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Membrane Surface Functionalization with Imidazole Derivatives to Benefit Dye Removal and Fouling Resistance in Forward Osmosis

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Water contaminated with low concentrations of pollutants is more difficult to clean up than that with high pollutant content levels. Membrane separation provides a solution for removing low pollutant content from water. However, membranes are prone to fouling, losing separation performances over time. Here we synthesized a neutral (IM-NH₂) and positively charged (IL-NH₂) imidazole derivatives to chemically functionalize membranes. With distinct properties, these imidazole grafts could tailor membrane physicochemical properties and structures to benefit forward osmosis (FO) processes for the removal of 20 – 100 ppm of Safranin O dye—a common dye employed in the textile industry. The water fluxes produced by IM-NH₂ and IL-NH₂-modified membranes increased by 67% and 122%, respectively, with DI water as the feed compared to that with the nascent membrane. A 39% flux increment with complete dye retention (~ 100%) was achieved for the IL-NH₂-modified membrane against 100 ppm of Safranin O dye. Regardless of the dye concentration, the IL-NH₂-modified membrane exhibited steadily higher permeation performance than the original membrane in long-term experiments. Reproducible experimental results were obtained with the IL-NH₂-modified membrane after cleaning using DI water, demonstrating the good antifouling properties and renewability of the newly developed membrane.

Abstract Graphic

TOC Graphic

Keywords: forward osmosis; FO membrane; membrane modification; imidazole derivatives; dye removal

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INTRODUCTION

Water pollution due to the discharge of industrial waste such as dyes and pigments is a longstanding environmental issue that has remained unsolved. These compounds are toxic, carcinogenic, and hazardous to living organisms.^{1,2} Advancements in traditional dye removal technologies such as adsorption, coagulation, biological degradation, and oxidation are adequate for processing large amounts of concentrated dye solutions.³⁻⁶ The problem lies in cleaning up wastewater with low dye concentrations. This is ascribed to the chemical stability of dyes; that is, i.e., they are difficult to degrade via aerobic digestion, oxidation, or using external stimuli such as heat and light. More importantly, these mitigation techniques can generate a large amount of toxic waste or sludge from the use of chemicals for dye removal, contributing towards toward secondary pollution.⁷ In recent years, membrane technology including ultrafiltration, nanofiltration, and reverse osmosis has been employed for such applications as toxic sludge is not produced, and these processes are easy to scale-up.⁸⁻¹² However, the high-energy consumption of these membrane processes, which is often exacerbated by membrane fouling, offsets their perceived green benefits and potential.^{8,11,12} These drawbacks of membrane separation can be overcome with forward osmosis (FO).^{13,14}

FO, a membrane process driven by the osmosis pressure gradient between a feed and draw solution to induce water flow across a semipermeable membrane, has been employed in dye removal.¹⁵⁻¹⁷ Different from other membrane processes, FO requires no hydraulic pressure to drive the system, lowering both fouling propensity and energy consumption without sacrificing high water recovery rates and excellent rejection of low molecular weight dyes.^{13,18} The key to all FO processes is the semipermeable membrane which determines the fouling resistance and water recovery efficiency of the separation process. Thin-film composite (TFC) membranes comprising a thin selective layer of polyamide (PA) deposited on porous supports of polysulfone (PSf), polyethersulfonepoly(ether sulfone) (PES), and sulfonated polyethersulfonepoly(ether sulfone) (sPES) have been widely used in FO processes.¹⁹ However, current FO membranes suffer from poor water recovery efficiency and selectivity, low fouling resistance, and renewability. These drawbacks can be overcome by chemical functionalization that alters surface properties and membrane structures.²⁰ A range of materials such as neutral amines, alcohols, zwitterions, and other compounds have been deployed to covalently functionalize membranes for better FO performance.¹⁹ However, such modifications are usually at the expense of lowering permeation flux.

Imidazole derivatives such as imidazole-based ionic liquids have been widely used for membrane modification due to their design flexibility, high stability, and environmental friendliness.^{21,22} These materials endow membranes with desirable properties to benefit applications in gas separation,²³ biofuel purification,²¹ wastewater treatment,²⁴ and desalination.²² However, most of the imidazole-based modification materials in those studies are synthesized with complicated procedures and/or under harsh conditions.^{23,25,26} Meanwhile, these substances are usually immobilized on membrane via physical blending.^{21,22,25} A problem frequently encountered in this approach is that modification materials leach into the solution due to a lack of affinity between modification material and membrane. Other approaches in the synthesis of imidazole-derivative functionalized membrane are achieved via multistep reactions²⁷ or free radical initiated reaction.²⁵ Some require treatment at high temperatures.²³ Such conditions are prone to cause defects on the resultant membrane surface.

To address the aforementioned problems, we propose novel imidazole-based modification materials synthesized through a single-step reaction and chemically immobilize them on membrane surface via a fast one-step reaction under mild conditions. These imidazole-based compounds were specially designed with distinct properties to identify the

factors affecting membrane separation performance. We previously reported that removal of unwanted species from water via FO separation can be enhanced through ionic grafting of membranes without sacrificing the water permeation flux.²⁰ Ionic grafts imbue membrane with desired physicochemical properties which are most likely responsible for this improvement. Here, we use this mechanism to purify dye-containing wastewater in FO processes via the novel FO membranes developed through chemical modifications. Specifically, we design two grafting agents both comprising (aminopropyl)imidazole to chemically functionalize the ready-made membranes. ~~The We will elaborate on the advantages in the synthesis strategies of the imidazole-based modifiers and membranes will be elaborated.~~ The impact of the differences in chemical structure and property of membrane modifiers on the interaction with both dye and water molecules will be elucidated. Membrane renewability and performance in dye removal and wastewater remediation will be demonstrated.

