

Cr (VI) separation by PolyHIPE membrane immobilized with Aliquat 336 by solvent-nonsolvent method

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Abstract. PolyHIPEs membrane prepared with styrene (St), divinylbenzene (DVB), and ethylhexyl acrylate (EHA) can yield a unique pore structure provided by large voids highly interconnected by many small window throats. With the advantageous pore structure, PolyHIPE presents a potential as a support for carrier facilitated transport membrane. Tricaprylmethylammonium chloride (Aliquat 336) can be efficiently incorporated into the PolyHIPE membrane by a two-step solvent-nonsolvent method to obtain an Aliquat 336-immobilized PolyHIPE membrane with good stability. The study of Cr (VI) transport through Aliquat 336-immobilized PolyHIPE membrane indicates that the membrane has high initial flux and maxima stripping flux ($J_f^0=15.01$ ($\mu\text{mol}/\text{m}^2\text{s}$), $J_s^{\text{max}}=6.15$ ($\mu\text{mol}/\text{m}^2\text{s}$)). The reusability study shows that the Aliquat 336-immobilized PolyHIPE membrane can maintain high Cr(VI) recovery efficiency even after 15 cycles of operations. The developed membrane was also used in the separation of Cr (VI) from other anions (i.e., SO_4^{2-} and NO_3^-) and other cations (i.e., Ni (II), Mg (II) and Cu (II)) with good selectivity.

Keywords: polyHIPE membrane; Cr(VI) separation; solvent-nonsolvent method

1. Introduction

Carrier facilitated transport membrane has been extensively studied for the applications in heavy metal ions separation from aqueous solutions. The focuses were to improve the selectivity of metal ion, the transport flux of the membrane and the stability of the liquid carrier phase held in the porous membrane support (Richard 2012). Membrane support is one of the factors that influence the performance of carrier facilitated transport membrane (Othman *et al.* 2016). To improve the performance of the membrane, many studies have focused on the search of new membrane support. The strategies for the developments of new membrane support included creating dense interface gel layers inside the pores (Neplenbroek *et al.* 1992), coating with surface layer (Kemperman *et al.* 1997), functionalization of membrane support (Jabera *et al.* 2005) and

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formation of composite membranes (Danesi *et al.* 1986, Arslana *et al.* 2009).

The structural characteristics of membrane support affect the performance of membrane. Membrane with high porosity and large pore size is preferable to allow higher transport flux (Othman *et al.* 2016, Dinkar *et al.* 2013). On the other hand, membrane with small pore can improve the stability of the organic extractant by the capillary effect (Dinkar *et al.* 2013). In addition, a porous membrane with high interconnectivity can have high transport efficiency (Tanko 2011). Therefore, a porous material with pore structure simultaneously containing above mentioned characteristics may provide a simple way to enhance the performance of the membrane. Highly porous PolyHIPE materials (porosity >74%) have a pore structure with spherical cavities, known as voids, and the interconnecting pores between each void and its neighbors, referred to as 'windows' (Silverstein 2014, Cameron 2005). With this advantageous pore structure, PolyHIPE may present a potential membrane support for carrier facilitated transport membrane.

Another important issue for carrier facilitated transport membrane is the extractant impregnation process. The incorporation of viscous extractant into a porous material normally requires organic solvent as a diluent. However, the instability of impregnated extractant and subsequent loss of membrane performance over time are partly attributed to the evaporation and emulsification of the solvent used to prepare the membrane, leading to membrane failure (Ferraz *et al.* 2007, Zha *et al.* 1995, Richard 2012). To achieve efficient impregnation of extractant into a porous membrane, a two-step solvent-nonsolvent method is proposed. The two-step solvent-nonsolvent method is based on the concept of phase segregation for the immobilization of extractant (Chen *et al.* 2013). In the solvent treatment step, the extractant can be incorporated into the swelled polymer matrix. In the nonsolvent treatment step, the extractant undergoes phase segregation, resulting in the immobilization of extractant.

In this study, the potential of PolyHIPE as a membrane support was demonstrated by the application for the application of heavy metal Cr (VI) wastewater treatment, with Aliquat 336 as the carrier. Aliquat 336, a quaternary ammonium salts, has been successfully used for Cr (VI) separation (Alonso and Pantelides 1996, Gherasim *et al.* 2011, Asai *et al.* 2006). The immobilization of Aliquat 336 into PolyHIPE membrane by solvent-nonsolvent process was evaluated in terms of the amount of extractant immobilized in PolyHIPE membrane and extractant stability. The performance of Aliquat 336-immobilized PolyHIPE membrane was studied by Cr (VI) transport study. The long term performance of the membrane was investigated by reusability study. The developed membrane was also used in the separation of Cr (VI) from other anions (i.e., SO_4^{2-} and NO_3^-) and other cations (i.e., Ni (II), Mg (II), and Cu (II)).

2. Experimental

2.1 Chemicals

Tricaprylmethylammonium chloride (Aliquat 336, $\text{CH}_3\text{N}[(\text{CH}_2)_7\text{CH}_3]_3\text{Cl}$) was obtained from Alfa Aesar. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) was purchased from Kanto Chemical (Tokyo, Japan). The chromium standard for Atom Adsorption analysis was obtained from J.T. Baker. Styrene (St), divinylbenzene (DVB), 2-ethylhexyl acrylate (EHA), sorbitanmonooleate (Span 80), azobisisobutyronitrile (AIBN), sodium hydroxide (NaOH) and hydrochloric acid (HCl) were obtained from Aldrich (Milwaukee, WI). All chemicals were of reagent grade and were used without further purification.

