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Selective transport of chromium (III), cobalt (II), barium (II) and strontium (II) ions through polymer inclusion membranes

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ABSTRACT

In the present work the separation of chromium(III), cobalt(II), barium(II) and strontium(II) from chloride solution using polymer inclusion membranes (PIMs) was investigated. PIMs doped with amide derivatives of 2-aminobenzoic acid [2-dodecanamidobenzoic acid (DABA), 2-tetradecanamidobenzoic acid (TABA), 2-palmitamidobenzoic acid (PABA) and 2-stearamidobenzoic acid (SABA)] as fixed carriers, cellulose triacetate (CTA) as base polymer and dioctyl phthalate (DOP) as a plasticizer have been prepared. The amide derivatives were prepared by reaction of 2-aminobenzoic acid with fatty acids (lauric, myristic, palmitic and stearic acid) in the presence of N,N`-dicyclohexylcarbodiimide (DCC) as dehydrating agent. The chemical structure of the prepared carriers was confirmed by Fourier transform infra-red (FTIR) and nuclear magnetic resonance (^{1}HNMR), while the prepared membranes were characterized using different techniques such as FTIR, X-ray diffraction and scanning electron microscopy (SEM). The competitive transport of Cr(III), Co(II), Ba(II) and Sr(II) ions through PIM was investigated and optimized as a function in transport time, pH, membrane composition, type of receiving phase and its concentration. Results showed that the initial flux of chromium(III) transport increased with different carriers in the order DABA < TABA < PABA < SABA through the cellulose triacetate membranes. The chromium(III) ions were transported with a highest rate, and the selectivity order was as follows: Cr(III) > Co(II) > Ba(II) > Sr(II). The best results of normalized initial flux and recovery were obtained for membranes containing 40% of each carrier. The obtained results showed that around 96.3% of Cr(III) was transported from the source phase containing equimolar mixture of all metals at pH 4.1 through PIM after 10 h into 3.0 M HCl using carrier SABA.

Keywords: Polymer inclusion membrane (PIM); Dioctyl phthalate (DOP); Cellulose triacetate (CTA); N;N′-dicyclohexylcarboimide (DCC)

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1. Introduction

Cr(III) is considered to be an essential trace element for proper functioning of living organisms, whereas Cr(VI) is toxic and causes cancer in humans. During wastewater treatment the less toxic Cr(III) often changes its oxidation state and becomes more toxic Cr(VI). Therefore, removal of both existing forms of chromium is very important for protection of the natural environment and human health [1,2].

In higher concentrations, cobalt is toxic to humans and to terrestrial and aquatic animals and plants [3]. Barium and strontium ions are the most toxic radio-nuclides present in radioactive liquid wastes arising out of different activities including: inadequate practices for the management and disposal of radioactive waste, accidental discharge of radioactive material to the environment, nuclear activities, testing of nuclear weapons, nuclear fuel cycle processes, etc. Both these ions are bone seeking elements and hence have carcinogenic effects [4–6].

General techniques for removal liquid radioactive waste are precipitation, solvent extraction and ion exchange but each process has some limitations in application [7]. In the

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last decades new technologies have been proposed. These include techniques which are becoming commercially available or utilized at least to some extent in full scale applications, such as membrane separation, electro dialysis and emerging technologies such as extractive metallurgy and selective adsorption [8].

Transport of metal ions across liquid membranes (LMs) is a strong tool, which combines extraction and stripping in one step of process. LMs play important role in science and technology, and many efforts were made for development of these kinds of membranes [9]. Liquid membrane systems include bulk liquid (BLMs), emulsion liquid (ELMs) and supported liquid membranes (SLMs) [10]. Polymer inclusion membranes (PIMs) were developed as an alternative of SLMs.

Separation methods based on polymeric inclusion membranes (PIMs) have received considerable attention due to the high stability of such membranes compared to that of supported liquid membranes [11]. These membranes are easy to prepare and have excellent mechanical properties [12]. It is envisaged that the development of metal selective PIMs will bring in a quantum jump in the field of separation science and technology [13]. These processes are important because of the use of selective carrier species which would increase the mass transfer and improve the selectivity of the process [14].

Konczyk et al. [15] studied facilitated transport of chromium(III) through polymer inclusion membrane (PIM) containing 2-ethylhexylphosphonic acid (DEHPA) as an ion carrier and tricaprylylmethyl ammonium chloride (Aliquat 336) as a plasticizer. Tor et al. [16] reported transport of Cr(III) through polymer inclusion membrane (PIM) with di(2-ethylhexyl)phosphoric acid (DEHPA) as carrier. According to the competitive transport of Cr(III), Cu(II) and Ni(II) through the PIM, the transport selectivity order was found as Cr(III) ≈ Cu(II) > Ni(II).

The competitive transport of cobalt-60, strontium-90 and cesium-137 radioisotopes across polymer inclusion membranes with 3,7-dinonyl-naphtalene-1-sulfonic acid (DNNS) was studied. The selectivity order of metal ions transported was found to be: Co(II) < Cs(I) < Sr(II) [17]. Lee et al. [18] studied the selective transport of Cs(I) and Ba(II) by a novel self-assembled isoguanosine ionophore through polymer inclusion and bulk liquid membranes. They reported that excellent Cs^+ flux and selectivity over the other alkali metal cations was observed in PIMs and bulk liquid membranes (BLMs). In the absence of Cs^+, this ionophore exhibits good Ba^{2+} selectivity in BLMs. Competitive transport of alkaline earth metal cations, i.e. Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, across plasticized cellulose triacetate PIMs by acyclic di-ionizablepolyethers were investigated by Eliasi [19]. For all studied acyclic polyethers, with increasing of the bridge length, the total flux of alkaline earth metal cations decreases. The best transported metal cation was barium, the values of molar Ba^{2+}/total ratio was very high and equal to 0.96.

Competitive transport of trace radionuclide ions, i.e., ^{137}Cs, ^{90}Sr, and ^{60}Co from $NaNO_3$ aqueous solutions across polymer inclusion membranes containing a mixture of dinonylnaphtalenesulfonic acid, and dibenzo-21-crown-7 as the carrier provide the selectivity order Cs(I) > Sr(II) > Co(II) [20]. Alamine 336 as an ion carrier used for separation of copper (II), cobalt (II), nickel (II) and cadmium (II) from aqueous solutions with polymer inclusion membranes [21].

The objective of the present work is to prepare a novel PIMs based on CTA as base polymer, DOP as plasticizer and some new amide derivatives of 2-amino benzoic acid as a new fixed carrier and use them for the selective extraction of chromium, cobalt, barium and strontium ions. We studied the behavior of the prepared carriers towards competitive transport of Cr(III), Co(II), Ba(II) and Sr(II) ions through a prepared membranes at different operating conditions such as, type of carrier and its wt%, contact time, pH of source and receiving phases.

2. Experimental and characterization techniques

2.1. Materials

Analytical-grade inorganic chemical chromium(III), cobalt(II), barium(II), and strontium(II) chlorides were obtained from Fluka. Organic reagents: cellulose triacetate (CTA), dioctyl phthalate (DOP), fatty acids (stearic, palmitic, myristic and lauric acid) and N,N`-dicyclohexylcarbodiimide (DCC) were purchased from Fluka and used without further purification. 2-amino benzoic acid, dichloromethane (CH_2Cl_2) was purchased from Sigma-Aldrich. Deionized water was used for preparing all aqueous solutions.

