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Application of full factorial design to study the simultaneous removal of copper and zinc from aqueous solution by liquid–liquid extraction

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ABSTRACT

The aim of this study is to investigate the zinc and copper removal by liquid–liquid extraction using a statistical method. The study is carried out in two steps: (1) the preliminary extraction tests are performed in order to identify the adequate operational conditions, such as the equilibrium time (=15 min) and the pH range (4.5–6.5). (2) A full factorial design at two levels is applied; the effects of the initial solution pH, the initial concentration of metals, the concentration of extractant, the type of initial solution (sulphate or chloride) and the stirring rate on the removal of each heavy metal are investigated. A first-order-polynomial equation is established. The analysis of variance (ANOVA) method is applied to determine the significant level of the main and interaction effects. The initial concentration of Zn is the most influential parameter on the extraction yield and the concentration of extractant. Di-2-ethylhexyl phosphoric acid is the most used one for the Cu(II) extraction yield. The coefficients of determination, calculated for statistical models obtained, are $R^2 = 0.908$ and $R^2 = 0.814$, respectively, for Zn and Cu and their p-values are 2.26E−07 and 9.01E−07. The interaction graphs have provided valuable information on the interactions factors for each model.

Keywords: Liquid–liquid extraction; Full factorial design; D_2EHPA; Simultaneous removal of metals

1. Introduction

The world production of copper and zinc in 2010 exceeded 10 million tons. These are used in a wide range of applications in many industrial processes [1,2]. Both in inorganic effluent from the industries [3] or leach liquors of some hydrometallurgy process, copper is often found in association with other divalent metals [4–6]. These leach liquors may be media chlorides or sulphates. Chloride is the most common medium in which all the precious metals, except silver, can be efficiently brought into solution [7]. Copper (II) is mainly recovered from sulphate solutions obtained by the leaching of oxide ores with sulphuric acid; contrary to copper (II) zinc (II) is often present in chloride weakly acidic solutions [8]. Several methods can be employed to remove heavy metals such as chemical precipitation, ion exchange [3,9], coagulation–flocculation, flotation, membrane filtration [3], chemical oxidation/reduction, reverse osmosis, electro dialysis [9] and liquid membrane [10].

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Liquid–liquid extraction is an important separation method that has been widely used in recovering of heavy metals [11–15]. In this technique two immiscible liquids are brought into contact, one is the organic phase containing the extractant and the second is the aqueous phase containing the solutes. Di-2-ethylhexyl phosphoric acid (D_2EHPA) is an extractant widely used for recovering heavy metals from aqueous solutions [12,15–18]. N-heptane is one of the organic diluents used to receive extractant [19].

The technique of statistical design for experiments can be applied for process characterization, optimization and modeling. It has been widely accepted in manufacturing industry for improving product performance and reliability, process capability and yield [20].

The studies devoted to application of statistic design experiment for heavy metals removing or separations by liquid–liquid extraction are very limited. Chang et al. [21] have studied the optimization of two process variables, namely extractant concentration and equilibrium pH (pH_{eq}), in Cu(II) extraction from aqueous solutions using response surface methodology by maximizing the percentage extraction. In another research work, these authors, in the aim to study the factors influencing Cu(II) extraction such equilibrium pH, extractant concentration, mixing time, salt concentration and organic to aqueous ratio, have applied the fractional factorial design [22]. Tsakiridis and Agatzini [23–25] have studied the solvent extraction of cobalt and nickel using factorial design of experiments and statistical analysis of the data to determine the main effects and interactions of the chosen factors, such as equilibrium pH, temperature, extractant concentration and aqueous/organic phase ratio, and the optimum conditions. Mellah and Benachour [15] have studied the effects of equilibrium pH, aqueous/organic phase ratio and extractant concentration, and their interactions on the extraction yield of zinc and cadmium by using a factorial design.

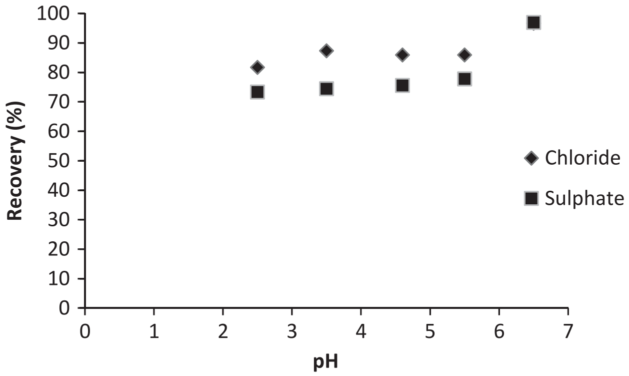

Fig. 1. Extraction of Cu(II) with D_2EHPA from chloride and sulphate media.

