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LCST-type thermo-responsive ionic liquid used as a recyclable and reusable cleaning agent for fouled membrane

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ABSTRACT

Lower-critical solution temperature (LCST)-type thermo-responsive ionic liquids used as recyclable and reusable cleaning agents for fouled membrane were investigated. Three thermo-responsive ionic liquids with different LCST, including P_{4444} maleic acid (P_1Mal), P_{4444} trifluoroacetic acid (P_1TFA) and P_{4444} p-toluenesulfonic acid (P_1TSO) were understudied. They can clean organic foulant, inorganic scaling foulant and combined organic foulant/inorganic scaling foulant. In studying the cleaning of the membrane fouled by bovine serum albumin or calcium sulfate, high cleaning efficiency could be obtained with shorter cleaning time. The used LCST-type thermo-responsive ionic liquid cleaning solution can be separated to ionic liquid-rich part and water-rich part by increasing the temperature above LCST. The ionic liquid in ionic liquid-rich part could be recycled by thermal method and filtration. In our study, the recycled ionic liquid retains significant membrane cleaning ability. The flux recovery ratio could reach to 95%.

Keywords: Ionic liquid; Lower-critical solution temperature; Membrane cleaning; Recycle

1. Introduction

Membrane separation technology is widely used in water treatment process. However, it can suffer the formation of foulant on the membrane surface, which can decrease the membrane performance, especially the water flux decline. The foulant is resulted from the dissolved matters and particles in feed solution, which can be classified as colloidal type organic or biological matters and inorganic scaling [1]. In the past decades, many works have been conducted to mitigate the water flux decline for different types of the membrane separation process. The research topics include the membrane surface modification and the post treatment of used membrane. In former case, many hydrophilic materials are used to modify the membrane to achieve the requirements. For example, different hydrophilic oligomer or monomer such as polyethylene glycol (PEG) [2], acrylic acid (AA) and 2-hydroxyethyl methacrylate (HEMA) have been coated or grafted on the membrane surface [3]. Poly(vinyl alcohol) (PVA), a common hydrophilic polymer, was introduced into polyamide layer of nanofiltration by Gohil and Ray [4]. Polymerized ionic liquid (PIL) is a hydrophilic material, which can be grafted on the membrane surface to enhance the antifouling ability

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of poly(vinyl alcohol) membrane [5]. Ji et al. [6] synthesized a new type of zwitterionic terpolymers and the antifouling membrane prepared through surface coating and cross-linked with their zwitterionic terpolymers. As to the post treatment of used membrane, many cleaning agents were used to recover the performance of fouled membrane. The strategies of membrane cleaning can be applied by the physical methods such as backwashing and turbulent mixing (mesh spacers and air scouring), or chemical methods that can break down the bond between the foulant and membrane. Ang et al. [7] investigated the chemical and physical aspect of organic-fouled reverse osmosis membrane. In their study, alkaline solution, chelating agent and surfactant were used to clean the organic-fouled membrane. Espinasse et al. [8] studied the chemical cleaning agents for fouled nanofiltration (NF) membrane. The chemicals they used include hydrochloric acid (HCl), sodium hydroxide (NaOH). In the study of Zhao et al. [9], the chemical cleaning agents used include acids (HCl, citric acid and acetic acids), surfactant (sodium dodecylbenzene sulfonate (SDBS), dodecyldimethyl betaine (BS-12), dodecyltrimethylammonium chloride (DTAC), cetyltrimethylammonium chloride (CTAC)). Aguiar et al. [10] also studied the cleaning of fouled nanofiltration membrane used in acid mine drainage. The chemical agent they used including HCl, phosphoric acid, citric acid, sulfuric acid, nitric acid, ethylenediaminetetraacetic acid (EDTA) and NaOH. In addition to these studies, Lee et al. [11] cleaned the fouled reverse osmosis membrane with concentrated salt solution. Although the cleaning efficiency is high enough to recover membrane performance, these cleaning agents become to be pollutants after membrane cleaning processes. The cleaning solution needs to be well-managed and well-disposed.

Ionic liquids (ILs) are liquid type organic salts at temperatures below 100°C. They are usually composed of organic cation and inorganic or organic anion. Ionic liquids have negligible vapor pressure, excellent thermal stability and low flammability. Ionic liquid can be used as extractant for metal ions [12–14] or proteins [15–17]. Ding et al. [18] synthesized functional guanidium ionic liquids being able to extract bovine serum albumin (BSA) with extracting efficiency of 90%. The anions were selected from the compound having carboxyl group, such as formic acid, acetic acid, propanoic acid and lactic acid. In another study, an imidazolium-sulfonate ionic liquid having the extracting efficiency of 80% for calcium ion was investigated by Kozonoi and Ikeda [19]. Obviously, the ionic liquids with carboxyl group or sulfonate group can be regarded as promising media for extraction application [20].

