

## Simple and cost-effective to fabricate P(VC/VAC) based anion exchange membranes for acid recovery via diffusion dialysis

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### ABSTRACT

A series of anion exchange membranes for acid recovery via diffusion dialysis were prepared by the reaction between vinyl chloride–acetate copolymer (P(VC/VAC)) and N-methylimidazole (NMI), and their diffusion dialysis performances were characterized with a simulated feed (1.0 M HCl + 0.2 M FeCl<sub>2</sub>). The resulting membranes exhibited high dialysis coefficients ( $U_{dt}$ ; 0.0116–0.0325 m/h) and the separation factors ( $S$ ) (26–36) at 25°C. At the same time, standardized techniques were used to evaluate diffusion dialysis-related performance such as ion exchange capacity, water uptake ( $W_R$ ), linear expansion rate, elongation at break ( $E_b$ ), tensile strength (TS), initial decomposition temperature and thermal decomposition temperature, etc. Surface morphologies of the prepared anion exchange membranes were determined through scanning electron microscopy analysis. Through the proposed method, in this report, toxic reagents (such as methyl iodide) for quaternization are not required to prepare the anion exchange membranes. The experimental work presented here provided the preparation method, which not only is simple and economical but also exhibits excellent membrane performance, suggesting it as one of the promising candidates for diffusion dialysis membranes fabrication.

*Keywords:* Diffusion dialysis; Anion exchange membrane; Acid recovery; P(VC/VAC)

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### 1. Introduction

As an effective and feasible method, diffusion dialysis (DD) technique was widely used for recovering acid from waste acid solutions [1–5]. In comparison with other methods, DD method not only has low cost and low energy consumption [6,7] but also performs with outstanding acid recovery efficiency and environmental-friendly process [8,9].

As illustrated in Fig. 1, DD technique not only depends on the membrane properties such as thickness and surface conditions [10] but also the other conditions, for example concentration gradients, fluid properties of two rooms [11], mixing condition and so on.

As the key part of DD technique, a high-performance anion exchange membrane should essentially acquire several main features: appropriate water uptake, a high anion permeability, good chemical and thermal stability, excellent dimensional stability (DS), and selective separation of acid and its salts from waste water solution [12]. Therefore, the issue of the membrane preparation technology has received considerable critical attention. In this work, the aim was to provide a newly developed approach for membrane preparation with the above requirements satisfied, demonstrating their effectiveness as promising contender for applications in acid recovery based on DD.

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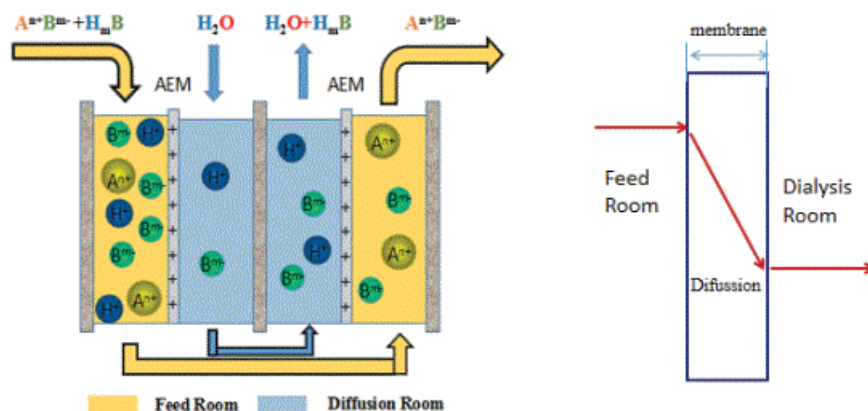


Fig. 1. Illustration of the DD principle for separation of  $A^m B^n$  and  $H_m B$ .

Results of recent studies on anion exchange membrane for acid recovery via DD are summarized as follows.

According to Table 1, it can be found that high acid DD coefficient ( $U_H$ ) normally requires high ion exchange rate (IEC) and water uptake ( $W_R$ ) of anion exchange membrane, while high IEC and water uptake have high negative influence upon the DS as well as the physical and mechanical strength of the membrane. Therefore, finding optimal polymer backbone for anion exchange membrane is one of the most frequently stated challenges for researchers.

At present, BPPO (brominated poly(2,6-dimethyl-1,4-phenylene oxide)) [22,23], PVDF (polyvinylidene fluoride) [24], PVA (polyvinyl alcohol) [25,26], PVC (polyvinyl chloride) [18], etc. are normally used to prepare anion exchange membrane for acid recovery based on DD. Nevertheless, although PVA-based membrane possesses high acid permeability, its application in DD is restricted because of its poor DS and high water uptake. On the other hand, BPPO and PVDF-based membranes possess good chemical and thermal stability, but their application in DD is limited by their low acid permeability and high price. P(VC/VAC) has been considered as one of the good candidates because it endows good membrane properties such as thermal stability and DD properties with low cost, which makes it suitable for industrial application [27].

Quaternary ammonium groups are commonly used for anion exchange membrane functional groups [28,29]. Imidazole groups can be used [30,31], since it has been confirmed that good DD performance can be obtained by using imidazole groups as the functional group of anion exchange membrane [32].

In this work, N-methylimidazole (NMI) and P(VC/VAC) are applied as raw materials to synthesize P(VC/VAC) grafted N-methylimidazole (PVC-g-NMI) via alkylation reaction [33,34]. By changing the content of N-methylimidazole with respect to P(VC/VAC), the obtained products are used for anion exchange membrane fabrication. Due to the existence of imidazole groups in the membrane structure, the obtained membranes have good physical and chemical stability comparing with the quaternary ammonium-based membranes indicated by previous studies. This project, therefore, sets out to prepare the membranes for acid recovery through DD by synthesizing P(VC/VAC)-g-NMI. In this study, a combination of quantitative and qualitative

approaches was used to evaluate the performance of the prepared membranes where a simulated acid waste water  $FeCl_2$  (0.2 M) and HCl (1 M) mixture is introduced and typical experiments are carried out. Furthermore, the results are discussed based on the relevant literature, and compared with the commercial membranes and other findings.

## 2. Experimental setup

### 2.1. Materials

Vinyl chloride–vinyl acetate copolymer (P(VC/VAC) with average polymerization degree of  $700 \pm 50$  is supplied by Hanwha Group (South Korea), Vinyl acetate is 10% and model is CP-710. N-Methylimidazole (NMI, 98%) is purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Other reagents possess analytical grade and were obtained from domestic chemical reagent companies. Deionized water (DI water) was used in all the experiments.

