Physicochem. Probl. Miner. Process., 58(6), 2022, 152997

http://www.journalssystem.com/ppmp

Physicochemical Problems of Mineral Processing

ISSN 1643-1049

Separation of Co from Ni and Li from chloride media using polymer inclusion membrane system with thiosalicylate based ionic liquid

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Abstract: The selective removal of cobalt(II) from aqueous chloride solutions containing nickel(II) and lithium(I) was studied. The facilitated transport of metal ions through polymer inclusion membranes (PIMs) with trihexyl(tetradecyl)phosphonium thiosalicylate [PR4][TS] under various conditions was analyzed. In order to optimize the separation process, several factors such as the ion carrier concentration in the membrane as well as of the effect of the concentration of the acids in the source/receiving phases were investigated. The results show that PIM containing 25% CTA as the polymer support, 40% NPOE as the plasticizer and 35% [PR4][TS] allow the selective recovery of more than 90% of cobalt(II) from 6 mol/dm^3 hydrochloric acid into 0.5 mol/dm^3 sulfuric acid.

Keywords: cobalt, lithium, Ionic liquids, polymer inclusion membranes

1. Introduction

Cobalt and lithium arerecognized as critical and strategic metals. Lithium has a low melting point and density. This metal is soft and light. Whereas, cobalt and nickel are hard ferromagnetic metals. They are very importantdue to their properties, wide range of applications and the high demand for the production of lithium-ion batteries (LIBs), which are used in many electronic devices such as telephones, personal computers, cameras, etc. Nevertheless, spent batteries require suitable recycling. The recovery of cobalt is among the most important stages in the hydrometallurgical technology of processing electronic waste. There are numerous literature reports regarding the possibility of recovering metals from waste (Pospiech, 2013; Chagnes and Pospiech, 2014; Wang et al. 2014; Winslow et al. 2018; Nguyen and Lee, 2020; Yuan et al. 2022;). The hydrometallurgical processes of leaching LIBs with hydrochloric acid (HCl) result in a leach liquor containing metals, mainly cobalt, lithium and nickel, sometimes manganese, copper, iron, zinc. The selective separation of Co(II) from the mixture of other metal ions is a key step in obtaining pure metal. A number of cobalt extracting agents are known, such as Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid) (Stefaniak et al., 2020), di(2-ethylhexyl)phosphoric acid (D2EHPA/DEHPA), tricaprylylmethylammonium chloride/trioctylmethylammonium chloride (Aliquat 336) (Kang et al. 2010; Swain et al. 2010; Cheng et al., 2019; Alvial-Hein et al. 2021), etc.

Recently, ionic liquids (ILs) have been investigated as an alternative to known extractants used for the separation of many metals from aqueous solutions such as Co(II) and Ni(II) (Rybka and Regel-Rosocka et al., 2012; Coll et al. 2012; Cholico-Gonzalez et al., 2015; Turgut et al. 2017; Diabate et al. 2018; Janiszewska et al., 2019). Task specific ionic liquids (TSILs) with coordinating anions are of particular importance. Fisher et al. (2011) reported that ILs based on phosphonium and ammonium cations containing functionalized anions (thiol-, thioether-, hydroxyl-, carboxylate-, thiocyanate , etc.) are useful for the removal of many heavy metalsfrom aqueous solutions. In particular, ILs containing the sulfur demonstrated very interesting extracting properties in separation processes. For instantce, trihexyl(tetradecyl)phosphonium thiosalicylate [PR4][TS] and tricaprylmethylammonium thiosalicylate [A336][TS] were used as extractants of Cu, Ag, Pt and Hg from aqueous solutions.

IL are also studied as the ion carrier for the synthesis of polymer inclusion membranes (PIMs). A polymer membrane based on cellulose triacetate (CTA) or poly(vinyl chloride) (PVC) separates

DOI: 10.37190/ppmp/152997

the source phase containing mixture of metal ions and the receiving phase. The ion carrier present in the membrane enables the selective transfer of metal ions from the source phase into the receiving phase (Nayl, 2010; Regel-Rosocka et al. 2012; Pospiech, 2015; Baczynska et al. 2016; Alguacil, 2017; Makowka and Pospiech 2019, 2021). The process conditions and the composition of the PIM membrane require detailed experimental studies to ensure high selectivity and efficiency.

