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Higher efficiency of triethanolamine-grafted anion exchange membranes for acidic wastewater treatment

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ABSTRACT

Acidic wastewaters are major industrial effluents that must be cleaned before release in natural waters, yet classical treatment methods are limited. Diffusion dialysis through anion exchange membranes (AEM) appears as a sustainable alternative because those membranes are cheap and highly selective, yet there is a need for improved membranes. Here we synthesized AEMs from brominated poly(2,6-dimethyl-1,4-phenylene oxide) using triethanolamine as an ion-exchange group for acid recovery. The prepared membranes were characterized by Fourier-transform infrared spectroscopy, scanning electron microscopy, and atomic force microscopy. Acid recovery was tested with a mixture of HCl and $FeCl_2$. Results show that increasing triethanolamine content into the membrane polymer matrix led to an increase of water uptake from 12% to 117%, ion exchange capacity from 1.28 to 2.29 mmol/g, and linear swelling ratio from 3.52% to 32.70%. The diffusion dialysis coefficient of acid (U_H^+) reached 23×10^{-3} m/h, which is higher than that actual membranes, of 0.37–20 × 10^{-3} m/h. U_H^+ increased with membrane triethanolamine content, which is explained by increasing H bonding of aqueous protons with membrane hydroxyl groups. U_H^+ also increased from 23×10^{-3} m/h at 25°C to 71×10^{-3} m/h at 55°C due to easier ion flow. Moreover, the separation factor (S) reached 495 at 25°C, which is higher than that of actual membranes, of 73–351. The diffusion dialysis coefficient of metal (U_{Fe}^{2+}) ranged from 0.0025 to 61 10^{-3} m/h. Membranes also showed excellent thermal, chemical and mechanical stability.

Keywords: Triethanolamine; Brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO); Anion exchange membrane; Water uptake; Acid recovery

1. Introduction

Acidic wastewaters are produced in large amounts from industrial processes such as electroplating, metallurgy, and mining. Acidic wastewaters induce two major issues, environmental pollution when effluents are discharged in rivers, and corrosion, which is costly [1,2]. Common processes for wastewater treatment include neutralization, crystallization, thermal decomposition, solvent extraction, precipitation, coagulation-flocculation, distillation, and electrodialysis [3,4], yet these processes have drawbacks such as cost, low selectivity, high energy and the use of toxic chemicals. Alternatively, diffusion dialysis through ion exchange membranes is actually under active research investigation because it is operationally cheaper, it consumes less energy and is potentially more efficient [5–16]. In particular, anion exchange membranes (AEM) are well-suited for acid separation and recycling [17–23], yet the performances of actual membranes are limited.

The diffusion dialysis process is driven by a gradient of compound concentration between the two sides of the ion exchange membrane. Ion exchange membranes can

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be classified into AEM and cation exchange membranes according to the ionic group attached to the polymeric backbone. Currently, AEMs are tested for acid recovery from industrial acidic wastewater. Membranes have been synthesized from polysulfone and polystyrene, by photo-initiated polymerization of 4-vinylpyridine with varying amounts of divinylbenzene in the pores of polypropylene, by surface modification and pore filling of various polymers [24–27]. Nonetheless, those membranes usually lack stability, and their hydrophobicity limits ion transfer during diffusion dialysis. Therefore, there is a need for cost-effective membranes that have long-term stability, higher selectivity, and permeation for acid recovery and wastewater treatment.

AEMs can be improved by modifying the polymeric backbone and functional groups [6,12,13,19,28]. Indeed, the polymeric backbone should be hydrophobic and mechanically stable. Actual polymeric backbones include poly(arylene ether ketone) [29,30], poly(arylene ether sulfone) [31–33], poly(fluorenyl ether ketone sulfone) [34], poly(vinyl alcohol) [35], poly(2,6-dimethyl-1,4-phenylene oxide) [36,37], and polyetherimide [38]. Besides, the ion exchange capacity (IEC) should be high because well connected ion-conducting channels improve the diffusion dialysis coefficient [39]. The anion permeability can be controlled by the functional groups such as guanidinium [40–43], sulfonium [44] and phosphonium [45–49].

Membranes including quaternary ammonium are cheap and easy to synthesize [10]. Here, a higher proton diffusion coefficient U_H^+ of 0.033 m/h and a high separation factor S of 95.45 at 25°C has been obtained with quaternary ammonium-functionalized poly(arylene ether) (QPAE-Br) membranes [28]. A diffusion dialysis coefficient U_H^+ of 0.019 m/h and a separation factor S of 127 was reported for series-connected hexacations cross-linked membranes [6]. Quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) membranes displayed IEC value of 2.07 mmol/g, diffusion coefficient U_H^+ of 0.020 m/h and a separation factor S of 73 at room temperature [50]. Highly charged hierarchical porous membranes increased the performance of diffusion dialysis with higher diffusion dialysis coefficient U_H^+ of 0.0273 m/h and a separation factor S of 86.5 at 25°C [51]. Poly(DMAEM-co-g-MPS) gave a diffusion dialysis coefficient U_H^+ of 0.016–0.029 m/h and a separation factor S of 23.3–87.7 [8]. PPO has good mechanical properties and allows easy membrane preparation for high acid recovery at room temperature [7,9,10].

Triethanolamine (TEA) appears as a better reagent for membrane preparation, compared to other quaternary ammonium groups. Indeed triethanolamine bears three highly hydrophilic hydroxyl groups ($^{-}$OH), which act as assisting groups to improve H$^+$ transfer during dialysis [12,13]. Secondly, the low acidity of triethanolamine, with pKa of 10.75, allows higher anion permeability because anions are dissociated easier from functional groups [16]. In addition, the high alkalinity of triethanolamine induces higher adsorption of water molecules on positive groups, which, in turn, facilitates the conduction of anions [16].