### 2.2. P(VC/VAC)-g-NMI polymer and membrane preparation

#### 2.2.1. Purification of P(VC/VAC)

20 g of vinyl chloride–vinyl acetate copolymer was dissolved in 100 mL toluene solvent. After precipitation (in water), leaching, washing, and drying ( $60^\circ C$  for 2 d), purified vinyl chloride–vinyl acetate copolymer was obtained.

#### 2.2.2. P(VC/VAC)-g-NMI polymer preparation

P(VC/VAC)-g-NMI polymer was synthesized by alkylation reaction [33,34] and the particular procedures are as follows: (i) 5 g of purified vinyl chloride–vinyl acetate copolymer was dissolved in 100 mL toluene to obtain a 5 wt.% solution in a 250 mL three-necked bottle, which was equipped with Allihn condenser; (ii) a certain amount of N-methylimidazole and aluminum trichloride were then added into the solution with magnetic stirring so as to achieve a homogeneous liquid; (iii) the mixture was by reflux reaction for 8 h at  $120^\circ C$ . The final P(VC/VAC)-g-NMI polymer was obtained after treatments of precipitation (in water), leaching, washing, and drying ( $60^\circ C$  for 2 d).

Table 1  
Recent research results on anion exchange membrane for acid recovery via diffusion dialysis

Num.	IEC (mmol/g)	$W_R$	$U_H$ (m/h)	$S (U_H/U_{Fe})$	Feed concentration	Temp. (°C)	Polymer backbone	Ref.
1	0.41–0.75	54.9%–81.3%	0.016–0.029	23.3–87.7	(1.28 M) HCl + (0.2 M) FeCl <sub>2</sub>	25	PVA	[13]
2	0.82–1.18	260%–310%	0.042–0.065	24.5–34	(1 M) HCl + (0.2 M) FeCl <sub>2</sub>	25	BPPO	[14]
3	1.86–2.13	410%–440%	0.045–0.063	19–21.5	(1 M) HCl + (0.2 M) FeCl <sub>2</sub>	25	BPPO	[15]
4	1.04–1.06	81%–146%	0.016–0.024	33.2–47.6	(1 M) HCl + (0.25 M) FeCl <sub>2</sub>	25	PVA	[16]
5	0.49–1.33	72.3%–153.3%	0.019–0.029	27.84–52.6	(1 M) HCl + (0.25 M) FeCl <sub>2</sub>	25	PVA	[17]
6	0.34–1.32	5.62%–24.8%	0.012–0.040	36–61	(0.81 M) HCl + (0.18 M) FeCl <sub>2</sub>	25	PVC	[18]
7	0.42–1.13	92%–122%	0.017–0.060	7.8–22.5	(0.81 M) HCl + (0.18 M) FeCl <sub>2</sub>	25	PVA	[19]
8	1.39–2.01	10.1%–28.5%	0.021	34.52	(1 M) HCl + (0.2 M) FeCl <sub>2</sub>	30	BPPO	[20]
9	1.08–1.67	19%–27%	0.021–0.028	19–25	(1.3 M) HCl + (0.2 M) FeCl <sub>2</sub>	25	PVDF	[21]

P(VC/VAC)-g-NMI polymers were prepared by changing the amount of N-methylimidazole as shown in Table 2.

### 2.2.3. Preparation of membrane

The above purified P(VC/VAC)-g-NMI polymer (Number A) was added in 100 mL toluene, the mixture was then stirred at 80°C for 8 h so as to achieve a complete dissolution and following cast onto polytetrafluoroethylene plates which were dried at 25°C under ventilated condition for 48 h. After peeling off from the polytetrafluoroethylene plate, the membranes were immersed into DI water for 48 h and the DI water was replaced every 8 h. The membranes were finally dried at 50°C under ventilated condition for 48 h. P(VC/VAC)-g-NMI membrane was prepared and named as membrane A. Membrane B, C, D, E were prepared according to the methods of preparation of membrane A. For comparison, P(VC/VAC) film was prepared through the same procedure as above.

### 2.3. Membrane characterizations

Water uptake ( $W_R$ ) was tested as below. The dried membrane samples were weighed and immersed into DI water for one and a half days at 25°C. Surfaces of the wet membranes are then carefully dried with tissue paper and the weight of wet membranes was accurately recorded. Water uptake was defined as the relative weight gain per gram of the dry membrane sample, which was calculated as follows:

$$W_R = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (1)$$

where  $W_{\text{dry}}$  and  $W_{\text{wet}}$  are the weight of dry and wet membranes, respectively.

IEC was monitored by adopting the Mohr method. Dry membranes were precisely weighed and converted into Cl<sup>-</sup> form in 1.0 M NaCl aqueous solution for 48 h at room temperature (25°C). Excessive NaCl was washed off with DI water. Then the membrane was immersed into 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution for 48 h at room temperature (25°C). Ion exchange capacities were obtained by testing the amount of

Table 2  
Amount of P(VC/VAC) and NMI of the starting materials for preparing P(VC/VAC)-g-NMI polymer

Number	P(VC/VAC) (g)	NMI (g)	TOL (mL)	AlCl <sub>3</sub> (g)
A	5	0.2	100	0.1
B	5	0.4	100	0.1
C	5	0.6	100	0.1
D	5	0.8	100	0.1
E	5	1.0	100	0.1

the exchanged Cl<sup>-</sup> via titration with 0.1 mol/L AgNO<sub>3</sub> aqueous solution.

DS affects application performance of anion exchange membrane. DS was monitored by linear expansion rate (LER) in 25°C water. The dried membrane was cut into dimension of 10 cm × 10 cm and recorded as  $L_{\text{DRY}}$ .  $L_{\text{WET}}$  is defined as the length of wet membrane, which was immersed into DI water for 72 h at 25°C. LER was calculated by the following equation:

$$\text{LER} = \frac{(L_{\text{WET}} - L_{\text{DRY}})}{L_{\text{DRY}}} \times 100\% \quad (2)$$

where  $L_{\text{DRY}}$  and  $L_{\text{WET}}$  represents the lengths of dry and wet membranes, respectively.