One type of ionic liquid called thermo-responsive ionic liquid, was deeply studied for many years. It can be classified into lower-critical solution temperature (LCST) type and upper-critical solution temperature (UCST) type [21]. In UCST type, the ionic liquid aqueous solution is immiscible below the critical temperature and it becomes to be a miscible when the system is heated above a critical temperature. In LCST-type, a homogeneous phase of the ionic liquid aqueous solution can be separated to water-rich phase and ionic liquid-rich phase when the ionic liquid aqueous solution is heated to above a critical temperature. Kohno and Ohno [22] investigated the phase separation behavior of LCST-type thermo-responsive ionic liquid/H_2O system, especially for the phosphonium-base ionic liquids. The mechanism of phase separation behavior of LCST-type phosphonium-base ionic liquid/H_2O system was also investigated in our previous paper [23].

In this study, LCST-type phosphonium-base ionic liquids with carboxyl group or sulfonate group were synthesized and used as cleaning agents for the fouled membrane. The clearing concept is based on the fact that protein or inorganic scaling can be extracted by the ionic liquid containing carboxyl group or sulfonate group. In investigating the clearing of fouled membrane, the LCST-type phosphonium-base ionic liquids under study are P_{4444} maleic acid (P_1Mal), P_{4444} trifluoroacetic acid (P_1TFA) and P_{4444} p-toluenesulfonic acid (P_1TSO). The foulants of fouled membrane include organic BSA foulant, inorganic calcium scaling foulant and the combined organic foulant/inorganic scaling foulant. After cleaning processes, the ionic liquid cleaning solution was heated to a temperature above LCST. The solution was separated to ionic liquid-rich phase and water-rich phase. The ionic liquid in ionic liquid-rich phase was recycled for reuse. Further treatment methods of the ionic liquid after phase separation, including thermal treatment and filtration, were investigated in this study.

2. Experimental

2.1. Materials

NF90-1812 nanofiltration spiral wound membrane was purchased from ASPRINN membrane technology. Tetrabutylphosphonium hydroxide (P_{4444}OH) aqueous solution (40 wt.% in H_2O) and trifluoroacetic acid (TFA) were purchased from Alfa Aesar. Maleic acid (Mal), p-toluenesulfonic acid (TSO), BSA, calcium sulfate ($CaSO_4$), hydrochloric acid (HCl), sodium dodecyl sulfate (SDS) and ethylenediaminetetraacetic acid tetra-sodium (EDTA-4Na) were all purchased from Sigma-Aldrich. Magnesium sulfate ($MgSO_4$) was purchased from SHOWA and sodium hydroxide was purchased from J.T. Baker.

2.2. Synthesis and characterization of ionic liquid

P_{4444}Mal, P_{4444}TFA and P_{4444}TSO were synthesized by the procedure described in our previous study [23] and denoted as P_1Mal, P_1TFA and P_1TSO respectively. The structure of these ionic liquids was confirmed by ^{1}H-NMR spectroscopy (Varian Unity Inova 500 MHz NMR, Agilent). The NMR spectra and structure formula are shown in Fig. 1. The viscosity of P_1Mal, P_1TFA and P_1TSO aqueous solution with different concentration were measured by Brookfield viscometer (Table 1).

2.3. LCST determination with macroscopic phase separation

Different concentrations of ionic liquid aqueous solutions were prepared and stand in water bath at 15°C until the solution was homogeneous and clear. Then, each solution was stepwise heated from 15°C to 100°C, every 5°C for 10 min. When the distinct two-phase stratification was observed, the temperature point was defined as the LCST with macroscopic phase separation.

2.4. Nanofiltration test

A cross-flow nanofiltration (NF) device was used to accesses the membrane performance and assembled in our laboratory shown in Fig. 2. The nanofiltration membrane was NF90-1812 with an effective area was 0.39 m². The permeate flux was determined at working pressure of 7 bar. 2,000 ppm $MgSO_4$ solution was used as the standard feed solution for determining the membrane performance (ASTM D4194-03). The NF performance including water flux (*J*) and salt rejection (*R*%) were evaluated and calculated by the following formulas:

$$J\left(\text{LMH}\right)=\frac{\Delta m_{\text{perm}}/\rho_{\text{perm}}}{A_{\text{eff}}\times\Delta t} \tag{1}$$

$$R\left(\%\right)=\frac{C_{\text{perm}}-C_{\text{feed}}}{C_{\text{feed}}}\times 1100\% \tag{2}$$

where Δm_{feed} is the weight changes of the permeate side; ρ_{feed} is the density of the permeate; A_{eff} is the effective membrane area and Δt is the measuring interval time. C_{perm} is the conductivity of permeate; C_{feed} is the conductivity of standard feed solution.