Here we present the first attempt to employ triethanolamine as a functional group in AEMs. Membrane properties were tailored by varying the triethanolamine content of the polymeric matrix. Membranes were characterized by Fourier-transform infrared spectroscopy (FTIR), and for morphology, IEC, water uptake, linear swelling ratio (LSR), thermal, chemical, and mechanical stability. Membranes were tested for acid recovery with a mixture of HCl and $FeCl_2$ by diffusion dialysis. The effect of temperature on the dialysis performance was also tested.

2. Experimental setup

2.1. Materials

PPO from Sigma-Aldrich (Germany). Triethanolamine, chlorobenzene, ethanol, chloroform, N-methyl-2-pyrrolidone (NMP), 2,2′-azobisisobutyronitrile (AIBN), N-bromosuccinimide (NBS), sodium chloride (NaCl), silver nitrate ($AgNO_3$), sodium sulfate (Na_2SO_4), potassium chromate (K_2CrO_4), hydrochloric acid (HCl), ferrous chloride ($FeCl_2\cdot 4H_2O$), methyl orange (MO) from Sinopharm Chemical reagent Co. Ltd, China. Distilled water was used.

2.2. Preparation of brominated PPO

Synthesis has been described [52] (Fig. 1). Typically, 6 g of PPO (50 mmol) is dissolved into 50 ml chlorobenzene in a round bottom flask containing a magnetic stirrer and reflexed condenser. 4.45 g NBS (25 mmol) and 0.25 g azobisisobutyronitrile (AIBN, 1.5 mmol) are added and the solution is stirred at 135°C for 3 h. After cooling to 25°C, the reaction mixture is poured into an excess of ethanol to precipitate the polymer. The polymer is filtered, washed with ethanol, re-dissolved into 60 mL chloroform then precipitated into an excess of ethanol. The polymer is collected as a light-yellow powder and dried under vacuum for 2 d at 40°C to yield brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) with a bromination ratio of 75%.

2.3. Fabrication of AEMs

We used the solution casting method to prepare membranes [7,53–57]. We prepared a 8%w solution by dissolving 0.8 g of BPPO into 10 mL of NMP. 0.15, 0.25, 0.35, or 0.45 g of triethanolamine were added to obtain membranes named TEA-19, TEA-31, TEA-44, and TEA-56 respectively, where 19, 31, 44, and 56 refer to the weight percentage (w%) of triethanolamine into the membrane matrix. The reaction mixture was stirred 12 h at 40°C then casted onto a glass plate at 60°C for 24 h. Membranes were peeled off from glass plates and cleaned with deionized water. The chemical structure of the prepared membrane is also shown in Fig. 1.

2.4. Characterization

2.4.1. Instrumentation

^{1}H-NMR (proton nuclear magnetic resonance) with DMX 300 NMR spectrometer operating at 300 MHZ was used to monitor the bromination of PPO. AEM was analysed for attenuated total reflectance with a Vector 22, Bruker, (Massachusetts, MA, USA) FTIR spectrometer at 4,000–400 cm^{-1}. Field-emission scanning electron microscopy (FE-SEM, Sirion 200, FEI Company, USA) and atomic force microscopy (AFM) were used to observe the membrane morphology. Membrane thermal stability was tested using a Shimadzu Corporation, (Kyoto, Japan) TGA-50H analyzer under nitrogen flow with a heating rate of 10°C/min from

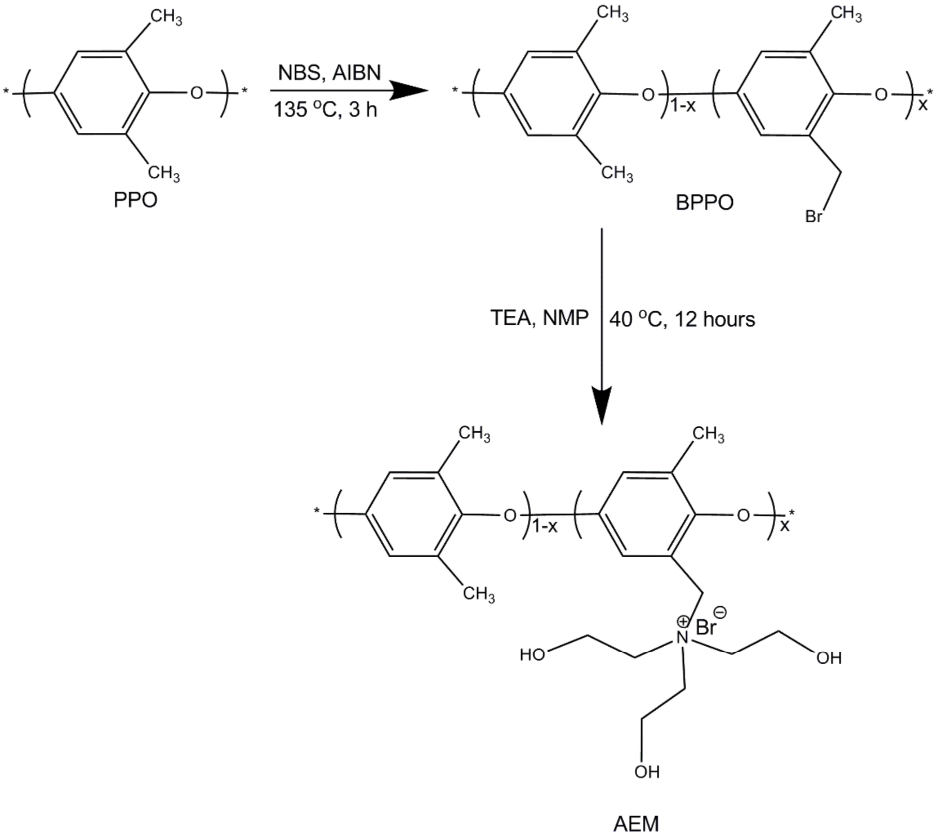

Fig. 1. Preparation of brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO)-based anion exchanged membranes. NBS: N-Bromo-succinimide; AIBN: 2,2′-azobisisobutyronitrile; TEA: triethanolamine, NMP: N-methyl-2-pyrrolidone, AEM: anion exchange membrane.

