A Separation of manganese (II) and cobalt (II) ions by D2EHPA/TBP-immobilized PolyHIPE membrane

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Abstract. The D2EHPA/TBP co-extractants immobilized PolyHIPE membrane can be used for the selective separation of Mn (II) from Co (II). By solvent-nonsolvent method, D2EHPA/TBP co-extractants can be effectively immobilized into PolyHIPE membrane. The pore structure of PolyHIPE membrane and the presence of TBP enhance the stability of immobilized co-extractants. The optimal operating conditions for the separation of Mn (II) and Co (II) are feeding phase at pH 5.5, sulfuric acid concentration in the stripping phase of about 50 g/L and stirring speed at 400 rpm. The D2EHPA/TBP co-extractants ratio of 5:1 shows synergetic effect on Mn/Co separation factor about 22.74. The removal rate and recovery rate of Mn (II) is about 98.4 and 97.1%, respectively, while for Co (II) the transport efficiency is insignificant. The kinetic study of Mn (II) transport shows that high initial flux, $J_f^o = 80.1$ (μmol/m^{2}s), and maxima stripping flux, $J_s^{max} = 20.8$ (μmol/m^{2}s), can be achieved with D2EHPA/TBP co-extractants immobilized PolyHIPE membrane. The stability and reusability study shows that the membrane can maintain a long term performance with high efficiency. High purity of Co (II) and Mn (II) can be recovered from the feeding phase and stripping phase, respectively.

Keywords: Mn (II) and Co (II) separation; D2EHPA; TBP; PolyHIPE membrane; separation factor

1. Introduction

Cobalt is an important metal in high-technology industries involving batteries, alloys, magnetic materials, and catalysts. The limited source and high demand of cobalt have posed a supply risk for this metal. The appearance of growing manganese contents in the potential cobalt ore has led to developments of Co/Mn separation technology in the ore processing plant to substitute the now less-effective classical cobalt precipitation method (Kongolo *et al.* 2000). In addition to cobalt ore mining, electronic products such as lithium ion batteries (LIBs) have emerged as possible secondary sources for cobalt. The separation processes like Co-Ni (Jeong *et al.* 2004, Juang 1993), Co-Zn (Alguacil and Alonso 2005), Co-Li (Swain *et al.* 2007) and Co-Mn (Alguacil 2002) have been investigated by supported liquid membrane (SLM) technique for the recovery of valuable metals from the waste cathodic materials of LIBs. Recently, many cathodic active materials contained Mn, which is much cheaper and less toxic compare to Co or Ni (Nitta *et al.* 2015). Therefore, the study of separation of manganese and cobalt is a significant issue for the effective recycling of the waste cathodic materials of LIBs. Nevertheless, the separation of Co (II) from Mn (II) poses a difficult problem because of their similar chemical and physical properties (Baba *et al.* 2014).

The separation of Mn (II) and Co (II) ion by SLM depends on the type of extractant. Several extractants such as Di-2-ethylhexyl phosphoric acid (D2EHPA) (Swain *et al.* 2004a, Swain *et al.* 2004b, Alguacil and Alonso 2005, Alguacil 2002), PC-88A (Akita and Takeuchi 1992), LIX84 (Lee *et al.* 2004), and Cyanex 921 (Alguacil *et al.* 2005) have been used for the extraction of Mn (II). Among them, D2EHPA has been identified as one of cheapest reagents for selective extraction of manganese over other metals (Zhang *et al.* 2010). Studies on the separation of metal ions have shown that instead of using a single extractant, mixtures of co-extractants can give rise to synergistic effects and better selectivity of metal extraction and separation in solvent extraction processes (Pospiech 2014a, Pospiech 2014b). Tributyl phosphate (TBP) is a widely used extractant modifier (Baaden *et al.* 2001), which can improve the extraction efficiency and enhance phase separation in solvent extraction (Fatmehsari *et al.* 2009). However, to our knowledge, no study focused on the application of the D2EHPA and TBP dual extractants immobilized SLM for the recovery and separation of Mn (II) and Co (II) using SLM technique. Therefore, the separation of Mn (II) and Co (II) by D2EHPA/TBP co-extractants in SLM deserves investigation.

One of the major concerns of SLM is the stability of incorporated extractant (Yang *et al.* 2007). The structural characteristics of membrane support can affect the stability of SLM. Porous membrane with high porosity and large pore size can allow higher transport flux (Othman *et al.* 2016, Dinkar *et al.* 2013). On other hand, the stability of the organic extractant can be improved for membrane with

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small pore due to the capillary effect (Dinkar *et al.* 2013). Highly porous PolyHIPE materials (porosity >74%) have a pore structure with spherical cavities, known as voids, and small interconnecting pores between each void and its neighbors, referred to as 'windows' (Silverstein 2014). With this advantageous pore structure, PolyHIPE present a potential membrane support for the carrier facilitated transport membrane (Chen *et al.* 2017).

For the immobilization of extractant into porous material, the extractant impregnation process is an important factor (Jerabek *et al.* 1996). The incorporation of viscous extractant into a porous material normally requires organic solvent as a diluent. However, the evaporation and emulsification of the solvent during the operation is partly responsible for the loss of stability of impregnated extractant and subsequent loss of membrane performance over time (Ferraz *et al.* 2007, Zha *et al.* 1995, Richard 2012). A modified impregnation process, namely two-step solvent-nonsolvent method, can achieve efficient impregnation of extractant into a porous membrane (Chen *et al.* 2013).

In this study, the separation of Mn (II) and Co (II) by D2EHPA/TBP co-extractants immobilized into PolyHIPE membrane by the solvent-nonsolvent method was investigated. The effects of operation condition, such as stirring speed, pH of feed solution, acid concentration in stripping solution, and synergetic effect of co-extractants ratio on the separation Mn (II) and Co (II) were determined. The transport kinetics study was examined in order to elucidate the facilitated transport mechanism for the diffusion of ion through D2EHPA/TBP immobilized PolyHIPE membrane. The stability and reusability of the membrane were evaluated to demonstrate the long term application of this new type of membrane.

2. Experimental

2.1 Materials

Styrene (St), divinylbenzene (DVB), 2-ethylhexyl acrylate (EHA), sorbitan monooleate (Span 80) and azobisisobutyronitrile (AIBN) used for the preparation of PolyHIPE membrane were obtained from Aldrich (Milwaukee, WI). Di-2-ethylhexul phosphoric acid (D2EHPA) and tributyl phosphate (TBP) were supplied by Aldrich (Milwaukee, WI, USA). Cobalt (II) sulfate heptahydrate ($CoSO_4 \cdot 7H_2O$), manganese sulfate ($MnSO_4 \cdot H_2O$), sulfuric acid and ethanol were also supplied by Aldrich (Milwaukee, WI, USA). The manganese and cobalt standards for Atom Adsorption analysis were obtained from J.T. Baker. All chemicals were of reagent grade and were used without further purification.

