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EXPERIMENTAL RESEARCHES ON METALS EXTRACTION WITH ORGANIC SOLVENTS BY NEW METHODS USING LIQUID MEMBRANES

Жидкостная мембрана, поддерживаемая полыми волокнами и пропитанная органическим растворителем М5640, разбавленным в керосине, является альтернативным способом извлечения меди из промышленных стоков с низким содержанием меди (500 частей на миллион). Скорость потока фильтруемой жидкости влияет на проницаемость мембраны. Оптимальное соотношение скорости потока фильтруемой жидкости и жидкости для десорбции были определены как 2080 мл/ч и 6264 мл/ч соответственно. При таких условиях можно считать, что сопротивление массопереносу является минимальным благодаря низкой плотности диффузионного граничного слоя.

The hollow fibers supported liquid membrane, impregnated with M5640 organic solvent diluted in kerosen, is an attractive technique for copper recovery from industrial wastewater with low content of copper (500 ppm). The flow rates of the feed solution influence the membrane permeability. The optimum set of flow rates for the feed solution and for the strip solution have been established at 2080 ml/h and 6264 ml/h, respectively. In the above mentioned conditions one may consider that the resistance to mass transfer was near the minimum due to the small thickness of the diffusion boundary layer.

1. Introduction

The industrial wastewaters can contains a lot of metals, such as Al, Ca, Cr, Cu, Fe, Hg, Ni, Pb, Zn which are very important to be recovered from the solutions. There are some techniques of interest, utilized to improve the recovery of the metals from industrial wastewater, such as: liquid-liquid extraction, ion exchange, liquid membrane. 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). Among these technologies the hollow fibers supported liquid membranes present the greatest advantages: the extraction and the reextraction 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. This paper has the main objective to investigate the copper extraction from industrial wastewater by using hollow fiber supported liquid membrane. The permeability variation with the flow rates of the feed solution was investigated.

2. Experimental system

Figures 1 shows a schematically representation of the experimental installation used in the research work. The experimental module was built by embeding the hollow fiber in the glass tube using epoxy resin. The hollow fiber was a microporous polypropylene fiber, type ACCUREL, designed by Enka Wuppertal Germania for ultra filtration installation. The physical characteristics of the fiber were – 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. The structure of the pores is presented in figure 2. The hollow fibers were impregnated with M5640 organic solvent di-

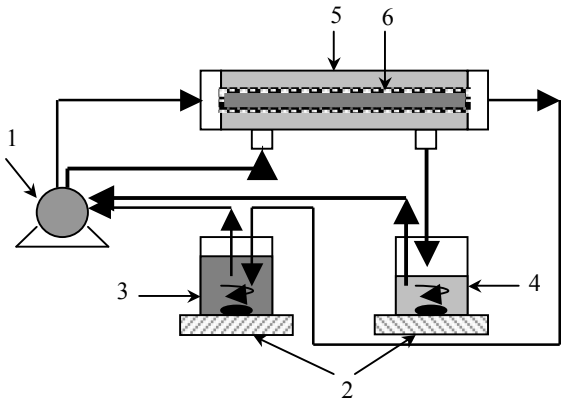

Fig.1. Schematically representation of the installation used in experimental work: 1 – peristaltic pump; 2 – magnetic stirring; 3 – feed solution bulk; 4 – strip solution bulk; 5 – glass tube; 6 – hollow fiber impregnated with M5640 diluted in kerosene

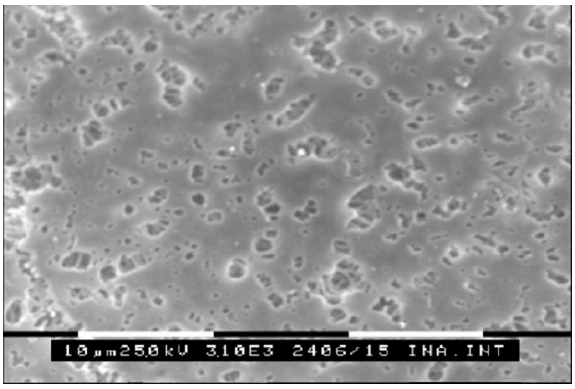

Fig.2. The structure of the hollow fiber pores (x 3100)

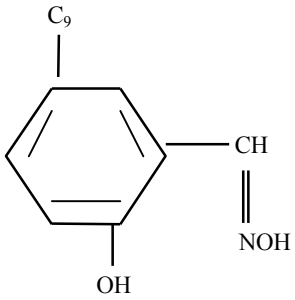

Fig.3. The M5640 structure

luted in kerosene by flowing the organic phase through the lumen. The M5640 reagent structure is presented in figure 3.

