Korean J. Chem. Eng., 39(4), 1011-1019 (2022)
DOI: 10.1007/s11814-021-0986-y

pISSN: 0256-1115
eISSN: 1975-7220

Selective separation of gallium from various ions by polymer inclusion membranes based on CTA/PVC blend using TOPO as carrier

Osman Tutkun† and Kurmancan Kaparova

Department of Chemical Engineering, Faculty of Engineering, Kyrgyz-Turkish Manas University, 56, Tynchtyk Avenue, Djal, 770043 Bishkek, Kyrgyzstan
(*Received 12 June 2021 • Revised 26 September 2021 • Accepted 16 October 2021*)

Abstract−Selective transport of gallium from HCl media containing other ions such as Zn, Co, and Ni, by polymer inclusion membranes (PIM), based on CTA/PVC blend using trioctylphosphine oxide (TOPO) as carrier and 2-nitrophenylpentyl ether (2-NPPE) as plasticizer is studied. The effect of various parameters such as the HCl concenration in the feed, HCl concenration in the stripping phase, carrier (TOPO) concentration, 2-NPPE concentration, the cellulose triacetate (CTA)/poly(vinyl chloride) (PVC) as the polymer-blend was experimentally studied and the optimum conditions were determined. It was possible to selectively extract gallium ions from the ions (Zn, Co, and Ni) in the acidic solutions. The separation factors of gallium over Zn, Co, and Ni, at the optimum conditions, were found to be of 963, 702, and 514, respectively, for the feed solution of 100 mg/dm^3 Ga, 1,000 mg/dm^3 Zn, 600 mg/dm^3 Co, and 600 mg/dm^3 Ni.

Keywords: Polymer Inclusion Membranes, Gallium Separation, Trioctyl Phosphine Oxide (TOPO), CTA-PVC Blend Membranes, Separation Factor

INTRODUCTION

Gallium has emerged as an important strategic metal that is extensively used in the manufacturing of semiconductor devices for photovoltaic cells and computers since it provides efficient optical transitions as well as high electron mobility [1,2]. It is usually produced as a byproduct of zinc refineries and Bayer liquor obtained during alumina production from bauxite; therefore it mostly is associated with aluminum, zinc and, germanium. The acidic sulfate or chloride solutions from hydrometallurgical production of zinc are an important source of gallium in addition to alkaline Bayer solutions for aluminum [3-6]. Gallium is also used in the medical application where ^{67}Ga ($t_{1/2}$=78 h) is used for palliation of bone pain due to metastatic bone lesions. Besides, accelerator-based production of ^{67}Ga and ^{68}Ga is largely achieved via nuclear reactions ^{67}Zn (p,n) ^{67}Ga, ^{68}Zn (p,2n) ^{67}Ga and ^{68}Zn (p,n) ^{68}Ga [7]. Selective separation of pure gallium radioisotopes produced by cyclotrons or nuclear reactors from the target material and target holder (Zn and Cu respectively) can be achieved by PIMs. Solvent extraction has been developed as a technique for the separation and recovery of metal ions in industrial effluent and discarded wastes [7-11]. While these processes are usually efficient and cost-effective, they present environmental and occupational hazards as the extractants are commonly toxic and corrosive organic diluents are often highly flammable. To reduce the environmental and economic burden, such as the use of large amounts of organic solvent and extractant, several liquid membrane separation techniques such as supported liquid membranes (SLMs) and emulsion liquid membranes (ELMs), have been studied [12-18]. Among all applications just a few have been commercialized [19,20]. Despite the potential advantages offered by these membranes, their operational complexity sharing the some of the hazards inherit to solvent extraction (SX) techniques and an inherent lack of stability have seriously limited their industrial application [21].

Polymer inclusion membranes (PIMs) are a new and very promising type of visibly homogeneous extracting membranes, which are suitable for the separation of ions and small organic molecules, which substantially reduces the hazards associated with SX-like techniques. PIMs entrap an extractant within a polymer matrix, often with the addition of plasticizer and/or modifier to improve their extraction characteristics. As the extractant is wholly encapsulated in the polymer, the exposure of workers to toxic extractants is minimized. The polymer replaces the organic diluent, which removes the fire hazard associated with conventional SX. PIMs have better stability compared to that of other liquid membranes, such as supported liquid membranes, which have been the mainstream of liquid membrane research. Recently, PIM-based research on extraction of metal ions and organics has been extensively reported, but no work on gallium extraction by PIM is available in the literature. PIMs are mechanically strong and stable, easy and safe to handle and reasonably simple to fabricate [22,23]. The base polymer plays a crucial role in providing the mechanical resistance of the membranes. Poly (vinyl chloride) (PVC) and cellulose triacetate (CTA) are used in the most of research study on PIMs area. Moreover, PVC-based membranes are very stable in aggressive solutions (like acidic and basic solutions), and possess remarkable mechanical strength and flexibility. CTA-based PIMs have good mechanical properties due to their crystalline structure, but are less chemically resistant than the PVC ones [24,25]. Another advantantage of PIMs to SX and ion-exchange based separation is that PIMs combine the extraction and stripping

†To whom correspondence should be addressed.
E-mail: osman.tutkun@manas.edu.kg
Copyright by The Korean Institute of Chemical Engineers.

processes. Polymer blends have been also used for taking into account that the properties of the multicomponent polymer systems are influenced by the nature of the polymers, their thermal behavior and their possible interactions. From this point of view, the PIMs based on a mixture of two polymers, such as CTA/PVDF (polyvinylidene fluoride) to separate lead and cadmium [26] and CTA/PBAT (poly(butylene adipate-co-terephtalate) for chromium removal [27], have been recently used.

The aim of the present work is to selectively separate gallium from the other ions such as zinc, cobalt and nickel in acidic solutions, through PIMs based on CTA/PVC polymer blends using TOPO as carrier. The fundamental parameters influencing the transport and separate gallium from zinc, cobalt and nickel ions have been reported and discussed: composition of base polymers (CTA and PVC), plasticizer (2-NPPE) concentration, carrier (TOPO) concentration, HCl concentrations in feed and strip solutions.

EXPERIMENTAL

1. Chemicals and Reagents

PIM is composed of a base polymer (PVC and/or CTA), an extractant TOPO (trioctylphosphine oxide), and a plasticizer 2-NPPE (2-nitrophenylpentyl ether). TOPO was purchased from Merck. $ZnSO_4 \cdot 7H_2O$, $CoSO_4 \cdot 7H_2O$, and $NiSO_4 \cdot 6H_2O$ are all from Merck and of analytical grade. PVC (M_w=80 kDa, Sigma-Aldrich), Cellulose Triacetate (CTA, M_w=72-74 kDa Sigma-Aldrich), gallium metal (99.99%, Strem Chemicals, USA), HCl (37%, Merck), Dichloromethane (CH_2Cl_2, Merck), Tetrahydrofuran (THF, Merck). All the chemicals unless otherwise stated are analytical reagent grade and used as received.