Acidic stability was obtained starting by immersing the weighed dry membrane samples into 65°C HCl (2.0 mol/L) aqueous solution for 168 h. Then the samples were transferred out and washed with DI water. After drying for 48 h at 50°C, the weight of dried membranes was measured again at 25°C. Percentage of mass change before and after was used to evaluate the acidic stability of membrane.

Tensile strength (TS) and elongation at break ( $E_b$ ) were measured by Instron universal tester (Model 1185, US) at room temperature (25°C).

Thermal stability of the membranes was determined by TGA-50H analyzer (Shimadzu Corporation, Japan) with a constant heating rate of 20°C/min from 40°C to 600°C under N<sub>2</sub> condition.

Fourier transform infrared spectroscopy (FTIR-ATR) of the membrane samples was recorded using FTIR spectrometer

(Nicolet 6700, Thermo Fisher Scientific) with a resolution of  $2\text{ cm}^{-1}$  and a spectral range of  $4,000\text{--}400\text{ cm}^{-1}$ .

The surface images of membranes were observed by scanning electron microscopy (SEM; JSM-7500F, JEOL of Japan).

#### 2.4. Diffusion dialysis

DD tests were taken through a DD device, which has a two-compartment cell separated by anion exchange membrane with an effective area of  $5.7\text{ cm}^2$ . Prior to DD experiments, the anion exchange membrane was first immersed into the simulated acid waste ( $1\text{ M HCl} + 0.2\text{ M FeCl}_2$ ) for 2 h and then rinsed with DI water to clean the solution. 100 mL feed solution and 100 mL DI water were filled into each compartment, respectively. During the experiment, two compartments were stirred vigorously to minimize concentration polarization. The diffusion time was set as 45 min and then the feed/osmotic solution was removed from the two sides. The HCl concentration of both sides was tested by titration method with  $0.05\text{ mol/L Na}_2\text{CO}_3$  aqueous solution, while  $\text{FeCl}_2$  concentration was determined by titration method with  $0.002\text{ mol/L KMnO}_4$  aqueous solution. All the experiments were conducted at room temperature ( $25^\circ\text{C}$ ).

The separation factor ( $S$ ) was calculated using the ratio of dialysis coefficients ( $U$ ) of the two species ( $\text{H}^+$  and  $\text{Fe}^{2+}$ ) presented in the solution.  $U$  can be calculated as below:

$$U = \frac{M}{At\Delta C} \quad (3)$$

where  $M$  is the amount of component transported (mol),  $A$  is the diffusion effective area ( $\text{m}^2$ ),  $t$  is the diffusion time (h) and  $\Delta C$  is the logarithm average concentration between the two compartment cells ( $\text{mol/m}^3$ ).  $\Delta C$  was calculated according to the equation below [26]:

$$\Delta C = \frac{C_f^0 - (C_f^t - C_d^t)}{\ln(C_f^0 / (C_f^t - C_d^t))} \quad (4)$$

where  $C_f^t, C_f^0$  is the feed concentrations at time  $t$  and 0, respectively.  $C_d^t$  is the dialysate concentration at time  $t$ .

According to the above equations (Eqs. (3) and (4)),  $U_{\text{H}}$  and  $U_{\text{Fe}}$  can be calculated. Separation factor ( $S$ ) was calculated according to the equation below:

$$S = \frac{U_{\text{H}}}{U_{\text{Fe}}} \quad (5)$$

### 3. Results and discussion

#### 3.1. FTIR spectra

The synthesis route of P(VC/VAC)-g-NMI polymer is shown in Fig. 2. As shown in Fig. 3, FTIR spectra of the membranes with the different degree of reaction and P(VC/VAC) film were exhibited to confirm the successful synthesis of P(VC/VAC)-g-NMI polymer. An obvious absorption peak was observed at  $2,928\text{ cm}^{-1}$ , which corresponds to the characteristic peak of asymmetric stretching vibration of  $-\text{CH}_2$  group in the main chain of P(VC/VAC). The typical absorption peak of P(VC/VAC) at  $1,730\text{ cm}^{-1}$  refers to stretching vibration of  $-\text{COOCH}_3$  group. The bending absorption peaks of C–C bond are at  $1,034\text{ cm}^{-1}$  [35]. The skeleton vibrations, representing C=C stretching in imidazole ring, are found in  $1,578\text{ cm}^{-1}$  region and C–H stretching bands are absorbed in  $1,367\text{ cm}^{-1}$  [36,37]. The bending vibration peaks of C–H and C–Cl bond are at  $-1,222$  and  $-599\text{ cm}^{-1}$ , respectively. By comparing FTIR spectra of membranes (A–E) and P(VC/VAC) film, membranes (A–E) appeared with clear absorption peaks of  $1,367$  and  $1,578\text{ cm}^{-1}$ , which are originated from the reaction of N-methylimidazole with P(VC/VAC). Hence, the successful synthesis of P(VC/VAC)-g-NMI polymer has been confirmed by the presence of C–N bonds.

#### 3.2. Water uptake ( $W_R$ ), IECs and LER

The water uptake is significantly critical to the fundamental properties of anion exchange membrane. The DD effect, microstructure, channel size and aggregation state of the membrane are all related to the water uptake

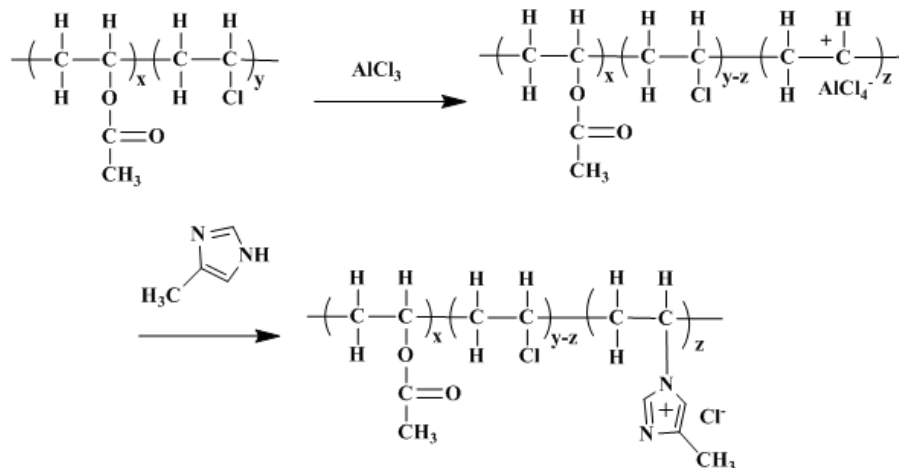


Fig. 2. Route of synthesis of P(VC/VAC)-g-NMI.