2.2 Preparation and characterization of PolyHIPE membrane

The PolyHIPE membrane was prepared as reported (Zhao *et al.* 2007). In a typical experiment, the continuous phase was an organic solution consisted of 3.0 g styrene (St), 6.0 g 2-ethylhexyl acrylate (EHA), 1.0 g divinylbenzene (DVB), 0.2 g azobisisobutyronitrile (AIBN) and 2.4 g Span 80. The dispersed phase (40.0 ml of DI-water) was added dropwise (within 30 min) to the organic solution stirring at 300 rpm. After the addition of water, the mixture was stirred at 400 rpm for another 30 min to obtain a viscous emulsion solution for membrane preparation. To prepare a thin membrane, the emulsion solution was placed in a mold with two flat polytetrafluoroethylene (PTFE) plates and circumscribed by spacers to adjust the thickness of the membrane. The thickness of membrane was controlled at $120 \pm 5 \mu\text{m}$. The mold was then tightly clamped and put in an oven pre-set at 60°C to start polymerization. After 48 h of polymerization, the PolyHIPE membrane was carefully retrieved. The PolyHIPE membrane was washed for three times in ethanol for 6 h to remove organic impurities and monomeric materials, followed by immersion in DI water for 1 h to remove inorganic residual. Finally, the PolyHIPE membrane was oven-dried at 50°C for 24 h.

The foam density of PolyHIPE was determined by dividing the mass by the volume of the sample. The volume was determined from the sample dimension measured by a digital micrometer (Mitutoyo) with $0.1 \mu\text{m}$ standard deviation and averaged over 10 readings. The pore structure and chemical structure of PolyHIPE membrane was observed by SEM (S-4700, Hitachi) and FT-IR spectrometer (NICOLET 6700, Thermo Electron), respectively.

The tensile testing of the PolyHIPE membrane was conducted according to ASTM D412. The Shore hardness of the PolyHIPE membrane was measured with SHAHE/LX-C 0-100 HC 2.5 mm. The flexibility of PolyHIPE was evaluated by following the standard test method protocol ASTM F137-08. By placing the specimen over a mandrel with different radius, the bent position of the specimen face was visually examined for breaks, cracks, or other damage. The testing was performed in an ambient environment within 5 min.

2.3 Immobilization of Aliquat 336 into PolyHIPE membrane by solvent-nonsolvent method

The Aliquat 336-immobilized PolyHIPE membrane was prepared by solvent-nonsolvent method according to previous study (Chen and Huang 2007). The solvent-nonsolvent process involves two sequential steps. In the solvent treatment step, the PolyHIPE membrane was immersed in 50 mL of Aliquat 336/solvent mixture for 12 h under continuous stirring at 25°C for the solvent to swell the polymer matrix and the incorporation of Aliquat 336 into the polymer matrix. In this study, two kinds of solvent were used, namely ethanol and acetone. In the nonsolvent treatment step, a specified amount of distilled and deionized water (polar nonsolvent), which is miscible with solvent and immiscible with Aliquat 336, was added to have final total water content equal to 70 vol.%. After 1h, the Aliquat 336-immobilized PolyHIPE membrane was removed and air-dried at 45°C for 12 h. The amount of immobilized Aliquat 336 was determined by the weight difference of the membrane before and after immobilization.

The stability of Aliquat 336-immobilized PolyHIPE membrane was investigated by immersing a piece of Aliquat 336-immobilized PolyHIPE membrane sample ($\sim 0.1 \text{ g}$) in 200 mL of water at pH 4 and 12. The stirring rate was kept at 450 rpm to simulate the stirring condition in the transport study. The stability of immobilized Aliquat 336 was determined by the dry-weight

difference before and after the immersion treatment. All data reported were average of three samples.

2.4 Membrane transport study

The membrane transport experiments were performed in a double-cell device with the membrane tightly clamped between the two cell compartments with volume of 120.0 mL. The contact area of the Aliquat 336/PolyHIPE membrane was 16.0 cm². The feeding phase was a Cr (VI) aqueous solution with varied initial pH adjusted with HCl. The stripping phase was a basic solution adjusted with NaOH. Transport experiments were conducted at room temperature (25.0 ± 0.1°C). Both the feeding and stripping phases were stirred at 450 rpm, which was determined in the pre-experiment of stirring rate effect. During the transport study, the concentration of Cr (VI) was measured with an Atomic Absorption Spectrometer (Perkin-Elmer Analyst 100) with a chromium cathode lamp (Perkin Elmer) at a wavelength of 357.9 nm. All data were average of three replicable determinations.

The removal and recovery rate of metal ion was defined according to Eqs. (1) and (2)

$$\text{Removal(\%)} = \frac{C_{fo} - C_f}{C_{fo}} \times \frac{V_f}{V_f} \times 100 \quad (1)$$

$$\text{Recovery(\%)} = \frac{C_s}{C_{fo}} \times \frac{V_s}{V_f} \times 100 \quad (2)$$

where C_{fo} (mol/L) is the initial concentration of metal ion in the feed solution. C_f (mol/L) and C_s (mol/L) is the metal ion concentration in the feeding and the stripping phase at a particular time, respectively. V_f and V_s is the volume of the feeding and stripping phase, respectively ($V_f = V_s$ in this study).

The long term performance of the membrane was evaluated by reusability study. The membrane reusability was performed by subsequent transport experiments of 8 h each, under the same conditions previously established. These repeated experiments were conducted with the same membrane as in the first run while both the feeding and stripping phases were renewed after each cycle.

