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Factorial design in optimization of extraction procedure for copper (II) using Aliquat 336 and Tri-*n*-butylphosphate based supported liquid membrane

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ABSTRACT

In the present paper, extraction procedure for copper (II) present in an aqueous sulphate media using a supported liquid membrane by chloride tri-*N*-octylmethylammonium (Aliquat 336) and Tri-*n*-butylphosphate from molar ratio 1:1, with polytetrafluoroethylene as a membrane support was studied. The effects of various parameters such as initial pH, potassium thiocyanate concentration and ammonium acetate concentration on the extraction yield, were carried out. By a calculation programme using Chemical Equilibrium in Aquatic System V. L20.1, the determination of the percentages of the present species before and after extraction were given in aqueous medium and on the membrane to be able to determine the relation between the nature of the extracted species and the extraction yield. The optimization process was carried out using 2^3 factorial designs. Initial pH (pH_i) of feed solution, the concentration of potassium thiocyanate and the concentration of ammonium acetate were regarded as factors in the optimization. Student's *t*-test on the results of the 2^3 factorial design with eight runs for copper (II) extraction demonstrated that the factor concentration of potassium thiocyanate in the levels studied are statistically significant. Under the optimum conditions the percentage of extracted copper (II) was 93.6% in one step.

Keywords: Supported liquid membrane; Optimization; Copper (II); Extraction; Factorial design

1. Introduction

Studies on the removal of heavy metals like copper, nickel, cadmium, cobalt, etc. have been reported in the literature [1–3]. The major component of solid wastes of metallurgical zinc industries is copper. Many methods are available, such as precipitation, electrolysis, nano-filtration and liquid–liquid extraction [4,5]. However, most of the pre-concentration and separation methods used for this purpose have some disadvantages such as the requirement for large amount of toxic solvents, time consuming nature of the procedures, probability of sample contamination, very sensitive to operational conditions, employment

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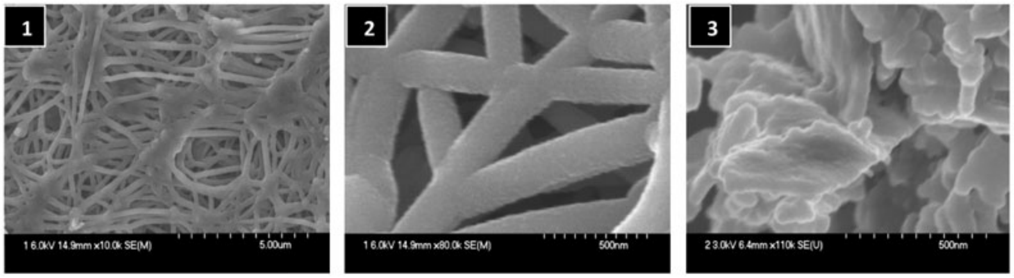


Scheme 1. (1) & (2) Membranes before impregnation. (3) Membrane after impregnation.

of environmentally unsafe and expensive chemical products [6,7].

Supported liquid membranes (SLMs) offer a potentially attractive alternative to process liquid–liquid and solid–liquid extractions, in that they combine the processes of extraction and stripping in a single unit operation. The advantages of SLMs are its simplicity and ease of operation [8]. For this, it was suggested for the recovery and the concentration of many metals and selective separations of trace amounts of metal ions [9,10]. The removal of copper (II) ions from aqueous solutions can be achieved by SLM extraction process [11–13].

Several membrane supports have been used to make SLMs such as polypropylene, polyvinylidene difluoride, polytetrafluoroethylene (PTFE) and silicones [14,15].

Procedures for optimization of factors by multivariate techniques [16–20] have been encouraged, as they are faster, more economical and effective, and allow more than one variable to be optimized simultaneously. In chemistry, the factorial design [21–23] has been widely used in several situations.