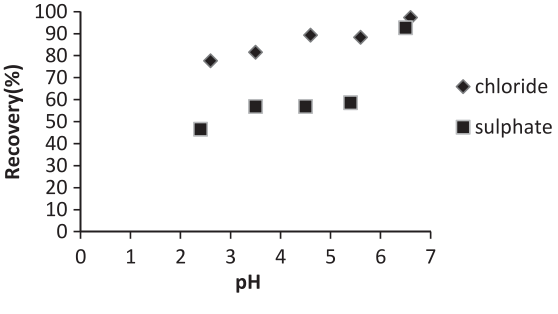

Fig. 2. Extraction of Zn(II) with D_2EHPA from chloride and sulphate media.

To contribute on innovation in this area, we carried out this work, which consists of the application of a full factorial design for simultaneous removal of zinc and copper from aqueous solutions by solvent extraction method. Two level full factorial designs are used to determine the prediction of the zinc and copper elimination by developing first-order models, and to examine the effects of main parameters and their interactions on yield of metals removal. In these models, the output parameter or response is the yield of metal extraction and the input ones are the process parameters, namely the pH of initial solution, initial concentration of metal, extractant concentration (D_2EHPA), medium type of the initial aqueous solution and stirring rate. It is be noted that in the models, qualitative parameter is included (medium type: chloride or sulphate) that would allow comparison between the metals removal.

Preliminary tests are conducted by classical method to determine the range of initial pH solution.

2. Experimental procedure

All chemicals used are of analytical grade purity and without further purification.

2.1. Materials and reagents

The chemicals used are D_2EHPA (98% Fluka) and n-heptane (Panréac 99%). The organic phases are prepared by dissolving the required volumes of the extractant (D_2EHPA) into n-heptane.

The stock of aqueous solutions, containing 100 mg/L of Zn(II) and Cu(II), respectively, is prepared by dissolving analytical grade sulphate or chloride salts in distilled water. The sulphate media are obtained from zinc sulphate heptahydrate $ZnSO_4.7H_2O$ (Panréac, > 99.5% purity) or copper sulphate pentahydrate ($CuSO_4.5H_2O$)

(Fluka, > 99% purity); those of chlorides are obtained from the zinc chloride $ZnCl_2$ (Panréac, > 98% purity) and copper chloride dehydrate $CuCl_2.2H_2O$ (EMerk 100%).

A pH meter (Mettler Toledo, Delta 320) is used to measure the pH of the aqueous phase before and after extraction. The concentrations of Cu(II) and Zn(II) in the aqueous phase after extraction are measured by flame atomic absorption spectrometry (Pye Unicam SOLAAR 969), while those in the organic phase are calculated by mass balance.

2.2. Experimental procedure

The batch experiments are carried out in the laboratory mixing vessel (6.2 cm in height and 7.5 cm in diameter) containing 50 ml each of the two phases (aqueous and organic). The mixture is shaken mechanically at room temperature (≈25°C) with a glass straight blade impeller welded to a glass shaft. After 30 min of contact time, the mixture is poured into a separatory funnel, in which a complete separation of two phases is obtained by settling. No third phase formation has been observed in the experimental conditions studied.

2.3. Experimental design and statistical treatments

The principle steps of statistically designed experiments are the choice of the experimental design type, determination of response variables, factors and their levels and statistical analysis of the data. A full factorial design (2^5) is run for all combinations of the levels of the factors; therefore the number of the conducted tests is equal to 32. Each factor is taken in a coded form, and is equal to +1 and −1, respectively.

The significance of the regression coefficients of the first-order model established is tested by a Student *t*-test. This test, based on the hypothesis that the true parameter is zero, is employed in multiple regressions to elucidate the significance of the factors. If the t value is greater than ($t_{1-\alpha}$, df) for a significant level α, with a degree of freedom (df), the term contributes significantly to observed response. The $\alpha = 0.05$, a priori level of significance, is chosen for all the regression analyses and other comparisons in this study.

The quality of fit of the regression model is expressed by the coefficient of determination, R^2. Analysis of variance (ANOVA) is applied to determine the statistical significance of regression model by using a Fisher *F*-test. The test is made by the comparison of two variances: the pure error variance and the lack of fit.

3. Results and discussion

The value ranges of parameters studied are selected on the basis of preliminary tests results. To determine the equilibrium time of extraction, the effect of contact time is studied. The extraction equilibrium is established after 10 min for copper in both media (chloride and sulphate) and for zinc in sulphate medium, but in chloride medium, it is equal to 15 min.

3.1. Determination of the initial pH range

The extraction of zinc and copper from the sulphate and chloride media are studied under the following conditions: D_2EHPA 10% (vol.), phase ratio $O/A = 1$ and initial pH range 2.5 ± 0.1–6.5 ± 0.1.

