



Choline chloride modification of nanofiltration membranes for improving heavy metal ions separation in wastewater

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ABSTRACT

The growing concern over heavy metal ion contamination in industrial wastewater, posing a significant threat to global public health, has led to a heightened interest in devising efficient removal methods. Nanofiltration, while promising, faces a substantial challenge in simultaneously achieving a high rejection of heavy metal cations and maintaining an elevated water permeance. In response, this study utilizes a simple approach by employing choline chloride with a quaternary ammonium group to modify the surface of PEI-TMC membrane, leading to the design of a high-performance PEI-TMC-CC membrane. The choline chloride modification optimized the surface morphology, hydrophilicity, roughness, and combined the Donnan exclusion effect as well as sieving effect, enabling the PEI-TMC-CC membrane to achieve an exceptional rejection of heavy metal ions while retaining a great water permeance. An impressive water permeance $10.0 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ was performed by the PEI-TMC-CC membrane, nearly three times that of traditional PEI-TMC membranes. Concurrently, the PEI-TMC-CC membrane demonstrated an impressive rejection of heavy metals Cd^{2+} , Pb^{2+} , Ni^{2+} , Zn^{2+} , and Cu^{2+} , reaching rejections of 98.3 %, 95.9 %, 98.1 %, 98.5 % and 99.1 %, respectively. Moreover, density functional theory (DFT) calculations confirmed the improved hydrophilicity of choline chloride molecules, aligning with experimental results. The modification of traditional nanofiltration membranes using cost-effective, hydrophilic, positively charged chemicals not only leads to significant performance improvements but also holds the potential to advance the development of positively charged nanofiltration membranes tailored for the removing of heavy metals cations from wastewater. This approach demonstrates promising prospects for industrial applications and further development.

1. Introduction

The environmental challenges arising from societal development are substantial, with industrial wastewater containing hazardous heavy metal cations (e.g., Cd^{2+} , Pb^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+}) posing a significant threat to public health [1–3]. As a consequence of the significant solubility of heavy metals and their resistance to degradation in water, coupled with their propensity for accumulation in organisms, they pose a threat to the well-being of all organisms [4]. Hence, the mitigation of heavy metals holds paramount importance for water purification.

Traditional approaches for eliminating heavy metal ions encompass chemical precipitation [5], adsorption [6], ion exchange [7,8], membrane separation [9,10]. Notably, membrane separation technology, characterized by low cost, simple operation, and environmentally friendliness, has garnered considerable attention in this context. Nanofiltration membrane technology operates at lower pressure levels than reverse osmosis and exhibits a superior ion selectivity in comparison to ultrafiltration [11]. As a result, nanofiltration has emerged as an efficient method for treating water contaminated with heavy metals.

At present, nanofiltration membranes based on positively charged

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selective layer [12–15], synthesized through the traditional interfacial polymerization of trimesoyl chloride (TMC) and polyethyleneimine (PEI), are extensively employed for the removing of heavy metal cations from wastewater. While conventional polyamide membranes have demonstrated effectiveness in removing significant quantities of heavy metal ions, their real-world performance is limited by the relatively low water permeance ($\sim 4 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$), which can be ascribed to the dense polyamide layer [16]. This limits the applicability of nanofiltration membranes in practical processes. Consequently, there is a critical need to not only enhance the membrane water permeance but also maintain their ability to reject heavy metals.

Enhancing water permeance in PEI-TMC membranes is currently addressed through the incorporation of nanomaterial additives and surface modifications, as predominant strategies in the field. Various nanomaterial additives have been employed to improve the membrane water permeance, such as carbon quantum dots [17], graphene oxide [18], MoS_2 [19] and C_3N_4 [20–22]. It is worth noting that, although nanomaterial additives can optimize the water permeance of polyamide membranes to some extent, their preparation typically involves complex synthesis processes and higher costs, rendering their practical application challenging. Surface modification is a straightforward and effective approach to improve the hydrophilic properties of membranes, consequently optimizing their water permeance. Recently, various molecules have been designed, synthesized, and utilized to enhance the water permeance and reinforce the positive charge of polyamide membranes, such as diaminoethimidazole bromide [23], quaternized tetrahydroxyethyl imidazolium [24], and quaternized bipyridine [25]. However, despite their effectiveness in enhancing the water permeance of positively charged polyamide membranes, the preparation of these molecules involves complex chemical processes, resulting in a obviously increase in membrane manufacturing costs, thereby rendering large-scale implementation difficult.

In this study, choline chloride (CC) with quaternary ammonium groups, a food additive known for its affordability and non-toxic nature, was chosen for the surface modification of a PEI-TMC membrane. This aims to endow the membrane with excellent hydrophilicity and great rejection of heavy metal cations, ensuring that the membrane modification process does not impose additional environmental impact while also guaranteeing economical characteristics. Choline chloride not only exhibits excellent hydrophilicity and features a positively charged quaternary ammonium group but also allows for effective interaction between the hydroxyl group of choline chloride and the acid chloride group of TMC, facilitating its grafting onto the membrane surface. This study systematically evaluates the separation performance of the PEI-TMC-CC for heavy metal cations at different concentrations. The grafting of choline chloride is expected to effectively enhance membrane hydrophilicity, consequently boosting the water permeance while retaining a great rejection of various heavy metal cations (including Cd^{2+} , Ni^{2+} , Cu^{2+} , Pb^{2+} , Mn^{2+}) with the combined Donnan exclusion effect and sieving effect. Simultaneously, analyses of chemical composition, morphology, zeta potential, and contact angle of the membranes were performed and discussed. Additionally, DFT results corroborate that choline chloride exhibits higher hydrophilicity compared to PEI, aligning with the findings observed in the experimental results.