2. Preparation of Polymer Inclusion Membrane (PIM)

In this study, PIM consisting of CTA alone as polymer support, 2-NPPE as a plasticizer, and TOPO as a carrier was prepared. The weighted amounts of CTA, plasticizer (2-NPPE), and carrier (TOPO) were dissolved in a 10-mL dichloromethane (casting solution) in a 50-mL beaker and was stirred on a magnetic stirrer at 350 rpm at room temperature for 2 hours, while glass covered on top. At the end of this period, the solution was poured into a Petri dish of 90-mm diameter. Dichloromethane was allowed to evaporate slowly over 24 h to obtain a polymer membrane with a smooth surface. For a PVC-base membrane, on the other hand, the weighted amounts of PVC, plasticizer (2-NPPE), and carrier (TOPO) were dissolved in a 10-mL tetrahydrofuran (casting solution) in a 50-mL beaker, and stirred on a magnetic stirrer at 350 rpm at room temperature for 2 hours. For the hybrid CTA/PVC membrane blends, however, the weighted amounts of CTA, TOPO and 2-NPPE were first dissolved in a 5-mL dichloromethane in a 50-mL beaker, and the weighted amount of PVC was dissolved in THF, in a separate 50-mL beaker. Having completely dissolved both polymer in about half an hour, the PVC solution was added into the CTA solution, which contained the weighted amounts of TOPO and 2-NPPE. No phase formation was observed during addition of both solutions, which were completely miscible. The combined solution was stirred in a magnetic stirrer for 2 hours and later was poured into a 90-mm diameter of Petri dish. The Petri dish was covered by a filter paper and weight put on it and allowed to evaporate slowly over 24 hours. After the evaporation of dichloromethane and THF, the obtained membranes were carefully peeled off the dish by immersion in cold water. The resulting membranes in this form exhibited good mechanical strength and were transparent films with thicknesses around 50-150 μm, depending mainly on the the amount of CTA and/or PVC. The average membrane thickness was measured by a micrometer (Insize Inc., USA). Considering that the transport process is enhanced when the membrane thickness decreases, there was a need to compare different membranes. Each membrane flux ($J_{exp,M}$) was normalized using as a reference the thinnest membrane. The normalized flux (J_N) was calculated by Eq. (1):

$$J_N = J_{exp,M} \times \frac{d_M}{d_R} \quad (1)$$

where d_R is the reference membrane thickness, d_M corresponds to the thickness of the membrane whose flux is normalized.

3. Transport Experiments

Membrane transport experiments were conducted in a compartment cell, as shown in Fig. 1. Each compartment had a volume capacity of 80 mL. The membrane was sandwiched between the two-compartment cell. The stirring rates in the both feed and stripping solutions were kept at a constant rate (700 rpm) using a digital mechanical stirrers at 20±1 °C to avoid concentration polarization conditions at the membrane interfaces and in the bulk of the solutions. About 0.5 mL of samples in volume was taken out at selected intervals for determination of metal ion concentration in feed and stripping solutions. The metal ion concentration was determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES, Perkin Elmer, Optima 5300DV) and by an inductively coupled plasma-mass spectrometer (ICP-MS, Perkin Elmer, Elan-DRC). The mass flux J of the metal ions through the membrane from the feed side to the strip side was calculated by Eq. (2):

$$J = \frac{\Delta(\text{Metal}) \cdot V}{S \cdot \Delta t} \quad (2)$$

where Δ(Metal) represents the variation of the metal ion concentration in the feed or strip phase at the time interval Δt, S the effective membrane area, and V the feed or strip phase volume. Two different values of the mass fluxes were determined: one measured from the decrease of metal ion concentration in the feed solution and the other one from the increase of the metal ion concentra-

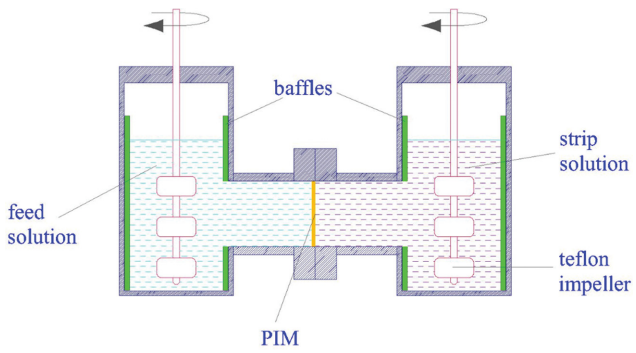

Fig. 1. Representation of the cell used to carry out the gallium transport.

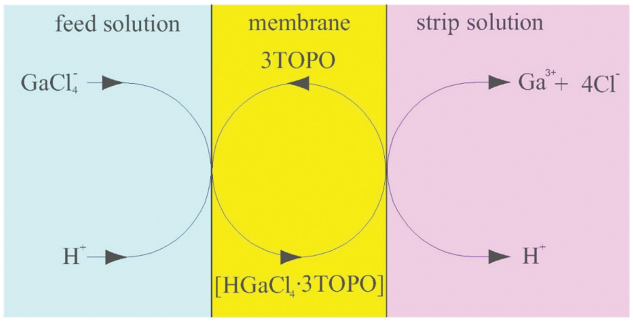

Fig. 2. Transport mechanism of gallium from the multicomponent acidic solutions.

tion in the strip solution.

4. Transport Mechanism

The following balance exists when TOPO extracts gallium from strong hydrochloric acids solutions [3,28,29]:

$$H^+_{(aq)} + GaCl^-_{4(aq)} + 3TOPO \rightarrow HGaCl_4 \cdot 3TOPO_{(org)} \quad (3)$$

When the organic phase, containing the ion-pair $HGaCl_4 \cdot 3TOPO$, is contacted 0.1 M hydrochloric acid or sulfuric acid solution the overall stripping reaction at the membrane-strip phase interface may be equivalently given by the following reaction:

$$HGaCl_4 \cdot 3TOPO_{(org)} \rightarrow 3TOPO_{(org)} + Ga^{3+}_{(aq)} + 4Cl^-_{(aq)} + H^+_{(aq)} \quad (4)$$

This was also confirmed by the emulsion liquid membrane study carried out on gallium extraction [17,18]. From Eqs. (3) and (4), the mechanism of selective separation of gallium is given in Fig. 2. Reactions 3 and 4 occur at the feed-membrane and membrane-strip solution interfaces, respectively.

RESULTS AND DISCUSSION

1. Effect of Hydrochloric Acid Concentration in the Feed Phase

The effect of hydrochloric acid concentration in the feed phase

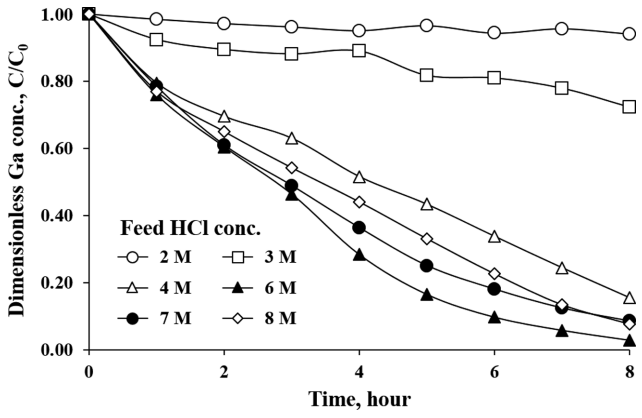

Fig. 3. Effect of HCl concentration in feed phase on the rate of gallium extraction (Carrier (TOPO): 30.1 wt%; Plasticizer (2-NPPE): 30.3 wt%; CTA: 19.8 wt%; PVC: 19.8 wt%; Strip phase: 80 mL 0.1 M HCl; Feed phase: 80 mL (100 mg/dm^3 Ga^{3+}, 1,000 mg/dm^3 Zn^{2+}, 600 mg/dm^3 Co^{2+}, 600 mg/dm^3 Ni^{2+}, (2-8 M HCl); Stirring rates of feed and strip phases: 700 min^{-1}).

