



Facilitated transport of Cr(III) through activated composite membrane containing di-(2-ethylhexyl)phosphoric acid (DEHPA) as carrier agent

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ABSTRACT

The facilitated transport of chromium(III) through activated composite membrane (ACM) containing di-(2-ethylhexyl) phosphoric acid (DEHPA) was investigated. DEHPA was immobilised by interfacial polymerisation on polysulfone layer which was deposited on non-woven fabric by using spin coater. Then, ACM was characterised by using scanning electron microscopy (SEM), contact angle measurements and atomic force microscopy (AFM).

Initially, batch experiments of liquid–liquid distribution of Cr(III) and the extractant (DEHPA) were carried out to determine the appropriate pH of the feed phase and the results showed that maximum extraction of Cr(III) was achieved at a pH of 4. It was also found that Cr(III) and DEHPA reacted in 1/1 molar ratio.

The effects of Cr(III) (in feed phase), HCl (in stripping phase) and DEHPA (in ACM) concentrations were investigated. DEHPA concentration varies from 0.1 to 1.0 M and it was determined that the transport of Cr(III) increased with the carrier concentration up to 0.8 M. It was also observed that the transport of Cr(III) through the ACM tended to increase with Cr(III) and HCl concentrations. The stability of ACM was also confirmed with replicate experiments.

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1. Introduction

Increasing accumulation of Cr(III) in the environment from industrial outputs caused great concern because accumulated Cr(III) had been reported to be toxic to animals and humans. Major anthropogenic sources of Cr(III) in the environment include metal extraction, metal fabrication, textile, leather tanning facilities, electroplating, surface finishing, paints, pigments and manufacture of batteries [1].

During the last decades, different methods (i.e. adsorption [2,3], precipitation [4] and membrane processes [5–8]) have been investigated to remove chromium from wastewater. Membrane process (e.g. reverse osmosis, ultrafiltration and electro dialysis [9]) has contributed to separation technology. Moreover, other separation procedures based on chemical interaction have also been studied and developed in the last decades with the main objective of increasing the selectivity of separation. Among these procedures, the supported liquid membranes (SLMs) have attracted much interest for separation and concentration of toxic and/or valuable solutes

due to the possibility to combine the extraction and stripping processes in one step [10].

The potential advantages of SLMs over traditional separation techniques are lower capital investments and operation costs, low energy and extractant consumption, high concentration factors, and high fluxes compared with solid membranes. SLMs can be used for the recovery of mercury [11,12] and metal ions [13–16], which are present together in leaching solutions of poly-metallic ores [17]. However, the main disadvantage of SLMs is short lifetime due to the progressive leakage of both extractant and solvent from the membrane. Therefore, different approaches have been suggested to stabilize SLMs [16,18–20], such as applying a thin polyamide layer covering the impregnated flat-sheet and hollow fiber support, which partially avoided the loss of carrier reagent from the membrane phase [9,21]. Recently, this concept was employed to develop activated composite membranes (ACMs) that have demonstrated high selectivity and more stable transport properties within long periods than corresponding SLMs [22,23]. ACMs containing different carriers have been used for separation of metal ions and some organic molecules particularly amino acids [24–27].

Because the transport of Cr(III) through ACM containing DEHPA was not considered before, in the present work, we evaluated the ACM containing DEHPA as a carrier in the facilitated transport of Cr(III). DEHPA was immobilised by interfacial polymerisation on

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polysulfone layer which was coated on a supporting non-woven fabric by using spin coater. First, surface characterization of the ACM was carried out by contact angle measurements, atomic force microscopy (AFM) and scanning electron microscopy (SEM). Then, the influence of DEHPA concentration as well as acidity of the stripping phase and initial concentration of Cr(III) on the transport properties of ACM has been investigated.

2. Materials and method

2.1. Chemicals

The chemical reagents used for ACM preparation and experiments, were hydrochloric acid, chromium(III) chloride, acetic acid, sodium acetate, sodium hydroxide, DEHPA, 1,3-phenylenediamine, 1,3,5-benzenetricarbonyl trichloride, *n*-hexane, *N,N*-dimethyl formamide (DMF) all from Merck Co. (Darmstadt, Germany). Polysulfone and sodium dodecyl sulfate were from Aldrich (Steinheim, Germany) and J.T. Baker (Dewenter, Holland), respectively.

2.2. Preparation of activated composite membrane

The schematic representation for the preparation of ACM is shown in Fig. 1(a and b) [24]. The design of the ACM is based on the addition of the selective carrier molecules to a solid compos-

ite membrane formed by a homogeneous hydrophilic stabilizing top layer (polyamide) and a macroporous hydrophobic membrane support layer (polysulfone).