2. Materials and methods

2.1. Materials and chemicals

Dimethyl sulfoxide (DMSO, 99.5 %) and Polyethersulfone (PES) used in this article were purchased from BASF, Germany. VWR International BVBA (Belgium) supplied the oil phase solvent n-Hexane (99 %). Trimesoyl chloride (TMC), polyethyleneimine (PEI), zinc chloride (ZnCl_2 , 99 %), lead chloride (PbCl_2 , 99 %), cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$, 99 %), copper nitrate ($\text{Cu}(\text{NO}_3)_2$, 98 %) and nickel nitrate ($\text{Ni}(\text{NO}_3)_2$, 99 %) were supplied by Sigma-Aldrich.

2.2. Fabrication of PEI-TMC-CC membranes

PES membrane was fabricated by the traditional phase inversion as the substrate of separation membrane. Firstly, PES polymer powder was dissolved in DMSO solvent to make a casting solution. The PES concentration of the casting solution is 16 wt%. On the non-woven fabric, a scraper was used to evenly spread the PES solution. It was then soaked in pure water to obtain a PES membrane. The interfacial polymerization method was used to fabricate the ion-selective layer on the PES substrate. Immerse the PES membrane in PEI solution (0.5 wt%, 10 ml) for 5 min. Then the solution is carefully removed by using an air gun. Then pour the TMC organic solution (0.1 wt%, 10 ml) on the membrane and keep it for 1 min to form a pre-prepared PEI-TMC. Finally, take the PEI-TMC out of the holder and heat it at 60 °C for 5 min to obtain the prepared PEI-TMC.

10 ml of choline chloride solutions of different concentrations were kept on the pre-prepared PEI-TMC for a certain period of time, and then the solution was carefully removed. Subsequently, the membrane was heated at 60 °C for different times to form a PEI-TMC-CC membrane. Finally, all membranes were placed in deionized water and placed in a refrigerator at 0–4 °C for 24 h. The detailed preparation method of PEI-TMC-CC membrane is shown in Fig. 1a. Table S1 shows the conditions for preparing nanofiltration membranes with different choline chloride concentration, grafting time, and heating time.

2.3. Membrane characterization

Here, the VERTEX80V Fourier transform infrared spectrometer (FT-IR) sourced from Bruker (Germany) was employed to examine the functional group composition present on the membrane. Elemental analysis of the membrane surface was conducted using a PerkinElmer's X-ray photoelectron spectroscopy (XPS). Morphological observations of the membrane surface were carried out by a Netherlands scanning electron microscope Philips XL30 FEG. Furthermore, surface topography and roughness assessments were carried out using a Dimension Icon SPM atomic force microscope supplied by Veeco Instruments Inc., USA. The hydrophilicity of the membrane was assessed using a contact angle meter, the OCA20, obtained from Dataphysical Instruments, Germany. Additionally, the charge characteristics of the membrane surface were got using the SurPASS 3 electrokinetic analyzer from Austria. The detailed information of molecular weight cut-off (MWCO) experiments can be found in Supporting information.

2.4. Nanofiltration performance tests

The cross-flow setup was employed to assess the nanofiltration performance of the prepared membranes. The nanofiltration area was 7.1 cm^2 during the separation performance test. Prior to the formal separation performance test, all prepared membranes were operated under 6 bar pressure for 30 min to stabilize their water permeance. The separation performance of the nanofiltration membrane was evaluated based on permeance (P) and rejection rate (R), calculated as follows:

$$P = V / (A \times \Delta p \times \Delta t) \quad (\text{Equation 1})$$

$$R (\%) = \left(1 - \frac{C_p}{C_f} \right) \times 100 \quad (\text{Equation 2})$$

where V denotes the permeance solution volume (L); A denotes the area (m^2) of effective separation; Δp denotes the pressure (bar) of operation and Δt denotes the filtration time (h), and; C_f and C_p denote the concentration (g/L) of feed and permeance solution, respectively.