2.2 Preparation of D2EHPA/TBP immobilized PolyHIPE membrane

The PolyHIPE membrane was prepared as reported (Chen *et al.* 2017). 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 stirred 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. The thickness of membrane was controlled at 120±5 μm with a mold with two flat polytetrafluoroethylene (PTFE) plates. After 48 h of polymerization at 60°C, the PolyHIPE membrane was washed with ethanol for 6 h, followed by immersion in DI water for 1 h. Finally, the PolyHIPE membrane was oven-dried at 50°C for 24 h.

The foam density of PolyHIPE was calculated by dividing the mass by the volume of the sample, which was determined from the sample dimension measured by a digital micrometer (0.1μm standard deviation, Mitutoyo) 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 characteristic of pore structure of PolyHIPE was evaluated by mercury porosimetry (Micromeritics AUTOPORE 9520, Micromeritics Instrument, Norcross, GA, USA) with maximum test pressure of 200 MPa.

Immobilization of extractants into PolyHIPE membrane was carried out by solvent-nonsolvent method according to previous study (Chen *et al.* 2017). The solvent-nonsolvent process involves two sequential steps. In the solvent treatment step, the PolyHIPE membrane was immersed in 50 mL of D2EHPA/TBP co-extractants mixture in ethanol under continuous stirring at 25°C for 12 h to allow the ethanol to swell the polymer matrix and the incorporation of extractants into the PolyHIPE membrane. In the nonsolvent treatment step, a specified amount of distilled and deionized water (polar nonsolvent), which is miscible with ethanol and immiscible with D2EHPA/TBP, was added to have a final total water content equal to 65 vol. %. Due to the fast elution of solvent by nonsolvent, phase segregation of organic extractants occurred inside the pore of the membrane, resulting in immobilization of extractants. After 1h, the D2EHPA/TBP-immobilized PolyHIPE membrane was air-dried at 45°C for 12 h. The amount of immobilized extractants was determined by the weight difference of the membrane before and after immobilization with the average of three samples.

2.3 Separation of Mn (II) and Co (II)

The separation experiments were conducted in a double-cell device with solution volume of 100 mL for each compartment. The contact area of the membrane was 16 cm^2. The feeding phase was an aqueous solution with varied initial pH adjusted with H_2SO_4. The stripping phase is a H_2SO_4 solution. Separation experiments were performed at room temperature (25.0 ± 0.1°C). During the separation operation, the concentration of Co (II) and Mn (II) ions in both phases was periodically measured with an Atomic Absorption spectrometer (Analyst 100, Perkin-Elmer) with manganese and cobalt cathode lamp (Perkin Elmer) at

wavelength of 240.7 and 279.5 nm, respectively. All data are averages of three replicable determinations. In this study, the prepared SLM was conditioned for 12 h in the cell between two phases of pure water. After this induction period of time, the ions were introduced to begin the transport study.

The removal and recovery rate of metal ions was defined as Eqs. (1) and (2)

$$Removal(\%) = \frac{[M]_{fo} - [M]_f}{[M]_{fo}} \times 100 \qquad (1)$$

$$Recovery(\%) = \frac{[M]_s}{[M]_{fo}} \times 100 \qquad (2)$$

where $[M]_{fo}$ is the initial concentration of metal ions in the feeding phase, $[M]_f$ and $[M]_s$ is the concentration of metal ions in the feeding and stripping phase, respectively.

The separation factor ($\beta_{Mn/Co}$) was determined as following (Mulder 1991)

$$\beta_{Mn/Co} = \frac{y_{Mn}/y_{Co}}{x_{Mn}/x_{Co}}, \qquad (3)$$

where y_{Mn} and y_{Co} are the concentration of Mn (II) and Co (II) in the stripping phase; x_{Mn} and x_{Co} are the concentrations of the components in the feeding phase.

3. Results and discussion

3.1 Characteristic of D2EHPA/TBP-immobilized PolyHIPE membrane

3.1.1 Immobilization of D2EHPA/TBP co-extractants by solvent-nonsolvent method

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 show that the pore structure of membrane has open voids interconnected with many smaller windows throats (Fig. 1). The pores of larger sizes can provide high flux, and the small interconnecting windows can provide capillary effect to hold the extractant (Chen *et al.* 2018). It is clear that the larger open voids are connected with many small windows to form passageways directed across the membrane.

The structure characteristics of PolyHIPE membrane were summarized as follows. The thickness of membrane is 120±5 μm. The foam density is 0.23±0.03 (g/cm³), and the porosity is 0.77±0.02. The diameter of the void is 10-15 μm and the diameter of interconnection window is less than 1.5 μm. The pore size of PolyHIPE membrane measured by mercury porosimetry shows a bimodal distribution with two distinct pore diameter regions (10-30 nm and 1000-9000 nm) with a "valley" within 30-1000 nm. The relative pore volume of the two distinct pore size ranges is 11.6% (10-30 nm) and 88.4% (1000-9000 nm), respectively. Other
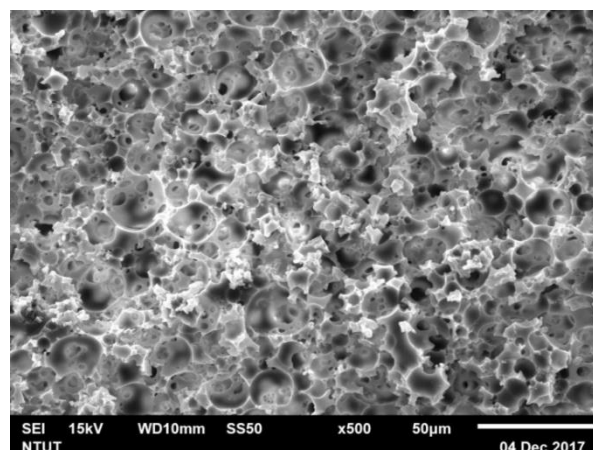

Fig. 1 SEM images of the PolyHIPE substrate

characteristic properties of PolyHIPE membrane obtained from mercury porosimetry measurement are bulk density (0.23 g/mL), skeletal density (1.095 g/mL), and porosity (0.77).