3. Results and discussion

3.1 Porous PolyHIPE membrane

In this study, the PolyHIPE membrane was prepared with monomer phase (30 wt.% St, 60 wt.% EHA and 10 wt.% DVB) and 80 vol.% aqueous phase dispersed with 24 wt.% of Span 80. The SEM images of PolyHIPE substrate (Fig. 1(a)) shows that the pore structure of membrane has open voids interconnected with many smaller windows throats. The diameters of the voids are 10-15 μm and the diameters of interconnection windows are less than 1.5 μm. The pores of larger sizes can provide high flux. The small interconnecting windows can provide capillary effect to hold the extractant (Kocherginsky *et al.* 2007). Fig. 1(b) shows the cross section of the pore structure of PolyHIPE membrane. It is clear that the larger open voids are connected with many small windows to form passageways directed across the membrane. The foam density is 0.23

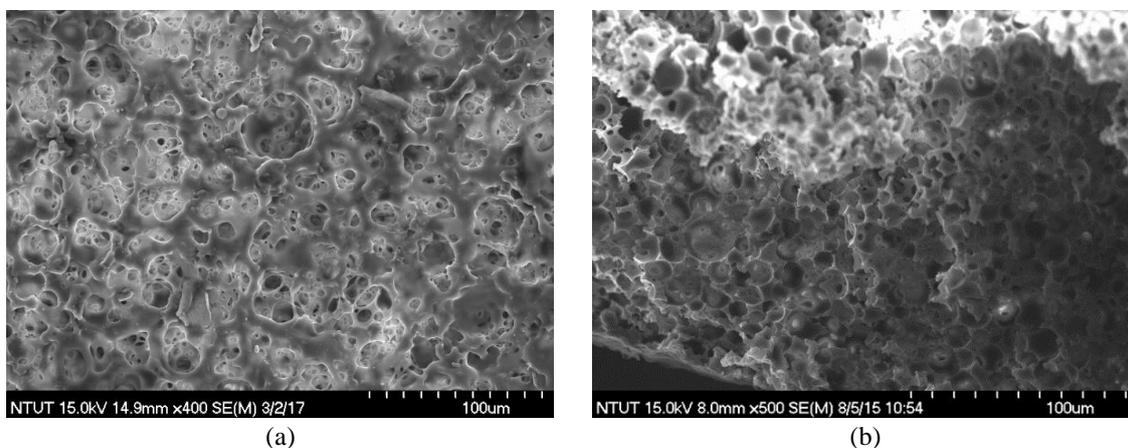


Fig. 1 SEM images of the PolyHIPE substrate: (a) top view (b) cross section

± 0.03 (g/cm³), and the porosity is 0.77 ± 0.02 .

In this study, the PolyHIPE is a poly(styrene-*co*-2-ethylhexyl acrylate) copolymer. The copolymer is cross-linked with DVB to provide the mechanical strength, and the segment of 2-ethylhexyl acrylate is to provide the flexibility. The averaged Young's modulus of the PolyHIPE substrate is about 1.25 ± 0.42 MPa. The significant variation of tensile testing results may be due to the high porosity of the substrate. The Shore hardness of the PolyHIPE membrane is about 52.6 ± 4.5 LX-C. The flexibility evaluated according to (ASTMF137-08) shows that the porous PolyHIPE can be bent over a cylindrical mandrel with diameter as small as 0.2 cm. The mechanical properties of PolyHIPE membrane film are acceptable for long term separation operation as demonstrated in the reusability study (Section 3.2.3).

3.2 Immobilization of Aliquat 336 on PolyHIPE membrane by solvent-nonsolvent method

3.2.1 Solvent-nonsolvent solution system

Immobilization of Aliquat 336 by the solvent-nonsolvent method involves mixing of Aliquat 336, solvent and nonsolvent. Therefore, the solution behavior of extractant/solvent/nonsolvent system is important. In this study, ethanol and acetone were selected as solvents, since both solvents can dissolve Aliquat 336 and swell the polymeric matrix of PolyHIPE membrane. The characteristics of ethanol and acetone are shown in Table 1. Water was selected as the nonsolvent, which is miscible with ethanol and acetone and immiscible with Aliquat 336. Fig. 2 shows the three-component phase diagrams of the ethanol/Aliquat 336/water and acetone/Aliquat 336/water mixture systems at 25°C and 1 atm. Because Aliquat 336 is soluble in ethanol and acetone and only marginally soluble in water, the phase diagrams show two regions. In the solvent-rich region, the mixture of solvent, Aliquat 336 and water forms a clear homogeneous phase. In the water-rich region, the mixture system shows two immiscible phases due to the low solubility of Aliquat 336 in water.

The variations of solution composition before and after the solvent-nonsolvent process in this study are also indicated on the phase diagrams. In the solvent treatment step, the composition of the Aliquat 336/solvent mixture is in the clear homogeneous region to ensure good incorporation

Table 1 Characteristics of solvents

Solvent	Surface tension (Vallero 2014) (N/m ⁻¹ at 20°C)	Viscosity (Haidekker <i>et al.</i> 2005) (cP)	Relative polarity (Christian 2003)	Diffusion coefficient in water (Cussler 1997) (cm ² /s)
Acetone	0.0236	0.32	0.355	1.16×10^{-5}
Ethanol	0.0236	1.2	0.654	0.84×10^{-5}