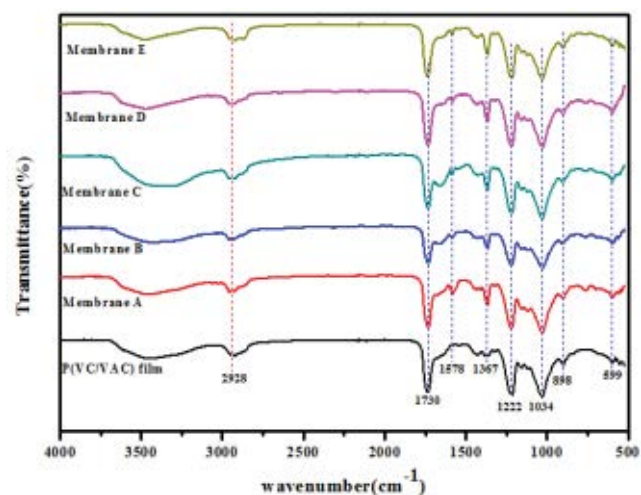


Fig. 3. FTIR spectra of anion exchange membranes (A–E) and P(VC/VAC) film.

of the membrane. Appropriate water uptake is beneficial to the performance of DD of the membranes, while excessive water uptake is detrimental to the DS of the membrane. According to Table 3, with the increase of IEC value from 0.29 to 1.12, the water uptake of the membrane increased from 6.8% to 24.5%, mainly due to hydrophobicity of P(VC/VAC) and hydrophilicity of N-methylimidazole. Through experiments, further analysis showed that increasing the content of N-methylimidazole in the membrane can effectively improve the water uptake of the membrane. In combination with Tables 3 and 4, a positive correlation was found between the LER and water uptake value of the membrane. As discussed earlier, increasing the water uptake of the membrane to appropriate degree facilitates the DD performance of the membrane; however if the water uptake is enormous, the membrane will swell leading to decrease in the DS of the membrane. As can be seen from Table 4, LER of different P(VC/VAC)-g-NMI membranes is 5.1%–12.1%, which is lower than those of many other PVA basement membranes [38,39], suggesting the improved DS in the process of application of membranes (A–E).

### 3.3. Thermal stability

Enhanced thermal stability is necessary for AEMs to perform effectively in DD. The short-term thermal stability of different P(VC/VAC)-g-NMI membranes was characterized using thermogravimetry (TGA) as shown in Fig. 4.

From Fig. 4, the initial decomposition temperature (IDT) and thermal decomposition temperature (Td) can

Table 3  
Ion exchange capacities (IECs) and water uptake ( $W_R$ ) of membranes (A–E)

Membrane	A	B	C	D	E
IEC	0.29	0.46	0.67	0.78	1.12
$W_R$ (%)	6.8	13.6	16.1	22.5	24.7

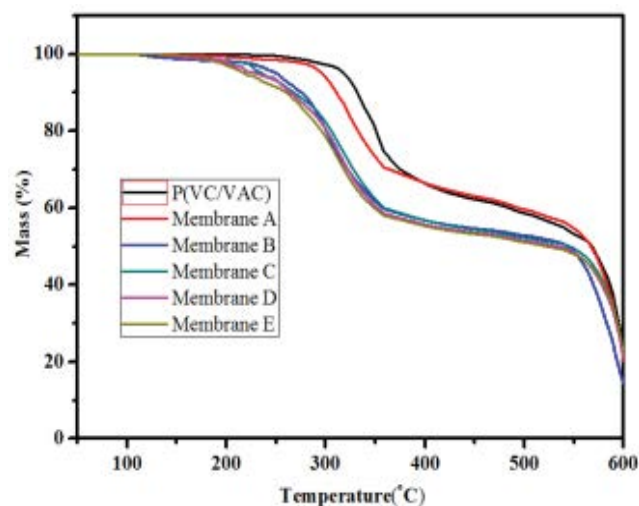


Fig. 4. TGA graphs of P(VC/VAC)-g-NMI membranes (A–E) and P(VC/VAC).

be determined, and the measurement results are shown in Table 5. According to the table, IDT values of these P(VC/VAC)-g-NMI membranes are in the range of 191°C–276°C and Td values are in the range of 215°C–292°C. The weight loss between 200°C and 300°C is ascribed to the degradation of imidazole groups [40] and the second degradation step occurred in the range of 340°C–360°C, which is linked to the main chain of the polymer backbone [41].

Reasons for the good thermal stability of the membranes are mainly due to the following two aspects: (1) imidazole groups are thermally stable in the P(VC/VAC)-g-NMI membranes [40], (2) the main chain of the polymer backbone is thermally stable, because Td and IDT values of the P(VC/VAC) appear at 295°C and 312°C, respectively [27].

The TGA data indicate that the membranes are stable up to 191°C, these prepared membranes have acceptable thermal stability in practical applications, where the operating temperature of DD process is usually below 100°C.

Table 4  
Thickness and linear expansion rate (LER) of P(VC/VAC) film and membranes (A–E)

	Membrane A	Membrane B	Membrane C	Membrane D	Membrane E	P(VC/VAC) film
P(VC/VAC)/NMI dosage (g)	5/0.2	5/0.4	5/0.6	5/0.8	5/1.0	5/0
Thickness ( $\mu\text{m}$ )	111	114	113	115	109	112
LER (%)	5.1	7.9	9.2	10.6	12.1	0.7

Table 5  
Td and IDT of the membranes A–E and P(VC/VAC)

Number	P(VC/VAC)	Membrane A	Membrane B	Membrane C	Membrane D	Membrane E
IDT (°C)	295	276	229	216	207	191
Td (°C)	312	292	246	231	226	215

Td is thermal decomposition temperature, which is defined as the temperature at 5% weight loss of P(VC/VAC)-g-NMI membranes A–E. IDT is the initial decomposition temperature determined from TGA thermograms.

### 3.4. Elongation at break ( $E_b$ ) and TS

Elongation at break reflects the flexibility of the membrane and TS represents the resistance of the membrane to mechanical force. As shown in Table 6, membrane A shows the biggest  $E_b$  and TS, while membrane E shows the lowest  $E_b$  and TS.

