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Preparation of polymer inclusion membrane with sodium diethyldithiocarbamate as a carrier reagent for selective transport of zinc ions

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ABSTRACT

This study reports the design of a new type of polymer inclusion membrane (PIM) for selective transport of zinc ion. Sodium diethyldithiocarbamate (NaDDTC) was incorporated in the cellulose acetate-based membrane as a carrier for Zn(II) ion. The PIMs were characterized using Fourier transform infrared spectroscopy, scanning electron microscopy, atomic force microscopy and contact angle measurements. The effects of parameters, including concentration of Zn(II) in the feed phase, HCl in the stripping phase and amount of NaDDTC incorporated in the membrane, on the transport of Zn(II) ion were studied. For 1×10^{-4} M of Zn(II) ion in the feed phase at pH 5.04, 96% of Zn(II) ion was transported through the PIMs prepared with 1.0 (wt%) diethyldithiocarbamate via 0.5 M HCl as a stripping phase. The diffusion of Zn(II) ions through the membrane was governed by complex formation between Zn(II) ion and NaDDTC in the membrane. Moreover, selective transport of Zn(II) ion was achieved in the presence of divalent metal ions involving Cu(II), Pb(II) and Ni(II). The prepared PIM provided reproducible transport efficiency, and it can be efficiently used in separation processes.

Keywords: Polymer inclusion membrane; Facilitated transport; Zinc; Sodium diethyldithiocarbamate

1. Introduction

Wastewater discharge into the environment is the primary reason for the heavy metal contamination. Accumulation of heavy metal species in human tissues is responsible for various disorders in humans such as kidney failures, nervous system disorders and bone damages. Therefore, treatment of water and wastewater containing heavy metals is of importance [1–3]. Up to now, various techniques such as adsorption, ion exchange and membrane-based technologies for the removal of the heavy metal ions have been reported [4–6]. Still, more effective and selective techniques for the removal of heavy metal ions from aqueous solutions are required.

Membrane processes (i.e., reverse osmosis, ultrafiltration and electrodialysis) have been widely used in the separation technology [7]. Transport across liquid membranes including bulk liquid membranes (BLMs), emulsion liquid membranes (ELMs) and supported liquid membranes (SLMs) [8] have emerged as alternative separation technique to membrane processes mentioned above [8–14]. In the system of SLMs, carrier-facilitated transport is an effective technique used in selective separation and concentration of metal ions [10,15]. On the other hand, lack of stability in these systems limits their upscale applications [16–21]. Polymer inclusion membranes (PIMs) have better stability compared with other types of liquid membranes including BLMs, ELMs and SLMs due to negligible loss of extractant or carrier reagent from the membrane. Therefore, PIMs are

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becoming of great interest for the transport and separation of chemical species [22–25]. PIMs are produced through a casting solution containing a carrier reagent (or an extractant), a modifier (or a plasticizer) and a base polymer (i.e., poly(vinyl chloride) or cellulose triacetate [CTA]). The feed and stripping phases are separated by the membrane, and in this system, organic solvents are not used to maintain the phase separation. Loss of carrier from the membrane is negligible, and small amount of carrier is often required, enabling the use of expensive extractant types [26]. Although PIMs are often accused of having low permeabilities due to the increase in the viscosity of the membrane support medium, various studies comparing transport efficiency of PIMs with traditional SLMs have reported that PIMs provided good long-term stabilities and fluxes comparable with those showed by SLMs [27]. For example, Schow et al. [28] studied the fluxes for K^+ ion through flat-sheet and hollow fiber SLMs and a PIM prepared using CTA and 2-nitrophenyl octyl ether (NPOE) as plasticizer, and a crown ether as carrier. They reported that PIM fluxes were three orders of magnitude larger than those obtained from flat-sheet and hollow fiber SLMs. On the basis of stability test performed for 80 d, they also indicated that no decrease in K^+ flux was observed for PIM. Paugam and Buffle [29] investigated the facilitated transport of Cu(II) through both SLM- and CTA-based PIM using lauric acid as carrier. They pointed out that Cu(II) transport was controlled by diffusion in both type of membranes, and on the basis of the correction for the difference in porosity and tortuosity, the diffusion coefficients were determined as 22 times lower in the PIM than in the SLM. Similarly, Aguilar et al. [30] investigated the transport of Cd(II) and Pb(II) through CTA-based PIM and SLM using Kelex 100 as carrier. Despite of the considerable difference in viscosity between PIM and SLM, in case of Pb(II), maximum permeability for the PIM system was about two times lower than that for SLM. The stability of PIM was tested by using the same membrane for 20 cycles, and no significant decrease in the permeability value was reported. Kim et al. [31] studied the selective transport of cesium over other alkali metal ions through PIM consisting of CTA–NPOE/tris(2-butoxyethyl) phosphate (TBEP) and calixcrown ethers as carriers. It was reported that PIM exhibited higher flux and more stability than corresponding SLM. Similar results were reported for the transport of Ag(I) ion through PIM containing acyclic polyether bearing amide and amine end-group in comparison with the SLM system [32].