MATERIALS AND METHODSMaterials and Methods

Synthesis and Characterizations of Imidazole Derivatives

The novel imidazole-based materials used for membrane modification were synthesized by a one-step reaction under mild conditions. The detailed information ~~was~~ provided in the ~~supporting information~~Supporting Information (SI).

Preparation of the PES Substrate and FO Membranes

A dope solution was prepared and deployed to fabricate the PES substrate ~~by~~ using an established method.²⁸ The TFC PA FO membranes were fabricated via interfacial polymerization.¹⁹ To modify the ready-made FO membrane, the surface of nascent PA layer was covered with solutions comprising different concentrations of the novel modification compounds (0.5 wt.%, 1.0 wt.%, 2.0 wt.%, and 3.0 wt.%) for varying ~~time at~~times of 5 min, 10 min, 20 min, and 40 min, respectively. After that, the resultant membranes were rinsed fully with DI water followed by stored in water bath for further experiments. The experimental details ~~were~~ included in the ~~SI~~Supporting Information.

Membrane Characterizations

The physicochemical and structural properties, morphological features, and mass transfer behavior of the membranes were studied systematically. The detailed procedures ~~were~~ disclosed in the ~~SI~~Supporting Information.

FO Processes. FO experiments were all performed on a custom-built FO set-up (Suzhou Faith & Hope Membrane Technology Co. Ltd.). Each membrane module in the FO system was tested at two different orientations: (1) pressure retarded osmosis (PRO) mode where the draw solution flows against the membrane selective layer and (2) FO mode where the draw solution flows against the porous support layer. Water flux (J_w , $L m^{-2} h^{-1}$, abbreviated as LMH) and solute loss (J_s/J_w), i.e., the ratio of salt flux (J_s , $gm^{-2} h^{-1}$, abbreviated as gMH) to water flux, were used to evaluate the performance of an FO membrane. The detailed information was given in the ~~SI~~.

FO Processes

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RESULTS AND DISCUSSIONResults and Discussion

Chemical Structure of Ionic Grafts

A key requirement of our strategy to employ modifiers of imidazole derivatives that enhance the separation performance of polymer membranes is a facile synthesis procedure. As shown in Figure 1, this was achieved via efficient one-step reactions at mild conditions. NMR and FTIR spectroscopy were employed here to reveal the chemical structures of new compounds synthesized in this work.

Figure 1. ~~The synthesis~~Synthesis scheme of IM-NH₂ and IL-NH₂ modification materials.

The ^1H NMR resonances for protons from the imidazole ring in IL-NH₂ ($\delta = 7.49$ – 8.82 ppm) were downfield shifted compared to those in IM-NH₂ ($\delta = 6.96$ – 7.59 ppm) (Figures 2(a) and 2(b)).^{29,30} This was mainly attributed to the electron deficiency resulting from the quaternization of imidazole ring in IL-NH₂. Likewise, the proton resonances of the side chain of propyl amine in IL-NH₂ ($\delta = 2.29$ – 4.36 ppm) were downfield shifted relative to those of IM-NH₂ ($\delta = 1.78$ – 3.92 ppm). This was due to the stronger electron-withdrawing behaviour of the positively charged imidazole ring in the former compound. A resonance at 3.88 ppm was also observed in IL-NH₂ which was from the methyl group connecting to the N atom of the imidazole ring.^{29,30} Proton resonances in the ^1H NMR spectra were consistent with the proposed structures. FTIR analyses revealed that the peak centered at 2900 cm^{-1} , correlated to stretching vibration of $-\text{CH}_2-/-\text{CH}_3-$, was present in the spectra of both compounds (Figure 2(e)). The higher absorbance intensity at 2900 cm^{-1} of IL-NH₂ was likely to be due to the additional methyl group connecting to the imidazole ring. There was a red-shift in the absorption of the imidazole ring from 620 cm^{-1} in IM-NH₂ to 580 cm^{-1} in IL-NH₂ resulting from the reduced electron cloud density in the imidazole ring of the latter due to quaternization.²⁰ We also observed peaks centered at 3400 cm^{-1} that corresponded to the amine functional group in both compounds synthesized here. These amine groups were crucial for the subsequent covalently grafting of these compounds on to the PA surface via an amidation reaction for membrane modification.

Figure 2. (a) The NMR spectra of IL-NH₂; (b) The NMR spectra of IM-NH₂; (c) The FTIR spectra of IL-NH₂ and IM-NH₂.

Membrane Modification and Characterization

TFC membranes studied here were fabricated by depositing a dense PA layer on to a PES support through interfacial polymerization between MPD and TMC.^{28,31} Excessive acyl chloride groups from the unreacted TMC on the nascent PA layer were utilized to react with the primary amino groups which were present in both IM-NH₂ and IL-NH₂ (Figure 3). This acylation reaction was the primary mechanism underpinning the grafting of functional modifiers on to the polymer membrane. Unlike other harsh modification techniques such as crosslinking via Schiff-base reaction or Michael addition reaction which was usually catalyzed by a strong base or acid in organic solvents,^{19,32,33} our approach minimized damage to the membrane surface. Our proposed technique enhanced membrane properties and structures benefiting FO processes, as shown in the following sections.

