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Research Works Referring to the Development of Copper Recovery by Hollow Fiber Supported Liquid Membranes Extraction

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Abstract

The present paper brings forward the experimentally results regarding the copper extraction from low concentrated sulfate solution (<1,57 $\cdot 10^{-2}$ mol/l) *by using the hollow fibers supported liquid membrane, impregnated with M5640 organic solvent (2-hidroxy-5-nonil-benzofenonoxima + organic ester modificator) diluted in kerosen.*

Key words: *copper, hollow fiber, extraction*

Introduction

Due to the stringent laws regarding the environmental protection, the worldwide specialists have stared to develop new technologies in order to remove and to recovery the toxic heavy metals from wastewater.

There have been reported known methods that have been widely applied to concentrate and to separate the metallic species, both in hydrometallurgical and wastewater treatment processes such as: liquid-liquid extraction, ion exchange extraction and liquid membrane extraction. The last method includes emulsion liquid membranes, bulk liquid membranes, resins impregnated with organic solvents and supported liquid membranes (flat sheet or hollow fibers supported liquid membranes) [7, 11].

The hollow fiber supported liquid membrane extraction is one of the newer technologies that could be applied to remove and to recover the toxic metals from wastewater. Due to the greater advantages offered by this techniques (the extraction and the re-extraction processes take place in a single stage; a species may be transported against the concentration gradient; high ratios membrane surface/aqueous solution volume and aqueous feed solution volume/strip solution volume; economical use of expensive and selective reagents; very good selectivity; small organic solvent inventory, etc.), a lot of extraction systems that are using the hollow fiber techniques were investigated by the worldwide specialists. Table 1 present some of these systems as reported in the literature.

The extraction mechanism in the hollow fiber supported liquid membrane is based on the ion exchange chemical reaction that occurs. The reversible chemical reaction responsible with the copper ions transfer from the aqueous feed solution in the liquid membrane is:

$$Cu^{2+} + 2HR \Leftrightarrow CuR_2 + 2H^+ \quad , \tag{1}$$

where : CuR_2 represent the CuR_2 concentration in the liquid membrane, mol/l;
Cu^{2+} - copper concentration in the aqueous feed solution, mol/l;
H^+ - hydrogen ion concentration in the aqueous feed solution, mol/l;
HR- reagent concentration in the liquid membrane, mol/l;

The hydrogen ion concentrations in the aqueous feed solution influence the copper extraction efficiency from the aqueous feed solution in the liquid membrane. At a higher hydrogen ion concentrations in the aqueous feed solution (small value of pH) the re-extraction process may occurs and at a smaller concentration of hydrogen ion concentration (high value of pH) the extraction process may occurs.

The aim of this paper is to study the Cu(II) extraction, at different pH values (different hydrogen ion concentrations), from synthetic wastewater using the hollow fiber supported liquid membrane impregnated with M5640 (hidroxy-oxima) diluted in kerosen.

Table 1. Extraction systems.

Metal recover	**Feed solution**	**Strip solution**	**Reagent***	**Diluent**	**Hollow fiber material**
Cu(II)	sulfate	H_2SO_4	LIX84[3]	kerosene	poly-propylene
Zn(II)	sulfate	H_2SO_4	PC88A[3]	kerosene	poly-propylene
Cu(II)	acid solution	H_2SO_4	LIX860[1]	Kermac 500-T	poly-tetrafluoro-ethylene
Cu(II), Co(II), Ni(II), Zn(II)	sulfate	H_2SO_4	LIX864[5]	kerosene	poly-tetrafluoro-ethylene
Cu(II), Zn(II)	sulfate	-	LIX984[8] + DEHPA[8]	n-heptane	poly-sulfone
Cu(II)	$CuCl_2$ + EDTA	-	Aliquat 336[10]	kerosene	poly-propylene
Cu(II)	sulfate	HCl	LIX64N[9]	kerosene	poly-propylene
Cu(II)	sulfate	H_2SO_4 or HCl	SME529[6] – chelating agent	dispersol	teflon/ poly-prolylene/ polyacrylo-nitrile
Cd Ni	sulfate	H_2SO_4	D2EHPA+ TBP[4]	kerosene	poly-propylene
Cr(IV)	Na_2CrO_4	NaCl	Aliquat 336[2]	kerosene	poly-propylene