Literature survey showed that the studies about the facilitated transport of Zn(II) ions through a PIM are very rare [33–35]. Therefore, the objective of this study was to prepare a PIM consisting of CTA as a polymer support, several plasticizers and sodium diethyldithiocarbamate (NaDDTC) as a carrier agent, and its application to the selectively facilitated transport of Zn(II) ions.

Dithiocarbamates have functional groups with sulfur, and therefore, they are considered as a suitable chelating agent for metal ions with soft acid character such as Cd, Pb and Cu [36]. NaDDTC is a chelating agent, which is able to form complexes with several elements, including Cu, Ni, Co, Fe, Cr, Mo, U, Se, Te, etc. These chelates are soluble not only in water but also in organic solvents such as CCl_4, $CHC1_3$, acetone, TBP, kerosene, etc. Therefore, NaDDTC has a wide application in spectrophotometric analysis and solvent extraction procedures [37].

In this study, Zn(II) ion was selected as model ion in the transport experiments because it can be found in the effluents of many industries including electroplating, rayon fiber manufacture and steel works [38]. Stripping of Zn(II) from the membrane was achieved using hydrochloric acid [36,39]. The effects of parameters including Zn(II) ion concentration in the feed phase, initial pH and stripping phase concentration, type of membrane plasticizers and existence of Ni(II), Cu(II) and Pb(II) on the transport of Zn(II) ions were studied.

2. Experimental

2.1. Chemicals

All chemical reagents used in this study were of analytical grade. Sodium diethyldithiocarbamate trihydrate solution ($NaDDTC.3H_2O$), dichloromethane, HCl, NaOH, NaCl, CH_3COOH, $Zn(NO_3)_2.4H_2O$, $Pb(NO_3)_2$, $Cu(NO_3)_2.3H_2O$ and $Ni(NO_3)_2.6H_2O$ were obtained from Merck (Germany). CTA, NPOE, tris(2-ethylhexyl)trimellitate (TEHM), bis-(2-ethylhexyl)adipate (BEHA), dibutyl phthalate (DBP) and 1-decanol (DOH) were obtained from Fluka (Switzerland).

2.2. PIM preparation procedure

A modified version of the procedure reported in reference [24] was followed for the preparation of PIMs. Briefly, 200 mg of CTA was dissolved in 20 mL of dichloromethane at room temperature. 2-NPOE (0.3 mL) in 5 mL of dichloromethane was then added. After this solution was stirred vigorously, a desired amount of NaDDTC in 5 mL of glacial acetic acid was added and stirred for 30 min in order to obtain a homogenous solution. The solution was rested overnight to evaporate the dichloromethane. The resulting membranes were recovered from glass plate surface by immersion into cold water. Finally, the PIMs were kept in distilled water for 2 h before it was used in the transport experiments.

2.3. Characterization of PIM surfaces

The PIMs were characterized by employing Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques and contact angle measurements. FTIR spectrum of the PIMs was recorded by an attenuated total reflection (ATR) FTIR spectrometer (PerkinElmer 100 FTIR) over the wave number range from 400 to 4,000 cm^{-1}. Surface images of the PIMs were obtained by using an SEM (ZEISS EVO-LS10) at 20 kV in high vacuum. The size of the PIMs was assessed by Scandium 5.0 software (Olympus Soft Imaging Systems, Japan). AFM images were recorded by a Veeco diCaliber instrument. Contact mode of AFM in air was employed in order to investigate the surface morphology with a scanning speed of 2 kHz. Silicon nitride cantilevers (antimony, ndoptFi) were used. The sessile drop method was followed to measure the contact angle of the PIMs. A 4-µL droplet of distilled water was placed on the PIM surface using a 0.10-µL syringe, and a horizontal beam comparator (KSV CAM 200) was employed to measure the contact angle.

2.4. Transport experiments

The transport experiments were performed in a Teflon cell consisting of two detachable chambers. The chambers were separated by the PIM (effective membrane area: 7.07 cm^2), and silicon rubber seals were used in order to prevent any leakage from the chambers. Each chamber was filled with equal volumes (40 mL) of the feed phase, and the stripping phase and both phases were stirred at 600 rpm throughout the experiment. Ionic strengths of the feed and stripping phases were equal by employing NaCl. All transport experiments were conducted for 4 h at a constant temperature (25°C ± 1°C).