Figure 3. Preparation processes of the pristine PA and modified FO membranes.

FTIR analyses revealed that the peak corresponding to unreacted acyl chlorides in the nascent PA layer (centered at 1780 cm^{-1}) disappeared when either IM-NH₂ or IL-NH₂ was introduced (Figure 4(a)). This was due to the amidation reaction between these functional groups with primary amines in both IM-NH₂ and IL-NH₂ compounds. This resulted in a significant intensification of peaks corresponding to amide groups centered at 1670 cm^{-1} .^{20,28} These findings clearly indicated the grafting of our novel imidazole-based compounds onto the membrane surface. These chemical grafts did not alter surface porosity of dense PA layers as the average pore diameter on modified PA layers was retained at 0.3 nm, well within the FO range. As a result, FO water permeability of these modified membranes was retained but salt rejection was significantly enhanced (Figure 4(b), and Table S1), overcoming the well-established trade-off between membrane surface modification and molecular transport.¹⁹ This was because IM-NH₂ or IL-NH₂ formed a loose layer on PA surface according to the SEM analysis below which did not adversely affect water transport but increased repulsion between the modified surface and solutes. Meanwhile IM-NH₂ and IL-NH₂ grafts enhanced surface hydrophilicity as water contact angles of membranes were reduced from 68° of the nascent PA membrane to 49° and 35° of the IM-NH₂ and IL-NH₂ modified membranes, respectively (Figure 4(c)). Grafting IL-NH₂ and IM-NH₂ compounds on the PA surface imbued the membrane with more hydrophilic amide groups ($-\text{CONH}-$), and hence improved the membrane hydrophilicity. There is an ionic imidazole ring in IL-NH₂ which made it more efficient in improving the membrane hydrophilicity, leading to a larger decline in the water contact angle. These grafts also impacted on membrane surface electronegativity (Figure 4(d)). The nascent PA membrane had an electronegative surface due to the deprotonation of carboxylic acid groups resulting from the hydrolysis of residual acyl chloride groups. Immobilizing the imidazole derivatives on membrane surface consumed the unreacted acyl chloride groups and simultaneously introduced cationic imidazolium rings to the membrane surfaces; the electronegative PA membrane surface was subsequently transformed into electron-positive surfaces. This also indirectly validated the covalent bonding of imidazole derivatives onto PA membranes.

Figure 4. Comparisons of (a) FTIR spectra and (b) pore size distribution of the PES substrate, pristine PA, and modified membranes; (c) water contact angle of the PA and modified membranes under different modification conditions (when concentration varied, the reaction time was 20 min; when the contact time varied, the modifier concentration was 1.0 wt %); (d) the zeta potential of the PA and modified FO membranes.

Introduction of IM-NH₂ and IL-NH₂ also impacted the surface morphology of membrane. Through SEM and AFM micrographs (Figures 5 and 6), we observed that the distinctive ridge-and-valley morphology of a typical PA membrane produced from interfacial polymerization^{34,35} was transformed into a compact leaf-like layer with imidazole grafts. Variations in graft content did not alter the morphology, possibly due to the formation of an ultrathin modification layer (Figure 5).

Figure 5. SEM images of the PA and modified membranes.

Changes in the surface morphology were quantified by the average roughness (R_a) and the root mean square roughness (R_q) estimated by using an AFM (Figure 6). Both R_a and R_q values were changed upon chemical modification. Surface roughness was reduced first as the graft content increased from 0 to 2.0 wt.% but increased again with higher grafting content. This was because with IM-NH₂ or IL-NH₂ grafted on to the PA membrane surface, thin modification layers started to build up, essentially filling up the “valleys” and hence smoothing the initial rough surface of the nascent PA membrane. However, the grafting of more modifiers on these smoothed surfaces created a rough surface resulting from the loose arrangement of imidazole derivatives on the outermost layer of membrane surface, causing increased surface roughness. Smooth membrane surfaces were favorable for impeding fouling that consequently improved FO separation performance over time. ^{28,36,37}

Figure 6. (a) The average roughness (R_a , nm) and root mean square roughness (R_q , nm) of the PA and modified membranes under the optimal modification conditions; (b) R_a of the IL-NH₂ membrane fabricated at varied IL-NH₂ concentrations.

Separation Performances of the Modified Membranes

The separation performances of the modified membranes were studied as a function of modifier concentration and modification duration (Figure 7). Higher modifier content and longer modification durations resulted in a trend of