25°C to 800°C. Membrane mechanical stability was measured using Q800 dynamic mechanical analyzer (DMA, TA Instruments, Kyoto, Japan) at a stretch rate of 0.5 N/min.

2.4.2. Ion exchange capacity

IEC of membranes was determined by Mohr's method. Typically, the dried membrane samples were immersed in 1 M NaCl for 48 h to convert the charged sites into the Cl^- form. Excess NaCl was removed from membranes by careful water cleaning then immersion into 0.5 M Na_2SO_4 for 48 h. The concentration of released Cl^- was determined by titration with 0.05 M $AgNO_3$ using K_2CrO_4 as an indicator, and was calculated using the following equation [53]:

$$\mathrm{IEC} = \frac{C_{\mathrm{AgNO_3}} V_{\mathrm{AgNO_3}}}{W_{\mathrm{Dry}}} \tag{1}$$

where m, V, and C depict the dry weight of the membrane sample, titer value during titration, and the concentration of $AgNO_3$ solution, respectively.

2.4.3. Water uptake and LSR

To measure water uptake of the prepared membranes, the dried membrane samples were weighed and then immersed in water for 24 h at room temperature. After removing the surface water with tissue paper, wet weight was measured. Water uptake was calculated from the mass difference before and after the complete drying of the membranes, using the following equation [57,58]:

$$W_{\mathrm{R}} = \frac{W_{\mathrm{WET}} - W_{\mathrm{DRY}}}{W_{\mathrm{DRY}}} \times 100\% \tag{2}$$

where W_{WET} and W_{DRY} depict the wet and dry weights of membrane samples, respectively.

The LSR was measured at 25°C. The membranes sample was cut into a 3 cm^2 × 3 cm^2 pieces. The ratio was obtained using the following equation [54]:

$$\mathrm{LER} = \frac{\left(L_{\mathrm{WET}} - L_{\mathrm{DRY}}\right)}{L_{\mathrm{DRY}}} \times 100\% \tag{3}$$

where L_{WET} and L_{DRY} denote wet and dry lengths of membrane samples, respectively.

2.4.4. Chemical stability

To investigate membrane chemical stability, membrane samples were immersed in $HCl/FeCl_2$ feed solution at 55°C. The change in weight as a function of immersion time was calculated to measure chemical stability.

2.4.5. Diffusion dialysis of $HCl/FeCl_2$

The acid recovery performance of anionic exchange membranes reported in our previous work [5,9]. Typically, the experiment was carried out in a two-compartment stack separated by the AEM. The effective area of the used membrane is 5.7 cm^2. The membrane sample is conditioned in the feed solution of 0.89 M HCl and 0.25 M $FeCl_2$ for 5 h, which stimulates waste acid solution prior to the test. One compartment of the stack is filled up with a 100 mL feed solution, while the other side with 100 mL deionized water during the experiment. Both solutions are stirred 60 min. vigorously in order to minimize the concentration polarization. Then both feed and permeate are taken from the different compartments. The concentrations of H^+ in both compartments were measured by titration, while Fe^{2+} concentration was measured by inductively coupled plasma spectrophotometry (ICP, Optima 7300 DV).

The dialysis coefficient U is calculated using the following equation [10]:

$$U = \frac{M}{At\Delta C} \tag{4}$$

where M is the concentration of the transported component in mol, A depicts the effective membrane area in m^2, t denotes the time in h, and ΔC represents the logarithm average concentration between the two chambers in mol/m^3. ΔC is measured as below [10]:

$$\Delta C = \frac{C_f^0 - \left(C_f^t - C_d^t\right)}{\ln\left[C_f^0 / \left(C_f^t - C_d^t\right)\right]} \tag{5}$$

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

Dialysis coefficient U_H and U_{Fe} can be measured using Eqs. (4) and (5). The separation factor S is ratio of dialysis coefficients U of the two species present in the solution. S is calculated by [10]:

$$S = \frac{U_H}{U_{Fe}} \tag{6}$$

3. Results and discussion

3.1. Bromination of PPO

Brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) was synthesized by the bromination of PPO by NBS as a brominating agent and AIBN as initiator. Bromination can occur either at the benzylic position or at the aromatic ring depending on the reaction condition and reagents [52,59]. In this research, it occurred at the benzylic position of PPO in refluxing chlorobenzene solution at 135°C. The structure and degree of BPPO were investigated by ^{1}H-NMR spectroscopy (Fig. 2). The benzyl bromide group is located at 4.3 ppm. The degree of bromination is 75%, it is the percentage of the integral area of the benzyl bromide group vs. the unreacted benzyl signal at 2.1 ppm.

