificial metal used was an iron electrode shown in Fig. 3. For each run, a fresh solution of copper sulphate and fresh electrode were used.

All reagents used in this study were analytical grade and distilled water was used to prepare all the copper sulphate and sulphuric acid solutions (($CuSO_4 \cdot 5H_2O$) 99% purity and H_2SO_4; 96% purity). Fractions of solution (5 cm^3) are sampled at regular intervals during 2 h (30, 60, 90, 120 min) for analysis by atomic absorption spectrophotometer (SCHIMADZU AA6500) connected to the micro-computer. The analysis is conducted with an oxidizing air–acetylene flame at 324.8 nm wavelength.

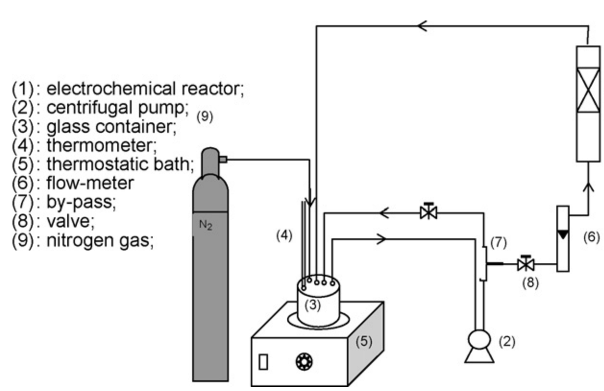

Fig. 1. Schematic representation of the experimental set-up.

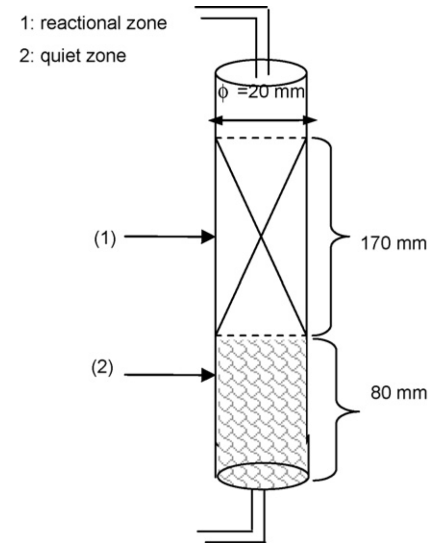

Fig. 2. Electrochemical reactor.

3. Design of experiments

Experimental design is widely used for controlling the effects of parameters in many processes. Its usage decreases number of experiments, using time and material resources. Furthermore, the analysis performed on the results is easily realized and experimental errors are minimized. Statistical method measures the effects of change in operating variables and their mutual interactions on process through experimental design way [9,13]. The three steps used in experimental design included statistical design experiments, estimation of coefficient through a mathematical model and analysis of the model's applicability [11–13].

In this study, four operating factors were chosen as independent variables, namely, initial copper concentration (x_1),

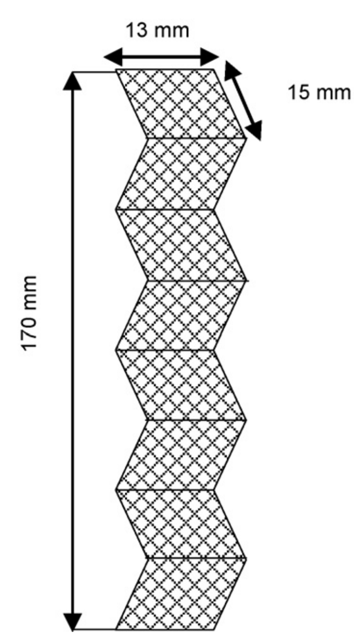

Fig. 3. Iron electrode.

temperature (x_2), solution pH (x_3) and flow rate (x_4), and the cementation yield as dependent output response variable which is expressed as (%):

$$y(\%) = \frac{[Cu^{2+}]_0 - [Cu^{2+}]_t}{[Cu^{2+}]_0} \times 100 \quad (2)$$

where $[Cu^{2+}]_0$ is the initial copper ions concentration (mg/L) and $[Cu^{2+}]_t$ is the copper ions concentration at time t (mg/L).

The original values of each factor and their corresponding levels are shown in Table 1.

The experiments were performed according to the central composite rotatable design (CCRD) matrix given in Table 2. This design is composed of 2^4 factorial design (runs 1–16; see Table 2), eight-star points (17–24) and 12 replicates runs (25–36). The stars points and the replicates are added to the factorial design to provide for estimation of curvature of model and to allow for estimation of experimental error [11–13].

