Poly(Homopiperazine–Amide) Thin-Film Composite Membrane for Nanofiltration of Heavy Metal Ions

Syed Ibrahim, Mahdi Mohammadi Ghaleh, Arun M. Isloor,*, Mona Bavarian, and Siamak Nejati*

ABSTRACT: The development of membrane-based technologies for the treatment of wastewaters and resources containing heavy metal ions is in high demand. Among various technologies, nanofiltration (NF) membranes are attractive choices, and the continuous development of novel materials to improve the state-of-the-art NF membranes is highly desired. Here, we report on the synthesis of poly(homopiperazine–amide) thin-film composite (HTFC)-NF membranes, using homopiperazine (HP) as a monomer. The surface charge, hydrophilicity, morphology, cross-linking density, water permeation, solute rejection, and antifouling properties of the fabricated NF membranes were evaluated. The fabricated HTFC NF membranes demonstrated water permeability of 7.0 ± 0.3 L/(m² h bar) and rejected Na₂SO₄, MgSO₄, and NaCl with rejection values of 97.0 ± 0.6, 97.4 ± 0.5, and 23.3 ± 0.6%, respectively. The membranes exhibit high rejection values of 98.1 ± 0.3 and 96.3 ± 0.4% for Pb²⁺ and Cd²⁺ ions, respectively. The fouling experiment with humic acid followed by cross-flow washing of the membranes indicates that a flux recovery ratio (FRR) of 96.9 ± 0.4% can be obtained.

1. INTRODUCTION

The deterioration and contamination of surface and ground-water resources by heavy metal ions mandate the need for advanced remediation technologies.1,2 Due to the hazardous impact of heavy metal ions on human health, complete removal of these ions from water resources is of critical importance.

The term “heavy metals” refers to elements with a specific gravity greater than 5.0 and atomic weight between 63.5 and 200.6 amu.3 Among various heavy metal contaminants, lead and cadmium are frequently detected in industrial wastewater.4 The current manufacturing schemes for car batteries, paints, fertilizers, pigments, etc., are among the main sources of these contaminants in water supplies. The overexposure of humans and animals to these metal ions can cause severe health problems. According to the World Health Organization, the maximum contaminant level (MCL) of lead in drinking water is 15 ppb. It is reported that the presence of 10 ppb of lead in drinking water could cause cognitive impairment.6 Furthermore, the intake of drinking water contaminated with lead above MCL is reported to be damaging to the kidneys, liver, and both nervous and reproductive systems. Similarly, there are serious concerns about the potential carcinogenic effect of cadmium on human health.7 Consequently, high demand exists for the development of schemes that allow for reducing the concentration of heavy metal ions in water resources. Chemical precipitation, ion exchange, flocculation, and electrochemical treatment are the conventional methods for treating water resources contaminated with heavy metal ions.7–9 However, all of these methods have their limitations. For instance, the chemical precipitation method is associated with the production of a large quantity of sludge and toxic fumes; it is suitable only for wastewater containing a high concentration of heavy metals.10 The low efficacy (~60–90%), the high cost of resin, and the difficulties involved with the regeneration of used resin make the ion-exchange process less viable for heavy metal removal.11

Currently, membrane-based purification is the most promising and scalable approach for the removal of heavy metal ions from contaminated water resources. Among all of the membrane-based techniques, reverse osmosis (RO) and nanofiltration (NF) are considered as the state-of-the-art technologies for water purification and desalination. NF plays a vital role in wastewater purification and desalination because it can be considered as the intermediate stage between RO and ultrafiltration (UF).12 Compared to RO, NF operates at lower pressures and exhibits complete rejection of the solute in the range of 100–1000 Da.13

Received: August 22, 2020
Accepted: October 12, 2020
Published: October 26, 2020
Recently, applications of NF have been extended from desalination to the removal of heavy metal ions, dyes, pharmaceutical waste, and pesticides from impaired water resources. The state-of-the-art NF membranes are thin-film composite (TFC) membranes, prepared via interfacial polymerization (IP). A TFC membrane consists of an active polyamide (PA) layer, in situ polymerized on a UF or microfiltration (MF) membrane. The TFC performance in NF primarily depends on the quality of the PA layer, which controls the permeability and solute rejection of the membrane. The properties of the PA layer can be adjusted by the proper choice of support, monomer miscibility of phases, reaction time, temperature, and post-treatment. Among these parameters, the selection of monomer and post-treatment is considered as a facile strategy to improve the TFC NF membrane. In the fabrication of TFC NF membranes for heavy metal removal, monomers such as m-phenylenediamine (MPD), polyethylenimine (PEI), piperazine (PIP), chitosan, poly(2-methacryloyloxyethyl phosphorylcholine-co-2-aminoethyl methacrylate), and poly(amidoamine) (PAMAM) and post-treatment using PEI are reported. The chlorine resistance of the membrane prepared by aliphatic and aromatic amines was evaluated. It was observed that the TFC membrane exhibited reduced water permeability and antifouling property of the TFC membrane. In another study, the chlorine resistance of the TFC membrane prepared by aliphatic and aromatic amines was evaluated. It was observed that the TFC membrane prepared with HP exhibited improved chlorine resistance than MPD. The increased chlorine resistance was attributed to the reduced basicity of HP compared to MPD. Furthermore, the preparation of TFC and thin-film nanocomposite (TFN) membranes using HP as an amine source is also patented for NaCl and Na2SO4 removal and organic solvent nanofiltration. However, no studies were performed to evaluate the heavy metal removal and antifouling property of the TFC membranes prepared using HP as a monomer.

In this study, we report on the synthesis of poly-(homopiperazine–amide) TFC (HTFC) nanofiltration (NF) membranes by reacting homopiperazine (HP) and trimesoyl chloride (TMC) at the aqueous–organic interface. The as-prepared HTFC NF membranes were further post-treated with ethylenediamine (EDA) in isopropanol alcohol (IPA) to fine-tune the HTFC NF membrane surface properties. To the best of our knowledge, heavy metal ion removal and antifouling properties of post-treated poly(homopiperazine–amide) TFC nanofiltration membranes have not been studied yet. The effect of post-treatment time on the NF membrane permeability, surface roughness, hydrophilicity, and heavy metal ion rejection was examined. Also, the antifouling property of the HTFC NF membranes was characterized using humic acid (HA) as a model foulant in the cross-flow filtration mode.

2. RESULTS AND DISCUSSION

2.1. Chemical Characterization of HTFC Membranes.
To confirm the chemistry of HTFC membranes, we characterized the membranes with attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR). Figure 1A presents the ATR-FTIR spectra of the PSF substrate and the HTFC membranes. All of the HTFC membranes exhibited peaks at 2967, 1293, 1242, and 1150 cm⁻¹, attributed to the characteristic aromatic C–H stretch, S=O asymmetric stretch, C=O–C stretch, and S=O symmetric stretch of the PSF support, respectively. Comparing the spectra of PSF and HTFC membranes, a new peak located at ~1625 cm⁻¹ in the FTIR spectra of all of the HTFC samples was observed. This peak was ascribed to the C=O stretching vibration of the amide group (amide I). This observation confirms the presence of the PA layer on the PSF substrate. The broad peaks located at ~3401 and 1725 cm⁻¹ were ascribed to the –OH and C=O stretches of the residual carboxylic acid groups, respectively.