Immobilization of D2EHPA/TBP co-extractants into PolyHIPE membrane by the solvent-nonsolvent method depends on the mixing behavior of extractants, solvent and nonsolvent. In this study, ethanol was selected as solvent, since ethanol can dissolve both D2EHPA and TBP and swell the polymeric matrix of PolyHIPE membrane. Water was selected as the nonsolvent, which is miscible with ethanol and immiscible with D2EHPA and TBP. Fig. 2 shows the three-component phase diagram of D2EHPA/ethanol/water, TBP/ethanol/water and D2EHP/TBP co-extractants/ethanol/water systems at 25°C and 1 atm. The phase diagram of D2EHPA/ethanol/water system shows two regions. In the ethanol-rich region, since water is miscible with ethanol and D2EHPA is soluble in ethanol, the mixture of solvent, D2EHPA 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 D2EHPA in water (about 1 vol.%) (Lee *et al.* 2011). Since the solubility of TBP in water (0.1-1 vol.% (Lee *et al.* 2011)) is close to that of D2EHPA, the phase diagram of TBP/ethanol/water is similar.

In this study, a mixture of D2EHP/TBP was used as co-extractants for the separation of Co (II) and Mn (II) ions. The phase diagram of D2EHP/TBP co-extractants/ethanol/water system shows similar trend (Fig. 2). The variations of solution composition of D2EHP/TBP co-extractants system before and after the solvent-nonsolvent process in this study are also indicated on the phase diagram. In the solvent treatment step, the composition of co-extractants/ethanol/water mixture is in the clear homogeneous region to ensure good incorporation of extractants molecules into the membrane matrix. In the nonsolvent treatment step, after the elution of ethanol by nonsolvent (water) the composition of mixture is in the phase segregation region to ensure immobilization of extractants.

Fig. 3 shows the effect of initial co-extractants D2EHPA/TBP (ratio of 5:1) content in ethanol on the amount of immobilized co-extractants by solvent-
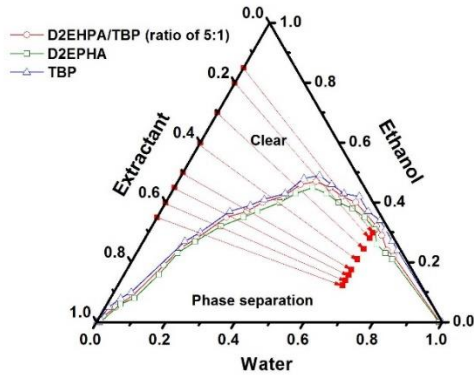
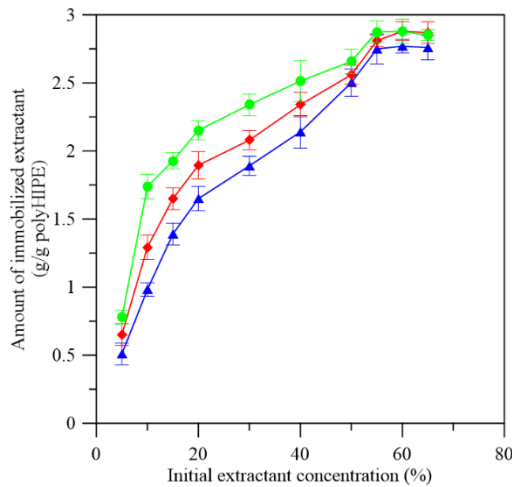Fig. 2 Phase diagrams of ethanol/extractants/water

Fig. 3 Amount of immobilized extractant into PolyHIPE membrane as function of initial extractant content. (♦) D2EHPA/TBP (ratio of 5:1), (▲) D2EHPA, (●) TBP

nonsolvent method. In general, the amount of immobilized co-extractants increases with increasing co-extractants concentration and levels off at about 55 vol.% for co-extractant of D2EHPA/TBP (ratio of 5:1). The highest amount of immobilized co-extractants into PolyHIPE membrane is 2.81 ± 0.08 g/g of PolyHIPE. The effect of initial concentration of single D2EHPA and TBP extractant on the amount of immobilized extractant was also evaluated. The highest amount of D2EHPA is about 2.75 ± 0.11 g/g of PolyHIPE. For TBP, the amount of immobilization is 2.85 ± 0.04, which is higher than that of D2EHPA and D2EHPA/TBP. It was indicated that TBP can make D2EHPA to be distributed more homogenously and uniformly in the pores of porous substrate (Bao *et al.* 20018). Furthermore, comparing the results of D2EHPA and D2EHPA/TBP systems, the presence of TBP can further enhance the immobilization of extractant. This may be due to the more polar nature of TBP (Zheng *et al.* 2018), which may have better interaction with the EHA moiety of PolyHIPE in this study.

3.1.2 Stability of D2EHPA/TBP co-extractants in PolyHIPE membrane

One major concern of D2EHPA/TBP-immobilized PolyHIPE membrane is the stability of immobilized co-
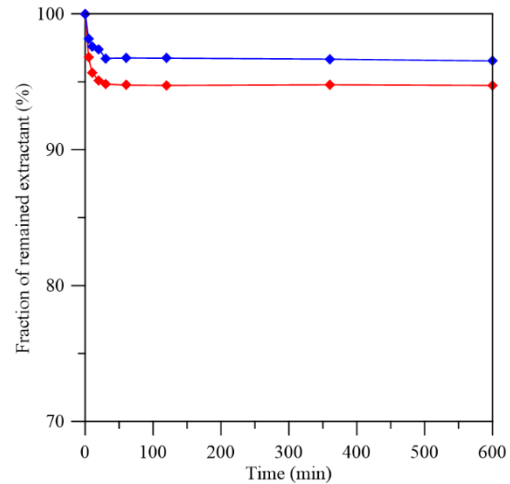

Fig. 4 Stability of (♦) D2EHPA-immobilized PolyHIPE membrane and (♦) D2EHPA/TBP-immobilized PolyHIPE membrane

extractants. The stability of the immobilized co-extractants in PolyHIPE membrane was evaluated by immersing a membrane sample in water solution under continuous stirring at 400 rpm. Fig. 4 shows that the amount of immobilized co-extractants decreases slightly (<5%) in the first 60 min of immersion period. This is probably due to the removal of co-extractants from the large pores in the surface region of PolyHIPE membrane. After 60 min, the remained amount of impregnated D2EHPA/TBP becomes stable (96.53%). For comparison, the stability of D2EHPA-immobilized PolyHIPE membrane was also evaluated. After 60 min, the remained amount of immobilized extractant in the membrane is about 94.73%. The higher stability of D2EHPA/TBP-immobilized PolyHIPE membrane may due to the present of TBP, which improves the stability of co-extractants.

For longer immersion time, the extractant-immobilized PolyHIPE membrane also shows long term stability. Based on above stability study, the amount of D2EHPA and D2EHPA/TBP co-extractants leached into the water phase corresponds to the content of D2EHPA and D2EHPA/TBP in water phase of about 0.03 and 0.02%, respectively, which is lower than the solubility of D2EHPA and TBP in water. Therefore, the long term stability of immobilized extractant can be attributed to the pore structure of PolyHIPE. The small windows in the PolyHIPE membrane provide higher capillary force to hold the extractant. This result indicates that the pore structure of PolyHIPE can effectively improve the stability of D2EHPA/TBP inside the membrane for long term operation.