2.2. Synthesis

2.2.1. Synthesis of carriers

0.02 mole fatty acid (stearic, palmitic, myristic or lauric acid) was dissolved in 25 ml of dichloromethane. Solution of 0.01 mole N,N`-dicyclohexylcarbodiimide (DCC) (2.06 g) in 25 ml of dichloromethane was added to above solution with stirring for 15 min. The mixture was filtered off to remove dicyclohexyl urea. 0.01 mole of 2-aminobenzoic acid (1.37 g) dissolved in 50 ml dichloromethane was added to the above filtrate solution and stirred for 2 h. The product was obtained by evaporating dichloromethane and the solid product washed with petroleum ether to remove liberated acid. Crystallization with petroleum ether, m.p. 115, 103, 91 and 83°C for DABA, TABA, PABA and SABA, respectively and the yield ranging from 84 to 88%. Purity and structure of synthesized carries were confirmed by FT-IR and ^{1}HNMR spectra.

2.2.2. Membranes preparation

The membranes were prepared according to the procedure reported in the previous paper [22]. 10 ml of cellulose triacetate solution in dichloromethane (10 g/l) as the base polymer, 10 ml of (mixture of DOP and carrier) solution in dichloromethane (9.85 g/l of DOP as plasticizer and 30 g/l of carrier) was mixed and stirred to obtain a transparent solution. This solution was poured into a Petri dish of a 6.0 cm diameter. After slow solvent evaporation overnight the resulting membrane was peeled off from the Petri dish by immersion in cold water. Then, the membrane was soaked for 12 h in distilled water to achieve their homogeneity. The average thickness of the membranes was determined as 45 ± 3, 49 ± 2, 52 ± 4 and 56 ± 3 µm with DABA, TABA, PABA and SABA carriers, respectively using a digital micrometer (Salu Tron Combi-D3).

2.3. Characterization techniques

2.3.1. FT-IR measurements

The IR spectra for prepared carriers and membranes were measured using FT/IR-BRUKER, Vector 22 (Germany) spectrophotometer.

2.3.2. Nuclear magnetic resonance spectra (^{1}HNMR)

The proton magnetic resonance spectra (in $CDCl_3$ as a solvent) for prepared carriers were recorded on Bruker 400 MHZ spectrophotometer. The chemical shift (ϑ) is given downfield relative to tetramethylesilan (TMS) as internal standard.

2.3.3. Scanning electron microscopy (SEM)

Scanning electron microscopy was used to show the cross section morphology of the prepared membranes. Micrographs were obtained using (QUANTA 250 SEG, HOLANDA) microanalyzer microscope.

2.3.4. X-Ray diffraction (XRD)

The X-ray diffraction of the prepared membranes were obtained from Diano X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å).

2.3.5. Determination of the metal ions concentration

Metal ions concentration was determined by using Hitachi atomic absorption Z-6100 polarized Zeeman spectrometer.

2.4. Transport studies

Transport studies were carried out in a permeation cell in which the membrane film (at the surface area of 7.06 cm^2) was tightly clamped between two cells as shown in Fig. 1. Both the source and receiving aqueous phases (160 mL each) were stirred at 800 rpm. The source phase was solution containing chlorides of Cr(III), Co(II), Ba(II) and Sr(II) ions at the concentration of 0.01 M for each metals. The receiving phase was 1.0 M aqueous solution of hydrochloric acid. The PIM transport studies were carried out at room temperature 25°C. Small samples (1 ml each) of the source and receiving phase were taken periodically using a sampling port with a syringe and analyzed to determine metal ions concentrations by atomic absorption spectroscopy method. The pH of source phase was adjusted using few drops of diluted NaOH solution and controlled by pH-meter.

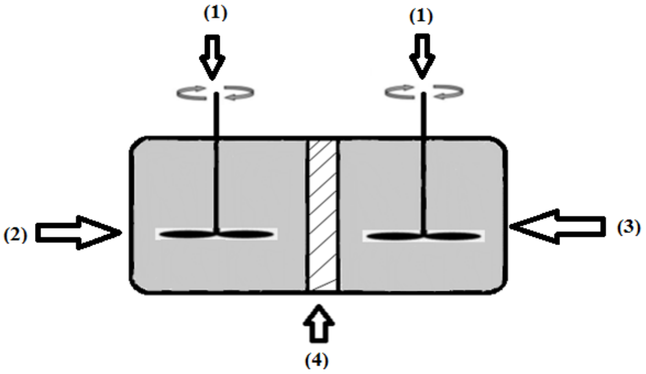


Fig. 1. A typical PIM experimental set up (1) Mechanical stirrer, (2) Source phase, (3) Receiving phase and (4) PIM.

The kinetic of the PIM transport was described by a first order transport rate equation in metal ion concentration:

$$\ln\left[\frac{c}{c_i}\right] = -kt \tag{1}$$

where *c* is the concentration (M) of metal ion in the source phase at given time, c_i is initial metal ion concentration (M) in the source phase, *k* is rate constant (s^{-1}), and *t* is time of metal transport (*s*).

To calculate the *k* values, plots of ln(c/c_i) with time were drawn. The rate constant value for the duplicate transport experiment was averaged. The relationship of ln(c/c_i) vs. time was linear, which was confirmed by high values of coefficient of determination (R-squared), i.e., which were mostly from 0.9764 to 0.9941.

The initial flux (J_i) was determined as equal to:

$$J_i = \frac{V}{A} \cdot k \cdot c_i \tag{2}$$

where *V* is volume of the source phase (m^3), and *A* is area of the effective membrane (m^2).

The selectivity coefficient *S* was known as the ratio of the initial fluxes for *M1* and *M2* metal ions, respectively:

$$S = J_{iM1}/J_{iM2} \tag{3}$$

The removal percent (*R*) of metal ions from the source phase into receiving phase was calculated as:

$$R = \frac{c_i - c}{c_i} \cdot 100\% \tag{4}$$

3. Result and discussion

Coupling of fatty acids (stearic, palmitic, myristic and lauric acid) with 2-aminobenzoic acid in the presence of DCC to afford the corresponding amide is shown in Fig. 2.

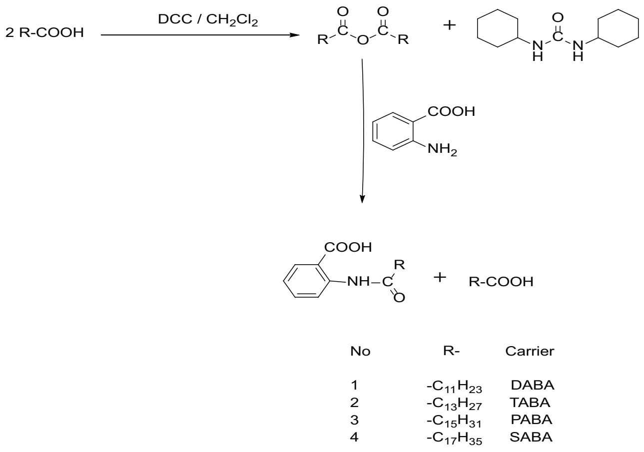


Fig. 2. The reaction of 2-aminobenzoic acid with fatty acids to afford DABA, TABA, PABA and SABA.

3.1. *Characterization of prepared carriers*

3.1.1. *FT–IR spectra of prepared carriers*

Figs. 3a–d show FT–IR spectra of the prepared carriers, which shown absorption peaks for all carriers at 1698 cm^{-1} attributed to C=O of carboxylic group and band at 1660 cm^{-1} for C=O of amide in fatty chain. The bands at 3326 and 3455 cm^{-1} assigned to NH and OH group, respectively. The bands at 2848 and 2917 cm^{-1} can be assigned to CH$_2$ group symmetry and asymmetry of fatty chain, respectively.