2.5. Membrane fouling & cleaning test

High fouling organic BSA solution and inorganic $CaSO_4$ solution were used to investigate the cleaning ability of ionic liquid. Due to the less fouling being observed for Mg^{2+} ion [24–25]. $MgSO_4$ was added to these two solutions for determining the salt rejection of the membrane before and after membrane cleaning. The salt rejection results can provide us information on whether the selectivity layer of the membrane was destructed by ionic liquid. Hence, the organic foulant solution includes 1,000 ppm BSA and

Table 1
Solution viscosity at different ionic liquid concentrations

Viscosity (cps)	5 wt.%	10 wt.%	20 wt.%	50 wt.%	70 wt.%
P_1Mal	7.3	8.3	9.3	13.2	20.2
P_1TFA	7.4	7.7	9.1	14.6	20.3
P_1TSO	7.4	7.6	9.2	14.8	27.5

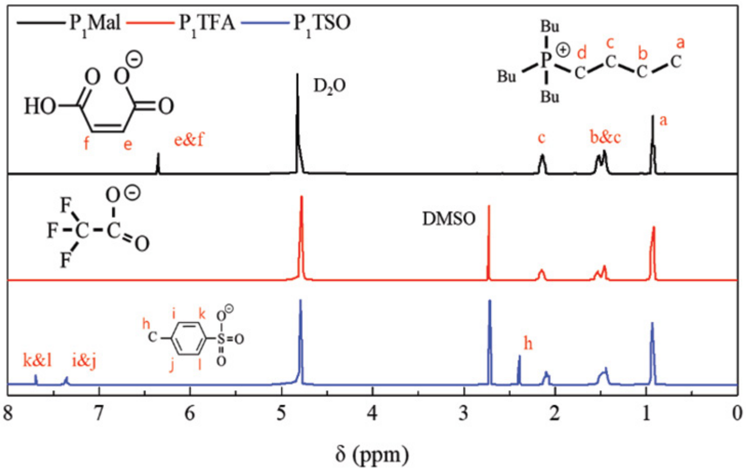

Fig. 1. The ¹H-NMR spectra and structure formula of P_1Mal; P_1TFA and P_1TSO.

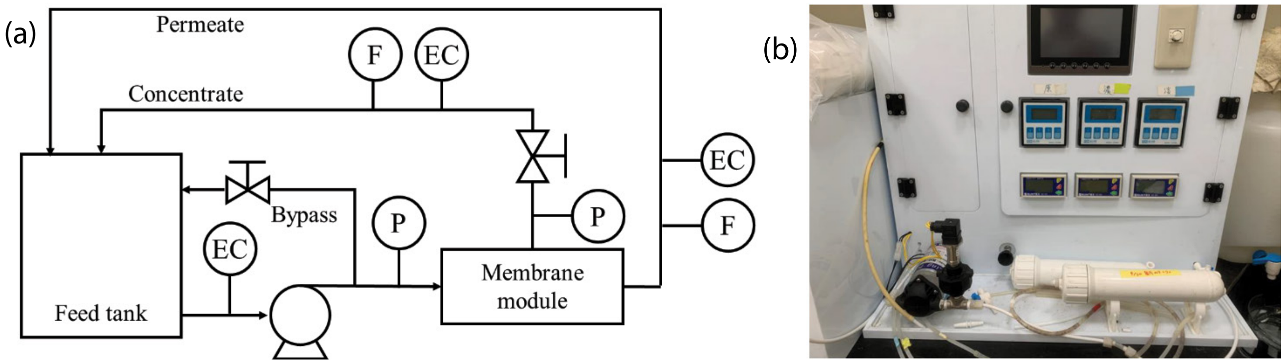

Fig. 2. The diagram (a) and photo (b) of the NF device.

2,000 ppm $MgSO_4$. The inorganic scaling solution includes 1,000 ppm $CaSO_4$ and 2,000 ppm $MgSO_4$. The combined organic fouling and inorganic scaling system includes 1,000 ppm BSA, 1,000 ppm $CaSO_4$ and 2,000 ppm $MgSO_4$. The permeate flux was determined at working pressure of 7 bar. The fouling test stopped when the permeate flux (denoted as J_F) was decreased around 15%~20%. The membrane cleaning agents then introduced into the NF device after water flushing for 10 min. The cleaned membrane performance was tested by the standard feed solution, the permeate flux after membrane cleaning denoted as $J_{C.}$ The flux decline ratio (FDR) and flux recovery ratio (FRR) were calculated by the following formulas:

$$\text{FDR} = \left(\frac{J - J_F}{J}\right) \times 100\% \tag{3}$$

$$\text{FRR} = \frac{J_c}{J} \times 100\% \tag{4}$$

The cleaning efficiency was described as normalized flux, calculated by the following formulas:

$$\text{Normalized flux} = \frac{J_t}{J_0} \tag{5}$$

where J_t is the water flux at certain time; J_0 is the water flux of the fresh NF90 that determined by standard solution. The value of J_0 was 44.75 ± 1.33 LMH.

3. Results and discussion

3.1. Phase separation temperature of three thermo-responsive ionic liquid solutions

When the thermo-responsive ionic liquid aqueous solution was heated above a critical transition temperature, a liquid–liquid phase separation was observed, which formed ionic liquid-rich phase and water-rich phase, shown in Fig. 3a. The phase separation temperatures of three thermo-responsive ionic liquid aqueous solutions at different concentrations are shown in Fig. 3b. From Fig. 3b it can be seen that the LCST value for the P_1Mal, P_1TFA and P_1TSO is around 21°C (at 40 wt.%), 28°C (at 30 wt.%) and 52°C (30 wt.%), respectively.