The correlation of the independent variables and the response were estimated by a second-order polynomial equation (3), using the least-square method as shown below:

$$y = b_0 + \sum_{j=1}^{k} b_j x_j + \sum_{\substack{u,\, j = 1 \\ u \neq j}}^{k} b_{uj} x_u x_j \sum_{j=1}^{k} b_{jj} x_j^2 + \varepsilon \quad (3)$$

Here y represents the copper cementation reaction yield; b_0 the value of fitted response at the center point of design, b_j, b_{uj} and b_{jj} are the linear, interaction and quadratic terms, respectively. The dimensionless x_j variables are related to the standardized

Table 1
Values and levels of operating parameters

Operating factors	Levels				
	−2	−1	0	1	2
Z_1: $[Cu^{2+}]_0$ (mg/L)	10	32.5	55	77.5	100
Z_2: T (°C)	20	30	40	50	60
Z_3: pH	1	2	3	4	5
Z_4: Q_v (mL/s)	0.46	1.44	2.42	3.40	4.38

Table 2
Experimental design and the results for copper cementation yield

Run no.	Natural values of parameters				Coded values of parameters					y (%)	$\hat{y}$ (%)
	Z_1	Z_2	Z_3	Z_4	x_0	x_1	x_2	x_3	x_4		
1	32.5	30	2	1.44	1	−1	−1	−1	−1	67.938	69.213
2	77.5	30	2	1.44	1	1	−1	−1	−1	73.223	73.415
3	32.5	50	2	1.44	1	−1	1	−1	−1	75.622	78.359
4	77.5	50	2	1.44	1	1	1	−1	−1	84.261	82.561
5	32.5	30	4	1.44	1	−1	−1	1	−1	81.948	82.957
6	77.5	30	4	1.44	1	1	−1	1	−1	86.865	87.159
7	32.5	50	4	1.44	1	−1	1	1	−1	88.382	86.855
8	77.5	50	4	1.44	1	1	1	1	−1	90.302	91.057
9	32.5	30	2	3.4	1	−1	−1	−1	1	81.714	83.269
10	77.5	30	2	3.4	1	1	−1	−1	1	87.055	87.471
11	32.5	50	2	3.4	1	−1	1	−1	1	92.938	92.415
12	77.5	50	2	3.4	1	1	1	−1	1	95.182	96.617
13	32.5	30	4	3.4	1	−1	−1	1	1	89.114	88.241
14	77.5	30	4	3.4	1	1	−1	1	1	91.414	92.443
15	32.5	50	4	3.4	1	−1	1	1	1	91.203	92.139
16	77.5	50	4	3.4	1	1	1	1	1	96.528	96.341
17	10	40	3	2.42	1	−2	0	0	0	84.622	83.178
18	100	40	3	2.42	1	2	0	0	0	91.848	91.582
19	55	20	3	2.42	1	0	−2	0	0	84.045	82.446
20	55	60	3	2.42	1	0	2	0	0	95.599	95.490
21	55	40	1	2.42	1	0	0	−2	0	80.913	79.070
22	55	40	5	2.42	1	0	0	2	0	92.404	92.538
23	55	40	3	0.46	1	0	0	0	−2	73.973	73.306
24	55	40	3	4.38	1	0	0	0	2	93.684	92.646
25	55	40	3	2.42	1	0	0	0	0	92.495	92.052
26	55	40	3	2.42	1	0	0	0	0	90.384	92.052
27	55	40	3	2.42	1	0	0	0	0	91.536	92.052
28	55	40	3	2.42	1	0	0	0	0	92.896	92.052
29	55	40	3	2.42	1	0	0	0	0	92.367	92.052
30	55	40	3	2.42	1	0	0	0	0	90.855	92.052
31	55	40	3	2.42	1	0	0	0	0	92.871	92.052
32	55	40	3	2.42	1	0	0	0	0	92.324	92.052
33	55	40	3	2.42	1	0	0	0	0	92.371	92.052
34	55	40	3	2.42	1	0	0	0	0	92.911	92.052
35	55	40	3	2.42	1	0	0	0	0	91.511	92.052
36	55	40	3	2.42	1	0	0	0	0	92.102	92.052

forms as following [11–13]:

$$x_j = \frac{Z_j - Z_j^0}{\Delta Z_j}, \quad j = 1, 2, \ldots, k, \quad Z_j^0 = \frac{Z_{j\max} + Z_{j\min}}{2},$$