3.2. Quaternization of brominated PPO

FTIR spectroscopy was used to check the quaternization of BPPO with triethanolamine. Fig. 3 shows the FTIR spectra of the pristine BPPO membrane and of the BPPO membrane containing 65% triethanolamine (TEA-56). The band at 1,608 cm^{-1} is due to C=C stretching in phenyl groups; the

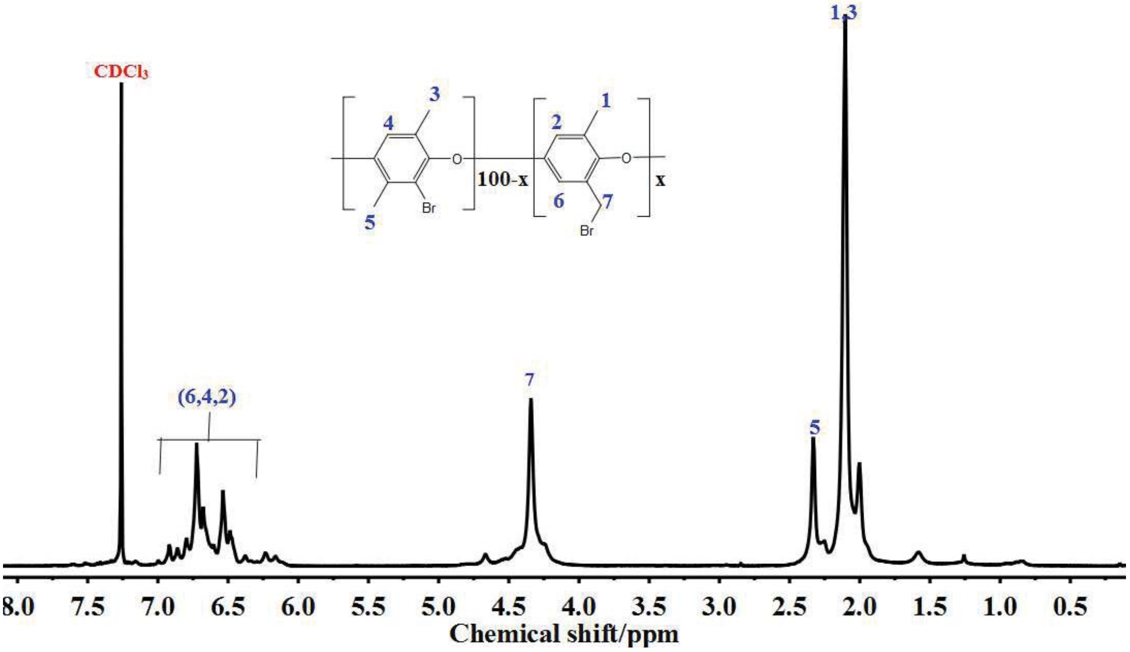

Fig. 2. ^{1}H-NMR spectrum of brominated poly(2,6-dimethyl-1,4-phenylene oxide) synthesized by bromination of poly(2,6-dimethyl-1,4-phenylene oxide). The presence of a peak at 4.3 ppm reveals the successful bromination at benzylic positions.

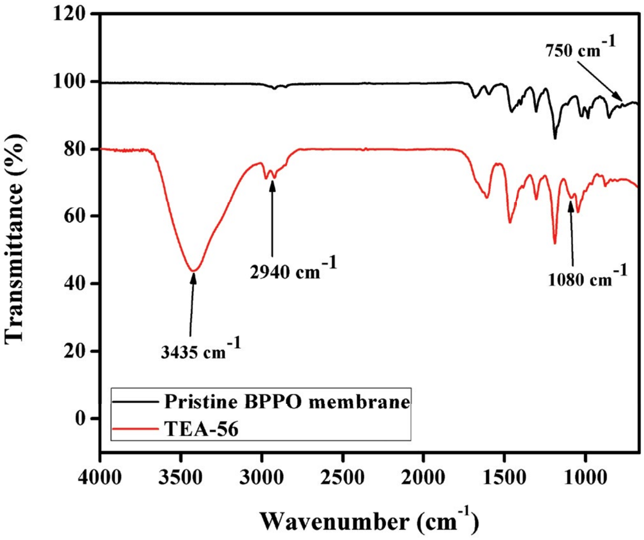

Fig. 3. Infrared spectra of pristine brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) and the membrane prepared with 56% triethanolamine (TEA-56), confirming successful synthesis.

peak at 1,190 cm^{-1} is characteristic of C–O–C stretching [60]. The bands at 1,446 cm^{-1} are attributed to –CH stretching (V and δ) [35]. Symmetrical and asymmetrical stretching of C–O are at 1,200 and 1,306 cm^{-1}, and those of phenyl groups at 1,470 and 1,600 cm^{-1} respectively [54]. The band at 750 cm^{-1} is attributed to C–Br stretching in the pristine BPPO membrane [61].

The triethanolamine-containing membrane shows a characteristic band at 1,080 cm^{-1} associated with C–N stretching, thus demonstrating the successful reaction of BPPO and triethanolamine. Other characteristic bands include –OH stretching of triethanolamine at 3,435 cm^{-1}; a peak at 2,940 cm^{-1} due to the $-CH_2$ group of triethanolamine attached to the BPPO backbone. Noteworthy, the signal for C–Br stretching in bromobenzyl groups at 750 cm^{-1} disappeared after the reaction of triethanolamine with BPPO [61,62]. Overall, our findings confirm the successful grafting of triethanolamine with the BPPO backbone.

3.3. Membrane morphology

The morphology of anionic exchange membranes prepared with 19% and 56% triethanolamine was studied by scanning electron microscopy (SEM) (Fig. 4a). Results show that membranes are free from any hole or crack in surfaces and cross-sections, thus confirming their homogeneous nature. Moreover, the membrane homogeneity is enhanced by increasing the concentration of triethanolamine into the membrane matrix. This finding is explained by higher miscibility with an increasing amount of triethanolamine into the polymer matrix. Overall, the homogeneous morphology of the membranes makes them suitable for acid recovery via diffusion dialysis. Membrane surfaces were also analyzed by AFM at room temperature (Fig. 4b). Results show again that the membranes are homogeneous without any phase separation.