increasing first and then decreasing in water flux but smaller solute loss under both FO and PRO modes (Figures 7(a) & 7(b)). This trend was associated with the changes in membrane properties. Grafting the imidazole derivatives onto membrane surface increased not only the hydrophilicity but also the thickness of membrane selective layer (Figures 4(e) & 5). The former contributed to increased water permeability whereas the latter reduced it due to the increase transfer resistance. The combined effects made the water fluxes of membrane exhibiting a rise–fall trend. On the other hand, the increased thickness and surface potential also enhanced the resistance of reverse salt diffusion and mutual repulsion between salt and membrane surface, both leading to an enhanced salt rejection. Consequently, the optimal separation performances of the individual IM-NH₂ and IL-NH₂ modified membranes were achieved with a 20-min modification process by using 1.0 wt.% of IM-NH₂ and 2.0 wt.% of IL-NH₂, respectively. Compared to the pristine PA membrane, the water fluxes of membranes modified with IM-NH₂ and IL-NH₂ were enhanced by 23% and 69%, achieving 11.0 and 15.0 LMH in PRO mode, respectively. These flux enhancements were also observed with the ionic membranes in FO mode, albeit on a slightly larger scale (Figure 7(e)). Notably, the IL-NH₂ modified membrane exhibited the best performance with a higher water permeation rate and smaller reverse solute flux (Figure 7(d)). The ionic imidazole ring in IL-NH₂ was key to a more hydrophilic and positively charged membrane surface, underpinning the more significant improvements in FO performance.

Figure 7. FO performance of the IL-NH₂ modified membrane as a function of (a) modification time (the concentration of IL-NH₂ is fixed at 1.0 wt.%), and (b) IL-NH₂ concentration (the modification time is fixed at 20 min); (c) and (d) comparison of FO performance of the pristine PA and modified membranes under the optimal modification conditions. Experimental conditions: DI water as the feed; 0.5 M MgCl₂ as the draw solution.

The separation performances of these membranes were further evaluated under different conditions by varying membrane orientation, draw solute category, and concentration (Figure 8).

Figure 8. FO performance comparisons of the original and modified FO membranes: (a) and (c) comparison of water flux; (b) and (d) comparison of reverse salt flux. DI water as the feed.

Regardless of operating mode, the water fluxes of all FO membranes studied here were enhanced with higher salt content in the draw solution. This was ascribed to a larger net driving force induced by a larger ~~trans-membrane~~ ~~transmembrane~~ pressure differential at a higher concentration of the draw solution. ~~Due to~~ ~~Because of~~ the effects caused by internal concentration polarization (ICP), the water fluxes of these membranes during FO operation were lower than those generated under the PRO mode. When draw solution flowed against the porous support layer (FO mode), molecules of draw solutes diffused into the membrane interior in view of the much smaller size of the hydrated radii of ionic species in draw solution (Na^+ 0.36 nm, Mg^{2+} 0.43 nm),³⁸ increasing the resistance to water flow and thus reducing the water transfer rate. Additionally, MgCl_2 as a draw solution generated a higher water flux when compared to a NaCl -based draw solution. This could be attributed to the Van't Hoff law where solutes that dissociated more ionic species would generate higher osmotic pressure at the same molar concentration.³⁹ Regardless of the type of draw solution employed in our experiments, the IL-NH₂-modified membrane demonstrated the best water transport properties ~~amongst~~ ~~among~~ all membranes studied here. This was due to the most hydrophilic and smoothest surface (Figures 4 (c) & (d) and 6) that best benefited water transportation. Meanwhile, the most electropositive feature of the IL-NH₂-modified membrane enhanced the electrostatic repulsion between membrane and draw solutes, leading to a comparable or smaller solute loss in FO processes. Furthermore, the optimal separation performances of the IL-NH₂ immobilized membrane outperformed other polymer membranes reported elsewhere (Table 1).⁴⁰⁻⁴³ The superior FO separation performances of the IL-NH₂-modified membranes make it potentially benefit the isolation of molecular dyes from water.

Table 1. FO ~~performance comparisons~~ ~~Performance Comparisons~~ of the IL-NH₂-modified membrane-Modified Membrane with other materials-modified ~~Other Material-Modified~~ FO ~~membranes recently reported~~ ~~Membranes Recently Reported~~ in the literature.

FO Membrane	Draw solution (M)	Water flux (LMH)		Reverse salt flux (gMH)		Refs.
FO membrane	draw solution (M)	PRO	FO	PRO	FO	refs
IL-NH ₂ membrane	1.0	21.3 ^K 21.3 ± 0.7 ^T ± 0.7	18.7 ^K 18.7 ± 0.5 ^T ± 0.5	3.25 ^K 3.2 5 ± 0.4 ^T ± 0.4	3.48 ^K 3.4 8 ± 0.8 ^T ± 0.8	This work
	1.5	26.2 ^K 26.2 ± 1.1 ^T ± 1.1	22.5 ^K 22.5 ± 0.7 ^T ± 0.7	4.16 ^K 4.1 6 ± 0.5 ^T ± 0.5	4.26 ^K 4.2 6 ± 0.5 ^T ± 0.5	
	2.0	29.8 ^K 29.8 ± 1.0 ^T ± 1.0	24.5 ^K 24.5 ± 0.9 ^T ± 0.9	4.47 ^K 4.4 7 ± 0.7 ^T ± 0.7	4.64 ^K 4.6 4 ± 0.5 ^T ± 0.5	
NIPS membrane	1.0	15.5	9.4	7.9	4.0	43
TIPS membrane	1.0	28.4	16.2	13.8	7.1	43
AM-PES membrane	2.0	29.4	18.1	7.3	4.1	40
TFC1,PA/PES	1.0	—	11.0	—	—	41
TFC2,PA/PES	1.0	—	17	—	—	41
PAN/PSf TFC	1.0	12.6	—	11.6	—	42

Note: DI water and NaCl are the respective feed and draw solutions. NIPS: non-solvent induced phase separation; TIPS: thermally induced phase separation; AM-PES: A stands for acrylic acid, and M stands for acrylamide; PES: poly(ether sulfone), poly(ether sulfone); PA: polyamide; PSf: polysulfone; PAN: polyacrylonitrile.