In general, there is negative correlation between  $E_b$  and TS, but both  $E_b$  and TS decrease with the increase of content of imidazole group (ion exchange group) in the prepared membranes. The main reasons are as follows: (1) the aggregation of imidazole group in the membranes affects the continuity of membranes formation, which leads to formation of defects in the membranes, resulting in simultaneous decay in both  $E_b$  and TS. (2) In the presence of two-phase separation between P(VC/VAC) polymer (with small polarity) and P(VC/VAC)-g-NMI polymer (with large polarity), the distance between molecules becomes larger, and inter-molecular forces become smaller, leading to weaker TS. (3) The inner plasticization within VAC chain segment in P(VC/VAC) provides the prepared membranes with higher  $E_b$  than that of porous membrane [23] or the hybrid membranes [25], The enhanced flexibility is favorable for membrane storage and transportation.

### 3.5. Acid stability

Long-term acid resistance is another main challenge for AEMs applied in DD for acid recovery, which is processed in acidic operating environment. To evaluate the acid resistance of the prepared membrane, the qualities of the membranes were recorded before and after immersing into aqueous HCl (2 mol/L) solutions for 168 h at 65°C. The quality maintenance of the membrane is shown in Table 7. It can be clearly observed that the quality maintenance of membrane A–E ranges from 99.2% to 99.8%. It is apparent from this table that the prepared membranes have stronger acid resistance. The enhanced acid resistance can be ascribed to the high stability of P(VC/VAC) backbone and imidazole group.

### 3.6. Membrane morphology

The surface morphology of membranes A–E was observed through SEM to determine the impact of NMI content to the membrane structure. The surface morphologies of membranes A–E are shown in Fig. 5.

The phase separation becomes more obvious with the increase of NMI content. The surface morphologies of membrane A and B are smooth and uniform. However, with increasing NMI content, slight phase separation was

Table 6  
Tensile strength (TS) and elongation at break ( $E_b$ ) of P(VC/VAC)-g-NMI membranes A–E

Membrane	A	B	C	D	E
$E_b$ (%)	206	193	172	156	135
TS (MPa)	23.2	21.8	20.6	19.5	18.6

Table 7  
Quality changes of the membranes (A–E) after immersion into 2 mol/L HCl solutions at 65°C for 168 h

Membrane	Quality maintenance
A	99.8
B	99.6
C	99.5
D	99.3
E	99.2

observed for membrane C. The aggregation of the particles can be observed on the surface through SEM image of the membranes D and E, and formation of defect appeared for membrane E. The clear phase separation in the membranes D and E, as shown in the SEM images, demonstrates the strong correlation between NMI content and degree of phase separation of membranes. By increasing the amount of NMI, large dosage of NMI promotes the reaction between NMI and P(VC/VAC). Therefore, with bigger amount of NMI, large aggregates and bigger degree of phase separation was observed in membranes D and E.

### 3.7. Diffusion dialysis

In order to better coordinate for the comparison with the previous experimental results, a simulated waste liquid of HCl/FeCl<sub>2</sub> mixture (1 M HCl + 0.2 M FeCl<sub>2</sub>) was prepared in typical experiments and data were applied to evaluate the DD performance. The corresponding results are demonstrated in Fig. 5.

As shown in Fig. 6, with the increased content of imidazole group (ion exchange group), the  $U_H$  value increases gradually from  $11.6 \times 10^{-3}$  m/h (membrane A) to  $32.5 \times 10^{-3}$  m/h (membrane E), and the  $U_{Fe}$  value increases gradually from  $0.32 \times 10^{-3}$  m/h (membrane A) to  $1.23 \times 10^{-3}$  m/h (membrane E). There are three reasons contributed to the increase of  $U_H$  and  $U_{Fe}$  value: (1) in general, the larger content of imidazole group (ion exchange group) in membrane leads to

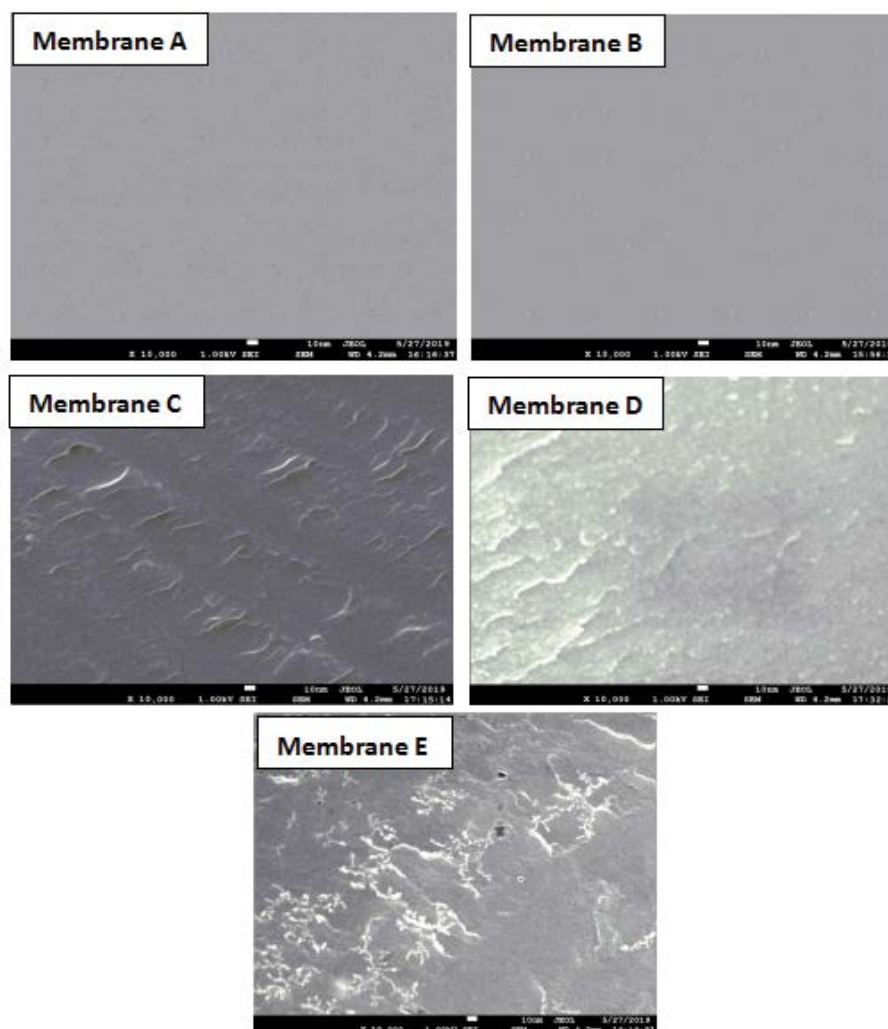


Fig. 5. Morphology of membranes A–E are the surface images with the magnification of 10,000 $\times$  by scanning electron microscopy.