3.1.2. *^{1}HNMR spectra of prepared carriers*

Table 1 represents the chemical shift (δ) of the prepared carriers in ^{1}H NMR spectra.

3.2. *Membranes characteristic*

3.2.1. *FT–IR spectra of prepared membranes*

The chemical structure of the prepared membranes was characterized using Fourier transform infra-red (FT-IR).

Fig. 4 shows the spectra of the different prepared membranes. Table 2 lists the peak values and the corresponding radical of the reference CTA, DOP and CTA + DOP + carriers membranes.

The obtained results showed that all corresponding values obtained from the spectrum of the CTA reference membrane, i.e. without plasticizer and carrier, are present in the prepared membranes spectra in addition to those of the carrier molecules. This result confirms the presence of plasticizer and carrier in the polymer matrix.

3.2.2. *X-Ray diffraction*

Figs. 5a–d show the X-ray curves for cellulose triacetate (CTA) + plasticizer + carriers membranes. Based on these figures, we can observe the following:

- The CTA membrane presents a single maximum at approximately 20° found in all polymers and corresponds

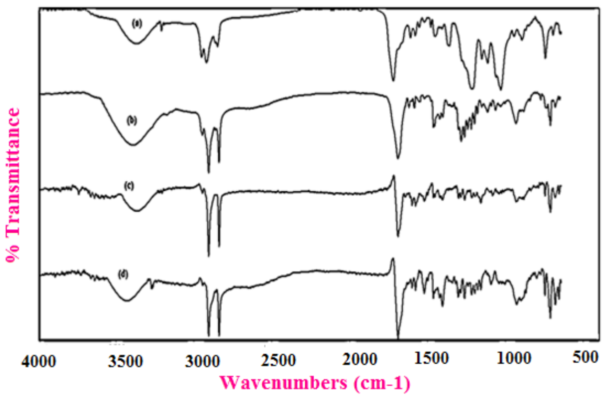


Fig. 3. FT-IR spectra of the prepared carriers (a) Carrier DABA, (b) Carrier TABA, (c) Carrier PABA and (d) Carrier SABA.

Table 1
The collected data of ^{1}HNMR of the prepared carriers

Carrier	δ (ppm)	Corresponding radical
DABA	0.83	(3H, CH$_3$)
	1.22	(16 H, CH$_2$ of fatty chain of lauric acid)
	1.75	(2H, $CO-\overset{\vert}{\underset{\vert}{C}}-CH_2$)
	2.44	(2H, COCH$_2$)
	6.66–8.14	(4H, CH aromatic)
	8.76	(1H, NH), which D$_2$O exchangeable
	10.98	(1H, OH), which D$_2$O exchangeable
TABA	0.83	(3H, CH$_3$)
	1.22	(20 H, CH$_2$ of fatty chain of myristic acid)
	1.75	(2H, $CO-\overset{\vert}{\underset{\vert}{C}}-CH_2$)
	2.44	(2H, COCH$_2$)
	6.66–8.14	(4H, CH aromatic)
	8.76	(1H, NH), which D$_2$O exchangeable
	10.98	(1H, OH), which D$_2$O exchangeable
PABA	0.83	(3H, CH$_3$)
	1.22	(24 H, CH$_2$ of fatty chain of palmitic acid)
	1.75	(2H, $CO-\overset{\vert}{\underset{\vert}{C}}-CH_2$)
	2.44	(2H, COCH$_2$)
	7.10–8.10	(4H, CH aromatic)
	8.76	(1H, NH), which D$_2$O exchangeable
	10.98	(1H, OH), which D$_2$O exchangeable
SABA	0.83	(3H, CH$_3$)
	1.22	(28 H, CH$_2$ of fatty chain of stearic acid)
	1.75	(2H, $CO-\overset{\vert}{\underset{\vert}{C}}-CH_2$)
	2.44	(2H, COCH$_2$)
	6.66–8.14	(4H, CH aromatic)
	8.76	(1H, NH), which D$_2$O exchangeable
	10.98	(1H, OH), which D$_2$O exchangeable

to the Van der Waals halo [23,24]. Thus, this material presents basically amorphous characteristics.

- The systems constituted by the mixture of CTA + DOP + carriers do not give any diffraction. It can be due to the absence of crystalline structure of the membrane which permits us to eliminate the mechanism of transfer of the ions by successive jumps between carrier complexing sites.

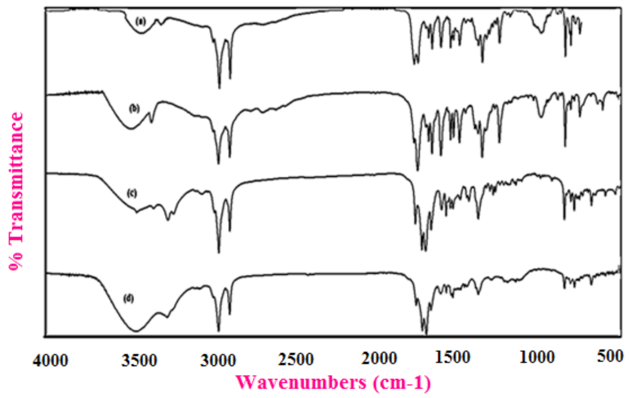


Fig. 4. FT-IR spectra of the prepared membranes (a) CTA + DOP + Carrier (DABA), (b) CTA + DOP + Carrier (TABA), (c) CTA + DOP + Carrier (PABA) and (d) CTA + DOP + Carrier (SABA).

Table 2
Peak values and the corresponding radicals in different membranes

Membrane	Peak value (cm^{-1})	Corresponding radical
CTA	3450–5550	O–H
	2935	C–H
	1739	C=O
	1526	COO$^-$
DOP	1726	C=O stretching of (COO)
	1077	C–O stretching of O–CH$_2$
	1285	C–O stretching of O=C–O
CTA + DOP + Carriers (DABA, TABA, PABA and SABA)	Same peaks of CTA and DOP	
	1698	C=O (carrier)
	1660	C=O (carrier)
	2848	C–H (carrier) symmetry
	2917	C–H (carrier) asymmetry
	3326	NH (carrier)
	3455	OH(carrier)