The polysulfone casting solution was prepared by dissolving the polymer (15%, w/w) in DMF by vigorous stirring for 12 h. Deposition of a polysulfone layer onto the non-woven fabric (Hollytex 3329) was performed by using spin coater (Laurell Model WS-400A-6NPP/LITE). The impregnated support was then immersed in a water bath at room temperature for 5 min to induce phase inversion polymerisation (Fig. 1a). A second polyamide layer containing the carrier was formed on the first layer by interfacial polymerisation, which resulted from interaction of two different phases: an aqueous 1,3-phenylenediamine solution and a *n*-hexane organic solution containing benzene-1,3,5-tricarbonyl chloride with DEHPA (Fig. 1b).

The diamine aqueous solution consisted of 3 g of 1,3-phenylenediamine in 50 mL of distilled water, containing 0.01 g of sodium dodecyl sulfate as an aqueous stabilizing agent. The organic solution contained 0.04 g of benzenetricarbonyl trichloride in 50 mL of *n*-hexane and desired concentration of DEHPA.

The ACM was washed with distilled water and dried in an oven at 60 °C for 60 min. The resulting membrane sheet was cut to produce 3.0 cm diameter circles that were placed into the transport cell. An inactivated composite membrane (blank membrane) was prepared similarly to that already described, though without including DEHPA.

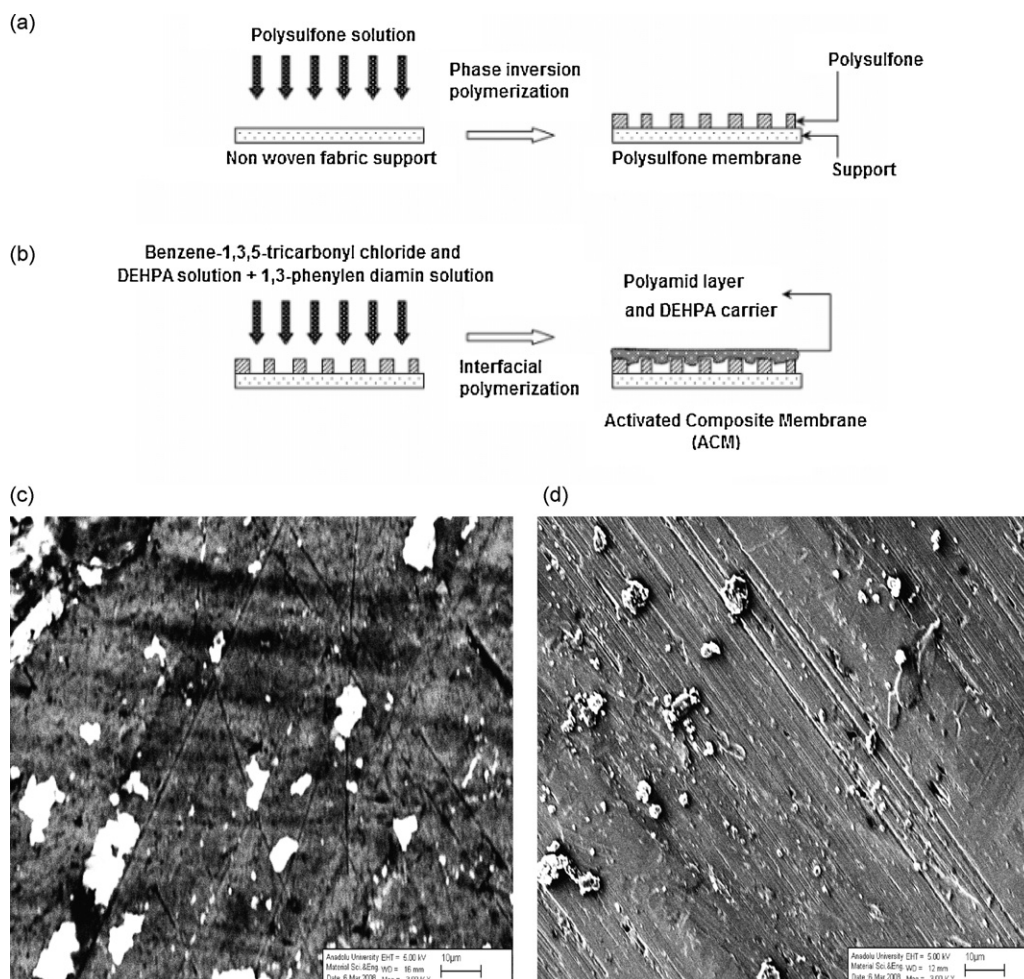


Fig. 1. Schematic representation of the laboratory manufacturing process for the ACM (a) support polymer deposition by spin coating, (b) deposition of the dense polyamid layer with DEHPA carrier, (c) SEM image of blank membrane and (d) SEM image of ACM containing 1.0 M DEHPA.