Figs. (1) and (2) show the effect of initial pH of the aqueous phase on the removal metals. As expected, the increase in pH (lower proton concentration) results in higher metal removal. Such behaviour is typical for the extraction of metal cations by cationic extractants as is the case of D_2EHPA, as shown by the following reaction [18]:

$$M^{m+}_{(aq)} + n(RH)_{2(org)} \rightleftarrows MR_2(RH)_{2n-2(org)} + mH^+_{(aq)} \qquad (1)$$

where M represents the metals: Zn and Cu; RH is the molecule of D_2EHPA; m: metal valence; n: stoichiometric coefficient and subscripts (aq) and (org) refer to the aqueous and organic species, respectively.

On the basis of these results, the best extraction yields of the Zn(II) and Cu(II) are obtained in the pH range 4.5–6.5, consequently, in the following experiments, the pH range will be 4.5 ± 0.1–6.5 ± 0.1.

L.R. Gouvea and his coworker [6] have reported a low recovery of Cu(II) in a range of $pH < 3.5$, when D_2EHPA is used as extractant; but others researchers [21,26,27] have obtained the Cu(II) extraction yields exceeding 90% using the same extractant in a range of $pH > 3$; these are in agreement with our results. However, this difference in results, obtained above, can be explained by the extractant dissolution—phenomenon which under some operating conditions (pH of the aqueous phase, concentration of metal, etc.) may take place and influence the extraction process [28].

3.2. Factorial design study

3.2.1. Conditions of design experiments

The values and levels of the five experimental input variables are presented in Table 1.

The matrix of the factorial design and the response values (Y_{Zn} and Y_{Cu}) are described in Table 2. Higher

Table 1
Design factors and their levels

Control factors	Code	Unit	Factor levels	
			Low (−1)	High (+1)
pH of initial solution	X_1	/	4.5	6.5
Initial concentration of metal [$(Zn)_0$ or $(Cu)_0$]	X_2	mg/L	25	75
Concentration of extractant (D_2EHPA)	X_3	(% vol.)	5	10
Medium type of initial aqueous solution	X_4	/	Sulphate	Chloride
Stirring rate	X_5	rpm	400	500

and lower levels of the variables were noted by (+1) and (−1), respectively. A first-order linear model for 5 independent variables with interaction terms is used to fit the experimental data, expressed by the simple Eq. (2):

$$\begin{aligned} Y = {} & A_0 + A_1X_1 + A_2X_2 + A_3X_3 + A_4X_4 + A_5X_5 + A_{12}X_1X_2 + A_{13}X_1X_3 + A_{14}X_1X_4 + \\ & A_{15}X_1X_5 + A_{23}X_2X_3 + A_{24}X_2X_4 + A_{25}X_2X_5 + A_{34}X_3X_4 + A_{35}X_3X_5 + A_{45}X_4X_5 + \\ & A_{123}X_1X_2X_3 + A_{124}X_1X_2X_4 + A_{125}X_1X_2X_5 + A_{134}X_1X_3X_4 + A_{135}X_1X_3X_5 + A_{145}X_1X_4X_5 + \\ & A_{234}X_2X_3X_4 + A_{235}X_2X_3X_5 + A_{245}X_2X_4X_5 + A_{345}X_3X_4X_5 + A_{1234}X_1X_2X_3X_4 + A_{1245}X_1X_2X_4X_5 \\ & + A_{1345}X_1X_3X_4X_5 + A_{1235}X_1X_2X_3X_5 + A_{2345}X_2X_3X_4X_5 + A_{12345}X_1X_2X_3X_4X_5 \end{aligned} \tag{2}$$

where A_0 is the value of the fitted response at the centre point of design, the A_i coefficients represent the linear effects or main effects and A_{ij}, A_{ijk}; A_{ijkl}, A_{ijklm} are the regression coefficients corresponding to the interaction effects. They are computed as below:

$$A_0 = \sum \frac{Y_i}{N}$$

$$A_i = \sum \frac{X_iY_i}{N}$$

$$A_{nj} = \sum \frac{X_{nj}X_{ji}Y_i}{N}$$

The percentage of each metal removed are calculated using the Eq. (3):

$$Y = \frac{(m_i - m_f)}{m_i} = \frac{C_{org.}V_{org}}{C_{org.}V_{org.} + C_{aq} \times V_{aq}}.100 \tag{3}$$

where m_i and m_f: initial and final mass of metal, respectively; C_{org}, C_{aq}: concentration of metal in organic and aqueous phase, respectively; V_{org}, V_{aq}: volume of organic and aqueous phase, respectively.

The results in Table 3 show that the zinc removal yields vary from 83.75 to 99.27%, while that of copper from 94.32 to 99.54%.