3.4. Ion exchange capacity

The IEC of the prepared membranes, measured by the Mohr's method, is given in Table 1. Results show that the IEC increases from 1.28 to 2.28 mmol/g by increasing the amount of triethanolamine in the polymer matrix. The IEC depicts the number of exchangeable ion-conducting groups and thus controls the ion conductivity and swelling ratio of membranes. The IEC also provides information on the membrane charge density, which is related to their conductivity and transport properties [54]. Our results thus imply higher anion permeability and, in turn, higher performance for diffusion dialysis.

3.5. Water uptake and linear swelling ratio

Table 1 depicts the water uptake of the membranes prepared with 19%–56% triethanolamine at room temperature. Results show an increase in water uptake from 12% to 117% with triethanolamine content. This finding implies that hydrophilicity can be controlled and that ion permeability and mechanical properties can be tailored for diffusion dialysis applications. Indeed, water molecules are involved in ion transport and, as a consequence, a moderate water uptake is required for higher anion permeability [16]. Nonetheless, too much water may reduce mechanical and dimensional stability. Overall, our membranes display a suitable water uptake for diffusion dialysis.

Table 1 presents linear swelling ratio (LSR) of prepared membranes. Results show that LSR increases from 3.51% to 32.70 % with increasing the amount of triethanolamine into the polymer matrix. These findings imply that the membranes exhibit excellent swelling resistance, which is required for diffusion dialysis.

3.6. Diffusion dialysis coefficient and separation selectivity

We used a mixture of HCl and $FeCl_2$ as a model of acidic wastewater to test the membrane performances, similarly to previous reports [7,9,13]. The diffusion dialysis coefficient of HCl (U_{H}^{+}) and metal (U_{Fe}^{2+}) of our membranes are shown in Fig. 5a. Results show that U_{H}^{+} ranges from 1.3 to 23 × 10^{-3} m/h, and that U_{Fe}^{2+} ranges from 0.0025 to 0.61 × 10^{-3} m/h at room temperature. Our membranes have thus higher U_{H}^{+} values than the commercial DF-120B membranes (4 × 10^{-3} m/h) [7], PVA-based hybrid membranes (11–18 × 10^{-3} m/h) [3] and PPO-based membranes (0.37–20 × 10^{-3} m/h) at 25°C [50].

The increase of U_{H}^{+} and U_{Fe}^{2+} with triethanolamine content is explained by higher water uptake and IEC, leading to enhanced membrane hydrophilicity. In addition, the free hydroxyl groups of triethanolamine are assistant functional groups that accelerate the transport of H^+ ions through hydrogen bonding [12]. The higher values of U_{H}^{+} is explained by the much smaller ionic radius of H^+ vs. Fe^{2+} [63].

The separation selectivity is calculated by the separation factor S, defined as a ratio of U_{H}^{+} to U_{Fe}^{2+}. Fig. 5b shows that our membranes have S ranging from 37 to 495 at room temperature. These values are much higher than that of the commercial DF-120B membrane [10], BPAES-based