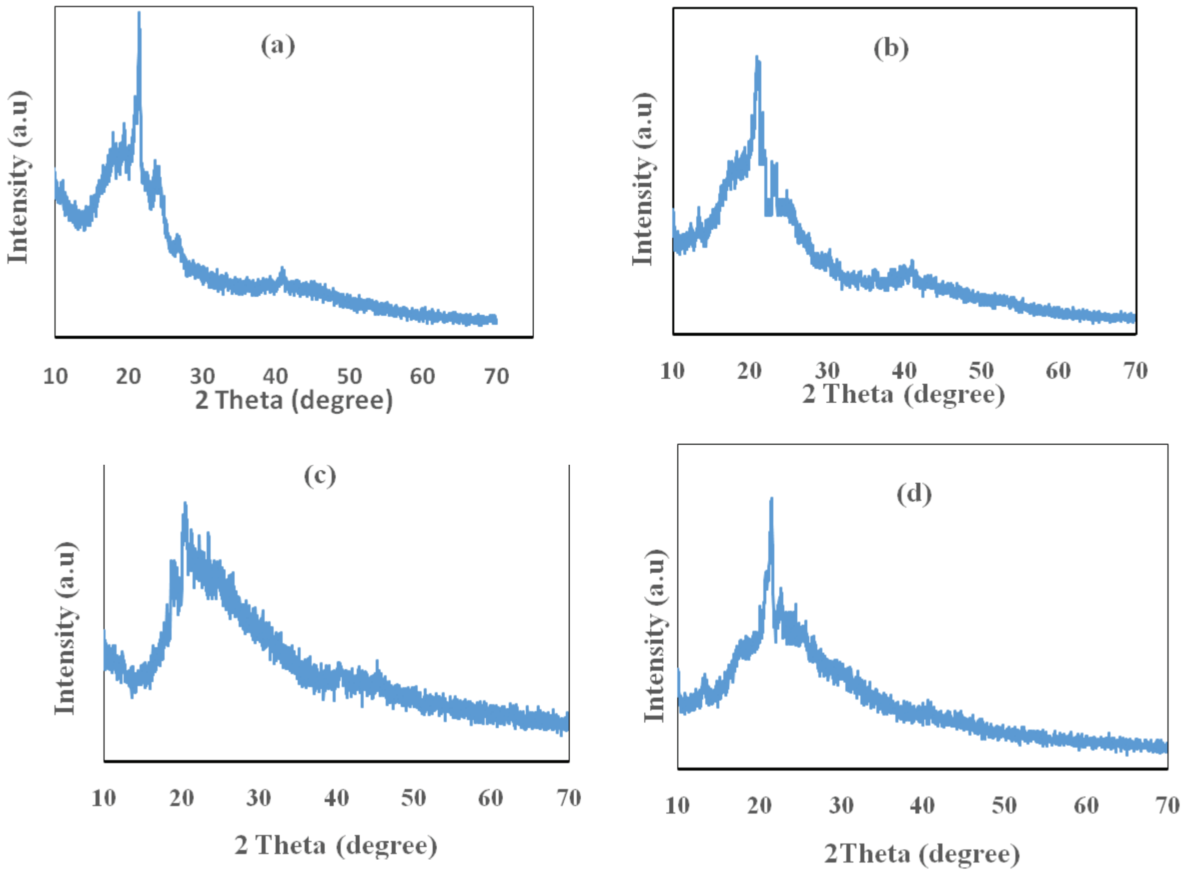


Fig. 5. X-Ray diffraction of the prepared membranes (a) CTA+ DOP + Carrier (DABA), (b) CTA + DOP + Carrier (TABA), (c) CTA + DOP + Carrier (PABA) and (d) CTA + DOP + Carrier (SABA).

3.2.3. Characterization by scanning electron microscopy (SEM)

The morphologies of cross section for the CTA + Plasticizer + carriers membranes (Figs. 6a–d) show that the CTA-plasticizer (DOP) and carriers membranes present a dense structure where the pores of membrane have been filled by the DOP and carriers molecules yielding a thick and less porous membrane.

3.3. Transport factors

3.3.1. Effect of transport time

Transport time is important role for metal ions transport because transport time can give information about mass transfer, kinetic reaction, membrane permeability and flux. To investigate the effect of transport time on studied metal ions transport, the concentration of Cr (III), Co (II), Ba (II) and Sr (II) in source phase was determined as a function of time (Fig. 7).

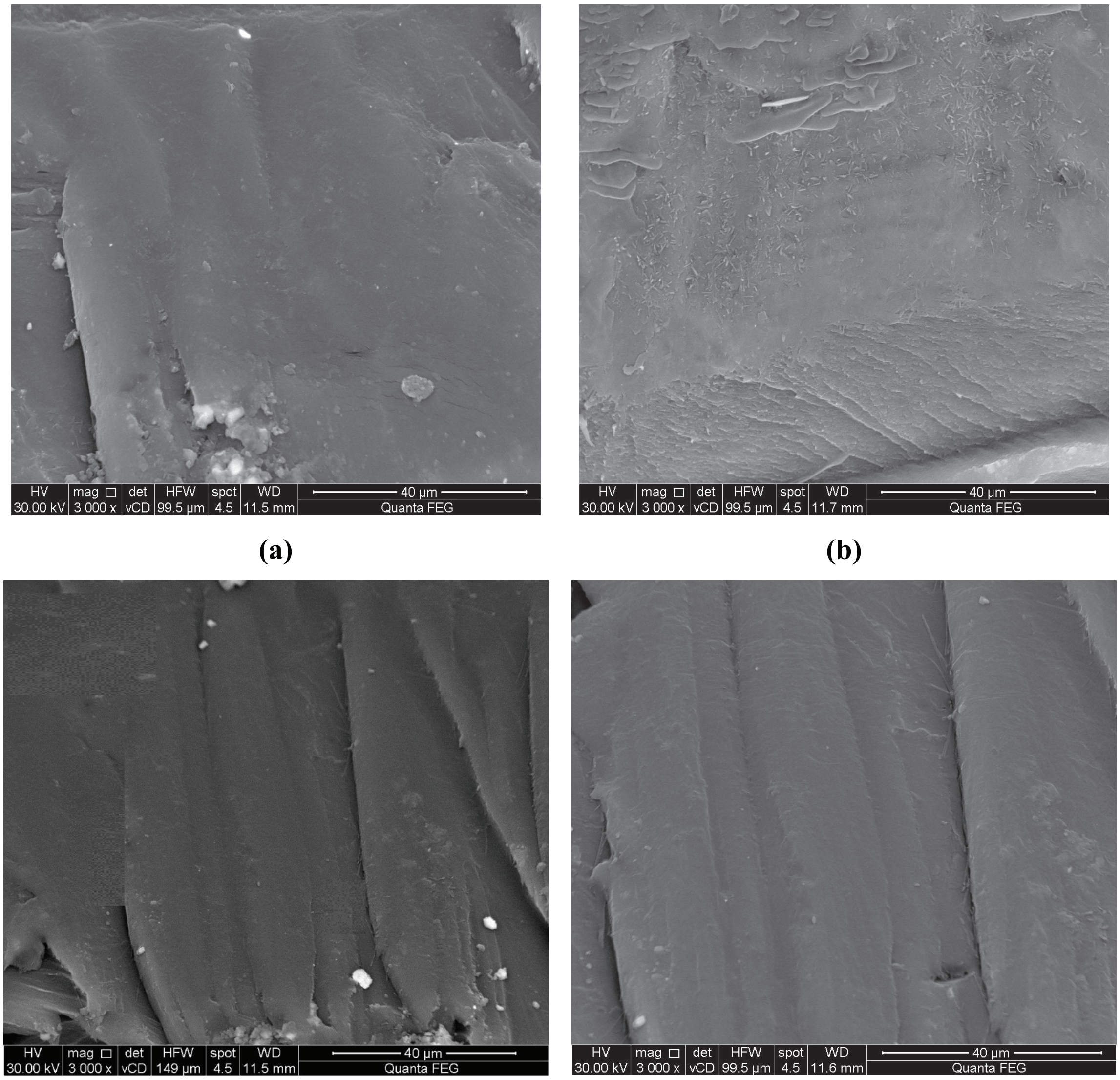
Extraction and transport of a metal cation by an acidic carriers governed by the exchange of the metal ion for protons of the carrier as shown in Eqs. (5), (6).

$$Cr^{3+}_{(aq)} + 3HR_{mem} \leftrightarrow CrR_{3mem} + 3H^{+}_{(aq)} \tag{5}$$

$$M^{2+}_{(aq)} + 2HR_{mem} \leftrightarrow CrR_{2mem} + 2H^{+}_{(aq)} \tag{6}$$

where HR represents the DABA, TABA, PABA or SABA carriers.