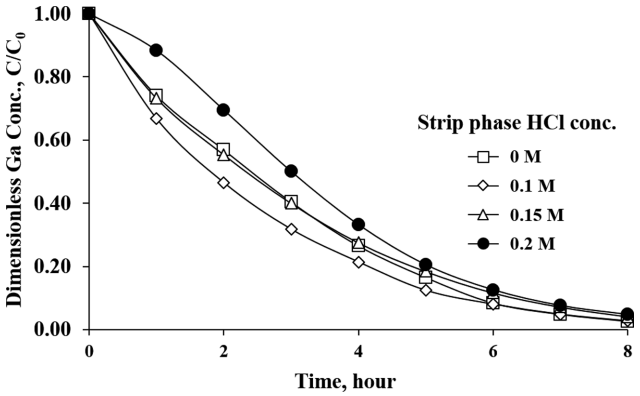

Fig. 4. Effect of acid concentration in strip phase on the rate of gallium extraction (Carrier (TOPO): 30.1 wt%; Plasticizer (2-NPPE): 30.3 wt%; CTA: 19.8 wt%; PVC: 19.8 wt%; Strip phase: 80 mL, 0-0.2 M HCl; Feed phase: 80 mL (100 mg/dm^3 Ga^{3+}, 1,000 mg/dm^3 Zn^{2+}, 600 mg/dm^3 Co^{2+}, 600 mg/dm^3 Ni^{2+}, 6 M HCl); Stirring rates of feed and strip phases: 700 min^{-1}).

on the extent of gallium extraction was investigated in the range of 2-8 M. It is clear from Fig. 3 that, the percentage of gallium extracted and transported increased with increasing HCl concentration, until a minimum was reached at 6 M HCl concentration within 8 hours. However, at higher HCl concentration (>6 M) transport efficiency decreased. Similar behavior in gallium systems was also reported previously [4,11,17,18,30,31]. This may be attributed to the fact that the initial rise in the rate of extraction with acidity was the formation, in greater amounts, of the extractable species, $HGaCl_4$. However, at higher acidity (hydrochloric acid molarity higher than 6 M), the extraction of HCl also occurred; this consequently reduced the extraction of gallium due to a competitive effect between $GaCl_4^-$ and HCl-TOPO complex, as reported by Judin and Bautista [32].

2. Effect of Stripping Reagent Concentration

Different concentrations of various stripping agents, such as nitric, sulfuric and hydrochloric acids and even water can be used to strip and recover gallium. The effect of hydrochloric acid concentration on the extent of gallium extraction was studied in the range of 0-0.2 mol/dm^3 HCl and is indicated in Fig. 4. It is found that the extraction percentage of gallium decreases with the increase in hydrochloric acid molarity from 0.1 to 0.2 M when considering 8 hours of extraction time. The highest extraction rate was observed at 0.1 M HCl of stripping concentration. This could be easily explained from Eq. (4) since the $HGaCl_4 \cdot 3TOPO_{(org)}$ complex at the membrane-strip interface tends to decompose as the stripping HCl concentration decreases. However, 0 M HCl concentration was found to be comparable to 0.15 M HCl. Similar behavior was also reported elsewhere [17,18,30,31,33,34].

3. Effect of Plasticizer Content

Plasticizers are compounds that are added to hard, stiff plastics to make membranes softer and more flexible. There is an interest in including these compounds in PIMs to improve the membrane chemical and mechanical stability for its continuous use. To test the selective separation of gallium from other ions of Zn, Co and Ni with plasticizer (2-NPPE) concentration, PIMs prepared with variable concentrations of this compound at fixed concentrations

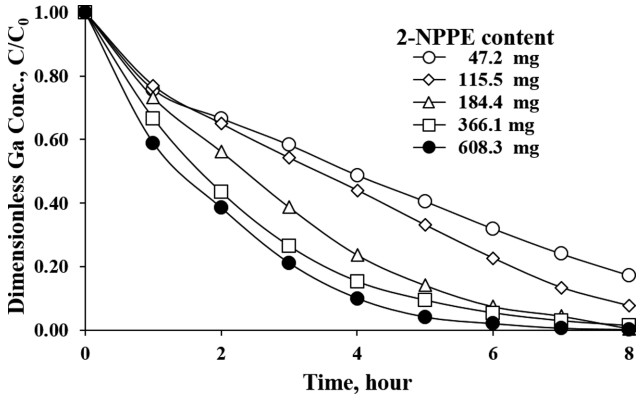

Fig. 5. Effect of plasticizer content on the rate of gallium extraction (Carrier (TOPO): 183.2 mg; Feed phase: 80 mL (100mg/dm^3 Ga^{3+}, 1,000 mg/dm^3 Zn^{2+}, 600 mg/dm^3 Co^{2+}, 600 mg/dm^3 Ni^{2+}, 6 M HCl); Strip phase: 80 mL 0.1 M HCl; Stirring rates of feed and strip phases: 700 min^{-1}).

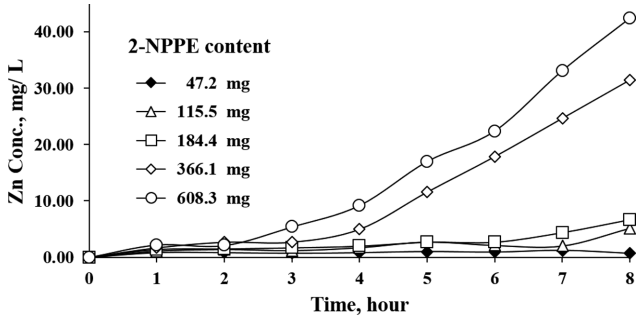

Fig. 6. Effect of 2-NPPE content on zinc concentration in strip phase (Carrier (TOPO): 183.2 mg; Polymer blend: (120.8 mg CTA+ 120.8 mg PVC); Feed phase: 80 mL (100 mg/dm^3 Ga^{3+}, 1,000 mg/dm^3 Zn^{2+}, 600 mg/dm^3 Co^{2+}, 600 mg/dm^3 Ni^{2+}, 6 M HCl); Strip phase: 80 mL 0.1 M HCl; Stirring rates of feed and strip phases: 700 min^{-1}).

of extractant (TOPO) and base polymer-blend (CTA plus PVC) were tested. From Fig. 5, it is found that the extraction percentage