3.1.3 Evaluation of D2EHPA and TBP interaction in PolyHIPE membrane

Fig. 5 shows the FTIR spectra of PolyHIPE. IR absorption frequencies at 699.5, 1452.7, 2856.2 and 2927 cm^{-1} are associated with the methylene group of styrene, while deformation of C-H of methyl group (CH_3) is at 1444.5 cm^{-1} (Derrick *et al.* 1999). The stretching vibration at 1726.4 cm^{-1} is the carbonyl group (C=O) of EHA. The peak at 1603 cm^{-1} is due to deformation and skeletal
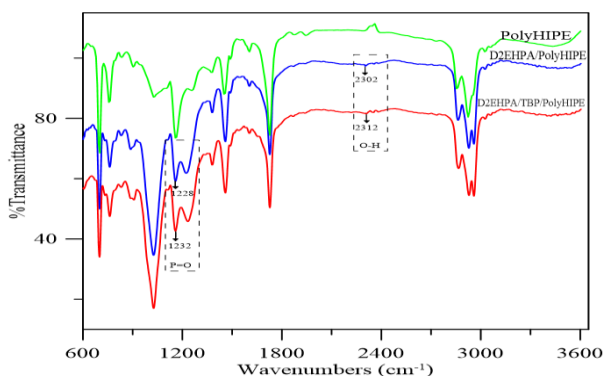
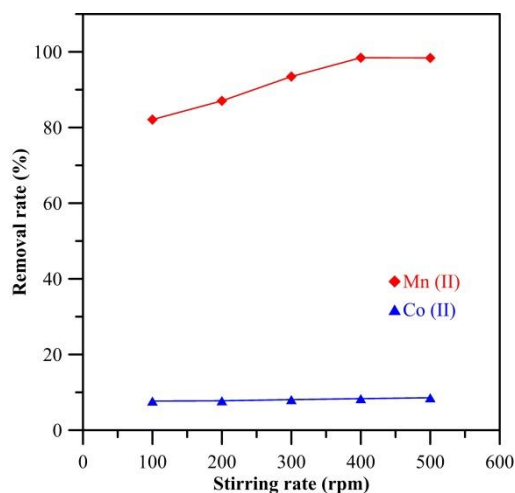Fig. 5 FT-IR spectrum of extractant immobilized PolyHIPE membrane

Fig. 6 Effect of stirring speed on the removal rate (%) of Co (II) and Mn (II). Feeding phase: [Co (II)]=[Mn (II)]=0.01 M at pH 5.5; stripping phase: [H$_2$SO$_4$]=50 g/L
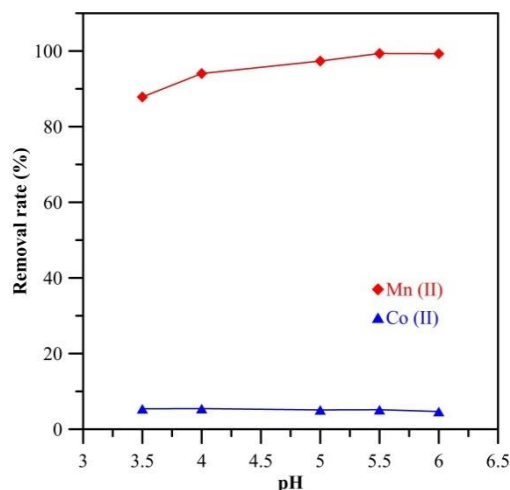

Fig. 7 Effect of the pH of feeding solution on the removal rate (%) of Mn (II) and Co (II). Feeding phase: [Mn(II)]=[Co(II)]=0.01 M; stripping phase: [H$_2$SO$_4$]=50 g/L; stirring speed=400rpm

vibrations of C-H in DVB (Singare *et al.* 2011). For D2EHPA-immobilized and D2EHPA/TBP-immobilized PolyHIPE, the P-O-C stretching frequency at 1224 cm^{-1} and P=O at 1280 cm^{-1} are characteristic peaks for both D2EHPA and TBP, while the characteristic peak at 1040 cm^{-1} is the characteristic peak of P-O-H of D2EHPA (Draa *et al.* 2004, Colthup *et al.* 1990).

The IR absorption frequencies assignments for D2EHPA/TBP-immobilized and D2EHPA-immobilized PolyHIPE show difference in the carbonyl group characteristic peak as compared with the spectrum of the PolyHIPE free of extractant. For D2EHPA-immobilized PolyHIPE, the stretching vibration of carbonyl group of EHA remains at 1726.0 cm^{-1}. For D2EHPA/TBP-immobilized PolyHIPE, the characteristic peak of carbonyl group of EHA shifts from 1726.4 cm^{-1} to about 1730 cm^{-1}, indicating possible interaction between TBP and the EHA moiety of PolyHIPE. This shift suggests a stronger tight bond of the phosphoryl group of TBP in the D2EHPA/TBP co-extractant immobilized PolyHIPE.

D2EHPA generally exits as dimers by hydrogen bonds by hydrogen bonds (Bao *et al.* 2018), which also can be seen in the FTIR spectrum (Fig. 5). As TBP is added, the stretching vibration of O-H and P=O in D2EHPA shifts to the higher wavenumbers (2292 to 2300 cm^{-1} for O-H and

1228 to 1232 cm^{-1} for P=O), indicating that part D2EHPA may be converted from dimers to monomers due to the break of hydrogen bonds. Therefore, D2EHPA can provide more reacting sites for adsorbing ion when it is changed from dimers to monomers, which is beneficial for the adsorption of metal ions.

3.2 The effects of operation parameters on the separation of Mn (II) and Co (II) by D2EHPA/TBP immobilized PolyHIPE membrane

3.2.1 Effect of stirring speed
The influence of stirring rate on the removal rate of ions was studied in order to obtain a suitable stirring operation condition. The stirring speed was varied between 100 and 500 rpm. The effect of stirring speed on Mn (II) and Co (II) removal rate after 10 h of operation is shown in Fig. 6. It was observed that removal rate of Mn (II) increased from 82.1% to 98.4% and increased from 7.6% to 8.6% for Co (II), as the stirring speed increases from 100 to 400 rpm. The removal rates remain constant as the stirring speed increases to 500 rpm. Therefore, the stirring speed of 400 rpm is considered to be sufficient for the experimental set up and is fixed in the followed experiments.