As it could be seen, transport rate depends on used carrier. The initial fluxes and selectivity coefficients of chromium(III), cobalt(II), barium(II) and strontium(II) ions



(a) **(b)**

(c) **(d)**

Fig. 6. Scanning electron microscopy of cross section for various membranes (a) CTA + DOP + Carrier (DABA), (b) CTA + DOP + Carrier (TABA), (c) CTA + DOP + Carrier (PABA) and (d) CTA + DOP + Carrier (SABA).

transport across PIMs using different carriers from aqueous source phase of equimolar mixture of all metals are shown in Table 3 and Fig. 7. The chromium(III) ions were transported with a highest rate and the selectivity order was as follows: Cr(III) > Co(II) > Ba(II) > Sr(II). The results showed that the equilibrium reached at 10 h after this time the concentration of dissolved Cr(III), Co(II), Ba(II) and Sr(II) remains constant until 24 h. Also, the PIM system allows the membrane to be used repeatedly for 12 cycles, without any loss of transport rate.

The initial flux of chromium(III) transport increased with different carriers in the order DABA < TABA < PABA > SABA. The observed trend is in accordance with increasing length of alkyl fatty chain in the corresponding carrier. On the basis of obtained results, it could be noticed that carriers with alkyl chain length from 11 to 17 carbon atoms are able to fast transport of tested chromium(III), cobalt(II), barium(II) and strontium(II) ions through PIM. This may be due to alkyl fatty chain has an effect on hydrophobic properties and the initial flux of the transported metal ions [27]. While the length of alkyl fatty chain increased the stability of carrier inside membrane increased. Although different molar concentration of carriers in membranes was used, the highest molecular weight carrier (lowest molar concentration) recorded highest rate. It means that transport rates of metal ions depend on: (i) molar concentration of carrier (ii) fatty acid chain length of carrier, but the latter is predominant which increased hydrophobicity of membrane. The maximum value of the initial flux for Cr(III) ions was equal to 6.4 × 10^{-5} mol/m^2·s (for carrier SABA).

3. 2. The effect of source phase pH

The PIMs containing DABA, TABA, PABA and SABA as an ion carriers and DOP as plasticizer in transport of Cr(III), Co(II), Ba(II) and Sr(II) at different pH values in source phase were examined. Fig. 8 shows the effect of pH of source phase on chromium(III), cobalt(II), barium(II) and strontium(II) ions transport through PIMs using different carriers. The concentration of chromium(III), cobalt(II),

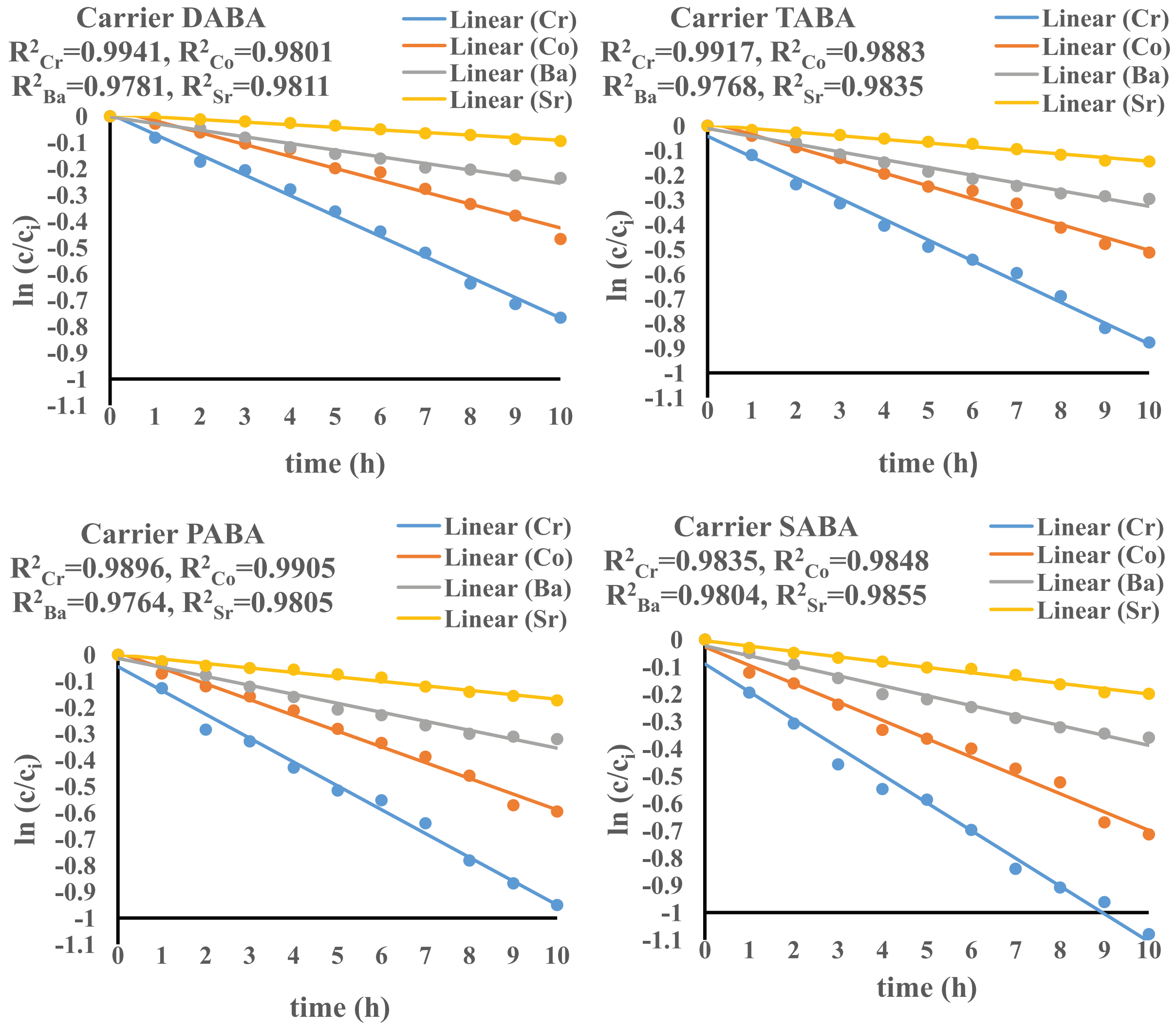


Fig. 7. Kinetics of Cr(III), Co(II), Ba(II) and Sr(II) transport though PIMs, source phase: c_M = 0.01 M, pH = 3.1; receiving phase: 1.0 M HCl.

Table 3
Initial flux and selectivity coefficients for competitive transport of Cr(III), Co(II), Ba(II) and Sr(II) ions across PIMs. Conditions: source phase: c_M= 0.01 M, pH = 3.1; receiving phase: 1.0 M HCl; membrane composition: carrier, 60 wt. %; DOP, 20 wt.% and CTA, 20 wt.%

Carrier	Metalions	$k \cdot 10^5$ (s^{-1})	$J_i \cdot 10^5$ (mol/m^2 s)	$S_{Cr(III)/M(II)}$
DABA	Cr(III)	2.2	4.9	Cr(III)>Co(II)> Ba(II)>Sr(II)
	Co(II)	1.3	2.9	1.7 3.1 7.9
	Ba(II)	0.70	1.6	
	Sr(II)	0.28	0.62	
TABA	Cr(III)	2.3	5.3	Cr(III)>Co(II)> Ba(II)>Sr(II)
	Co(II)	1.4	3.3	1.6 2.8 5.7
	Ba(II)	0.88	1.9	
	Sr(II)	0.41	0.93	
PABA	Cr(III)	2.5	5.7	Cr(III)>Co(II)> Ba(II)>Sr(II)
	Co(II)	1.7	3.8	1.5 2.6 5.2
	Ba(II)	0.95	2.2	
	Sr(II)	0.47	1.1	
SABA	Cr(III)	2.8	6.4	Cr(III)>Co(II)> Ba(II)>Sr(II)
	Co(II)	1.9	4.2	1.5 2.8 5.3
	Ba(II)	1.0	2.3	
	Sr(II)	0.54	1.2	