2.3. Procedure

The experimental study includes both batch experiments for liquid–liquid distribution and membrane transport experiments.

2.3.1. Liquid–liquid distribution

Batch experiments of liquid–liquid distribution of Cr(III) and the extractant (DEHPA) were carried out to determine the appropriate chemical conditions for membrane transport experiments [28]. Therefore, equal volumes (20 mL) of aqueous and organic phases were shaken for 2 h in a stoppered flask. The aqueous phase contained 0.001 M of Cr(III) and the organic phase was 0.1 M DEHPA in *n*-hexane. The distribution of the Cr(III) was measured by the determination of Cr(III) in aqueous solution before and after phase equilibration, using Continuum Source Atomic Absorption Spectrometer (ContrAA 300, Analytik jena). The spectral line used for Cr(III) was 357.9 nm.

2.3.2. Transport experiments

A two-compartment cell described in our previous paper [5] was used in the transport experiments. The membrane was clamped tightly between two compartments of 40 mL capacity.

The effects of the DEHPA concentration of ACM, Cr(III) concentration of the feed phase and HCl concentration of the stripping phase on the transport of Cr(III) were investigated. 0.001, 0.005 and 0.01 M of Cr(III) solutions with different ionic strengths (from 0.05 to 0.5 M adjusted with NaCl) and a pH of 4 (by using 0.1 M acetic acid/acetate buffer) were used as the feed phase for each system. The acidity of the feed phase was chosen according to the liquid–liquid distribution results. 0.05, 0.1 and 0.5 M of HCl were evaluated as stripping phase.

Equal volumes (40 mL) of feed and stripping phase were placed in the respective compartments of the cell that were separated by the prepared ACM. In each experiment, the stirring rates of both phases were equal and kept constant at 600 rpm throughout the experiment. All experiments were performed at $25 \pm 1^\circ\text{C}$.

The transport of Cr(III) was observed by determining its concentration in the feed and stripping phases. For this purpose, samples of 1 mL were periodically withdrawn (every 30 min) over 3 h, and analysed by ContrAA 300. Each analytical value reported is the mean of two replicates.

3. Results and discussion

The results obtained correspond to surface characterization, liquid–liquid distribution and membrane transport.

3.1. Surface characterization

3.1.1. Scanning electron microscopy (SEM)

The change in the surface of blank membrane and ACM was observed by using SEM (JEOL 5600-LU). Membranes were fixed with conductive glue and covered with a thin (10–20 nm) Au layer [29] in order to get SEM pictures.

Fig. 1(c) and (d) show SEM images of blank membrane and ACM surface, respectively. As can be seen from Fig. 1(c) and (d), the difference between the surface morphology of the blank membrane and ACM indicated that DEHPA was covered onto the membrane surface by interfacial polymerization. The surface of ACM (Fig. 1(d)) seems to be quite compact but with some heterogeneity. This heterogeneity may be attributed to the variation of the polymerization process taking place in the presence of large amounts of the carrier [26].

3.1.2. Contact angle measurements

The sessile drop method was used to measure the contact angle of the prepared membranes [30]. A 4 μL droplet of distilled water was placed on the membrane surface by means of a 0.10 mL syringe and contact angle was measured by a horizontal beam comparator (KSV CAM 200).

Contact angle measurement is used to investigate the hydrophilicity of the material surfaces [31]. In the present study, contact angle measurements were taken at room temperature. For blank membrane (containing no DEHPA) and ACM containing 0.5 and 1.0 M of DEHPA, contact angles were found to be $(78 \pm 11)^\circ$, $(68 \pm 1)^\circ$ and $(63 \pm 4)^\circ$, respectively [$n = 3$]. The results indicate that ACMs containing DEHPA have lower contact angle values compared to the blank membrane, which means that ACM surface has more hydrophilic character than that of blank one. The results are in agreement with contact angle measurements from previous work [32].

3.1.3. Characterization of membrane surface morphology by AFM

AFM images were obtained by using Veeco diCaliber instrument. The speed of scanning was 2 kHz. Tapping mode of AFM in air was used to investigate the membrane surface morphology. Silicon nitride cantilevers (antimony, ndoptFi) were employed. Several AFM images (of ca. $1.0 \mu\text{m} \times 1.0 \mu\text{m}$) of different parts of the membrane were analysed properly in order to obtain the roughness (*Ra*) parameter.

