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Selective Transport of Bismuth from Heavy Metal Solution by Ionic Liquid-Based Polymer Inclusion Membrane IL-PIM

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Abstract: Bismuth is an important critical metal which is under risk of supply. It is mainly found and extracted at trace amounts in copper, lead, tin and gold mining by-product. In this work, we present the results of the selective transport of trace bismuth Bi(III) from a solution of heavy metals by an Ionic liquids-based Polymer Inclusion Membranes (PIM), using the task-specific ionic liquid: trihexyl(tetradecyl) phosphonium salicylate (THTDPS), as extractant and ion carrier. The TS-IL was first synthesized by exchanging the inorganic anion of trihexyl(tetradecyl) phosphonium chloride Cyphos IL 101 with the organic anion of sodium salycilate. Important parameters influencing extraction and transport have been examined and optimized. The studied PIM is composed of 50% CTA, and 50% THTDPS without any additional chemical (modifier or plasticizer). The performance and stability of the PIM was carried out in depth. The selective transport of Bi(III) from a solution containing the heavy metals: Pb(II), Cu(II), Cd(III), Ni(II) was carried out. The feed phase is composed of trace concentration of the metal ions (10 $mg.L^{-1}$) in 1M HCl. The optimal receiving phase conditions were studied and the best composition is EDTA 0.05M at pH 5. The PIM exhibits a good selectivity towards Bi(III), and the transport rates are reported to be 74.8 ± 9% for Bi(III), against 62.23%, 14.8 ± 9%, 3.15 ± 3.15%, and 2.5 ± 2.5% for Cd(II), Pb(II), Cu(II), and Ni(II), respectively. The study of the stability shows that the PIM can be used up to 5 cycles of extraction-back extraction without significant decrease in the efficiency.

Keywords: Ionic Liquids, Polymer inclusion membranes, Metal separation

Introduction

The extraction, separation, and recovery of strategic metal ions at trace amounts, either from ores in mines industry, or from end-of-life electronic materials in the recycling industry, or from different industrial wastewater recycling systems, constitute a very large domain of investigation. Bismuth (III) is rare and expensive, this latter attracts a lot of interest because it is the most harmless heavy metal, and has the status of a "green element". It is widely used in various fields such as the manufacture of special alloys and in the pharmaceutical, cosmetic, and medicinal industry. The special properties of Bismuth (III) make it very interesting to study (Mohan, 2010).

- Selection and peer-review under responsibility of the Organizing Committee of the Conference

The first work to report the use of polymer inclusion membranes in the extraction and separation of Bi was published by Kazemi et al. (2021). The optimal conditions were investigated. The PIM that demonstrated the most effective extraction is composed of 50% D2EHPA as ion carrier and PVC as base polymer. The PIM selectivity showed a minimal co-extraction of other metals, the stability and reusability demonstrated consistent extraction and back-extraction efficiency over 15 cycles.

Ghaderi et al.(2022), investigated the selective extraction and back extraction of Bi from chloride solution. The study of the optimal conditions led to the development of a PIM composed of 40% CTA as base polymer, 25% trioctylamine (TOA) as ion carrier, and 35% TBP as plasticizer. The speciation was also investigated and it is reported that Bi(III) is extracted under anionic complex $BiCl_5^{2-}$. The PIM showed high selectivity toward Bi(III) in the presence of other heavy metals and inorganic anions.

The first work that achieved direct transport of Bi(III) (Meziani et al., 2022), carried out a comparative study on the extraction, recovery and transport of Bi(III) using ionic liquids as ion carriers. The ionic liquids are the quaternary ammonium salt Aliquat 336, and quaternary phosphonium salt trihexyltetradecylphosphonium chloride THTDPCl, respectively. PIMs are composed of 30% CTA as base polymer, 45% NPOE as plasticizer, and 25% ionic liquid IL. In the reusability study both PIMs showed efficient extraction efficiency even after 7 cycles. THTDPCl-based PIM is showed to be the most stable.

The first application of PIM separation process for the recovery of Bi(III) from real industrial samples are reported by Kazemi and Yaftian, (2024). Kazemi investigated the application of a PVDF-HFP based PIM in the selective extraction and back extraction of Bi(III) from Zinc electrowinning sludge sample. The optimal PIM composition is 60% PVDF-HFP as base polymer and 40% D2EHPA as ion carrier. The PIM is used on the selective extraction of Bi(III) from real zinc electrowinning sludge sample, and the separation was highly efficient.

In this work, a new ionic liquid trihexyltetradecylphosphonium salicylate THTDPS was used as ion carrier in a polymer inclusion membrane for the extraction, and transport of Bi from a chloride medium. The PIM is composed of 50% cellulose triacetate CTA as polymer and 50%THTDPS.