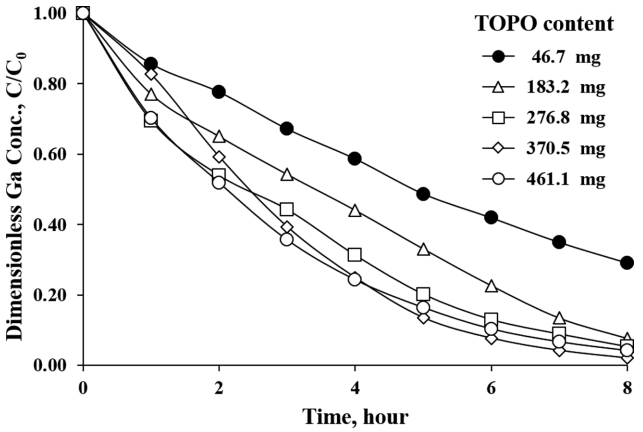

Fig. 7. Effect of carrier (TOPO) content on the rate of gallium extraction (2-NPPE: 26.3 wt %; Feed solution: 80 mL (100 mg/dm^3 Ga^{3+}, 1,000 mg/dm^3 Zn^{2+}, 600 mg/dm^3 Co^{2+}, 600 mg/dm^3 Ni^{2+}, 6 M HCl; Strip solution: 80 mL 0.1 M HCl; Stirring rates of feed and strip phases: 700 min^{-1}).

of gallium increases with the increase in 2-NPPE content from 47.2 to 608.3 mg within 8 hours. The increase in the rate gallium extraction with the increase of plasticizer content could be explained considering the plasticization effect, which turns the membrane into a better medium for plasticizer and carrier movements, as argued by Rodriguez de San Miguel et al. [6].

When the 2-NPPE content increased from 47.2 to 638.3 mg, or concentrations of 10.0 to 58.9 wt%, the percentage of gallium extraction at 8 hrs, increased from 82.8% to 99.8%, respectively. Fig. 6 indicates the zinc concentration in strip phase versus time. As the 2-NPPE content increases from 47.2 to 184.4 mg, zinc concentration slightly increases, that is, up to 5.1 mg/dm^3, dimensionless concentration (C/C_o) being 0.003, as shown in Fig. 6. However, the 2-NPPE content of 366.1 mg (30.3 wt% 2-NPPE) onwards zinc concentration sharply increases up to 42.4 mg/dm^3 at 8 hours. On the other hand, for all 2-NPPE contents the cobalt ions were hardly extracted into strip phase and the nickel ions did not appear in the strip phase within the limit of detection, as shown in Table 1.

Table 1. The percentages of extraction of zinc, cobalt and nickel ions into strip phase (Carrier (TOPO): 183.2 mg; Polymer blend: (120.8 mg CTA+ 120.8 mg PVC); Feed phase: 80 mL (105.2 mg/dm^3 Ga^{3+}, 1,000 mg/dm^3 Zn^{2+}, 600 mg/dm^3 Co^{2+}, 600 mg/dm^3 Ni^{2+}, 6 M HCl); Strip phase: 80 mL 0.1 M HCl; Stirring rates of feed and strip phases: 700 min^{-1})

	Strip solution					
Time (hrs)	Zn		Co		Ni	
	C, mg/dm^3	C/C_o	C, mg/dm^3	C/C_o	C , mg/dm^3 (*)	C/C_o
0	0	0	0	0	<0.5	<0.001
1	2.1	0.003	<0.4	<0.001	<0.5	<0.001
2	2.2	0.003	<0.4	<0.001	<0.5	<0.001
3	5.4	0.007	<0.4	<0.001	<0.5	<0.001
4	9.2	0.011	0.5	0.001	<0.5	<0.001
5	17.0	0.021	0.8	0.001	<0.5	<0.001
6	22.4	0.028	1.0	0.002	<0.5	<0.001
7	33.1	0.041	1.3	0.002	<0.5	<0.001
8	42.4	0.053	1.7	0.003	<0.5	<0.001

*Limit of detection; C/C_o: Dimensionless concentration

4. Effect of Carrier (TOPO) Concentration

The effect of TOPO content in the range of 46.7 to 461.1 mg on the gallium rate of extraction was studied, as indicated in Fig. 7. The gallium rate of extraction increased as the TOPO content increased from 46.7 to 370.5 mg, or concentration of 9.87 to 46.2 wt%, but then with further increase in the carrier content above 370.5 mg did not result in a higher transport rate, probably due to the increase in the membrane viscosity. This depressed the ion-carrier complex in the membrane, or low solubility of the carrier in the plasticizer, as reported also [6,35-42].

5. Effect of CTA Composition in the Base Polymer-Blend (CTA/PVC)

The effect of CTA composition in the base polymer-blend (CTA/PVC), that is carrier- and plasticizer-free, on the extraction of gallium has been studied. The feed solution is the aqueous solution, which consisted of 100 mg/dm^3 Ga, 1,000 mg/dm^3 Zn, 600 mg/dm^3 Co, and 600 mg/dm^3 Ni. The membranes are composed of the base polymer-blends of CTA and PVC, plasticizer and carrier. The total concentration of the base polymer-blend was kept constant at 34.4 wt%, while maintaining the plasticizer- and carrier concentrations at 26.3 wt% and 39.4 wt%, respectively. The plasticizer- and extractant-free CTA concentration was varied between 0 and 100 wt%. It was observed that with the increase in CTA concentration, the percentage of gallium extraction increased, as indicated in Fig. 8(a), and 80 wt% CTA and 20 wt% PVC exhibited the maximum extraction efficiency. The same effect is also shown in Fig. 8(b), wherein an increase in CTA concentration also causes an increase in the percentage of gallium extraction in the strip phase. From Fig. 8(a), it can be concluded that the CTA compositon of 80 wt% in polymer blend is the one which gives the maximum percentage of extraction efficiency of gallium, that is, 95.3% at 8 hours.