Dye Removal via the IL-NH₂-Modified Membrane in FO

Using a cationic dye solution containing 20 – 100 ppm of Safranin O (Table S2), a widely used dye in the textile and dye industries, as the feed solution, and 2.0 M MgCl₂ as the draw solution, we evaluated the FO performance of both the pristine membrane and cationic membrane grafted with IL-NH₂ (Figure 9). The water flux of the cationic membrane was reduced by 21% when we changed the feed solution from DI water to a 100 ppm dye solution. This was due to a reduction in the effective osmotic pressure differential across the membrane, and membrane fouling by dyes present in the feed. Compared to the pristine membrane, the cationic IL-NH₂ membrane demonstrated a larger water permeation increment at a higher dye content. Immobilization of the cationic IL-NH₂ altered the membrane surface to become more hydrophilic, electropositive, and smoother (Figures 4 (e), 4 (d) & 5). This made the dye foulant less easily adhering to the membrane surface, enhancing the membrane fouling resistance and hence increasing water flux increment from 28% to 39% relative to the nascent PA membrane (Figure 9 (a)). The cationic imidazolium ring in IL-NH₂ on the membrane surface was key for rejecting cationic dyes via electrostatic repulsion. The same charges on both the target molecule and the cationic graft along with the reduction in roughness of the membrane selective layer minimized the build-up of dye molecules on the modified membrane surface and pores, efficiently improving the anti-fouling behavior of the modified membrane. Regardless of the surface properties of membrane, a complete dye retention (~ 100%) was achieved for both the PA and IL-NH₂-modified membranes against Safranin O dye in the studied ranges (Figure 9 (a)).

Figure 9. Performance comparison of the pristine and modified membranes: (a) Comparison of dye rejection and water flux in 30 min. (b) Comparison of water flux in 600 min. Experimental conditions: Safranin O solution (20 – 100 ppm) as feed solution, 2.0 M MgCl₂ as draw solution, FO mode. (c) Membrane fouling tests. Experimental conditions: Safranin O solution (100 ppm) as feed solution, 2.0 M MgCl₂ as draw solution, FO mode.

The water flux of the pristine PA membrane was reduced as a function of operating duration (Figure 9(b)). This obvious decline in water transport was due to severe membrane fouling as dye content built up on the membrane surface during the long-term operation. At higher dye concentrations, the reduction in initial water flux was even more pronounced due to a lower net driving force and more severe fouling propensity. Longer operation durations (up to 10 h) reduced the normalized flux of the nascent PA membrane from 100% to 75% against a dye solution with a 100 ppm initial concentration. By contrast, these drawbacks of the nascent PA membrane in dye-containing water treatment were overcome with the cationic IL-NH₂ graft. Regardless of the dye content, the IL-NH₂-modified membrane demonstrated a steady water reclamation performance during long-term operation and a slighter difference with the initial water flux. With a 100 ppm dye solution as the feed, the cationic IL-NH₂ membrane maintained a flux ratio of 90% of the initial water flux in 10 h (Figure 9(c)). Other than being more hydrophilic that led to a higher water flux, the more superior anti-fouling properties of the cationic membrane also prevented the buildup of dye content and formation of concentration polarization that could reduce water flux.

A 15-min physical washing protocol was applied to clean the membranes employed in these studies. Without the additional features provided by the functional IL-NH₂, the pristine PA membrane was less effective in treating dyeing wastewater during long-term FO operation. We were not able to fully recover the water flux of pristine membranes after the first dye removal cycle. This was because of the limitations of physical hydraulic washing to clean fouled membranes. In contrast, the water flux of the IL-NH₂-modified membrane was fully recovered and a slow loss in water flux was observed due to less fouling tendency. The mutual repulsion efficiently prevented dye foulants from depositing on the membrane surface or entrapped in the pores.^{1,9,44} The presence of IL-NH₂ graft clearly improved the anti-fouling properties of membrane.

Conclusions

We demonstrated the design of novel imidazole derivatives to imbue a traditional PA-PES TFC membrane with better properties for FO water reclamation from low concentration dye solutions. Through changes in the structure and property of our newly developed compounds, we elucidated the impact and importance of charges during the removal of dye compounds and inorganic salts. The presence of a positive charge was essential to create electrostatic repul-

sion that underpinned the rejection of cationic dyes, whilst the efficient control over the deposition of ultrathin modification layers enhanced surface hydrophilicity to improve water flux. These advantages of our newly developed membranes were harnessed to tackle one of the most complicated environmental issue—solutions containing low concentrations of pollutants. The novel cationic IL-NH₂ membrane could be potentially employed for the treatment of industrial wastewater containing positively-charged ions.

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Supporting Information

Supporting Information Available

Starting materials and chemicals; syntheses and characterizations of the imidazole derivatives; preparation of the PES substrate and FO membranes; membrane characterizations; FO processes.

Starting materials and chemicals; syntheses and characterizations of the imidazole derivatives; preparation of the PES substrate and FO membranes; membrane characterizations; FO processes (PDF)

Author Contributions These authors contribute J.G. and Q.Y. contributed equally to this work.

