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ORIGINAL RESEARCH PAPER

REMOVAL OF COPPER IONS USING ALIQUAT 336/TBP BASED SUPPORTED LIQUID MEMBRANE

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Abstract: The sorption of copper (II) present in an aqueous media using a supported liquid membrane (SLM) by chloride tri-N-octylmethylammonium (Aliquat 336) and Tri-n-butylphosphate (TBP) from molar ratio 1:1, with polytetrafluoroethylene (PTFE) as a membrane support was studied. The effects of various parameters as initial pH, KSCN concentration and ammonium acetate concentration on the extraction yield were carried out. By a calculation program using CHEAQS 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 2^3 factorial design achieve the best conditions of recovery procedure. The recovery of copper (II) is almost quantitative (94 %), in one step.

Keywords: *copper removal, extraction, factorial design, optimization, supported liquid membrane*

INTRODUCTION

Research and development in the treatment of copper by various processes were intensified in recent years. Many methods are available, such as precipitation, electrolysis, nano-filtration and liquid-liquid extraction [1, 2]. However, most of the preconcentration /separation methods used for this purpose have some disadvantages, such as the requirement of large amount of toxic solvents, time consuming nature of the procedures, probability of sample contamination, very sensitive operational conditions, employment of environmentally unsafe and expensive chemical products [3, 4].
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 [5]. For this, it was suggested for the recovery and the concentration of many metals and selective separations of trace amounts of metal ions [6, 7]. The removal of copper ions can be achieved by supported liquid membrane extraction process (SLM) [8-10].
Several membrane supports have been used to make SLMs, such as: polypropylene (PP), polyvinylidene difluoride (PVDF), polytetra-fluoroethylene (PTFE) and silicones [11, 12].
The objective of our work concerns the recovery of copper (II) on a supported liquid membrane type polyethylene impregnated by a mixture of Chloride tri-N-octylmethylammonium / tri-butylphosphate (Aliquat 336 / TBP- molar ratio 1:1). The influence of operating variables such as ammonium acetate concentration, KSCN concentration and initial pH of the 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 [13]. The effects of the various parameters will be studied by using a 2^3 full factorial design.

MATERIALS AND METHODS

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 were purchased from Merk. TBP was provided from Aldrich.
The liquid membrane support was a microporous polytetrafluoroethylene (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 (Figure 1).

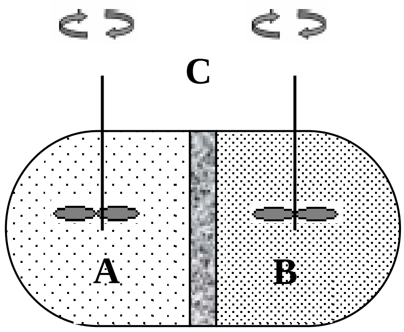

Figure 1. *Cellule of Lewis*

Apparatus

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

Impregnating liquid membrane

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

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 ambient temperature. SLM extraction was studied in discontinuous extraction mode.

RESULTS AND DISCUSSION

A conventional solvent extraction system which is carried out in two steps, either, for separation or pre-concentration of copper ions from its source solution, can be illustrated in bulk solutions as shown in Figure 2.

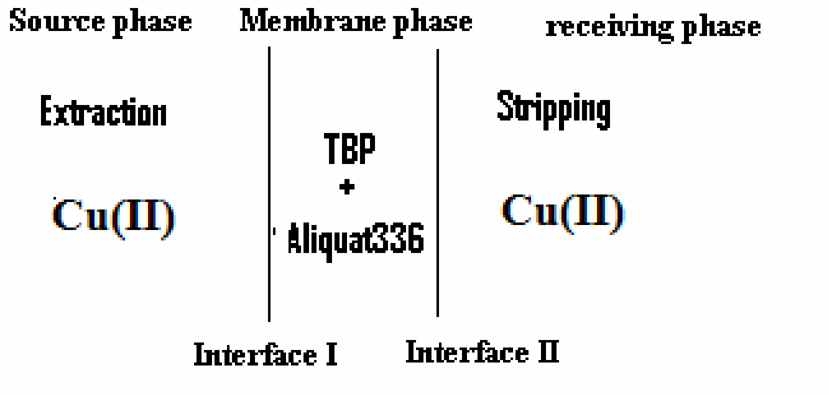

Figure 2. *Metal ion transport illustration in liquid membrane*

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 (%).

$$Y(\%) = \frac{C_0 - C_t}{C_0} x100 \qquad (1)$$

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 species present in the feed phase before extraction and after extraction, have been quantified by the program Chemical Equilibrium in Aquatic System (CHEAQS) [14].
The optimal extraction yields by Aliquat 336/TBP function from percentages of the species present in the feed phase have been investigated.

