Application of Pseudo-Emulsion Based Hollow Fiber Strip Dispersion (PEHFSD) for Recovery of Zn(II) Using TBP-3PC10 Mixture as Carrier

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The recovery of Zn(II) from chloride solutions using pseudo-emulsion based hollow fiber strip dispersion (PEHFSD) technique with TBP-3PC10 (tributyl phosphate and 1-(3-pyridyl)undecan-1-one oxime) mixture was investigated. The influence of several parameters, among them the concentration of the oxime as modifier of the organic phase was studied. The extractants proposed showed to be appropriate carriers in PEHFSD process and the overall mass transfer coefficient of Zn(II) permeation was found to be 1.0×10^{-6} m/s for the mixtures tested.

1. Introduction

For many years, for industrial scale zinc(II) has been extracted from the hydrochloric acid solution with tributyl phosphate (TBP). Using this type extractant Zn(II) can be extracted in inert chlorocomplex form of $ZnCl_2$ and anionic forms of chlorocomplexes $ZnCl^{3-}$ and $ZnCl_4^{2-}$. Zinc extraction with TBP is affected by many factors such as chloride ions concentration inthe aqueoussolution and the concentration of the extractant in the organic phase. TBP is also a good extractant of organic and inorganic acids, used to regenerate spent nuclear fuel in the PUREX process.

In the case of the Zn(II) extraction from acidic chloride solutions, it is a major disadvantage that TBP co-extracts the mineral acid to the organic solution reducing the extraction of zinc(II) [1]. Due to such extensive use of TBP, it was decided to test the synthesized compound - oxime of 1-(3-pyridyl)undecan-1-one (3PC10) (Figure 1.) as modifier of organic phase to improve TBPextraction properties. The modifier in the extraction process can be defined as a substance whichadded to the organic phase changes the properties of this phase. Modifiers can improve extraction, reduce the surface tension at the interface, so that the extracted compounds can be easier moved to the organic phase. The role of the modifier is also to prevent the formation of third phase [2].

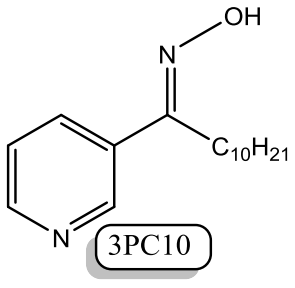

Figure 1. Modifier of TBP- oxime of 1-(3-pyridyl)undecan-1-one

The aim of this work was to study the possibility of using the novel mixture of extractants – TBP-3PC10 for the recovery of Zn(II) from chloride medium using the PEHFSD technique.

2. Experimental

2.1 Reagents

The non-commercial extractant-oxime of 1-(3-pyridyl)undecan-1-one (3PC10) was synthesized in a two stage reaction . In the first stage 1-(3-pyridyl)undecan-1-one was synthesized by treating 3-pyridylcarbonitrile with decylmagnesium bromide in Grignard reaction. In the second stage, the ketone was treated with hydroxylamine hydrochloride in the presence of sodium hydroxide (at pH = 7) [3-5].A purity of the final product-1-(3-pyridyl)undecan-1-one oxime was confirmed by NMR spectroscopy.

1-(3-pyridyl)undecan-1-one oxime (**3PC10**): ^{1}H NMR ($CDCl_3$) δ in ppm: 9.10 (s, 1H, OH); 8.65 (d, 1H, $H_{py}(2)$); 8.30 (d, 1H, $H_{py}(6)$); 8.25 (d, 1H, $H_{py}(4)$); 7.70 (t, 1H, $H_{py}(5)$); 2.80 (t, 2H, CH_2); 1.55 (q, 2H, CH_2); 1.45-1.15 (m, 18H, CH_2); 0.90 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ in ppm: 157.0 (oxime C=N); 149.3 ($C_{py}(6)$); 147.2 ($C_{py}(2)$); 133.7 ($C_{py}(4)$); 132.2 ($C_{py}(5)$); 122.9 ($C_{py}(3)$); 62.8 (-CH_2(CNOH)); 31.6 (CH_2); 29.8 (CH_2); 29.6 (CH_2); 29.3 (CH_2); 29.1 (CH_2); 26.2 (CH_2); 25.6 (CH_2); 22.5 (CH_2); 14.0 (CH_3).