bigger water uptake in the membrane. Under the same content of imidazole group (ion exchange group) conditions, the water uptake increases in the membrane, which could enhance  $H^+$  and  $Fe^{2+}$  content in the membrane, enhancing the concentration gradient between membrane and diffusion chamber. The bigger concentration gradient could accelerate the diffusion of  $H^+$  and  $Fe^{2+}$  ions from membrane to diffusion chamber, resulting in the increase in  $U_H$  and  $U_{Fe}$  values. (2) The phase separation can reduce the resistance of ions ( $H^+$  and  $Fe^{2+}$ ) to pass through the membrane, which is beneficial for the motion of  $H^+$  and  $Fe^{2+}$  ions, so  $U_H$  and  $U_{Fe}$  values become high accordingly. (3) As schematically shown in Fig. 7, the  $-COOCH_3$  groups existed in P(VC/VAC) backbone are considered as auxiliary functional group for  $H^+$  transport [18,42,43], the oxygen in  $-COOCH_3$  groups exist exposed electrons, which can absorb  $H^+$  ions,  $H^+$  concentration in anion exchange membranes become high, the concentration gradient between membrane and diffusion chamber is enhanced, so  $U_H$  values are higher than that of commercial membrane DF-120 ( $9 \times 10^{-3}$  m/h), which was produced by Shandong Tianwei Membrane Technology Co., Ltd, China.

As can be seen from Fig. 6, as the content of imidazole group (ion exchange group) increases, the separation coefficient of anion exchange membrane decreases from 36 (membrane A) to 30 (membrane B), increases to 33 (membrane C), and decreases to 26 (membrane E). Comparing with commercial membrane DF-120 (18.5) [44], the separation coefficients of membranes A–E are higher than that of commercial membrane. Arising from the increase in the imidazole group (ion exchange group), both the IEC and  $W_R$  of the membranes increase and the phase separation of the membranes becomes bigger. The high IEC is beneficial to the enhanced separation coefficient. On the other hand, the increase of  $W_R$  and phase separation of the membranes is unfavorable to the improvement of separation coefficient. Therefore, no certain trend of separation coefficient was observed through the combination of IEC,  $W_R$  and phase separation.

Together these results provide important insight that the  $U_H$  and separation coefficient of the prepared membranes are all higher than those of commercial membranes DF-120 (0.009 m/h for  $U_H$ , 18.5 for  $S$ ). Therefore, the P(VC/VAC)-g-NMI membranes have potential applications as DD for acid recovery.

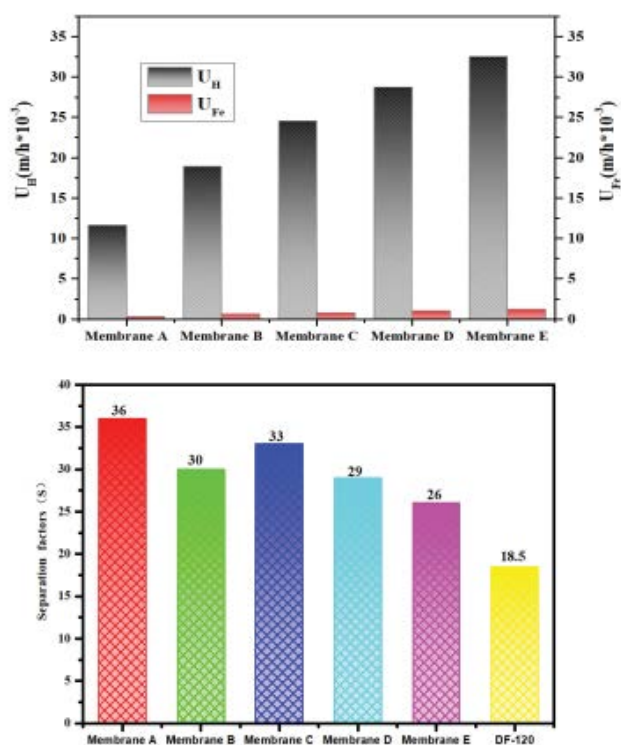


Fig. 6. (a) Hydrochloric acid (HCl) and ferrous chloride ( $FeCl_2$ ) dialysis coefficients and (b) separation factor.

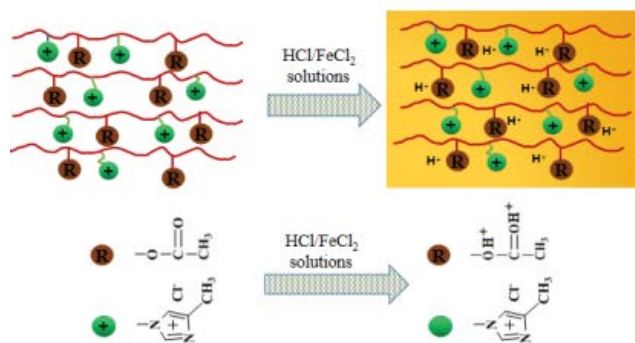


Fig. 7. Schematic representation for ions diffusion in anion exchange membrane with the presence of assistant functional groups  $-(CO)OCH_3$ .

#### 4. Conclusion

In this study, we have successfully prepared P(VC/VAC) based graft polymer anion exchange membrane with P(VC/VAC) and NMI. The results showed that with the increase of the content of NMI, IEC increased from 0.29 to 1.12 mmol/g and water uptake ( $W_R$ ) was between 6.8% and 24.7%, and LER is in the range of 5.1%–12.1%. The membranes showed good thermal stability with thermal decomposition temperature ( $T_d$ ) ranged from 215°C to 292°C and IDT in the range of 191°C–276°C. The acid resistance was excellent and weight maintenance was 99.2%–99.8% in 2 mol/L HCl for 168 h at 25°C. With the increase in the content of NMI, the permeability of  $H^+$  ( $U_{H^+}$ ) increased and the separation coefficient

( $S$ ) decreases first, then increased and finally decreases,  $U_{H^+}$  and  $S$  values are all higher than that of commercial membrane (DF-120). Overall, we predict that this simple and cost-effective method to fabricate anion exchange membrane will have potential applications in DD for acid recovery.