The feed solution volume ($V = 1000$ cm^3) is a synthetic aqueous feed solution with a low copper concentration ($C_0 = 500$ ppm) that circulates, in laminar condition, through the fiber lumen by using a peristaltic pump. The strip solution volume ($V = 500$ cm^3), that is an acid solution with 200 g/l H_2SO_4, circulates in co-current with the feed solution, through the tube glass. Both solutions are recycled in the process.

3. Permeability evaluation

To evaluate the membrane permeability, Danesi model [1] valid for the case of aqueous feed solution with low copper content was used. The relationships are:

$$\ln \frac{C_{in}}{C_{in}^0} = -\frac{A}{V} P^* \frac{\varphi}{\varphi + 1}, \quad (1)$$

$$T = \frac{A}{V} t, \quad (2)$$

$$K = P^* \frac{\varphi}{\varphi + 1}, \quad (3)$$

$$\varphi = \frac{RU}{P^* L \varepsilon}, \quad (4)$$

$$P^* = \frac{KRU}{RU - KL\varepsilon}. \quad (5)$$

Where: $C_{in} = C_0$ represents de copper concentration at time $t = 0$, ppm; $C_{in}^0 = C_t$ is the 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 feed solution at time t, cm^3; $A = 2\pi RLN\varepsilon$, total internal surface of the hollow fiber, cm^2; t is the extraction time, s; R is the internal radius of fiber, cm; $N = 1$, number of fibers; L is the fiber length, cm; ε is the fibers porosity, %; $U = Q_t/A_t$, equivalent linear velocity, cm/s; Q_t is the flow rate of the feed solution, cm^3/s; $A_t = \pi R^2 N$, cross section of the fibre, cm^2; K is the slope of the plot $\ln C_0/C_t$ versus f(T), cm/s.

4. Results and discussion

The membrane permeability varies with the flow rates of the aqueous solution. To study this influence, the flow rates of the feed solution have been modified in the limits 126 up to 5208 ml/h and for the strip solution from 378 to 10808 ml/h. The concentration of the reagent in the organic phase was 10 % M5640 in kerosene. The pH of the feed solution was kept constant at a value of 2. Taking into con-