3.2.2. Development of regression model equation

The values of yields shown in Table 3 are used to estimate all coefficients of the polynomial regression equation Eq. (2). The statistical significance of these coefficients is determined by student's *t*-test and that of the model equation by Fisher's test [29]. The proportion of variance explained by the model obtained is given by the multiple coefficient of determination, R^2.

The statistical analysis for each of response variables (Y_{Zn} and Y_{Cu}) is summarized in Table 4.

According to the student's *t*-test results, the main and interaction coefficients did have not similar effects on the metals elimination. The initial concentration (X_2) is the variable that has the greatest effect on the Zn(II) removal yield and the concentration of the extractant (X_3) is the variable that has the greatest effect on the Cu(II) removal yield. By analyzing the results of Table 3, it can be seen that for the Zn(II) removal yield, all the main effects (A_1–A_5) of regression model are significant, but for the interaction effects, only the following coefficients: A_1A_2, A_2A_5, A_3A_4, A_3A_5, A_4A_5, $A_2A_3A_4$ and $A_3A_4A_5$ are significant; for the Cu(II) removal, only the followings main and

Table 2
Experimental design matrix and results

Run	Factor					Response	
	X_1	X_2	X_3	X_4	X_5	Y_{Zn}	Y_{Cu}
1	−1	−1	−1	−1	−1	90.1	96.5
2	1	−1	−1	−1	−1	93.4	96.7
3	−1	1	−1	−1	−1	83.7	96.1
4	1	1	−1	−1	−1	85.9	96.8
5	−1	−1	1	−1	−1	96.7	98.4
6	1	−1	1	−1	−1	97.0	98.8
7	−1	1	1	−1	−1	93.7	98.5
8	1	1	1	−1	−1	98.3	98.8
9	−1	−1	−1	1	−1	95.9	95.8
10	1	−1	−1	1	−1	97.2	95.9
11	−1	1	−1	1	−1	95.0	95.3
12	1	1	−1	1	−1	96.6	99.5
13	−1	−1	1	1	−1	99.3	98.4
14	1	−1	1	1	−1	99.0	98.6
15	−1	1	1	1	−1	91.9	98.1
16	1	1	1	1	−1	97.3	98.2
17	−1	−1	−1	−1	1	98.0	96.1
18	1	−1	−1	−1	1	94.8	96.7
19	−1	1	−1	−1	1	88.0	96.0
20	1	1	−1	−1	1	94.5	97.4
21	−1	−1	1	−1	1	97.0	94.3
22	1	−1	1	−1	1	97.0	98.2
23	−1	1	1	−1	1	89.5	98.5
24	1	1	1	−1	1	93.4	98.9
25	−1	−1	−1	1	1	94.4	96.2
26	1	−1	−1	1	1	95.4	96.7
27	−1	1	−1	1	1	89.3	95.7
28	1	1	−1	1	1	88.1	98.4
29	−1	−1	1	1	1	98.0	98.5
30	1	−1	1	1	1	96.8	98.5
31	−1	1	1	1	1	85.8	98.0
32	1	1	1	1	1	90.1	98.2

interaction effects (A_1, A_2, A_3, $A_1A_2A_3$, $A_1A_2A_4$, $A_1A_3A_4$, $A_2A_3A_4$, $A_2A_4A_5$) are significant; it should be noted that no interaction effect between two variables is significant. The level of significance of each coefficient is given as p-value compared to $\alpha = 0.05$.

The t-value is a measure of the effect importance compared to standard error of parameter effect. Figs. (3) and (4) represent the absolute values of t-student of the significant parameters of the two regression models. As shown in Fig. 3, the coefficient (A_2) of the initial concentration of Zn(II) is the most influential factor affecting extraction yield, while the type of medium (A_4) has the lowest importance; when the stirring speed and type of medium are at the same level (both are + 1 or −1), their interaction effect (A_{45}) is the most unfavorable on the Zn(II) removal, because this factor is negative.

Fig. 4 shows that the coefficient (A_3) of extractant concentration is the most important parameter on Cu (II) removal and while that of medium type (A_4) is the smallest one. All significant interaction parameters have almost the same importance.

