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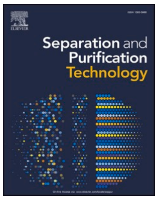

Enhanced anti-fouling performance through integrated coagulation and membrane co-deposition modification for sustainable water treatment

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ABSTRACT

Membrane fouling remains a significant challenge limiting the widespread use of membrane technology in water treatment, particularly in ultrafiltration (UF) processes. To address this, we proposed a "coagulation + membrane modification" strategy to enhance fouling mitigation. The UF membranes were modified with polydopamine (PDA)-polyethyleneimine (PEI) and zwitterions via co-deposition. We investigated membrane morphology, physicochemical properties, hydrophilicity, permeability, and anti-fouling performance. Results showed that both PDA-PEI and zwitterions produced a more uniform and smoother deposited layer, while only PDA-PEI reduced the membrane contact angle by approximately 43 %, significantly improving surface hydrophilicity. Membranes modified with PDA-PEI exhibited exceptionally high permeability (159.02 $L \cdot m^{-2} \cdot h^{-1}$) and a high humic acid (HA) rejection rate (91.25 %). Additionally, the PDA-PEI-modified membrane demonstrated excellent antifouling properties, achieving a flux recovery ratio of over 95 % after three cycles. Furthermore, this strategy was applied to actual water treatment, where it outperformed single coagulation or membrane modification alone. The combined approach achieved removal rates of approximately 100 %, 87 %, 92 %, and 84 % for turbidity, TOC, HA, and NOR, respectively, in real water samples. Notably, the strategy showed strong antifouling performance with a specific flux of 0.9 and a flux decline rate of just 10 %, highlighting its considerable potential for improving the fouling resistance of UF processes in water treatment.

1. Introduction

Water scarcity is a significant challenge threatening human health and sustainable development. Compared with traditional water treatment processes, membrane technology is a well-established method owing to its simple operation and cost-effectiveness. Ultrafiltration (UF) is widely integrated into the water treatment field due to its advantages, such as its excellent removal efficiency, relatively low energy consumption, compact treatment installations, simplicity of operation and reasonable operational and capital cost [1,2]. However, a drawback of UF technology that inevitably restricts its extensive application is its propensity for membrane fouling, which is caused by undesirable pore adsorption, cake layer formation and concentration polarization [3]. It has been demonstrated that membrane fouling will inevitably lead to a flux decline, shorter membrane life and deterioration of water quality, resulting in higher operating costs and deceleration of the UF commercialization process [4]. Therefore, numerous types of research have been carried out to approach its multiple applications and mitigate membrane fouling.

Up to now, several common substrate materials such as polyacrylonitrile (PAN), polyvinyl chloride (PVC), polyvinylidene fluoride (PVDF), polyethersulfone (PES) and polysulfone (PSF) have been utilized for the fabrication of UF membranes due to their better thermal and chemical corrosion-resisting capacities [5–9]. However, the hydrophobicity of these materials is the main reason for membrane fouling and permeability degradation. To minimize this unintended

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consequence, improving the membrane surface hydrophilicity to impart the membrane antifouling properties has been recognized as an effective method for alleviating membrane fouling.

There are various methods for improving membrane hydrophilicity, such as surface coating and grafting [10–12], incorporating hydrophilic nanoparticles [13,14] and blending with hydrophilic polymers [15,16]. Among these surface modification methods, introducing surface-modifying macromolecules (SMMs) into the host membrane polymer would be an essential method [17,18]. The key features of SMM included that, firstly, they could mix with the base polymer and prepare the modified membranes using a single casting step, as opposed to the multi-step processing required to prepare composite membranes. Secondly, they are entrenched in the polymer matrix and would not leach out like other additives. Thirdly, they would migrate to the membrane surface after casting and impart the membrane's different characteristics [19]. For the fabricated membranes, the SMMs migrated to the surface, rendering the surface either hydrophobic [20,21] or hydrophilic [22], depending on the functional group of the added SMMs. In recent years, surface treatment using polydopamine (PDA) has been increasingly studied due to its simplicity, versatility, effortless control, stability of the coating, and low damage to the membranes, and some studies focused on developing a kind of low-cost, super hydrophilicity, and fouling resistance of hydrophobic membranes with PDA/PEI as a modified coating [23,24].

Meanwhile, hydrophilic nanomaterials have been widely introduced into membrane material due to their simple operation and excellent effects. A kind of UF membrane was fabricated by adding modified MoS_2 nanoparticles with polydopamine (PDA) and polyethyleneimine (PEI) into the PES membrane, and the results indicated that the permeability, rejection and antifouling capability of the modified membrane were improved compared with the pristine membrane [25]. Similarly, both nano-porous metal–organic frameworks (MOFs) and organic PDA layer have been introduced into the PES membranes as a novel dopant to prepare UF membranes, and the obtained membranes incorporated with MOFs@PDA exhibited exceptionally high permeability at about 209.02 $L\cdot m^{-2}\cdot h^{-1}$, high BSA rejection at about 99.12 % and significant improvements in flux recovery ratio at about 82 % [26]. Both excellent antifouling properties could be attributed to the formation of the porous structure and the improvement of the membrane hydrophilicity.

In addition, conventional chemical coagulation is still regarded as an effective pretreatment technology for UF membrane fouling. This technology is essential to ensure UF performance and reduce unnecessary damage to the membranes [27–29]. Aluminum (Al) salts and iron salts (Fe) are commonly used inorganic coagulants for the pre, treatment of water treatment [30,31], and relevant research results show that both of them could enhance the membrane permit and substantially mitigate membrane fouling [31–34]. However, the coagulant concentration should be strictly controlled as the coagulant dosage could affect the degree of membrane fouling, while the spatial distribution of the formed micros and particles plays a critical role in improving the cake layer microstructure [34,35]. Meantime, some researchers highlighted that Al-based salts were active in the typical pH range between 6 and 8 and could remove about 34 %-53 % of natural organic matter (NOM). At the same time, iron species were active at pH between 4 and 6, and the NOM removal rate was only 28 %-40 % [29].