The AFM images are presented in Fig. 2(a) and (b) for blank membrane and ACM containing 1.0 M of DEHPA, respectively. The relatively high mean roughness values have been commonly found

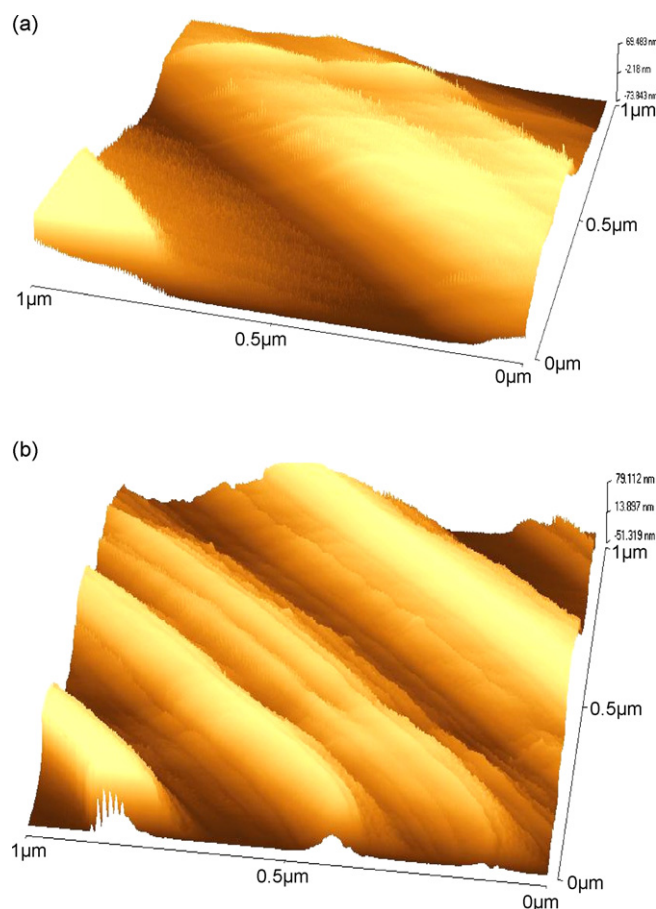


Fig. 2. AFM images of blank membrane (a) and ACM containing 1.0 M DEHPA (b).

on the top layer of aromatic co-polyamide composite membranes [33,34]. Kwak et al. [35] reported that the surface roughness is enhanced when polyamides are meta-oriented due to the presence of free amide groups that are unbound to other amide groups by hydrogen bonding as a consequence of a large intermolecular N–HO distance. The roughnesses (R_a) obtained from blank membrane and ACM surfaces are 18 ± 3 and 9 ± 4 nm, respectively [$n = 5$]. In other words, blank membrane surface showed a R_a value distinctively higher than that of ACM. This may be attributed to the filling of surface pores with the carrier molecules (Fig. 2).

The nodule sizes for blank membrane and ACM are 34 ± 5 and 35 ± 6 nm, respectively [$n = 5$]. The results indicate that nodule sizes are similar for blank membrane and ACM. According to Kesting [36], the nodule sizes correspond to macromolecular nodules. The small variation of the nodule sizes, between the membranes, can also be attributed to the presence of carriers either in the depressions or the pores at the membrane surface without being fully incorporated inside the nodule. Since the interaction between the carrier and the macromolecules are thus limited, the size of the nodule is unaffected by the presence or absence of the carriers in the membrane [37].

As seen in Fig. 2(a) and (b), there are some zones of the polyamide coating that exhibit remarkable valleys, which are probably caused by the polymerization process and coating procedure. These topographic aspects are present for both the blank membrane and ACM. We assume that these defects appear during the preparation procedure as a consequence of friction forces when synthesizing the polyamide layer by interfacial polymerization. Nevertheless, it is important to notice that although this is a theoretical drawback, membrane transport still occurs properly. Similar observation was reported by Macanás et al. [38].

3.2. Liquid–liquid distribution

The experimental data, expressed in terms of mol fraction in the organic phase at different pH of aqueous solution, are represented in Fig. 3. Under the given conditions maximum extraction of Cr(III) was achieved above a pH of 4. CrOH^{2+} is the dominant species in aqueous solution at a pH below 6.5, while insoluble $\text{Cr}(\text{OH})_3$ species dominates between pH 6.5 and 10.5 [39]. More-