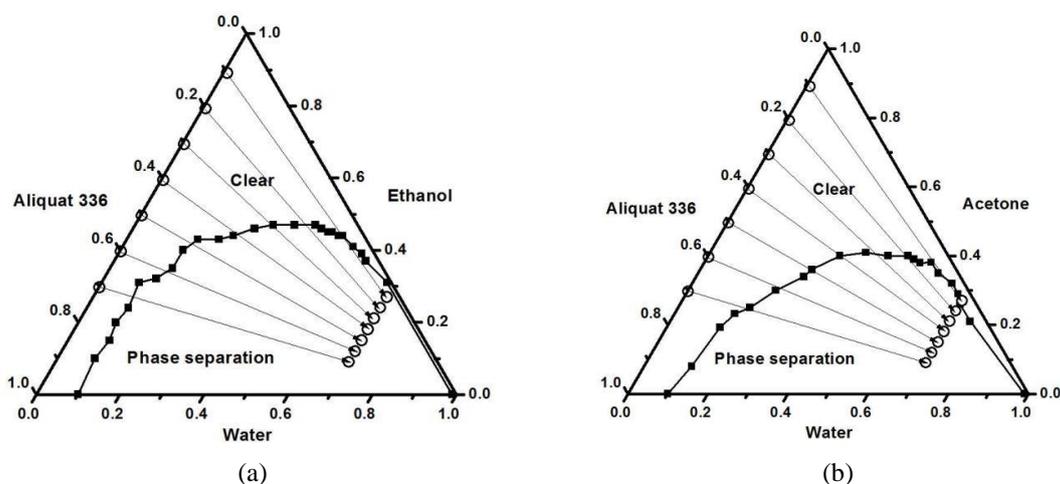


Fig. 2 Phase diagrams of (a) ethanol/Aliquat 336/water; (b) acetone/Aliquat 336/water systems at 25°C and 1 atm

of Aliquat 336 molecules into the membrane matrix. In the nonsolvent treatment step, the composition of mixture is in the phase segregation region to ensure immobilization of Aliquat 336.

3.2.2 Aliquat 336/PolyHIPE membrane

(a) Effect of solvent composition on the amount of immobilized Aliquat 336

Fig. 3 shows the effect of initial Aliquat 336 concentration in ethanol and acetone mixtures on the amount of immobilized Aliquat 336 by solvent-nonsolvent method. In general, the amount of immobilized Aliquat 336 increases with increasing Aliquat 336 concentration and levels off at about 60 vol.% of Aliquat 336. The amount of immobilized Aliquat 336 is affected by solvent property. For ethanol, the highest amount of immobilized Aliquat 336 into PolyHIPE membrane is 2.77 ± 0.01 g/g of PolyHIPE, while for acetone the value is about 2.24 ± 0.01 g/g of PolyHIPE. This is probably due to the higher solubility of Aliquat 336 in acetone (as shown in Fig. 1), resulting in higher elution of Aliquat 336 along with acetone toward water during the nonsolvent treatment step. Therefore, ethanol is selected as the solvent system in this study. Based on the density of Aliquat 336 (0.884 g/cm³) and the foam density of PolyHIPE (0.23 g/cm³), the theoretical saturated amount of Aliquat 336 is about 2.96 g/g of PolyHIPE.

For comparison, the impregnation of Aliquat 336 was also conducted by only solvent impregnation step with ethanol as solvent. The highest amount of impregnated Aliquat 336 is about 19% lower than that of solvent-nonsolvent process. It is clear that the solvent-nonsolvent method can improve the efficiency of Aliquat 336 immobilization.

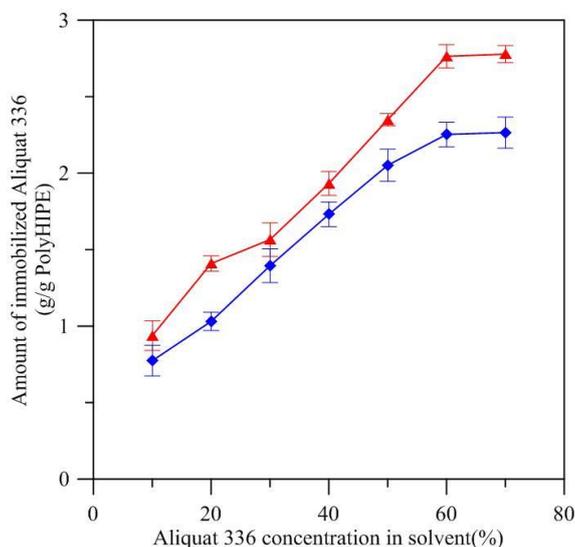


Fig. 3 Amount of immobilized Aliquat 336 into PolyHIPE membrane as function of initial Aliquat 336 concentration. (▲) Ethanol, (◆) Acetone

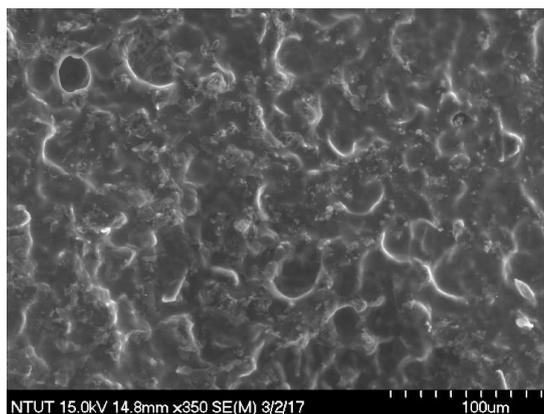


Fig. 4 SEM of Aliquat 336-immobilized PolyHIPE membrane treated with 50 vol.% of Aliquat 336

The amount of immobilized Aliquat 336 also affects the flexibility of the membrane. The flexibility test shows that the flexibility of PolyHIPE membrane remains the same (i.e., bent over a cylindrical mandrel with 0.2 cm in diameter) until the initial Aliquat 336 concentration equal to 50 vol.% (in ethanol). For initial Aliquat 336 concentration higher than 60 vol%, however, the flexibility of PolyHIPE membrane decreases (with Aliquat 336 leaching out during the flexibility test). Therefore, in the followed experiments, the immobilization of Aliquat 336 is carried out with 50 vol.% of initial Aliquat 336 concentration in ethanol. The SEM image shows that after immobilization of Aliquat 336, the cavity of open voids and the smaller open windows of PolyHIPE membrane cannot be clearly identified (Fig. 4).

