Zinc(II) Membrane-Extraction by *N*-decyloxy-1-(3-pyridyl)ethanoimine Using Pseudo-Emulsion Based Hollow Fiber Strip Dispersion (PEHFSD) Processing

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The extraction of zinc(II) ions from chloride solutions through pseudo-emulsion based membrane strip dispersion (PEHFSD) using *N*-decyloxy-1-(3-pyridyl)ethanoimine or tributylphosphate as the extractants was investigated. The metal ions transport was investigated as a function of the composition of the organic membrane phase. The overall mass transfer coefficient of permeation was calculated from the experimental data, the values being found in the range of 1.8×10^{-7}–2.3×10^{-6} m/s. The best results in terms of the kinetics of extraction were obtained for the pyridine extractant. The recovery of zinc with pyridine (0.05 M, 0.1 M) and with TBP (1.4 M, 2.9 M) extractants attained values of ~75% and 85–95%, respectively, using water as the strippant. The removal of zinc from aqueous solution exceeded 95% in most cases.

1. Introduction

The *Supported Liquid Membrane* technology (SLM) is a membrane-based solvent extraction method that uses a micro-porous hydrophobic membrane as supporting layer [1]. This membrane, often polypropylene, is impregnated with an organic solvent containing the specific carrier molecules for metal ion extraction [2]. The SLM-technology results, according to the industrial needs, into a strongly reduced disposal of metal waste. This technique not only reduces and avoids waste, but also aims at the recovery of valuable products. The vast majority of industrial effluents and waste water, such as mining water, etching or pickling baths, dilute leach solutions generated during hydrometallurgy, electroplating rinse liquors, etc. may carry Zn(II), Cu(II), Co(II) etc. in low concentrations [3]. SLM membranes also include hollow fiber membranes.

Since many years the scientists have been writing about the advantage of the Pseudo-Emulsion Hollow Fiber Strip Dispersion (PEHFSD) technique offers a potential attractive alternative to the conventional processes because it combines the process of extraction and stripping in a single unit operation. Furthermore, the consumption of the extractant is much smaller than in the classical extraction. An important advantage of hollow fiber membranes is that compact modules with very high membrane surface areas can be formed. The diameter of hollow fibers varies over a wide range,

from 50 to 3000 μm. Pseudo-emulsion system is a very promising method for treatment of liquid waste streams with toxic or valuable metal ions [4].

The aim of this work was to study the possibility of using the non-comercial extractant - *N*-decyloxy-1-(3-pyridyl)ethanoimine (3PC1-OC10) for recovery of Zn(II) from chloride solutions using the PEHFSD technique and compare the results with those obtained with the classical extractant tributylphosphate (TBP).

2. Experimental

2.1 Reagents

N-decyloxy-1-(3-pyridyl)ethanoimine (Figure 1.) was synthesized according procedure described in previous papers [5]. Toluene (ACS reagent, Chem-Lab NV, Belgium) and decan-1-ol (Merck, Germany) were used as components of the organic phase. Sodium chloride (ACS reagent, Panreac, Spain), hydrochloric acid (35%) (AR reagent; VWR, USA), sodium sulfate (ACS reagent, AppliChem, Germany) and zinc(II) chloride (anhydrous) (ACS reagent, Chem-Lab NV, Belgium) were used to compose the aqueous phase.

The organic phase used in the extraction studies contained the synthesized compound (0.05 M or 0.1 M) and toluene (Carlo Erba, France) as a diluent with a 10% (v/v) addition of decan-1-ol (Merck, Germany). Tributyl phosphate (Rhodia, Netherlands) was also used as a carrier being diluted in ShellSol D70 (aliphatic diluent; aromatic content <0.01%, Drogas Vigo, Portugal).

The aqueous solutions before and after tests were analyzed for zinc(II) concentration by AAS using a Perkin Elmer - AAnalyst 200 at 213 nm in the air-acetylene flame.
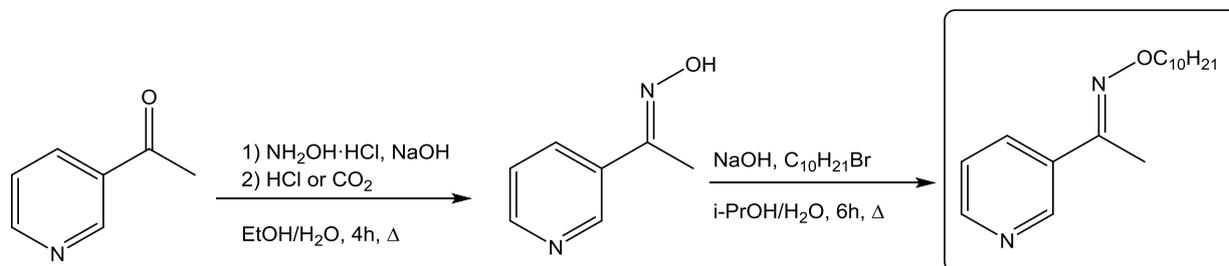
Figure 1. Two-step synthesis of *N*-decyloxy-1-(3-pyridyl)ethanoimine

2.2 PEHFSD experiments

The experimental setup used for carrying out PEHFSD experiments is shown in Figure 2. The HF experiments were carried out in a polypropylene microporous fiber module Liqui-Cel® Extra-Flow (2.5×8 inch) G501, supplied by Celgrad (USA). The module length and diameter were 28 and 7.7 cm, respectively. The module contained ~10,800 fibers with the effective fiber length 15.6 cm and inner and outer diameters of the fibers were equaled to 214 and 300 μm [6].