The effects of experimental parameters (i.e., initial pH [1.0–6.0], feed phase concentration of Zn(II) [1 × 10^{-4}–1 × 10^{-3} M], NaDDTC.3H_2O concentration in the casting solution [0.5–5.0 wt%], stripping phase (HCl) concentration [0.1–1.0 M]) on the transport of Zn(II) through the PIM were studied. Moreover, the effects of various competitive ions including Ni(II), Cu(II) and Pb(II) on the transport of Zn(II) were studied.

The permeability coefficient (P) was employed to evaluate the influence of the studied parameters on the transport of Zn(II). P is defined as indicated in Eq. (1) [40]:

$$P = \frac{dC}{C} \cdot \frac{1}{dt} \cdot \frac{V}{A} \tag{1}$$

Integration of Eq. (1) produces Eq. (2):

$$\ln \frac{C_o}{C_t} = \frac{A}{V} \cdot P \cdot t \tag{2}$$

where P is the permeability coefficient (m/s); C_0 is the initial feed phase concentration of Zn(II); and C_t is the feed phase concentration of Zn(II) at time t (s). A denotes the effective membrane area (7.07 cm^2), and V is the volume of the feed phase (mL). Thus, the slope of the linear plot of $\ln(C_0/C_t)$ vs. time provides the permeability coefficient.

Recovery of Zn(II) can also be defined according to Eq. (3):

$$\text{Recovery}(\%) = 100 \cdot \left(\frac{C_s}{C_o}\right) \tag{3}$$

where C_s is the stripping phase concentration of Zn(II) at time t, and C_0 is the initial feed phase concentration of Zn(II).

Concentration of Zn(II) in the feed or stripping phases was determined by periodically withdrawing 1 mL of solution from the feed or stripping phases (every 1 h) over 4 h. Zn(II) concentration of the samples were determined by a continuum source atomic absorption spectrometer (ContrAA 300, Analytik Jena) in air-acetylene flame system at wavelength of 213.8 nm. In the competitive transport experiments, Ni(II), Cu(II) and Pb(II) concentration was determined on ContrAA 300 in air-acetylene flame at wavelength of 232.0, 324.8 and 217.0 nm, respectively. Each reported analytical data is the mean of two replicates. pH measurements were achieved by a pH-meter (Thermo 420A+) equipped with a combined glass–Ag/AgCl electrode.

3. Results and discussion

3.1. Characterization of PIM

FTIR spectra of blank membrane (black line), NaDDTC.3H_2O (blue line) and PIM containing 1.0 wt% of NaDDTC.3H_2O (red line) are depicted in Fig. 1. For blank membrane, the band appeared at around 1,749 cm^{-1} can be attributed to stretching vibrations of the carbonyl group. The bands at 1,228 and 1,047 cm^{-1} can be assigned to the stretching modes of C–O single bonds. The bands at 2,927 and 2,856 cm^{-1} correspond to C–H bonds. Infrared (IR) spectra of both blank membrane and PIM are similar because of their similar structure. By considering the bands observed for blank membrane, NaDDTC.3H_2O and PIM, it can be concluded that PIM was successfully prepared. This conclusion is also supported by differences between the AFM, SEM images of blank membrane and PIM and contact angle measurements.

Fig. 2 shows the AFM images of surface of blank membrane and PIM prepared with 1.0 wt% of NaDDTC. The blank membrane has a non-porous surface character. As it is seen in Fig. 2, the difference between the surface of blank membrane and PIM can be attributed to the inclusion of the carrier (NaDDTC) into the CTA membrane support.

Fig. 3 presents the SEM images of the blank membrane and PIM. Fig. 3(a) shows that blank membrane has smooth surface. However, Fig. 3(b) clearly indicates that NaDDTC is dispersed throughout the membrane support, which means that inclusion of NaDDTC.3H_2O into the membrane support was achieved.

Contact angle measurements are employed to study the hydrophilicity of the material surfaces [41]. In this study, contact angle measurements were taken at room temperature for blank membrane and PIM with 1.0 and 5.0 wt% of NaDDTC, and the contact angles were determined to be 57° ± 3°, 61° ± 4° and 74° ± 4°, respectively (n = 3). Contact angle values of the PIM increased with increasing amount of NaDDTC in the membrane. Increase in the contact angle corresponds to a decrease in the wettability of the membrane surface. It is also likely that higher carrier concentration led to a higher contact angle due to the capillary force working from the membrane pore, which prevented the movement of the water droplet on the surface by leading to the higher contact angle [42].