We performed XPS measurements to analyze the elemental composition and cross-linking density of the formed PA layer on the PSF support. Figure 1B shows the survey spectra of the control and fabricated HTFC membranes. The main features of the spectra are the sharp peaks assigned to C 1s, N 1s, and O 1s. The small peak around 497 eV is associated with Na KLL from sodium hydroxide, which was used to neutralize the as-formed HCl during IP. The high-resolution C 1s, N 1s, and O 1s core electron spectra of the sample before (HTFC-IPA) and after (HTFC-3) post-treatment can be found in Figure 2; the XPS spectra for all samples can be found in the Supporting Information. The C 1s core electron spectrum of all samples shows four peaks centered at 284.3, 285.3, 287.2, and 291.2 eV ascribed to C=O, C=O, C=O, and shake-up features, respectively. Three distinct peaks also were identified in N 1s core electron spectra of different samples, centered at 398.2, 399.2, and 400 eV. These peaks were attributed to C=NH/
CNH₂, N−C, and N−C=O species, respectively. The O 1s core electron spectra show two distinct peaks centered at 530.8 and 532.3 eV. These peaks are assigned to C=O and O−H species, respectively.

Elemental analysis was used to find the degree of cross-linking for samples before and after EDA treatment. For the untreated samples (control and HTFC-IPA), the degree of cross-linking (X) was directly correlated to the O/N ratio. For the detailed calculations, see Figure S2, Supporting Information. Table 1 includes the surface elemental composition (atomic %), O/N ratios, as well as the estimated degree of cross-linking for samples before and after EDA treatment. The O/N ratios for the control and HTFC-IPA membranes were about 1.0 and 1.24, respectively. Thus, by correlating the O/N to the cross-linking density, the control membrane exhibited a degree of cross-linking of 58.3%. However, this value fell to 40.3% after the sample was treated with IPA (HTFC-IPA). This reduction in the degree of cross-linking was attributed to the removal of unreacted monomers and hydrolysis of the acid chloride group in the PA layer by the water-miscible solvent IPA, which reduced further cross-linking during heat treatment.

From the XPS elemental analysis, it can also be deduced that the O/N ratio decreases from 1.25 (HTFC-1) to 0.96 (HTFC-3) post-treatment with EDA.

Table 1. XPS Elemental Composition of HTFC Membranes

| Membrane   | Atomic concentration (%) | O/N ratio | X (%) | XEDA (%) |
|------------|--------------------------|-----------|-------|----------|
| Control    | C 1s 72.72 ± 0.03, O 1s 13.4 ± 0.02, N 1s 13.43 ± 0.05, Na 1s 0.44 ± 0.02 | 1.0       | 1.0   | 58.3     |
| HTFC-IPA   | C 1s 73.71 ± 0.02, O 1s 13.73 ± 0.05, N 1s 11.08 ± 0.03, Na 1s 1.16 ± 0.03, Cl 2p 0.31 ± 0.03 | 1.24      | 1.24  | 40.3     |
| HTFC-1     | C 1s 70.74 ± 0.03, O 1s 14.99 ± 0.03, N 1s 11.98 ± 0.02, Na 1s 2.01 ± 0.03, Cl 2p 0.28 ± 0.02 | 1.25      | 1.25  | 23.7     |
| HTFC-2     | C 1s 72.21 ± 0.04, O 1s 13.52 ± 0.05, N 1s 12.07 ± 0.03, Na 1s 1.84 ± 0.05, Cl 2p 0.35 ± 0.02 | 1.12      | 1.12  | 24.1     |
| HTFC-3     | C 1s 72.61 ± 0.02, O 1s 13.14 ± 0.04, N 1s 13.67 ± 0.02, Na 1s 0.25 ± 0.05, Cl 2p 0.33 ± 0.02 | 0.96      | 0.96  | 40.3     |

Scheme 1. Synthetic Scheme of Poly(Homopiperazine–Amide) Thin-Film Composite (HTFC) Membrane Preparation

In the first step, homopiperazine (HP) and trimesoyl chloride (TMC) reacted via the Schotten–Baumann reaction to give polyamide-I. In the second step, ethylenediamine (EDA) was post-treated with the as-formed polyamide-I layer to react with the residual acyl chloride group and yield polyamide-II.
3). The slight reduction of the O/N ratio after post-treatment (cross-linking using EDA) is due to the additional nitrogen atoms covalently attached to the PA network. To define the degree of cross-linking for the samples that went through EDA treatment, we estimated the concentration of \( \text{HN-} \text{C} \) species using the chemical state and elemental analysis data provided in Tables S1–S3, Supporting Information. To do so, we looked at the C 1s and O 1s spectra simultaneously. First, we subtracted the concentration of \( \text{O-}\text{H} \) groups from the concentration of \( \text{C}==\text{O} \) species in the O 1s spectrum. Here, according to the proposed chemical structure after EDA treatment (Scheme 1), the \( \text{C}==\text{O} \) species are connected to either N atoms present in the HP rings (\( \text{O}==\text{C}==\text{N} \)) or NH groups of the linkers (\( \text{O}==\text{C}==\text{NH} \)). If we multiply the resultant value by two, it will be approximately equal to the total concentration of \( \text{C}==\text{N} \) groups located in the HP rings. Subsequently, by subtracting the concentration of \( \text{C}==\text{N} \) groups located in the HP rings from the total concentration of \( \text{C}==\text{N} \) in the C 1s spectrum, we found the equivalent concentration of \( \text{C}==\text{NH} \) species in the linkers. We defined the cross-linking density of the treated samples (\( X_{\text{EDA}} \)) to be the ratio of \( \text{C}==\text{NH} \) species to the total \( \text{C}==\text{N} \) concentration, as shown in eq S1, Supporting Information. As shown in Table 1, the \( X_{\text{EDA}} \) value for HTFC-1 was about 23.7%, and it increased to about 24.1 and 40.3% for the HTFC-2 and HTFC-3 samples, respectively. This enhancement in the degree of cross-linking shows the effectiveness and evolution of EDA treatment with reaction time.

Another critical property of the PA layer is the surface morphology of the as-prepared HTFC membranes. For this reason, the morphology of membranes was characterized using scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques. The cross-section SEM images of the control and an HTFC membrane are shown in Figure 3, where the thickness of the PA layer was measured to be \( \sim 80 \) nm. Figure 3A shows the formed nodular and globular structures on the surface of the control and HTFC-IPA membranes. The AFM height images of the control and HTFC-IPA membranes, shown in Figure 3B, confirm the presence of a globular structure on the top layer.

Figure 3. (A) Top-surface SEM and (B) AFM two-dimensional (2D) images of the control and HTFC-IPA NF membranes. The control membrane was not washed with IPA, whereas the HTFC-IPA membrane was washed with 20 mL of IPA for 1 minute at 20 °C. Both SEM and AFM images depict the presence of nodular and globular structures of control and HTFC-IPA membranes.