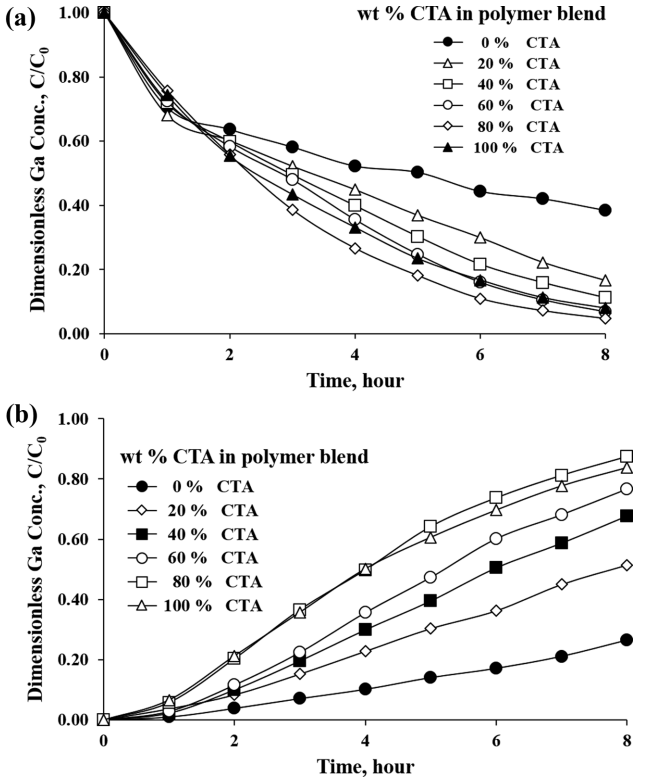

Fig. 8. (a) Effect of CTA concentration in polymer-blend on the rate of gallium extraction (Polymer blend: 34.4 wt% (CTA: 0-100%); Plasticizer (2-NPPE): 26.3 wt%; Carrier (TOPO): 39.4 wt%; Feed solution: 80 mL (100 mg/dm^3 Ga^{3+}, 1,000 mg/dm^3 Zn^{2+}, 600 mg/dm^3 Co^{2+}, 600 mg/dm^3 Ni^{2+}, 6 M HCl); Strip phase: 80 mL 0.1 M HCl; Stirring rates of feed and strip phases: 700 min^{-1}). (b) Effect of CTA concentration in polymer-blend on the rate of gallium extraction (Polymer blend: 34.4 wt% (CTA: 0-100%); Plasticizer (2-NPPE): 26.3 wt%; Carrier (TOPO): 39.4 wt%; Feed solution: 80 mL (100 mg/dm^3 Ga^{3+}, 1,000 mg/dm^3 Zn^{2+}, 600 mg/dm^3 Co^{2+}, 600 mg/dm^3 Ni^{2+}, 6 M HCl); Strip phase: 80 mL 0.1 M HCl; Stirring rates of feed and strip phases: 700 min^{-1}).

PVC and CTA are the most widely used base polymers in PIMs since they provide a high mechanical strength to the membranes compatible with most carriers. To examine the effect of the polymer matrix Kozlowski and Walkowiak [43] studied the transport of chromium ions from 0.10 M HCl aqueous solution, through PIM with trioctyl amine (TOA) as a carrier, CTA or PVC as the base polymer, 2-NPPE as the plasticizer, into a 0.10 M NaOH aqueous solution as the strip phase. They found that the chromate ions were transported through CTA polymer inclusion membranes with higher rate in comparison with PIM with PVC matrix. The cause of this has been attributed to the fact that CTA has more hydrophilic properties than PVC and also due to the necessity to deliver a large amounts of carrier, which has the additional plasticizing properties [44]. For this reason they stated that a higher amount of TOA in PVC-based PIM, above 1.25 M based on plasticizer volume, is required to cause the inclusion formation in the organic phase of membranes, which is characterized by high degree of dispersion, as argued by Kozlowski and Walkowiak [44]. Similar behavior to the work of Kozlowski and Walkowiak [44] was also observed by Kebiche-Senhadji et al. [36]. They compared PIMs containing Aliquat 336 and CTA or PVC for the extraction of Cr (VI), that is, the extraction efficiency obtained with the CTA-based PIMs was higher than that with the PVC-based PIMs up to the Aliquat 336 concentration of 1.17 M; however, above this value, the PVC-based PIMs exhibited slightly higher percentages of Cr (VI) extraction. Baczynska et al. [45] also reported that better transport ability of CTA membranes towards Zn (II) compared with PVC membranes was obtained, and they stated that the differences in the structure of the two polymers undoubtedly played a crucial role in the permeability of the membranes. However, they also reported that the type of carrier used seems to influence the transport less than the matrix type.

6. Effect of CTA Composition in the Base Polymer-Blend (CTA/PVC) on the Initial Flux

The influence of CTA composition in the base polymer-blend (CTA/PVC) on the initial gallium flux was studied from 0 to 100 wt% of CTA concentration. The feed solution is the aqueous solution, which consisted of 100 mg/dm^3 Ga, 1,000 mg/dm^3 Zn, 600 mg/dm^3 Co, and 600 mg/dm^3 Ni. Fig. 9 indicates the gallium fluxes determined from Eq. (2), based on the concentration profiles in the feed and strip solutions. From Fig. 9, both fluxes increased with an increase in CTA composition and reached the maximum when the CTA composition was 80 wt%, as was also shown in Fig. 8.

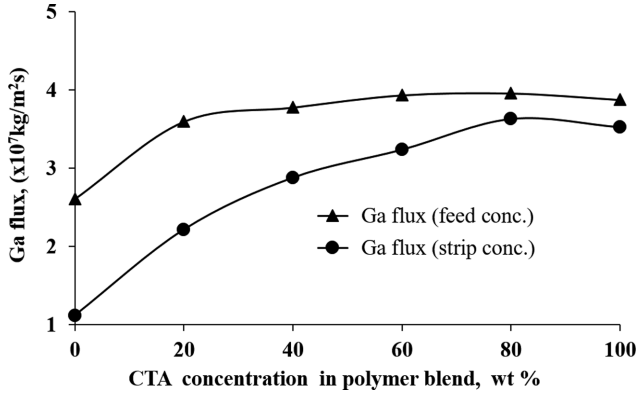

Fig. 9. Effect of CTA concentration in polymer-blend on gallium flux (Polymer blend: 34.4 wt% (CTA: 0-100%); Plasticizer (2-NPPE): 26.3 wt%; Carrier (TOPO): 39.4 wt%; Feed solution: 80 mL (100 mg/dm^3 Ga^{3+}, 1,000 mg/dm^3 Zn^{2+}, 600 mg/dm^3 Co^{2+}, 600 mg/dm^3 Ni^{2+}, 6 M HCl); Strip phase: 80 mL 0.1 M HCl; Stirring rates of feed and strip phases: 700 min^{-1}).

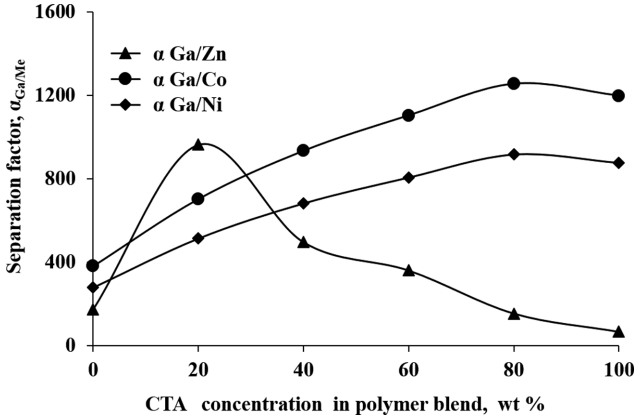

Fig. 10. Effect of CTA concentration in polymer-blend on separation factor of gallium over the other ions (Polymer blend: 34.4 wt% (CTA: 0-100%); Plasticizer (2-NPPE): 26.3 wt%; Carrier (TOPO): 39.4 wt%; Feed solution: 80 mL (100 mg/dm^3 Ga^{3+}, 1,000 mg/dm^3 Zn^{2+}, 600 mg/dm^3 Co^{2+}, 600 mg/dm^3 Ni^{2+}, 6 M HCl); Strip phase: 80 mL 0.1M HCl; Stirring rates of feed and strip phases: 700 min^{-1}).