Study of the extraction conditions

Effects of potassium thiocyanate concentration

The effect of concentration of KSCN on copper (II) sorption was studied at initial *p*H equal to 2 and fixed concentration of ammonium acetate equal to 1M, by stirring with and adding of KSCN in the feed solution, from concentration 0.01M to 0.1M. Results are summarized in Figure 3.
Figure 3 shows that the influence of the KSCN concentration on extraction of copper is important. Changing the ionic strength by the addition of an electrolyte influences sorption in at least two ways:
- by affecting interfacial potential and therefore the activity of electrolyte ions and adsorption,
- by affecting the competition of the electrolyte ions and adsorbing anions for sorption sites [15,16].

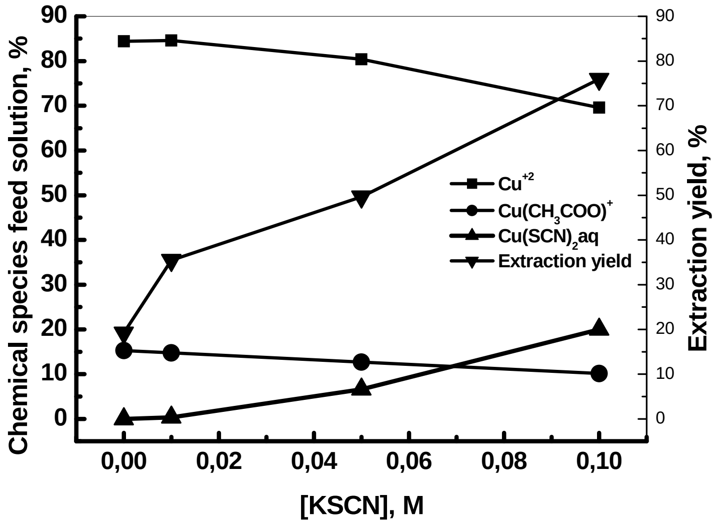

Figure 3. *Effect of the KSCN concentration on the chemical species present in the feed solution and the yield of extraction*
T=20° C, Va=450 rpm, $[Cu^{2+}]_0$ = 0.01 M, pHi = 2, $[CH_3COONH_4]$ = 1 M, Aliquat 336/TBP (molar ratio 1:1).

From the Figure 3, it can be observed that the increase in the yield of the extraction with that of the concentration of the 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 [14], although the Cu(II) specie remain always majority compared to the others.
The increases in the percent copper 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 for the sorbent via removal of oxygenated complexes as soluble cyanocomplexes, increasing thereby the number of sorption sites and hence the sorption of copper(II) species [17].

Effects of ammonium acetate concentration
Results study of effect ammonium acetate in presence of fixed KSCN concentration to 0.1M and an initial *p*H equal to 2, by stirring with adding of acetate concentration in the feed solution, from 0.1M to 2M, are summarized in Figure 4.

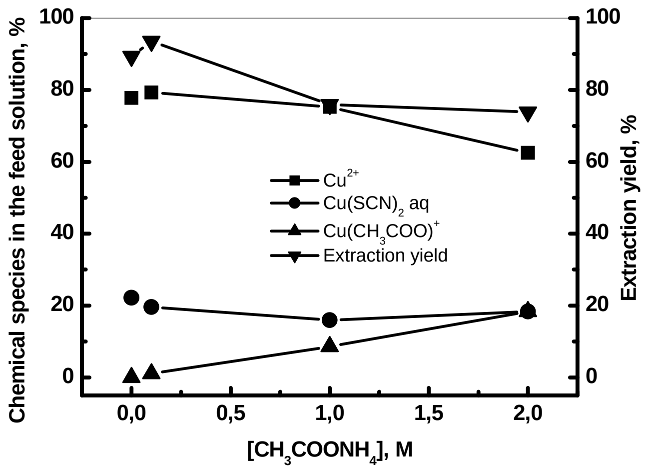

Figure 4. *Effect of the CH_3COONH_4 concentration on the chemical species present in the feed solution and on the yield*
$[Cu^{2+}]_0$ = 0.01 M, pHi = 2, [KSCN] = 0.1 M, T = 20° C, Va = 450 rpm, Aliquat 336/TBP (molar ratio 1:1)

It can be observed that a synergistic effect on the extraction yield is obtained in the 0-0.1M domain of ammonium acetate. From 0.1M to 1M ammonium acetate, the extraction yield decrease with the increasing concentration of specie $[Cu(CH_3\,COO)]^+$. The best yield (94 %) was obtained in the following conditions: initial *p*H = 2, [KSCN] = 0.1M, $[CH_3\,COONH_4]$ = 0.1M.