Method

Reagents

All reagents were analytical grade. trihexyltetradecylphosphonium (Cyphos IL 101) and sodium salycilate $C_7H_5NaO_3$ were provided by Sigma-Aldrich. Bismuth (III) solutions were prepared from Bismuth Oxyde Bi_2O_3, provided by Sigma-Aldrich. Chloride acid (HCl), nitric acid (HNO_3), and sulfuric acid were respectively provided by Sigma-Aldrich, CHEMINOVA, and MERCK. Acetone and Chloroform are considered as industrial grade, and were respectively provided by Janssen Chimica, and CARLO ERBA

PIM Preparation

PIMs were prepared following the procedure already described by (Fontàs et al., 2007) . A chloroform solution of CTA (200 mg in 20 mL), and the ionic liquid with the same mass (200mg) were poured into a 9.0 cm diameter flat bottom glass Petri-dish. The dish was set horizontally and covered loosely. The solution was allowed to evaporate over 24 h at room temperature. The film was then carefully peeled out from the bottom of the Petri dish.

Apparatus

All metal samples were analysed using a flame atomic absorption spectrometer (AAS) (Schimadzu AA6800). Bi at λ= 223.1 nm, Pb at λ = 283.3 nm, Cd at λ =228.8 nm, Cu at λ = 324.8 nm.

Results and Discussion

Effect of Bi Concentration

The effect of Bi concentration and the maximum extraction capacity of the PIM is investigated by putting in contact different solutions of Bi at different concentrations from 5 mg L^{-1} to 150 mg L^{-1} with PIM1 (50%CTA-50%THTDPS). The results are shown in Figure 1.

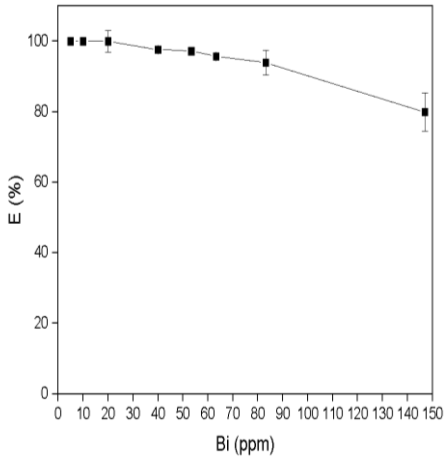

Figure 1. Extraction of Bi(III) at different concentrations. PIM1 = 50%CTA50%THTDPS. Feed phase: 1M HCl, V=10ml. time: 24h**.**

Figure 1 shows that from an initial concentration of 5 mg L^{-1} until 80 mg L^{-1} the extraction efficiencies don't go below 90%. And it decrease to 79.9% ±5.4% for an initial concentration of 150 mg. L^{-1}.

Recovery of Bi from Loaded PIM

PIMs loaded at different concentrations from previous experiments were put in contact with two different stripping solutions (1M HNO_3 and 0.05M EDTA at pH 5) at a volume V=10mL for 4 hours agitation time. The results are shown in figure 2. As can be observed, the chelating agent EDTA is the most suitable for the back-extraction of Bi from loaded PIM.

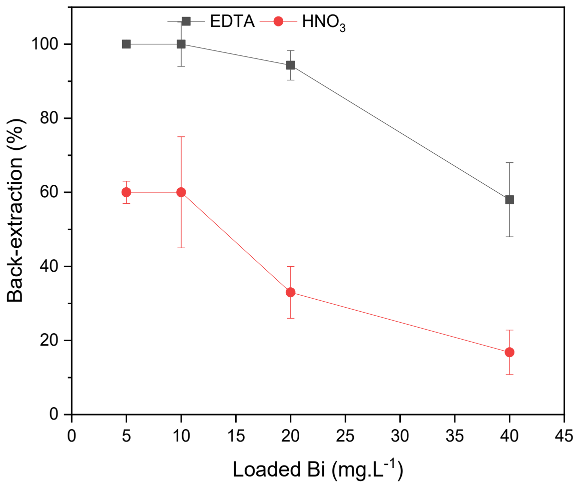

Figure 2. Back-extraction of Bi from different loaded-PIMs using EDTA (black) and HNO_3 (red) as stripping agents. [EDTA]=0.05M at pH 5. [HNO_3]=1M. Time: 4 h.

Reusability

The reusability of the PIM was studied by carrying out several cycles of extraction-back-extraction. Figure 3 highlights the results of the extraction and back-extraction. As can be observed, the extraction efficiency started to decrease below 90% only at the 6th cycle (89.5% ±6.3%). In the case of the back-extraction efficiencies, the nearly complete recovery of the metal is performed for every cycle.

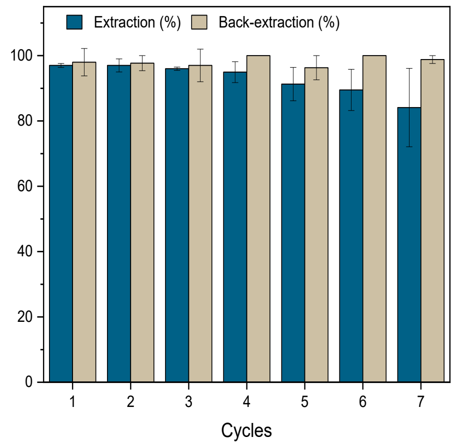

Figure 3. Reusability of PIM (50%CTA-50%THTDPS).