The estimated average roughness (\( R_s \)) factor of the control membrane surface is about 36% higher than that of the HTFC-IPA sample. The difference in \( R_s \) was ascribed to the molecular rearrangement induced by treating the membrane with an organic solvent, resulting in irreversible structural deformation of the PA layer.\(^{33,34}\) We did not note any trend in the roughness factor of the membranes as a function of post-treatment processing. Nonetheless, our HTFC membranes show lower roughness compared with that shown in most published works.\(^{35,46}\) The top-surface SEM and AFM images of HTFC-1, HTFC-2, and HTFC-3 can be found in Figure S3B.

Figure 4A presents the \( \zeta \)-potential for all of the HTFC membranes in the pH range of 5–9. As shown, all of the as-

![Figure 4](https://dx.doi.org/10.1021/acsomega.0c04064)

prepared HTFC membranes demonstrated a positive charge below pH 6.2, which favors the rejection of divalent or multivalent ions via the Donnan effect.\(^{47}\) The isoelectric point (IEP) of the control membrane was found to be at pH 6.47. Compared with the control samples, the IEP for the HTFC-1 membrane declines to pH 6.25. The reduced IEP (slightly increased negative charge) was attributed to the removal of unreacted monomers and oligomer during the post-treatment process. Because of the unreacted amine removed during the post-treatment, the unreacted acyl group (\( \text{COCl} \)) in the PA layer hydrolyzed in the presence of water, forming a COOH group. As a result, the HTFC-1 membrane becomes more

![Figure 4](https://dx.doi.org/10.1021/acsomega.0c04064)
negative than the control membrane. By increasing the post-treatment time, we expect the unreacted carboxylic groups to be cross-linked by EDA, which results in an increased IEP.

Another way to characterize the polarizability of the surface is to evaluate the wettability of the surfaces by measuring the water contact angle (CA).46 As shown in Figure 4B, the control membrane has the lowest water CA of 16.9° due to the higher $R_a$ value when compared to all other HTFC membranes. According to the Wenzel model, the increased surface roughness will reduce the contact angle.48 Here, an increase in the contact angle was noted as a function of the treatment process, with the HTFC-3 membrane demonstrating the highest contact angle of all surfaces. This trend in the CA values was attributed to the increased cross-linking density and the reduced availability of free carboxylic acid groups in the PA layer.49

2.2. HTFC Membrane Performance. The water permeability and effective solute rejection of the HTFC membranes can be tuned by adjusting the cross-linking density of the PA layer and post-treatment.50 Often, increasing the cross-linking density results in the formation of a tighter polymeric network, which causes enhanced solute rejection and reduced water permeability. Here, we showed that post-treatment with organic solvent and amine group results in creating an NF membrane with a reduced cross-linking density and a positively charged surface. The aliphatic nature of the used diamine and the organic solvent allows the NF to swell and cross-link with an extended degree of motion compared to the cross-linking of the rigid aromatic precursors. Thus, the NF membrane prepared by diamine cross-linking is expected to have a more open structure and a positive charge, as evidenced by the IEP measurement.

To estimate the nominal pore size and the solute rejection efficiency of the PA layer, we evaluated the rejection values for different molecular weight PEGs; the MWCO of all of the membranes was also estimated. As shown in Figure 5A, the MWCO values of the control, HTFC-IPA, HTFC-1, HTFC-2m, and HTFC-3 membranes were 253, 260, 272, 266, and 326 D, respectively. The corresponding Stokes radius ($r_p$) values for these membranes were estimated to be 0.36, 0.37, 0.38, 0.37, and 0.42 nm. The MWCO values of all of the NF membranes were in the same range except for the HTFC-3 membrane. The slight decrease in PEG rejection was ascribed to the extended post-treatment processing time. We postulate that during post-treatment, not only the amidation reaction between EDA and TMC happens, but also the removal of the low-molecular-weight PA layers occurs. Consequently, structural defects are prone to be formed. The latter could be the reason leading to a slight reduction in PEG rejection, increasing the MWCO of the HTFC-3 membrane.

We also measured the water permeability, $A$, of all of the HTFC membranes. The data are presented in Figure S4. By comparing the pristine control membrane with the HTFC-1 NF membrane, an increase in the $A$ parameters from 3.6 ± 0.4 to 7.0 ± 0.3 L/(m² h bar) can be noted. This increase in water permeability was attributed to the post-treatment process. Additionally, the pristine membranes demonstrated a higher cross-linking density, as reflected in Table 1, which can contribute to the inferior permeability of these membranes. When the EDA solution post-treatment time was increased, water permeability decreased. This change was ascribed to the
increased cross-linking density of the active layer. EDA molecules in IPA reacted with unreacted acid chloride and resulted in a higher cross-linking density. These results are in agreement with the literature, indicating that the permeability of the NF membrane mainly depends on the porosity of the PA layer, surface hydrophilicity, and PA-layer thickness.

To evaluate the performance of the membranes in rejecting the solute, we chose divalent and monovalent salts such as Na₂SO₄, MgSO₄, and NaCl and prepared feed solutions with 2000 ppm concentration of these salts. The rejection and permeation data for the NF membranes are shown in Figure S5B,C. All of the NF membranes demonstrated more than 94% rejection toward Na₂SO₄ and MgSO₄. Subsequently, all of the HTFC NF membranes exhibited below 30% rejection for NaCl. The improved rejection of MgSO₄ was attributed to the Donnan exclusion effect. The control and HTFC-1 membranes were negatively charged, while HTFC-2 and HTFC-3 membranes were positively charged at pH 7 (Figure 4A). Therefore, in the cases of the control and HTFC-1 membranes, the SO₄²⁻ ions were electrostatically repelled. Also, Mg²⁺ ions were rejected to maintain electrical neutrality. On the other hand, for the HTFC-2 and HTFC-3, Mg²⁺ ions were rejected via electrostatic repulsion. Additionally, the Stokes radius values for the HTFC-2 and HTFC-3 membranes were estimated to be 0.37 and 0.42 nm, respectively, while the hydrated ionic radius values of SO₄²⁻, Mg²⁺, Cl⁻, and Na⁺ ions are reported to be 0.4, 0.43, 0.33, and 0.36 nm, respectively. As a result, the Na₂SO₄ rejection mechanism for HTFC-2 and HTFC-3 membranes depends on size exclusion. The obtained results are well aligned with the literature.

From a practical point of view, operational stability is one of the main requirements for the NF membrane. For this reason, an HTFC-1 membrane was chosen to be characterized for long-term tests (24 h) due to better permeability and salt rejection. As shown in Figure S5D, the HTFC-1 membrane demonstrated promising stability, permeability, and salt rejection over 24 h. The obtained results indicated that the as-prepared HTFC membranes are suitable for desalination.