Two different values of the fluxes were determined: one obtained from the decrease of the metal ion concentration in the feed solution (J_f) and the other determined from the increase of the metal ion concentration in the strip solution (J_s). The differences in the values of J_f and J_s indicate the retention of metal ion within the membrane phase, as shown in Fig. 9. Both fluxes increased as the CTA concentration increased, but the differences in the two fluxes decreased as the CTA concentration in the polymer blend increased. This was also observed by Rodriguez de San Miguel et al. [46]. The decrease in the gap between the fluxes with the increase in the CTA concentration may be explained by considering the effect, which turns the membrane morphology into a better medium that enhances the diffusivity of the metal-ion complex and thus causes an increase in the flux. The percentage of gallium retention sharply decreased from 136% to 7%, as CTA composition increased from 0 to 100 wt%. Similar behavior was also observed in almost all studies that the PIMs with CTA give higher fluxes than that with PVC, as reported elsewhere [23,36,43-45]. However, the gallium flux increased from 2.609×10^{-7} to 3.87×10^{-7} kg/m^{2}s, as the CTA composition increased from 0 to 100 wt% at 8 hrs in the feed solution, giving an increase of 48.6%, as shown in Fig. 9.

This is the first and only study in the literature for the extraction and the selective separation of gallium from multicomponent acidic solutions on PIMs. Therefore, there is no other study to compare yet. However, the selectivity of gallium over the ions of zinc, cobalt and nickel for the similar feed solutions by emulsion liquid membranes (ELMs) is given in Table 2. It is observed from Table 2 that, the selectivities $\alpha_{Ga/Zn}$, $\alpha_{Ga/Co}$ and $\alpha_{Ga/Ni}$ obtained from this PIM study are quite higher than those obtained by ELM work. This also proves that PIMs always give higher separation factors than those of ELMs.

7. Effect of CTA Concentration on Separation Factor of Gallium over other Ions

The separation factors (α_{ij}) of gallium with respect to the other metal ions that exist in the solutions are indicated in Fig. 10. The separation factor (α_{ij}) is given by Eq. (5):

$$\alpha_{ij}=\frac{(C_i/C_j)_{strip}}{(C_i/C_j)_{feed,\,o}} \tag{5}$$

where C_i and C_j are the concentrations of i and j components in the stripping and the initial feed phases, respectively.

At the end of experiments, in 8 hours, the PIM membrane selec-

Table 2. The comparison of separation factors, of gallium over the ions of zinc, cobalt and nickel, obtained from this study (PIM) and those obtained from ELM work [17,18]

Liquid membrane type	Separation factor, $\alpha_{Ga/Me}$			Reference
	$\alpha_{Ga/Zn}$	$\alpha_{Ga/Co}$	$\alpha_{Ga/Ni}$	
PIM* (Base polymer/Plasticizer/Carrier) CTA-PVC/2-NPPE/TOPO)	963.3	702.4	513.5	This study
ELM (Surfactant/Diluent/Carrier)**				
(ECA 4360J/Kerosene/TOPO)	28.3	16.2	43.1	[17]
(ECA 4360J/Kerosene/TBP)	44.8	15.5	43.8	[18]

PIM*: Membrane (20 wt% CTA+ 80% wt PVC); $\alpha_{Ga/Me}$ values in 8 hrs

ELM**: $\alpha_{Ga/Me}$ values in 30 mins; PIM: Polymer inc. memb.; ELM: Emul. liq. memb

tivity of gallium with respect to the other ions (Zn, Co and Ni) was reasonably high, as shown in Fig. 10. The separation factors of gallium against CTA concentration in the CTA/PVC blend, excluding the other membrane components, are indicated in Fig. 10. At 8 hours the separation factor of gallium with respect to zinc ($\alpha_{Ga/Zn}$) increased as the CTA concentration increased up to 20% w/w, but further increase in the CTA concentration, $\alpha_{Ga/Zn}$ exponentially decreased, giving a maximum value of approximately 963, at 20 wt% of CTA in the blend; while the separation factors of gallium over Co and Ni increased continuously with the increase in the CTA concentration. From Fig. 10 the separation factors of gallium over Zn, Co, and Ni, at the optimum CTA concentration of 20 wt%, were found to be of 963, 702, and 514, respectively, for the feed solution of 100 mg/dm^3 Ga, 1,000 mg/dm^3 Zn, 600 mg/dm^3 Co, and 600 mg/dm^3 Ni. On the other hand, at 8 hour gallium separation factors over Zn, Co and Ni for pure PVC were found to be 173.8, 381.1 and 278.4, and that for pure CTA were 65.7, 1198 and 876, respectively, as indicated in Fig. 10. However, as the CTA composition decreased from 100 wt% to 20 wt%, the gallium flux also decreased from 3.878×10^{-7} to 3.599×10^{-7} kg/m^{2}s, that is, causing a decrease of 7.2% in the flux, as shown in Fig. 9. This is significant that gallium can be selectively separated from such ions as zinc, cobalt an nickel, which exist in the leach solutions of a zinc refinery [17,18].

8. Optimum Conditions

The optimum conditions were experimentally determined from the effects of the parameters studied as follows:

- Plasticizer (2-NPPE) concentration: 30.3 wt%
- Carrier (TOPO) concentration: 46.0 wt%
- Polymer blend: 23.7 wt% (20 wt% CTA+80 wt% PVC)
- HCl concentration in the feed solution: 6 M
- HCl concentration in the strip solution: 0.1 M

9. Effect of the Initial Gallium Feed Concentration on the Flux

The influence of the initial Ga concentration on the transport in the feed solution on gallium flux by TOPO was investigated at optimum conditions. The variation of gallium concentration in the feed was studied from 49.2 to 238.5 mg/dm^3 using optimum parameters, as given in Fig. 11. The results of Ga transport flux through the membrane as a function of Ga concentration is indicated in Fig. 11. The results show that the Ga flux values gradually increased by increasing the gallium concentration of the feed solution from 1.82×10^{-7} to 4.05×10^{-7} kg/m^{2}s for the upper curve, based on Ga concentration profile on the feed solution. Similar behavior was also observed for the lower curve, based on the gallium concentration profile on the strip solution. This behavior is in accordance with the fact that the higher the concentration in the feed solution, the higher driving force for the gallium transfer, and thus the higher the gallium flux, as shown in Fig. 11. This is in agreement with the tendency reported in the literature [35,36,44,47-49]. However, no metal loading behavior for carrier up to the Ga concentration of 248 mg/dm^3 in the feed solution was observed. From Fig. 11 it was also observed that the retention of gallium ion within the membrane phase occurred, and increased as the initial Ga concentration increased.