The objective of our work concerns the recovery of copper (II) on a SLM of type polyethylene impregnated by a mixture of chloride tri-*N*-octylmethylammonium and tri-*n*-butylphosphate (Aliquat 336/TBP-molar ratio 1:1). The influence of operating variables such as ammonium acetate concentration, potassium thiocyanate concentration and initial pH of aqueous solution on the extraction yield was studied. Nowadays, factorial designs have proved their usefulness, and are widely used in the statistical planning of experiments to obtain empirical linear models relating process response to process factors [24]. The effects of the various parameters will be studied by using a 2^3 full factorial design.

2. Experimental

2.1. Reagents and chemicals

Copper sulphate and the ammonium acetate were purchased from Prolabo. The potassium thiocyanate was provided from Fluka. Sulphuric acid, hydrochloric acid and Aliquat 336 (tricaprylmethylammonium chloride $CH_3N[(CH_2)_7CH_3]_3Cl$) were purchased from Merck. TBP was provided from Aldrich.

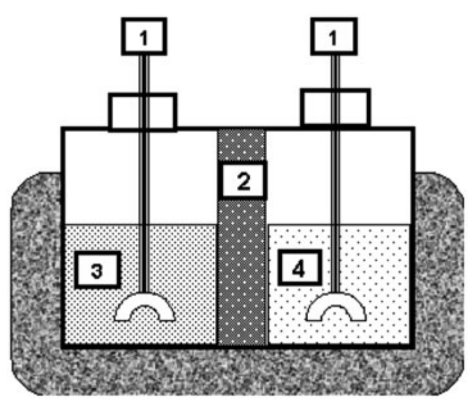
The liquid membrane support was a microporous PTFE film with nominal porosity of 75%, an average pore size of 0.2 μm and a total thickness of 175 μm (Millipore FG). The membrane was procured from Millipore, Ireland. The membrane was placed between two PTFE blocks (Scheme 2).

2.2. Apparatus

A Perkin-Elmer atomic absorption spectrophotometer assisted by microcomputer (model A Analyst 300) and a Consort C831 pH metre with combined glass electrode were used for concentration copper (II) ions and pH measurements, respectively.

2.3. Impregnating liquid membrane

While the PTFE membranes were easier to wet, SLMs needed more than 12 h [15]. Liquid membrane was prepared by impregnating the support during 24 h in a mixture (Aliquat 336/TBP, molar ratio 1:1) and diluted in acetone.



Scheme 2. Schematic representation of apparatus used for SLM system. (1) Motor with agitator, (2) membrane, (3) source phase, (4) striping phase.

The Millipore Fluoropore (PTFE 04700) membrane support, before and after impregnation have been scanned by electron microscopy, model Hitachi FEG S4700 with 16.0 and 23.0 kV (Scheme 1).

2.4. Membrane equipment

After impregnating and installation of the membrane, the strip and feed channels were flushed with water for 10 min at a flow rate of $10\,cm^3\,min^{-1}$ to remove the excess of the organic solvent from the surface of the membrane. The feed solution was pumped through the feed channel. All experiments were performed at 20˚C. SLM extraction was studied in discontinuous extraction mode.

3. Synergic ion transport mechanism in liquid membrane system

A conventional solvent extraction system which is carried out in two steps, either, for separation or preconcentration of copper (II) ions from its source solution [25–27], can be illustrated in bulk solutions as shown in Scheme 3.

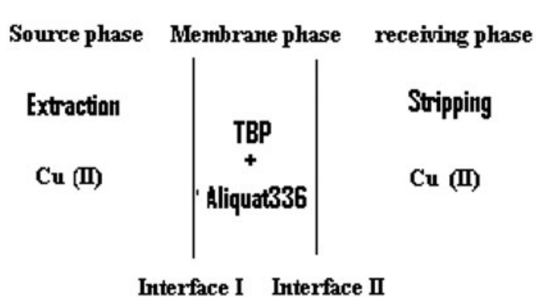
The combination of liquid anion exchanger (Aliquat-336, R^+ Cl^-) and solvating extractant (TBP), can be used for the continuous pumping of metal ion from source to receiving phase through liquid membrane phase using salt medium [28].