barium(II) and strontium(II) ions remaining in the source phase was measured at different pH ranging from 1.1 to 4.1. The results showed that chromium(III), cobalt(II), barium(II) and strontium(II) ions transport through all carriers were optimum at pH 4.1, which achieved highest recovery for chromium(III), cobalt(II), barium(II) and strontium(II) ions transport. The R (%) values obtained from Fig. 8 point out the preferable formation of complex in membranes with carriers as an ion carrier [25,26]. It is known that chromium(III) may exist in different ionic pH-dependent forms. In more acidic aqueous solutions (pH ≤ 3.1) chromium occurs mainly in the form of Cr^{3+} while at pH 4.1 there exist $Cr(OH)^{2+}$ (60%) besides Cr^{3+} (40%) species [28]. The action between the chromium ions and the carrier at the interface between the aqueous source and the organic membrane can be described as shown in Eqs. (5), (7):

$$Cr(OH)^{2+}_{(aq)} + 2HR_{mem} \leftrightarrow Cr(OH)R_{2mem} + 2H^{+}_{(aq)} \quad (7)$$

where HR represents the DABA, TABA, PABA or SABA. Initial flux (J_i) and selectivity (S) values of Cr(III), Co(II), Ba(II) and Sr(II) transport across membranes at different source phase pH are presented in Table 4.

3.3.3. Effect of membrane composition

Experiments of Cr(III), Co(II), Ba(II) and Sr(II) transport across PIMs with different carriers under variable membrane composition were carried out at pH 4.1. Changes of the membrane composition resulted from different amount of CTA and concentration of the carrier in PIMs; the concentration of the plasticizer (DOP) was constant. The composition and normalized (average) values of initial flux using different carriers characterizing the membranes used in the processes are shown in Table 5. The best results of initial flux and recovery are obtained for CTA membranes containing 40% of all carriers. In case of CTA membranes, the transport parameters of Cr(III), Co(II), Ba(II) and Sr(II) ions increased with increasing the carrier content up to 40% and decreased for higher content above 40% for all used carriers. This may be due to saturation of membrane active sites.

3.3.4. Type of receiving phase

The initial flux of membrane system for Cr(III), Co(II), Ba(II) and Sr(II) transport is considerably dependent on the nature of stripping agent for Cr(III), Co(II), Ba(II) and Sr(II) ions used in receiving phase (Table 6). Results show that highest flux and recovery favors when the receiving phase is HCl), whereas Cr(III) ions recorded highest flux through different carriers using HCl as receiving phase as follows: 8.5×10^{-5}, 9.1×10^{-5}, 12.5×10^{-5} and 14.8×10^{-5} mol/m^2·s, for carriers DABA, TABA, PABA and SABA, respectively. Using water as receiving phase showed the lowest recovery for Cr(III), Co(II), Ba(II) and Sr(II) ions transport through different membranes using different carriers. This lower percentage may be due to weak complexing ability than membrane complex constituents. This makes lower in rate constant and flux in comparison with HCl, HNO_3 and H_2SO_4.

3.3.5. Effect of different concentrations of receiving phase

The selective transport of Cr(III), Co(II), Ba(II) and Sr(II) ions through all carriers was recorded at different concentration of receiving phase (HCl) ranging from 1.0–3.0 M. Table 7 shows that highest removal percentage

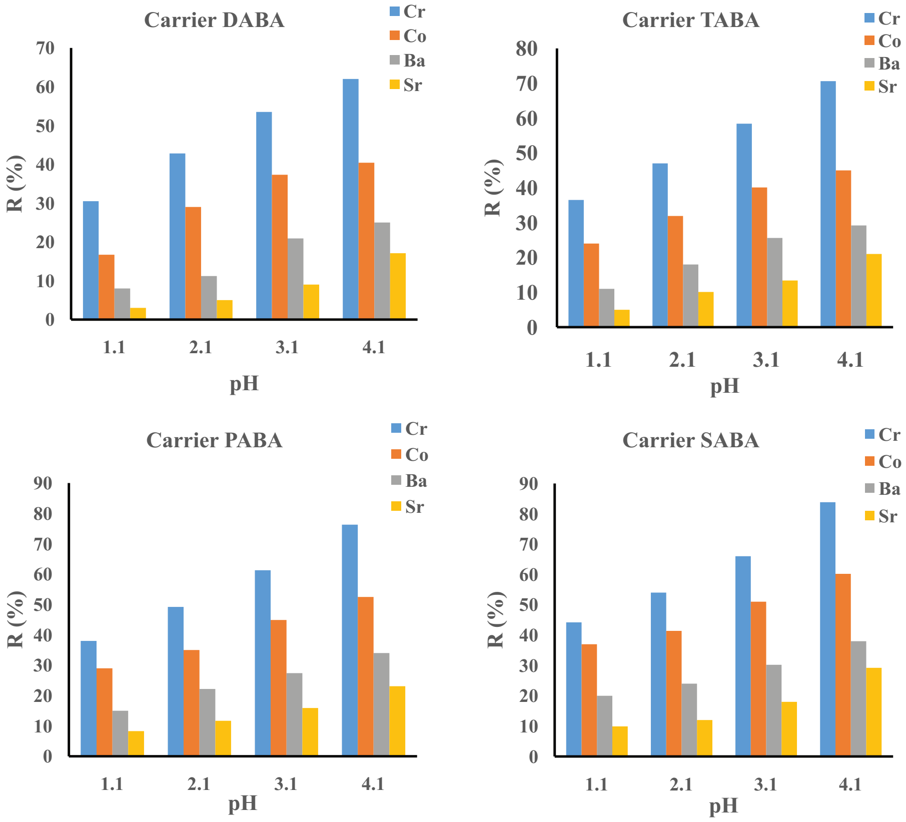


Fig. 8. Removal (%) of Cr(III), Co(II), Ba(II) and Sr(II) ions from chloride aqueous solutions in PIM transport at different pH after 10 h, 60 % of carrier, source phase: c_M = 0.01 M and receiving phase: 1.0 M HCl.

Table 4
Initial flux and selectivity coefficients for competitive transport of Cr(III), Co(II), Ba(II) and Sr(II) ions at different pH using different carriers across PIMs

pH	Metal ions	$J_i \cdot 10^5$ (mol/m^2·s)				$S_{Cr(III)/M(II)}$			
		Carrier DABA	Carrier TABA	Carrier PABA	Carrier SABA	Carrier DABA	Carrier TABA	Carrier PABA	Carrier SABA
1.1	Cr(III)	2.3	2.9	3.0	3.7	Cr<Co<Ba<Sr	Cr<Co<Ba<Sr	Cr<Co<Ba<Sr	Cr<Co<Ba<Sr
	Co(II)	1.2	1.7	2.2	2.9	1.9 12 4.3	1.7 4.0 7.4	1.4 3.0 5.5	1.3 2.6 5.6
	Ba(II)	0.53	0.73	1.0	1.4				
	Sr(II)	0.19	0.39	0.55	0.66				
2.1	Cr(III)	3.5	4.0	4.3	5.0	Cr<Co<Ba<Sr	Cr<Co<Ba<Sr	Cr<Co<Ba<Sr	Cr<Co<Ba<Sr
	Co(II)	2.2	2.4	2.7	3.4	1.6 4.7 11	1.7 3.1 6.0	1.6 2.7 5.5	1.5 2.9 6.2
	Ba(II)	0.75	1.3	1.6	1.7				
	Sr(II)	0.32	0.67	0.78	0.81				
3.1	Cr(III)	4.9	5.3	5.7	6.4	Cr<Co<Ba<Sr	Cr<Co<Ba<Sr	Cr<Co<Ba<Sr	Cr<Co<Ba<Sr
	Co(II)	2.9	3.3	3.8	4.2	1.7 3.1 7.9	1.6 2.8 5.7	1.5 2.6 5.2	1.5 2.8 5.3
	Ba(II)	1.6	1.9	2.2	2.3				
	Sr(II)	0.62	0.93	1.1	1.2				
4.1	Cr(III)	6.1	7.7	9.1	12	Cr<Co<Ba<Sr	Cr<Co<Ba<Sr	Cr<Co<Ba<Sr	Cr<Co<Ba<Sr
	Co(II)	3.3	3.8	4.7	5.8	1.9 3.4 5.1	2.0 3.5 5.1	1.9 3.5 5.4	2.1 4.0 5.5
	Ba(II)	1.8	2.2	2.6	3.0				
	Sr(II)	1.2	1.5	1.7	2.2				

Conditions: 60 % of carrier, source phase: c_M = 0.01 M; receiving phase: 1.0 M HCl.