PIM made of 50% CTA+ 50%THTTPS is a promising membrane for the selective extraction and transport of Bi. It is of paramount importance to take into account the SL extraction performances, and the possible complete recovery via the chelating agent EDTA and the reusability for several cycles.

Transport Experiments

Transport experiments were carried out by putting the PIM in the middle of a transport cell separating two compartments: the feed phase, and the receiving phase. Each phase has a volume of V= 150ml and the diameter of the circular contact area of the PIMs is d= 1cm. HNO_3, EDTA, and NaCl were employed as stripping agents. Figure 2 shows that EDTA gives the highest transport rate of 70.6% ± 2%, after 24 hours, followed by HNO_3 which is slightly less efficient with a transport rate of 65% ± 2% and NaCl exhibited a very weak transport rate of 16.5%.

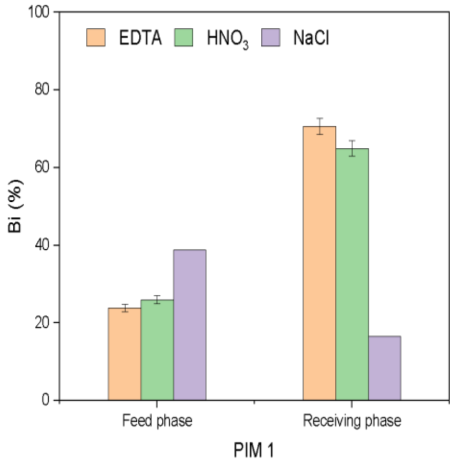

Figure 4. effect of different receiving phases on the transport rate of Bi. Feed phase: 20mg L^{-1} Bi in HCl 1M. V: 150ml. T= 24H. [HNO3] = 1M, [NaCl] =3M, [EDTA] = 0.05M at pH5. PIM= PIM 1.

Selective Transport of Bi from a Solution of Heavy Metals

Competitive transport of Bi (III) from mixture composed of the heavy metal ions Cd (II), Cu (II), Pb (II), and Ni (II) was carried out. The transport was carried out under the same optimal conditions previously determined for individual Bi (III) transport. The feed phase is composed of [Bi]= [Cd]= [Cu]= [Pb]= [Ni]= 10 mg L^{-1} in 1M HCl and the receiving phase is EDTA 0.05M at pH 5. Metals rate in the feed and receiving phases, and separation factors Bi/ Metal are summarised in table 1. The best separation is obtained with Cu and Ni with a separation factor $SF_{Bi/Metal}$ >>>100 followed by Pb with a significant separation $SF_{Bi/Metal}$ = 42.7±42. Finally, Cd was the least separated with $SF_{Bi/Metal}$=2.1±0.98. The presence of other heavy metal ions didn't affect the transport efficiency of Bi which is reported to be 74.8%±9%. As can be observed, there is a co-transport of the element Cd with an efficiency of 62.2%.

Table 1. Separation of Bi from heavy metals. T= 24 hours. [M]= 10 mg L^{-1}. [EDTA]= 0.05 M. pH= 5.

Metals (M)	Feed phase (%)	Receiving phase (%)	D	$SF_{Bi/Metal}$
Bi	17.2 ± 8	74.8 ± 9	3.54 ± 1.9	
Cd	34.38	62.23	1.65	2.14 ± 0.98
Cu	95 ± 5	3.15 ± 3.15	0.033 ± 0.033	Quant
Ni	96.7 ± 3.3	2.5 ± 2.5	0.026 ± 0.026	Quant
Pb	85.2 ± 9	14.8 ± 9	0.1855 ± 0.1245	42.685 ± 42.065

Conclusion

The obtained results prove the great potential of this separation process and open up perspectives to further optimisations for specified applications. The complete extraction and back-extraction of Bi can be carried out at in a concentration rang that goes from 5 mg L^{-1} to 20 mg L^{-1}. Moreover, the reusability of the PIM exhibited a possible use of 5 cycles of extraction and back-extraction without significant decrease in the efficiency. The selective transport of bismuth from a heavy metal Pb, Cu, Cd, and Ni solution is successfully carried out by using the optimal conditions and Bi was separated from all the divalent metals. Only Cd was co-transported with Bi.

The results promise the conception of a PIM separation process for the practical use in the recovery of Bi from primary or secondary sources. Further works will be done, in the aim to optimize the PIM composition and reduce the intremembrane interactions, using other environmentally friendly chemical agents, and perform practical separations using real mineral/recycling samples.

Scientific Ethics Declaration

* The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM Journal belongs to the authors.

Conflict of Interest

* The authors declare that they have no conflicts of interest

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