The transport of copper (II) ion with potassium thiocyanate was explained as follows.

The liquid anion exchanger is converted into appropriate anion form.

At high concentration of KSCN and low initial pH value:

$$(Cu^{2+},\ SO_4^{2-}) + 2(K^+,\ SCN^-) \rightleftharpoons (Cu^{2+},\ 2SCN^-) + (2K^+,\ SO_4^{2-}) \quad (1)$$



Scheme 3. Metal ion transport illustration in SLM.

$$\overline{(R^+,\ Cl^-)} + (K^+,\ SCN^-) \rightleftharpoons \overline{(R^+,\ SCN^-)} + (K^+,\ Cl^-) \quad (2)$$

The $(R^+,\ SCN^-)$ has high affinity for $(Cu^{2+},\ 2SCN^-)$

$$\overline{2(R^+,\ SCN^-)} + (Cu^{2+},\ 2SCN^-) \rightleftharpoons \overline{[Cu(SCN)_4]^{2-},\ 2R^+} \quad (3)$$

TBP has high affinity towards solvation complex formation with $(Cu^{2+}$, $2SCN^-)$ at interface I (Scheme 3).

$$(Cu^{2+},\ 2SCN^-) + \overline{2TBP} \rightleftharpoons \overline{Cu(SCN)_2 \cdot 2TBP} \quad (4)$$

The formation of ion pair and solvated complex with liquid anion exchanger, solvating extractant and $(Cu^{2+}$, $2SCN^-)$, take place as synergic extractions at interface I as follows.

$$(Cu^{2+},\ 2SCN^-) + \overline{2(R^+,\ SCN^-)} + \overline{2TBP} \rightleftharpoons \overline{[Cu(SCN)_4]^{2-}, 2\ R^+ \cdot 2TBP} \quad (5)$$

In order to study the kinetics of copper (II) extraction with Aliquat 336/TPB mixture at different times, the variable taken as a response was the extraction yield Y (%).

$$Y\ (\%) = \frac{c_0 - c_t}{c_0} \times 100 \quad (6)$$

where c_0 and c_t are the initial concentration and concentration at time "t" of copper (II) in $mol\,L^{-1}$, respectively.

Under various experimental conditions, the copper (II) species present in the feed phase before extraction and after extraction, have been quantified by the programme Chemical Equilibrium in Aquatic System [29].

The optimal extraction yields by Aliquat 336/TBP function from percentages of the species present in the feed phase have been investigated.

4. Results and discussion

4.1. Study of the extraction conditions

4.1.1. Effects of potassium thiocyanate concentration

The effect of concentration of KSCN on copper (II) extraction was studied at initial pH equal to 2.0 and fixed concentration of ammonium acetate equal to

1 M, by stirring with and adding of KSCN in the feed solution, from concentration 0.00 to 0.10 M. Results are summarized in Fig. 1.

Fig. 1 shows that the influence of the KSCN concentration on the extraction of copper (II) is important. Changing the ionic strength by the addition of an electrolyte influences the transport of metal ion in at least two ways:

- by affecting interfacial potential and, therefore, the activity of electrolyte ions.
- by affecting the competition of the electrolyte ions [30].

From Fig. 1, it can be observed that the increase in the yield of the extraction with that of the concentration of KSCN is accompanied by a relative decrease of the percentage of the Cu(II) specie and an increase in the percentages of $Cu(SCN)_2$ and $Cu(CH_3COO)^+$ species, although the Cu (II) specie remain always in majority compared to the others.

The increases in the percentage of copper (II) removal with the increase of the KSCN salt concentration, in aqueous phase, can be assigned to the following facts: (i) the K^+ effect lowers the solubility of Cu(II) salt and (ii) the SCN^- acts as an *in situ* regenerating agent via removal of oxygenated complexes as soluble cyanocomplexes, increasing thereby the extraction yield of copper (II) species [31].