The volume of the feed solution in the experiments was 800 cm^3 and the same volume of pseudo emulsion, organic and striping solutions (400 cm^3 for each). The organic phase used in the HF studies contained *N*-decyloxy-1-(3-pyridyl)ethanoimine and toluene with 10% (v/v) addition of decan-1-ol or TBP diluted in ShellSol D70. The concentration of the 3PC1-OC10 was 0.05 and 0.1 M,

whereas the concentration of TBP was 1.4 M (40% v/v) and 2.9 M (80% v/v). The feed solution, containing zinc(II) chloride (1.0 g/L of Zn), sodium chloride (1 M) and hydrochloric acid (1 M), was pumped through the hollow fibers. The stripping phase (H₂O) was dispersed into the organic phase, containing the extractant. The pseudo-emulsion flows through the shell side of the membrane module and the aqueous feed phase flows through the tube side. The overpressure on the tube side was in the range of 20-40 kPa to avoid the transport of the organic phase from entering the hollow fibers through the micropores to the feed solution. The flow rate of the aqueous phase was kept at 290-300 mL/min, whereas the flow rate of the pseudo-emulsion phase was kept at 260-270 mL/min. The experiments were conducted at room temperature (typically 23 ºC).
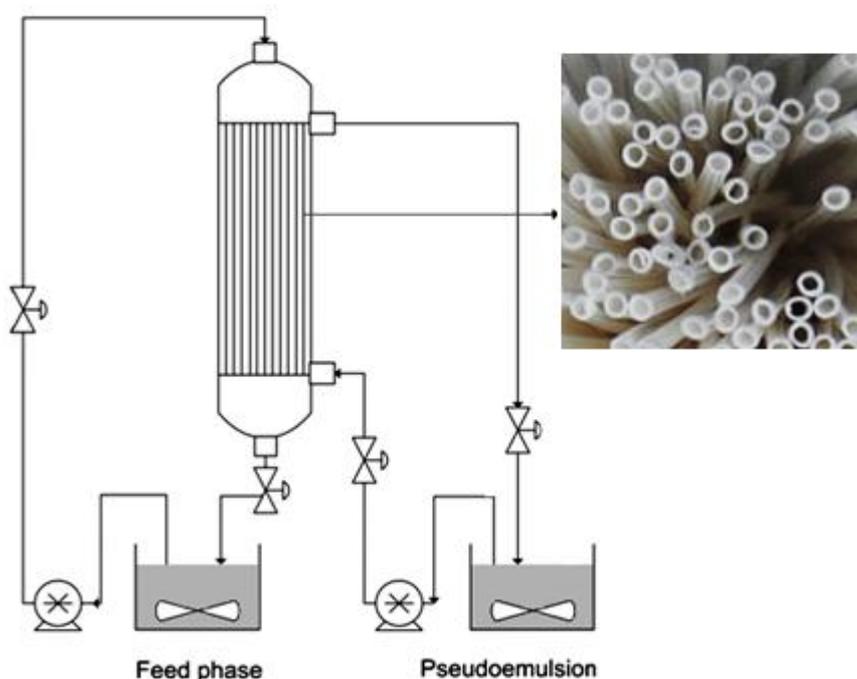
Figure 2. PEHFSD experimental setup

2.3 Calculations

The analysis of the results was made on the basis of the overall mass transfer coefficient of Zn(II) permeation K_P. According to the model for the transport of metal ions in PEHFSD operating in the recycling mode presented in previous studies [7,8], the following linear relationship was derived:

$$V_{aq} \ln \frac{[Zn]_{aq,0}}{[Zn]_{aq}} = St \tag{1}$$

where V is the volume of the phase, t is the time and aq and 0 refer to the aqueous feed phase and initial value, respectively. Thus, the coefficient K_P can be estimated from the slope S of this linear relationship being given as:

$$K_P = -\frac{u_{aq} r_i}{2L} \ln\left[1 - \left(\frac{S}{Q_{aq}}\right)\right] \qquad (2)$$

where u is the linear velocity, Q is the flow rate, r_i is the inner radius of the fiber and L is the fiber length.

3. Results and Discussion

Table 1 summarizes experimental data from PEHFSD experiments using 3PC1-OC1 and TBP as the carriers. Figure 3 illustrates the determination of the overall mass transfer coefficient of zinc permeation from Equations (1) and (2).