3.2.2 Effect of the pH of feeding phase
pH effect was investigated for both feeding and stripping phases. Fig. 7 shows the effect of initial pH of feeding phase on the removal rate of Mn (II) and Co (II). As the pH increased from 3.5 to 5.5, the removal rate of Mn (II) increased from 87.8% to 98.4 %, while the removal rate of Co (II) increased slightly from 7.9% to 8.7%. This may be due to the higher dissociation of phosphoric acid functional group (P-OH) at higher pH. The higher removal rate of Mn (II) than Co (II) in feed solution may be due to that the oxygen contained functional group of D2EHPA has higher affinity towards Mn (II) ion than Co (II) (Bruce 2014). However, it was point out that the higher dissociation of phosphoric acid may result in dissolution
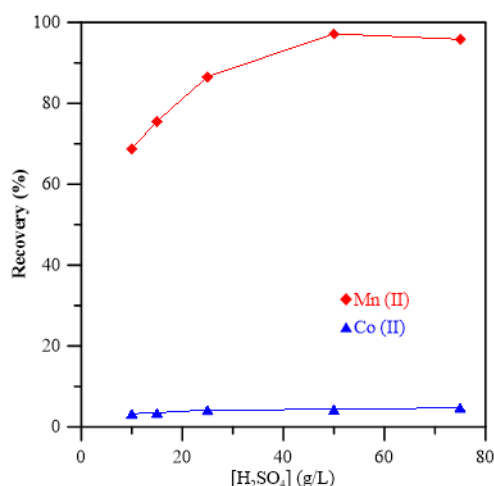
Fig. 8 Effect of the sulfuric acid concentration of stripping phase on the recovery rate (%) of Mn (II) and Co (II). Experimental condition: feeding phase: [Mn(II)]=[Co(II)]=0.01 M at pH 5.5; stirring speed:400rpm

and lose of D2EHPA in aqueous phase (Huang and Juang 1986). Nevertheless, in this study, the continuous increase of Mn (II) removal rate indicates that the dissolution of D2EHPA may be limited due to the pore structure of PolyHIPE membrane. Therefore, the removal rate of both Mn (II) and Co (II) remains constant even for pH higher than 5.5.

3.2.3 Effect of sulfuric acid concentration of stripping phase

In this study, the stripping reagent was sulfuric acid, which is effective for Mn (II) stripping from D2EHPA extractant (Biswas *et al.* 2005). The effect of sulfuric acid concentration in the stripping phase on the separation of Mn (II) and Co (II) by PolyHIPE memebrane was also evaluated. The stripping phase was adjusted with different concentration of sulfuric acid ranging from 10 to 75 g/L. Fig. 8 shows that the recovery rate of Mn (II) increases with increasing H_2SO_4 concentration in the stripping solution and levels off at 50 g/L. The recovery rate at 50 g/L of sulfuric acid is 97.1%, indicating that at this concentration sufficient protons can replace the Mn (II) metal ions from Mn(II)-D2EHPA/TBP complex. Furthermore, it was pointed out that in sulfuric acid solution, Mn (II) ion has a tendency to form complexes with sulfate and bisulfate ion (Batchu *et al.* 2014), which may enhance the stripping of Mn (II) from the membrane. On the other hand, the recovery rate of Co (II) remains almost constant at 4.4% for all range of acid concentration.

3.2.4 Effect of D2EHPA/TBP co-extractants ratio

The effect of the ratio of D2EHPA/TBP co-extractants in PolyHIPE membrane on the separation of Mn (II) and Co (II) was carried with different D2EHPA/TBP ratio of 1:0, 5:1, 5:3 and 0:1 (Table 1). For single D2EHPA extractant, the removal rate of Mn (II) (91.5%) is much higher than that of Co (II) (7.3%), indicating that immobilized D2EHPA has higher affinity toward Mn (II) ion. For single TBP, the removal rates of both Mn (II) and Co (II) ions are negligible.

Table 1 Separation of Mn (II) and Co (II) using extractant immobilized-PolyHIPE membrane

D2EHPA/TBP vol. ratio	Removal rate (%)		Recovery rate (%)		Separation factor ($\beta_{(Mn/Co)}$)
	Mn (II)	Co (II)	Mn (II)	Co (II)	
1:0	91.5	7.3	83.4	3.8	21.95
5:1	98.4	8.6	97.1	4.1	22.74
5:3	81.2	6.3	71.3	3.9	18.28
0:1	<0.5	<0.5	<0.5	<0.5	--

Note. Feeding phase: [Co(II)]=[Mn(II)]=0.01 M at pH 5.5; stripping phase: [H_2SO_4]=50 g/L; stirring speed=400rpm

For D2EHPA/TBP ratio of 5:1, the removal rate of Mn (II) increases to 98.4%, while for Co (II) the removal rate is about 8.6%. This may be partly due to the fact that more D2EHPA can be changed from dimers to monomers in the presence of TBP (Fig. 5), which provides more reacting sites for Mn (II). Furthermore, it was suggested that the addition of TBP can increased the lipophilic nature of extracted complex (Fatmehsari *et al.* 2009). However, increasing added amount of TBP to make D2EHPA/TBP co-extractant ratio of 5:3 results in decrease of separation efficiency. Apparently, this is due to that increasing the TBP content, which does not adsorb Mn(II) and Co(II), decreases the amount of D2EHPA available for metal adsorption inside the PolyHIPE membrane. These results suggest that appropriate D2EHPA/TBP ratio is important for the synergetic effect on the separation efficiency of Mn (II) and Co(II). Table 1 also shows the separation factor $\beta_{(Mn/Co)}$. The performance of the D2EHPA/TBP-immobilized PolyHIPE membrane for separation of Mn (II) and Co (II) is comparable with other system (Alguacil 2002).

Based on these experiment results, in the followed study, the operation parameters are set up as: stirring speed at 400rpm, feeding phase at pH 5.5 and sulfuric acid concentration in the stripping phase of 50 g/L, with PolyHIPE membrane immobilized with D2EHPA/TBP co-extractants ratio of 5:1.

3.3 Transport of Mn (II) through D2EHPA/TBP-immobilized PolyHIPE membrane

For D2EHPA/TBP co-extractant system, the separation of Mn (II) and Co (II) ions is achieved due to the high selectivity of Mn (II) over Co (II). Since the overall recovery rate of Co (II) is less than 5% and the recovery rate of Mn (II) is higher than 97%, the major concern of this study is the transport behavior of Mn (II) through D2EHPA/TBP-immobilized PolyHIPE membrane, which will govern the separation efficiency of the membrane.