3.2. Zn(II) transport experiments

3.2.1. Effect of plasticizer type

PIMs were prepared using various plasticizer including NPOE, TEHM, BEHA, DBP and DOH to reveal the effect of plasticizer on the transport of Zn(II) by keeping the amount of carrier and CTA in the PIM constant. The result in Table 1 showed that initial fluxes, permeability and recovery factor were obtained with plasticizer in the order of NPOE > DOH > BEHA > DBP > TEHM. The obtained result can be attributed to the viscosity and dielectric constant of plasticizers examined in this study (Table 1). The highest transport efficiency was recorded when the plasticizer NPOE with the highest dielectric constant was used. The plasticizer with high dielectric constant exhibits relatively high polarity. This kind of plasticizer is particularly preferred for the preparation of PIM because they provide better transport efficiency [43,44].

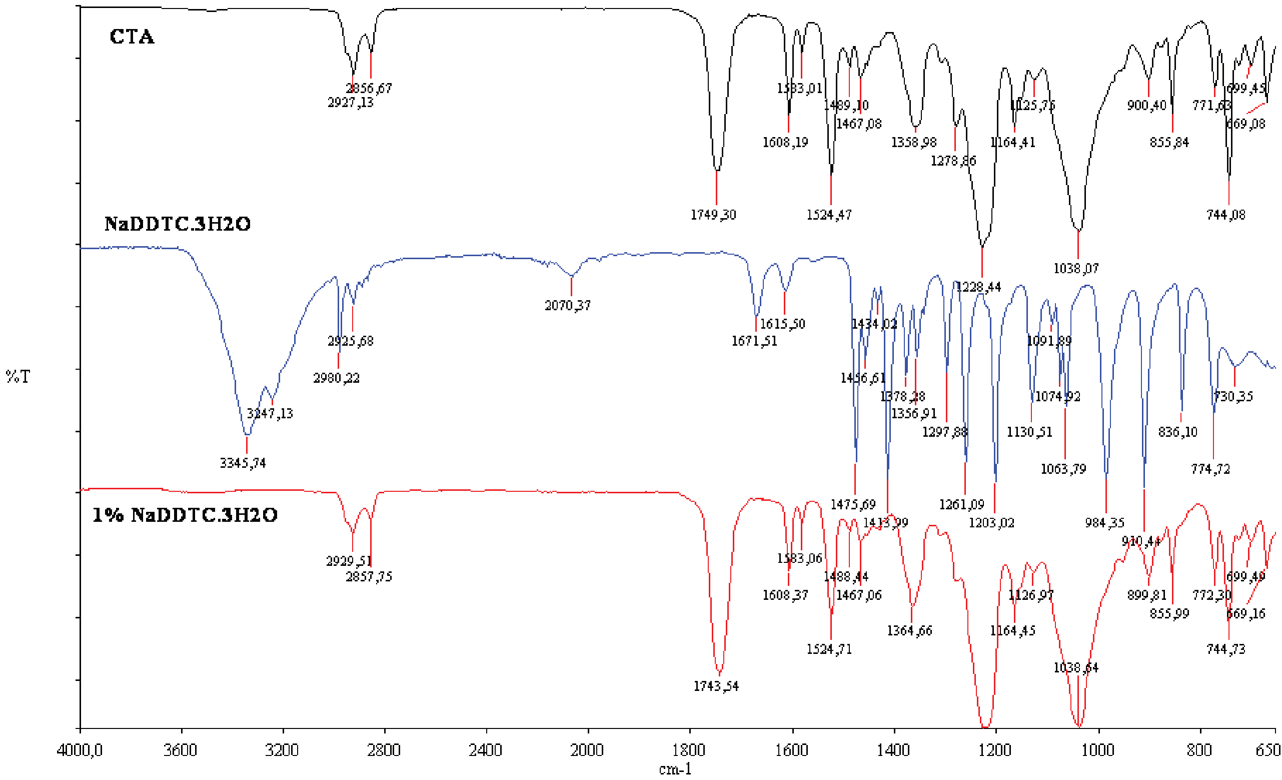

Fig. 1. FTIR spectrum of blank membrane (black line), PIM containing 1.0 wt% of NaDDTC.3H_2O (red line) and NaDDTC.3H_2O (blue line).