3.2. BSA fouled membrane cleared by ionic liquid

The membrane was fouled by organic BSA foulant solution. The organic BSA foulant solution includes 1,000 ppm BSA and 2,000 ppm $MgSO_4$. P_1Mal was used as membrane cleaning agent. The variables affecting cleaning performance include the concentration of membrane cleaning agent, cleaning time and cleaning strategies (flush and immerse). The concentration effect on cleaning efficiency was first studied. The cleaning time was set at 30 min (25 min immerse and 5 min flush) and 25°C. The results are shown in Fig. 4. It can be seen that the FRR increases

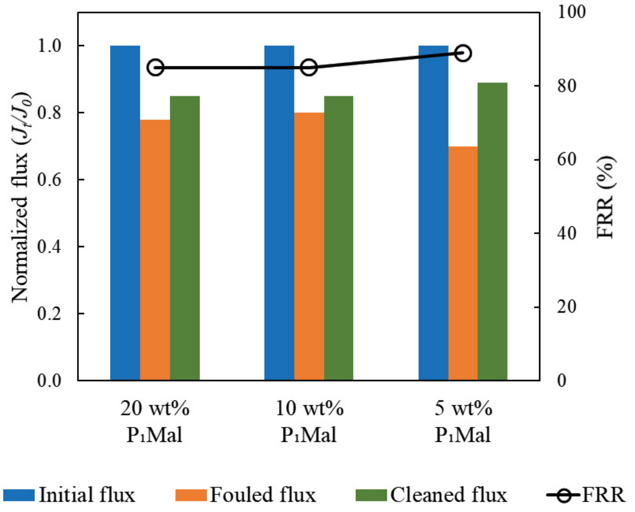

Fig. 4. Cleaning efficiency for BSA fouled membrane at different concentrations of P_1Mal.

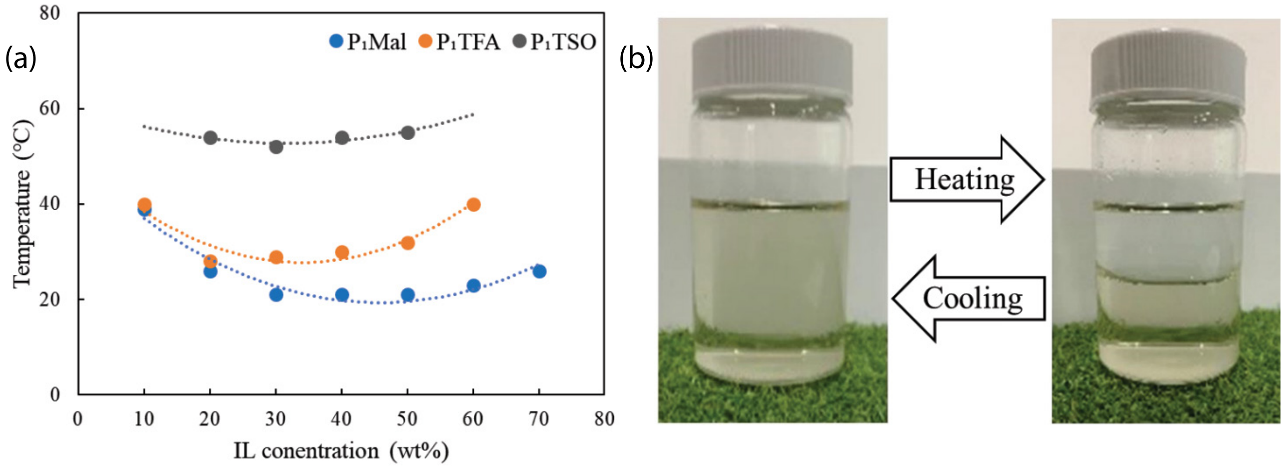

Fig. 3. (a) The phase separation temperature curves of three LCST-type ionic liquids and (b) The phase separation behavior before and after LCST: (left) clear solution; (right) phase separation.

when the P_1Mal concentration was decreased from 20 wt.% to 5 wt.%. The solution viscosity may be an affecting factor. Lower solution viscosity is observed at lower concentration of P_1Mal, shown in Table 1. At lower solution viscosity, ionic liquid can easily penetrate into the fouling layer and the structure of the fouling layer is loosed. Then the foulant on the membrane is easily extracted and flushed away.

The optimum cleaning time and the cleaning strategies were investigated. The results are shown in Fig. 5. The results of Fig. 5a show that the lower cleaning efficiency was observed at cleaning time of 1 min. It might be that the shorter contact time between P_1Mal and the foulant. When the cleaning time was increased to 10 min (immerse time with 5 min and flush time with 5 min), the FRR was increased from 87% to 93%. However, further increasing the immerse time to 25 min, the FRR slightly decreased from 93% to 90%, it might be that the negative zeta potential of NF90 (–10 to –20 mV), which attracted the cation of P_1Mal on the membrane and block the pores of NF90 [26]. From above analysis, we can see that the optimal cleaning condition was ionic liquid concentration of 5 wt.%, immerse time with 5 min and flush time with 5 min at 25°C.