4.1.2. Effect of ammonium acetate concentration

Results of the study of effect ammonium acetate in the presence of fixed KSCN concentration to 0.1 M and an initial pH equal to 2, by stirring with the addition of acetate concentration in the feed solution, from 0.1 to 2 M, are summarized in Fig. 2.

It can be observed that a synergistic effect on the extraction yield is obtained in the 0–0.1 M domain of ammonium acetate. From 0.1 to 1 M ammonium acetate, the extraction yield decrease with the increasing concentration of specie $[Cu(CH_3\ COO)]^+$.

The best yield (93.56%) was obtained in the following conditions: initial pH = 2, [KSCN] = 0.1 M, $[CH_3COONH_4]$ = 0.1 M.

4.1.3. Effect of the initial pH

The effect of solution pH on the extraction of copper (II) ions from the aqueous solution was investigated in the pH range of 2.0–6.7 using 50 mL of 0.01 M of Copper (II) ion solutions, in the presence of $[CH_3COONH_4]$ = 1 M and [KSCN] = 0.1 M. The results are summarized in Fig. 3. It can be observed that the extraction efficiency decreases when the initial pH increase. At the initial pH = 2.0 of the feed solution, the extraction efficiency is the better.

These results are in good agreement with those described by previous work [10]. It is the pH where copper is in the free form Cu^{2+} to 82 and 18% in the form of $Cu(SCN)_2$. The increasing of $Cu(SCN)_3^-$

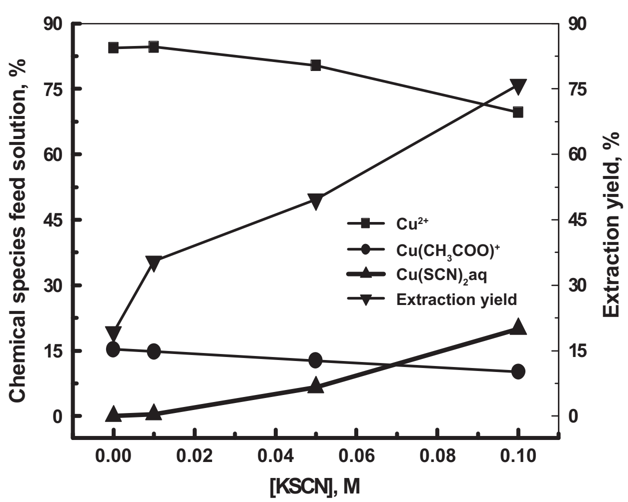


Fig. 1. Effect of the KSCN concentration on the chemical species present in the feed solution and the yield of extraction. $T = 20$°C, $V_a = 450$ rpm, $[Cu^{2+}]_0 = 0.01$ M, $pH_i = 2.0$, $[CH_3COONH_4] = 1$ M, Aliquat 336/TBP (molar ratio 1:1).

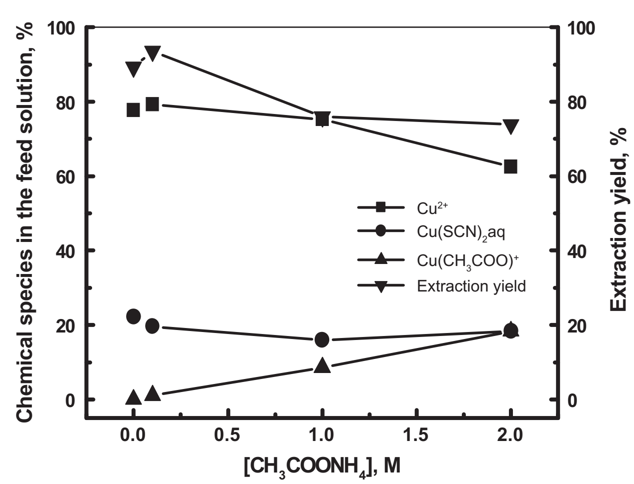


Fig. 2. Effect of the CH_3COONH_4 concentration on the chemical species present in the feed solution and on the yield. $[Cu^{2+}]_0 = 0.01$ M, $pH_i = 2.0$, [KSCN] = 0.1 M, $T = 20$°C, $V_a = 450$ rpm, Aliquat 336/TBP (molar ratio 1:1).