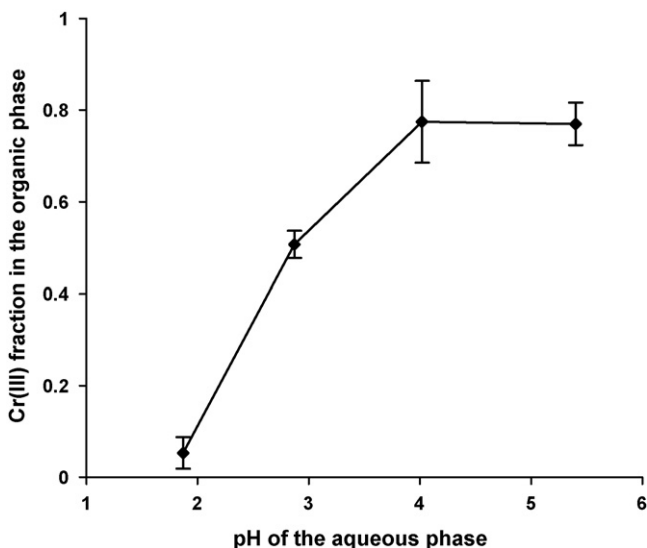


Fig. 3. Influence of the aqueous feed pH in the liquid–liquid distribution of Cr(III) by using DEHPA as extractant in *n*-hexane, bars indicate the precision of each reported value [$n = 3$].

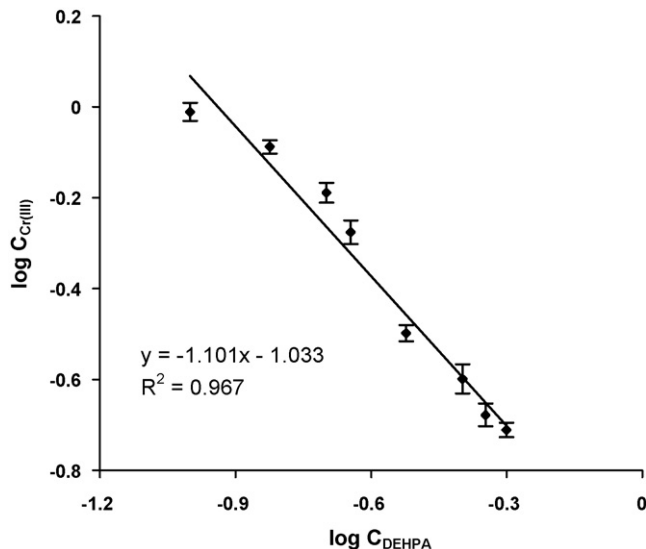
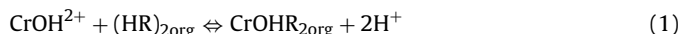


Fig. 4. Stoichiometry plot for the transport of Cr(III) through ACM containing DEHPA as carrier, Bars indicate the precision of each reported value [$n = 3$].

over, DEHPA is dissolved in the membrane phase as a dimer form in non-polar solvents [13]. This is a consequence of the extraction reaction below taking place between the CrOH^{2+} species and the DEHPA in the organic phase.



where HR is the extractant (DEHPA) in molecular form.

The plot of $\log C_{\text{Cr(III)}}$ versus $\log C_{\text{DEHPA}}$ is shown in Fig. 4, which has an equation and R^2 as $y = -1.101(\pm 0.084)x - 1.033(\pm 0.053)$ and 0.967, respectively. The slope value (-1.101 ± 0.084) reveals that one molecule of DEHPA involved in the transport of the one molecule of CrOH^{2+} through the ACM. Hence, stoichiometric equation can be arrived as shown in Eq. (1). The obtained result was supported by Ref. [40] which reported that trivalent chromium and DEHPA react in 1/1 molar ratio.

For transport experiments, pH 4 was selected as an optimum pH of the feed phase to ensure the maximum Cr(III) transport by ACM. Moreover, in such conditions, the solubility of DEHPA in aqueous phase should be also considered. Gumi et al. [26], who investigated the facilitated transport of Pb(II) and Cd(II) by ACM containing DEHPA, reported that solubility of DEHPA at a pH of 4 is negligible because only 4% of total DEHPA in organic phase was determined in aqueous phase at this pH.

3.3. Membrane transport experiments

As mentioned above, the HCl concentration in the stripping phase, Cr(III) concentration in the feed phase and the concentration of the membrane carrier (DEHPA) were selected as key chemical variables for the membrane transport system. These parameters were varied in order to determine their particular influence on the Cr(III) transport.

3.3.1. Effect of carrier concentration

The carrier concentration of membrane has a significant effect on metal ion transport across the membrane. It is generally expected to increase with the carrier concentration [26]. The experiments were carried out for different DEHPA concentrations of 0.1, 0.5, 0.8 and 1.0 M.