The salt rejection performance of membrane was investigated before and after cleaning. The results are shown in Fig. 5b. It can be seen that salt rejection performance of membrane were not affected by all of the cleaning strategies. It means that the membrane was not destructed by P_1Mal in our experimental condition.

The membrane cleaning efficiencies of P_1TFA and P_1TSO were also investigated at the same fouling conditions and optimum membrane cleaning strategies (immerse time with 5 min, flush time with 5 min at 25°C respectively. The cleaning results are shown in Fig. 6. For comparison, the cleaning efficiencies of P_1Mal and the traditional cleaning agent at 30°C for 30 min are also shown in Fig. 6. The results in Fig. 6a. indicate that the cleaning efficiency of thermo-responsive ionic liquids are better than that of the traditional cleaning agents because higher cleaning efficiency can be obtained with shorter cleaning time and without heating [27].

3.3. Inorganic scaling and the combined organic fouling/inorganic scaling fouled membrane cleared by ionic liquid

The membrane was fouled by inorganic scaling and combined organic fouling/inorganic scaling foulant respectively. In studying the ionic liquid clearing for membrane fouled by inorganic scaling (calcium sulfate), the cleaning efficiency of P_1Mal, P_1TFA, P_1TSO and 0.6 wt.% EDTA was investigated. Ionic liquid can remove calcium sulfate scale by acid dissolution of scale and then calcium ion can be extracted. The anion of ionic liquid is related to the reactivity of ionic liquid with water or other compounds. For the same cation, the anions of the ionic liquids may be selected from various Lewis acids and non-Lewis acids. The cleaning strategy of ionic liquid solution was immersing time with 5 min and flush time with 5 min at 25°C. The cleaning strategies of EDTA solution was immersing time with 25 min and flush time with 5 min at 30°C. The cleaning results are shown in Fig. 6b. The results indicated the FRR of P_1Mal, P_1TFA, P_1TSO and EDTA were 93%, 99%, 93% and 90%, respectively. In our study, the cation is tetrabutylphosphonium. The anions are Mal, TFA and TSO. TFA has three highly electronegative fluorine atoms which withdraw electron density via induction. Its conjugate base can stabilize the negative charge. In comparison to two other acids, TFA is stronger acid. Hence P_1TFA shows a higher FRR value than others. In combined organic fouling/inorganic scaling foulant, 0.6 wt.% EDTA with NaOH was used as membrane cleaning agent in addition to ionic liquid cleaning agents. The results of Fig. 6c show that the FRRs of four cleaning agents were almost equal and higher than 90%.

In summary, the results presented in previous sections reveal that BSA or calcium ion foulants can be removed from fouled membrane by the LCST-type thermo-responsive ionic liquid containing carboxyl group or sulfonate group. The extract ability and chelating ability of ionic liquids are the main driving forces for membrane cleaning. For the combined BSA/Ca^{2+} foulant, ionic liquid can penetrate into the organic/inorganic dense fouling layer and then the loosened BSA and Ca^{2+} can be removed by ionic liquid. In order to provide better understanding, a clear schematic diagram

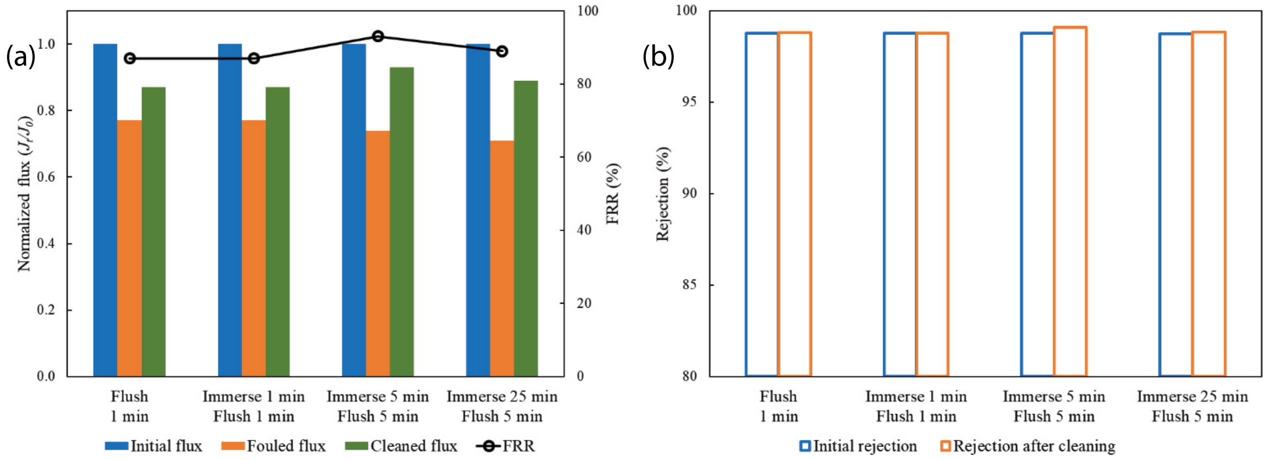

Fig. 5. Membrane cleaning efficiencies (a) and salt rejection (b) for different cleaning strategies.