Effect of the initial pH

The effect of solution *p*H on the sorption of Cu(II) ions from the aqueous solution was investigated in the *p*H range of 2.0 – 6.7 using 50 mL of 0.01 M of Cu(II) ion solutions, in presence of $[CH_3COONH_4]$ = 1 M and [KSCN]=0.1 M (Figure 5).

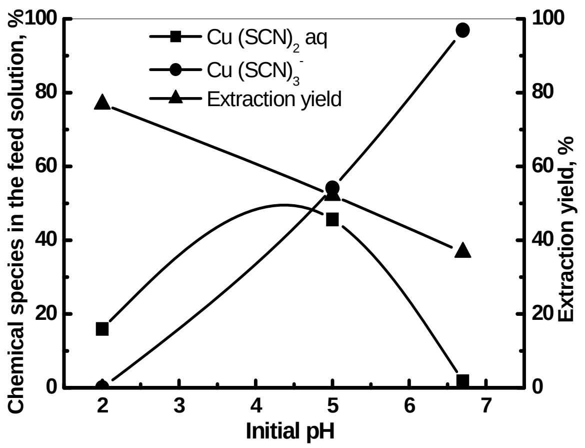

Figure 5*. Effect of the initial pH on the chemical species present in the feed solution and on the yield*
$[Cu^{2+}]_0$ = 0.01 M, $[CH_3COONH_4]$ = 1 M, [KSCN]=0.1M, T = 20° C, Va = 450 rpm, Aliquat 336 / TBP (molar ratio 1:1)

It can be observed that the extraction efficiency decreases when the initial *p*H increase. The extraction efficiency for meat is better when the initial *p*H of feed solution is 2. These results are in good agreement with those described by previous work [7]. It is the *p*H where copper is in the free form Cu^{2+} to 82 % and 18 % in the form $Cu(SCN)_2$. The increasing of $Cu(SCN)_3^-$ specie is responsible of the decreasing of the extraction yield. For higher *p*H values (*p*H = 6.7), Cu(II) ions precipitate in the form of hydroxide.

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 *p*Hi feed solution, the concentration of potassium thiocyanate (C_1) and of the concentration of ammonium acetate (C_2).

A wide range between low and high levels as 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 Table1. The Mathematica 5.0 software was used to calculate the equation coefficients in factorial design study.

***Table 1**. 2^3 factorial design matrices and the responses*

N°	pH	C_1, M	C_2, M	X_1	X_2	X_3	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

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

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

$$\text{Yield,\%}=52.96 -9.098\ X_1 + 19.29\ X_2 - 5.188\ X_3 - 3.903\ X_1X_2 \\ - 2.523\ X_2X_3+0.671\ X_1X_3-0.048\ X_1X_2X_3 \quad (2)$$

where: X_j (j = 1 to 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 *p*H, C_1, C_2, respectively.

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 corresponding effect involved and the way it acts upon yield extraction (favourable or detrimental), respectively (Table 2). 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 [18-20]. The Student's t significance test was carried out on coefficients of Equation (3) by analysing the repeated values shown in Table 1.

$$\text{Yield, \%} = 52.96 - 9.098\ X_1 + 19.29\ X_2 - 5.188\ X_3 - 3.903\ X_1X_2 - 2.523\ X_2X_3 \qquad (3)$$

Table 2. *Model coefficients and their corresponding effects upon yield extraction of Cu(II)*

Reduced variables and their interactions	**Coefficient's equation**	**Expected effect on the yield extraction**
X_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_1X_3	0.671	No significant binary interaction of X_1 and X_3
X_2X_3	- 2.523	(–) weak detrimental binary interaction of X_2 and X_3
$X_1X_2X_3$	-0.048	No significant interaction between X_1, X_2 and X_3

(+) Favorable or positive effect; (-) detrimental or negative effect.

The first observations from Table 2 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 on the other hand the effect of *p*H_i feed solution (X_1) and CH_3COONH_4 concentration (X_3) have a negative effect.
The interactions between two parameters were unfavorable between *p*H_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 ($X_1X_2X_3$).

CONCLUSIONS

The extraction efficiency for the extraction of copper ion in a supported liquid membrane system by Aliquat 336/TBP was investigated as a function of various parameters such as initial *p*H, 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 [0.01M – 0.1M].
The results showed that the yield of extraction decreases when the initial *p*H increase. The extraction efficiency for copper is better at initial *p*H equal to 2.

The experimental design is the only 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 sorption. 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 initial *p*H=2.0, KSCN concentration (0.1 M) and CH_3COONH_4 concentration (0.1 M).

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