Table 1. Exemplary results obtained for aqueous feed solutions containing 1.0 g/L Zn(II), 1 M HCl and 1 M NaCl; strippant: water.

Organic phase	Extraction				Recovery	K_P (m/s)
	15 min	30 min	1 h	2 h		
0.05 M 3PC1-OC10	45%	77 %	96%	-	76%	4.8×10^{-7}
0.1 M 3PC1-OC10	91%	97%	-	-	74%	2.3×10^{-6}
1.4 M (40%) TBP	20%	38%	62%	90%	85%	1.8×10^{-7}
2.9 M (80%) TBP	50%	73%	92%	96%	95%	5.7×10^{-7} [7]
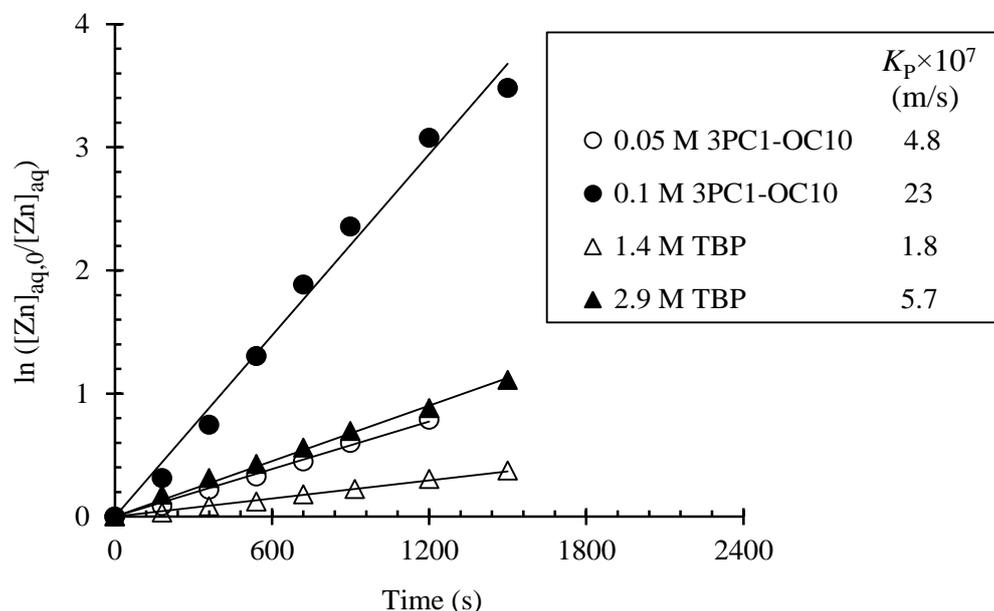
Figure 3. Influence of type and concentration of extractant (3PC1-OC10 or TBP) on zinc transport. Aqueous feed phase: 1.0 g/L Zn(II), 1 M HCl and 1 M NaCl; pseudo-emulsion: (3PC1-OC10 or TBP) and H_2O.

The bests result in terms of mass transfer rate was attained with 0.1 M of 3PC1-OC1. Actually, the extraction efficiency was 97% for 30 min and it was 91% for 15 min of permeation time. The decrease in the concentration of the pyridine extractant from 0.1 M to 0.05 M made the kinetics of the extraction slower, the overall mass transfer coefficient K_P being reduced from 2.3×10^{-6} to 4.8×10^{-7} m/s. It is worth mentioning that the use of 0.05 M 3PC1-OC1 and 80% TBP led to similar kinetics of zinc extraction, as noted from % extraction along time and K_P values (Table 1), as well as from the straight lines depicted in Figure 3. It should be emphasized that in this case the molar concentration of TBP is 58 times higher than that of 3PC1-OC1. The reduction in the concentration of TBP from 80% to 40% decreased the K_P value from 5.7×10^{-7} to 1.8×10^{-7}. Nevertheless, the use of 40% and 80% TBP in the membrane allowed recovering zinc with a very high yield, i.e. 85% and 95%, respectively, after 2 h of permeation. On the other hand, the recovery attained with the pyridine extractant was lower (74-76%), since part of the metal extracted to the organic phase was not stripped with water. However, the stripping process was found more efficient if water was substituted by 5% Na_2SO_4 aqueous solution (data not shown).

4. Conclusion

The novel extractant *N*-decyloxy-1-(3-pyridyl)ethanoimine showed to be a potential carrier of zinc(II) ions from chloride solution using pseudo-emulsion based membrane strip dispersion technique. The efficiency of extraction for a feed phase containing 1.0 g/L of Zn(II) attained very high values (i.e., 96-97%), being comparable to those obtained with the conventional extractant TBP. Nevertheless, the pyridine extractant exhibited a faster kinetics of permeation; the overall mass transfer coefficient of Zn(II) was of the same order of magnitude when the concentration of 3PC1-OC10 in the membrane was much smaller than that of TBP. The recovery of zinc in water (strippant) was found to be in the range of 74-95%. .

Acknowledgement

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