(b) Stability of immobilized Aliquat 336

The stability of the Aliquat 336-immobilized PolyHIPE membrane was investigated by

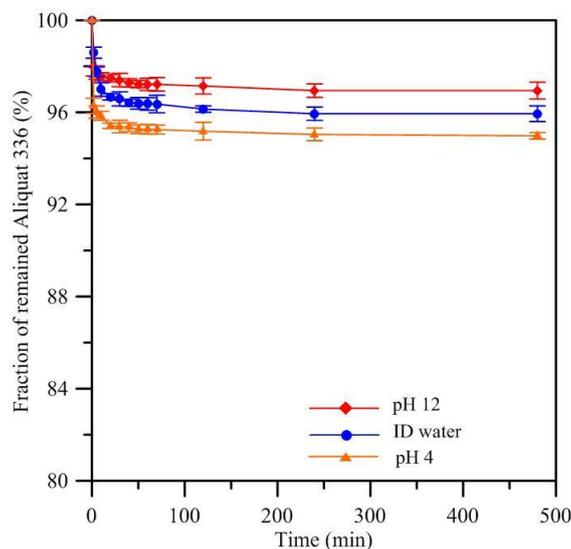


Fig. 5 Stability of Aliquat 336-immobilized PolyHIPE membrane under stirring condition 450 rpm

immersing a membrane sample in water solution under continuous stirring at 450 rpm. Fig. 5 shows that the amount of immobilized Aliquat 336 decreases slightly in the first 20 min of immersion. This is probably due to the removal of Aliquat 336 from the large pores in the surface region of PolyHIPE membrane. After 20 min, the amount of immobilized Aliquat 336 becomes stable. For membrane immersed in water solution at pH 4, 7 and 12 after 8 h of immersion, the amount of immobilized Aliquat 336 remained in the membrane is about 95.05%, 96.12% and 96.94%, respectively. The difference may be due to the pH effect on the solubility of Aliquat 336 in water (Xu *et al.* 2003). The good stability of immobilized Aliquat 336 (>95%) is attributed to the pore structure of PolyHIPE. The small windows in the PolyHIPE membrane provide higher capillary force to hold the Aliquat 336.

3.2 Transport behavior of Cr (VI) through Aliquat 336-immobilized PolyHIPE membrane

3.2.1 pH effect

In general, pH is one of the most important factors affecting the separation of Cr (VI). pH effect was investigated for both feeding and stripping phases. Fig. 6(a) shows the effect of initial pH in the feeding phase on the removal rate of Cr (VI). After 8 h, the removal rate of Cr (VI) increases from 93.7% to 98.3% with initial pH in the feeding phase increased from 2 to 5. The slightly lower removal rate at pH 2 may be due to that Cr (VI) may form condensation products of large chromate aggregate as $\text{Cr}_3\text{O}_{10}^{2-}$ and/or $\text{Cr}_4\text{O}_{13}^{2-}$ at low pH (Weckuysen *et al.* 1996), which have lower mobility (Chen *et al.* 2013). In addition, the decrease in Cr (VI) extraction at acidic pH may also be explained by the fact that Cr(VI) will form H_2CrO_4 as a non-anionic species, which does not participate in the anion exchange process (Saha *et al.* 2004). Therefore, in the transport study the pH of the feeding phase is fixed at pH 4.

The effect of pH in the stripping phase can be evaluated by the recovery rate of Cr (VI), while keeping the pH in the feeding solution at pH 4. Fig. 6(b) shows that the Cr (VI) recovery rate