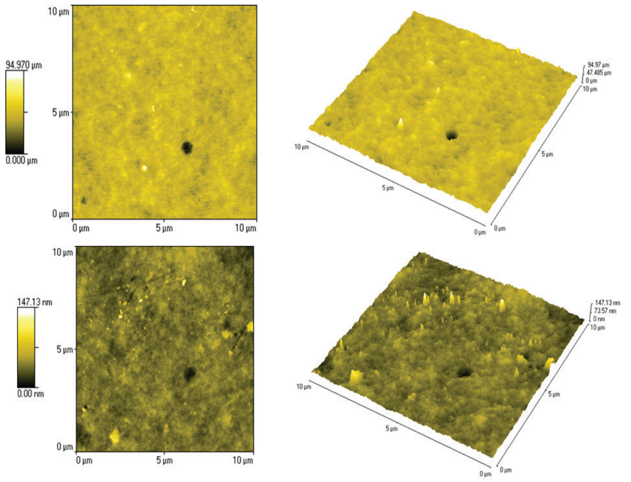

Fig. 2. AFM images of blank membrane and PIM containing 1.0 (wt%) of NaDDTC.3H_2O.

3.2.2. Initial pH effect and Zn(II) transport mechanism

Zn(II) transport experiments were carried out at initial pH of 1.5, 2.2, 3.1, 4.2, 5.1 and 6.0 to reveal the effect of initial pH of the feed phase on the transport. In each pH measurement, a deviation of ±0.1 was recorded. Fig. 4 shows that efficient transport of Zn(II) through the PIM with NaDDTC can be achieved when the initial pH of the feed phase is equal to or higher than 5.04. This result is in good agreement with our

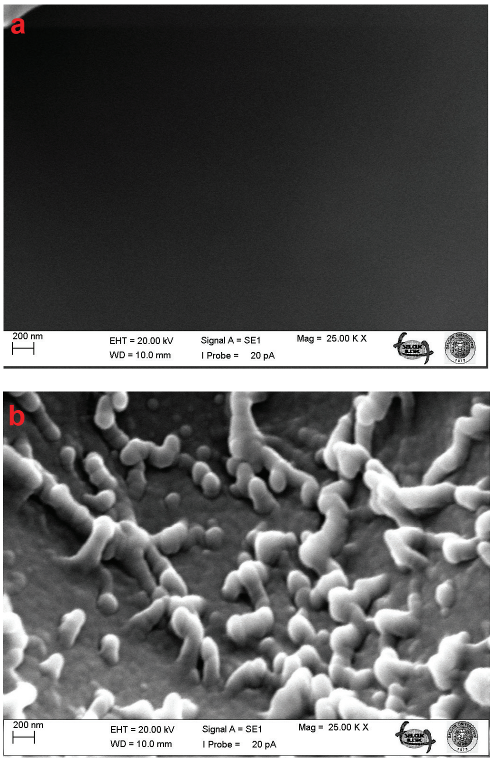

Fig. 3. SEM images of blank membrane (a) and PIM containing 1.0 (wt%) of NaDDTC.3H_2O (b).

previous work [45], which reports the selectively facilitated transport of Zn(II) through a PIM containing Cyanex 272 as a carrier reagent.

Zinc ion exists as Zn^{2+} in the feed phase under specified conditions of the present study (at pH 5.1 and ionic strength of feed phase: 0.5 M maintained with NaCl) [46]. It is likely that the extraction of Zn(II) from the feed phase occurred by means of the interaction between positively charged zinc ion and negatively charged diethyldithiocarbamate (DDTC).

A possible Zn(II) transport mechanism through PIM can be described as follows: NaDDTC forms complex with Zn(II) ions at the feed phase–membrane interface. The resulting complex diffuses across the PIM, and it was decomplexed by HCl at interface between the membrane-stripping phases. This explanation is suggested on the basis of reference [37], which described the transport of selenite through a solid SLM using NaDDTC, as carrier between HCl solutions. This mechanism, called as facilitated transport, has been mentioned in earlier report [45].

3.2.3. Effect of carrier concentration

Metal ion transport through the membrane is considerably affected by the carrier concentration in the membrane. PIMs were prepared at four different amount of NaDDTC (0.5, 1.0, 3.0 and 5.0 wt%). It was observed that increase in the amount of NaDDTC up to 1.0 wt% improved the transport of Zn(II) (Fig. 5). This can be linked to the stoichiometry of the Zn(II)–NaDDTC complex is 1:2 [47]. Hence, increasing the NaDDTC content of PIMs produced enhancement in the transport. However, there is no significant change in the transport efficiency of the PIMs when amount of NaDDTC in the casting solution exceeded 1.0 wt%. In other words, all the reactive sites do not contribute to the transport when carrier concentration of the PIM is higher than 1.0 wt%.