The authors declare no competing financial interest.

References

- (1) Ito, T.; Adachi, Y.; Yamanashi, Y.; Shimada, Y. Long-Term Natural Remediation Process in Textile Dye-Polluted River Sediment Driven by Bacterial Community Changes. *Water Res.* **2016**, *100*, 458–465. [10.1016/j.watres.2016.05.050](https://doi.org/10.1016/j.watres.2016.05.050).
- (2) Li, M.; Wang, X.; Porter, C. J.; Cheng, W.; Zhang, X.; Wang, L.; Elimelech, M. Concentration and Recovery of Dyes from Textile Wastewater Using a Self-Standing, Support-Free Forward Osmosis Membrane. *Environ. Sci. Technol.* **2019**, *53*, 3078–3086. [10.1021/acs.est.9b00446](https://doi.org/10.1021/acs.est.9b00446).
- (3) Sekar, S.; Surianarayanan, M.; Ranganathan, V.; MacFarlane, D. R.; Mandal, A. B. Choline-Based Ionic Liquids-Enhanced Biodegradation of Azo Dyes. *Environ. Sci. Technol.* **2012**, *46*, 4902–4908. [10.1021/es204489h](https://doi.org/10.1021/es204489h).
- (4) Kyzas, G.; Lazaridis, N.; Kostoglou, M. Modelling the Effect of Pre-Swelling on Adsorption Dynamics of Dyes by Chitosan Derivatives. *Chem. Eng. Sci.* **2012**, *81*, 220–230. [10.1016/j.ces.2012.07.007](https://doi.org/10.1016/j.ces.2012.07.007).
- (5) Natarajan, S.; Bajaj, H. C.; Tayade, R. J. Recent Advances Based on the Synergetic Effect of Adsorption for Removal of Dyes from Waste Water Using Photocatalytic Process. *J. Environ. Sci.* **2018**, *65*, 201–222. [10.1016/j.jes.2017.03.011](https://doi.org/10.1016/j.jes.2017.03.011).
- (6) Yao, Y.; Wang, L.; Sun, L.; Zhu, S.; Huang, Z.; Mao, Y.; Lu, W.; Chen, W. Efficient Removal of Dyes Using Heterogeneous Fenton Catalysts Based on Activated Carbon Fibers with Enhanced Activity. *Chem. Eng. Sci.* **2013**, *101*, 424–431. [10.1016/j.ces.2013.06.009](https://doi.org/10.1016/j.ces.2013.06.009).
- (7) Katheresan, V.; Kansedo, J.; Lau, S. Y. Efficiency of Various Recent Wastewater Dye Removal Methods: A Review. *J. Environ. Chem. Eng.* **2018**, *6*, 4676–4697. [10.1016/j.jece.2018.06.060](https://doi.org/10.1016/j.jece.2018.06.060).
- (8) Abdi, G.; Alizadeh, A.; Zinadini, S.; Moradi, G. Removal of Dye and Heavy Metal Ion Using a Novel Synthetic Polyethersulfone Nanofiltration Membrane Modified by Magnetic Graphene Oxide/Metformin Hybrid. *J. Membr. Sci.* **2018**, *552*, 326–335. [10.1016/j.memsci.2018.02.018](https://doi.org/10.1016/j.memsci.2018.02.018).
- (9) Cheng, S.; Oatley, D. L.; Williams, P. M.; Wright, C. J. Characterisation and Application of a Novel Positively Charged Nanofiltration Membrane for the Treatment of Textile Industry Wastewaters. *Water Res.* **2012**, *46*, 33–42. [10.1016/j.watres.2011.10.011](https://doi.org/10.1016/j.watres.2011.10.011).
- (10) Cao, X.-L.; Yan, Y.-N.; Zhou, F.-Y.; Sun, S.-P. Tailoring Nanofiltration Membranes for Effective Removing Dye Intermediates in Complex Dye-Wastewater. *J. Membr. Sci.* **2020**, *595*, 117476. [10.1016/j.memsci.2019.117476](https://doi.org/10.1016/j.memsci.2019.117476).
- (11) Zhu, J.; Tian, M.; Hou, J.; Wang, J.; Lin, J.; Zhang, Y.; Liu, J.; Van der Bruggen, B. Surface Zwitterionic Functionalized Graphene Oxide for a Novel Loose Nanofiltration Membrane. *J. Mater. Chem. A* **2016**, *4*, 1980–1990. [10.1039/C5TA08024J](https://doi.org/10.1039/C5TA08024J).