2.2.1. Heavy Metal Ion Removal and Antifouling Study. To explore the versatility of the as-prepared HTFC membranes, we tested the heavy metal ion rejection efficiency of all of the HTFC NF membranes, presented in Figure 6A. All of the HTFC membranes exhibited >97% Pb²⁺ and >94% Cd²⁺ ion rejection at pH 5. As Pb²⁺ and Cd²⁺ ions form insoluble metal hydroxides at above pH 7, in this study, the rejection experiment was performed at pH 5. In a review of the metal ion rejection results, the HTFC NF membranes demonstrated higher rejection toward Pb²⁺ than Cd²⁺ ions. This is unexpected, as Pb²⁺ ions are smaller than Cd²⁺ ions. The reason for the higher rejection of Pb²⁺ over Cd²⁺ can be explained as follows: (i) higher normalized volume charge density and (ii) lower ionic strength of the Pb(NO₃)₂ solution than the Cd(NO₃)₂ solution and (iii) increased hydrated stability of Pb²⁺ at pH 5 than Cd²⁺. The increased hydrated stability of Pb²⁺ bestowed better charge—charge repulsion between the Pb²⁺ ions and the positively charged membrane surface. Therefore, Pb²⁺ ions were rejected by >97% when compared to the Cd²⁺ ions (>94%). The heavy metal ion rejection ability of the as-prepared membrane was compared with the literature, and the results were comparable to most of the membranes and superior to some of the NF membranes reported (Table 2).

Figure 6. (A) Pb²⁺ and Cd²⁺ rejection of the HTFC-1 membrane at pH 5, 150 psi (10.3 bar), and 20 °C. The filtration was performed with 10 ppm of Pb(NO₃)₂ and Cd(NO₃)₂ aqueous solution individually. (B) Antifouling performance of the control, HTFC-IPA, HTFC-1, HTFC-2, and HTFC-3 membranes with 200 ppm of aqueous humic acid (HA) as feed at 150 psi (10.3 bar) and 20 °C. Water permeability was measured in the first 8 h using DI water as a feed solution. Then, the feed solution was replaced with 200 ppm aqueous HA, and filtration was continued for another 8 h. Finally, the membranes were washed with DI water, and again the water permeability was measured for another 8 h using DI water as feed.

The rejection of higher metal ions (Pb²⁺ and Cd²⁺) of all of the as-prepared membranes was attributed mainly to the NF membrane surface charge. As all of the prepared NF membranes were positively charged at pH 5, the metal ions (Pb²⁺ and Cd²⁺) were rejected via electrostatic repulsion (Donnan effect). The positive charge on the control and HTFC-IPA NF membrane at pH 5 was attributed to the higher cross-linking density, which led to the reduced unavailability of the free carboxylic acid group. For HTFC-1, HTFC-2, and HTFC-3 membranes, the presence of EDA increased the positive charge. However, the membrane HTFC-3 membrane demonstrated slightly reduced metal ion rejection owing to the increased r_p value (0.42 nm) compared to other NF membranes prepared.

Fouling of the NF membrane is one of the bottlenecks during membrane filtration. The presence of NOM, such as HA in the wastewater, will affect the NF membrane flux by adsorbing on the membrane surface. In this study, the antifouling ability of all of the prepared NF membranes was analyzed for 24 h and is represented in Figure 6B. As shown, all of the NF membranes exhibited a sudden drop in water permeability when the feed solution was changed from water to HA solution. The sudden drop in water permeability was ascribed to the deposition of HA molecules on the membrane surface, which acted as a barrier for the water molecule in passing through the membrane. Then, the control and all HTFC NF membranes’ antifouling efficiencies were evaluated by measuring the flux recovery ratio (FRR) and are depicted in Figure S5. In general, the TFC NF membranes prepared with PIP as the monomer exhibited FRR in the range of 60—70%.
However, in this study, simple water washing of all of the NF membranes prepared using HP as a monomer bestowed FRR of >94%. When compared to all of the NF membranes prepared in this study, the HTFC-1 membrane demonstrated higher FRR (96.9%) and water permeability.

Table 2. Comparison of Heavy Metal Removal Capacity of As-Prepared NF Membranes with the Literature

| membrane                  | water permeability, A (L/(m² h bar)) | metal ion          | rejection (%) | ref |
|---------------------------|--------------------------------------|--------------------|---------------|-----|
| Dow membrane NF90        | 7.14 Pb²⁺ [Pb(NO₃)₂]                | 91–94              |               | 58  |
| Dow membrane NF270       | 13.2 Pb²⁺ [Pb(NO₃)₂]                | ~60                |               | 59  |
| Polybenzimidazole/polyethersulfone dual-layer hollow fiber membrane | 0.826 Cd²⁺ [Cd(NO₃)₂] | ~68               |               |     |
| Matrimid/PEI/Nexar       | 2.4 Cd²⁺ [Cd(NO₃)₂]                 | 93                 |               | 60  |
| PAN/SPEB blend           | 7.62 Pb²⁺ [Pb(NO₃)₂]                | 98.9               |               |     |
| PIP/PEI-Ag/H₂N-NH₂       | 8.0 Pb²⁺ [Pb(NO₃)₂]                 | 98.6               |               | 62  |
| Tetrahydroterephthalate/PES | 10.0 Pb²⁺ [Pb(NO₃)₂]             | 96.5               |               |     |
| ED-γ-MWCNT/PES           | 8.0 Pb²⁺ [Pb(NO₃)₂]                 | 97.4               |               | 63  |
| PEI-CNCs                 | 5.98 Pb²⁺ [Pb(NO₃)₂]                | 90.5               |               | 64  |
| HTFC-1                   | 7.0 Pb²⁺ [Pb(NO₃)₂]                 | 98.1               |               | 65  |

4. EXPERIMENTAL SECTION

4.1. Materials. Polysulfone (PSF, Mₙ ~22 000), homopiperazine (HP, 98%), sodium hydroxide (NaOH, >98%, pellets), lead nitrate (Pb(NO₃)₂, 99.9%), cadmium nitrate tetrahydrate (Cd(NO₃)₂·4H₂O, 98%), humic acid sodium salt (HA), and ethylenediamine (EDA, >99%) were purchased from Sigma-Aldrich. 1,3,5-Benzenetricarboxylic acid chloride (TMC, 98%) was purchased from Acros. Poly(ethylene glycol) (PEG) of different molecular weights and N,N'-dimethylformamide (DMF, anhydrous, 99.8%) were purchased from Loba Chemie. Isopar-G was purchased from Univar. Poly(ethylene terephthalate) nonwoven fabric (PET, K801 3249) was purchased from Hollytex. Isopropyl alcohol (IPA, >99.8%), sodium chloride (NaCl, >99.5%), anhydrous sodium sulfate (Na₂SO₄, >99.0%), and anhydrous magnesium sulfate (MgSO₄, >98.0%) were obtained from Fisher Scientific.

4.2. Fabrication of Nanofiltration Membranes. The PSF beads were dried in a vacuum (~25 in Hg) at 60 °C for 12 h to remove adsorbed water. The PSF supports were fabricated through the nonsolvent induced phase separation (NIPS) method. Briefly, 15 wt % PSF was dissolved in DMF and stirred for 8 h at 60 °C. The solution was deaerated by keeping the dope solution at room temperature for 6 h without stirring. The nonwoven PET fabric was secured on the glass plate by taping it from the backside and preevted with DMF; the excess DMF was removed by Kimwipes (Kimberly-Clark). The dope solution was poured on the fabric and cast on the wet PET using a casting knife (Gardco) with an adjustable gap set at 50 mils. After the solution was cast, the substrates were immediately immersed in a coagulation bath containing water. After gelation (5 min), the membranes were transferred to another water bath and soaked for 24 h to remove the residual solvent. The as-prepared PSF support membrane exhibited a thickness of ~100 μm measured by a micrometer at different locations. The PSF substrate membranes were stored in deionized water at 4 °C until use.