The results of ANOVA are given in Table 4. The F-ratio calculated is 15.64 (>critical $F = 2.30$) for the model of Zn(II) removal and that for the Cu(II) removal model is 12.61 (>critical $F = 2.37$). The Fisher

Table 3
Estimated effects and student's *t*-test for the yield of Zn(II) and Cu(II) removal (%) using 2^5 full factorial design

	Removal of Zn			Removal of Cu		
Variable	Effect	*t*-value	*p*-value	Effect	*t*-value	*p*-value
Mean	93.78	320.2	3.2E−37	97.39	1,015	8.9E−36
X_1	0.89	3.041	0.00336	0.50	5.252	6.1E−05
X_2	−2.46	−8.42	3.9E−08	0.25	2.626	0.00997
X_3	1.26	4.321	0.00018	0.78	8.138	5.6E−07
X_4	0.60	2.038	0.02787	0.10	1.075	0.15025
X_5	−0.65	−2.23	0.01901	−0.13	−1.32	0.10356
X_1X_2	0.81	2.785	0.00591	0.13	1.355	0.09839
X_1X_3	0.17	0.587	0.28212	−0.15	−1.55	0.07163
X_1X_4	−0.21	−0.71	0.2417	0.01	0.117	0.45415
X_1X_5	−0.26	−0.89	0.19346	0.11	1.16	0.13276
X_2X_3	−0.08	−0.29	0.3882	−0.03	−0.37	0.35795
X_2X_4	−0.15	−0.52	0.30358	−0.08	−0.87	0.20038
X_2X_5	−0.83	−2.83	0.00538	0.11	1.166	0.13148
X_3X_4	−0.87	−2.98	0.00388	0.02	0.228	0.41145
X_3X_5	−0.95	−3.23	0.00219	−0.16	−1.65	0.06075
X_4X_5	−1.49	−5.09	3.3E−05	0.15	1.544	0.07241
$X_1X_2X_3$	0.40	1.355	0.09565	−0.34	−3.54	0.00162
$X_1X_2X_4$	−0.23	−0.8	0.21674	0.28	2.893	0.0059
$X_1X_2X_5$	0.24	0.822	0.21076	−0.14	−1.51	0.07643
$X_1X_3X_4$	0.17	0.587	0.28212	−0.28	−2.92	0.00561
$X_1X_3X_5$	0.07	0.245	0.40439	0.11	1.173	0.13021
$X_1X_4X_5$	−0.06	−0.2	0.42076	−0.19	−1.94	0.03628
$X_2X_3X_4$	−0.80	−2.72	0.00678	−0.33	−3.41	0.00212
$X_2X_3X_5$	−0.37	−1.27	0.10977	0.17	1.779	0.04849
$X_2X_4X_5$	−0.46	−1.59	0.0642	−0.24	−2.51	0.01252
$X_3X_4X_5$	0.99	3.382	0.00156	0.14	1.414	0.08961
$X_1X_2X_3X_4$	0.42	1.44	0.08302	−0.04	−0.46	0.32765
$X_1X_2X_3X_5$	−0.28	−0.95	0.17713	−0.05	−0.48	0.31857
$X_1X_2X_4X_5$	−0.41	−1.4	0.08916	0.04	0.469	0.32309
$X_1X_3X_4X_5$	−0.003	−0.01	0.4958	−0.04	−0.43	0.33685
$X_2X_3X_4X_5$	0.44	1.504	0.07446	−0.06	−0.68	0.25252
$X_1X_2X_3X_4X_5$	0.42	1.44	0.08302	0.19	1.981	0.0338

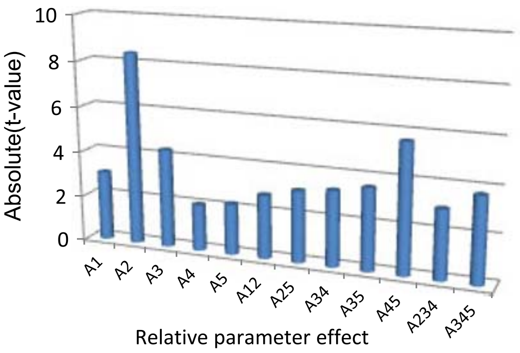

Fig. 3. Comparison between the parameters significance of the Zn removal model.

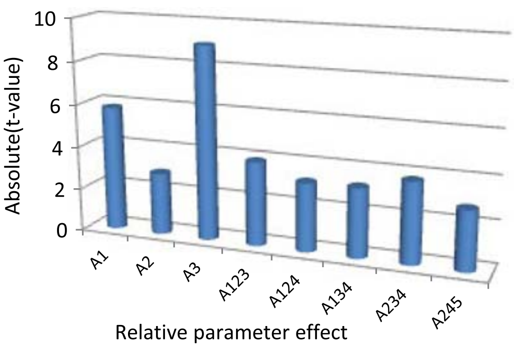

Fig. 4. Comparison between the parameters significance of the Cu removal model.

F-tests with the very low probability values [p-value of models is 2.26619E−07 and 9.01885E−07 for the yield of Zn(II) and Cu(II) removal, respectively] demonstrate that the regression models are significant at 95% of confidence interval.