In this work, [PR4][TS] was applied as the carrier for the synthesis of PIM based on cellulose triacetate (CTA) for the facilitated transport of Co(II) from a hydrochloric acid solution containing Ni(II) and Li(I). PIM with [PR4][TS] as the ion carrier was used for the competitive transport of cobalt(II), nickel(II) and lithium(I) for the first time. The main aim of this work was to develop optimal conditions for the effective and selective recovery of Co(II), such as the carrier concentration in the membrane, the concentration of hydrochloric acid and sulfuric acid in the source phase and the receiving phase, respectively.

2. Materials and methods

2.1. Chemicals

The inorganic chemicals: cobalt(II) chloride ($CoCl_2 \cdot 6H_2O$), lithium chloride (LiCl), nickel(II) chloride ($NiCl_2 \cdot 6H_2O$), hydrochloric acid (HCl), sulfuric acid (H_2SO_4) were of an analytical grade (POCh, Poland). The organic reagents such as trihexyl(tetradecyl)phosphonium thiosalicylate [PR4][TS] (purity≥97%), cellulose triacetate (CTA), dichloromethane, 2-nitrophenyl octyl ether (NPOE) were of an analytical reagent grade (Aldrich).

2.2. Polymer inclusion membranes (PIMs)

PIMs were synthesized according to the procedure presented in previous works (Pospiech, 2013; Pospiech, 2015; Makowka and Pospiech, 2019, 2020). The mixture containing appropriate amounts of CTA (1.25 g CTA/100 cm^3),[PR4][TS],(0.1 M), 10% NPOE was prepared for the synthesis of PIM. The membrane was formed by the evaporation of dichloromethane from the prepared mixture.

2.3. Transport experiment

The transport experiment through PIMs and the research methodology were described in detail in previous works (Pospiech, 2013; Pospiech, 2015; Makowka and Pospiech, 2019, 2020). The volumes of the source phase and the receiving phase were the same (100 cm^3 each). The source phase contained 0.02 mol/dm^3 Co(II) and 0.002 mol/dm^3 Li(I) and 0.002 mol/dm^3 Ni(II) in a hydrochloric acid solution. The surface of the membrane was 12.6 cm^2. The aqueous source and the receiving phases were pumped with a peristaltic pump (PP1B-05A type, Zalimp). The concentrations of metal ions were analyzed by means of an atomic emission spectrometer MP-AES 4200 (Agilent). The kinetics of the metal ion transport was described by the first-order reaction (Danesi, 1984):

$$ln\left(\frac{c}{c_i}\right) = -kt \qquad (1)$$

In order to calculate rate constant (k), a diagram of the dependence of $\ln(c/c_i)$ vs. time was prepared for each transport of metal ions. Permeability coefficient (P) and initial flux (J_i) were calculated according to the equations presented in previous works (Pospiech, 2013; Pospiech, 2015).