2.5. Stability performance evaluation

The membrane long-term stability was assessed through extended

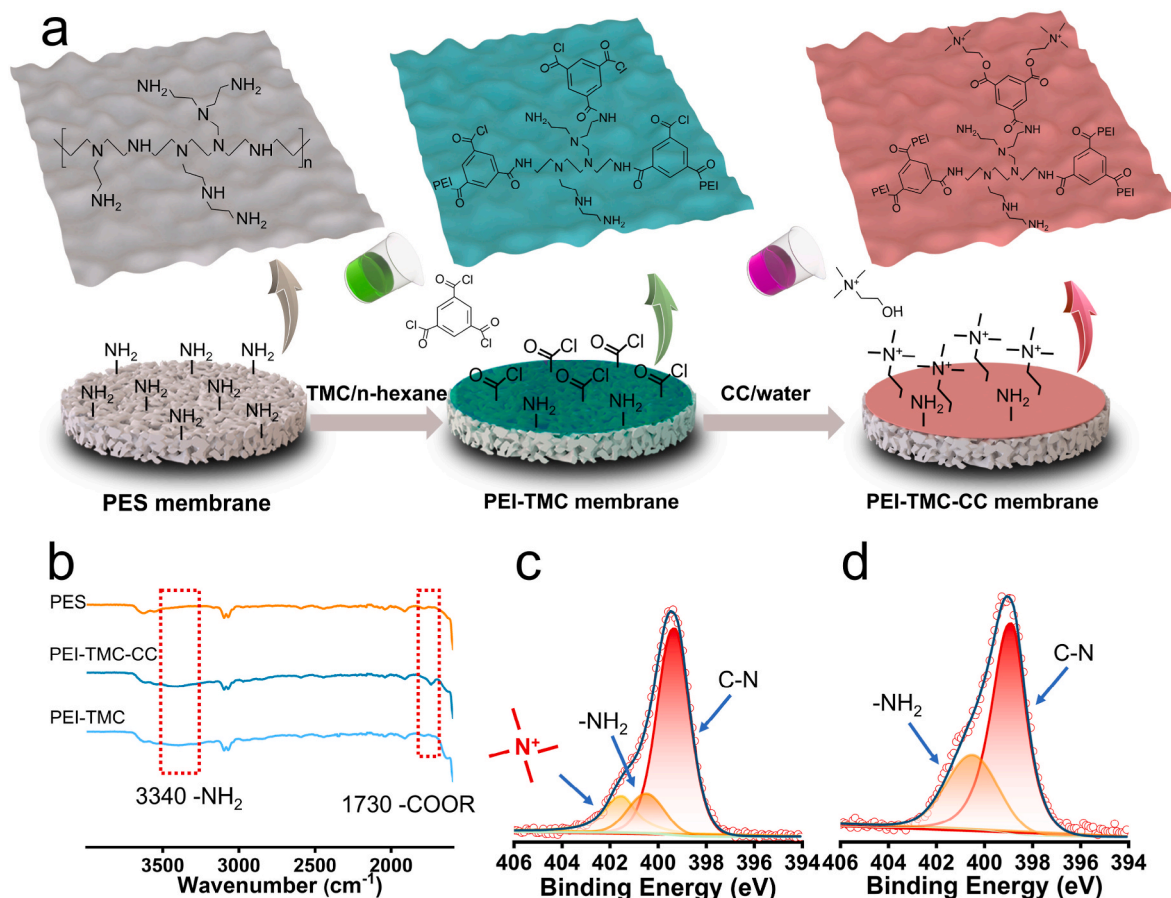


Fig. 1. (a) Schematic depiction of the fabrication procedure for the PEI-TMC-CC membrane. (b) FT-IR spectra of PES, PEI-TMC, and PEI-TMC-CC membranes. N 1s core-level XPS spectra: (c) PEI-TMC-CC membrane and (d) PEI-TMC membrane.

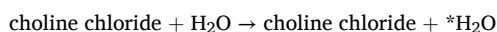
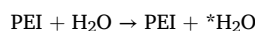
testing. This involved evaluating the membrane's stability by testing water permeance and rejection of a mixed heavy metal solution (200 ppm ZnCl₂, 200 ppm PbCl₂, 200 ppm Cd(NO₃)₂, 200 ppm Cu(NO₃)₂, and 200 ppm Ni(NO₃)₂) over a period of 10-day.

2.6. Anti-scaling performance evaluation

The detailed information of anti-scaling testing can be found in Supporting information.

2.7. Density functional theory

In the density functional theory (DFT) framework, calculations utilized the Perdew-Burke-Ernzerhof functional within the generalized gradient approximation. Ultrasoft pseudopotentials were employed to describe core electrons and atomic nuclei. The plane wave basis was defined with specific charge density (300 Ry) and kinetic energy (30 Ry) cutoffs. The Brillouin zone was sampled at the gamma point (k-point). To mitigate interactions between periodic images along the z direction, a ~10 Å vacuum layer was introduced. Prior to calculations, the structures of choline chloride and PEI models were relaxed (as depicted in Figs. S1–2). Protonation of the -NH₂ group in PEI was achieved by adding protons and re-optimizing the geometry, resulting in protonated PEI (illustrated in Fig. S3). The optimized structures of choline chloride and protonated PEI in the presence of H₂O are displayed in Figs. S4–5, respectively. Additionally, the free energy was computed according to the following reaction:



where ^{*}H₂O denotes the adsorbed H₂O on the CC or PEI. The energy differences (ΔE) were calculated following the methodology introduced by Nørskov [26], where ΔE denotes the computed reaction energy. The PW module from the Quantum ESPRESSO package was employed for the DFT calculations [27].