TBP (Rhodia, Netherlands) and toluene (Carlo Erba, France) were used as components of the organic phase. Sodium chloride (ACS reagent, Panreac, Spain), hydrochloric acid (35%) (AR reagent; VWR, USA); 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 in 0.025 and 0.05M and TBP and toluene as the diluents.

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.

2.2 Pseudo-emulsion based membrane strip dispersion tests

The PEHFSD experiments were carried out in the commercial membrane module, Liqui-Cel® Extra-Flow (2.5×8 inch) produced by CELGARD (USA)[6]. Experimental module system is shown in Figure 2. Further module (contactor G501) details are given in Table 1.

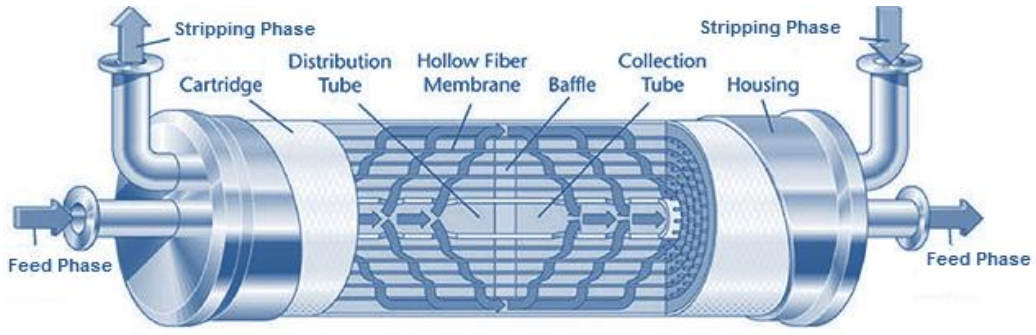

Figure 2. Commercial module hollow fiber

Table 1. Characteristics of hollow fiber membrane module [6,7]

Type of module : G501 (contactor)	
Module length (cm)	28
Module diameter (cm)	7.7
Case inner diameter (cm)	5.55
Centre tube diameter (cm)	2.22
Number of fibers	~10,800
Fiber	X50 – polypropylene
Effective fiber length (cm)	15.6
Inner diameter of the fibers (µm)	214
Outer diameter of the fibers (µm)	300
Pore size (µm)	0.03
Porosity (%)	40
Tortuosity	2.6
Inner interfacial area (m^2)	1.13
Area per unit volume (cm^2/cm^3)	28

The volume of the pseudo-emulsion phase used in the experiments was 800 cm^3, therein 400 cm^3 of the organic solution (0.025 or 0.05M of 3PC10 dissolved in TBP/toluene) and 400 cm^3 of strippant (H_2O). The aqueous phase (800 cm^3) contained zinc(II) in 1 g/L. All tests were carried out for around 2–2.5 h. The samples of the aqueous and pseudo-emulsion phases were collected at regular time intervals, during the process. The overpressure on the tube side was in the range of 20-40 kPa. Both phases were pumped to the module by two pumps capable of variable flows; 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 200–280 mL/min. The experiments were conducted at room temperature.

3. Results and Discussion

Several tests using PEHFSD liquid membrane configuration were carried out by varying the composition of the organic phase. Exemplary results are displayed in Table 2. The analysis of the kinetics of the extraction was made on the basis of the overall mass transfer coefficient of Zn(II) permeation K_P. This coefficient was calculated according to the model for the transport of metal ions in PEHFSD operating in the recycling mode presented in a previous study [1]. Figure 3 illustrates the linear relationships obtained, which allow to derive K_p values.

As observed, the addition of a small concentration (0.025–0.05 M) of the non-commercial 3PC10 extractant in the membrane phase, which contains 50% of TBP, strongly increased the extraction rate. In fact, the overall mass transfer coefficient K_P was almost four times higher in the presence of the pyridineketoxime reagent. On the other hand, the mixtures TBP-3PC10 and TBP (100%) led to comparable K_P values ($1.0–1.4 \times 10^{-6}$ m/s). The increase in the concentration of 3PC10 from 0.025 to 0.05 M had no significant effect on the kinetics of zinc extraction, the K_P values being