3. Results and discussion

3.1. Effect of carrier concentration in PIMs on their transport and separation properties

The composition of the polymer membrane has a significant influence on the efficiency and cost effectiveness of the PIM method as well as on the kinetics of the metal ion transport. The concentration of the ion carrier in the membrane is of particular importance. Therefore, the effect of [PR4][TS] the concentration in PIM on the transport of Co(II), Ni(II) and Li(I) was investigated. The concentration of [PR4][TS] was varied from 0.25 to 2 mol/dm^3 (based on the volume of plasticizer). 0.5 mol/dm^3 H_2SO_4 was used as the receiving phase. The source phase contained 0.02 mol/dm^3 Co(II), 0.002 mol/dm^3 Li(I) and 0.002 mol/dm^3 Ni(II) in 6 mol/dm^3 HCl. The results indicate that only Co(II) was transported from the feed solution into the receiving phase, while Ni(II) and Li(I) ions remained in the source phase. As can be seen from Fig. 1, initial flux (J_i) for the transport of Co(II) increases with an increasing carrier concentration up to 1.5 mol/dm^3 and then its value slightly decreases. PIM with a different concentration of ion carrier differed in thickness (Table 1). The kinetic parameters of the transport of Co(II) through PIMs are listed in Table 1. It can be concluded that both a low and too high concentration of the carrier can adversely affect the transport properties of the membrane. The conducted research allows the optimal carrier concentration in the membrane to be determined as 1.5 mol/dm^3. This PIM contained: 25% w/w CTA, 40% w/w NPOE and 35% w/w [PR4][TS]. Other researchers found that some ion carriers (i.e. ammonium salts, phosphonium salts) can have the properties of a plasticizer (Kozlowski et al., 2006; Regel-Rosocka, 2012; Turgut et al., 2017). In this case, [PR4][TS] can also act as a plasticizer. Therefore, it is observed that the concentrated carrier [PR4][TS] and plasticizer NPOE can form a film on the membrane surface. This causes the viscosity to increase which limits the transport of Co(II) through PIM and reduces the transport rate.

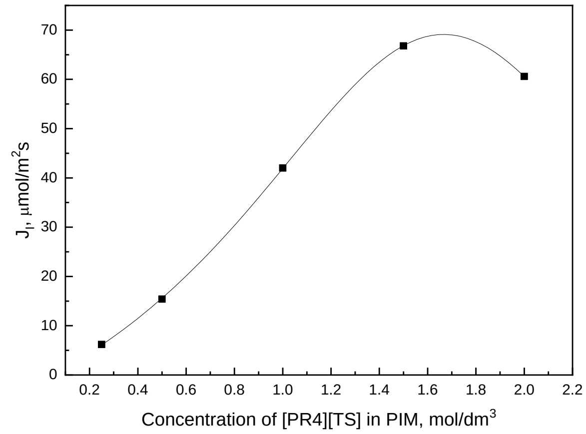

Fig. 1. Effect of [PR4][TS] concentration on initial flux of Co(II). Conditions: source phase 0.02 mol/dm^3 Co(II), 0.002 mol/dm^3 Li(I) and 0.002 mol/dm^3 Ni(II) in 6 mol/dm^3 HCl; receiving phase: 0.5 mol/dm^3 H_2SO_4

Table 1. Kinetic parameters for Co(II) transport depending on carrier concentration in PIM. Conditions as in Fig. 1

[PR4][TS], mol/dm^3	Rate constant, k, h^{-1}	Permeability coefficient, P, µmol·s^{-1}	Recovery factor, %	PIM thickness, µm
0.25	0.014	0.310	19.5	75
0.5	0.035	0.795	42.9	82
1.0	0.095	2.100	77.6	84
1.5	0.151	3.340	91.6	88
2.0	0.137	3.031	88.3	92

3.2. Effect of hydrochloric acid

In hydrochloric acid solutions Co(II) ions exist as the anionic chloro-complexes (Rybka and Regel-Rosocka, 2012). Thus, the concentration of this acid can have a significant impact on the transport rate of metal ions. The effect of the concentration of hydrochloric acid in the source phase on the transport of metal ions was investigated using PIM containing 25% w/w CTA, 40% w/w NPOE and 35% w/w [PR4][TS]. The aqueous source phase contained 0.02 mol/dm^3 Co(II), 0.002 mol/dm^3 Li(I) and 0.002 mol/dm^3 Ni(II) at variable concentrations of HCl. This concentration was varied between 0.5 mol/dm^3 to 6 mol/dm^3. Fig. 2 shows the dependence of the cobalt(II) recovery (RF, %) versus time for the transport of metal ions at various HCl concentrations. Other metals (Ni(II) and Li(I)) were not detected in the receiving phase, which proves the high selectivity of the process.Table 2 presents the kinetic parameters such as rate constant (k), permeability coefficient (P) and initial flux (J_i).