* ***LIX84***- *anti-2-hydroxy-5-nonyl acetophenoneoxime;* ***PC88A***-*2-ethylhexylphosphonic acid mono-2-ethylhexylester;* ***LIX860*** *-5-dodecylsalicylaldoxime;* ***LIX864***-*LIX860 and HS-LIX64 (2-hydroxy-5-nonylbenzophenone oxime and 5, 8-diethyl-7-ydroxydodecan-6oxime);* ***LIX984***-*LIX860 and LIX84;* ***Aliquat 336***-*tri-n-octylmethylammonium chloride;* ***D2EHPA*** *-di(2-ethylhexyl)phosphoric acid;* ***TBP***-*tri-n-butyl phosphate.*

Research Methodology

Figure 1 shows a schematically representation of the experimental installation used in the present research work.

Using the peristaltic pump type Watson-Marlow, the feed solution volume ($V = 1000\ cm^3$) circulates through the hollow fiber lumen and the strip solution volume ($V = 500\ cm^3$) circulates in co-current, through the glass tube. Both solutions are recycled in process. The flow rates used in the experimental work were: $Q_{feed} = 0.577\ cm^3/s$; $Q_{strip} = 1.74\ cm^3/s$. In the experimental studies, a synthetic aqueous feed solution with an initial copper concentration $C_0 = 7{,}86 \cdot 10^{-3}$ mol/l has been used. Aiming to study the permeability variation with the pH of the feed solution, aqueous synthetic feed solution with different values of pH (pH = 0.71; 1.5; 2; 3.7; 4.5) were used. The strip solution was an acid solution with 2.04 mol/l H_2SO_4.