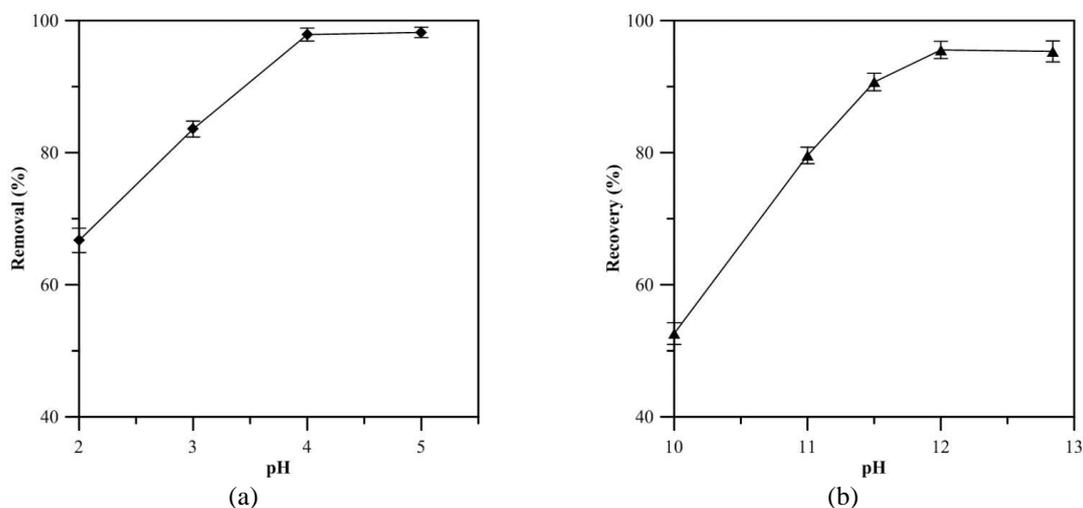


Fig. 6 (a) Effect of pH in the feeding phase: feeding phase [Cr(VI)]=53 mg/L; stripping phase: NaOH solution at pH 12; stirring rate: 450 rpm. (b) Effect of pH in the stripping phase: feeding phase: [Cr(VI)]=53 mg/L at pH=4; stripping phase: NaOH solution; stirring rate: 450 rpm.

increases from 63% to 97% as the initial pH in the stripping phase increased from 10 to 12.5. The increasing of the Cr (VI) recovery rate is due to the increasing OH^- concentration in the stripping phase. At pH 12, the Cr (VI) recovery rate levels off at about 97 %.

3.2.2 Kinetic of Cr (VI) transport

Kinetic study provides essential information for designing full-scale separation process. For a well-mixed feeding and stripping phases (stirring rate at 450 rpm), it can be assumed that the mass transfer between the bulk phases (feeding and stripping phases) and the membrane interface is an immediate process. The sequence of transport phenomena involves: extraction of Cr(VI) by Aliquat 336, diffusion of Cr(VI) through the Aliquat 336-immobilized membrane, followed by stripping of Cr(VI). Therefore, the transport of Cr (VI) through PolyHIPE membrane can be described by a kinetic law of two consecutive first order irreversible reaction (3) (Mehmet *et al.* 2011).



where Cr(VI)_f and Cr(VI)_s represents the Cr(VI) ions in the feeding and stripping phase, respectively, while Cr(VI)_m is the Cr(VI)-Aliquat 336 complex in the membrane phase. k_1 and k_2 is the first order apparent rate constant of the extraction and the stripping reaction, respectively. Both of the “apparent rate constants” are function of extraction reaction, stripping reaction and the solute diffusion rate (Zhang *et al.* 2009).

The transport rate of Cr (VI) can be expressed by the following differential equations Eqs. (4)-(6)

$$\frac{dR_f}{dt} = -\alpha k_1 R_f \quad (4)$$

$$\frac{dR_m}{dt} = \alpha k_1 R_f - \beta k_2 R_m \quad (5)$$

$$\frac{dR_s}{dt} = \beta k_2 R_m \quad (6)$$

where α and β is the ratio of membrane contact area to the volume of the feeding and stripping phase, respectively ($\alpha=\beta=16 \text{ m}^2/\text{m}^3$ in this study). R_f , R_m and R_s is the dimensionless concentrations of Cr(VI) in feeding, membrane, and stripping phase, respectively. They are defined as

$$R_f = \frac{C_f}{C_{fo}} \quad (7)$$

$$R_m = \frac{C_m}{C_{fo}} \quad (8)$$

$$R_s = \frac{C_s}{C_{fo}} \quad (9)$$

Combining Eqs. (4)-(6) and integration of these differential equations yield

$$R_f = e^{-16k_1 t} \quad (10)$$

$$R_m = \frac{k_1}{k_2 - k_1} \left(e^{-16k_1 t} - e^{-16k_2 t} \right) \quad (11)$$

$$R_s = 1 - \frac{k_2}{k_2 - k_1} e^{-16k_1 t} + \frac{k_1}{k_2 - k_1} e^{-16k_2 t} \quad (12)$$

Fig. 7 shows the kinetic variation of reduced concentrations of the feeding phase, stripping phase and membrane phase, of which the amount of Cr (VI) in the membrane phase is determined by mass balance ($C_m=C_{fo}-C_f-C_s$). In all cases, R_f decreases bi-exponentially with time (Eq. (10)), R_s follows a monotonically increasing sigmoid-type curve (Eq. (12)), while the time evolution of R_m presents a maximum (Eq. (11)). The fitted parameters are $k_1=1.23 \times 10^{-5} \text{ m/s}$ and $k_2=9.55 \times 10^{-5} \text{ m/s}$ ($R^2>0.98$).

The performance of Cr (VI) separation by the Aliquat 336-immobilized PolyHIPE membrane can be quantified by the maxima stripping flux (J_s^{max}) and initial feeding flux (J_f^0) values, which can be determined from the kinetic model. The kinetic curve of R_m in the membrane phase has a characteristic maximum, which can be characterized by two parameters, namely t_{max} and $(R_m)_{\text{max}}$. By taking the derivative $dR_m/dt=0$, the time for R_m to reach a maximum, t_{max} , can be obtained from Eq. (13) and Eq. (14), respectively

$$t_{\text{max}} = \frac{\ln \frac{k_2}{k_1}}{k_2 - k_1} \quad (13)$$

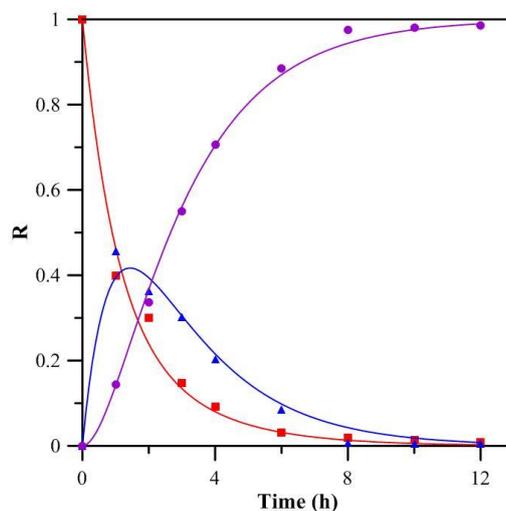


Fig. 7 The kinetic behavior of R_f (■), R_m (▲) and R_s (●): Feeding phase: Cr (VI) (53 mg/L), pH 4; stripping phase: pH12; stirring rate: 450 rpm

$$(R_m)_{\max} = \left(\frac{k_1}{k_2} \right)^{\frac{k_2}{k_2 - k_1}} \quad (14)$$