1.0×10^{-6} m/s. It is worth mentioning that if an organic phase with 0.05 M of 3PC10 (without TBP) was used, the expected value for K_P would be much lower (i.e., 4.9×10^{-7}m/s [8]), which also emphasizes the importance of the presence of TBP in the mixture. Hence, the mixture TBP-3PC10 showed to be a potential carrier of Zn(II) ions from acidic chloride solution. In addition, the recovery of Zn(II) was verified to be very high (95-100%), the overall extraction/stripping performance being more attractive than that of single TBP. As stated before, one major disadvantage of the use of TBP is due to HCl co-extraction to the organic solution reducing the extraction of zinc(II). Therefore, the study ought to be further intensified to optimize the concentration of the oxime modifier in the organic phase, as well as the amount of TBP under various compositions of the feed phase.

Table 2. 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 15 min	Extraction 30 min	Extraction 1 h	Extraction 2 h	Recovery	K_P (m/s)
1.8 M (50% v/v) TBP	28%	50%	78%	96%	87%	2.8×10^{-7}
3.6 M (100%) TBP	77%	95%	97%	93%	92%	1.4×10^{-6}
0.025 M 3PC10+1.8M TBP	70%	95%	99%	99%	~100%	1.0×10^{-6}
0.05 M 3PC10+ 1.8 M TBP	67%	94%	99%	100%	95%	1.0×10^{-6}

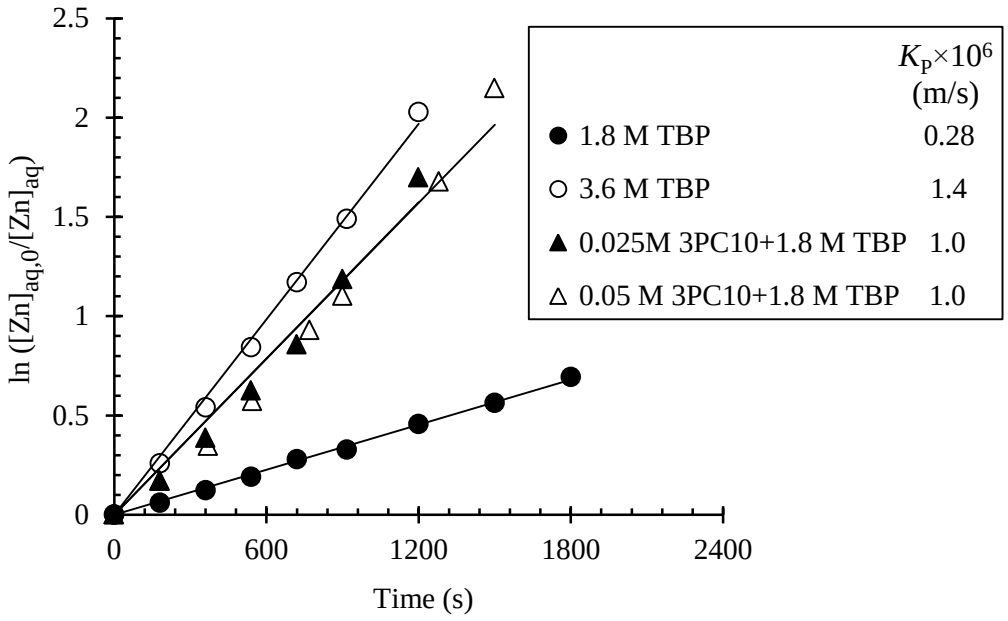

Figure 3. Influence of composition of the organic phase on zinc transport. Aqueous feed phase: 1.0 g/L Zn(II), 1 M HCl and 1 M NaCl; pseudo-emulsion: (3PC10+TBP or TBP) and H_2O.

4. Conclusion

The mixture TBP-3PC10 (tributyl phosphate and 1-(3-pyridyl)undecan-1-one oxime) showed to be a potential extractant of zinc(II) ions from chloride solution using pseudo-emulsion based membrane strip dispersion technique. The recovery of zinc from a feed phase containing 1 g/L of solute attained very high values (i.e., 95-100%) by using 0.025-0.05 M of 3PC10 diluted in TBP/toluene, the yield being higher than that achieved with 100% of TBP in the membrane. In what concerns the kinetics of extraction, the results obtained with the mixtureTBP-3PC10 were found comparable to those obtained with 100% of TBP. Further studies are necessary to optimize the concentration of 3PC10 in the mixture under variable feed compositions.

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