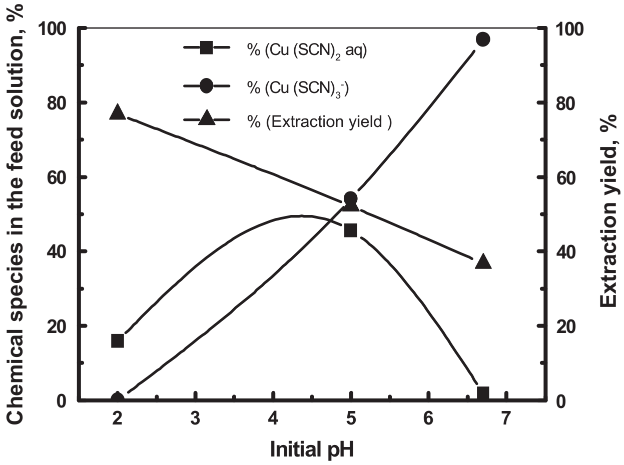


Fig. 3. Effect of the initial pH on the chemical species present in the feed solution and on the yield. $[Cu^{2+}]_0 = 0.01$ M, $[CH_3COONH_4] = 1$ M, [KSCN] = 0.1 M, $T = 20$°C, $V_a = 450$ rpm, Aliquat 336/TBP (molar ratio 1:1).

specie is responsible for the decreasing of the extraction yield. For higher pH values (pH = 6.7), Cu(II) ions precipitate in the form of hydroxide.

4.2. Factorial design study

In order to examine the interaction between the studied factors on the copper (II) extraction, a 2^3 factorial design had been used, by varying three key variables, namely pH_i feed solution, the concentration of potassium thiocyanate (C_1) and of the concentration of ammonium acetate (C_2) [30–34].

An adequate selection of these parameters is an essential requirement for establishing an accurate polynomial model (Eq. (7)). A wide range between low and high levels was considered in order to observe clearly the effect of each factor on the yield. The design matrix of a 2^3 factorial design and their responses are shown in Table 1. The Mathematica 5.0 software was used to calculate the equation coefficients in factorial design study.

The regression equation of matrices is represented by the following expression:

$$\begin{aligned}\text{Yield }(\%) = {} & 52.96 - 9.098\ X_1 + 19.29\ X_2 - 5.188\ X_3 \\ & - 3.903\ X_1X_2 - 2.523\ X_2X_3 \\ & + 0.671\ X_1X_3 - 0.048\ X_1X_2X_3 \end{aligned} \quad (7)$$

where X_j ($j = 1$–3): reduced variable which takes two values: −1 (low level) and + 1 (high level); low level = 2 (low value−mean)/range; high level = 2 (high value−mean)/range; mean = (high value + low value)/2; range = (high value−low value). X_1, X_2, X_3 are the reduced variables of pH, C_1, C_2, respectively.

For the sake of reproducibility, one must check whether this model accurately describes the process investigated by determining which coefficients could be neglected, through Student's t test and Fisher's test. The model adequacy strongly depends on the accuracy of the experiment. In the current experiment, the main errors arise from volume and weight measurements. For this purpose, three additional attempts at the central point (0, 0, 0) are required for estimating the average error in the value of each coefficient, on the basis of the random variance [35–37]. The calculations made are summarized in Table 2.