In summary, we developed a new thin-film composite nanofiltration (NF) membrane using homopiperazine as a monomer. The influence of post-treatment with (EDA)/IPA on the NF membrane performances was studied. The as-prepared HTFC NF membranes exhibited low surface roughness, confirmed by AFM. The ζ-potential analysis revealed that the negatively charged PA layers of HTFC membranes became positively charged by simple EDA post-treatment. The optimized NF membrane prepared with 2 wt % HP, 0.15 wt % TMC, and post-treatment with EDA in IPA for 1 min demonstrated a pure water permeability of 7.0 ± 0.3 L/(m² h bar) and salt rejections of 97.0 ± 0.6, 97.4 ± 0.5, 23.3 ± 0.6, 98.1 ± 0.3, and 96.3 ± 0.4% for Na₂SO₄, MgSO₄, NaCl, PbCl₂, and CdCl₂, respectively. When fouled with HA, the NF membrane exhibited a flux recovery ratio of 96.9 ± 0.4% upon cross-flow washing. Overall, the as-prepared NF membranes are promising separation materials for brackish water desalination and the removal of heavy metal ions.
performing interfacial polymerization (IP) on the prepared PSF support. All of the TFC membranes were prepared at room temperature (20 °C) and relative humidity of 60%. In brief, PSF substrates were sandwiched between the glass plates and HDPE frames, creating wells 1 cm deep. Next, 30 mL of DI water containing 2 wt % HP and 0.35 wt % NaOH was poured on the substrate, and the substrate was allowed to rest for 2 min. The excess HP solution was drained by keeping the frame in the vertical position for 1 min. The residual droplets of the HP solution were removed by gently paddling the support, using a Kimwipe. In the second step, 30 mL of Isopar-G solution containing 0.15 wt % TMC was poured into the well and left for 1 min to allow the reaction to complete. Subsequently, the excess solution was drained by keeping the frame in a vertical position for 1 min. The as-formed PA membranes were cured in a convective oven for 8 min at 60 °C. The feed solution was circulated using a Hydra-Cell pump (Wanner Engineering Inc., Minneapolis, MN). The temperature of the feed solution was maintained using a VWR recirculating chiller. The cross-flow rate of the feed solution was measured using a digital flow sensor in a vertical position for 1 min. The as-formed PA membranes were cured in a convective oven for 8 min at 60 °C. The ionic conductivities of both the feed and permeate were measured using a conductivity meter (Oakton CON 2700), calibrated using 0.01 M KCl standard solution. For the heavy metal removal efficiency calculations, Pb(NO3)2 and Cd(NO3)2 were used as salts. To evaluate the removal efficiency, 10 ppm aqueous solutions of these salts were used and the experiments were performed at 150 psi (10.3 bar), 20 °C, and pH 5. The metal ion concentrations, in both the feed and permeate, were determined using an inductively coupled plasma mass spectrometer (ICP-MS) (ThermoFisher iCAP RQ). The % rejection (R) was calculated using eq 3

\[
\%R = \left(1 - \frac{c_p}{c_f}\right) \times 100
\]

where \(c_p\) and \(c_f\) are the permeate and feed conductivities, respectively.

4.3. Characterization of HTFC NF Membranes. The transport properties of NF membranes were characterized using a custom-made cross-flow stainless steel membrane cell with an active area of 19 cm². All of the measurement was done at 20 °C. The feed solution was circulated using a Hydra-Cell pump (Wanner Engineering Inc., Minneapolis, MN). The temperature of the feed solution was maintained using a VWR recirculating chiller. The cross-flow rate was monitored by a flow sensor. The volumetric flow rate \(F\) for the permeate was measured using a digital flow meter (Tovatech FlowCal 5000), connected to a PC. All of the experiments were replicated six times. For each measurement, before collecting water flux \(J_w\) and solute rejection, each membrane was compacted at 170 psi (11.7 bar) for 1 h using DI water, allowing for permeate flux to reach the steady-state condition. For each condition, \(J_w\) (L/(m²·h)) and water permeability \(A\) (L/(m²·h·bar)) were measured at 150 psi (10.3 bar) using the following equations:

\[
J_w = \frac{F}{A_m}
\]

\[
A = \frac{J_w}{\Delta p}
\]

where \(F\) is the permeate flow rate (L/h), \(A_m\) is the effective membrane area of the membrane in the module (m²), and \(\Delta p\) is the operating pressure (bar).

The solute rejection efficiency of the NF membrane for NaCl, Na2SO4, and MgSO4 was measured using a feed solution with the dissolved solid concentration of 2000 ppm. All of the measurements were conducted at 150 psi (10.3 bar) and 20 °C. The molecular weight cutoff (MWCO) of the membrane was determined by filtering PEG molecules with different molecular weights (200, 400, 600, and 1000 Da) at 150 psi (10.3 bar) and 20 °C. The concentration of PEG in both the feed and permeate, were determined using an inductively coupled plasma mass spectrometer (ICP-MS) (ThermoFisher iCAP RQ). The PEG rejection curve was plotted, and the MWCO of the membrane was defined to be the equivalent PEG molecular weight at the rejection value of 90%. The Stokes radius \(r_p\) (nm) of the PEG was also determined according to eq 5

\[
r_p = 16.73 \times 10^{-12} \times \text{MW}^{0.557}
\]

where MW is the molecular weight of the PEG used.

The antifouling performance of all of the HTFC membranes was evaluated using a feed solution containing 200 ppm of HA. For this purpose, the membrane sample was loaded into the measurement cell and the water permeability \(J_w\) was measured at 150 psi (10.3 bar) for 8 hours. Then, we replaced the feed solution with an aqueous solution containing 200 ppm HA and continued the filtration at the same condition for another 8 h. The permeate flux \(J_w\) was measured continuously. Once the membrane fouled with the HA solution, the feed solution was replaced with RO water. The fouled membrane was washed under the cross-flow condition, at 10 psi and 20 °C, to remove the loosely adhered HA

Table 3. Poly(Homopiperazine–Amide) Thin-Film Composite (HTFC) Membrane Parameters

| membrane     | HP (wt %) | TMC (wt %) | NaOH (g) | post-treatment |
|--------------|-----------|------------|----------|---------------|
| control      | 2         | 0.15       | 0.1      | no post-treatment |
| HTFC-IPA     | 2         | 0.15       | 0.1      | IPA washed    |
| HTFC-1       | 2         | 0.15       | 0.1      | 1 wt % EDA in IPA for 1 min |
| HTFC-2       | 2         | 0.15       | 0.1      | 1 wt % EDA in IPA for 2 min |
| HTFC-3       | 2         | 0.15       | 0.1      | 1 wt % EDA in IPA for 3 min |

*HP, homopiperazine; TMC, 1,3,5-benzenetricarboxylic acid chloride; EDA, ethylenediamine; IPA, isopropyl alcohol.