Mathematical models for predicting the metal removal in the studied range can be represented by the following equations:

$$Y_{Zn} = 93.78 + 0.89X_1 - 2.64X_2 + 1.26X_3 + 0.60X_4 - 0.65X_5 + 0.81X_1X_2 - 0.83X_2X_5 + \\ -0.87X_3X_4 - 0.95X_3X_5 - 1.49X_4X_5 - 0.80X_2X_3X_4 + 0.99X_3X_4X_5 \quad (4)$$

$$Y_{Cu} = 97.39 + 0.5X_1 + 0.25X_2 + 0.78X_3 - 0.34X_1X_2X_3 + 0.28X_1X_2X_4 - 0.28X_1X_3X_4 \\ -0.33X_2X_3X_4 - 0.24X_2X_4X_5 \quad (5)$$

Positive sign and negative sign in front of the terms indicate synergistic effect and antagonistic one, respectively. The R^2 values for Eqs. (4) and (5) are 0.908 and 0.814, respectively. This indicated that 90.8 and 81.4% of the total variation in the Zn(II) and Cu(II) removal, respectively, are attributed to the experimental variables studied. The closer the R^2 value to unity, the better the model will be; it will give predicted values which are closer to the actual values for the response. The R^2 of 0.908 for Eq. (4) is considered relatively high, indicating there was a good agreement between the experimental and the predicted of the Zn(II) removal; the R^2 of 0.814 for Eq. (5) is considered as moderate to validate the fit; this value of least squares regression can be attributed to the degree of freedom involved in the model.

These equations reveal the effect of individual and interaction variables on Zn(II) and Cu(II) elimination from aqueous solution. As can be seen from Eq. (4), medium type of initial solution, its pH and concentration of extractant have a positive effect, while initial concentration of zinc and the stirring rate have a negative effect on the Zn(II) removal from aqueous solution in the range of variation of each variable studied. Eq. (5) shows that all the main factors, statistically significant, have a positive effect on the Cu(II) removal yield.

These two models show that the influential factors on the yield are not the same; consequently the optimal conditions of the two responses will be different.

To test the models developed, additional experiments are conducted. The results obtained are summarized in Table 5; as it can be seen, there is a small difference between the experimental and simulated values, and this therefore confirms that the models predict well the yield of metal removal by liquid–liquid extraction.

3.3. Analysis of the parameters effects on the removal of metals

The removal yield of the zinc and copper is affected by initial pH (X_1). This parameter plays a part in the interaction effects and particularly in the case of copper removal. Statistically, in both the cases, it is not the most important parameter in the range of study.

Table 4
ANOVA models

Source	Zn(II)			Cu(II)		
	Degree of freedom	Sum of square	Mean of square	Degree of freedom	Sum of square	Mean of square
Model	12	515.304	42.942	8	43.5947	5.4493375
Residual	19	52.158	2.745	23	9.9341875	0.4319212
Total	31	567.462	18.305	31	53.5288875	1.72673831
F-ratio	15.64			12.61		
p-value	2.26619E−07			9.01885E−07		
R^2	0.908			0.814		

Table 5
Comparison between the experimental and simulated values

	Experimental value	Model response	Error (%)
Cu(II)	99.22	98.28	0.95
	99.07	98.08	1.07
Zn(II)	95.56	95.52	0.99
	96.98	95.34	1.69

In the case of zinc removal, although the initial concentration (X_2) is the most important parameter, its interaction effects play less important role. The initial concentration of copper is the least important parameter among the main effects of variables, and its interaction effects have roughly the same importance.

The concentration of D_2EHPA (X_3) is a parameter that may influence the removal of metals; its interaction effects are involved in several terms of the both models (Eqs. (4) and (5)).

Compared to the other parameters studied, the type of medium (X_4) is not an important parameter in the range of study for removing the zinc; in the case of copper removal, its influence is statistically not significant. However, its interaction effects in the two cases are not statistically negligible.

In the case of the zinc removal, the stirring rate (X_5) has statistically little effect, but it is involved in many effects of interaction. It has no effect in the case of copper, and its interaction effects are very limited.

3.3.1. Study of interaction effects

The graphical interactions analysis of each variables pair allowed determining their influence on the removal of the metals. This kind of analysis has previously been applied with good results for developing extraction methods [30].

In the previous mathematical models Eqs. (4) and (5), only the effects statistically significant are retained. The importance of possible interaction effects on metal removal is determined, X_4 is fixed at high level (+1: sulphate medium) or low level (−1: chloride medium); for each case, pair of factors is selected and the others parameters are fixed at their average level ($X_i = 0$, $i \neq 4$). Then, the yield of removal is computed with models at the high level (+1), low level (−1) and high and low level for each pair of variables.

Only the cases involving the interaction effects are described in the following paragraphs. The interaction effects are more numerous in the case of Zn(II) recovery than in that of Cu(II).