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#### Abbreviations

P(VC/VAC)	—	Vinyl chloride–acetate copolymer
NMI	—	N-Methylimidazole
DI	—	Deionized
DD	—	Diffusion dialysis
IEC	—	Ion exchange capacity
$W_R$	—	Water uptake
LER	—	Linear expansion rate
TS	—	Tensile strength
$E_b$	—	Elongation at break
IDT	—	Initial decomposition temperature
$T_d$	—	Thermal degradation temperature
SEM	—	Scanning electron microscopy
$U_{H^+}$	—	Dialysis coefficient of HCl
$U_{Fe^{2+}}$	—	Dialysis coefficient of $FeCl_2$
$S$	—	Separation factor

#### References

- [1] A. Agrawal, K.K. Sahu, An overview of the recovery of acid from spent acidic solutions from steel and electroplating industries, *J. Hazard. Mater.*, 171 (2009) 61–75.
- [2] P. Wang, C. Wu, M. Sun, X. Zhang, Y. Wu, Porous P84 co-polyimide anion exchange membranes for diffusion dialysis application to recover acids, *Desal. Water Treat.*, 108 (2018) 40–48.
- [3] K.M. Imran, L. Rafael, P. Pepijn, R. Aziz Ur, A. Saima, N. Muhammad, S. Aqeela, Z. Shagufta, M. Mujahid, BPPO-based anion exchange membranes for acid recovery via diffusion dialysis, *Materials*, 10 (2017) 266.
- [4] Z. Palatý, H. Bendová, Continuous dialysis of sulphuric acid and magnesium sulphate, *Sep. Purif. Technol.*, 76 (2011) 400–406.
- [5] V. Chavan, C. Agarwal, V.C. Adya, Ashok, K. Pandey, Hybrid organic-inorganic anion-exchange pore-filled membranes for the recovery of nitric acid from highly acidic aqueous waste streams, *Water Res.*, 133 (2018) 87–98.
- [6] K.M. Imran, A.N. Mondal, C. Cheng, J. Pan, K. Emmanuel, L. Wu, T. Xu, Porous BPPO-based membranes modified by aromatic amine for acid recovery, *Sep. Purif. Technol.*, 157 (2016) 27–34.
- [7] K.M. Imran, Liang Wu, Md.M. Hossain, J. Pan, J. Ran, A.N. Mondal, T. Xu, Preparation of diffusion dialysis membrane for acid recovery via a phase-inversion method, *Membr. Water Treat.*, 6 (2015) 365–378.
- [8] J.Y. Kim, C.H. Shin, H. Choi, W. Bae, Recovery of phosphoric acid from mixed waste acids of semiconductor industry by diffusion dialysis and vacuum distillation, *Sep. Purif. Technol.*, 90 (2012) 64–68.