Accordingly, the PEG rejection curve was plotted, and the MWCO of the membrane was defined to be the equivalent PEG molecular weight at the rejection value of 90%. The Stokes radius \(r_p\) (nm) of the PEG was also determined according to eq 5

\[
r_p = 16.73 \times 10^{-12} \times \text{MW}^{0.557}
\]
molecules from the membrane surface. After the washing cycle, the water permeability ($J_w$) was measured at the same condition (10.3 bar, 20 °C) and the flux recovery ratio (FRR) was calculated using the following equation:

$$\text{FRR}(\%) = \frac{J_w}{J_{wo}} \times 100$$  \hspace{1cm} (6)

The detailed instrumental characterization of the HTFC NF membrane is given in the Supporting Information S1.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04064.

Characterization of HTFC nanofiltration membranes; calculation of the degree of cross-linking; high-resolution C 1s, N 1s, and O 1s XPS core electron spectra for HTFC nanofiltration membranes; calculation of the degree of cross-linking of the control and HTFC-IPA NF membranes; flux recovery ratio of HTFC membranes; XPS chemical states and elemental analysis for the HTFC-1 membrane; and XPS chemical states and elemental analysis for the HTFC-3 membrane (PDF)

## AUTHOR INFORMATION

### Corresponding Authors

Arun M. Isloor — Membrane Technology Laboratory, Department of Chemistry and Apache Solutions LLP, Science and Technology Entrepreneurs Park, National Institute of Technology Karnataka, Surathkal, Mangalore 575025, India; orcid.org/0000-0003-2038-3494; Email: isloor@yahoo.com

Siamak Nejati — Department of Chemical and Biomolecular Engineering, University of Nebraska—Lincoln, Lincoln, Nebraska 68588-8286, United States; orcid.org/0000-0002-1807-2796; Email: snejati2@unl.edu

### Authors

Syed Ibrahim — Membrane Technology Laboratory, Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Mangalore 575025, India; orcid.org/0000-0001-9460-8620

Mahdi Mohammadi Ghaheni — Department of Chemical and Biomolecular Engineering, University of Nebraska—Lincoln, Lincoln, Nebraska 68588-8286, United States; orcid.org/0000-0002-9824-450X

Mona Bavarian — Department of Chemical and Biomolecular Engineering, University of Nebraska—Lincoln, Lincoln, Nebraska 68588-8286, United States; orcid.org/0000-0001-7689-773X

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.0c04064

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

S.N. appreciates the kind support of Nebraska Environmental Trust (NET) under grant # 18–178. S.I. and A.M.I. thank the Director of NITK Surathkal, India, for his support and encouragement. A.M.I. expresses gratitude to VGST, Department of Science & Technology, and the Government of Karnataka for the Young Scientist and CESEM awards. S.I. is indebted to the Department of Science and Technology (DST) India, University of Nebraska, Indo-US Science and Technology Forum (IUSSTF), and the Daughtery Water for Food Institute (DWFI) for supporting and funding of the WARI internship. The research was performed in part in the Nebraska Nanoscale Facility: National Nanotechnology Coordinated Infrastructure and the Nebraska Center for Materials and Nanoscience, which are supported by the National Science Foundation under Award ECCS: 1542182, and the Nebraska Research Initiative.

## REFERENCES

1. Werber, J. R.; Osuji, C. O.; Elimelech, M. Materials for next-generation desalination and water purification membranes. Nat. Rev. Mater. 2016, 1, No. 16018.

2. Ibrahim, G. P. S.; Isloor, A. M.; Inamuddin; Asiri, A. M.; Ismail, N.; Ismail, A. F.; Ashraf, G. M. Novel, one-step synthesis of zwitterionic polymer nanoparticles via distillation-precipitation polymerization and its application for dye removal membrane. Sci. Rep. 2017, 7, No. 15889.

3. Praveen, S. K.; Majumder, C. B. Novel biofiltration methods for the treatment of heavy metals from industrial wastewater. J. Hazard. Mater. 2008, 151, 1–8.

4. Mondal, M.; Dutta, M.; De, S. A novel ultrafiltration grade nickel iron oxide doped hollow fiber mixed matrix membrane: Spinning, characterization and application in heavy metal removal. Sep. Purif. Technol. 2017, 188, 155–166.

5. Moideen, K. I.; Isloor, A. M.; Ismail, A.; Obaid, A.; Fun, H.-K. Fabrication and characterization of new PSF/PSU UF blend membrane for heavy metal rejection. Desalin. Water Treat. 2016, 57, 19810–19819.

6. Abdullah, N.; Gohari, R.; Yusof, N.; Ismail, A.; Juhana, J.; Lau, W.; Matsuura, T. Polysulphone/hydrous ferric oxide ultrafiltration mixed membrane preparation, characterization and its adsorptive removal of lead (II) from aqueous solution. Chem. Eng. J. 2016, 289, 28–37.

7. Fu, F.; Wang, Q. Removal of heavy metal ions from wastewaters: a review. J. Environ. Manage. 2011, 92, 407–418.

8. Barakat, M. New trends in removing heavy metals from industrial wastewater. Arabian J. Chem. 2011, 4, 361–377.

9. Yang, X.; Wan, Y.; Zheng, Y.; He, F.; Yu, Z.; Huang, J.; Wang, H.; Ok, Y. S.; Jiang, Y.; Gao, B. Surface functional groups of carbon-based adsorbents and their roles in the removal of heavy metals from aqueous solutions: A critical review. Chem. Eng. J. 2019, 366, 608–621.

10. Bolisetty, S.; Mezzenga, R. Amyloid–carbon hybrid membranes for universal water purification. Nat. Nanotechnol. 2016, 11, 365.

11. Inglezakis, V. J.; Stylianou, M. A.; Gkantzou, D.; Loizidou, M. D. Removal of Pb (II) from aqueous solutions by using cinominolite and bentonite as adsorbents. Desalination 2007, 210, 248–256.

12. Mohammad, A. W.; Tesw, Y. H.; Ang, W. L.; Chung, Y. T.; Oxlery-Radcliffe, D. L.; Hilal, N. Nanofiltration membranes review: Recent advances and future prospects. Desalination 2015, 356, 226–254.

13. Wang, Z.; Wang, Z.; Lin, S.; Jin, H.; Gao, S.; Zhu, Y.; Jin, J. Nanoparticle-templated nanofiltration membranes for ultrahigh performance desalination. Nat. Commun. 2018, 9, No. 2004.

14. Syed Ibrahim, G. P.; Isloor, A. M.; Bavarian, M.; Nejati, S. Integration of Zwitterionic Polymer Nanoparticles in Interfacial Polymerization for Ion Separation. ACS Appl. Polym. Mater. 2020, 2, 1508–1517.

15. Li, Q.; Liao, Z.; Fang, X.; Xie, J.; Ni, L.; Wang, D.; Qi, J.; Sun, X.; Wang, L.; Li, J. Tannic acid assisted interfacial polymerization based loose thin-film composite NF membrane for dye/salt separation. Desalination 2020, 479, No. 114343.

16. Yoon, Y.; Westerhoff, P.; Snyder, S. A.; Wert, E. C.; Yoon, J. Removal of endocrine disrupting compounds and pharmaceuticals by
nanofiltration and ultrafiltration membranes. Desalination 2007, 202, 16–23.