Based on the above analysis, a “coagulation + membrane modification” work was proposed to enhance this work's permeability performance and antifouling ability. Firstly, a series of UF membranes modified by PDA-PEI and some zwitterions, including betaine (BA) and sulfobetaine methacrylate (SBMA), were prepared, and the resultant membranes were comprehensively characterized. Then, the separation behaviors and antifoam membranes were evaluated to obtain the optima-modified membrane. Finally, the “coagulation + membrane modification” process evaluated the separation performance and antifouling ability given simulated and actual water, respectively. The results enhanced our understanding of coagulation mechanisms and provided a reference for the practical application of improving the antifouling ability of the UF process in water treatment.

2. Materials and methods

2.1. Membrane and reagents

Polysulfone (PSF) ultrafiltration membrane (GC-UF0201, MWCO of 20000) was provided by Guochu Technology. The following substances were supplied by Maclean Biochemical Technology Co Ltd: HCl, NaOH, Dopamine (DA), Trimethylol aminomethane, polyethyleneimine (PEI), Betaine (BA), sulfobetaine methacrylate (SBMA), poly aluminium chloride (PAC), Norfloxacin (NOR) and Humic acid (HA). All the reagents were analytical grades and used without further purification. Deionized water was used in all experiments.

2.2. Preparation of modified membrane

2.2.1. Preparation of modified solution

To obtain a PDA/PEI modified precipitated solution, Tris-HCl buffer solution (pH = 8.5) was prepared first, and then 2 g/L dopamine hydrochloride and 2 g/L polyethyleneimine were dissolved in the buffer solution. Since PDA tends to form free DA particles at high concentrations or temperatures, the newly prepared solution was shaken vigorously and conducted at 25 ℃ to avoid the formation of large PDA particles. PDA-PEI-betaine (PDA-PEI-BE) and PDA-PEI-sulfobetaine methacrylate (PDA-PEI-SBMA) were performed by similar steps except that PDA, PEI, betaine and SBMA were added simultaneously in the second step.

2.2.2. Membrane preparation by co-deposition modification

All of the UF membranes were prepared by co-deposition modification, as shown in Fig. 1. Firstly, the membrane was cut into a circular piece with a radius of 53 mm and soaked in deionized water for 2 h. Afterwards, the cleaned membrane was exposed to air at room temperature for 3 h to dry the surface and fix it into the self-assembled membrane deposition device. The UF membranes were modified by co-deposition of PDA and PEI. The freshly prepared PDA-PEI solution was immediately placed into the round holder to contact the UF membrane for variable co-deposition durations (i.e.,6h, 8 h, 10 h, 12 h, 14 h, and16h) by oscillating at a constant temperature on a Table concentrator (25 ℃, 65r/min). After the co-deposition, the membranes were removed and washed with deionized water three times and dried at 25 ℃ before use. In addition, zwitterionic monomers, such as BA and SBMA, possess a unique molecular structure of cationic and anionic moieties, could not only remove foulants, but increase hydrophilic properties, and control particle aggregation. Meanwhile, BA and SBMA exhibited good synergy with PDA and are considered to be some of the most excellent antifouling agents in membrane modification. Therefore, zwitterionic monomers were introduced in our study. The preparations of other modified membranes were accomplished using similar methods, and these membranes were denoted as PDA-PEI, PDA-PEI-BA, and PDA-PEI-SBMA, respectively.

2.3. Characterizations

The prepared modified membranes' surface chemical structures and compositions were characterized by Raman spectroscopy and X-ray Photoelectron Spectroscopy (XPS; PHI 5400 ESCA system) instrument. The hydrophilicity of the membranes was tested by a contact angle goniometer (JC2000DF, Shanghai Zhong Chen Digital Technology Equipment Co., Ltd.). The surface morphologies of the membranes were observed by Field emission scanning electron microscope (FE-SEM, MIRA4 Tescan, Czech Republic).

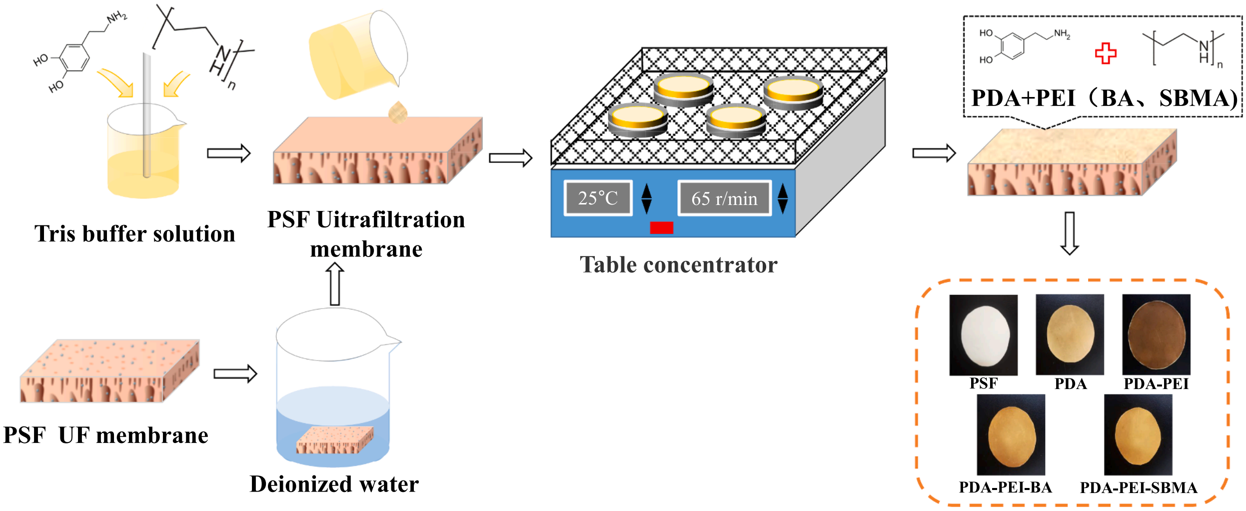


Fig. 1. Schematic diagram of modified UF membranes preparation.