In order to elucidate the transport mechanism of Mn (II) through D2EHPA/TBP-immobilized PolyHIPE membrane, the transport kinetics of the ion through membrane was investigated. The kinetic data was described with suitable model. The transport of ions by the carrier across the support liquid membrane was proposed to involve five consecutive steps (Benjjar *et al.* 2012).

(1) Diffusion of ion from feeding phase to the interface.

(2) Formation of ion-extractant complex at the feed phase-membrane interface.

(3) Diffusion of ion-extractant complex through the membrane.

(4) Dissociation of ion-extractant complex at the stripping phase-membrane interface, to release the ion into the stripping phase.

(5) Diffusion of the ion from the interface to the stripping phase.

Steps (1) and (5) can be assumed to be a fast process under effective stirring. Steps (2) and (4) is related to the formation and dissociation of the ion-extractant complex at the interfaces. The extraction and stripping reaction of Mn (II)-D2EHPA/TBP complex can be written as

$$M_{aq}^{2+} + 2(HL)_{org.} + TBP_{org.} \Leftrightarrow M(L)_2.TBP_{org} + 2H_{aq}^+. \qquad (4)$$
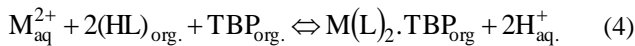
where the subscript aq. is the aqueous phase and org. is the organic phase. For step (3), the characteristics of membrane pore structure is the critical factor affecting the diffusion of ion-extractant complex through the membrane.

3.3.1 Kinetic of Mn (II) transport

Kinetic study of Mn (II) through D2EHPA/TBP immobilized PolyHIPE membrane can provide essential information for the evaluation of separation process in this study. The transport of Mn (II) through the PolyHIPE membrane can be assumed to follow the sequence as: adsorption of Mn (II) by D2EHPA/TBP co-extractants immobilized in the PolyHIPE membrane, diffusion of Mn (II) ion through the pores of the membrane, followed by stripping of Mn (II) by sulfuric acid. Therefore, the transport kinetics of Mn (II) through PolyHIPE membrane can be described as two consecutive first order irreversible reactions (5) (Mehmet *et al.* 2011), with two "apparent rate constants" as a function of extraction reaction, stripping reaction and the solute diffusion rate (Zhang *et al.* 2009).

$$Mn(II)_f \xrightarrow{k_1} Mn(II)_m \xrightarrow{k_2} Mn(II)_s \qquad (5)$$
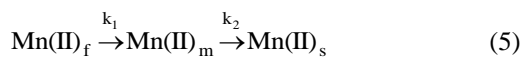
where $Mn(II)_f$ and $Mn(II)_s$ represents the Mn (II) ions in the feeding and stripping phase, respectively, while $Mn(II)_m$ is the Mn(II)-D2EHPA complex in the membrane phase. k_1 and k_2 is the first order apparent rate constant of the extraction and the stripping reaction, respectively.

The transport rate of Mn (II) can be expressed by the following differential equations Eqs. (6)-(8)

$$\frac{dR_f}{dt} = -\alpha k_1 R_f \qquad (6)$$

$$\frac{dR_m}{dt} = \alpha k_1 R_f - \beta k_2 R_m \qquad (7)$$

$$\frac{dR_s}{dt} = \beta k_2 R_m \qquad (8)$$

where α and β is the ratio of membrane contact area to the volume of the feeding and stripping phase, respectively

($\alpha=\beta=16$ m^2/m^3 in this study). $R_f=C_f/C_{fo}$, $R_m=C_m/C_{fo}$ and $R_s=C_s/C_{fo}$ is the dimensionless concentration of Mn (II) in feeding, membrane and stripping phase, respectively.

Integration of Eqs. (6)-(8) yield

$$R_f = e^{-16k_1 t} \qquad (9)$$

$$R_m = \frac{k_1}{k_2 - k_1}\left(e^{-16k_1 t} - e^{-16k_2 t}\right) \qquad (10)$$

$$R_s = 1 - \frac{k_2}{k_2 - k_1}e^{-16k_1 t} + \frac{k_1}{k_2 - k_1}e^{-16k_2 t} \qquad (11)$$

Fig. 9 shows the kinetic variation of reduced concentrations of the feeding phase, stripping phase and membrane phase, of which the amount of Mn (II) in the membrane phase is determined by mass balance ($C_m=C_{fo}-C_f-C_s$). In this case, R_f decreases exponentially with time (Eq. (9)), R_s follows a monotonically increasing sigmoid-type curve (Eq. (11)), while the time evolution of R_m presents a maximum (Eq. (10)). The fitted parameters are $k_1=6.6\times10^{-6}$ m/s and $k_2=6.1\times10^{-6}$ m/s ($R^2>0.98$).

In this study, the performance of Mn (II) transport through the D2EHPA/TBP-immobilized PolyHIPE membrane is evaluated based on the initial feeding flux (J_f^o) and maxima stripping flux (J_s^{max}) values. The initial feeding flux at $t=0$ can be described by Eq. (12) (Mehmet *et al.* 2011)

$$J_f^o = \frac{V_f}{A_{F/M}}\frac{dC_f}{dt}\bigg|_{t=0} = \frac{V_f}{A_{F/M}}16k_1C_{fo} \qquad (12)$$

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. The initial flux obtained in this study is $J_f^o = 80.1$ (μmol/m^{2}s).

The maxima stripping flux can be described by Eq. (13) (Mehmet *et al.* 2011).

$$J_s^{max} = -\frac{V_s}{A_{F/M}}\frac{dC_s}{dt}\bigg|_{t=t_{max}} = -\frac{V_s}{A_{F/M}}16k_2C_{fo}(R_m)_{max} \qquad (13)$$

where $(R_m)_{max}$ can be obtained from the kinetic curve of R_m in the membrane phase. 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 $(R_m)_{max}$. By taking the derivative $dR_m/dt=0$, the time for R_m to reach a maximum t_{max} and $(R_m)_{max}$ can be obtained from Eq. (14) and Eq. (15), respectively

$$t_{max} = \frac{\ln\frac{k_2}{k_1}}{16(k_2 - k_1)} \qquad (14)$$

$$(R_m)_{max} = \left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_2 - k_1}} \qquad (15)$$
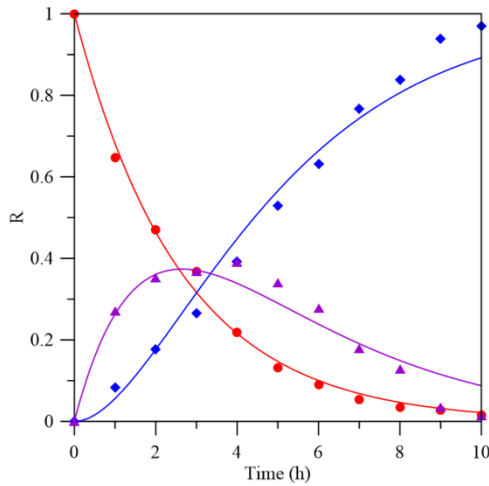
Fig. 9 The variations of Mn (II) concentration with respect to time: $R_f(\bullet)$, $R_m(\blacktriangledown)$ and $R_s(\blacklozenge)$. Feeding phase: [Mn(II)]=[Co(II)]=0.01 M at pH 5.5; stripping phase: [H₂SO₄]=50 g/L; stirring speed=400rpm

Based on the values of $(R_m)_{max}$ = 0.401 and t_{max} = 2.81 h, the maxima stripping flux in this study is J_s^{max} = 20.8 (μmol/m²s).