(17) Caus, A.; Vanderhaegen, S.; Braeken, L.; Van der Bruggen, B. Integrated nanofiltration cascades with low salt rejection for complete removal of pesticides in drinking water production. Desalination 2009, 241, 111–117.

(18) Xu, G-R.; Xu, J-M.; Feng, H-J.; Zhao, H-L.; Wu, S-B. Tailoring structures and performance of polyamide thin film composite (PA-TFC) desalination membranes via sublayers adjustment-a review. Desalination 2017, 417, 19–35.

(19) Wang, H.; Li, L.; Zhang, X.; Zhang, S. Polyamide thin-film composite membranes prepared from a novel triamine 3,5-diaminono-(4-aminophenyl)benzamide monomer and m-phenylenediamine. J. Membr. Sci. 2010, 353, 78–84.

(20) Park, S-J.; Kwon, S-J.; Kwon, H-E.; Shin, M-G.; Park, S-H.; Park, H.; Park, Y-J.; Nam, S-E.; Lee, J-H. Aromatic solvent-assisted interfacial polymerization to prepare high performance thin film composite reverse osmosis membranes based on hydrophobic supports. Polymer 2018, 144, 159–167.

(21) Khoshidi, B.; Thundat, T.; Fleck, B.; Sadrzadeh, M. Thin film composite polyamide membranes: parametric study on the influence of synthesis conditions. RSC Adv. 2015, 5, 54985–54997.

(22) Khoshidi, B.; Thundat, T.; Fleck, B. A.; Sadrzadeh, M. A Novel Approach Toward Fabrication of High Performance Thin Film Composite Polyamide Membranes. Sci. Rep. 2016, 6, No. 22069.

(23) Kim, S. H.; Kwak, S-Y.; Suzuki, T. Positron annihilation spectroscopic evidence to demonstrate the flux-enhancement mechanism in morphology-controlled thin-film-composite (TFC) membrane. Environ. Sci. Technol. 2005, 39, 1764–1770.

(24) Paul, M.; Jons, S. D. Chemistry and fabrication of polymeric nanofiltration membranes: A review. Polymer 2016, 103, 417–456.

(25) Zhu, W-P.; Gao, J.; Sun, S-P.; Zhang, S.; Chung, T-S. Poly(amide-dendrimer) dendrimer (PAMAM) grafted on thin film composite (TFC) nanofiltration (NF) hollow fiber membranes for heavy metal removal. J. Membr. Sci. 2015, 487, 117–126.

(26) Gao, J.; Wang, K-Y.; Chung, T-S. Design of nanofiltration (NF) hollow fiber membranes made from functionalized bore fluids containing polyethyleneimine (PEI) for heavy metal removal. J. Membr. Sci. 2020, 603, No. 118022.

(27) Bera, A.; Trivedi, J. S.; Kumar, S. B.; Chandel, A. K. S.; Haldar, S.; Jowrakaj, S. K. Anti-organic fouling and anti-biofouling poly-(piperazineimine) thin film nanocomposite membranes for low pressure removal of heavy metal ions. J. Hazard. Mater. 2018, 343, 86–97.

(28) Zhang, S.; Peh, M. H.; Thong, Z.; Chung, T-S. Thin Film Interfacial Cross-Linking Approach To Fabricate a Chitosan Rejecting Layer over Poly(ether sulfone) Support for Heavy Metal Removal. Ind. Eng. Chem. Res. 2015, 54, 472–479.

(29) Wang, T.; Qiblawey, H.; Sivaniah, E.; Mohammadian, A. Novel methodology for facile fabrication of nanofiltration membranes based on nucleophilic nature of polydopamine. J. Membr. Sci. 2016, 511, 65–75.

(30) He, Y.; Liu, J.; Han, G.; Chung, T-S. Novel thin-film composite nanofiltration membranes consisting of a zwitterionic co-polymer for selenium and arsenic removal. J. Membr. Sci. 2018, 559, 299–306.

(31) Kumano, A.; Matsuyama, H. Development and Characterization of a New Composite Nanofiltration Hollow Fiber Membrane. Solvent Extr. Res. Dev. Jpn. 2012, 19, 89–99.

(32) Konagaya, S.; Watanabe, O. Influence of chemical structure of isophthaloyl dichloride and aliphatic, cycloaliphatic, and aromatic diamine compound polyamides on their chlorine resistance. J. Appl. Polym. Sci. 2000, 76, 201–207.

(33) Waite, W. A. Composite Semipermeable Membrane. U.S. Patent US4,802,984 1989.

(34) Dom, E.; Hermans, S.; Koekelbergbs, G.; Vankelecom, I. Solvent Resistant Thin Film Composite Membrane and Its Preparation. U.S. Patent US9,943,809 2018.

(35) Kamiyama, Y.; Yoshioka, N.; Nakagome, K. Composite Semipermeable Membrane. U.S. Patent US4,619,761 1998.

(36) Wang, H.; Yeager, G. W.; Suriano, J. A.; Rice, S. T. Thin Film Composite Membranes Incorporating Carbon Nanotubes. U.S. Patent US8,591,741 2013.

(37) Waite, W. A. Selectively Permeable Barriers. U.S. Patent US8,147,533 2012.

(38) Kumar, R.; Isloor, A. M.; Ismail, A. F.; Rashid, S. A.; Matsuura, T. Polyethylene–Chitosan blend ultrafiltration membranes: preparation, characterization, permeation and antifouling properties. RSC Adv. 2013, 3, 7855–7861.

(39) Zhang, Z.; Kang, G.; Yu, H.; Jin, Y.; Cao, Y. Fabrication of a highly permeable composite nanofiltration membrane via interfacial polymerization by adding a novel acyl chloride monomer with an anhydride group. J. Membr. Sci. 2019, 570–571, 403–409.

(40) Karan, S.; Jiang, Z.; Livingston, A. G. Sub–10 nm polyamide nanofilms with ultrafast solvent transport for molecular separation. Science 2015, 348, 1347–1351.

(41) Moulder, J. F.; Chastain, J. Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data, Physical Electronics Division; PerkinElmer Corporation, 1992.

(42) Kwon, Y. N.; Tang, C. Y.; Leckie, J. O. Change of chemical composition and hydrogen bonding behavior due to chlorination of cross-linked polyamide membranes. J. Appl. Polym. Sci. 2008, 108, 2061–2066.

(43) Guo, S.; Chen, X.; Wan, Y.; Feng, S.; Luo, J. Custom-tailoring loose nanofiltration membrane for precise biomolecule fractionation: new insight into post-treatment mechanisms. ACS Appl. Mater. Interfaces 2020, 12, 13327–13337.

(44) Shin, M. G.; Kwon, S. J.; Park, H.; Park, Y-J.; Lee, J-H. High-performance and acid-resistant nanofiltration membranes prepared by solvent activation on polyamide reverse osmosis membranes. J. Membr. Sci. 2020, 595, No. 117590.

(45) Lai, G. S.; Lau, W. J.; Goh, P. S.; Ismail, A. F.; Tan, Y. H.; Chong, C. Y.; Krause-Rehberg, R.; Awad, S. Tailor-made thin film nanocomposite membrane incorporated with graphene oxide using novel interfacial polymerization technique for enhanced water separation. Chem. Eng. J. 2018, 344, 524–534.