3. Results and discussion

3.1. Characterization of membranes

The FT-IR was carried out to analyze the chemical properties of the fabricated membranes (Fig. 1b and S6). A peak corresponding to -NH₂ vibration in PEI-TMC-CC and PEI-TMC is observed at ~3340 cm⁻¹, indicating the presence of amino group (-NH₂) from PEI on membranes. Importantly, a new peak at 1723 cm⁻¹ can be clearly observed in the FT-IR spectrum of PEI-TMC-CC, indicating that choline chloride was successfully grafted on the membrane surface. In the FT-IR spectra of PEI-TMC and PEI-TMC-CC membranes, a novel distinctive peak approximately at 1645 cm⁻¹ is discernible, corresponding to the vibrational mode of C=O in amide, thereby corroborating the polyamide layer formation [28]. On the other hand, due to the vibration peak brought by PES at 970 cm⁻¹, it is difficult to clearly observe the -N⁺ group at the same position, which is consistent with the reports in the literature [29]. In conclusion, the above results confirmed that choline chloride was effectively grafted on the membrane.

To assess the impact of choline chloride modification in PEI-TMC-CC, the N 1s core-level XPS spectra of PEI-TMC and PEI-TMC-CC are depicted in Fig. 1c and d. A distinct peak corresponding to the -N⁺ group

emerges at 400.8 eV in the PEI-TMC-CC N 1s spectra, indicating the stable grafting of choline chloride onto the surface of membrane [13]. On the other hand, a new peak corresponding to the $-\text{COOR}$ group was observed at 533.5 eV in the O 1s spectra of PEI-TMC-CC (Fig. S7), suggesting the choline chloride grafted onto the membrane surface with the ester bond [11]. These findings are consistent with the FT-IR analysis, confirming the stability of choline chloride grafted onto the membrane.

The water contact angle serves as a crucial parameter in assessing hydrophilicity of membranes. Fig. 2a illustrates the water contact angles of PES, PEI-TMC, and PEI-TMC-CC membranes. Evidently, the water contact angle of PEI-TMC is lower than that of the PES, attributed to the enhanced hydrophilicity conferred by the amino groups of PEI. Moreover, the lowest water contact angle of the surface-modified PEI-TMC-CC, indicating that the additional hydrophilic choline chloride further enhances the hydrophilicity of membrane. The enhanced hydrophilicity plays a crucial role in expediting mass transfer across the membrane and boosting water permeance.

The charge information of the fabricated membrane was assessed by the zeta potential measurement, as depicted in Fig. 2b. The PEI-TMC exhibits a high zeta potential in the low pH range, attributed to the amino groups protonation from the PEI, increasing the positive charges of the membrane. As the pH increases, deprotonation of the amino group occurs, leading to a decrease in zeta potential, a phenomenon consistent with findings in the literature. Furthermore, the PEI-TMC-CC membrane, modified by choline chloride with quaternary ammonium groups, exhibits higher zeta potential than PEI-TMC, which can contribute to the rejection of heavy metal cations.

AFM and SEM analyses were carried out to observe the morphology of PES, PEI-TMC, and PEI-TMC-CC membranes. The surface morphology of PES, PEI-TMC, and PEI-TMC-CC membranes are depicted in Fig. 3. Fig. 3a shows a smooth surface of the pure PES membrane, aligning with observations reported in the literature [12]. Simultaneously, the violent chemical reaction between the amino groups of PEI and the acid chloride groups of TMC resulted in the ring-like morphology on the membrane (Fig. 3d), consistent with a prior literature report [12]. The surface morphology of PEI-TMC-CC membrane was performed by SEM and displayed in Fig. 3g. Notably, the surface of the PEI-TMC-CC appears more uniform than PEI-TMC, indicating a gentle chemical reaction between PEI and choline chloride. This observation supports the successful grafting of choline chloride on the membrane, which also similar to the literature [14,15]. The cross-sectional image of unmodified PEI-TMC and surface modified PEI-TMC-CC is depicted in Fig. 3e and h. Clearly visible in the cross-sectional images is the polyamide layer present in PEI-TMC and PEI-TMC-CC. The selective layer thickness ~ 89 nm of the PEI-TMC is observed, aligning well values reported in previous studies. It is noteworthy that the selective layer thickness ~ 145 nm in the PEI-TMC-CC is thicker than the selective layer in the PEI-TMC (Fig. 3h). This increase is attributed to the grafting of CC molecules onto the

polymer network structure. The additional thickness in the PEI-TMC-CC membrane results from a second reaction between the $-\text{OH}$ groups on the choline chloride molecules and the incompletely reacted acid chloride groups on the surface of membrane. The average surface roughness of the PEI-TMC is higher than the PEI-TMC-CC as depicted in Fig. 3f and i, indicating that the grafting of choline chloride onto the polymer network structure leads to a smoother membrane surface. The above analysis further proves the successful grafting of choline chloride on the membrane.