$$\Delta Z_j = \frac{Z_{j\max} - Z_{j\min}}{2}$$

where $Z_{j\max}$ and $Z_{j\min}$, respectively, represent the maximum and the minimum level of factor j in natural unit. The residual error ε that supposed to have Gaussian distribution [$\varepsilon \approx N(0, \sigma^2)$], was estimated by the difference between the predicted ($\hat{y}$) and the observed value (y) [11–13]. The coefficients of the fitted equation can be obtained from Eq. (3) as follows:

$$B = [X^{\mathrm{T}}X]^{-1}[X]^{\mathrm{T}}Y \tag{4}$$

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

4. Results and discussion

4.1. Results

The results of second-order central composite design experiments are collected in Table 2. The model coefficients (Eq. (3)) are estimated by standard least-square regression technique using "EXCEL" software. From statistical point of view, three tests are required to evaluate the adequacy of the model; Student's t-test which is about the significance of factors, R-square test and Fisher tests.

The estimated t values for particular process parameters can be calculated as follows:

$$t_j = \frac{|\text{coefficient of process parameter}|}{\sigma_{b_j}} = \frac{|b_j|}{\sigma_{b_j}} \quad \text{with}$$

$$\sigma_{b_j}^2 = C_{jj}\sigma_{\mathrm{rep}}^2 \quad \text{and} \quad \sigma_{\mathrm{rep}}^2 = \frac{\sum_{i=1}^{n_0}(y_i - \bar{y}_0)^2}{n_0 - 1} = 0.67$$

where $\sigma_{b_j}^2$ is the coefficients variance; C_{jj} the diagonal terms of $[X^{\mathrm{T}}X]^{-1}$matrix; σ_{rep}^2 the replication variance; y_i the observed value of cementation yield for ith central point; $\bar{y}_0$ the average value of cementation yield for the central point and n_0 is the repetition number of experiments at the center work domain.

The tabulate t value for 5% level of significance and 11 degrees of freedom ($f = 12 - 1 = 11$) is $t_{0.05}(11) = 2.201$. It is found that all individual effects are significant at 5% of significance level and only the interactions ($x_1 \times x_2$), ($x_1 \times x_3$), ($x_1 \times x_4$), and ($x_2 \times x_4$) are not significant. Therefore, they are excluded from the regression equation.

The test of reliability for predicting equation has been carried out by Fisher's variance ratio test known as F-test. The F-ratio is given by the following form:

$$F = \frac{\sigma_{\mathrm{res}}^2}{\sigma_{\mathrm{rep}}^2} \quad \text{with} \quad \sigma_{\mathrm{res}}^2 = \frac{\sum_{i=1}^{N}(y_i - \hat{y}_i)^2}{N - \ell}$$

Table 3
Fisher test for cementation yield

Residual variance, σ_{res}^2	1.63
Replication variance, σ_{rep}^2	0.67
Estimated F value	2.432

where σ_{res}^2 is the residual variance; N the total number of observations ($N = 36$); ℓ the number of coefficients in the regression equation ($\ell = 11$); y_i the observed value of cementation yield for ith observation and $\hat{y}_i$ is the estimated value of cementation yield for ith observation.

Table 3 gives the values of σ_{res}^2, $\sigma_{\mathrm{rep}}^2$and F estimated for regression equation.

The upper degree of freedom ($f_1 = N - \ell$) and the lower degree of freedom ($f = n_0 - 1$) are 25 and 11, respectively. The tabulated F value for 5% level of significance is between 2.57 and 2.61. The estimated F value is much less than this interval. Hence, it can be concluded that the two variances are equal and the most of the response variation can be explained by the regression. Furthermore, the test of significance of regression confirms at the established predicting equation gives an excellent fitting to observed data.

Finally, R^2-value is found to be 96.6% and Table 2, shows that the difference between the measured and the predicted values do not exceed 3%. Therefore, all those results indicate that the model can adequately represent the data.