The maxima stripping flux and initial feeding flux at $t=0$ can be described by Eq. (15) and Eq. (16), respectively (Mehmet *et al.* 2011)

$$J_s^{\max} = - \frac{V_s}{A_{F/M}} \frac{dC_s}{dt} \Big|_{t=t_{\max}} = - \frac{V_s}{A_{F/M}} 16k_2 C_{fo} (R_m)_{\max} \quad (15)$$

$$J_f^o = \frac{V_f}{A_{F/M}} \frac{dC_f}{dt} \Big|_{t=0} = \frac{V_f}{A_{F/M}} 16k_1 C_{fo} \quad (16)$$

where $A_{F/M}$ is the membrane contact area (cm^2), V_f and V_s is the volume of the feeding phase and stripping phase, respectively.

Based on the values of $(R_m)_{\max}=0.413$ and $t_{\max}=1.61$ h, $J_f^o=15.01$ ($\mu\text{mol}/\text{m}^2\text{s}$) and $J_s^{\max}=6.15$ ($\mu\text{mol}/\text{m}^2\text{s}$). It is clear that the performance of the Aliquat 336-immobilized PolyHIPE membrane is comparable with other studies with different extractant and membrane (Table 2). It is also worth to point out that even for trace concentration of Cr (VI), the residual amount of Cr (VI) is less than 0.5 ppm after 10 h of separation to meet the environmental regulation standard.

3.2.3 Long term operation performance

Long term performance of separation is one of the criteria for practical applications of membrane. In this study, the long term performance of the Aliquat 336-immobilized PolyHIPE membrane was evaluated based on the removal and recovery rates of Cr (VI) obtained from 15 sequential cycles. These repeated experiments were conducted with the same membrane as in the first run while both the feeding and stripping phases were renewed every 8 h. As can be seen (Fig.

Table 2 Comparison of the Cr (VI) transport efficiency by different membranes

[Cr(VI)] ₀ (mol/l)	Feeding phase pH	Membrane type/base polymer	Carrier	Stripping phase	J_o ($\mu\text{mol}/\text{m}^2\text{s}$)	Membrane thickness σ (μ)	Ref.
2.0×10^{-4}	0.12	PIM/CTA	Calix[4]arene	Acetic acid/ammonium acetate buffer at pH5	2.253	42	Kaya <i>et al.</i> 2013
2.0×10^{-3}	1	PIM/CTA	Aliquat 336	0.1M NaOH	8.84	28	Kozlowski <i>et al.</i> 2005
2.3×10^{-4}	1.2	PIM/CTA	Aliquat 336	0.1M NaOH	3.11	80	Keblache-Senhadjia <i>et al.</i> 2010
1.8×10^{-6}	8	PIM/CTA	Aliquat 336	1M NaNO ₃	0.002	62	Scindia <i>et al.</i> 2005
1.0×10^{-3}	1	ACM	Cyanex 923	0.5M NaOH	10.91	90	Arslana <i>et al.</i> 2009
1.0×10^{-3}	1	ACM	Cyanex 923	0.5M NaOH	11.94	25	
3×10^{-4}	2	SLM	CYPHOS IL101	1M NaOH	5.5	125	Rodríguez <i>et al.</i> 2014
7.5×10^{-4}	0	SLM	Cyanex 921	5 g/L Hydrazine sulfate.	6.7	125	Alguacil <i>et al.</i> 2003
1.0×10^{-3}	4	SLM/PolyHIPE	Aliquat 336	pH 12	15.1	120	This study

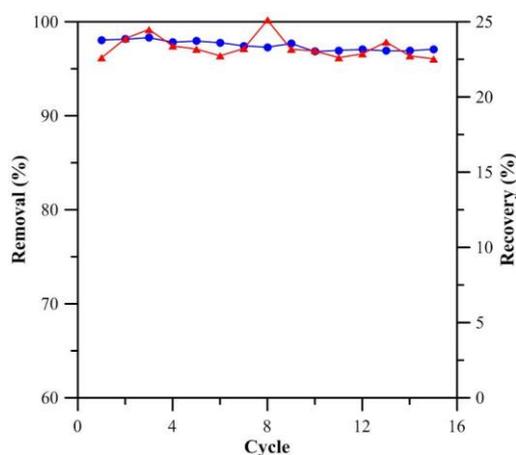


Fig. 8 Removal and recovery rates in consecutive separation cycle: (●) removal, (▲) recovery. Feeding phase: [Cr(VI)] = (53 mg/L) at pH 4; stripping solution: NaOH solution at pH 12; stirring rate: 450 rpm

8), the removal rate remains higher than 97% and the recovery rate remains approximately 96%, after 15 consecutive cycles. Therefore, the Aliquat 336-immobilized PolyHIPE membrane is effective for long-term Cr (VI) separation operation. The results of long term performance also indicate that the membrane has good hydraulic stability.