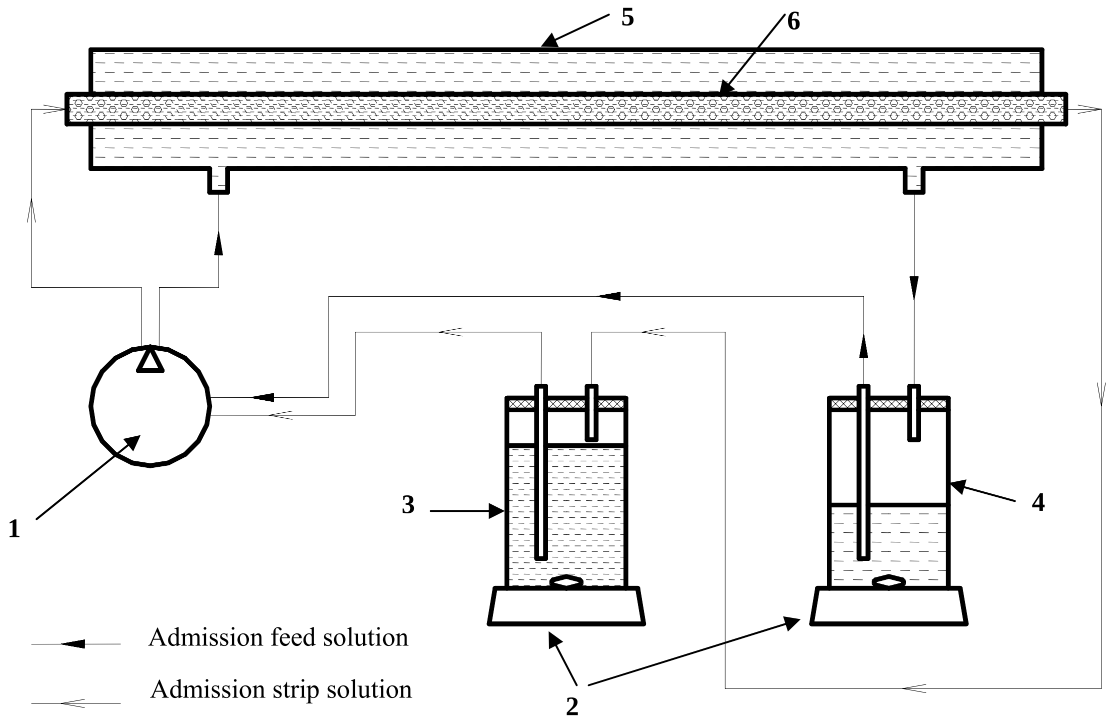


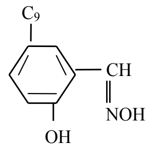
Fig. 1. Schematic representation of the installation used in experimental work:
1- peristaltic pump; 2-magnetic stirring; 3-feed solution bulk; 4-strip solution bulk;
5, 6-experimental module (5-glass tube; 6-hollow fiber impregnated with M5640 in kerosene).

The hollow fiber was embedded in the glass tube by using the epoxy resin. The hollow fiber used was a micro-porous polypropylene fiber, type ACCUREL, designed by Enka Wuppertal Germany for ultra filtration installation, with the following physical characteristics:

- internal diameter: 0.15 cm;
- thickness wall: 0.03 cm;
- length: 25 cm;
- porosity: 75 %.

The average pore diameter (determined with a scanning electronic microscope Philips SEM 515) was $0.04 \cdot 10^{-4}$ cm, [7]. The structure of the pores is presented in figure 2.

The hollow fibers were impregnated with M5640 solvent diluted in kerosene by flowing the organic phase through the hollow fiber lumen. The M5640 reagent's structure is:



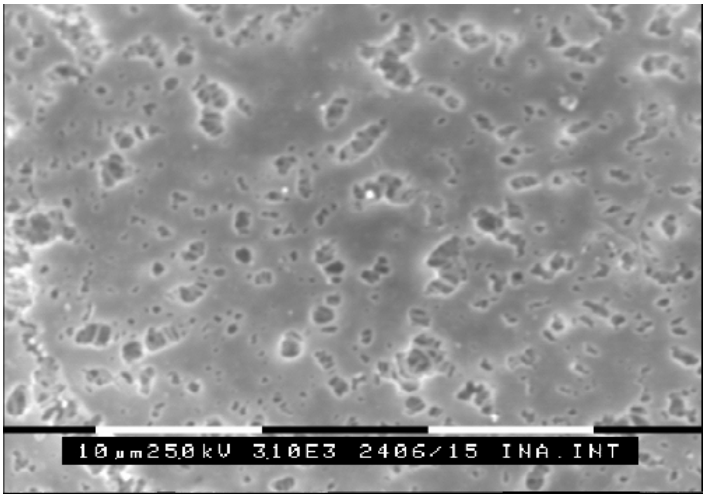


Fig.2. The structure of the hollow fiber pores (x 3100).

The M5640 reagent is manufactured by the AVICIA Chemicals. This reagent is on of the organics solvents industrial utilized for the selective extraction of the copper from sulfate aqueous solutions and present a good selectivity against Fe, Zn and other impurities existent in the copper solutions [11]. The reagent characteristics are:

- molecular weight 365;
- density (at 25^0C) 0.95 – 0.97;
- viscosity (at 25^0C) 500 cP.

Experimental Results

In order to investigate the pH influences on the copper extraction efficiency five extraction processes were proceeded each at different aqueous feed solution pH values, [7]. Figure 3 present the copper variation in the feed solution with the extraction time, for different aqueous feed solution pH values.

The copper concentration in the aqueous feed solution was determined by atomic absorption with a device type AAS 30 CARLZEISS JENA with the following characteristics: measurement field min. 0.5 ppm ($7.,86 \cdot 10^{-6}$ mol/l), precision grade A .

The *pH* of the feed solution was determined with a digital device type PH-10 with the following characteristics: measurement field 0 ÷ 14, precision grade 0.1 % from the measurement field ± 1 digit.

Table 2 presents the copper extraction efficiency at different aqueous feed solution pH values.