The model equation for copper cementation by iron obtained after performing 36 experiments and discarding the insignificant effects is as follows:

$$\begin{aligned}\hat{y} = {} & 92.052 + 2.101x_1 + 3.261x_2 + 3.367x_3 + 4.835x_4 \\ & - 1.312x_2x_3 - 2.193x_3x_4 - 1.168x_1^2 - 0.771x_2^2 \\ & - 1.562x_3^2 - 2.269x_4^2\end{aligned} \tag{5}$$

4.2. Discussion

The regression equation obtained above (Eq. (5)), shows that initial copper cementation, temperature, pH and flow rate all have an individual influence on the reaction yield of copper cementation. Flow rate (x_4) has the strongest effect on the response since coefficient of x_4 ($b_4 = +4.835$) is large than the coefficients of the other investigated factors. Positive sign of this coefficient indicates that there is a direct relation between flow rate and reaction yield; in other words, copper recovery increase with increasing flow rate. This effect is explained in literature [14,15] by an increase in mass transfer rate due to the decrease of diffusional boundary layer thickness at high flow rate. The order for factors strength on cementation yield following flow rate was found as pH (x_3), temperature (x_2) and initial copper concentration (x_1); all being positive in sign.

Concerning pH effect, literature results [6,14] show that for some substrates such as iron (Fe), which is used in this study, cementation rate decreases at high solution acidity because of the adsorption of hydrogen formed at metal surface which lead to the decrease in reduction sites of metallic ions present in solution. In other words, it is recommended to work with high values of solution pH (between 3 and 5) in the case of this sacrificial metal at the interval of pH investigated. These results are in agreement with that obtained by regression equation, where the coefficient of pH parameter is positive ($b_3 = +3.367$). This means that, increasing of pH has a positive effect on reaction yield of copper by iron in the work domain studied.

According the regression equation, temperature (x_2) has a positive effect on the response ($b_2 = +3.261$) which has been explained [4,16,17] by the decrease in solution viscosity with consequence increases of the bulk diffusivity of copper ions and so of the mass transfer coefficient.

The significance interactions found by the design of experiments for copper cementation yield are essentially between flow rate and solution pH (x_3x_4) and between temperature and pH (x_2x_3).

5. Optimization

In this work, the model equation is used to find the direction in which the variables should be changed in order to optimize cementation reaction yield. The corresponding two dimensional response surfaces of the quadratic model are shown in Fig. 4a–c. The figures are drawn in pH–flow rate plan (the most important two factors affecting the response) for various level of temperature (−2, 0, +2) at optimal initial copper concentration ($[Cu^{2+}]_0 = 75.25$ mg/L) using "MATLAB 7.0" software.

The surface contour plots of mutual interactions between the variables (Fig. 4) are found to be elliptical. The stationary point or central point is the point at which the slope of the contour is zero in all directions. The coordinates of the central point within the highest contour level in each of these figures will correspond to the optimum values of the respective parameters. The maximum predicted yield is indicated by the surface confined in the smallest curve of the contour diagram.

The analysis of these figures indicates clearly the significance influence of flow rate and its interaction with solution pH. The optimum cementation yield in all conditions (Fig. 4a–c) increases in the direction of the increase in the temperature and it reaches 99.6% cementation yield at high flow rate and low pH values (Fig. 4c). This result may be explained by the fact that at high solution acidity, the reaction of corrosion is accelerated, as