3.2. Optimization of membrane fabrication conditions

Fig. 4 displays the pure water permeance of PEI-TMC-CC membranes fabricated by different experimental conditions. As depicted in Fig. 4a, with an increase in choline chloride concentration from 0.0 wt% to 1.5 wt%, the water permeance initially rises from $3.3 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ to $10.0 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. This increase is ascribed to the enhanced hydrophilicity of the membrane with rising choline chloride concentration, leading to an overall improvement in water permeance. However, as the choline chloride concentration further increases to 1.5 wt%, the pure water permeance experiences a decline, possibly due to the modified layer becoming overly dense. Simultaneously, the presence of positively charged $-\text{N}^+$ groups resulting from choline chloride grafting on the membrane surface contributes to the membrane's excellent rejection performance. When modifying the membrane surface using grafting methods, the grafting time is also a crucial parameter. As shown in Fig. 4b, with the increase in grafting time, the pure water permeance of the membrane initially rises, then stabilizes almost entirely, with only a slight decrease. The initial increase in water permeance can be ascribed to the grafted choline chloride, enhancing the membrane permeance. The subsequent stabilization of permeance may suggest that surface grafting is nearly complete after 10 min, with the slight decrease potentially attributed to an increase in the thickness of selective layer due to the excessive grafting time. On the other hand, the heating time after membrane surface modification also appears to be critical. When unheated, the membrane demonstrates a low Mg^{2+} rejection and a great water permeance, possibly due to insufficient dense of the unheated polyamide layer (Fig. 4c). As the heating time increases, the water permeance initially decreases from $14.1 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ to $12.3 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and then to $10.0 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, while the Mg^{2+} interception gradually increased to 98.3 %, which may be ascribed to the denser selective layer as the heating time increases (Fig. 4c). As the heating time continues to increase, the rejection of Mg^{2+} remains stable, while water permeance noticeably decreases. This indicates that prolonged heating results in an excessive density of the polyamide membrane, reducing its water permeance. The pure water permeance of the PEI-TMC-CC membrane with a heating time of 5.0 min ($10.0 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) is approximately three times that of the conventional PEI-TMC

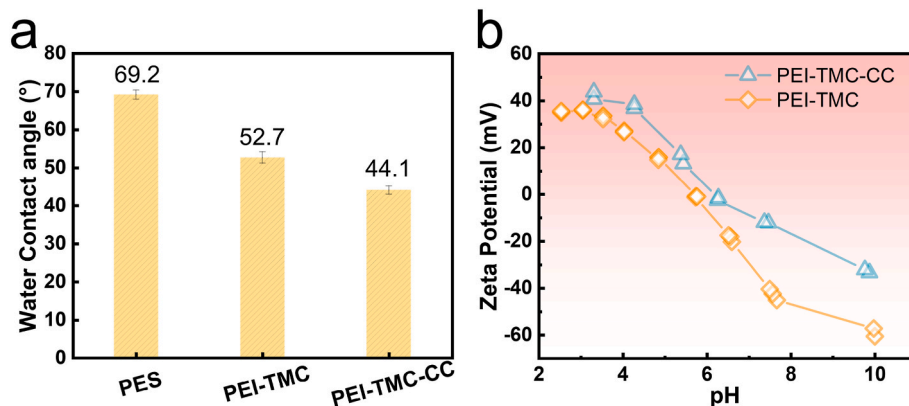


Fig. 2. (a) Water contact angle of PES, PEI-TMC and PEI-TMC-CC membranes. (b) Zeta potential of the PEI-TMC and PEI-TMC-CC membranes.