3.3.2 Modeling and parameters of Mn (II) diffusion

The effective diffusivity D^* is the key and most convenient parameter to describe the process of diffusion through porous membrane, since the value of D^* is directly related to the pore structure characteristics of PolyHIPE membrane, such as tortuosity and constrictivity. In this study, since the bulk phase is effectively stirred, the film diffusion of Mn (II) between bulk phase and membrane interface can be considered as a fast process, and the aqueous concentration $[C]_f$ and $[C]_s$ is uniform throughout the feeding and stripping phase, respectively. Therefore, the concentration of metal ion complex changes linearly inside the membrane (Huang *et al.* 2008, Velicky *et al.* 2014, Rhlalou *et al.* 2000). Assuming that the rate-determining step is the diffusion of Mn (II)-extractant through the membrane, the formation and dissociation of the Mn (II)-D2EHPA complex at the interfaces is a fast process (Benjjar *et al.* 2012). The determination of effective diffusion coefficient generally can be achieved from the relationship observed between the flux and the concentration of diffusant in the membrane phase (Velicky *et al.* 2014).

From the Fick's First Law, the diffusion flux inside the membrane (J_m) can be defined as Eq. (16).

$$J_m = D^* \frac{d[AC]}{dl} = D^* \frac{[AC]_f - [AC]_s}{l} \qquad (16)$$

where D^* is the effective diffusion coefficient of Mn (II)-D2EHPA/TBP complex inside the membrane, $[AC]$ is the concentration of Mn (II)-D2EHPA/TBP complex in the membrane phase, subscripts f and s refer to the feeding and stripping interfaces of the membrane, and l is the membrane thickness. Since the stripping phase is at high concentration of sulfuric acid, the dissociation of Mn (II)-D2EHPA/TBP
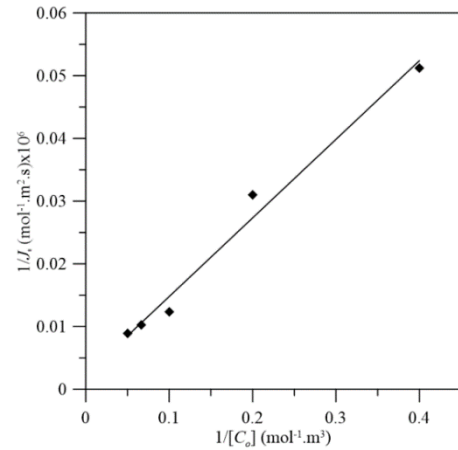

Fig. 10 Plots of $1/J_0$ vs. $1/[C]_o$, for the transport of Mn (II) across the D2EHPA/TBP-immobilized PolyHIPE membrane. Feeding phase: [Mn (II)]=[Co (II)] at pH 5.5; stripping phase: [H₂SO₄]=50 g/L; stirring speed=400rpm

is a fast process and the concentration of complex $[AC]_s$ is practically nil. On the other hand, the formation of complex is a fast heterogeneous equilibrium (Benjjar *et al.* 2012). Therefore, the concentration of complex $[AC]_f$ can be related to the concentration of Mn (II) in the feeding phase according to the mass action law, Eq. (17)

$$[AC]_f = K[A][C]_f \qquad (17)$$

where K is the formation constant of the Mn (II)-D2EHPA/TBP complex, $[A]$ and $[C]_f$ is the concentration of the D2EHPA/TBP in the membrane phase and the concentration of Mn (II) in the feeding phase, respectively. The total carrier concentration $[A]_o$ immobilized in the membrane is constant, equal to the sum of the concentrations $[A]$ and $[AC]_f$ (Eq. (18)). Therefore, the concentration of complex $[AC]_f$ can be related to the concentration of Mn (II) in the feeding phase by Eq. (19).

$$[A]_o = [A] + [AC]_f \qquad (18)$$

$$[AC]_f = \frac{[A]_o \times K \times [C]_f}{1 + K \times [C]_f} \qquad (19)$$

Since the formation of Mn (II)-complex is assumed to be a fast process, based on the quasi-steady state assumption $J^o_m \approx J^o_f$, the initial flux can be described as

$$J_f^o = \left(\frac{D^*}{l} \right) \frac{\left([A]_o K [C]_{fo} \right)}{1 + K [C]_{fo}} \qquad (20)$$

The postulated mechanism indicates that J^o_f is related to the effective diffusion coefficient and formation constant of Mn (II)-D2EHPA/TBP complex. In order to test the proposed relationship, Eq. (20) is rearranged to a linear form as Eq. (21).

$$\frac{1}{J_f^o} = \left(\frac{l}{D^*} \right) \left(\frac{1}{[A]_0 K} \right) \left(\frac{1}{[C]_{fo}} \right) + \left(\frac{l}{D^*} \right) \left(\frac{1}{[A]_0} \right) \qquad (21)$$

Transport experiments were carried out with $[C]_{fo}$ varied in the range 0.0025-0.02 M. By plotting the values of $1/J_f^o$ vs. $1/[C]_{fo}$, the effective diffusion coefficient and formation constant of the complexes can be obtained from the slope and intercept, respectively.

$$D^* = \frac{l}{[\overline{A}]_o \times \text{intercept}} \quad (22)$$

$$K = \frac{\text{intercept}}{\text{slope}} \quad (23)$$

Fig. 10 shows that the plot of $1/J_0$ vs. $1/[C]_o$ is linear with high correlation coefficient (R^2=0.99). Hence, the experimental results are in agreement with a mechanism in which the diffusion of the complex is the rate-determining step. From to the slope and intercept of above result (Fig. 10), the effective diffusion coefficient D^* is about 5.32×10^{-8} m^2 s^{-1} and the formation constant K is about 17.99 mol^{-1}L. Since D^* is directly related to the porosity (0.77), tortuosity (1.18) and constrictivity factor (3.3×10^{-3}) of PolyHIPE membrane (Chen *et al.* 2018), according to the equation $D^* = D\beta\Phi/\tau$ (Epstein 1989) we can obtain the diffusion coefficient (D) of Mn (II)-complex in the pore space equal to 1.77×10^{-5} m^2 s^{-1}.