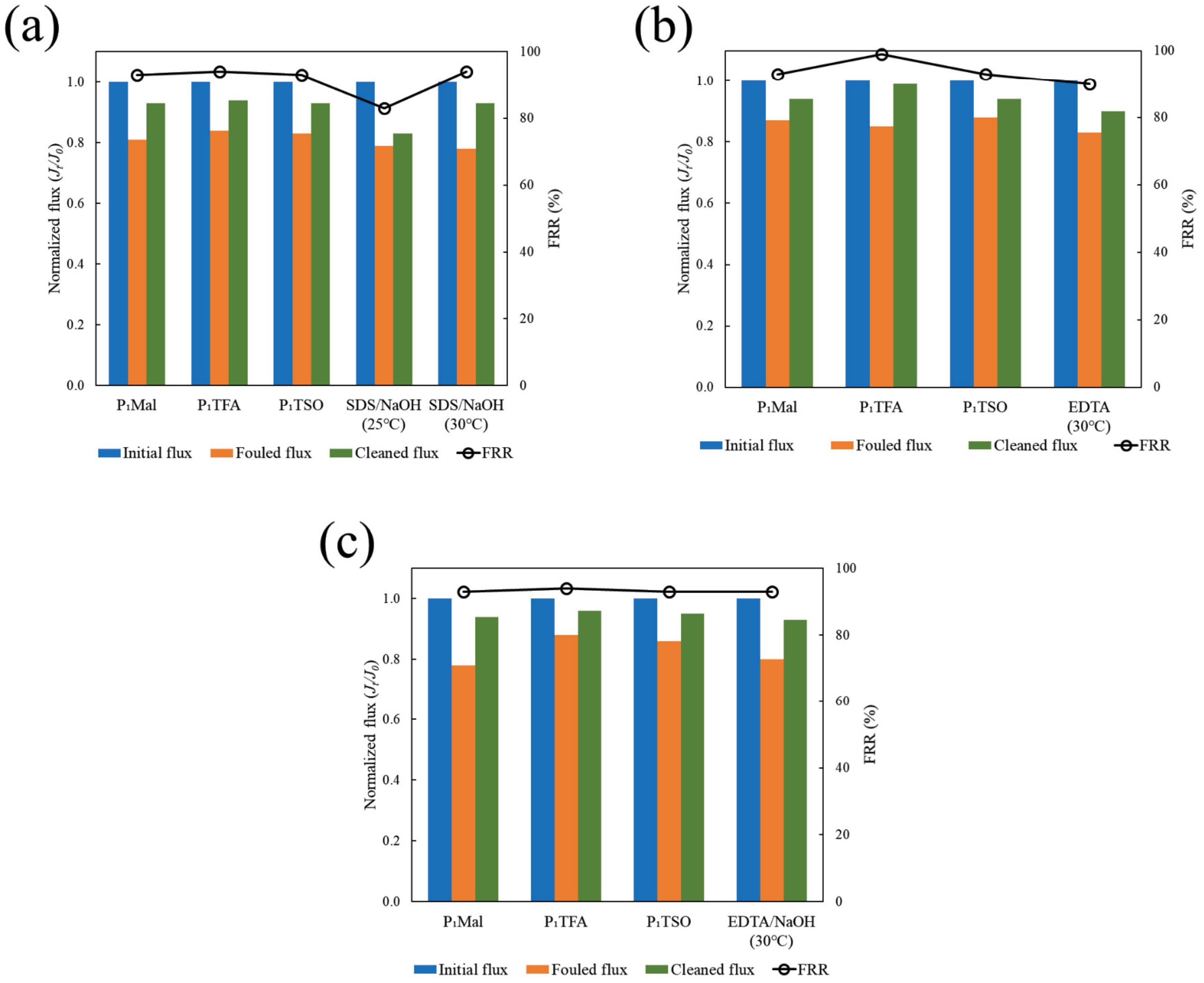

Fig. 6. Cleaning efficiency for different cleaning agents with (a) BSA fouled membrane, (b) $CaSO_4$ fouled membrane and (c) BSA/$CaSO_4$ fouled membrane.