- [9] K.M. Imran, K. Majeda, A. Fares, Fabrication and characterization of pyridinium functionalized anion exchange membranes for acid recovery, *Sci. Total Environ.*, 686 (2019) 90–96.
- [10] T. Hayat, M. Ijaz Khan, M. Farooq, A. Alsaedi, M. Waqas, T. Yasmeen, Impact of Cattaneo-Christov heat flux model in flow of variable thermal conductivity fluid over a variable thicked surface, *Int. J. Heat Mass Trans.*, 99 (2016) 702–710.
- [11] M.I. Khan, M. Waqas, T. Hayat, A. Alsaedi, A comparative study of Casson fluid with homogeneous-heterogeneous reactions, *J. Colloid Interface Sci.*, 498 (2017) 85–90.
- [12] J. Luo, C. Wu, T. Xu, Y. Wu, Diffusion dialysis-concept, principle and applications, *J. Membr. Sci.*, 366 (2011) 1–16.
- [13] A.N. Mondal, C. Cheng, M.I. Khan, M.M. Hossain, K. Emmanuel, L. Ge, B. Wu, Y.B. He, J. Ran, X. Ge, N.U. Afsar, L. Wu, T. Xu, Improved acid recovery performance by novel Poly(DMAEM-co- $\gamma$ -MPS) anion exchange membrane via diffusion dialysis, *J. Membr. Sci.*, 525 (2017) 163–174.
- [14] X. Lin, S. Kim, D.M. Zhu, Ezzatollah Shamsaei, T. Xu, X. Fang, H.T. Wang, Preparation of porous diffusion dialysis membranes by functionalization of polysulfone for acid recovery, *J. Membr. Sci.*, 524 (2017) 557–564.
- [15] X. Lin, E. Shamsaei, B. Kong, J.Z. Liu, Y. Hu, T. Xu, H.T. Wang, Porous diffusion dialysis membranes for rapid acid recovery, *J. Membr. Sci.*, 502 (2016) 76–83.
- [16] F. Mao, G. Zhang, J. Tong, T. Xu, Y. Wu, Anion exchange membranes used in diffusion dialysis for acid recovery from erosive and organic solutions, *Sep. Purif. Technol.*, 122 (2014) 376–383.
- [17] M. Irfan, E. Bakangura, N.U. Afsar, J. Ran, T. Xu, Augmenting acid recovery from different systems by novel Q-DAN anion exchange membranes via diffusion dialysis, *Sep. Purif. Technol.*, 201 (2018) 336–345.
- [18] C.L. Cheng, Z. Yang, Y. He, A.N. Mondal, E. Bakangura, T. Xu, Diffusion dialysis membranes with semi-interpenetrating network for acid recovery, *J. Membr. Sci.*, 493 (2015) 645–653.
- [19] C. Cheng, P. Li, Y. He, X.H. Hu, K. Emmanuel, Branched PVA hybrid membrane for acid recovery via diffusion dialysis, *Chem. Eng. Technol.*, 42 (2019) 1180–1187.
- [20] L. Wang, F. Zhang, Z. Li, J. Liao, Y. Huang, Y. Lei, N.W. Li, Mixed-charge poly(2,6-dimethyl-phenylene oxide) anion exchange membrane for diffusion dialysis in acid recovery, *J. Membr. Sci.*, 549 (2018) 543–549.
- [21] Prem P. Sharma, V. Yadav, A. Rajput, V. Kulshrestha, Acid resistant PVDF based copolymer alkaline anion exchange membrane for acid recovery and electrodialytic water desalination, *J. Membr. Sci.*, 563 (2018) 561–570.
- [22] T. Xu, W. Yang, Sulfuric acid recovery from titanium white (pigment) waste liquor using diffusion dialysis with a new series of anion exchange membranes-static runs, *J. Membr. Sci.*, 183 (2001) 193–200.
- [23] F. Sun, C. Wu, Y. Wu, T. Xu, Porous BPPO-based membranes modified by multisilicon copolymer for application in diffusion dialysis, *J. Membr. Sci.*, 450 (2014) 103–110.
- [24] X. Zuo, S. Yu, X. Xu, J. Xu, R. Bao, X. Yan, New PVDF organic-inorganic membranes: The effect of SiO<sub>2</sub> nanoparticles content on the transport performance of anion-exchange membranes, *J. Membr. Sci.*, 340 (2009) 206–213.
- [25] L. Zou, Y. Wu, G. Zhang, Separation of acidic HCl/glyphosate liquor through diffusion dialysis and electrodialysis, *Desal. Water Treat.*, 105 (2018) 199–208.
- [26] Y.H. Wu, J. Luo, L. Zhao, G. Zhang, C. Wu, T. Xu, QPPO/PVA anion exchange hybrid membranes from double crosslinking agents for acid recovery, *J. Membr. Sci.*, 428 (2013) 95–103.
- [27] J. Maiti, N. Kakati, P. Basumatary, S.P. Woo, Y.S. Yoon, Imidazolium functionalized poly(vinyl chloride-co-vinyl acetate)-based anion exchange membrane, *Int. J. Hydrogen Energy*, 41 (2016) 5776–5782.
- [28] T.S. Mayadevi, S. Sung, J.E. Chae, H.J. Kim, T.H. Kim, Quaternary ammonium-functionalized poly(ether sulfone ketone) anion exchange membranes: the effect of block ratios, *Int. J. Hydrogen Energy*, 44 (2019) 18403–18414.
- [29] M. Cong, Y. Jia, H. Wang, M. Wang, Preparation of acid block anion exchange membrane with quaternary ammonium groups by homogeneous amination for electro-dialysis-based acid enrichment, *Sep. Purif. Technol.*, 238 (2020) 116396.
- [30] P. Yang, B. Zhang, H. Wu, L. Cao, X. He, Z. Jiang, Imidazolium-functionalized carbon nanotubes crosslinked with imidazole poly(ether ether ketone) for fabricating anion exchange membranes with high hydroxide conductivity and dimension stability, *Electrochim. Acta*, 318 (2019) 572–580.
- [31] X. Dua, Z. Wang, W. Liu, J. Xua, Z. Chen, C. Wang, Imidazolium-functionalized poly(arylene ether ketone) cross-linked anion exchange membranes, *J. Membr. Sci.*, 566 (2018) 205–212.
- [32] K. Emmanuel, C.L. Cheng, B. Erigene, A.N. Mondal, M.M. Hossain, M.I. Khan, N.U. Afsar, G. Liang, L. Wu, T. Xu, Imidazolium functionalized anion exchange membrane blended with PVA for acid recovery via diffusion dialysis process, *J. Membr. Sci.*, 497 (2016) 209–215.
- [33] A. Mehrdad, N. Noorani, Permeability behavior of polyvinyl chloride-ionic liquid ionomer for CO<sub>2</sub>/CH<sub>4</sub> separation, *Sep. Purif. Technol.*, 226 (2019) 138–145.
- [34] Q. Che, Z. Zhu, N. Chen, X. Zhai, Methylimidazolium group-modified polyvinyl chloride (PVC) doped with phosphoric acid for high temperature proton exchange membranes, *Mater. Design*, 87 (2015) 1047–1055.
- [35] Y. Wu, C. Wu, Y. Li, T. Xu, Y. Fu, PVA-silica anion-exchange hybrid membranes prepared through a copolymer crosslinking agent, *J. Membr. Sci.*, 350 (2010) 322–332.
- [36] H. Wu, W. Jia, Y. Liu, An imidazolium-type hybrid alkaline anion exchange membrane with improved membrane stability for alkaline fuel cells applications, *J. Mater. Sci.*, 52 (2017) 1704–1716.
- [37] J. Ran, L. Wu, J.R. Varcoe, A.L. Ong, Simon D. Poynton, T. Xu, Development of imidazolium-type alkaline anion exchange membranes for fuel cell application, *J. Membr. Sci.*, 415–416 (2012) 242–249.
- [38] C. Wu, Y. Wu, J. Luo, T. Xu, Y. Fu, Anion exchange hybrid membranes from PVA and multi-alkoxy silicon copolymer tailored for diffusion dialysis process, *J. Membr. Sci.*, 356 (2010) 96–104.
- [39] J.J. Gu, C. Wu, Y. Wu, J. Luo, T. Xu, PVA-based hybrid membranes from cation exchange multisilicon copolymer for alkali recovery, *Desalination*, 304 (2012) 25–32.
- [40] C. Yang, S. Wang, L. Jiang, J. Hu, W. Ma, G. Sun, 1,2-Dimethylimidazolium-functionalized cross-linked alkaline anion exchange membranes for alkaline direct methanol fuel cells, *Int. J. Hydrogen Energy*, 40 (2015) 2363–2370.
- [41] J. Hu, C. Zhang, J. Cong, H. Toyoda, M. Nagatsu, Y. Meng, Plasma-grafted alkaline anion-exchange membranes based on polyvinyl chloride for potential application in direct alcohol fuel cell, *J. Power Sources*, 196 (2011) 4483–4490.
- [42] S. Yadav, K. Soontarap, M.S. Jyothi, M. Padaki, R.G. Balakrishna, J.Y. Lai, Supplementing multi-functional groups to polysulfone membranes using *Azadirachta indica* leaves powder for effective and highly selective acid recovery, *J. Hazard. Mater.*, 369 (2019) 1–8.
- [43] K. Emmanuel, B. Erigene, C. Cheng, A.N. Mondal, M.M. Hossain, M.I. Khan, N.U. Afsar, L. Ge, L. Wu, T. Xu, Facile synthesis of pyridinium functionalized anion exchange membranes for diffusion dialysis application, *Sep. Purif. Technol.*, 167 (2016) 108–116.
- [44] C. Cheng, Z. Yang, J. Pan, B. Tong, T. Xu, Facile and cost effective PVA based hybrid membrane fabrication for acid recovery, *Sep. Purif. Technol.*, 136 (2014) 250–257.