Thus, with a 95% confidence (i.e. $\alpha = 0.05$), and for a 2 variance (i.e. for three attempts at central point), one assessed the value of $t_{v,1-\alpha/2}$ as being equal to 1.27. Therefore, at this $(1-\alpha)$ level, the confidence range for all the coefficients estimated using 8 runs

Table 1
2^3 factorial design matrices and the responses

Experiment no.	Factors levels						Response function
	pH	C_1, M	C_2, M	X_1	X_2	X_3	Extraction yield (%)
1	2	0.01	1	−1	−1	+1	35.48
2	2	0.01	0.1	−1	−1	−1	42.25
3	2	0.1	1	−1	+1	+1	76.92
4	2	0.1	0.1	−1	+1	−1	93.59
5	5	0.01	1	+1	−1	+1	26.53
6	5	0.01	0.1	+1	−1	−1	30.42
7	5	0.1	1	+1	+1	+1	52.16
8	5	0.1	0.1	+1	+1	−1	66.34
(9, 10, 11, 12)[a]	3.5	0 .05	0.55	0	0	0	56.74, 57.28, 55.17, 56.93

Note: [a]Four additional tests at the central point (0, 0, 0) for the calculation of the Student's t test, using SLM extraction.

Table 2
Model adequacy tests and variance analysis

Feature	Symbol	Value
Parameter number	P	3
Level number	L	2
Number of experimental attempts	N	12
Number of tests at (0, 0, 0) point	n	4
Model variance	v	3
Average yield at (0, 0, 0) point	$y_o = \sum y_{0i}/4$	56.53
Random variance	$S^2 = \sum (y_{0i} - y_0)^2/v$	1.308
Square root of variance	S	1.143
Risk factor (chosen arbitrary)	α	0.05 (95%)[a]
Student's t test factor	t_v	4.3[b]
Average error on the coefficient value (trust range)	$\Delta b_i = \pm t_{v_{1-\alpha/2}} S/N^{0.5}$	±1.738
Number of remaining coefficients	R	8
Model response at (0, 0, 0)	b_0 (y_{000})	52.96
Discrepancy on average yield	$d = y_0 - y(0,\ 0,\ 0) = y_0 - b_0$	3.57
Error on average yield discrepancy	$\Delta d = \pm t_{v_{1-\alpha/2}} S(/N + 1/n)^{0.5}$	3.887
Average yield for the 12 attempts	$y_m = \sum y_i/8$	54.15
Residual variance	$S_r^2 = \sum (Y_i - Y_m)^2/(N - R)$	1010.68
Degrees of freedom	v_1	3
Residual degrees of freedom	v_2	7
Observed Fisher's test	$F_{obs} = Sr^2/S^2$	772.635[c]
Fisher-Snedekor law	$F_{0.95,3,7}$	8.89[d]

Notes: [a]$\alpha = 0.05$ was arbitrary chosen. In this case, one regarded that a 95% confidence may be satisfactory.
[b]Student law with 2 degrees of freedom at a 95% confidence ($t_{2,\ 0.975}$).
[c]After removing the less significant coefficients.
[d]See Fisher-Snedecor tables.

Table 3
Model coefficients and their corresponding effects upon yield extraction of copper (II)

Reduced variables and their interactions	Coefficient's equation	Expected effect on the yield extraction
Y_0	52.96	High average extracting capacity of Aliquat 336/TBP
X_1	−9.098	(− −) Weak detrimental individual effect of X_1
X_2	19.29	(+ +) Strong advantageous individual effect of X_2
X_3	−5.188	(− −) Weak detrimental individual effect of X_3
X_1X_2	−3.903	(−) Weak detrimental binary interaction of X_1 and X_2
X_2X_3	−2.523	(−) Weak detrimental binary interaction of X_2 and X_3

Notes: (+) Favourable or positive effect; (−) detrimental or negative effect.

($N = 8$), will be $\Delta b_i = \pm 1.7387$ at 95% confidence. From the Student's tests, it results that $|b_i| < |\Delta b_i|$ for b_1b_3, $b_1b_2b_3$. Consequently, these coefficients must be removed from the mathematical model because they do not display significant effect upon the response function, being shaded by their average error. Consequently, the final form of the polynomial model that describes the copper (II) extraction is the following:

$$\text{Yield (\%)} = 52.96 - 9.098\ X_1 + 19.29\ X_2 - 5.188\ X_3 - 3.903\ X_1X_2 - 2.523\ X_2X_3 \qquad (8)$$