The transport efficiency of Co(II) rises with increasing acid concentration. We can observe that the increasing ionic strength rises the extracting ability of [PR4][TS] because then the thermodynamic activity of the metal salt extracted also grows. The presence of chloride ions and an increment in their concentration in the feed phase positively influences the results of cobalt ion transport. Leyma et al. (2016) reported that chloride anions function as a salting out agent. Blitz-Raith et al. (2007) also observed that the recovery of Co(II) across PIM with Aliquat 336 increased with rising HCl concentration. This can be justified as follows: the chloro-complexes of Co(II) form ion-pairs with cations coming from the ion carrier at the membrane/solution interface. When the hydrochloric acid concentration is higher than 5 mol/dm^3, the concentration of anionic chloro-complexes of Co(II) is also higher. Cobalt complexes such as [$HCoCl_3$] and [H_2CoCl_4] are present in concentrated hydrochloric acid solutions. The ion carrier [PR4][TS] extracts the metallic species through an anion exchange, and as Co(II) forms anionic complexes in chloride solutions, it is possible to transfer it from HCl solutions. Transport of Co(II) is effective from the concentrated HCl in the source phase, because the $CoCl_4^{2-}$ complex predominates as the chloride concentration increases.

Table 2. Kinetic parameters for transport of Co(II) in depending on HCl concentration in source phase. Conditions as in Fig. 2

[HCl], mol/dm^3	Rate constant, k, h^{-1}	Permeability coefficient, P, μmol·s^{-1}	Initial flux, J$_i$, μmol·m^{-2}s^{-1}	Recovery factor after 16 h, %
1	0.031	0.665	13.3	39.8
2	0.042	0.930	18.6	51.6
4	0.123	2.72	54.4	85.4
6	0.151	3.34	66.8	91.6

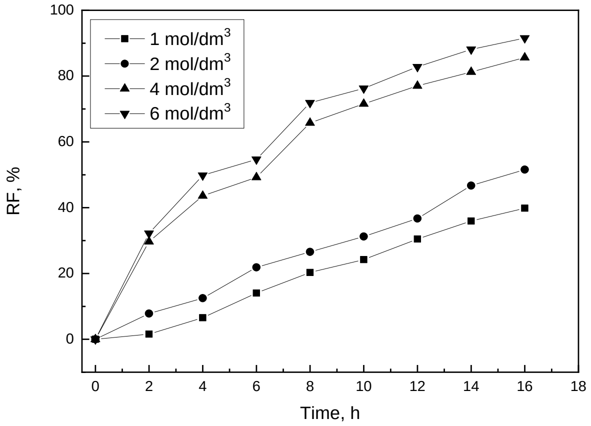

Fig. 2. Effect of HCl concentration on recovery factor of Co(II) (RF, %). Conditions: source phase 0.02 mol/dm^3 Co(II), 0.002 mol/dm^3 Li(I) and 0.002 mol/dm^3 Ni(II) in HCl solutions; receiving phase: 0.5 mol/dm^3 H_2SO_4. PIM: 25% w/w CTA, 40% w/w NPOE and 35% w/w [PR4][TS]

3.3. Effect of H_2SO_4 concentration in the receiving phase

It is very important to investigate the influence of the stripping phase composition on the transport of metal ions in order to making this process more efficient. The effect of the H_2SO_4 concentration in the receiving phase on the transport of Co(II) from 6 mol/dm^3 HCl was studied using PIM containing 25% w/w CTA, 40% w/w NPOE and 35% w/w [PR4][TS]. Fig. 3 shows the plot of $\ln c/c_i$ versus H_2SO_4 concentration for Co(II). Other metals remained in the feed phase.

The kinetic parameters are presented in Table 3. It can be obseved that the transport rate was the highest when the concentration of sulfuric acid in the receiving phase was low. Raising the acid concentration is not conducive to increasing the efficiency of the transport of metal ions. The percentage of Co(II) recovery varied from 91.6 to 32.1 % as the concentration of H_2SO_4 varied from 0.5 to 2 mol/dm^3, respectively. Thus, 0.5 M sulfuric(VI) acid can be considered a suitable receiving phase. During the stripping, the metal-ion carrier complex disintegrates at the interface (the membrane/the receiving phase) and Co(II) ions pass into the aqueous receiving phase. The released carrier particles can again be involved in the transfer of metal ions from the source phase. High concentration of sulfuric acid(VI), which is dissociated into ions (H^+, HSO_4^-, SO_4^{2-}) negatively affects the disintegration of the metal-ion carrier complex.