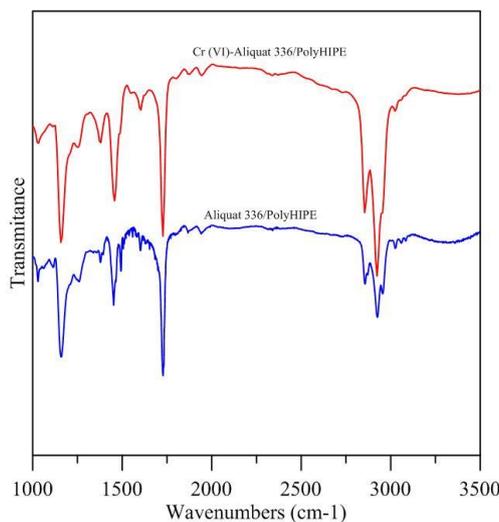


Fig. 9 FT-IR spectrum of Aliquat 336/PolyHIPE membrane

Due to the strong oxidation power of Cr (VI) solution, the stability of chemical structure of membrane is important for practical application. The FT-IR spectrum shows the characteristic peaks for Aliquat 336-immobilized PolyHIPE (Fig. 9). These bands at 699.5, 1452.7, 2856.2 and 2923.4 cm^{-1} are associated with the methylene group of styrene (Derrick *et al.* 1999). The stretching vibration of carbonyl group (C=O) of EHA is seen at 1726.4 cm^{-1} . The peak at 1603 cm^{-1} is due to deformation and skeletal vibrations of C-H in DVB (Singare *et al.* 2011). Therefore, the PolyHIPE substrate is consisted of polystyrene-EHA chains cross-linked with DVB. The peak at 1461.8 cm^{-1} and 1261 cm^{-1} is the characteristic peak for quaternary amine due to $(\text{CH}_3)\text{N}^+$ and -C-N stretching vibration for Aliquat 336, respectively.

Fig. 9 also shows the FT-IR spectrum of Aliquat 336-immobilized PolyHIPE membrane after 15 sequential cycles. The characteristic peaks of the PolyHIPE substrate are almost identical with that of initial membrane, indicating that the chemical structure of the membrane is stable. However, characteristic peak of -C-N stretching vibration is shifted from 1261 cm^{-1} to 1250 cm^{-1} for Cr (VI)-loaded Aliquat 336, indicating the bonding between Cr (VI) and the functional groups of Aliquat 336.

3.4 Separation of Cr (VI) from mixed ion solution

Industrial wastewaters contain mixtures of metal ions and other anionic species, which may affect the separation of Cr (VI). In this study, the Aliquat 336-immobilized PolyHIPE membrane was used for the recovery of Cr (VI) from a simulated wastewater mixture with the composition based on the wastewater from a local electroplating plant: Cr(VI) (53mg/L), Ni(II) (87.45 mg/L), Mg(II) (24.77 mg/L), Cu(II) (32.4 mg/L), SO_4^{2-} (245.0 mg/L), NO_3^- (84.30 mg/L) at pH 4.0. Table 3 shows the results of separation. The recovery rate of Cr (VI) is as high as 95.1% even under the interference of high concentration of anionic SO_4^{2-} and NO_3^- . The separation factor of Cr (VI)/ SO_4^{2-} and Cr (VI)/ NO_3^- is 27.44 and 11.34, respectively. The high separation factor demonstrates that Aliquat 336-immobilized PolyHIPE membrane has potential for practical application in the recovery of Cr (VI) from industrial wastewater.

Table 3 Separation of Cr(VI) from mixture solution by Aliquat 336/PolyHIPE membrane

Ion matter	Recovery (%)	Separation factor ($\alpha_{(A/B)}$)*
Cr(VI)	95.79	1
Cationic interference		
Ni(II)	1.19	77.07
Mg(II)	0.88	108.85
Cu(II)	0.91	105.26
Anionic interference		
SO ₄ ²⁻	3.49	27.44
NO ₃ ⁻	8.44	11.34

* $\alpha_{(A/B)} = \frac{y_A/y_B}{x_A/x_B}$, where y_A and y_B is the concentration of component A and B in the stripping phase,

respectively; x_A and x_B is the concentration of the component A and B in the feeding phase, respectively (Marcel 1991).

4. Conclusions

With the advantageous pore structure, PolyHIPE presents a potential as the support of carrier facilitated transport membrane. In this study, the feasibility of Aliquat 336-immobilized PolyHIPE membrane for wastewater treatment is demonstrated by Cr (VI) separation. By solvent-nonsolvent method, the amount of immobilized Aliquat 336 in the porous PolyHIPE membrane is as high as 2.77 ± 0.01 g/g of PolyHIPE. Due to the capillary effect provided by the small windows, the immobilized Aliquat 336 can have good hydraulic stability. The kinetic study of Cr (VI) separation shows that high initial flux and stripping flux ($J_f^o = 15.01$ ($\mu\text{mol}/\text{m}^2\text{s}$), $J_s^{\text{max}} = 6.15$ ($\mu\text{mol}/\text{m}^2\text{s}$)) can be achieved by Aliquat 336/PolyHIPE membrane. The reusability study shows that the Aliquat 336-immobilized PolyHIPE membrane can maintain high performance efficiency (over 96%) and chemical structure stability even after 15 consecutive cycles of operation. The developed membrane can be used in the separation of Cr (VI) from other anions, such as SO₄²⁻ and NO₃⁻, with good selectivity. The experimental results demonstrate the potential of practical application of this new type of membrane for trace Cr (VI) recovery.

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