The individual effects and the interactions of the parameters were discussed on the basis of the sign and the absolute value of each coefficient. These coefficients features will define the strength of the

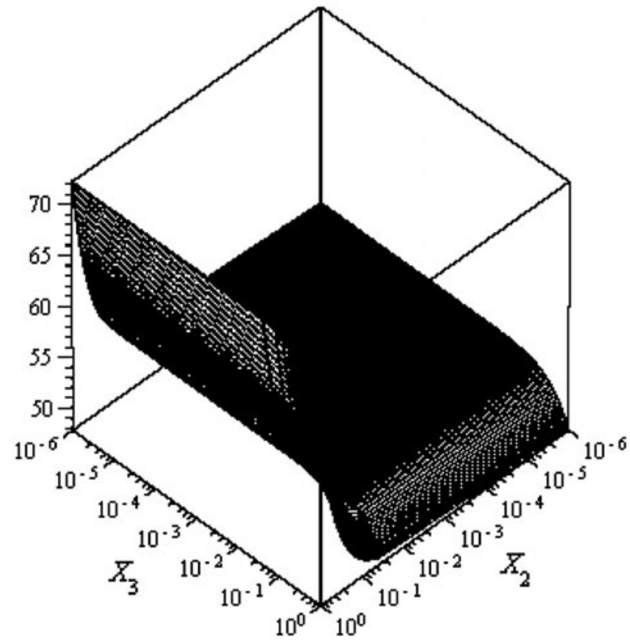


Fig. 4. 3D representation of the yield extraction (%) of copper (II) at fixed pH_i feed solution $X_1 = 0$, X_2: potassium thiocyanate concentration and X_3: ammonium acetate concentration.

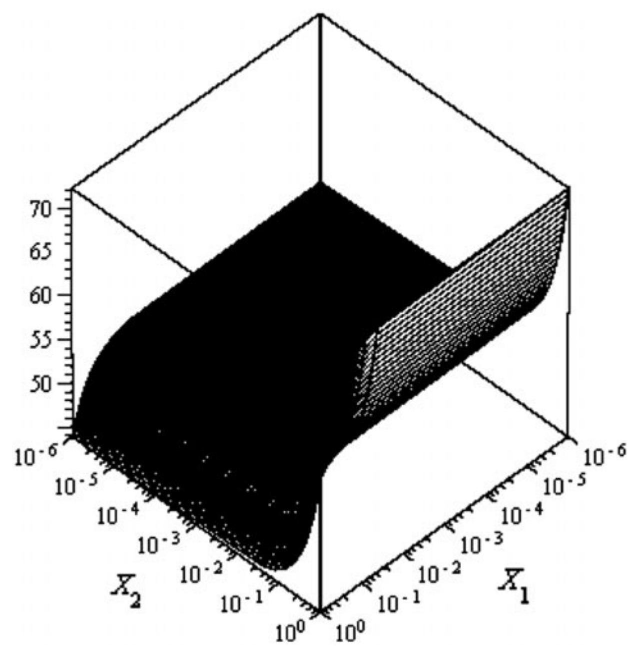


Fig. 5. 3D representation of the yield extraction (%) of copper (II) at fixed potassium thiocyanate concentration $X_2 = 0$, X_1: pH_i feed solution and X_3: ammonium acetate concentration.

corresponding effect involved and the way it acts upon yield extraction (favourable or detrimental),