2.4. *Separation performance*

The filtration behavior of the prepared membranes was tested in a lab-made cross-flow filtration device (effective membrane area: 2.81 × 10^{-3} m^2). Firstly, the bio-modified membranes were pre-compacted by filtrating the pure water at ambient temperature for 0.5 h to obtain a stable permeation. Subsequently, the filtration performance of the modified membranes was evaluated. The prepared membranes' flux (J) and solute rejection (R) were measured using the following Eqs. (1) and (2), respectively:

$$J = \frac{V}{A \bullet \Delta P \bullet \Delta t} \tag{1}$$

where v (L) represents the volume of permeate at time interval of Δt(h), ΔP (bar) denotes the applied pressure, and A (m^2) is effective area of the membranes.

$$R(\%) = 1 - \frac{C_p}{C_f} \tag{2}$$

where C_p (mol/L) and C_f(mol/L) represent the corresponding solution concentration in permeation and feed solutions, respectively.

Lastly, 20 mg/L polyaluminum chloride (PAC) was used as a coagulant. A combined coagulation-membrane modification process was adopted to treat simulated and actual water, respectively, and the separation performance was evaluated.

2.5. *Antifouling properties*

To test the antifouling property of the modified membranes, pristine PSF membrane and PDA-PEI, PDA-PEI-BA and PDA-PEI-SBMA modified membranes (modification time was set at 8 h) were chosen to carry out the antifouling experiment. This study used HA as a typical pollutant, and 8 mg/L HA solution (pH = 7) was used as feed water. The membrane was first operated with deionized water at 0.5 MPa for 30 min to obtain a stable state. The humic acid aqueous solution was filtrated by the UF process, which consisted of three cycles, and each cycle included a contamination phase (120 min), a cleaning phase (10 min) and a deionized water filtration phase (20 min). The flux decline rate (FDR) and flux recovery rate (FRR) were calculated using the following Eqs. (3) and (4), respectively:

$$FDR(\%) = \left(1 - \frac{J_p}{J_w}\right) \times 100\% \tag{3}$$

$$FRR(\%) = \frac{J_R}{J_w} \times 100\% \tag{4}$$

where J_w (L/m^2·h·bar), J_p (L/m^2·h·bar) and J_R (L/m^2·h·bar) represent the initial flux, the flux after UF process and the flux after membrane cleaning, respectively.

3. Results and discussion

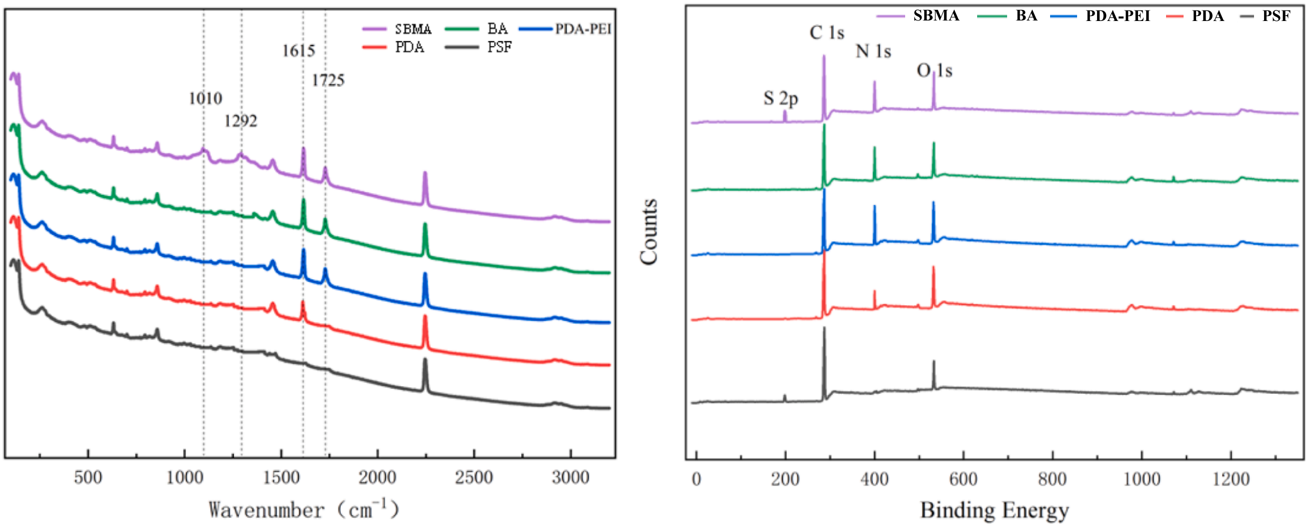
3.1. *Characterization of modified membranes*

3.1.1. *Analysis of membrane surface chemical structure*

As shown in Fig. 2a, compared with the pristine PSF membrane, the other four modified membranes showed a more substantial vibration peak at 1615 cm^{-1}, attributed to the N–H bending vibrations. The peak in the PDA-PEI-modified membrane was more evident than in the PDA-modified membrane. The reason was that many N–H bonds existed in both PDA and PEI molecules. Besides, in the PDA-PEI, PDA-PEI-BE, and PDA-PEI-SBMA modified membranes, a new vibration peak at 1725 cm^{-1} appeared, attributed to the C = N absorption vibration peak. The Schiff base reaction between the primary amine group on PEI and the C = O double bond on the benzene ring in the quinone dopamine molecule generated this vibration peak. For the PDA-PEI-SBMA modified membrane, two new vibration peaks at 1080 cm^{-1} and 1292 cm^{-1} represented the S = O group and the sulfonate functional group, respectively. These changes in the characteristic peaks indicated the existence of PDA, PEI, BA and SBMA on the membrane surface, and the modification was successful.

The surface chemical compositions for the membranes and the surface elemental compositions are shown in mole ratios in Table 1. As shown in Fig. 2b, the pristine PSF membrane had no nitrogen, but it was observed for the other four modified membranes. Moreover, evident differences were observed for the peak intensities and atomic compositions, as shown in Table 1. In the PDA-modified membrane, the content of the O element (14.5 %) was significantly higher than that of the N element (5.8 %). The O/N molar ratio was about 2.41, while for the PDA-PEI modified membrane, the O element and N element content were 14.2 % and 14.8 %, respectively, and the O/N ratio is close to 1. The content of the N element in the modified membrane is increased due to the addition of the PEI molecule. The reason was that the PDA molecule had C, N and O elements, while C and N elements were in the PEI molecule.