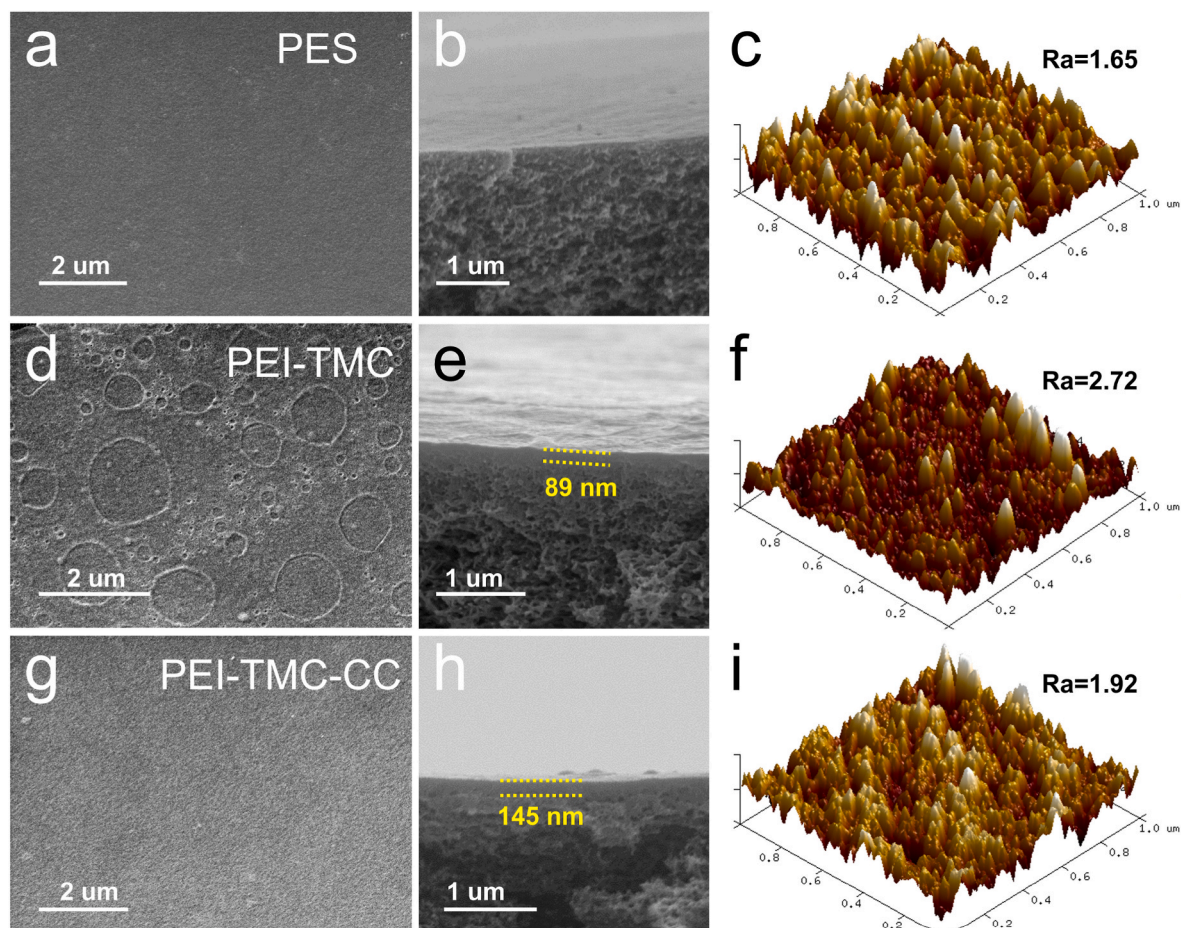


Fig. 3. The surface, cross-section, and AFM information of (a, b, c) PES, (d, e, f) PEI-TMC and (g, h, i) PEI-TMC-CC membranes.

membrane without choline chloride modification ($3.3 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$). More importantly, as the membrane permeance undergoes changes, the rejection of cations in the MgCl_2 solution remains consistently high, ensuring the effective removal of divalent cations. Therefore, the optimal membrane manufacturing reaction conditions, balancing both permeance and rejection, were found to be a grafting and heating time of 10 min and 5 min, as well as the choline chloride concentration of 1.0 wt %. On the other hand, the molecular weight cutoff (MWCO) of the PEI-TMC-CC membrane (310 Da) was higher than that of the PEI-TMC membrane (258 Da). Meanwhile, the average pore size of the membrane decreased from 0.48 nm to 0.46 nm with the grafting of CC (Fig. 4d), indicating that the successful grafting of CC reduced the average pore size of the membrane and enhanced the retention of heavy metal ions by enhancing the sieving effect.

3.3. Nanofiltration performance test

Fig. 5 presents the membrane separation performance of the PEI-TMC-CC for heavy metal cations solutions of varying concentrations and types. In Fig. 5a, it is evident that the PEI-TMC-CC exhibits a great removal rate for heavy metal cations (Cd^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , and Pb^{2+}) at a concentration of 200 ppm. Notably, even for Pb^{2+} , which has the smallest hydrated cation radius, the membrane achieves a rejection rate of over 96 %. Moreover, as illustrated in Fig. 5a, the PEI-TMC-CC membrane continues to maintain its rejection of heavy metal cations (1000 ppm). However, with a further increase in the heavy metal cations concentration of the solution, a slight reduction in permeance is observed. The decrease in membrane permeance may be attributed to the increase in osmotic pressure resulting from the high heavy metal

cations concentration in the feed solution. Fig. 5b demonstrates that the water permeance of the PEI-TMC-CC membrane remains relatively constant as the operating pressure increases from 2 bar to 6 bar. Concurrently, the PEI-TMC-CC membrane maintains a high retention rate of heavy metals in a mixed heavy metal ion solution, indicating its stable pressure resistance and excellent heavy metal ion retention capacity. Fig. 5c shows the long-term stability of the PEI-TMC-CC membrane. Over the 10-day test period, both the permeance and rejection rate of the PEI-TMC-CC for heavy metal ions remained stable. On the other hand, nanofiltration membrane for treating heavy metal wastewater frequently encounters the issue of scaling during application. Anti-scaling testing has demonstrated that the PEI-TMC-CC membrane exhibits superior anti-scaling performance. For further details and discussion, please refer to the Supporting Information. This suggests that PEI-TMC-CC holds good potential for industrial applications. The nanofiltration performance of membranes regarding heavy metal removal reported in the previous studies and PEI-TMC-CC are shown in Fig. 5d and Table S3 [30–38]. It is evident that the PEI-TMC-CC exhibits a great permeance and a commendable ion rejection rate. This observation highlights the superior performance of the PEI-TMC-CC in removing divalent heavy metal ions, underscoring its strong competitiveness compared to membranes reported in the literature. Meanwhile, the price of choline chloride is much lower than that of reported molecules or materials for membrane modification (Table S4), further confirming the affordability of this material.