In order to quantify the transport through the membrane, a flux model is used giving the following expression for the rate of ion

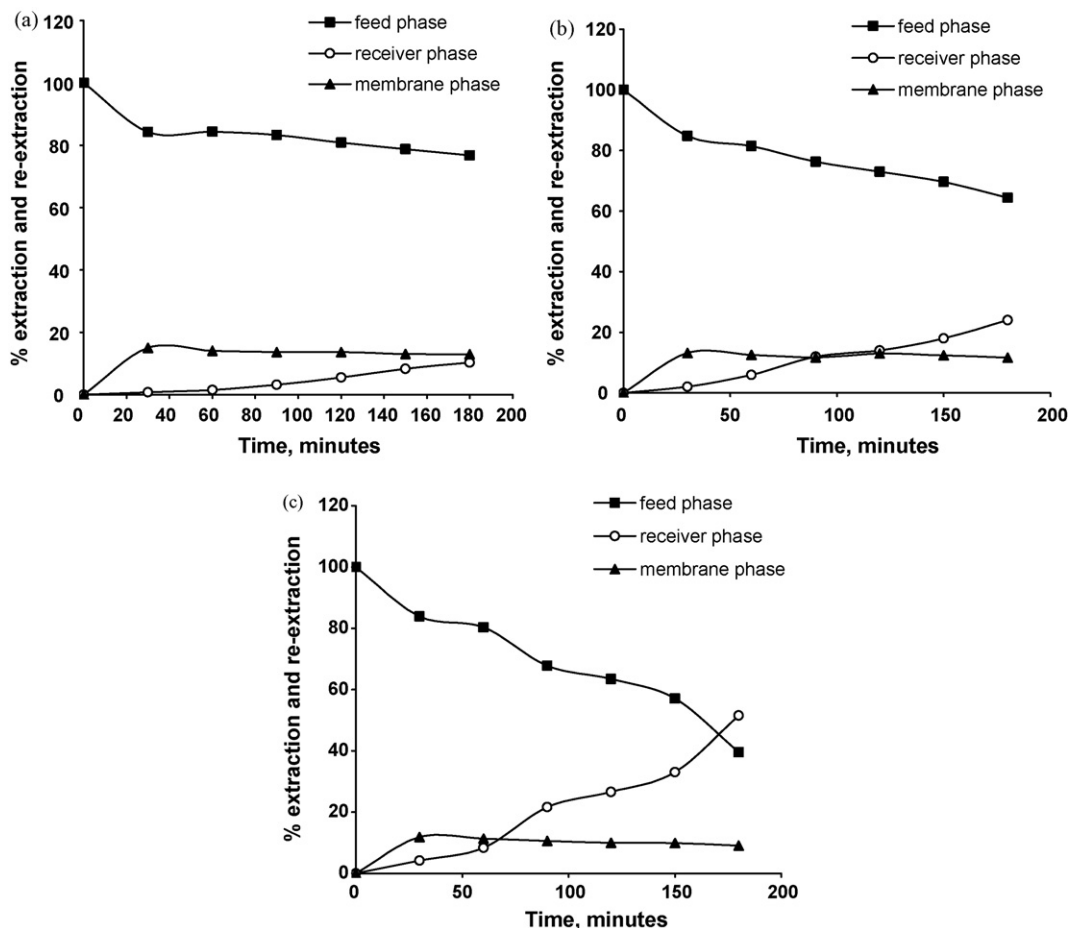


Fig. 5. Extraction/re-extraction time-histories for different HCl concentration of stripping phase (a) 0.05 M HCl, (b) 0.1 M HCl, (c) 0.5 M HCl (experimental conditions: feed phase: 0.001 M Cr(III) solution at pH 4.0 ± 0.1 , ACM containing 0.5 M DEHPA).

transfer through the membrane (J , mol/cm² s)

$$J = \left(\frac{V_s}{S_m} \right) \left(\frac{dC}{dt} \right) \quad (2)$$

where V_s is the volume of the stripping phase, S_m the effective membrane area (7.07 cm²), C the concentration of Cr(III) ion in the stripping phase and t the time.

The effect of DEHPA concentration on the transport was investigated under following experimental conditions: feed phase: 0.001 M Cr(III) solution at pH 4.0 ± 0.1 , receiver phase: 0.1 M HCl. The flux values (J) of $(0.69 \pm 0.10) \times 10^{-7}$, $(1.17 \pm 0.04) \times 10^{-7}$, $(1.45 \pm 0.05) \times 10^{-7}$ and $(1.07 \pm 0.04) \times 10^{-7}$ mol/cm² s were estimated for DEHPA concentrations of 0.1, 0.5, 0.8 and 1.0 M, respectively. The results clearly indicate that transport of Cr(III) increases with an increase in the DEHPA concentration up to 0.8 M in the membrane. At a lower carrier concentration the interface between the feed phase and the membrane may not be saturated by the carrier [41]. However, a decrease in Cr(III) transport was observed for ACM containing 1.0 M of DEHPA. This decrease of flux may be attributed to morphological change of the membrane surface, which is related to the variation of the polymerization process taking place in the presence of large amounts of the carrier [25,26].

