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COPPER EXTRACTION FROM DILUTED SOLUTIONS USING HOLLOW FIBER SUPPORTED LIQUID MEMBRANES

Экспериментально исследовалось извлечение меди из сточных вод с использованием жидкостной мембраны, поддерживаемой полыми волокнами и пропитанной органическим растворителем M5640. Коэффициент проницаемости увеличивается при увеличении pH фильтруемого раствора. При высоких концентрациях ионов водорода в фильтруемом растворе процесс управляется CuR_2, проникающим сквозь жидкостную мембрану. При низкой концентрации ионов водорода проницаемость перестает зависеть от этого фактора, и процесс управляется диффузией сквозь водный диффузионный слой, образуемый на границе фильтруемого раствора и жидкостной мембраны. Экспериментальные исследования проводились по модели Данези.

The copper extraction from wastewater using hollow fiber supported liquid membrane impregnated with M5640 was experimentally investigated. The permeability coefficients rise by raising the pH of the feed solution. At high concentration of hydrogen ions in the feed solution the process was controlled by diffusion of CuR_2 through the liquid membrane. At small concentration of hydrogen ions, the permeability become independently with this factor and the process was controlled by diffusion through the aqueous diffusion layer formed at the interface feed solution-liquid membrane. The experimental studies were in accordance with Danesi model assumptions.

1. Introduction

Due to the greatest advantages offered by the supported liquid membrane over the other techniques (the extraction and the re-extraction processes take place in a single stage; economical use of expensive and selectively reagents; very good selectivity; small organic solvent inventory, etc), this method was selected to study the recovery of copper from diluted aqueous solutions. The main objective of this paper was to investigate the pH influence on the membrane permeability, in the case of copper extraction with hollow fibers supported liquid membrane, impregnated with M5640 (hidroxy-oxima) diluted in kerosen.

2. Experimental

A. The extraction equilibrium constant

Using the liquid-liquid extraction techniques, the distribution coefficient of copper has been determined. Two sets of experimental work were effectuated in the following conditions:

a) 20 cm^3 organic phase (10 % M5640 diluted in kerosen) was contacted with 20 cm^3 feed solution (490 ppm copper concentration, pH = 0,67; 2; 3; 3.8);

b) 20 cm^3 organic phase (5 %, 10 %, 25 %, 80 %, 100 % M5640 diluted in kerosen) was contacted with 20 cm^3 feed solution (490 ppm copper concentration, pH = 2).

The extraction time was 10 minutes in both cases.

The extraction equation is:

$$Cu^{m+}_{aqueous} + nHR_{organic} \Leftrightarrow$$

$$\Leftrightarrow Cu(R)_m(HR)_{(n-m)organic} + mH^+_{aqueous}. \quad (1)$$

The extraction equilibrium constant is:

$$K_{ech} = \frac{[Cu(R)_m(HR)_{(n-m)organic}][H^+]^m_{aqueous}}{[Cu^{m+}_{aqueous}][HR]^n_{organic}}. \quad (2)$$

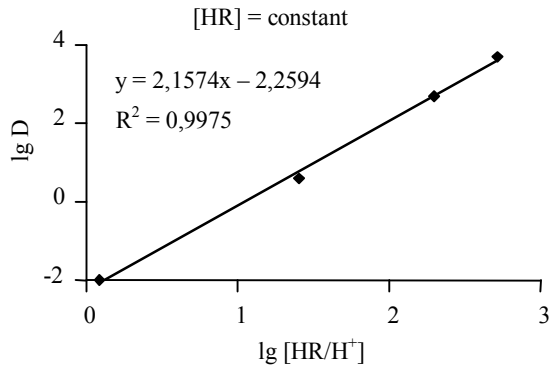


Fig.1. The distribution coefficient variation with pH_{eq} at constant concentration of extractant