On the other hand, compared with pristine PSF membrane, the S element was not detected in PDA, PDA-PEI and PDA-PEI-BA modified



(a)

(b)

Fig. 2. Chemical structure characterization. Raman spectrum (a) and XPS wide scan spectra (b).

Table 1
Elemental composition of pristine PSF and modified membranes.

Membranes	C 1(%)	O 1 s (%)	N 1 s (%)	S 2p (%)	O/N
Pristine PSF	85.4	13.8	/	0.8	/
PDA	79.7	14.5	5.8	/	2.41
PDA-PEI	71	14.2	14.8	/	1.17
PDA-PEI-BA	71	14.6	14.4	/	1.03
PDA-PEI-SBMA	69	15	13.9	2.1	1.8

membranes. The reasons might be that the co-deposited layer was very thick, the PSF membrane was fully covered, and the X-ray could detect no evident PSF substrate signal. Besides, the concentration of S element in the PDA-PEI-SBMA membrane increased obviously due to the presence of S element in SBMA. In summary, comparing the surface chemical structure and composition of the PSF membrane and the modified membranes, it could be proved that the adopted modified substances PDA, PEI and zwitterions in this study could be well deposited on the surface of the PSF membrane.

3.1.2. Surface morphology of membranes

The surface morphology of the pristine PSF membrane and other modified membranes are presented in Fig. S1. It could be observed that the PSF membrane surface was relatively smooth, and no apparent pores were observed. However, for the PDA-coated membranes, there were numerous parties on the PDA-coated surface. It has been PDA-contested that the PDA-coated layer may be composed of aggregated nanoparticles, which is related to the formation mechanism of PDA [36]. Notably, the aggregated PDA nanoparticles would block the membrane pores, resulting in a noticeable decrease in membrane flux. Therefore, although the PDA modification could improve the hydrophilicity of the membrane surface to a certain extent, the blockage of the membrane pores might lead to the aggravation of membrane fouling, which is consistent with most studies in the literature [37,38]. For the PDA-PEI-modified membrane, smooth wrinkles appeared, and aggregated nanoparticles disappeared. Since the cross-linking reaction between PEI and the PDA molecule occurred, the self-polymerization of PDA was destroyed, and the aggregated PDA nanoparticles on the membrane surface gradually disappeared. This suggested that introducing PEI could inhibit the formation of PDA aggregates, contributing to the mitigation of membrane fouling. Besides, compared with the PDA-PEI modified membrane, the wrinkles on the PDA-PEI-BE membrane surface were reduced, and the PDA-PEI-SBMA membrane surface was smoother, indicating that a uniform zwitterion polymer layer could be formed on the surface of the two modified membranes, and the introduction of zwitterions was conducive to improving the smooth degree of the membrane surface.

3.1.3. Water contact angles

The impact of modified materials on membrane surface hydrophilicity was evaluated using dynamic water contact angle measurements, as shown in Fig. S2. The water contact angle of the pristine PSF membrane was 47°. Then, the initial measurement dropped to 34° and 27° in the PDA-modified and PDA-PEI-modified membranes, respectively, indicating that PDA and PDA-PEI modification imparted increased hydrophilicity. The reason for this phenomenon was that both PDA and PEI molecules contained a large number of hydrophilic groups (such as –OH, $-NH_2$), which could increase the water adhesion ability of the membrane, and the hydrophilic functional groups had a strong attraction to water molecules and formed a hydration shell on the membrane. After the introduction of BA, however, the water contact angle increased. By introducing SBMA, the modified membranes encompassed a more significant number of hydrophilic functional groups sulfonates from SBMA; accordingly, the water contact angle was reduced, and the hydrophilicity of the membrane was improved. However, it is also worth noting that although some studies have reported that sulfobetaine groups are capable of creating a hydration layer from free water molecules through electrostatic interactions and hydrogen bonding, thus making the membrane more hydrophilic [39], the value of its water contact angle was not significantly higher than that of PDA-PEI modified membrane, therefore, considering the comprehensive properties of the membranes and the fact that PEI can simultaneously minimize PDA aggregation through covalent polymerization of dopamine, PDA-PEI modified membrane could be selected in our subsequent study.

3.2. Membrane performance analysis

3.2.1. Flux and rejection rate

To ensure the efficiency and quality of water treatment, UF membranes must have a high flux and rejection rate, especially for wastewater containing high concentrations of pollutants. The three modified membranes' performance at different modification times was evaluated by flux and HA rejection rate. As shown in Fig. 3, it can be seen that the flux of all three modified membranes decreased with the extension of modification time. Compared with the PDA-PEI-modified membrane, the introduction of BA and SMBA could improve the permeability of the membranes under the same conditions, which further demonstrated the introduction of zwitterions was conducive to improving membrane permeability. On the other hand, the rejection rate of PDA-PEI modified membrane decreased gradually with the extension of modification time.

In contrast, PDA-PEI-BA and PDA-PEI-SBMA membranes showed the opposite trend, which may be attributed to the positive charge on the surface of the membranes. For the solution with pH = 7, the ionization of HA negatively charged the solution, and the electrostatic repulsion with the membrane surface was relatively weak. However, the introduction of zwitterions reduced the positive charge on the surface of the membrane. It increased the electrostatic repulsion between the membrane and the solution, increasing the rejection rate. Accordingly, for the PDA-PEI modified membrane, with the extension of modification time, the PDA-PEI deposited layer became thicker, and the positive charge on the membrane surface gradually increased, making a more substantial electrostatic attraction effect. Thus, the rejection rate decreased with the modification time.

On the contrary, for both PDA-PEI-BA and PDA-PEI-SBMA membranes, with the extension of time, more amphoteric ions were introduced to the surface of the membranes, and the electrostatic repulsion was enhanced. Therefore, the rejection rate for HA increased. It is worth noting that when the modification time was set at 8h, the PDA-PEI modified membrane presented a controlled flux but maintained a retention rate of more than 90 %.