These findings can be also attributed to the contact angle measurement studies presented in section 3.1. The PIM with 5 wt% carrier had contact angle of 74° ± 4°, which is higher than those of blank PIM (57° ± 3°) and PIM with 1 wt% of carrier (61° ± 4°). Thus, higher contact angle or lower wettability of the surfaces produced lower permeability, hence lower Zn(II) transport. But, it should be stated that no detectable movement of the Zn(II) ions through the blank PIM means that the transport of Zn(II) ions through the PIM is accomplished by the carrier. Hence, PIMs with 1 wt% carrier were used in further experiments.

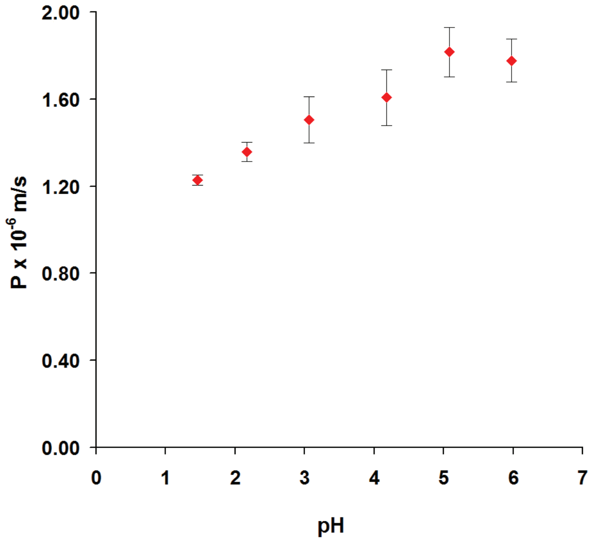

Fig. 4. Effect of initial pH of the feed phase on the transport of Zn(II) through the PIM (feed phase: 1×10^{-3} M Zn(II), stripping phase: 0.5 M HCl, PIM containing 1.0 wt% of $NaDDTC.3H_2O$).

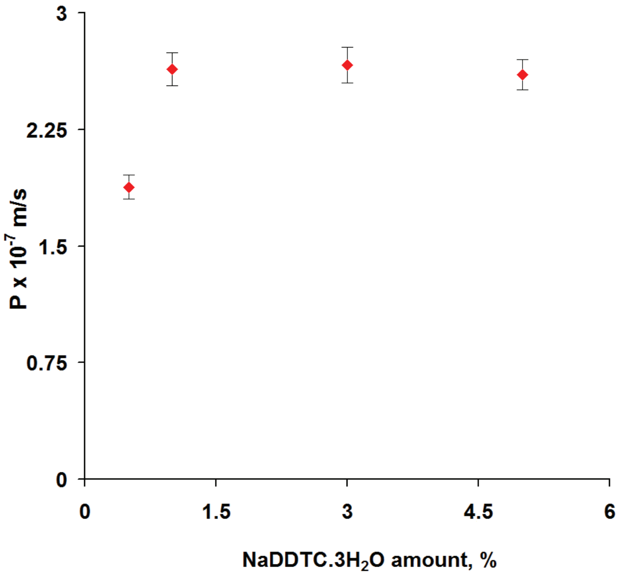

Fig. 5. Effect of $NaDDTC.3H_2O$ amount on the transport of Zn(II) through the PIM (feed phase: 1×10^{-3} M Zn(II), initial pH of the feed phase: 5.1 ± 0.1, stripping phase: 0.5 M HCl).

Table 1
The parameters for the transport of Zn(II) through PIM with different plasticizer

Plasticizer	Viscosity (cP)	Dielectric constant (ε_r)	$J_i \times 10^{-8}$ [mol/(cm^2.s)]	$P_i \times 10^7$ (m/s)	RF (%)
NPOE	11.1 (25°C)	24 (25°C)	3.95	3.95	96
TEHM	12.5 (na)	4.95 (na)	0.85	0.85	20
BEHA	13.7 (na)	5 (na)	1.69	1.69	42
DBP	16.6 (25°C)	6.58 (20°C)	1.69	1.69	39
DOH	5.4 (na)	5.19 (na)	1.97	1.97	43

Note: RF: Recovery factor and na: not available.

3.2.4. Effect of Zn(II) concentration of feed phase

Fig. 6 shows that the effect of the concentration of Zn(II) on its transport was studied at different concentration in the range of 1 × 10^{-4}–1 × 10^{-3} M. Increasing the ion concentration in the feed phase from 1 × 10^{-4} to 1 × 10^{-3} M decreased the transfer percentage from 100% to 71% for 6 h of transport. We reported similar findings in our previous paper [48], which described facilitated transport of Cr(VI) through an activated composite membrane containing Cyanex 923 as carrier reagent. This finding is also in agreement with result reported in reference [35].