For comparison, the diffusion coefficient for the Mn(II)-D2EHPA/TBP complex was also estimated using Wilke-Chang equation (Eq. (24)) (Wilke and Chang 1955).

$$D = 7.4 \times 10^{-8} (\varphi M)^{1/2} \frac{T}{\eta V^{0.6}} \quad (24)$$

where M and η is the molecular weight and viscosity of solvent, and φ is the "association parameter" (φ =1). Since the PolyHIPE is filled with D2EHPA/TBP, which can be treated as solvent in this case, M = 313.078 g/mol and $\eta_{\text{D2EHPA/TBP}} = (x_{\text{D2EHPA}} v_{\text{D2EHPA}}^{1/3} + x_{\text{TBP}} v_{\text{TBP}}^{1/3})^3$ =33.32 cp (Gambill 1959). The value of V=0.207$\times 10^3$ cm^3/mol can be calculated by summing the contribution of atoms, which consist of the solute molecule (i.e., Mn(II)-D2EHPA/TBP complex) as suggested by Wilke-Chang (Wilke and Chang 1955, Huang *et al.* 2008). For T=298 K, D = 4.78×10^{-7} m^2 s^{-1}.

Compared to the diffusion coefficient estimated from Wilke-Chang equation (Eq. (24)), the value of D obtained from D^* seems to be very high. This suggests that the transport of Mn (II) through D2EHPA/TBP-immobilized PolyHIPE membrane may not be a pure diffusion process. One possible explanation is the jumping transport mechanism as suggested by many literatures (Rajewski and Lobodzin 2016). The characteristic of jumping transport is to be faster than the diffusion (Benjjar *et al.* 2012). Therefore, for the conditions in this study the assumption of jumping transport seems to be correct.

3.3 Reusability of D2EHPA/TBP-immobilized PolyHIPE membrane

The reusability of D2EHPA/TBP-immobilized PolyHIPE membrane for the separation of Mn (II) and Co
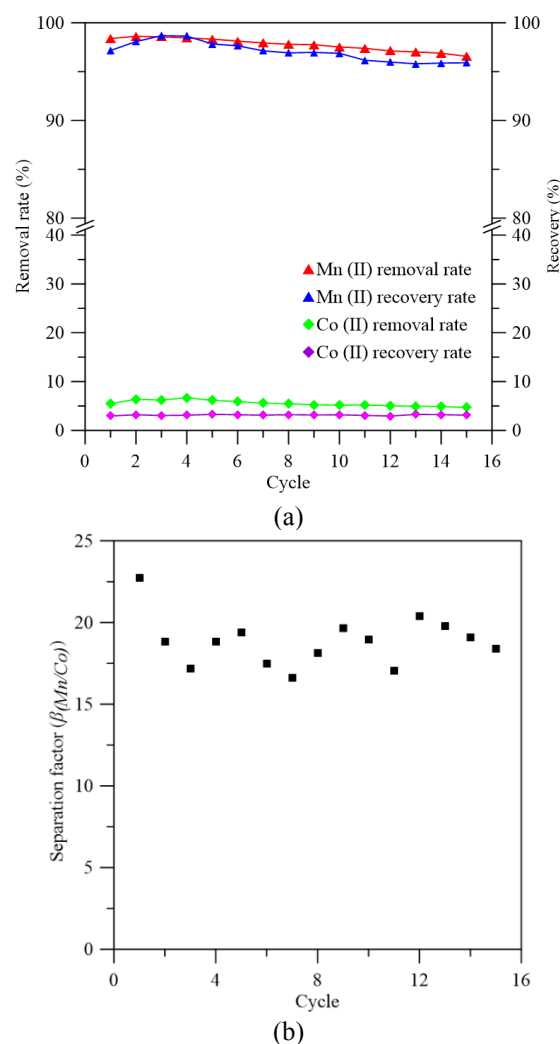

(a)

(b)

Fig. 11(a) Removal and recovery rates and (b) separation factor in consecutive cycle. Feeding phase: [Mn(II)]=[Co(II)]=0.01 M at pH 5.5; stripping phase: [H₂SO₄]=50 g/L; stirring speed=400 rpm

(II) was evaluated. Fig. 8(a) shows that after 15 sequential cycles of 10 h separation, the removal rate of Mn (II) drops slightly from 98.4% to 97.1%, while the recovery rate drops slightly from 97.2% to 95.9% after 15 cycles. On the other hand, the removal and recover rate of Co (II) remain almost constant. The reusability of the membrane also reflects the good hydraulic stability of D2EHPA/TBP-immobilized PolyHIPE membrane. Fig. 11(b) shows the separation factor remains as high as 18.39 ever after 15 sequential cycles of separation operations. From Fig. 11, it is clear that after the removal of Mn (II) (>97.1%), the high purity of Co (II) can be recovered from the feeding phase, while the high purity of Mn (II) can be recovered in the stripping phases.

4. Conclusions

By solvent-nonsolvent method, D2EHPA/TBP co-extractants can be effectively immobilized into PolyHIPE membrane with the amount of 2.81±0.08 g/g of PolyHIPE. The characteristic pore structure of PolyHIPE membrane

and the presence of TBP enhances the stability of immobilized co-extractants in the membrane. Optimal operating conditions for the separation of Mn (II) and Co (II) are as feeding phase pH of 5.5, sulfuric acid concentration in the stripping phase of about 50g/L and stirring speed at 400 rpm. The ratio of D2EHPA/TBP co-extractant of 5:1 in PolyHIPE membrane shows synergetic effect on Mn (II) and Co (II) separation. Under these conditions, the separation factor ($\beta_{Mn/Co}$) is about 22.74. The removal rate and recovery rate of Mn (II) is about 98.4 and 97.1%, respectively, while for Co (II) the transport efficiency is insignificant. The kinetic study of Mn (II) transport shows that high initial flux, $J_f^0 = 80.1$ (μmol/m^{2}s), and maxima stripping flux, $J_s^{max} = 20.8$ (μmol/m^{2}s), can be achieved by D2EHPA/TBP co-extractants immobilized PolyHIPE membrane. With the combined advantages of PolyHIPE structure and the synergetic effect of co-extractants, the stability and reusability study shows that the membrane can maintain high recovery efficiency (about 95%) even after 15 consecutive cycles of separation operation. After the removal of Mn (II) (>97.1%), the high purity of Co (II) can be recovered from the feeding phase, while the high purity of Mn (II) can be recovered in the stripping phases. The experimental results demonstrate the potential of application of this new type of membrane for Mn (II) and Co (II) separation.

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