3.2.2. *Antifouling ability*

During the UF process, pollutant molecules would deposit or adsorb on the surface and the inside pores of the membrane, causing a flux decrease in flux. Fig. 4 shows the time-dependent fluxes. In our study, the ratio of the flux after the UF process J_p (L/m^2·h·bar) to the initial flux J_w (L/m^2·h·bar) was adopted as normalized water flux. It could be observed that the fluxes for three modified membranes decreased dramatically due to the adsorption or deposition. After 120 min of HA ultrafiltration, the membranes were cleaned and then placed in deionized water; the fluxes of all the membranes recovered partially. Fig. 5 presented the pollution degree and flux recovery degree of the three modified membranes, where the green area represented the flux recovery rate (FRR), and the orange area represented the flux decline rate (FDR). It could be seen that with the introduction of BA and SBMA, the FRR of the modified membranes was slightly reduced but remained at more than 90 %. After three cycles, it was still maintained at a high level, indicating that all the modified membranes had good antifouling properties for HA. Compared with PDA-PEI-BA and PDA-PEI-SBMA-modified membranes, PDA-PEI-modified membranes presented the best antifouling properties with the highest FRR, which might be attributed to the increased hydrophilicity. Furthermore, the HA molecules might be grafted onto the modified membrane surface during the UF procedure. Then, the molecules tend layer decreases the position of HA molecules and suppresses formation.

In summary, PDA-PEI-8 modified membrane showed better performance in terms of flux, rejection rate and anti-fouling ability, therefore, PDA-PEI-8 modified membrane was utilized in subsequent study.

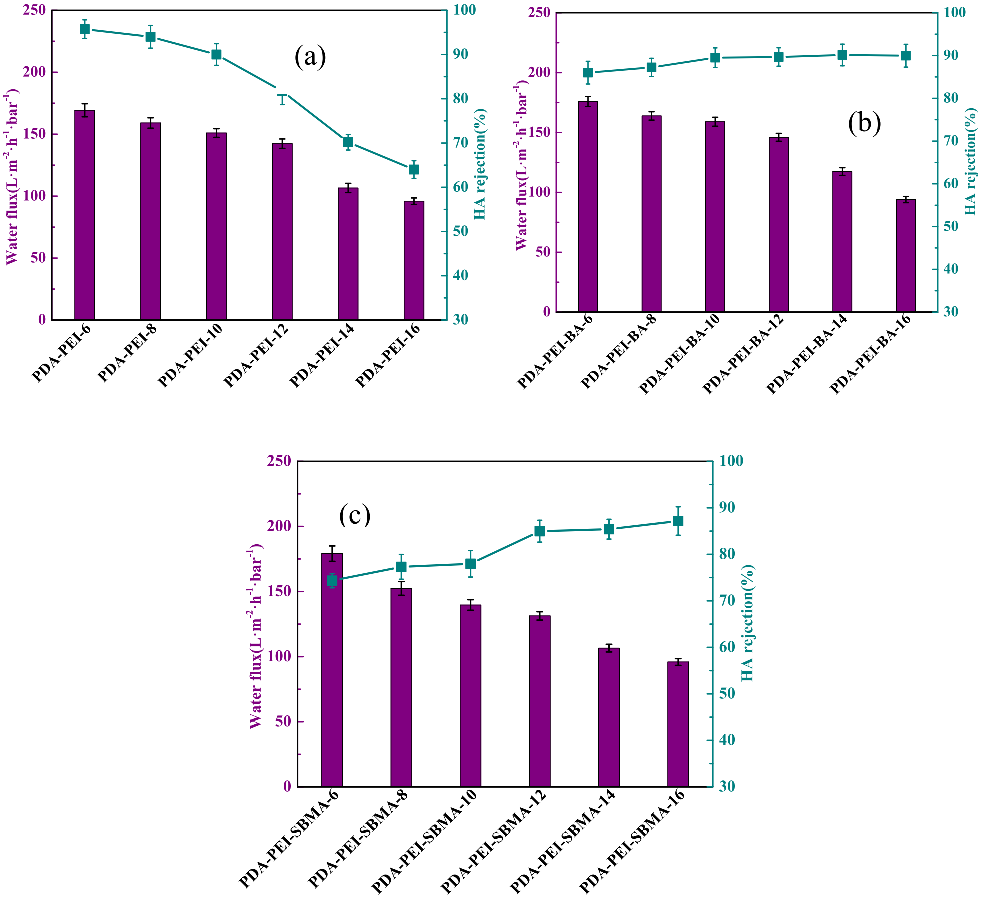


Fig. 3. Water flux and HA rejection of modified membranes with different coating times (a) PDA-PEI modified membranes (b) PDA-PEI-BA modified membranes; (c) PDA-PEI-SBMA modified membranes.

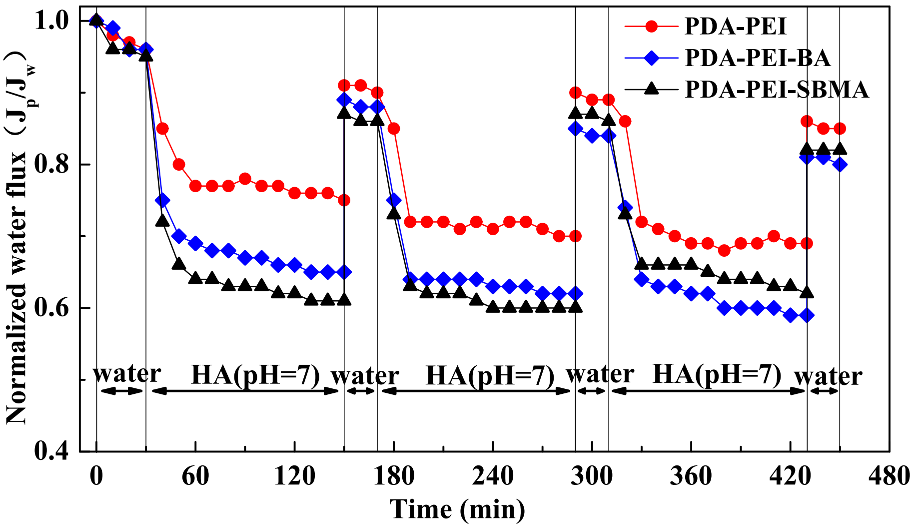


Fig. 4. Time-depended fluxes of different modified membranes.