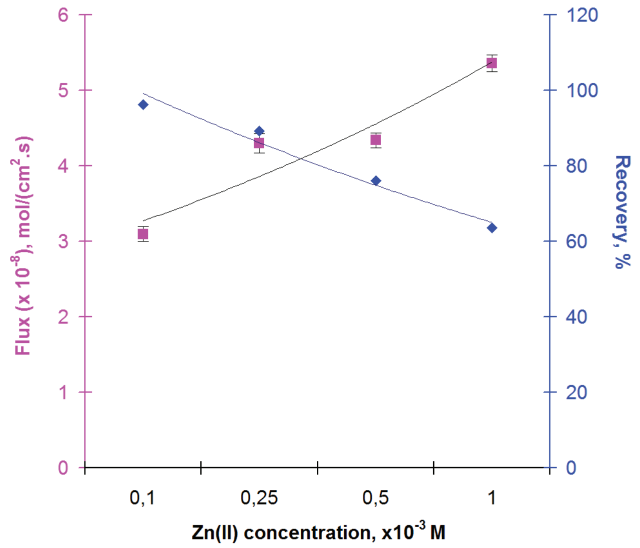

Fig. 6. Effect of Zn(II) concentration of the feed phase on the transport (initial pH of the feed phase: 5.0 ± 0.1, stripping phase: 0.5 M HCl, PIM containing 1.0 wt% of NaDDTC.3H_2O).

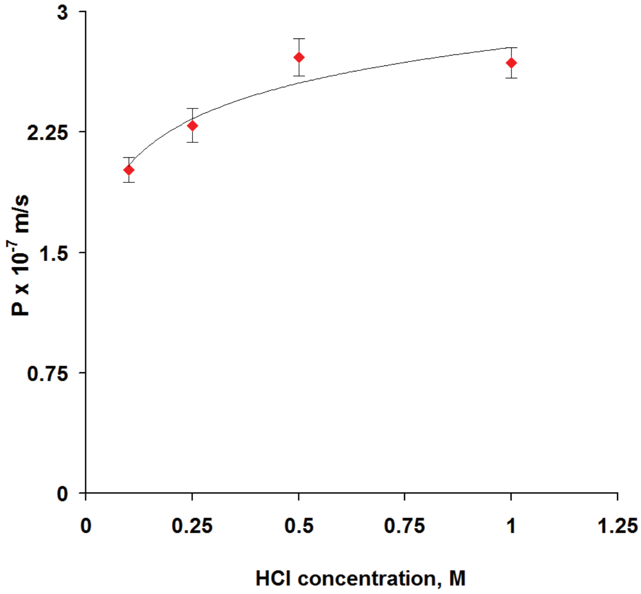

Fig. 7. Effect of stripping phase concentration on the transport of Zn(II) (feed phase: 1 ×10^{-3} M Zn(II), initial pH of the feed phase: 5.0 ± 0.1, PIM containing 1.0 wt% of NaDDTC.3H_2O).

Flux values, defined in Eq. (4) [49], are employed to assess the influence of the Zn(II) concentration on the transport:

$$J = P \cdot C_o \tag{4}$$

For different concentration of Zn(II) from 1 × 10^{-4} to 1 × 10^{-3} M, the flux values were recorded in the range between (3.09 ± 0.08) × 10^{-8} and (5.36 ± 0.04) ×10^{-8} mol/(cm^2 s). These results are expectable as higher concentration yields a higher flux according to Eq. (4). As the Zn(II) concentration increases, the complexation rate at the feed phase–PIM interface increases, which also results in the increase of the decomplexation rate at the PIM-stripping phase interface. Moreover, amount of Zn(II) inside the membrane was determined on the basis of mass balance. As a result, no retention of Zn(II) in the membrane was recorded, and the time lag was not observed during the transport.

3.2.5. Influence of stripping phase concentration

Since the extraction takes place at the interface of the feed phase–PIM, the extraction of Zn(II) occurs via a simultaneous back extraction step at the opposite side of the PIM. During the back extraction step, the extractant or carrier is regenerated, and the metal ions are stripped. As a result, the extraction efficiency is influenced by type and concentration of the reagents in the stripping phase. On the basis of the study [37], which described the transport of selenite through an SLM using NaDDTC, HCl was used as stripping phase. Moreover, HCl was used in the stripping solution in many other studies about the facilitated transport of metal ion [40,42,45]. Therefore, in this study, HCl was used as stripping phase. The effect of various HCl concentration in the range of 0.1–1.0 M on Zn(II) transport was investigated. By considering the HCl concentration of stripping phase, the ionic strength of the feed phase was also adjusted to 0.1–1.0 M by using NaCl. As it is depicted in Fig. 7, an increase in HCl concentration enhanced the transport of Zn(II). This behavior corresponds to the expected transport mechanism of metal ions through the PIM [50].