Table 5
Optimization of membrane ingredients to study kinetics parameters, flux, recovery and selectivity coefficient for competitive transport of Cr(III), Co(II), Ba(II), and Sr(II) ions across PIM using different carriers

Membrane composition			Metal ions	$J_i \cdot 10^5$ (mol/m²·s)				R (%)				$S_{Cr(III)/M(II)}$			
				Carrier				Carrier				Carrier			
CTA (%)	DOP (%)	Carrier (%)		1	2	3	4	1	2	3	4	1	2	3	4
60	20	20	Cr(III)	3.9	4.8	6.6	8.0	46	53	65	72	Cr(III)<Co(II) <Ba (II)<Sr(II) 1..6 2.8 5.1	Cr(III)<Co(II) <Ba (II)<Sr(II) 1.7 3.0 5.1	Cr(III)<Co(II) <Ba (II)<Sr(II) 1.9 3.3 6.0	Cr(III)<Co(II) <Ba (II)<Sr(II) 1.8 3.6 5.7
			Co(II)	2.4	2.9	3.4	4.4	32	37	42	50				
			Ba(II)	1.4	1.6	2.0	2.2	20	22	27	30				
			Sr(II)	0.76	0.95	1.1	1.4	11	14	16	20				
40	20	20	Cr(III)	8.5	9.1	13	15	74	77	86	91	Cr(III)<Co(II) <Ba (II)<Sr(II) 2.1 3.9 4.5	Cr(III)<Co(II) <Ba (II)<Sr(II) 2.0 3.5 4.3	Cr(III)<Co(II) <Ba (II)<Sr(II) 2.0 4.25.0	Cr(III)<Co(II) <Ba (II)<Sr(II) 1.9 4.2 4.8
			Co(II)	4.1	4.6	6.4	8.0	48	52	64	72				
			Ba(II)	2.2	2.6	3.1	3.6	30	33	39	43				
			Sr(II)	1.9	2.1	2.6	3.1	26	28	34	39				
20	20	60	Cr(III)	6.1	7.7	9.1	12	62	71	76	84	Cr(III)<Co(II) <Ba (II)<Sr(II) 1.9 3.4 5.1	Cr(III)<Co(II) <Ba (II)<Sr(II) 2.0 3.5 5.1	Cr(III)<Co(II) <Ba (II)<Sr(II) 1.9 3.5 5.4	Cr(III)<Co(II) <Ba (II)<Sr(II) 2.14.0 5.5
			Co(II)	3.3	3.8	4.7	5.8	40	45	53	60				
			Ba(II)	1.8	2.2	2.6	3.0	25	29	34	38				
			Sr(II)	1.2	1.5	1.7	2.2	17	21	23	29				

Conditions: source phase: $c_M = 0.01$ M, pH = 4.1; receiving phase: 1.0 M HCl, Carrier 1: DABA, Carrier 2: TABA, Carrier 3: PABA and Carrier 4: SABA.

Table 6
Initial flux and removal (%) for competitive transport of Cr(III), Co(II), Ba(II) and Sr(II) ions in different receiving phases using different carriers across PIMs

Receiving phase	Metals ions	$J_i\cdot10^5$ (mol/m^2·s)				R (%)			
		Carrier 1	Carrier 2	Carrier 3	Carrier 4	Carrier 1	Carrier 2	Carrier 3	Carrier 4
Water	Cr(III)	2.9	3.3	5.1	5.9	37	41	56	61
	Co(II)	1.5	1.8	2.9	3.2	22	24	37	39
	Ba(II)	0.88	1.2	1.4	1.8	13	18	20	25
	Sr(II)	0.32	0.71	0.88	1.3	5.0	11	13	19
H_2SO_4(1.0 M)	Cr(III)	6.5	7.5	9.4	10	64	70	78	80
	Co(II)	3.3	3.7	4.5	5.1	41	44	51	56
	Ba(II)	1.3	1.6	2.1	3.0	18	23	29	38
	Sr(II)	0.95	1.4	1.8	2.0	14	20	25	27
HNO_3(1.0 M)	Cr(III)	7.4	8.2	12	13	69	73	84	86
	Co(II)	3.6	4.1	5.4	5.8	44	48	58	60
	Ba(II)	1.8	2.1	2.4	3.3	25	29	32	41
	Sr(II)	1.2	1.6	2.1	2.5	18	23	28	33
HCl(1.0 M)	Cr(III)	8.5	9.1	13	15	74	77	86	91
	Co(II)	4.1	4.6	6.4	8.0	48	52	64	72
	Ba(II)	2.2	2.6	3.1	3.6	30	33	39	43
	Sr(II)	1.9	2.1	2.6	3.1	26	28	34	39

Conditions: source phase: c_M = 0.01 M, pH = 4.1; membrane composition: 40 wt.% carrier, 20 wt.% DOP and 40 wt.% CTA, Carrier 1: DABA, Carrier 2: TABA, Carrier 3: PABA and Carrier 4: SABA.

Table 7
Removal (%) for competitive transport of Cr(III), Co(II), Ba(II) and Sr(II) ions in different concentration of receiving phase using different carriers across PIMs

Concentration of HCl	Metals ions	R (%)			
		Carrier DABA	Carrier TABA	Carrier PABA	Carrier SABA
1.0	Cr(III)	74	77	86	91
	Co(II)	48	52	64	72
	Ba(II)	30	33	39	43
	Sr(II)	26	28	34	39
2.0	Cr(III)	78	81	90	92
	Co(II)	49	55	68	74
	Ba(II)	31	35	44	47
	Sr(II)	29	33	39	42
3.0	Cr(III)	84	88	92	96
	Co(II)	53	57	70	76
	Ba(II)	33	37	45	51
	Sr(II)	31	35	41	47

Conditions: source phase: c_M = 0.01 M, pH = 4.1; membrane composition: 40 wt.% carrier, 20 wt.% DOP and 40 wt.% CTA, receiving phase HCl.

for all metals, which recorded at optimum concentration 3.0 M of HCl for all carriers. Which carrier SABA showed highest recovery for chromium ions reached to 96.3% at 3.0 M of HCl.