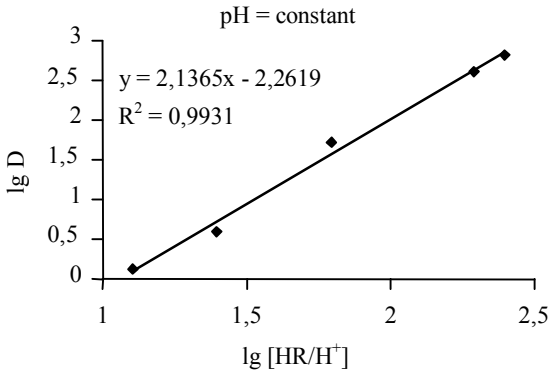


Fig.2. The distribution coefficient variation with M5640 reagent concentration at constant values of pH_{eq}

The distribution coefficient is:

$$D = \frac{[Cu(R)_m(HR)_{(n-m)organic}]}{[Cu^{m+}_{aqueous}]}. \qquad (3)$$

The equilibrium constant can be determined by using the following equation:

$$\lg D = n\lg[HR] - m\lg[H^+] + \lg K_{ech}. \qquad (4)$$

Where: m represent the number of hydrogen molecules/moll of extracted copper; n is the number of extractant molecules/moll of extracted copper; $[H^+]$ is the hydrogen ion concentration in the feed solution, mol/l; [HR] is the extractant concentration in the liquid membrane, mol/l.

The experimental data presented in Fig.1 and 2 allowed us to calculate the equilibrium constant by means of equations (3, 4). The obtained value was $K_{ech} \cong 5{,}5 \cdot 10^{-3}$.

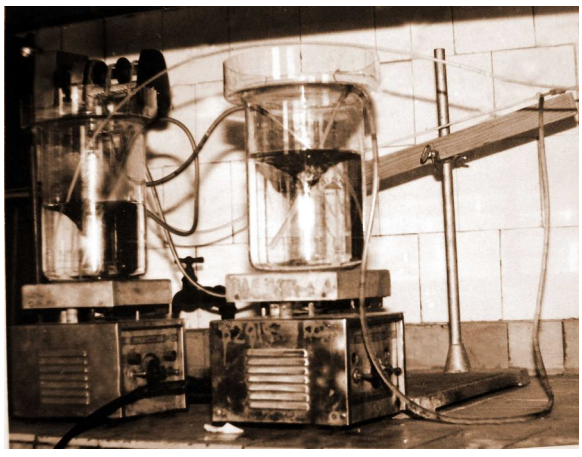


Fig.3. The installation used in the experimental work

B. Membrane permeability variation with the pH of the feed solution.

a. Experimental system

Figure 3 depicts the experimental installation used in the research work. The hollow fiber was a microporous polypropylene fiber, type ACCUREL with – internal diameter: 0,15 cm; thickness wall: 0,03 cm; length: 25 cm; porosity: 75 %. The hollow fibers were impregnated with M5640 (hidroxy-oxima) organic solvent diluted in kerosene by flowing the organic phase through the lumen.

The synthetic feed solution circulates, in laminar condition, through the fiber lumen by using a peristaltic pump and the strip solution (200 g/l H_2SO_4) circulates in co-current with the feed solution, through the tub glass. Both solutions are recycled in process.

Aiming to study the permeability variation with the pH of feed solution, aqueous synthetic liquors with different values of pH (pH = 0,9; 1,4; 2; 3,7; 4,5) were used. The concentration of the reagent in the organic phase was 10 % M5640 in kerosene.

b. Theoretical backgrounds

The permeability coefficients, for different values of pH, have been determined by using the Danesi model [1]:

$$\ln\frac{C_{in}}{C^0_{in}} = -\frac{A}{V}P^*\frac{\varphi}{\varphi+1}t, \qquad (5)$$

$$\varphi = \frac{RU}{P^*L\varepsilon}. \qquad (6)$$

Where: $C_{in} = C_0 = 500$ ppm represents de copper concentration at time $t = 0$; $C^0_{in} = C_t$ is the