3.2.6. Stability of the PIMs

The transport efficiency of the PIMs produced in four different batches of 1.0 wt% NaDDTC solution was studied under the specified conditions (initial pH of the feed phase:

Table 2
The change in the permeability coefficient with sequential transport experiment (initial pH of the feed phase: 5.04 ± 0.01, concentration of Zn(II): 1 × 10^{-3} M, HCl concentration in the stripping phase: 0.5 M, transport time: 4 h)

Transport cycle	Permeability coefficient, $P \times 10^{-6}$ m/s
1	5.85 ± 0.06
2	5.65 ± 0.04
3	5.36 ± 0.04

Table 3
Comparison of the carrier reagent, pH, processing time and selectivity order for selective separation through various membrane techniques with PIM used in this study

Membrane technique	Carrier reagent	pH	Processing time, h	Selectivity order	Reference
PIM	NaDDTC	5	4	Zn > Cu ≈ Pb > Ni	This study
PIM	DEHPA	2	24	Zn > Cu	[52]
PIM	Cyanex 301	3	24	Pb > Cd > Zn	[26]
PIM	Cyanex 302	3	24	Cd > Zn > Pb	[26]
ACM[a]	Cyanex 301	3	24	Pb, Cd > Zn	[26]
ACM	Cyanex 302	3	24	Cd > Pb > Zn	[26]
BLM[b]	Aliquat 336	3	4	Zn > Ni > Cd	[53]
PIM	DEHPA	4	72	Zn > Cu	[13]
HFSLM[c]	LIX84	2	2	Cu > Zn	[54]

[a] Activated composite membrane.
[b] Bulk liquid membrane.
[c] Hollow fiber supported liquid membrane.

5.04 ± 0.01, concentration of Zn(II): 1 × 10^{-3} M, HCl concentration in the stripping phase: 0.5 M). It was observed that transport efficiency of the PIMs was reproducible (relative standard deviation: ≤4%, mean transport percentage: 96%).

The stability of the PIM was examined by evaluation of the permeability coefficients from three sequential experiments. In the experiments, the same membrane was used under the mentioned experimental conditions. As it is seen in Table 2, the permeability coefficient did not change: (5.36 ± 0.04–5.85 ± 0.06) × 10^{-6} m/s, within all transport cycles (each cycle: 4 h), demonstrating that the PIMs have a potential to be utilized in the long-term separation processes.

3.2.7. Selectivity studies

The most common matrix constituents that can be found in real samples, e.g., alkali and alkaline earth elements, did not react with NaDDTC. However, metal ions that are capable of reacting with NaDDTC may reduce the extraction efficiency of Zn(II). Therefore, the effects of Cu(II), Pb(II) and Ni(II) on the transport of Zn(II) through the prepared PIM were studied. In these experiments, the transport efficiency of the PIMs from four different batches of 1.0 wt% NaDDTC solution was assessed under the specified conditions: initial pH of the feed phase: 5.04 ± 0.01, Zn(II); other metal ion concentration: 1 × 10^{-3} M; stripping phase: 0.5 M HCl. The results showed that Pb(II), Ni(II) and Cu(II) were transported through the PIM with transport percentage of 26%, 20% and 27%, respectively. This result can be attributed to the constant (β_2) of complex formation between Zn(II), Pb(II), Ni(II) and Cu(II) with DDTC, which are 11.4, 18.3, 12.9 and 23.9, respectively [47,51]. In other words, value of complex formation constants indicates the strength of the complex. A higher value of the constant means difficult stripping of corresponding ion, hence, difficult transport. Moreover, in the presence of these ions, Zn(II) was transported by giving a transport percentage of 73%, which was lower compared with the transport of Zn(II) from the feed phase containing only-Zn(II) ions (96%). This result may be probably due to the negative salting-out effect on the transport of Zn(II) through PIM [49]. A comparison for the transport of metal ion through various membrane techniques by means of carrier reagent, pH of feed phase, processing time and selectivity order for various metal ions in the previously reported studies with presented study are shown in Table 3. In our study, the comparable results with previous studies were obtained.

4. Conclusions

This study showed that inclusion of NaDDTC in the CTA structure was achieved, and the obtained PIM could be successfully used for the facilitated transport of Zn(II) ions. Moreover, in the presence of competitive divalent ions including Pb(II), Ni(II) and Cu(II), selectively transport of Zn(II) ions were achieved by prepared PIM. The results also showed that the transport efficiency of the PIM was reproducible and it can be suggested for the long-term separation processes.

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