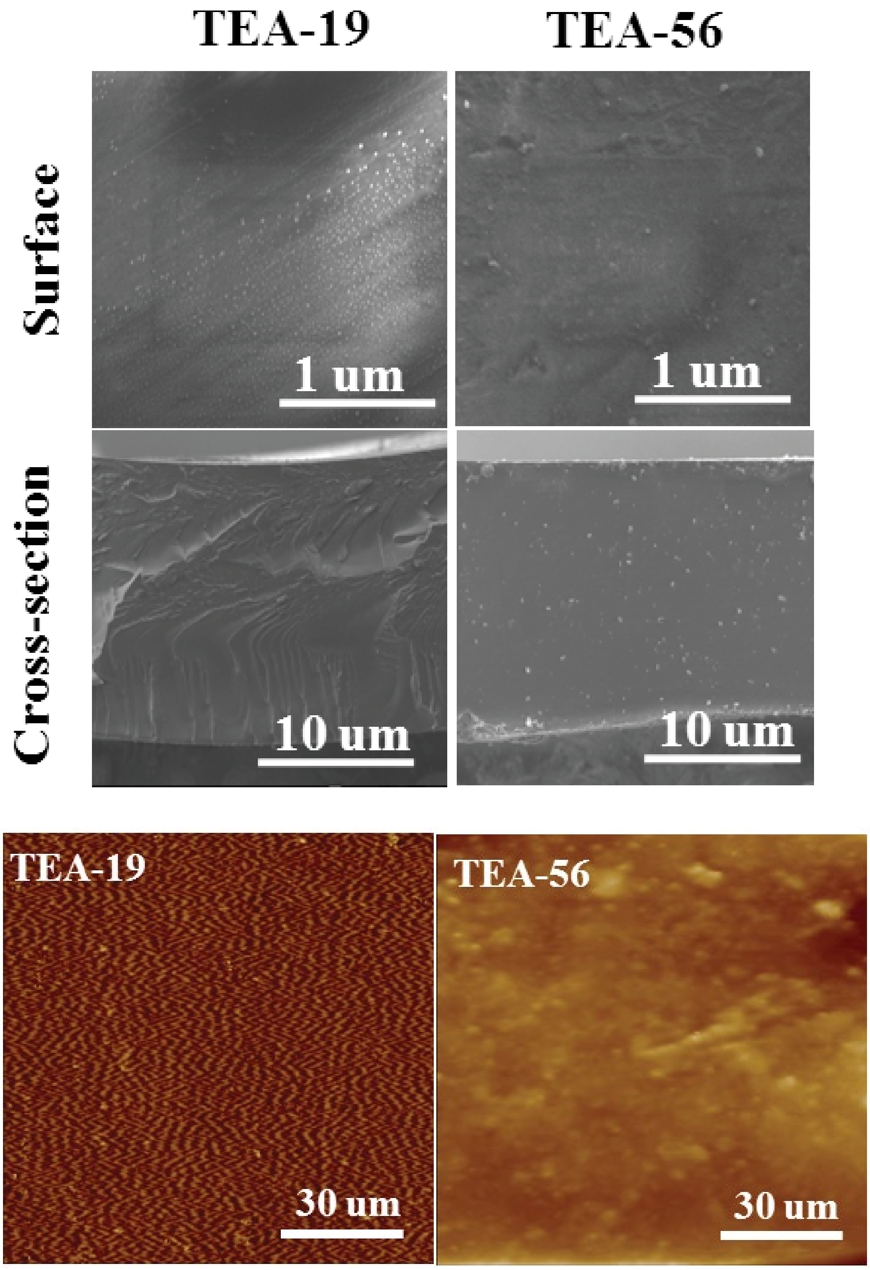

Fig. 4. (a) Surface and cross-section of anionic exchange membranes prepared with 19% (TEA-19) and 56% triethanolamine (TEA-56), analyzed by scanning electron microscopy (SEM). (b) Analysis by atomic force microscopy. Results show that membrane surfaces and sections are homogeneous.

Table 1
Theoretical ion exchange capacity (IEC), experimental ion exchange capacity, water uptake (W_R), and linear swelling ratio (LSR) of anionic exchange membranes prepared with 19%, 31%, 44%, and 56% of triethanolamine (TEA). Results show that all factors increase with triethanolamine amount in the polymer matrix at 25°C

Membranes	IEC_T (mmol/g)	$IEC_{Exp.}$ (mmol/g)	W_R (%)	LSR (%)
TEA-19	1.10	1.28 ± 0.06	12.0 ± 0.60	3.52 ± 0.18
TEA-31	1.60	1.71 ± 0.90	37.14 ± 1.86	10.53 ± 0.53
TEA-44	2.03	1.93 ± 0.10	49.35 ± 2.47	15.52 ± 0.78
TEA-56	2.40	2.29 ± 0.11	117 ± 5.85	32.70 ± 1.64

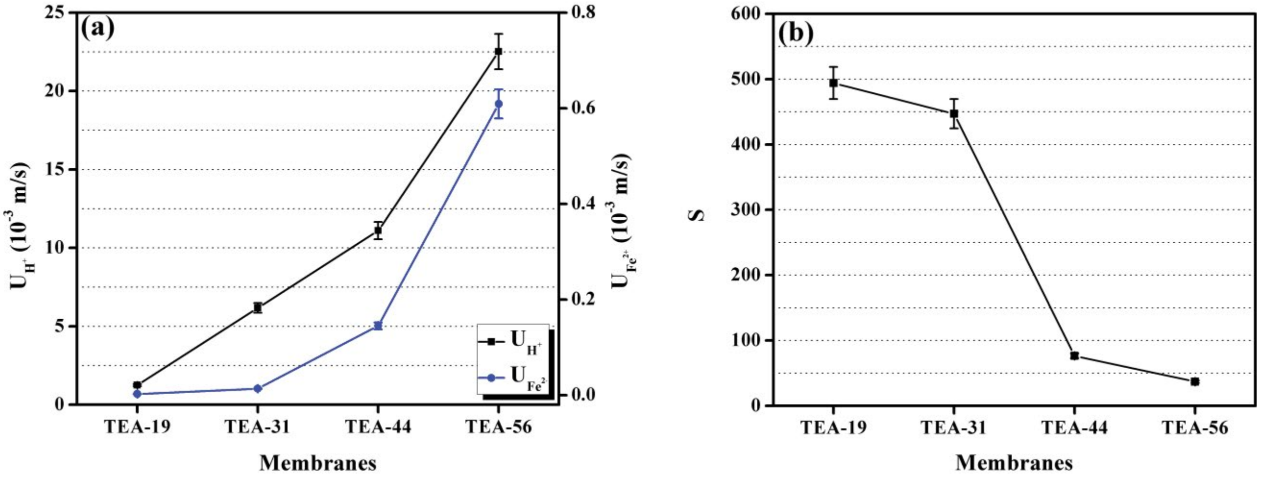

Fig. 5. (a) Diffusion dialysis coefficient of acid, U_H^+, and metal, U_{Fe}^{2+}, and (b) separation factor S for membranes prepared with 19%–56% of triethanolamine (TEA). Results show an increase of U and a decrease of S with triethanolamine content.

membranes [6] and BPPO-Im/GO membranes based membranes [18]. Furthermore, our results show that S decreases with triethanolamine content (Fig. 5b). This decrease is explained by higher water uptake and swelling ratio (Table 1), which enlarges the spaces between polymer chains and, in turn, favors the permeability of Fe^{2+}.

3.7. Effect of temperature

We selected the anionic exchange membrane prepared with 56% triethanolamine to test the effect of temperature, from 25°C to 55°C, on the performance of diffusion dialysis of H^+ and Fe^{2+} (Fig. 6a). Results show an increase of U_H^+ from 23 to 71 × 10^{-3} m/h, and of U_{Fe}^{2+} from 0.61 to 4.2 × 10^{-3} m/h with temperature. These findings agree with enhanced ion transport at higher temperatures [63,64]. Further, the effect of temperature on the separation factor S is shown in Fig. 6b. Data shows that S decreases from 37 to 17 with temperature. This finding is explained by the easier transfer of Fe^{2+} vs. H^+ at higher temperatures [63,64]. Overall the high U_H^+ values of our membrane imply an excellent diffusion dialysis performance at various temperatures.