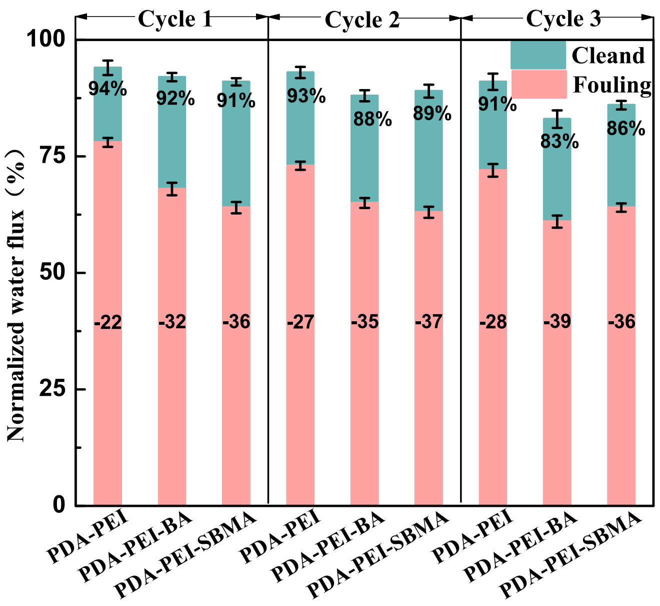


Fig. 5. Flux recovery rate (FRR, green area) and flux decline rate (FDR, orange area) of modified membranes after three cycles.

3.3. Separation performance of the integrated process

The removal rates of turbidity, TOC, HA and NOR in simulated water and actual water by the integrated coagulation-membrane modification process were shown in Fig. 6. As shown in Fig. 6a, the turbidity removal rates in simulated water for pristine membrane, PDA-PEI modified membrane, coagulation-pristine membrane and coagulation-membrane modification membrane were 63 %, 90 %, 95 %, and 98 %, respectively. Compared with the pristine membrane, the turbidity removal rate of membrane modification was increased by 27 %, and that of the coagulation process was increased by 32 %, indicating that coagulation had an excellent removal effect on suspended matter and most of the turbidity could be removed. After combining coagulation and membrane modification, the turbidity removal rate was further improved to about 100 %. The variation trend of the four membranes was similar to that of simulated water for actual water, indicating that the proposed integrated process could effectively remove turbidity in actual water.

Fig. 6b presented the TOC removal rates in simulated water and actual water. It could be found that the TOC removal rates of the four processes were only 14 %, 83 %, 45 % and 92 %, respectively. The removal rate is lower for pristine PSF membranes due to the larger membrane pore size. Compared with the pristine membrane, the PDA-PEI modified layer played an excellent role in TOC rejection, and the removal rate was increased by nearly 70 %. One possible reason was that the organic matter in the simulated water was mainly HA with considerable molecular weight, and the pore size of the modified layer was much smaller than that of the macromolecular organic matter. Thus, the sieving effect is the primary removal mechanism. Coagulation-membrane modification exhibited the highest TOC removal rate of more than 90 %. The excellent TOC removal rate is attributed to the fact that the hydrophilic acid macromolecules of HA were readily adsorbed and captured by the porous and loose aluminium hydroxide flocs formed in raw water during the coagulation process and then the net sweeping flocs. However, compared with simulated water, the four processes showed a lower TOC removal rate in actual water, at about 10 %, 79 % ，30 %, and 87 %, respectively. The reason was that compared with the simulated water containing only HA, the organic composition in the actual water was more complex, and the TOC removal rate was lower under the same condition. It is worth noting that due to the low turbidity of the actual water, fewer porous and loose alumina hydroxide flocs were formed in the coagulation stage, and the organic matter adsorbed and captured was significantly reduced. Hence, the TOC removal rate in the simple coagulation process was reduced by 15 %. However, as expected, the TOC removal rate of the combined coagulation-membrane modification process could still be up to 87 %. The results verified that the integrated process could have an excellent removal effect on the organic matter in the actual water.

In addition, the removal rates of HA in simulated water and actual water by the four processes were analyzed in Fig. 6c. By comparison; it was easy to find that the trend of HA removal rate of the four membranes was similar to that of TOC removal rate, and higher than the TOC removal rate under the same conditions. As expected, the removal rate of HA by the integrated coagulation-membrane modification process was almost 100 %, which could be further improved based on single membrane modification, indicating that coagulation could effectively promote the removal of HA by a modified membrane. The excellent removal effect could be attributed to the fact that during the coagulation process, the residual hydrolyzed aluminium nanoparticles adsorbed on the surface of the modified membranes and then combined with the PDA-PEI modified layer to increase the removal rate of HA. For actual water, since the organic matter in the actual water was not only from HA, the removal rate of HA by the four processes was higher than that of