3.4. DFT calculation

Density functional theory methods are commonly employed to

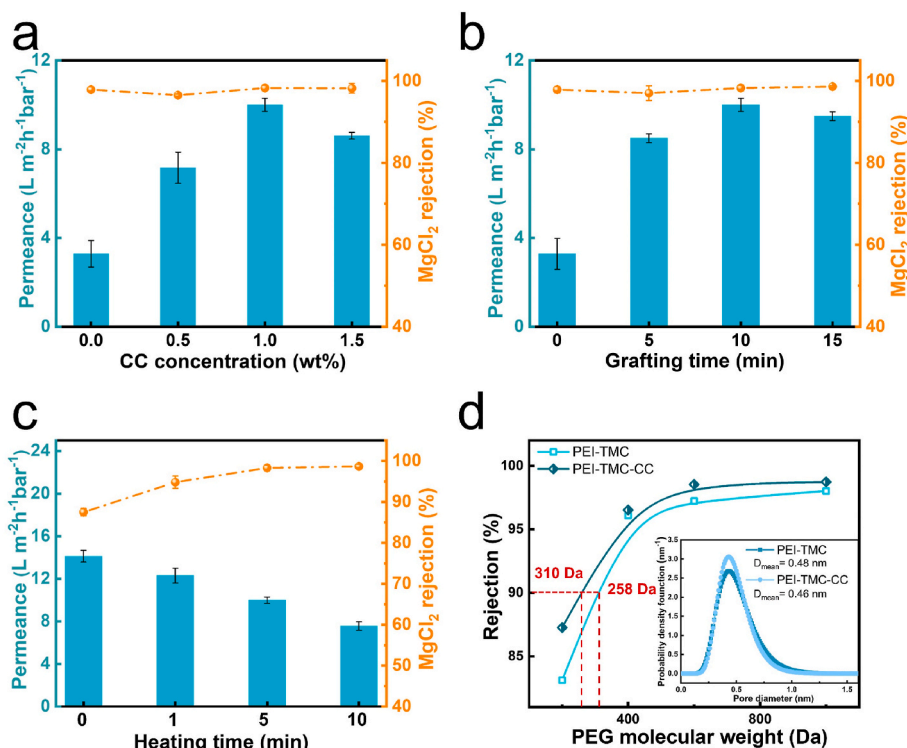


Fig. 4. The $MgCl_2$ (1000 ppm) rejection and water permeance of membrane with (a) different CC concentrations, (b) different grafting time, and (c) different heating time. (d) Molecular weight cut-off and pore size distribution.

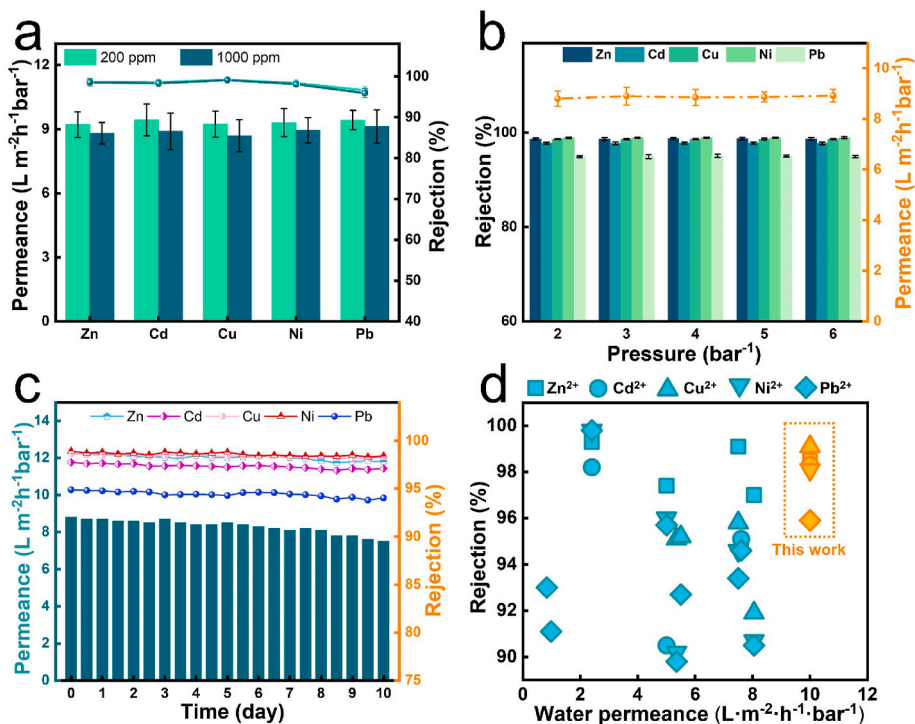


Fig. 5. (a) Rejection and permeance of the PEI-TMC-CC for heavy metal cations ($ZnCl_2$, $Cd(NO_3)_2$, $Cu(NO_3)_2$, $Ni(NO_3)_2$ and $PbCl_2$) with 200 ppm and 1000 ppm concentration (detailed pH value of heavy metal solution was present in Table S2). (b) Rejection and permeance of the PEI-TMC-CC for mixed heavy metal solution with different pressure. (c) Long-term stability of the PEI-TMC-CC for mixed heavy metal solution at 6 bar. (d) Comparison of the heavy metal cations rejection and water permeance of the PEI-TMC-CC membrane with the membranes in previous studies.