3.8. Comparison of various membranes

Fig. 7 compares the performances of our membranes with reported membranes [3,7,17,35,50,63,65–68]. Two parameters are displayed, the diffusion dialysis coefficient of acid U_H^+ and the separation factor S. Results show that our membranes have the second-highest U_H^+ value and the highest separation factor S. Therefore our membranes are very promising for acid recovery from industrial wastewater by diffusion dialysis.

3.9. Thermal and chemical stability

We selected the AEM prepared with 56% triethanolamine to test the thermal stability from 30°C to 800°C by thermogravimetric analysis. Fig. 8a shows the thermogravimetric curves of pristine membranes and membranes

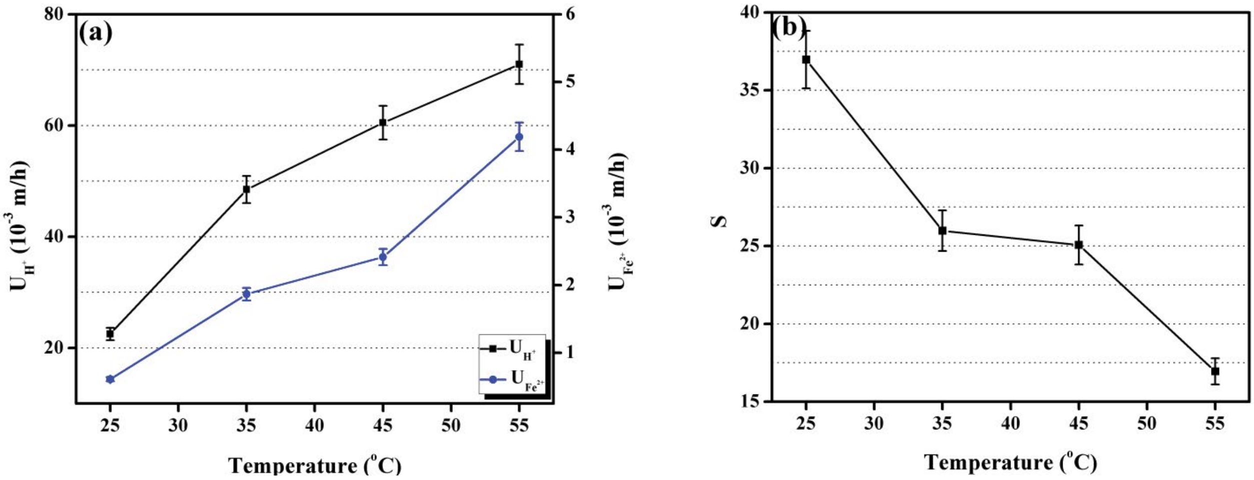

Fig. 6. (a) Diffusion dialysis coefficient of acid (U_H^+) and metal (U_{Fe}^{2+}) and (b) separation factor (S) for the membrane prepared with 56% triethanolamine (TEA-56). Results show an increase of U and a decrease of S with temperature.

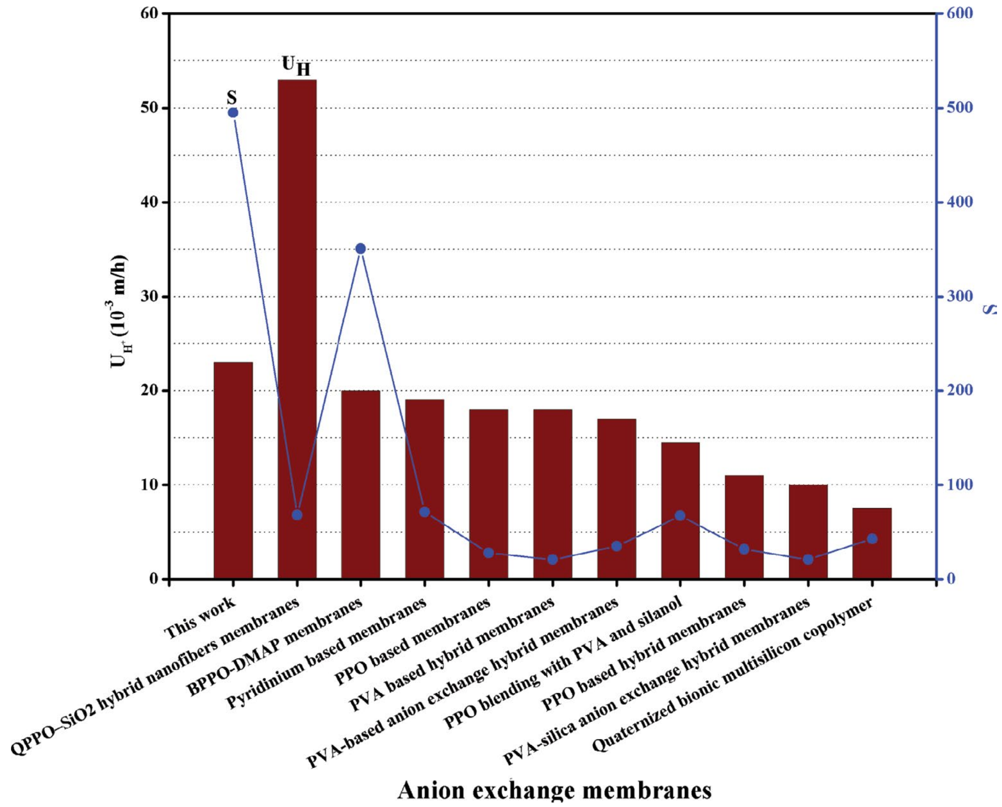

Fig. 7. (a) Comparison of membrane performances. Diffusion dialysis coefficients of acid U_{H}^{+} and separation factor S of our membranes ('this work') vs. reported membranes employing HCl/FeCl$_2$ as the model acidic waste solution.