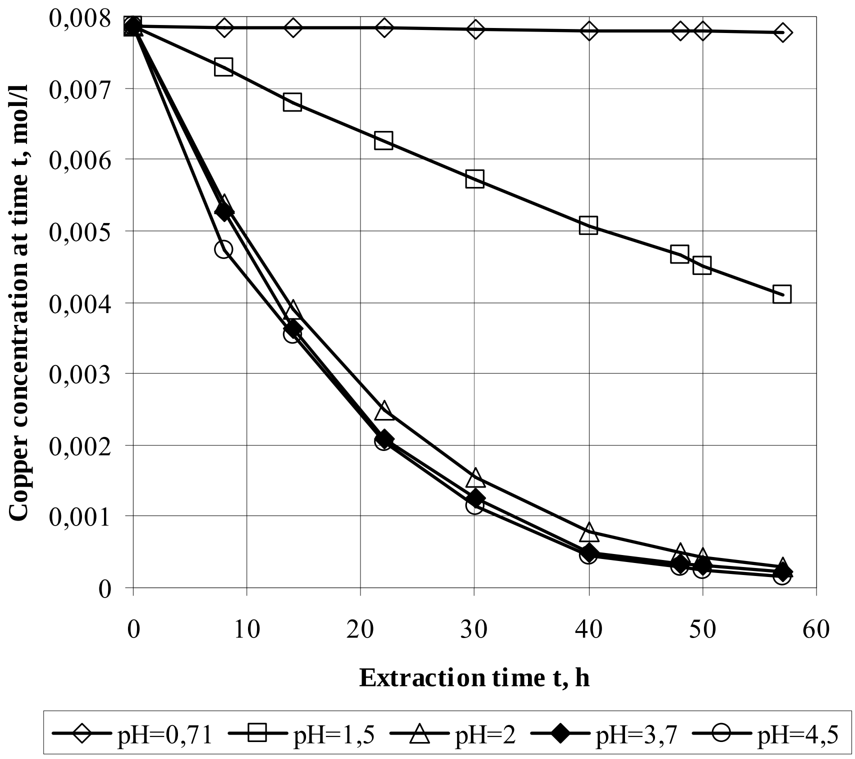


Fig.3. Variation of the copper concentration in the aqueous feed solution for different values of pH.

Table 2. Copper extraction efficiency at different pH values of the feed solution.

pH Feed solution	Extraction time, h	Initial copper concentration in the feed solution, mol/l	Final copper concentration in the feed solution, mol/l	Copper extraction efficiency, %
0.71	57	0.007867	0.007773	1.2
1.5	57	0.007867	0.004091	48
2	57	0.007867	0.000283	96.49
3.7	57	0.007867	0.000220	97.2
4.5	57	0.007867	0.000157	98

Conclusions

The focus of this research was to extract the copper from sulfate aqueous solution by using the hollow fiber supported liquid membrane impregnated with M5640 organic solvent diluted in kerosene, at different values of the pH aqueous feed solution.

The pH of the aqueous feed solution influences the copper extraction efficiency. The copper efficiency extraction from the aqueous feed solution is increasing with the decreasing of the concentration of the hydrogen in the aqueous feed solution.

At a value of pH equal with 2 the extraction efficiency of copper from sulfate aqueous solution is 96.49 % after 57 extraction hours by using the hollow fiber supported liquid membrane impregnated with M5640 organic solvent diluted in kerosene. By increasing the pH of the feed solution above this value, the copper efficiency is increasing but the selectivity of the copper is decreasing [7, 11].

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Cercetări privind extracţia cuprului prin membrane lichide pe suport solid de tip fibră tubulară

Rezumat

În lucrare se prezintă cercetările experimentale privind extractia cuprului din solutii apoase diluate de sulfat de cupru (<1,57 $\cdot 10^{-2}$ mol/l) folosind membrane lichide pe support solid de tip fibră tubulară, impregnate cu solventul organic M5640 (2-hidroxi-5-nonil-benzofenon oximă + modificator ester organic) diluat in kerosen.