- (12) Xia, Q.-C.Q.-C.; Yang, W.-J.W.-J.; Fan, F.; Ji, M.; Wang, Y.; Wang, Z.-Y.Z.-Y.; Cao, X.-L.X.-L.; Xing, W.; Sun, S.-P.S.-P. Encapsulated Polyethyleneimine Enables Synchronous Nanostructure Construction and In Situ Functionalization of Nanofiltration Membranes. *Nano. Lett.* **2020**, *20*, 81588185–819210.1021/acs.nanolett.0c03288.
- (13) Liao, X. L.; Zhang, W. H.; Ge, Q. A Cage-Like Supramolecular Draw Solute that Promotes Forward Osmosis for Wastewater Remediation and Source Recovery. *J. Membr. Sci.* **2020**, *600*, 1117862, 1117862–1010.1016/j.memsci.2020.1117862.
- (14) Cath, T.; Childress, A.; Elimelech, M. Forward Osmosis: Principles, Applications, and Recent Developments. *J. Membr. Sci.* **2006**, *281*, 70–8710.1016/j.memsci.2006.05.048.
- (15) Saren, Q.; Qiu, C. Q.; Tang, C. Y. Synthesis and Characterization of Novel Forward Osmosis Membranes Based on Layer-By-Layer Assembly. *Environ. Sci. Technol.* **2011**, *45*, 5201–520810.1021/es200115w.
- (16) Zhao, P.; Gao, B.; Xu, S.; Kong, J.; Ma, D.; Shon, H. K.; Yue, Q.; Liu, P. Polyelectrolyte-Promoted Forward Osmosis Process for Dye Wastewater Treatment - Exploring the Feasibility of Using Polyacrylamide as Draw Solute. *Chem. Eng. J.* **2015**, *264*, 32–3810.1016/j.cej.2014.11.064.
- (17) Perreault, F.; Jaramillo, H.; Xie, M.; Ude, M.; Nghiem, L. D.; Elimelech, M. Biofouling Mitigation in Forward Osmosis Using Graphene Oxide Functionalized Thin-Film Composite Membranes. *Environ. Sci. Technol.* **2016**, *50*, 5840–584810.1021/acs.est.5b06364.
- (18) Bell, E. A.; Holloway, R. W.; Cath, T. Y. Evaluation of Forward Osmosis Membrane Performance and Fouling During Long-term Osmotic Membrane Bioreactor Study. *J. Membr. Sci.* **2016**, *517*, 1–1310.1016/j.memsci.2016.06.014.
- (19) Xu, W.; Chen, Q.; Ge, Q. Recent Advances in Forward Osmosis (FO) Membrane: Chemical Modifications on Membranes for FO Processes. *Desalination* **2017**, *419*, 101–11610.1016/j.desal.2017.06.007.
- (20) Chen, Y.; Ge, Q. A bifunctional Zwitterion that Serves as Both a Membrane Modifier and a Draw Solute for Forward Osmosis Wastewater Treatment. *ACS Appl. Mater. Inter. Interfaces* **2019**, *11*, 36118–3612910.1021/acsami.9b13142.
- (21) Rdzanek, P.; Marszałek, J.; Kamiński, W. Biobutanol Concentration by Pervaporation Using Supported Ionic Liquid Membranes. *Sep. Purif. Technol.* **2018**, *196*, 124–13110.1016/j.seppur.2017.10.010.
- (22) Zhang, J.; Qin, Z.; Yang, L.; Guo, H.; Han, S. Activation Promoted Ionic Liquid Modification of Reverse Osmosis Membrane Towards Enhanced Permeability for Desalination. *J. Taiwan Inst. Chem. Eng.* **2017**, *80*, 25–3310.1016/j.jtice.2017.07.027.
- (23) Liu, B.; Zhou, R.; Bu, N.; Wang, Q.; Zhong, S.; Wang, B.; Kita, Hidetoshi, HK. Room-Temperature Ionic Liquids Modified Zeolite SSZ-13 Membranes for CO₂/CH₄ Separation. *J. Membr. Sci.* **2017**, *524*, 12–1910.1016/j.memsci.2016.11.004.
- (24) Hu, F.; Fang, C.; Wang, Z.; Liu, C.; Zhu, B.; Zhu, L. Poly (N-vinyl imidazole) gel Composite Porous Membranes for Rapid Separation of Dyes Through Permeating Adsorption. *Sep. Purif. Technol.* **2017**, *188*, 1–1010.1016/j.seppur.2017.06.024.
- (25) Reis, R.; Dumée, L.-P.L. P.; He, L.; She, F.; Orbell, J.-D.J. D.; Winther-Jensen, B.; Duke, M.-C.M. C. Amine Enrichment of Thin-Film Composite Membranes via Low Pressure Plasma Polymerization for Antimicrobial Adhesion. *ACS Appl. Mater. Inter. Interfaces* **2015**, *7*, 14644–1465310.1021/acsami.5b01603.
- (26) Zhao, Z.; Zhang, A.; Wang, X.; Lu, P.; Ma, H. Controllable Modification of Polymer Membranes by LDDLT Plasma Flow: Grafting Acidic ILs into PPF Membrane for Catalytic Performance. *J. Membr. Sci.* **2018**, *553*, 99–11010.1016/j.memsci.2018.02.044.
- (27) Davari, S.; Omidkhan, M.; Abdollahi, M. Improved Antifouling Ability of Thin Film Composite Polyamide Membrane Modified by a pH-Sensitive Imidazole-Based Zwitterionic Polyelectrolyte. *J. Membr. Sci.* **2018**, *564*, 788–79910.1016/j.memsci.2018.07.050.
- (28) Xu, W.; Ge, Q. Novel Functionalized Forward Osmosis (FO) Membranes for FO Desalination: Improved Process Performance and Fouling Resistance. *J. Membr. Sci.* **2018**, *555*, 507–51610.1016/j.memsci.2018.03.054.
- (29) Yen, S. K.; Haja, N. F. M.; Su, M.; Wang, K. Y.; Chung, T.-S. Study of Draw Solutes Using 2-Methylimidazole-Based Compounds in Forward Osmosis. *J. Membr. Sci.* **2010**, *364*, 242–25210.1016/j.memsci.2010.08.021.
- (30) Xu, K.; Thieme, N.; Breit, B. Atom-Economic, Regiodivergent, and Stereoselective Coupling of Imidazole Derivatives with Terminal Allenes. *Angew. Chem.* **2014**, *126*, 2194–219710.1002/ange.201309126.