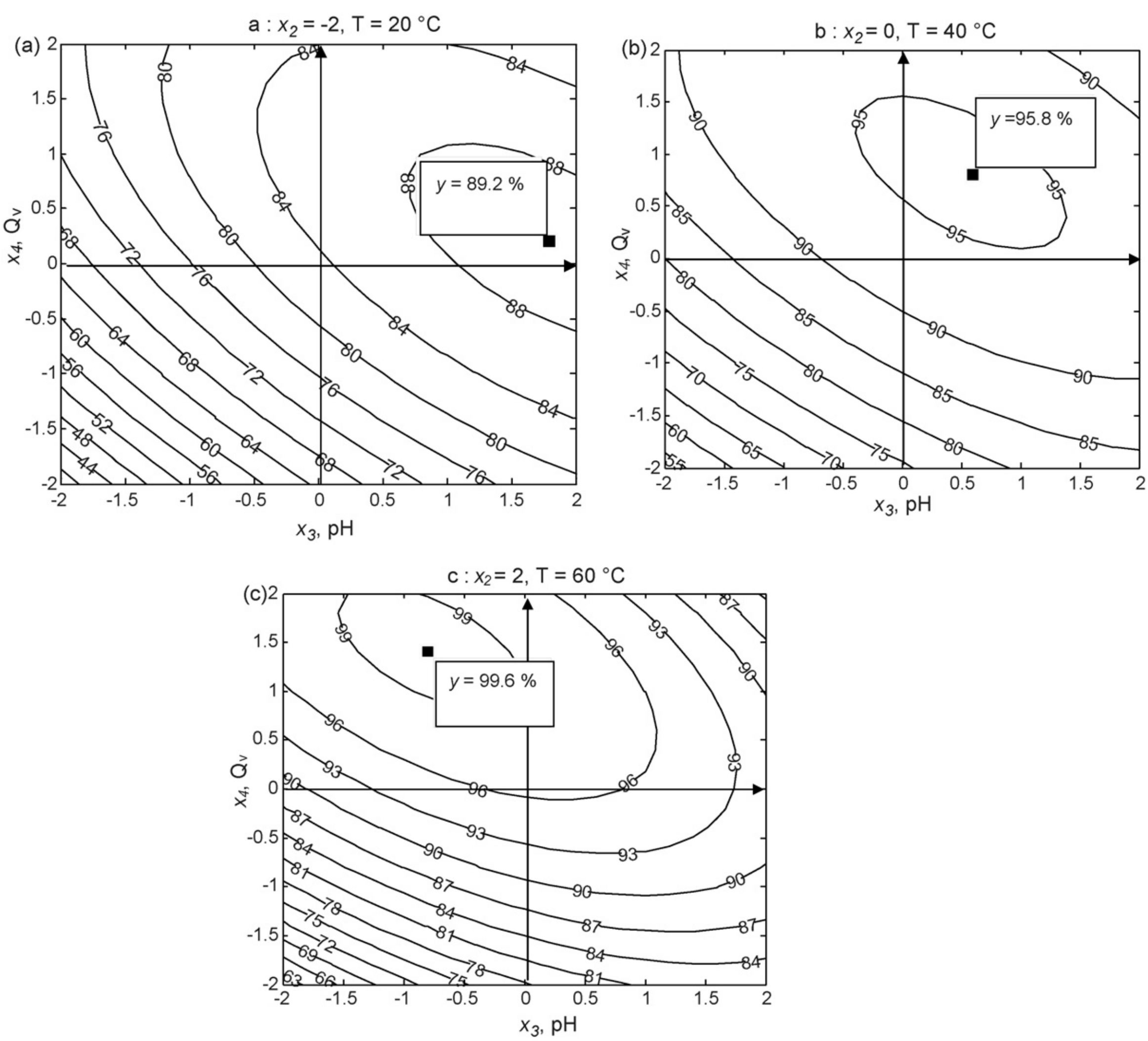

Fig. 4. (a–c) Surface contour plots for copper cementation yield at optimum value of initial copper concentration for different levels of temperature.

consequences; the reaction of hydrogen formation is accelerated too. To avoid the adsorption of hydrogen at the surface of iron and it occupation of active sites, it is recommended to increase flow rate to allow the reduction of copper ions present in solution.The corresponding conditions of the best cementation yield are follows:

$$x_1 = 0.90, \text{ corresponding to } [\mathrm{Cu}^{2+}]_0 = 75.25\,\mathrm{mg/L};$$

$$x_2 = 2, \text{ corresponding to } T = 60\,^{\circ}\mathrm{C};$$

$$x_3 = -0.8, \text{ corresponding to pH } = 2.2;$$

$$x_4 = 1.4, \text{ corresponding to } 3.79\,\mathrm{mL/s}$$

Under economical considerations, 95.8% cementation yield (Fig. 4b) can be easily reached in working at moderate temperature ($T = 30$–$40\,^{\circ}$C) and average solution acidity (pH 3 or 4).

6. Conclusion

The present work is a convivial tool for the determination of the optimal conditions of the cementation process functioning. It shows that experimental design is an appropriate method to optimize the cementation process of a laboratory-scale tubular reactor containing volumetric electrode of iron. The influence of various operating parameters namely: initial copper concentration, temperature, pH and flow rate in cementation yield has been investigated by using statistical method called central composite rotatable design (CCRD) to determine the optimum cementation conditions.

The quadratic model for copper cementation yield is developed using “EXCEL” software. The validity of regression equation has been controlled by statistical approaches. The optimal conditions determined by using surface contour plots are, initial copper cementation 75.25 mg/L, the temperature 60 °C, the pH 2.2 and the flow rate 3.79 mL/s. Under these conditions, the copper cementation yield obtained is 99.6%. In order to remedy to the overconsumption of iron at high solution acidity and for an economical considerations, 95.8% cementation yield can be easily obtained at moderate temperature (30–40 °C) and average pH solution (3–4).

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