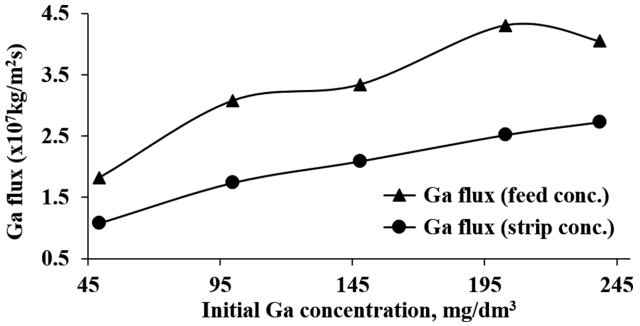

Fig. 11. Effect of initial gallium concentration on Ga flux in the optimum conditions (Polymer blend: 23.7 wt% (CTA: 20 wt%; PVC: 80 wt%); Carrier (TOPO): 46.0 wt%; Plasticizer (2-NPPE): 30.3 wt%; Feed solution: 80 mL (100 mg/dm^3 Ga^{3+}, 1,000 mg/dm^3 Zn^{2+}, 600 mg/dm^3 Co^{2+}, 600 mg/dm^3 Ni^{2+}; Feed HCl: 6 M; Strip solution: 80 mL 0.1 M HCl); Stirring rates of feed and strip phases: 700 min^{-1}).

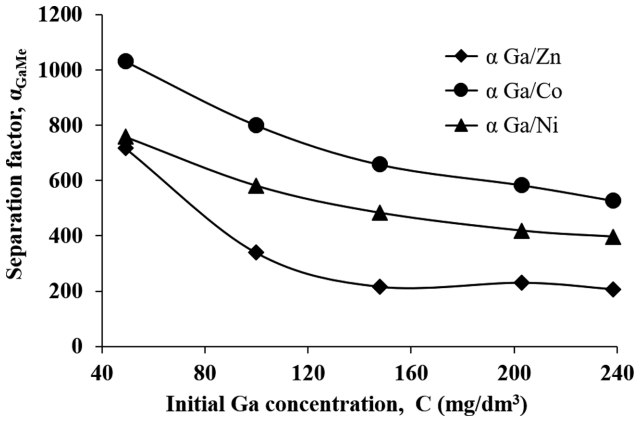

Fig. 12. Effect of initial gallium concentration on separation factor in the optimum conditions (Polymer blend: 23.7 wt% (CTA: 20 wt%; PVC: 80 wt%); Carrier (TOPO): 46.0 wt%; Plasticizer (2-NPPE): 30.3 wt %; Feed phase: 80 mL (100 mg/dm^3 Ga^{3+}, 1,000 mg/dm^3 Zn^{2+}, 600 mg/dm^3 Co^{2+}, 600 mg/dm^3 Ni^{2+}; Feed HCl: 6 M; Strip phase: 80 mL 0.1 M HCl); Stirring rates of feed and strip phases: 700 min^{-1}).

On the other hand, the influence of the initial Ga concentration on separation factors of gallium over the other metal ions, in the optimum conditions, was also determined, as shown in Fig. 12. The initial gallium concentration was tested from 49.2 to 238.5 mg/dm^3 using optimum parameters. From Fig. 12, all separation factors decreased as the initial Ga concentration increased.

CONCLUSIONS

PIM systems containing TOPO as carrier, 2-NPPE as plasticizer and CTA/PVC blends as base polymer were investigated to transport and selectively separate gallium ions from the ions of zinc, cobalt and nickel from chloride media. From this study, the following conclusions can be drawn:

1. As the 2-NPPE content increased from 47.2 to 608.3 mg, or the percentages of 10.0 to 58.9 wt% in the membrane, the gallium flux (J_f) also increased from 3.01×10^{-7} to 4.13×10^{-7} kg/m^{2}s; but after

2-NPPE content of 184.4 mg or 30.3 wt%, the zinc concentration in the strip phase increased from 5.1 to 42.4 mg/dm^3, in 8 hrs. Thus, the gallium separation factor over zinc was somewhat affected, but the gallium separation factors over cobalt and nickel were not affected.

2. As the TOPO content increased from 46.7 to 370.5 mg, the percentages of 9.88 to 46.2 wt% in the membrane, the gallium rate of extraction also increased. However, further increase in the carrier content above 370.5 mg did not result in a higher transport rate, rather slightly declined, probably due to the increase in the membrane viscosity, which depresses the ion-carrier complex in the membrane.

3. The plasticizer- and carrier-free CTA concentration was varied between 0 and 100 wt% for the feed solution, which consisted of 100 mg/dm^3 Ga, 1,000 mg/dm^3 Zn, 600 mg/dm^3 Co, and 600 mg/dm^3 Ni. 80 wt% CTA and 20 wt% PVC exhibited the maximum extraction efficiency. The gallium flux in the feed solution (J_f) increased from 1.82×10^{-7} to 4.05×10^{-7} kg/m^{2}s, and the flux in the strip solution (J_s) also increased in this range. 80 wt% CTA and 20 wt% PVC in the blend exhibited the maximum extraction efficiency of gallium, that is, 95.3%.

4. Two different values of the fluxes for feed (J_f) and strip solutions (J_s) were determined, and the differences in the values of J_f and J_s indicate the retention of metal ions within the membrane phase. However, the retention of metal ions decreased as the CTA composition increased.

5. In the 8 hours as the CTA concentration increased from 0 to 20 wt%, the separation factor of gallium over zinc ($\alpha_{Ga/Zn}$) also increased, but further increase in the CTA concentration, $\alpha_{Ga/Zn}$ exponentially decreased, giving approximately a maximum value of 963, at 20 wt% of CTA in the blend; while the separation factors of gallium over Co and Ni increased continuously with the increase in the CTA concentration. The separation factors of gallium over Zn, Co, and Ni, in the optimum CTA concentration of 20 wt%, were found to be of 963, 702, and 514, respectively, for the feed solution of 100 mg/dm^3 Ga, 1,000 mg/dm^3 Zn, 600 mg/dm^3 Co, and 600 mg/dm^3 Ni. On the other hand, in the 8 hour gallium separation factors over Zn, Co and Ni for pure PVC were found to be 173.8, 381.1 and 278.4, and that for pure CTA were 65.7, 1198 and 876, respectively. Therefore, it is significant that gallium could be selectively separated and extracted from the ions of zinc, cobalt and nickel that exist in the leach solutions of zinc refinery.

6. In the optimum conditions, as the initial gallium feed concentration increased from 49.2 to 238.5 mg/dm^3, the flux increased from 1.82×10^{-7} to 4.05×10^{-7} kg/m^{2}s, that is, an increase of 122.5% in the flux. However, the separation factors of Ga over Zn, Co and Ni decreased in this direction, that is, for Zn from 737 to 208, for Co from 1,060 to 532, and for Ni from 777 to 402.

7. When the polymer blends are used as the base polymers at different weight ratios, it could cause a positive synergy by increasing the membrane selectivity, extraction efficiency and the flux. Generally, the flux and selectivity are inversely proportional; however, as the CTA concentration increased from 0 to 20 wt%, the Ga flux and the separation factor of gallium over zinc ($\alpha_{Ga/Zn}$) also increased, but further increase in the CTA concentration, $\alpha_{Ga/Zn}$ exponentially decreased, giving approximately a maximum value of 963, at 20 wt% of CTA in the blend; while the separation factors of gallium over Co and Ni increased continuously with the increase in the CTA concentration.

ACKNOWLEDGEMENT

The authors wish to thank the Kyrgyz-Turkish Manas University, Kyrgyzstan for providing facilities and financial support.