- (31) Liu, Z.; Qi, L.; An, X.; Liu, C.; Hu, Y. Surface Engineering of Thin Film Composite Polyamide Membranes with Silver Nanoparticles Through Layer-By-Layer Interfacial Polymerization for Antibacterial Properties. *ACS Appl. Mater. Interf.* **2017**, *9*, 40987–40997 [10.1021/acsami.7b12314](#).
- (32) Hegab, H. M.; Elmekawy, A.; Barclay, T. G.; Michelmoro, A.; Zou, L.; Saint, C. P.; Ginic-Markovic, M. Fine-Tuning the Surface of Forward Osmosis Membranes via Grafting Graphene Oxide: Performance Patterns and Biofouling Propensity. *ACS Appl. Mater. Interf.* **2015**, *7*, 18004–18016 [10.1021/acsami.5b04818](#).
- (33) Romero-Vargas Castrillón, S.; Lu, X.; Shaffer, D. L.; Elimelech, M. Amine Enrichment and Poly(ethylene glycol) (PEG) Surface Modification of Thin-Film Composite Forward Osmosis Membranes for Organic Fouling Control. *J. Membr. Sci.* **2014**, *450*, 331–339 [10.1016/j.memsci.2013.09.028](#).
- (34) Duong, P. H.; Chisca, S.; Hong, P. Y.; Cheng, H.; Nunes, S. P.; Chung, T. S. Hydroxyl Functionalized Polytriazole-Co-Polyoxadiazole as Substrates for Forward Osmosis Membranes. *ACS Appl. Mater. Interf.* **2015**, *7*, 3960–3973 [10.1021/am508387d](#).
- (35) Wu, X.; Shaibani, M.; Smith, S. J. D.; Konstas, K.; Hill, M. R.; Wang, H.; Zhang, K.; Xie, Z. Microporous Carbon from Fullerene Impregnated Porous Aromatic Frameworks for Improving the Desalination Performance of Thin Film Composite Forward Osmosis Membranes. *J. Mater. Chem. A* **2018**, *6*, 11327–11336 [10.1039/C8TA01200H](#).
- (36) Chuang, Y. M.; Jack, K. S.; Cheng, H. H.; Whittaker, A. K.; Blakey, I. Using Directed Self Assembly of Block Copolymer Nanostructures to Modulate Nanoscale Surface Roughness: Towards a Novel Lithographic Process. *Adv. Funct. Mater.* **2013**, *23*, 173–183 [10.1002/adfm.201200564](#).
- (37) Valtiner, M.; Kristiansen, K.; Greene, G. W.; Israelachvili, J. N. Effect of Surface Roughness and Electrostatic Surface Potentials on Forces Between Dissimilar Surfaces in Aqueous Solution. *Adv. Mater.* **2011**, *23*, 2294–2259 [10.1002/adma.201003709](#).
- (38) Nightingale, E. R. Phenomenological Theory of Ion Solvation. Effective Radii of Hydrated Ions. *J. Phys. Chem.* **1959**, *63*, 1381–1387 [10.1021/j150579a011](#).
- (39) Lewis, G. N. The Osmotic Pressure of Concentrated Solutions, and the Laws of the Perfect Solution. *J. Am. Chem. Soc.* **1908**, *30*, 668–683 [10.1021/ja01947a002](#).
- (40) Khorshidi, B.; Bhinder, A.; Thundat, T.; Pernitsky, D.; Sadrzadeh, M. Developing High Throughput Thin Film Composite Polyamide Membranes for Forward Osmosis Treatment of SAGD Produced Water. *J. Membr. Sci.* **2016**, *511*, 29–39 [10.1016/j.memsci.2016.03.052](#).
- (41) Qiu, M.; Wang, J.; He, C. A Stable and Hydrophilic Substrate for Thin-Film Composite Forward Osmosis Membrane Revealed by In-Situ Cross-Linked Polymerization. *Desalination* **2018**, *433*, 1–9 [10.1016/j.desal.2018.01.021](#).
- (42) Shokrollahzadeh, S.; Tajik, S. Fabrication of Thin Film Composite Forward Osmosis Membrane Using Electrospun Polysulfone/Polyacrylonitrile Blend Nanofibers as Porous Substrate. *Desalination* **2018**, *425*, 68–76 [10.1016/j.desal.2017.10.017](#).
- (43) Wu, Q. Y.; Xing, X. Y.; Yu, Y.; Gu, L.; Xu, Z. K. Novel Thin Film Composite Membranes Supported by Cellulose Triacetate Porous Substrates for High-Performance Forward Osmosis. *Polymer* **2018**, *153*, 68150–74160 [10.1016/j.polymer.2018.08.017](#).
- (44) An, A. K.; Guo, J.; Jeong, S.; Lee, E. J.; Tabatabai, S. A. A.; Leiknes, T. High Flux and Antifouling Properties of Negatively Charged Membrane for Dyeing Wastewater Treatment by Membrane Distillation. *Water Res.* **2016**, *103*, 362–371 [10.1016/j.watres.2016.07.060](#).