In addition, a blank experiment was performed with no present carrier in the membrane. No detectable movement of the Cr(III) ions through the blank membrane suggests that the transport of Cr(III) ions through the ACM is fulfilled by the carrier.

3.3.2. Effect of stripping phase concentration

The influence of the concentration of the stripping phase on the transport was also studied. The concentration of hydrochloric acid used as stripping agent [26,42] was varied from 0.05 to 0.5 M. In this case, the ionic strength of feed phase was maintained constant at 0.05–0.5 M with NaCl. When the acid concentration increases the extraction and re-extraction process of Cr(III) also increases, so its transport rate increases, as shown in Fig. 5.

Cr(III) amount inside the membrane at each time was calculated by subtracting the mole of Cr(III) ions in phases (feed and stripping) to the original amount, corresponding to feed phase at the beginning of the experiment. As seen in Fig. 5, Cr(III) amount inside the membrane rose at the beginning and decreased slowly. The first 30 min of the procedure was related to the charge of the membrane and the rest corresponded to the progressive discharge of Cr(III) ion into the stripping phase. The charge of the membrane results in a lag for the transport of Cr(III). In other words, a time-lag profile was observed because of the Cr(III) accumulation in ACM.

The suggested mechanism for the transport of Cr(III) ion through ACM is shown schematically in Fig. 6. This suggested mechanism involves several stages, which include: a complexation reaction between the Cr(III) and the carrier at the feed phase–ACM interface, diffusion of the complex formed through the ACM, release of Cr(III) in the stripping phase via a decomplexation reaction of the complex at the ACM–stripping phase interface [9]. This mechanism enables the transfer process to be carried out even at very low solute concentrations, and even against a solute concentration gradient;

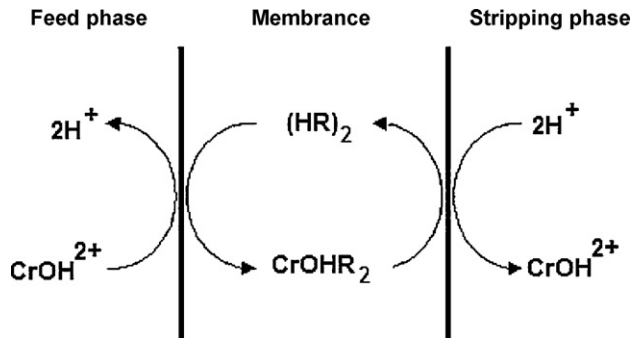


Fig. 6. Suggested mechanism for transport Cr(III) through ACM containing DEHPA as carrier.

this is known as facilitated transport, and has been reported by several authors [43,44]. In this system the driving force is the difference in H_3O^+ concentration between the feed and stripping phases. Fig. 5 shows that Cr(III) amount inside the membrane also slightly increased with decrease of stripping phase concentration. If the Cr(III)–DEHPA complex is not adequately stripped, the membrane phase becomes saturated with complex and the transport rate may therefore decrease [45].

3.3.3. Effect of Cr(III) concentration

In order to assess the influence of the Cr(III) concentration on its transport through ACM, the transport experiments were carried out at three different concentrations: 0.001, 0.005 and 0.01 M. Results are shown in Fig. 7. It is observed that for a transfer time of 180 min, upon increasing the concentration of Cr(III) in the feed phase, the transfer percentage increases. Transfer percentages observed were 24.1, 28.9 and 38.8%, for Cr(III) concentrations of 0.001, 0.005 and 0.01 M, respectively. At the end of 180 min processing, the percentage amounts of Cr(III) inside the membrane were 11.2, 13.2 and 21.0%, respectively. In addition, flux of Cr(III) show an increase; these values were observed to be $(1.17 \pm 0.04) \times 10^{-7}$, $(7.22 \pm 0.25) \times 10^{-7}$ and $(2.16 \pm 0.09) \times 10^{-6}$ mol Cr(III)/cm² s, respectively. Namely, as the Cr(III) concentration increases, the complexation rate in feed