(46) Lai, G.; Lau, W.; Gray, S.; Matsuura, T.; Gohari, R. J.; Subramanian, M.; Lai, S.; Ong, C.; Ismail, A.; Emazadah, D.; Ghanbari, M. A practical approach to synthesize polyamide thin film nanocomposite (TFN) membranes with improved separation properties for water/wastewater treatment. J. Mater. Chem. A 2016, 4, 4134–4144.

(47) Childress, A. E.; Elimelech, M. Relating nanofiltration membrane performance to membrane charge (electrokinetic) characteristics. Environ. Sci. Technol. 2000, 34, 3710–3716.

(48) Wenzel, R. N. Surface roughness and contact angle. J. Phys. Chem. A 1949, 53, 1466–1467.

(49) Gorgojo, P.; Jimenez-Solonmen, M. F.; Livingston, A. G. Polyamide thin film composite membranes on cross-linked polyamide supports: Improvement of RO performance via activating solvent. Desalination 2014, 344, 181–188.

(50) Li, M.; Lv, Z.; Zheng, J-J.; Hu, J.; Jiang, C.; Ueda, M.; Zhang, X.; Wang, L. Positively Charged Nanofiltration Membrane With Dendritic Surface for Toxic Element Removal. ACS Sustainable Chem. Eng. 2017, 5, 784–792.

(51) Ji, J.; Dickson, J.; Childs, R.; McCurry, B. Mathematical model for the formation of thin-film composite membranes by interfacial polymerization: porous and dense films. Macromolecules 2000, 33, 624–633.

(52) Bano, S.; Mahmood, A.; Kim, S-J.; Lee, K-H. Graphene oxide modified polyamide nanofiltration membrane with improved flux and antifouling properties. J. Mater. Chem. A 2015, 3, 2065–2071.

(53) Zhu, J.; Yuan, S.; Uliana, A.; Hou, J.; Li, J.; Li, X.; Tian, M.; Chen, Y.; Volodin, A.; de Bruggen, B. V. High-flux thin film composite membranes for nanofiltration mediated by a rapid co-deposition of polydopamine/piperazine. J. Membr. Sci. 2018, 554, 97–108.
Brant, J.; Lecoanet, H.; Hotze, M.; Wiesner, M. Comparison of Electrokinetic Properties of Colloidal Fullerenes (n-C60) Formed Using Two Procedures. Environ. Sci. Technol. 2005, 39, 6343−6351.

Marcus, Y. Ionic radii in aqueous solutions. Chem. Rev. 1988, 88, 1475−1498.

Trivedi, J. S.; Bhalani, D. V.; Bhadu, G. R.; Jewrajka, S. K. Multifunctional amines enable the formation of polyamide nanofilm composite ultrafiltration and nanofiltration membranes with modulated charge and performance. J. Mater. Chem. A 2018, 6, 20242−20253.

Ibrahim, G. S.; Isloor, A. M.; Inamuddin; Asiri, A. M.; Ismail, A.; Kumar, R.; Ahamed, M. I. Performance intensification of the polysulphone ultrafiltration membrane by blending with copolymer encompassing novel derivative of poly(styrene-co-maleic anhydride) for heavy metal removal from wastewater. Chem. Eng. J. 2018, 353, 425−435.

Saikaew, W.; Mattaraj, S.; Jiraratananon, R. Nanofiltration performance of lead solutions: effects of solution pH and ionic strength. Water Supply 2010, 10, 193−200.

Al-Rashdi, B. A. M.; Johnson, D. J.; Hilal, N. Removal of heavy metal ions by nanofiltration. Desalination 2013, 315, 2−17.

Zhu, W.-P.; Sun, S.-P.; Gao, J.; Fu, F.-J.; Chung, T.-S. Dual-layer polybenzimidazole/polyethersulfone (PBI/PES) nanofiltration (NF) hollow fiber membranes for heavy metals removal from wastewater. J. Membr. Sci. 2014, 456, 117−127.

Thong, Z.; Han, G.; Cui, Y.; Gao, J.; Chung, T.-S.; Chan, S. Y.; Wei, S. Novel nanofiltration membranes consisting of a sulfonated pentablock copolymer rejection layer for heavy metal removal. Environ. Sci. Technol. 2014, 48, 13880−13887.

Jia, T.-Z.; Lu, J.-P.; Cheng, X.-Y.; Xia, Q.-C.; Cao, X.-L.; Wang, Y.; Xing, W.; Sun, S.-P. Surface enriched sulfonated polyarylene ether benzonitrile (SPEB) that enhances heavy metal removal from polyacrylonitrile (PAN) thin-film composite nanofiltration membranes. J. Membr. Sci. 2019, 580, 214−223.

Moradi, G.; Zinadini, S.; Rajabi, L. Development of the tetrathioterephthalate filler incorporated PES nanofiltration membrane with efficient heavy metal ions rejection and superior antifouling properties. J. Environ. Chem. Eng. 2020, 8, No. 104431.

Peydayesh, M.; Mohammadi, T.; Nikouzad, S. K. A positively charged composite loose nanofiltration membrane for water purification from heavy metals. J. Membr. Sci. 2020, 611, No. 118205.

Hoang, M. T.; Pham, T. D.; Pham, T. D.; Verheyen, D.; Nguyen, M. K.; Pham, T. T.; Zhu, J.; Van der Bruggen, B. Fabrication of thin film nanocomposite nanofiltration membrane incorporated with cellulose nanocrystals for removal of Cu(II) and Pb(II). Chem. Eng. Sci. 2020, 228, No. 115998.

Tang, C. Y.; Leckie, J. O. Membrane Independent Limiting Flux for RO and NF Membranes Fouled by Humic Acid. Environ. Sci. Technol. 2007, 41, 4767−4773.

Mansourpanah, Y.; Momeni Habili, E. Preparation and modification of thin film PA membranes with improved antifouling property using acrylic acid and UV irradiation. J. Membr. Sci. 2013, 430, 158−166.

Vrijenhoek, E. M.; Hong, S.; Elimelech, M. Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes. J. Membr. Sci. 2001, 188, 115−128.

Gao, S.; Zhu, Y.; Gong, Y.; Wang, Z.; Fang, W.; Jin, J. Ultrathin Polyamide Nanofiltration Membrane Fabricated on Brush-Painted Single-Walled Carbon Nanotube Network Support for Ion Sieving. ACS Nano 2019, 13, 5278−5290.

Lin, J.; Ye, W.; Baltar, M.-C.; Tang, Y. P.; Bernstein, N. J.; Gao, P.; Balta, S.; Vlad, M.; Volodin, A.; Sotto, A.; et al. Tight ultrafiltration membranes for enhanced separation of dyes and Na2SO4 during textile wastewater treatment. J. Membr. Sci. 2016, 514, 217−228.

Seidel, A.; Elimelech, M. Coupling between chemical and physical interactions in natural organic matter (NOM) fouling of nanofiltration membranes: implications for fouling control. J. Membr. Sci. 2002, 203, 245−255.