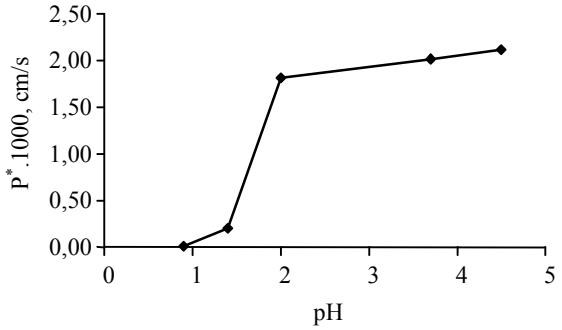


Fig.4. The permeability variation with the pH of the feed solution

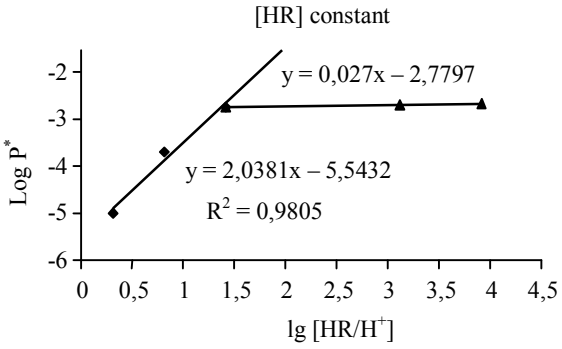


Fig.5. Log $[HR/H^+]$ vs.Log P^*

copper concentration at time t, ppm; P^* is the modified coefficient of permeability, cm/s; ϕ is the correction factor; V is the volume of the feed solution at time t, cm^3; A is the total internal surface of the hollow fiber, cm^2; t is the extraction time, s; R is the internal radius of the fiber, cm; L is the fiber length, cm; ε is the fibers porosity, %; $U = Q_t/A$ is the equivalent linear velocity, cm/s.

3. Results and discussion

Taking into consideration equation (5), from the graphic's slope, ln C_0/C_t versus $f\left(\frac{A}{V}t\right)$, the permeability coefficient can be determinate.

Figure 4 presents the membrane permeability variation with the pH of the feed solution. The process can be controlled by diffusion through the aqueous diffusion layer or by diffusion through the liquid membrane according to equations 7, 8 [2] and figure 5.

$$\log P^* = \log\left(\frac{D_0}{d_0\tau}\right) + \log K_{ech} - 2\log[H^+] + 2\log[\overline{HR}]. \quad (7)$$

Where: K_{ech} represents the equilibrium constant; $[H^+]$ is the hydrogen ion concentration in the feed solution, mol/cm^3; $[\overline{HR}]$ is the molar concentration of the extractant in the liquid membrane, mol/cm^3; D_0 is the diffusion coefficient of CuR_2 in the liquid membrane, cm^2/s; d_0 is the wall thickness of the hollow fibers, cm; τ is the tortuosity factor that taking into consideration the pores' form.

$$\log P^* = \log\left(\frac{D_a(R-d_a)}{d_a R}\right). \quad (8)$$

Where: d_a represents the thickness of the aqueous diffusion layer, cm; D_a is the copper diffusion coefficient in the feed solution, cm^2/s.

The two slopes exhibited by the plot of the experimental data in Fig.5 shows that the process is controlled by two mechanisms. At high concentration of hydrogen ions in the feed solution the process is controlled by diffusion of CuR_2 through the liquid membrane. At low concentration of hydrogen ions, the permeability becomes independent on this factor and the process is controlled by diffusion through the aqueous diffusion layer formed at the interface of the feed solution-liquid membrane. From the intercept of the two straight lines in the plot (Fig.5) the diffusion coefficient of CuR_2 in the liquid membrane, was calculated by means of eq. (7). The obtained value was $D_0 = 2{,}07 \times 10^{-5}$ cm^2/s. Using the limiting value of the permeability coefficient for this mechanism and eq. (8), a mass transfer coefficient $\left(\frac{D_a(R-d_a)}{d_a R} = 1{,}6\times10^{-3}\right)$ in the aqueous diffusion layer was obtained.

4. Conclusions

The membrane permeability varies with the pH of the feed solution. At high concentration of hydrogen ions in the feed solution the process was controlled by diffusion of CuR_2 through the liquid membrane. At small concentration of hydrogen ions, the permeability is controlled by diffusion through the aqueous diffusion layer formed at the interface feed so-

lution-liquid membrane. The experimental results agree with Danesi's model assumptions.

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