4. Conclusion

The polymer inclusion membranes (PIMs) containing amides derived from 2-aminobenzoic acid and fatty acids as ion carriers and dioctyl phthalate (DOP) as the plasticizer provide an attractive alternative to conventional solvent extraction methods for the separation of Cr(III), Co(II), Ba(II) and Sr(II) ions. The results show that Cr(III) can be effectively recovered from aqueous acidic chloride solutions containing Co(II), Ba(II) and Sr(II) ions in hydrometallurgical process of transport across the PIM with amides. This result may be due to the smallest ionic radius of chromium(III) compared to the ionic radii of Co(II), Ba(II) and Sr(II). The PIM containing amides with different fatty chain influenced the rate of transport of chromium, cobalt, barium and strontium ions, which length of alkyl fatty chain increased the rate of transport increased, this may be due to alkyl fatty chain have an effect on hydrophobic properties and the initial flux of the transported metal ions. Which the length of alkyl fatty chain increased the stability of carrier inside membrane increased. The highest flux of chromium(III) ions was obtained by transport through the PIM containing 40 wt.% carrier, 20 wt.% DOP and 40 wt.% CTA. The obtained results showed that recovery of Cr(III) ions reached to 96.3% into 3.0 M hydrochloric acid as the receiving phase after 10 h using carrier SABA.

References

[1] J. Kotas, Z. Stasicka, Chromium occurrence in the environment and methods of its speciation, Environ. Pollut., 107 (2000) 263–283.

[2] V. Gomez, M.P. Callao, Chromium determination and speciation since 2000, Trends Anal. Chem., 25 (2006) 1006–1015.

[3] K.W. Bruland, J.R. Donat, D.A. Hutchins, Interactive influences of bioactive trace metals on biological production in oceanic waters, Limnol. Ocenaogr., 36 (1991) 1555–1577.

[4] G. Gurboga, H. Tel, Preparation of TiO_2–SiO_2 mixed gel spheres for strontium adsorption, J. Hazard. Mater., B120 (2005) 135–142.

[5] S.P. Mishra, V.K. Singh, Radiotracer technique in adsorption study XIII. Adsorption of barium and strontium ions on chromium (IV) oxide powder, Appl. Radiat. Isot., 46 (1995) 847–853.

[6] M. Torab-Mostaedi, A. Ghaemi, H. Ghassabzadeh, M. Ghannadi-Maragheh, Removal of strontium and barium from aqueous solutions by adsorption onto expanded Perlite, Can. J. Chem. Eng., 89 (2011) 1247–1254.

[7] F. Bari, N. Begum, S.B. Jamaludin, K. Hussin, Extraction and separation of Cu(II), Ni(II) and Zn(II) by Sol-Gel silica immobilized with Cyanex 272, Hydrometallurgy, 96 (2009) 140–147.

[8] J.L. Cortina, N. Miralles, M. Aguilar, A.M. Sastre, Solvent impregnated resins containing di(2-ethyl-hexyl)phosphoric acid. II. Study of the distribution equilibria of Zn(II), Cu(II) and Cd(II), Solvent Extr. Ion Exch., 12 (1994) 371–391.

[9] V.S. Kislik, Liquid Membranes. Principles and Application in Chemical Separation and Wastewater Treatment. Amsterdam, The Netherlands 2010.

[10] J. de Gyves, E.R. de S. Miguel, Metal ion separations by supported liquid membranes, Ind. Eng. Chem. Res., 38 (1999) 2182–2202.

[11] P.K. Mohapatra, P.N. Pathak, A. Kelkar, V.K. Manchanda, Novel polymer inclusion membrane containing amacrocyclicionophore for selective removal of strontium from nuclear waste solution, New. J. Chem., 28 (2004) 1004–1009.

[12] S.D. Kolev, G. Argiropoulos, R.W. Cattrall, I.C. Hamilton, R. Paimin, Mathematical modelling of membrane extraction of gold(III) from hydrochloric acid solutions, J. Membr. Sci., 137 (1997) 261–269.

[13] R. Tripathi, A.K. Pandey, S. Sodaye, B.S. Tomar, S.B. Manohar, S. Santra, K. Mahata, P. Singh, S. Kailas, Backscattering spectrometry studies on metal ion distribution in polymer inclusion membranes, Nucl. Instrum. Method. Phy. Res., B 211 (2003) 138–144.

[14] L. Wang, R. Paimin, R.W. Cattrall, W. Shen, S.D. Kolev, The extraction of cadmium(II) and copper(II) from hydrochloric acid solutions using an Aliquat 336/PVC membrane, J. Membr. Sci., 176 (2000) 105–111.

[15] J. Konczyk, C. Kozlowski, W. Walkowiak, Removal of chromium(III) from acidic aqueous solution by polymer inclusion membranes with D2EHPA and Aliquat 336, Desalination, 263 (2010) 211–216.

[16] A. Tor, G. Arslan, H. Muslu, A. Celiktas, Y. Cengeloglu, M. Ersoz, Facilitated transport of Cr(III) through polymer inclusion membrane with di(2-ethylhexyl)phosphoric acid (DEHPA), J. Membr. Sci., 329 (2009) 169–174.

[17] C.A. Kozlowski, W. Walkowiak, Competitive transport of cobalt-60, strontium-90, and cesium-137 across polymer inclusion membranes with DNNS, J. Membr. Sci., 297 (2007) 181–189.

[18] S.C. Lee, J.D. Lamb, M. Cai, J.T. Davis, Cs^+ and Ba^{2+} selective transport by a novel self-assembled isoguanosine ionophore through polymer inclusion and bulk liquid membranes, J. Inclusion Phenom. Mac. Chem., 40 (2001) 51–57.

[19] B. Amiri-Eliasi, Metal ion separation by proton-ionizable macrocyclic and acyclic polyether ligands. Doctoral dissertation. Texas Tech University, Lubbock, USA, 2000.

[20] C. Kozlowski, W. Walkowiak, W. Pellowski, J. Koziol, Competitive transport of toxic metal ions by polymer inclusion membranes, J. Radioanal. Nucl. Chem., 253 (2002) 389–394.

[21] Y. Yildiz, A. Manzak, B. Aydýn, O. Tutkun, Preparation and application of polymer inclusion membranes (PIMs) including Alamine 336 for the extraction of metals from an aqueous solution, Mater. Technol., 48 (2014) 791–796.

[22] M. Ulewicz, J. Szczygelska-Tao, J.F. Biernat, Transport of Zn(II), Cd(II) and Pb(II) across polymer inclusion membrane doped with imidazole azocrown ethers, Desalination, 214 (2007) 352–364.

[23] N.S. Murthy, S.T. Correal, H. Minor, Structure of the amorphous phase in crystallisable polymers: Poly (ethyleneterephtalate), Macromolecules., 24 (1991) 1185–1189.

[24] G. Vancso, D. Snetvy, I. Tomka, Structural changes during polystyrene orientation: A study of optical birefringence and wide angle x-ray scattering, J. Appl. Polym. Sci., 42 (1991) 1351–1359.

[25] G. Arslan, A. Tor, Y. Cengeloglu, M. Ersoz, Facilitated transport of Cr(III) through activated composite membrane containing di (2 ethylhexyl)phosphoric acid (DEHPA) as carrier agent, J. Hazard. Mater., 165 (2009) 729–735.

[26] R. Tayeb, C. Fontas, M. Dhahbi, S. Tingry, P. Seta, Cd(II) transport across supported liquid membranes (SLM) and polymeric plasticized membranes (PPM) mediated by Lasalocid A, J. Membr. Sci., 42 (2005) 189–193.

[27] M. Ulewicz, E. Radzymińska-Lenarcik, Transport of metal ions across polymer inclusion membrane with 1-alkylimidazole, Physicochem. Probl. Miner. Process., 46 (2011) 119–130.

[28] R.L. Ramos, L.F. Rubio, R.M.G. Coronado, J.M. Baron, Adsorption of trivalent chromium from aqueous solution onto activated carbon, J. Chem. Technol. Biotechnol., 62 (1995) 64–67.