prepared with 56% triethanolamine. Results show that weight loss takes place in three successive steps, corresponding to evaporation of adsorbed water at 80°C–130°C, thermal deamination, and thermal oxidation of the polymer backbone. The second step at 230°C–240°C is explained by the degradation of quaternary ammonium groups [10]. The last step around 415°C is due to the degradation of the polymer backbone. Overall, our membranes have excellent thermal stability below 300°C.

The chemical stability of the membrane was also tested by immersion into HCl/FeCl$_2$ for 2 weeks at 55°C (Fig. 8b). Results show a weight loss of about 15%, in agreement

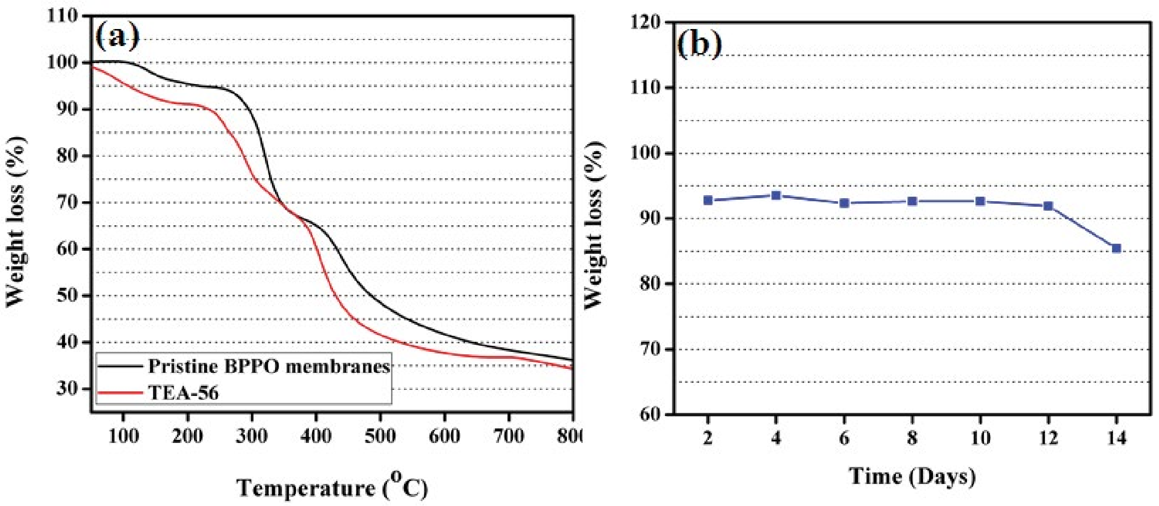

Fig. 8. (a) Thermogravimetric analysis of the pristine membrane and the membrane prepared with 56% triethanolamine (TEA-56) and (b) Weight loss of the TEA-56 membrane after immersion in HCl/FeCl$_2$ feed solution for two weeks at 55°C, showing high chemical stability.

Table 2
Tensile strength (TS) and elongation at break of the prepared anion exchange membranes

Membranes	TEA-19	TEA-31	TEA-44	TEA-56
TS (MPa)	31.85	31.38	23.51	19.27
E_b (%)	12.53	18.0	38.88	39.47

with our previous reported membranes [10]. Moreover, we also observed that the color of our membrane is unchanged after two weeks of immersion in $HCl/FeCl_2$ feed solution at 55°C. Overall, our AEMs display good chemical stability and are thus promising for acid recovery from wastewater.

3.10. Mechanical stability

We studied membrane mechanical stability by measuring tensile strength (TS) and elongation at break (E_b) of AEMs prepared with 19%–56% triethanolamine, in the wet state (Table 2). Results show that TS ranges from 19.27 to 31.85 MPa. These values are higher than our previously reported AEM [58], which implies that the membranes of this work have excellent mechanical stability. The elongation at break ranges from 12.53% to 39.47%, which are lower than hybrid AEMs [12]. TS decreases and elongation at break increases with triethanolamine content. The decrease in TS with enhanced IEC agrees with previous research [21]. The membrane prepared with 56% triethanolamine displays excellent flexibility due to lower tensile strength and higher elongation at break. By contrast, the AEM prepared with 19% triethanolamine exhibits high tensile strength and low elongation at break.

4. Conclusion

We prepared AEMs from PPO and triethanolamine by solution casting method. The successful synthesis was confirmed by FTIR spectroscopy. The homogeneous morphology was confirmed by SEM and AFM. Membranes exhibited optimal IEC and water uptake essential for diffusion dialysis applications. Membranes showed IEC of 1.28 to 2.29 mmol/g, water uptake of 12%–117%, LSR of 3.52% to 32.70%. The IEC, water uptake, and LSR increase with triethanolamine content into the polymer matrix. The membranes were tested for acid recovery by diffusion dialysis. Results showed that membranes exhibit high value of U_{H^+}, of $1.3–23 \times 10^{-3}$ m/h, and of separation factor, from 37 to 495, at room temperature. Membranes exhibit higher chemical, thermal, and mechanical stability. Overall, our findings reveal that the triethanolamine-functionalized AEMs are promising candidates for acid recovery from industrial acidic wastewater by diffusion dialysis.

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