Interaction graphs Fig. 5(A), obtained for the pH of initial solution (X_1) and concentration of extractant (X_3) do not show a similar behaviour. There is no effect of pH (X_1) on Cu(II) and Zn(II) yields when the (X_3) is fixed at (+1 or 10% vol.) and (−1 or 5% vol.), respectively, but at −1 and + 1, the yields are influenced by the pH (X_1). The yields for both metals are improved when the interaction parameters vary in same direction.

The plots of Fig. 5(B) show the interaction effects between the initial concentration of metal (X_2) and the extractant concentration (X_3). There is no effect of the initial concentration of metal when the (X_3) is fixed at (−1 or 5% vol.) on the Cu(II) removal from chloride medium; in this case, the interaction effect is less significant compared to the remaining cases (for both metals). In these previous cases, when the extractant concentration is fixed at low (−1 or 5% vol.) or high level (+1 or 10% vol.), the initial concentration of metal influences the removal yield. It is also worth to note that the improvement of Cu(II) extraction from sulphate medium is obtained when the values of pair parameters (X_2 and X_3) range from (−1 or 25 ppm,−1 or 5% vol.) to (+1 or 75 ppm, +1 or 10% vol.), i.e. both variables vary in the same direction; but in the case of Zn(II) extraction, to improve the yield, the values of pair parameters (X_2, X_3) must vary from (+1,−1) to (−1, + 1), i.e. both parameters vary in the opposite directions.

The interaction effects between the pH of initial solution (X_1) and initial concentration of metal (X_2) are shown in the Fig. 5(C). Except the case of Cu(II) extraction from chloride medium, in all others cases, when the initial concentration of metal is fixed at its low level (−1 or 5% vol.), the pH does not affect the yield of extraction. In these cases, similar behaviour is obtained.

It is possible to improve the extraction of Cu(II), regardless of the extraction medium, by varying the values of pair parameters (X_1 and X_2) from (−1 or 4.5,−1 or 25 ppm) to (+1 or 6.5, + 1 or 75 ppm), i.e. both variables vary in the same direction; but in the case of Zn(II) extraction, to improve the yield, X_2 must decrease regardless of the direction of change in X_1.

The interaction graphs shown in Fig. 5(D) are obtained in the case of the Zn(II) removal. In sulphate medium, when the stirring rate (X_5) is fixed at its high level (+1 or 500 rpm), the pH of initial solution (X_1) does not affect the yield; it is noted, also, that the variation of X_5 from (−1 or 400 rpm) to (+1 or 500 rpm) resulted in a decreasing of the removal yield regardless of pH change; but in the chloride medium, when these two parameters vary in the same direction, the yield may be improved.

The plots in Fig. 5(E) show that an interaction effect between the extractant concentration (X_3) and stirring