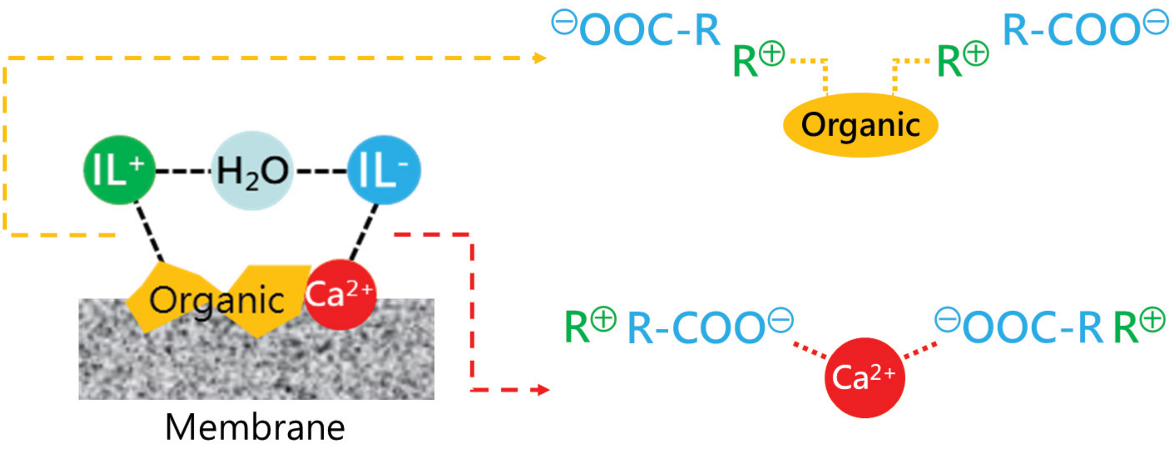

Fig. 7. Schematic diagram of ionic liquid clearing for fouled membrane.

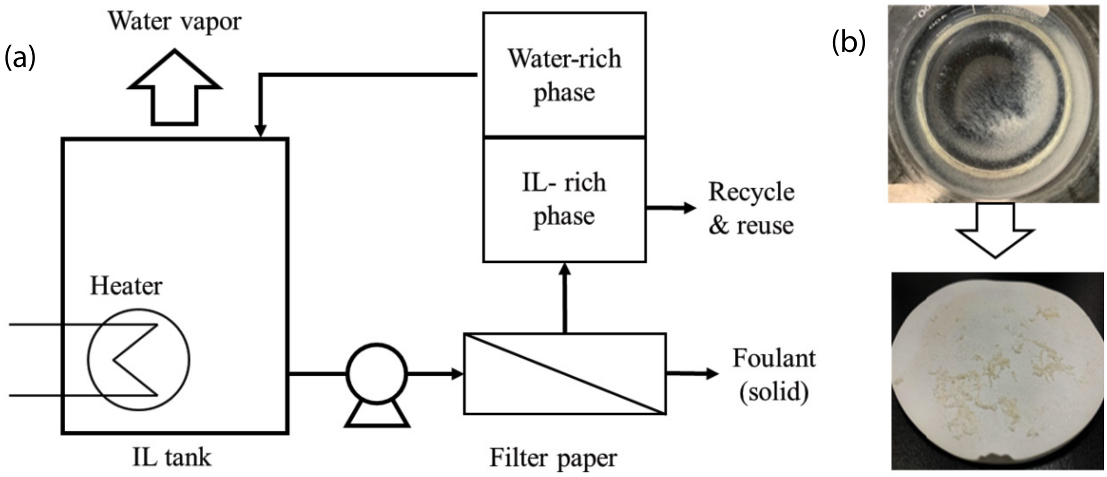

Fig. 8. (a) Diagram of ionic liquid recycling system and (b) foulants precipitated in ionic liquid solution and removed by filter paper.