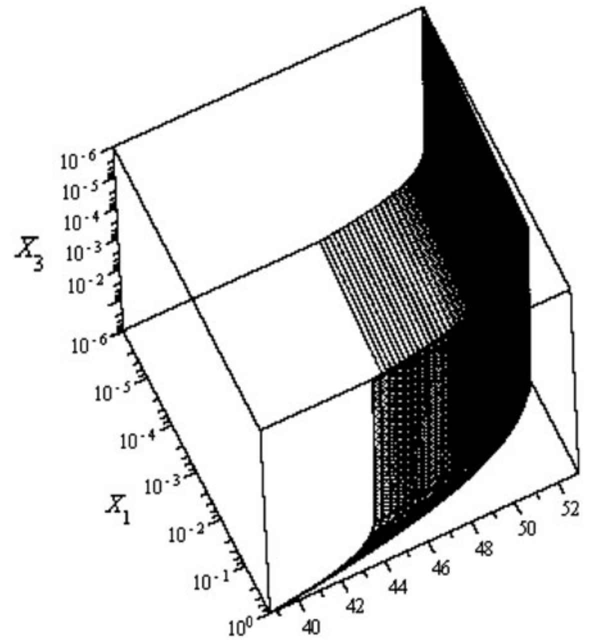


Fig. 6. 3D representation of the yield extraction (%) of copper (II) at fixed ammonium acetate concentration $X_3 = 0$, X_1: pH_i feed solution and X_2: potassium thiocyanate concentration.

Table 4
Specific regression functions with one fixed variable

Fixed coded variable	Polynomial model
$X_1 = 0$	$Y_1 = 52.96 + 19.29X_2 - 5.188X_3 - 2.523X_2X_3$
$X_2 = 0$	$Y_2 = 52.96 - 9.098X_1 - 5.188X_3$
$X_3 = 0$	$Y_3 = 52.96 - 9.098X_1 + 19.29X_2 - 3.903X_1X_2$

respectively (Table 3). For the sake of the reproducibility, one must check whether this model accurately describes the process investigated by determining which coefficients could be neglected, through Student's *t*-test [34–37]. The Student's *t* significance test was carried out on coefficients of Eq. (7) by analysing the repeated values shown in Table 1.

The first observations from Table 3 already allow making the following statements:

- The individual effect of KSCN concentration (X_2) has a positive effect on the yield of the extraction for SLM and on the other hand, the effect of pH_i feed solution (X_1) and CH_3COONH_4 concentration (X_3) has a negative effect.

- The interactions between two parameters were unfavourable between pH_i and KSCN concentration (X_1X_2), then between KSCN concentration and CH_3COONH_4 concentration (X_2X_3).
- No significant effect must be involved simultaneously between the three parameters ($X_1X_2X_3$).
- Graphical determination was achieved both by calculations and by using 2D representation of the extraction yield as a function of KSCN concentration and pH_i feed solution, maintaining constant the CH_3COONH_4 concentration, etc.

The shape of the response surface was plotted three times by fixing successively the three parameters at the central values. The vicinity around these central values is supposed to include the optimum, and the resulting 3-D representations of the response function, as illustrated by Figs. 4–6, according to the equations in Table 4.

5. Conclusion

The extraction efficiency for the extraction of copper (II) ions in a SLM system by Aliquat 336/TBP was investigated as a function of various parameters such as initial pH, KSCN and CH_3COONH_4 concentrations.

The individual effect of KSCN concentration is important for SLM extraction but its combined effect with CH_3COONH_4 concentration has a synergistic effect on the yield of the extraction only in the interval of concentration [0.01–0.1 M].

The results showed that the yield of extraction decreases when the initial pH increase. The extraction efficiency for copper (II) is better at initial pH equal to 2.

Application of factorial designs allowed the optimization of a procedure for the determination of copper (II), based on membrane liquid extraction, using a smaller number of experiments.

The experimental design is a way to investigate the entire influence of a given parameter, to assess its individual effect as an isolated variable, along with its binary interactions as a couple with each other parameter and its possible synergy when acting simultaneously with the other variables. In order to achieve the best conditions for Cu(II) uptake by Aliquat 336/TBP from aqueous solution a full 2^3 factorial designs were employed for screening the factors that would influence the overall optimization of a batch procedure of extraction. Individual effect of CH_3COONH_4 concentration is weak detrimental, but her combined effect with KSCN concentration became important. This optimization showed that the best initial conditions were copper (II) concentration equal to 0.010 M, initial pH = 2.0, KSCN concentration (0.1 M) and CH_3COONH_4 concentration (0.1 M) with extraction yield of 93.6% in one step.

Acknowledgements

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