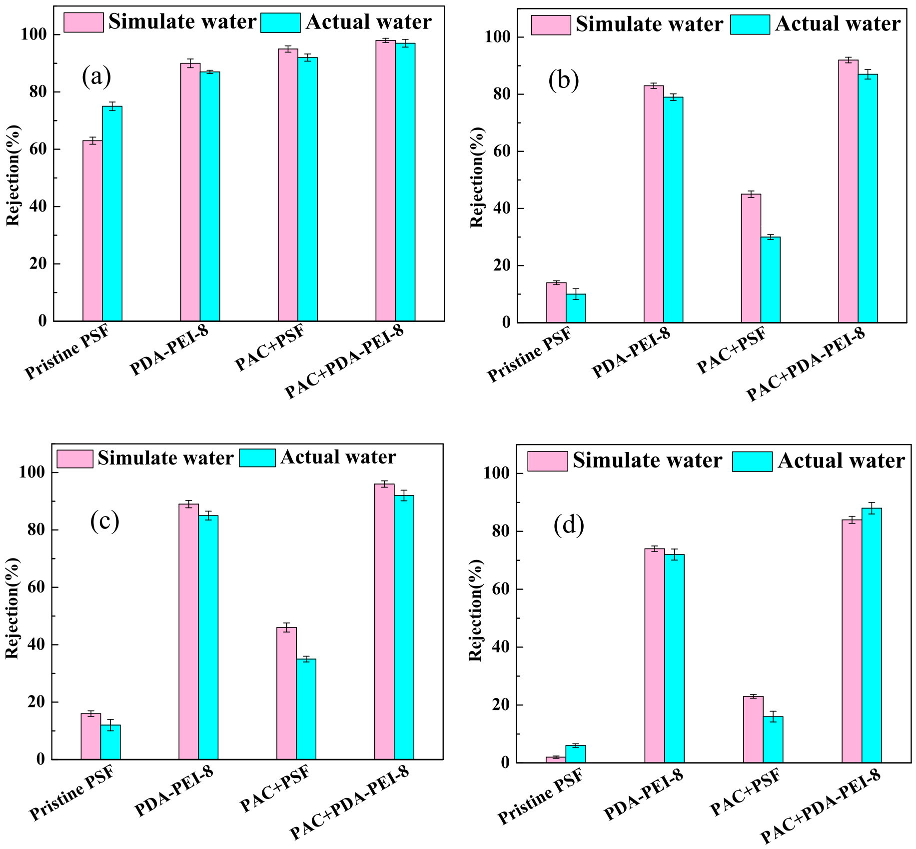


Fig. 6. Separation performance of the integrated process for simulated water and actual water (a) Turbidity removal rates (b) TOC removal rates (c) HA removal rates (d) NOR removal rates.

TOC. The removal rate of HA was significantly reduced by the coagulation process alone due to the decreased turbidity and HA content in actual water, leading to a poor coagulation effect. Similarly, the integrated process maintained a reasonable HA removal rate of up to 92 %.

Finally, Fig. 6d presented the four processes' removal of NOR from simulated and actual water. It could be seen that the NOR removal rate of the four membranes was lower than that of HA in both simulated and actual water. The reason might be that compared with macromolecular organic pollutant HA, the molecular weight of antibiotic NOR was much smaller, which was close to (even smaller) the pore size of the modified membrane. Accordingly, the highest removal rate was only 84 %. Meanwhile, the pristine PSF membrane had little effect on NOR rejection, and the removal rate was increased by 67 % after modification, then the integrated process further improved the NOR removal effect. Different from the removal of TOC and HA, there was almost no difference between the removal rate of NOR in actual water and that in simulated water, and similarly, the integrated process had excellent NOR removal performance in actual water.

3.4. *Antifouling ability of integrated process of coagulation and membrane modification*

Membrane fouling has always been one of the bottlenecks restricting further widespread applications of membranes. In this study, the antifouling abilities of the four membranes were evaluated by the specific flux within two hours. For simulated water, as shown in Fig. 7a, within two hours, the particular flux of the pristine membrane continued to decline and finally stabilized at 0.5, which decreased by 50 %. For the PDA-PEI modified membrane, the specific flux sharply reduced in the first 20 min, gradually levelled off and decreased to about 0.72. The flux decline in the PDA-PEI modified membrane mainly occurred in the first 20 min, possibly due to the sharp increase of fouling on the membrane surface and the rapid formation of a stable filter cake layer. The layer could also trap the fouling, so the flux decline slowed after 20 min. After introducing the coagulation process, the membrane presented better antifouling performance, and the flux decline rate was much lower than that of the pristine PSF membrane filtration alone. The reason was that coagulation could precipitate pollutants and improve the input water quality. The integrated process significantly enhanced the antifouling performance of the membrane. The specific flux eventually stabilized at about 0.9, and the flux decline rate was only 10 %. One possible reason was that the residual particles of coagulant hydrolysate combined with the PDA-PEI layer to form the Al-PDA-PEI composite layer, which further improved the hydrophilicity and reduced the roughness of the membrane and weakened the interaction between foulants and membrane surface.

Meanwhile, for actual water, the trend of specific flux in the four conditions was almost the same as that in the simulated water; the difference was that the composition of pollutants in the actual water was more complex, and the turbidity was lower than that in actual water, the specific flux of the pristine membrane and coagulation-pristine membrane stabilized at 0.3 and 0.5, respectively, which were lower than that in the simulated water under the same conditions, indicating that the membrane fouling in the actual water was more serious. The specific flux of both modified and coagulation-modified membranes was higher than that in simulated water, especially in the integrated process, which achieved comparable antifouling performance to simulated water. The excellent antifouling performance can still be explained in two aspects. Firstly, coagulation could effectively remove macromolecular pollutants in the water, improve the influent quality, and alleviate membrane fouling. Secondly, PDA-PEI on the modified me quickly formed a loose porous Al-PDA-PEI composite layer with residual particles of coagulant