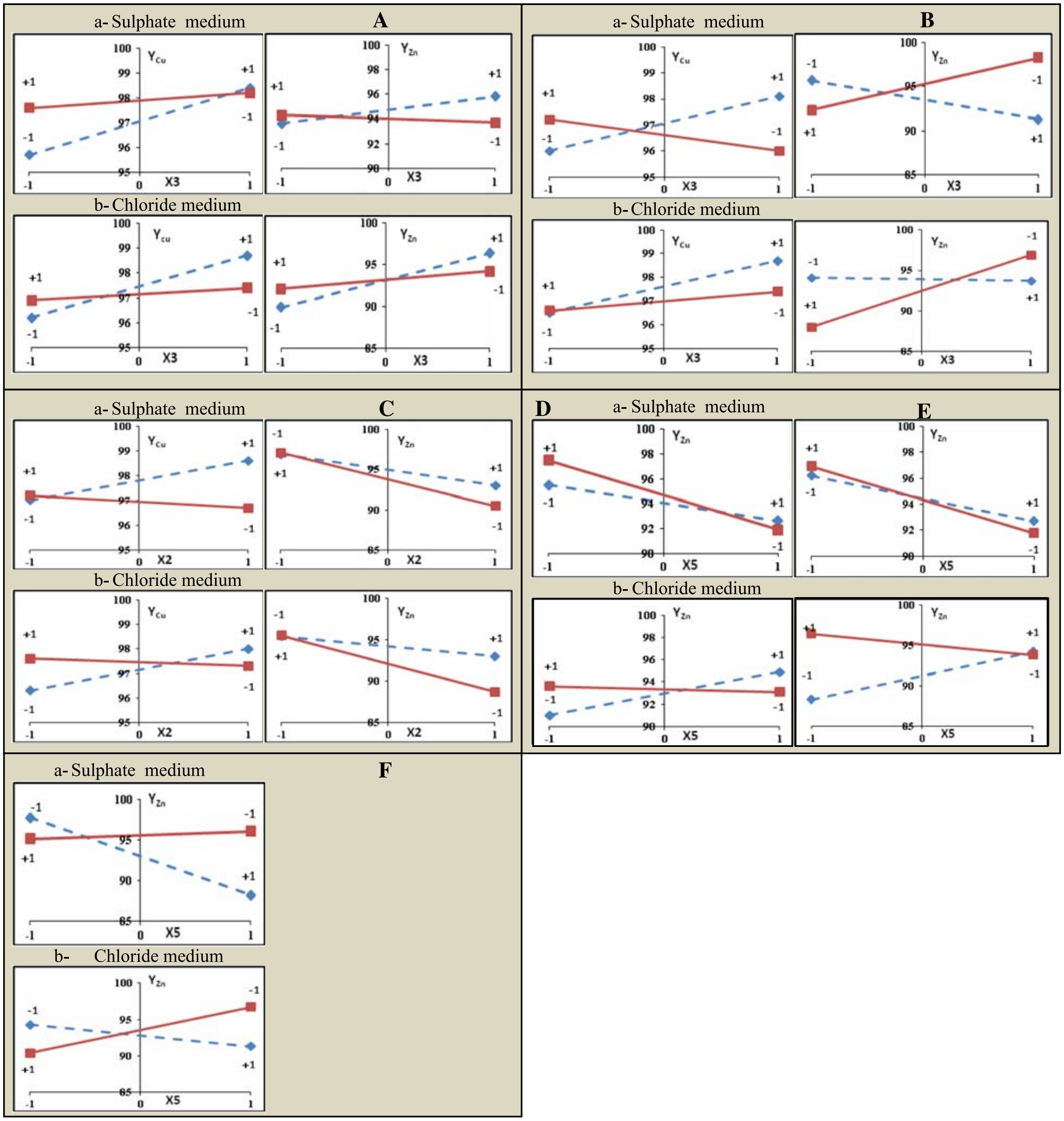

Fig. 5. Plots of interaction effects: (A: X_1–X_3; B: X_2–X_3; C: X_1–X_2; D: X_1–X_5; E: X_3–X_5; F: X_2–X_5).

rate (X_5) on the Zn(II) removal is very small in sulphate medium; when the X_5 is fixed at its low or high level (−1 or + 1), no effect of extractant concentration on the yield can be obtained. In chloride medium, when stirring rate (X_5) is fixed at its high level (+1), the extractant concentration (X_3) does not affect the yield; however, at its low level (−1), the effect of X_3 on the yield is significant. It is possible to improve the extraction of Zn(II) from chloride medium by varying the values of pair parameters (X_5 and X_3) from (−1 or 5% vol.,−1 or 400 rpm) to (+1 or 10% vol., + 1 or 500 rpm), i.e. both variables vary in the same direction.

Plots in Fig. 5(F) show the interaction effects between the initial concentration of Zn(II) (X_2) and stirring rate (X_5); they are approximately the same behaviour. When the stirring rate is fixed at (+1 or 500 rpm), the variation of removal yield in sulphate medium is better than one obtained in chloride medium, this result is inverted at low level (−1 or 400 rpm). In both media, to increase the extraction yield, X_2 must vary from (+1) to (−1) when X_5 ranges between $(-1, +1)$.

4. Conclusion

Liquid–liquid extraction can be used as efficient technical to remove the Zn(II) and Cu(II) from aqueous solutions. When the pH ranges between 4.5 and 6.5, the removal yield of these metals, using D_2EHPA as extractant, can exceed 90%.

To study the elimination process, full factorial design is applied. Regression models are developed to analyze the process variables (factors) by identifying the significant factors contributing to the elimination of metals. The significance models have been established with 95% of confidence interval. The effects of interaction between factors must be taken into account, because some influence the yield of extraction. The values of model parameters can contribute to the choice of parameters for process optimization. These parameters will be different for Zn(II) and Cu (II) removal studies.

Nomenclature

D_2EHPA	di-2 ethylhexylphosphoric acid
O/A	phase ratio of organic and aqueous phase
X_1	pH of initial solution
X_2	initial concentration of metal
X_3	concentration of extractant (D_2EHPA)
X_4	medium type of initial aqueous solution
X_5	stirring rate
A_i	linear effects or main effects
A_{ij}, A_{ijk}; A_{ijkl}, A_{ijklm}	regression coefficients corresponding to the interaction effects
Y	response values
m_i and m_f	initial and final mass of metal, respectively
C_{org}, C_{aq}	concentration of metal in organic and aqueous phase, respectively
V_{org}, V_{aq}	volume of organic and aqueous phase, respectively
R^2	coefficient of determination
t	student parameter
α	significant level
df	degree of freedom
F	fisher parameter
p	probability
ANOVA	analysis of variance
ppm	part per million

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