investigate intermolecular interactions, with the interaction force involving water molecules serving as a determinant of the substance's hydrophilicity or hydrophobicity [39]. In Fig. 6a, it is evident that

compared to PEI [39], water molecules exhibit a greater adsorption affinity to choline chloride, indicating that water molecules are more likely to adsorb on choline chloride, thereby confirming the superior

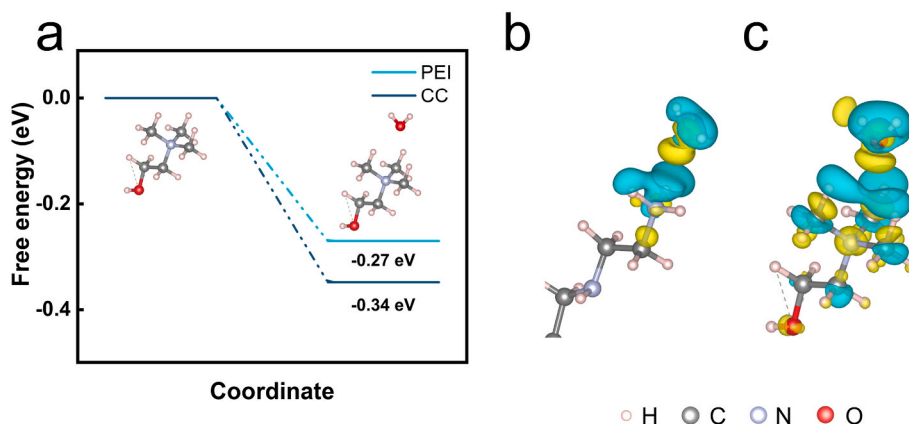


Fig. 6. (a) Relative free energy profile of the H_2O adsorption on the PEI and CC. DFT calculations for the electron density difference between (b) PEI (part of PEI, detail in supporting information) and (c) choline chloride with H_2O .

hydrophilicity of choline chloride. Furthermore, charge density difference analysis, illustrated in Fig. 6b–c and S8–9, reveals a more substantial charge transfer between choline chloride and H_2O compared to PEI, aligning with the results of free energy analysis. On the other hand, both PEI and CC react with TMC, and the interaction between the reaction products and water is also crucial. Models of PEI-TMC composites and CC-TMC composites were optimized to simulate the products formed from the reactions of PEI and CC with TMC (Fig. S10). Interestingly, the free energy changes associated with water adsorption on these composites are comparable to the results observed without TMC (Fig. S11). This further indicates that CC offers superior hydrophilicity. The DFT results above confirm that choline chloride exhibits superior hydrophilicity, consistent with the experimental findings.

4. Conclusion

In summary, the grafting of choline chloride onto the PEI-TMC surface effectively improves the membrane hydrophilicity and water permeance. This method enhances the membrane's capability to intercept heavy metal ions in heavy metal wastewater while markedly enhancing water permeance. The introduction of choline chloride not only adds positive charges to the PEI-TMC but also augments its hydrophilicity, thereby enhancing water permeance. The resulting PEI-TMC-CC exhibits outstanding water permeance at $10.0 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, approximately three times that of the unmodified membrane. Simultaneously, the PEI-TMC-CC maintained a high heavy metal ions rejection over 10-day of long-term stability testing. Additionally, the membrane demonstrates a high rejection performance for Zn^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , and Pb^{2+} . The rejection of Zn^{2+} , Ni^{2+} , Cu^{2+} , and Cd^{2+} all exceed 98 %, while the rejection of Pb^{2+} is approximately 96 %. These findings underscore the membrane's effectiveness in removing heavy metal ions from wastewater. Furthermore, DFT calculations confirm the increased hydrophilicity of choline chloride molecules. The findings of this study suggest that the modification of nanofiltration membranes using cost-effective and highly hydrophilic quaternary ammonium choline chloride holds significant promise for industrial applications.

CRediT authorship contribution statement

Junwei Li: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Yihao Song:** Conceptualization, Methodology, Writing – review & editing. **Daliang Xu:** Methodology, Resources, Data curation, Writing – review & editing, Investigation. **Xi Zhang:** Methodology, Investigation, Formal analysis, Data curation. **Jiale Du:** Conceptualization, Methodology, Investigation. **Riri Liu:** Writing – review & editing, Formal analysis. **Rui Zhao:** Writing – review & editing, Formal analysis. **Qin Chen:** Writing –

original draft, Investigation. **Alexander Volodine:** Methodology. **Raf Dewil:** Methodology. **Qieyuan Gao:** Methodology, Supervision, Writing – review & editing. **Bart Van der Bruggen:** Methodology, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.memsci.2024.123079>.

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