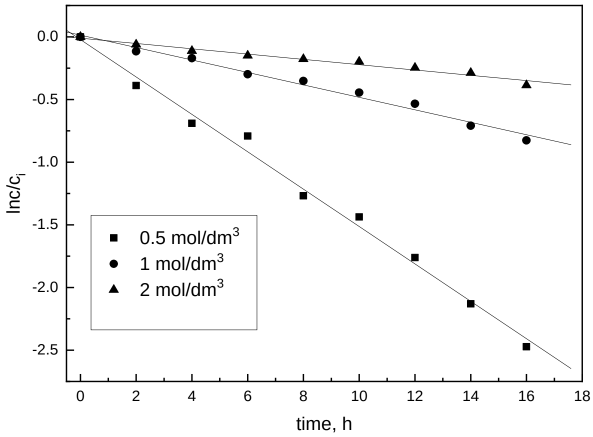

Fig. 3. Effect of H_2SO_4 concentration in receiving phase on the kinetics of Co(II) transport. Conditions: source phase 0.02 mol/dm^3 Co(II), 0.002 mol/dm^3 Li(I) and 0.002 mol/dm^3 Ni(II) in 6 mol/dm^3 HCl solutions; receiving phase: H_2SO_4, PIM: 25% w/w CTA, 40% w/w NPOE and 35% w/w [PR4][TS]

Table 3. Kinetic parameters for transport of Co(II) in depending on H_2SO_4 concentration in receiving phase. Conditions: source phase 0.02 mol/dm^3 Co(II), 0.002 mol/dm^3 Li(I) and 0.002 mol/dm^3 Ni(II) in 6 mol/dm^3 HCl solutions; receiving phase: H_2SO_4. PIM: 25% w/w CTA, 40% w/w NPOE and 35% w/w [PR4][TS]

H_2SO_4, mol/dm^3	Rate constant, k, h^{-1}	Permeability coefficient, P, μmol·s^{-1}	Initial flux, J$_i$, μmol·m^{-2}s^{-1}	Recovery factor after 16 h, %
0.5	0.151	3.340	66.8	91.6
1	0.049	1.070	21.4	56.3
2	0.022	0.489	9.77	32.1

3.4. The stability of PIM

The stability of the membrane was evaluated by using the same membrane (PIM: 25% w/w CTA, 40% w/w NPOE and 35% w/w [PR4][TS] over three cycles of the transport (conditions as in Fig. 1). The transport efficiency of Co(II) was sufficiently high after the first transport cycle (RF = 91.6%). The recovery factor for Co(II) was slightly lower after the second cycle (RF = 86.4%). The efficiency of Co(II) transport was much lower (67.3%) in the third cycle of the transport because after each extraction-stripping step, a slight amount of [PR4][TS] was leached from the membrane surface. When the concentration of the ion carrier in the PIM becomes too low, it affects the transport efficiency.

4. Conclusion

In the transport of Co(II) through PIM using phosphonium ionic liquid [PR4][TS] as the carrier, excellent selectivity and permeation of this metal ion was obtained. The transport rate is influenced by the HCl concentration in the source phase, H_2SO_4 concentration in the receiving phase, and the concentration of the ion carrier in the membrane. The transport of metal ions through PIM containing PIM: 25% w/w CTA, 40% w/w NPOE and 35% w/w [PR4][TS] made it possible to recover more than 90% of Co(II). A too high concentration of the ion carrier in the membrane reduces its transport and separation properties. Long-lasting transport across PIM is a drawback of this system. This transport was more effective when the concentration of HCl in the source phase was high, i.e. 6 mol/dm^3. A low concentration of sulfuric acid in the receiving phase favors a better recovery of cobalt(II) from the solution.

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