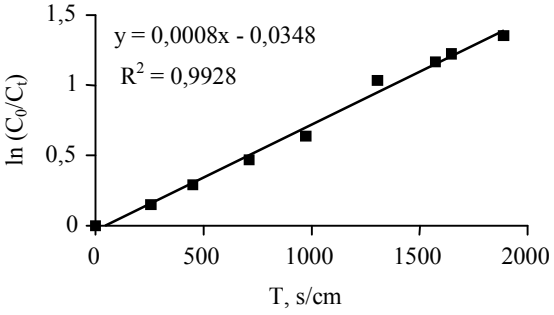

Fig.4. ln C_0/C_t vs. T, Q_{feed} = 126 ml/h
Q_{strip} = 378 ml/h

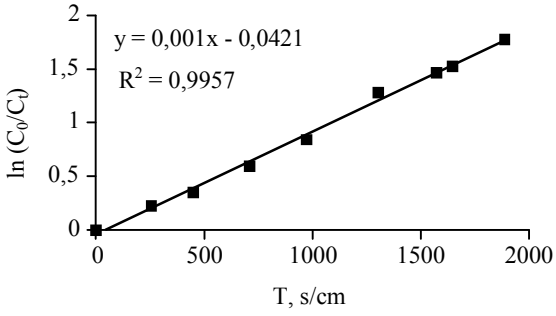

Fig.5. ln C_0/C_t vs. T, Q_{feed} = 360 ml/h
Q_{strip} = 1087 ml/h

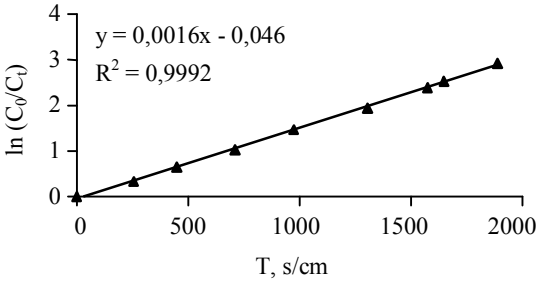

Fig.6. ln C_0/C_t vs. T, Q_{feed} = 1470 ml/h,
Q_{strip} = 4600 ml/h

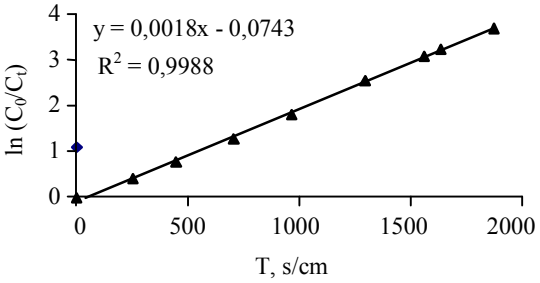

Fig.7. ln C_0/C_t vs. T,
Q_{feed} = 2080 ml/h, Q_{strip} = 6264 ml/h

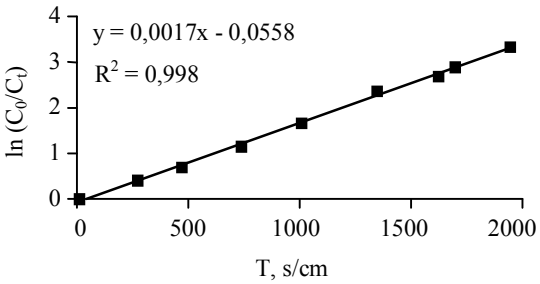

Fig.8. ln C_0/C_t vs. T,
Q_{feed} = 3850 ml/h, Q_{strip} = 8490 ml/h

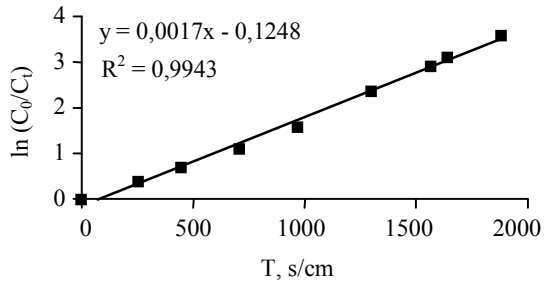

Fig.9. ln C_0/C_t vs. T,
Q_{feed} = 4832 ml/h, Q_{strip} = 9125 ml/h

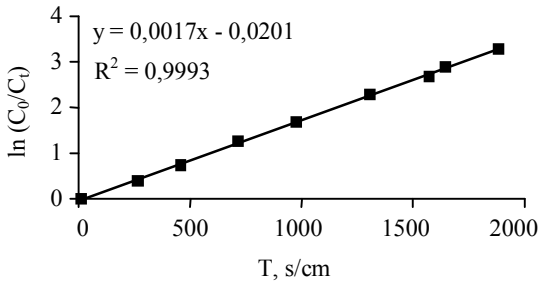

Fig.10. ln C_0/C_t vs. T,
Q_{feed} = 5208 ml/h, Q_{strip} = 10808 ml/h

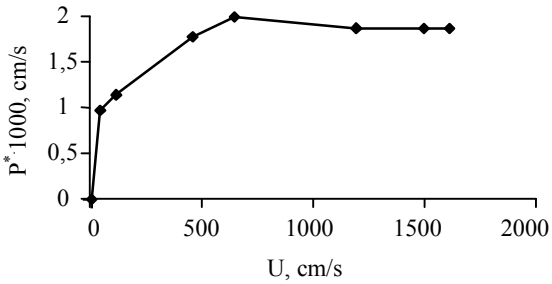

Fig.11. The permeability variation with the equivalent linear velocity of the feed solution

sideration equations (1, 2) and plotting ln $C_0/C_t = f(T)$ a straight line is obtained. The slope of the straight line is the K values from the equation (3). The membrane permeability coefficient is obtained by using equation (5).

The experimental data plotted in Fig.4-10 allowed us to determine the permeability coefficients for different values of flow rates of the feed solution. Table 1 presents the permeability coefficients obtained for different flow rates and Fig.11 shows the permeability variation with equivalent linear velocity of the aqueous feed solution.

Table 1-The permeability coefficients for different flow rates of the feed solution

Q_t, ml/h	U, cm/s	K, cm/s	P^*, cm/s	ϕ
126	1,981599	0,0008	0,000889	8,9
360	5,661713	0,001	0,001046	21,64
1470	23,11866	0,0016	0,001628	56,79
2080	32,71212	0,0018	0,001825	71,69
3850	60,54887	0,0017	0,001712	141,46
4832	75,99277	0,0017	0,001709	177,8
5208	81,90611	0,0017	0,001708	191,72

The permeability system increases by increasing the equivalent linear velocity of the feed solution, reaching a maximum value at U = 32,71 cm/s. The optimum set of flow rates for the feed solution and for the strip solution have been established at 2080 ml/h and 6264 ml/h, respectively. Higher values for the flow rates bring practically no improvement to the permeability of the system.

4. Conclusions

The Danesi model assumptions were verified for the experimental conditions presented in this paper. The membrane permeability was a function of the flow rates of the feed solution. The permeability coefficients rise by raising the flow rates of the feed solution. The maximum value of the membrane permeability is obtained when the thickness of the aqueous diffusion layer, presented at the feed solution-liquid membrane interface, is at a minimum. The copper extraction by using the hollow fiber supported liquid membrane is an economic and efficient technique.

REFERENCES

1. P.R. Danesi, A simplified model for coupled transport of metal ions through hollow-fiber supported liquid membranes, Journal of Membrane Science, 20, p. 231-248, 1984.