DECLARATION OF COMPETING INTEREST

The authors do not have any conflict of interest in the publication of the interest.

REFERENCES

1. B. Gupta, N. Mudhar, I. Zarena Begum and I. Singh, *Hydrometallurgy*, **87**, 18 (2007).
2. R. R. Moskalyk, *Miner. Eng.*, **16**(10), 921 (2003).
3. I. Mihaylov and P. A. Distin, *Hydrometallurgy*, **28**, 13 (1992).
4. Z. S. Abisheva, I. A. Blaida, E. I. Ponomareva and A. M. Rozen, *Hydrometallurgy*, **37**, 393 (1995).
5. S. Raiguel, W. Dehaen and K. Binnemans, *Dalton Transact.*, **49**(11), 3532 (2020).
6. E. Rodriguez de San Miguel, J. C. Aquilar, M. T. C. Rodriguez and J. de Gyves, *Hydrometallurgy*, **57**, 151 (2000).
7. I. M. Ahmed, Y. A. El-Nadi and N. E. El-Hefni, *Hydrometallurgy*, **131-132**, 24 (2013).
8. M. S. Lee, J. G. Ahn and E. C. Lee, *Hydrometallurgy*, **63**, 269 (2002).
9. X. Zhang, G. Yin and Z. Hu, *Talanta*, **59**, 905 (2003).
10. W.-S. Chen, S.-H. Huang, F.-C. Chang, J.-E. Chang and Y.-N. Wang, *Desal. Water Treatment*, **54**, 1452 (2015).
11. I. M. Ahmed, Z. H. Ismail and M. M. Hamed, *J. Radioanal. Nucl. Chem.*, **317**(2), 969 (2018).
12. A. Assadian and A. Ahmadi, *Mineral. Eng.*, **148**, 106207 (2020).
13. J. Draxler and R. J. Marr, *Chem. Eng. Process*, **20**, 319 (1986).
14. N. Parthasarathy, M. Pelletier and J. Buffle, *Anal. Chim. Acta*, **35**, 183 (1997).
15. F. J. Alguacil, *Revista de Metalurgia*, **38**(6), 419 (2002).
16. N. Alizadeh, S. Salimi and A. Jabbari, *Sep. Purif. Technol.*, **28**, 173 (2002).
17. R. A. Kumbasar and O. Tutkun, *Hydrometallurgy*, **75**(1-4), 111 (2004).
18. R. A. Kumbasar and O. Tutkun, *Sep. Sci. Technol.*, **41**(12), 2825 (2006).
19. X. J. Zhang, J. H. Liu and T. S. Lu, *Water Treatment*, **2**, 127 (1987).
20. J. Draxler, W. Fürst and R. J. Marr, *J. Memb. Sci.*, **38**, 281 (1988).
21. S. D. Kolev, in *Encyclopedia of analytical science*, P. Worsfold, A. Townshend and C. Poole eds., Elsevier, Amsterdam (2005).
22. A. M. St John, R. W. Cattrall and S. D. Kolev, *J. Memb. Sci.*, **364**(1-2), 354 (2010).
23. L. D. Nghiem, P. Mornane, I. D. Potter, J. M. Perera, R. W. Cattrall and S. D. Kolev, *J. Memb. Sci.*, **281**, 7 (2006).
24. C.-V. I. Gherasim, G. Bourceanu, R.-I. Olariu and C. Arsene, *J. Memb. Sci.*, **377**, 67 (2011).
25. S. Kagaya, R. W. Cattrall and S. D. Kolev, *Anal. Sci.*, **27**, 653 (2011).

26. N. Abdellaoui and O. Arous, *Macromol. Symp.*, **386**(1), 201800244 (2019).
27. F. Sellami, O. Kebiche-Senhadji, S. Marais, N. Couvrat and K. Fatyeyeva, *React. Funct. Polym.*, **139**, 120 (2019).
28. Y. Hasegawa, T. Shimada and M. Nitsu, *J. Inorg. Nucl. Chem.*, **42**, 1487 (1980).
29. K. Yamamoto and N. Katoh, *Anal. Sci.*, **15**, 1013 (1999).
30. T. Sato, T. Nakamura and S. Ishikawa, *Solvent Extr. Ion. Exch.*, **2**(2), 201 (1984).
31. B. Gutierrez, C. Pazos and J. Coca, *J. Chem. Tech. Biotechnol.*, **61**, 241 (1994).
32. V. Judin and R. G. Bautista, *Metallurgical Trans. B*, **17B**, 259 (1986).
33. K. Fujinawa, M. Akiyama, A. Shono, N. Imaishi and M. Hozawa, *Kagaku Kogaku Ronbunshu*, **15**, 381 (1989).
34. I. Kirgios, K. Schügerl and W. Degener, US Patent, 5,326,441 (1994).
35. S. P. Kusumocahyo, T. Kanamori, K. Sumaru, S. Aomatsu, H. Matsuyama, M. Teramoto and T. Shinbo, *J. Memb. Sci.*, **244**, 251 (2004).
36. O. Kebiche-Senhadji, S. Tingry, P. Seta and M. Benamor, *Desalination*, **258**, 59 (2010).
37. B. Pospiech, *Sep. Sci. Technol.*, **47**(9), 1413 (2012).
38. S. Mohebali, M. Nazari, A. Rahbar-Kelishami and P. Davoodi-Nasab, *Desal. Water Treat.*, **64**, 173 (2017).
39. C. Zidi, R. Tayeb and M. Dhahbi, *J. Hazard. Materials*, **194**, 62 (2011).
40. Y. Yildiz, A. Manzak and O. Tutkun, *Desal. Water Treat.*, **57**(10), 4616 (2016).
41. X. Meng, C. Gao, L. Wang, X. Wang and W. Tang, *J. Membr. Sci.*, **493**, 615 (2015).
42. P. Venkateswaran, A. Navaneetha and K. Palanivelu, *J. Environ. Sci.*, **19**, 1446 (2007).
43. C. A. Kozlowski and W. Walkowiak, *J. Membr. Sci.*, **266**, 143 (2005).
44. C. A. Kozlowski and W. Walkowiak, *Water Res.*, **36**, 4870 (2002).
45. M. Baczynska, M. Regel-Rosocka, M. Nowicki and M. Wisniewski, *J. Appl. Polym. Sci.*, **132**(30), 42319 (2015).
46. E. Rodriguez de San Miguel, A. V. Garduno-Garcia, J. C. Aguilar and J. de Gyves, *Ind. Eng. Chem. Res.*, **46**, 2861 (2007).
47. H. K. Haghighi, M. Irannajad and D. Moradkhani, *Physicochem. Probl. Miner. Process.*, **55**(1), 225 (2019).
48. S. Rehman, G. Akhtar, M. A. Chaudry, K. Ali and N. Ullah, *J. Membr. Sci.*, **389**, 287 (2012).
49. S. P. Kusumocahyo, K. Sumaru, T. Iwatsubo, T. Shinbo, T. Kanamori, H. Matsuyama and M. Teramoto, *J. Membr. Sci.*, **280**(1-2), 73 (2006).