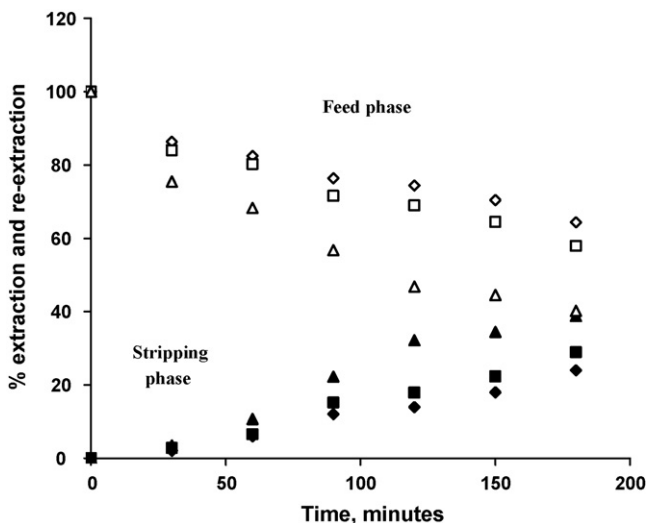


Fig. 7. Extraction/re-extraction time-histories for different Cr(III) concentration in feed phase (triangles, squares and diamonds indicate to 0.001, 0.005 and 0.01 M of Cr(III), respectively, filled and empty symbols correspond to Cr(III) concentration in stripping and feed phase, respectively. Experimental conditions: pH of feed phase 4.0 ± 0.1 , ACM containing 0.5 M DEHPA, stripping phase: 0.1 M HCl).

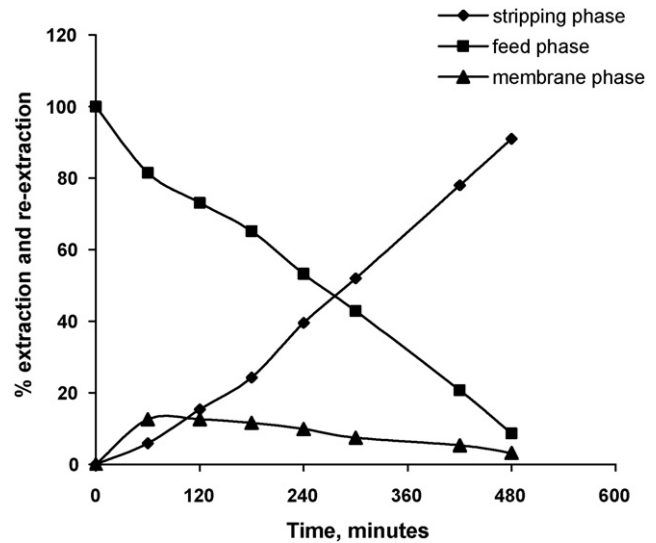


Fig. 8. Extraction/re-extraction time-histories for 0.001 M of Cr(III) in feed phase. Experimental conditions: pH of feed phase 4.0 ± 0.1 , ACM containing 0.5 M DEHPA, stripping phase: 0.1 M HCl).

phase–ACM interface increases, and depending on this, the decomplexation rate in the ACM–stripping phase interface increases [46].

In order to improve the transport percentage, effective membrane area or transport time should be increased. In this study, the effective membrane area is constant (7.07 cm²) because of the transport cell used. However, it was seen that to achieve a transfer of approximately 90% of 0.001 M Cr(III) through ACM containing 0.5 M DEHPA with 0.1 M HCl strippant requires 480 min (Fig. 8).

3.3.4. Stability of the ACM

The stability of the ACM was evaluated according to the flux values obtained from six sequential experiments on Cr(III) transport from feed phase containing 0.001 M of Cr(III) through the same ACM containing 0.5 M of DEHPA. The flux of around 1.20×10^{-7} mol/cm² s does not change with transport cycles (each cycle: 6 h). The results indicate that ACMs can be used in the long-term separation experiments.

4. Conclusion

The facilitated transport of chromium(III) through an activated composite membrane (ACM) containing di-(2-ethylhexyl) phosphoric acid (DEHPA), not considered before, was investigated. The following conclusions can be derived from the results of the present study:

- (i) The differences between the SEM images of blank and ACM indicated that carrier (DEHPA) was immobilised on the polysulfone layer. This result was supported by the topographic aspects from AFM images represented that DEHPA was deposited onto the blank membrane.
- (ii) The ACMs containing 0.5 M and 1.0 M DEHPA have lower contact angle values compared to the blank membrane, which means that ACM surface has more hydrophilic character than that of blank membrane. In addition, increasing DEHPA concentration also increased the hydrophilicity of ACM surface.
- (iii) According to the liquid–liquid distribution, maximum extraction of Cr(III) by DEHPA was achieved at a pH of 4.
- (iv) It was found that Cr(III) and DEHPA reacted in 1/1 molar ratio.

- (v) It was determined that the transport of Cr(III) increased with the carrier concentration up to 0.8 M.
- (vi) It was also observed that the transport of Cr(III) through the ACM increased with increasing Cr(III) and HCl concentrations.
- (vii) The flux values from membrane stability experiments indicated that ACMs can be used in the long-term Cr(III) transport.

Acknowledgments

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