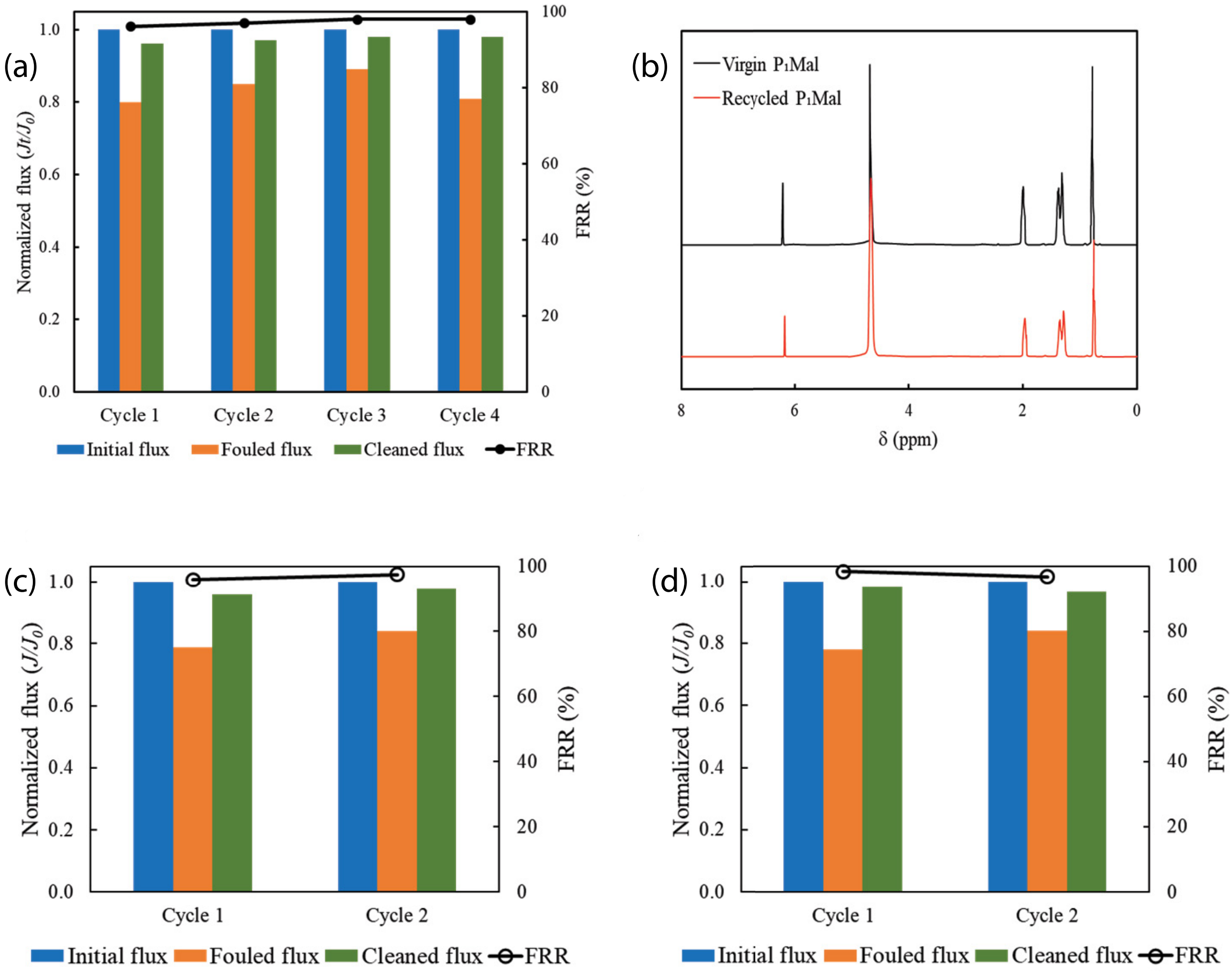

Fig. 9. (a) Membrane cleaning efficiencies of the cyclic cleaning tests and (b) ^{1}H-NMR of virgin and recycled P$_1$Mal. The cleaning efficiency between fresh and recycled (c) P$_1$TFA and (d) P$_1$T$_s$O.

of organic foulant or inorganic scaling foulant fouled membrane cleaned by ionic liquid is depicted in Fig. 7.

3.4. Recycling of used ionic liquid after cleaning fouled membrane

In recycling ionic liquid from the used LCST-type thermo-responsive ionic liquid cleaning solution, the LCST of thermo-responsive ionic liquid solution is an important parameter. Recycling study was demonstrated by P_1Mal. P_1Mal solution (5 wt.%) containing foulants (BSA/$CaSO_4$) was first concentrated to higher concentration (40 wt.%) for getting lower phase separation temperature. At temperature above the LCST (21°C) of P_1Mal, the phase separation occurred. The cleaning solution can be separated to ionic liquid-rich part and water-rich part. The foulants (BSA/$CaSO_4$) and residual water in ionic liquid part can then be removed by thermal method and the following filtration process, shown in Fig. 8a. In thermal process, the foulants precipitated and the water is vaporized out. The foulants could be removed by filtration through a 1 μm filter, shown in Fig. 8b. Then all of non-volatile ionic liquid could be recycled. The cleaning performance of recycled P_1Mal was tested. The results, shown in Fig. 9a, indicated that the recycled P_1Mal (recycling for four times) had retains comparable cleaning efficiency as virgin P_1Mal. ^{1}H-NMR spectrum of recycled P_1Mal and virgin P_1Mal are shown in Fig. 9b. The spectrum results indicated that no other chemical shift peak was observed. Therefore, P_1Mal can be used as recyclable and reusable cleaning agent for fouled membrane. Both P_1TFA and P_1TSO had 97% and 96% of cleaning efficiencies after recycling with the same methods as P_1Mal, shown in Fig. 9c and d.

4. Conclusion

In this study, LCST-type thermo-responsive ionic liquids used as cleaning agents for fouled membrane were investigated. In comparison to traditional cleaning agents. The benefit of these ionic liquid cleaning agents is that they can obtain same or higher cleaning efficiency with shorter cleaning time. In clearing the membrane fouled by BSA, $CaSO_4$ and BSA/$CaSO_4$, the optimal cleaning concentration was 5 wt.%. The cleaning strategies were immersing time with 5 min and flush time with 5 min at 25°C. The FRRs of three ionic liquids were all higher than 90%. The used thermo-responsive ionic liquid cleaning solution could be separated to ionic liquid-rich part and water-rich part by increasing the temperature above LCST. The ionic liquid in ionic liquid-rich part can be recycled by thermal method and filtration process. The recycled ionic liquid shows the same cleaning efficiency as the virgin ionic liquid. Hence, the LCST-type thermo-responsive ionic liquid is a recyclable and reusable cleaning agent for fouled membrane.

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