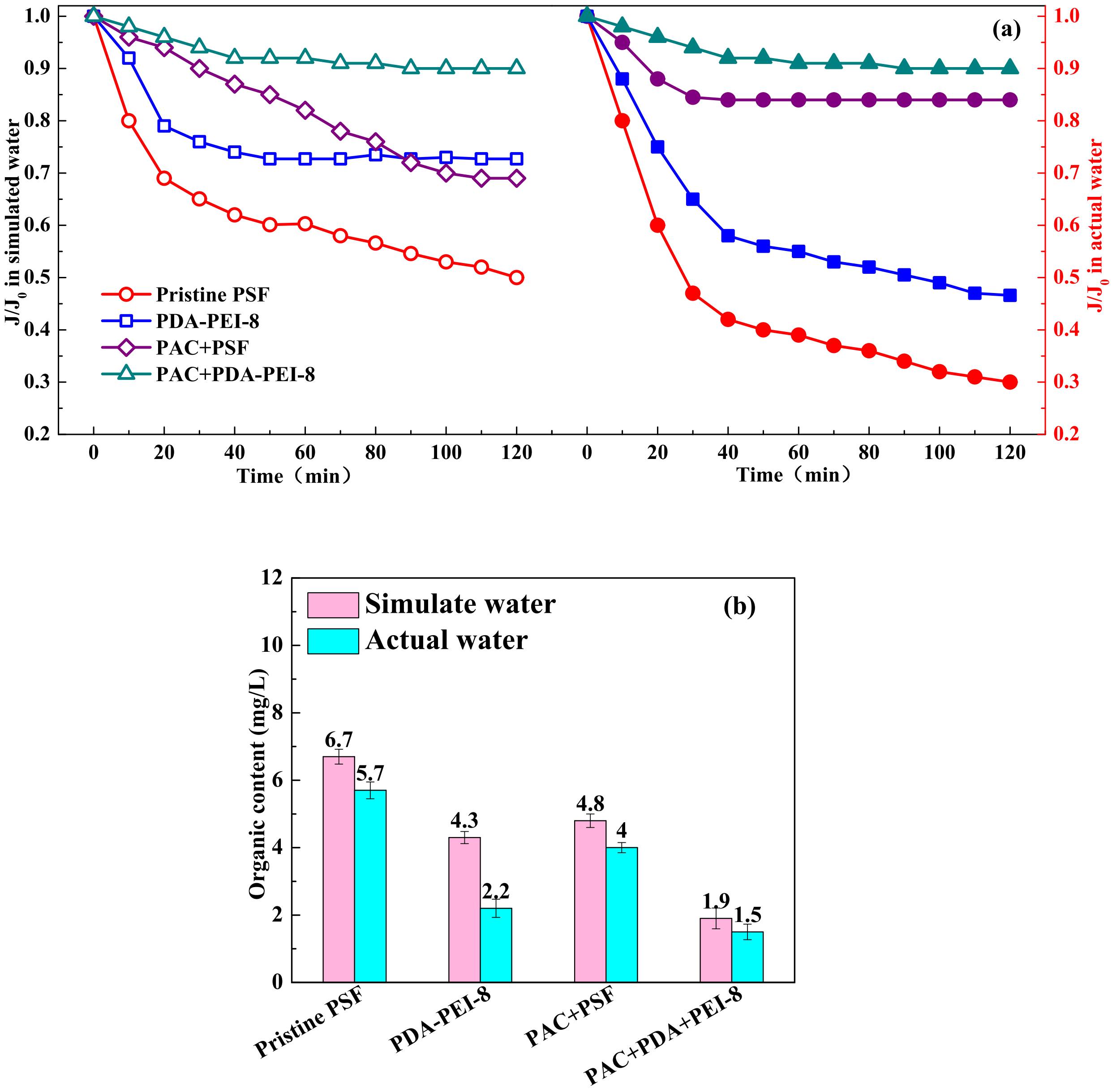


Fig. 7. Antifouling abilities of the integrated process for simulated water and actual water (a) J/J_0 values (b) Organic content in the fouling layers.

hydrolysate, which reduced membrane fouling by interacting with pollutants.

Fig. S3 shows the SEM analysis of membrane fouling under the above four conditions for simulated and actual water. Both in simulated and actual water, it could be seen that the surface of the fouled pristine membrane was covered with both large and small molecules of pollutants, and the membrane fouling was relatively severe. Then, after coagulation pretreatment, the macromolecular contaminants on the surface of the membrane were significantly reduced, and the remaining pollutants were mainly small molecules. This was because coagulant PAC mostly removed macromolecular pollutants. The results indicated that coagulation could alleviate membrane fouling to some extent.

Similarly, the co-deposition modification could also effectively alleviate membrane fouling, but the surface was still covered with some fouling substances. As expected, the surface pollutants were significantly reduced after the integrated process was treated. All the above results further demonstrated that the proposed coagulation-membrane modification process could effectively alleviate membrane fouling.

To further characterize the antifouling ability of the membranes, the organic contents of the fouling layers on the membrane surface under the above four conditions were evaluated and depicted in Fig. 7b. It could be seen that for both simulated and actual water, the organic content in the fouling layer on the membrane surface decreased significantly after the treatment by the integrated coagulation-membrane modification process. For simulated water, organic content in the fouling layer decreased from 6.7 mg/L for the pristine membrane to 1.9 mg/L for the integrated process. For actual water, organic content in the fouling layer decreased from 5.7 mg/L for the pristine membrane to 1.5 mg/L for the integrated process, indicating that the proposed integrated process could effectively reduce the content of organic matter on the fouling membrane surface and exhibit excellent antifouling performance for complex actual water.

4. Conclusions

In this study, an integrated process combining coagulation and membrane modification was proposed to mitigate membrane fouling. The key findings are summarized as follows:

Membrane Modification: The PSF ultrafiltration membrane was modified through co-deposition of PDA-PEI and zwitterionic monomers including BA and SBMA. Chemical structure analysis confirmed that PDA, PEI, and the zwitterions could be successfully deposited on the membrane surface.

Surface Morphology and Hydrophilicity: Surface morphology comparisons of the modified membranes showed that the introduction of both PDA-PEI and zwitterion polymers improved surface smoothness. However, water contact angle measurements revealed that zwitterions did not significantly enhance the membrane's hydrophilicity compared to PDA-PEI modification alone.

Flux and HA Rejection: The flux and humic acid (HA) rejection of the modified membranes were time-dependent. After the co-deposition for 8 h, the PDA-PEI-8 membrane exhibited an exceptionally high flux (159.02 L $m^{-2}\cdot h^{-1}$) and a high HA rejection rate (91.25 %). Additionally, this membrane demonstrated superior antifouling properties, with a flux recovery ratio (FRR) of over 90 %, attributable to its enhanced hydrophilicity.

Integrated Process Performance: The integrated coagulation and membrane modification process was evaluated using both simulated and actual water samples. Compared with coagulation or membrane modification alone, the integrated system achieved better removal of turbidity, TOC, HA, and NOR. Furthermore, it significantly improved antifouling performance, with a specific flux of up to 0.9 and a flux decline rate of only 10 %.

CRediT authorship contribution statement

Ying Liu: Project administration, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft. **Shichao Gong:** Data curation, Formal analysis, Investigation, Resources. **Meng Zhang:** Formal analysis, Investigation, Resources. **Xinbo Zhang:** Funding acquisition, Investigation, Methodology, Project administration, Supervision, Writing – review & editing. **Huizhong Wang:** Formal analysis, Methodology. **Haitao Wen:** Methodology, Resources. **Suyun Chang:** Data curation, Formal analysis, Resources. **Wenshan Guo:** Methodology, Writing – review & editing. **Huu Hao Ngo:** Conceptualization, Investigation, 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.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2025.131407.

Data availability

Data will be made available on request.

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