

Combining Magnetic Ion Exchange Media and Microsand before Coagulation as Pretreatment for Submerged Ultrafiltration: Biopolymers and Small Molecular Weight Organic Matter

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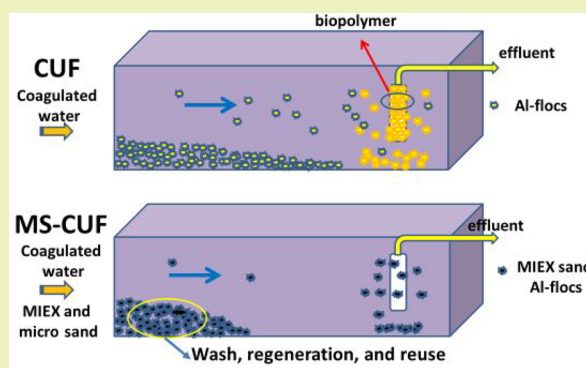
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S Supporting Information

ABSTRACT: In order to reduce the fouling of ultrafiltration (UF) systems caused by influent organic matter and microbial activities in the membrane tank, a novel pretreatment process has been evaluated involving the combination of magnetic ion exchange media (MIEX), microsand, and alum coagulation. Using a continuous flow bench-scale UF membrane apparatus and synthetic water, the influence of MIEX and microsand with alum pretreatment on membrane fouling was studied in comparison to a conventional pretreatment by alum alone. It was found that the continuous addition of low doses of MIEX and microsand substantially reduced (~50%) membrane fouling for nearly 60 days of operation, both in terms of reversible and irreversible fouling. MIEX adsorption increased the removal of dissolved organic matter, particularly hydrophobic and proteinaceous substances, and some fractions of humic-type substances, while the addition of microsand increased the density of flocs, and thus improved the removal of flocs and microorganisms (with flocs) in the membrane tank. As a consequence, the UF membrane with the MIEX/microsand pretreatment had a much reduced cake layer and accumulated material within membrane pores; in particular, the cake layer had much less protein-type and polysaccharide-type substances.

KEYWORDS: Ultrafiltration, Membrane fouling, MIEX, Microsand, Precoagulation, Combined pretreatment, Drinking water, Magnetic ion exchange media



INTRODUCTION

Membrane separation, particularly in the form of ultrafiltration (UF), is a particularly advantageous treatment method for drinking water and is becoming an increasingly important unit process. The greatest limitation to the wider development of UF technology is membrane fouling, which is caused by the accumulation of organic matter (especially biopolymers) and microorganisms on or within the membrane.^{1–4} In order to mitigate membrane fouling, some methods of pretreatment such as coagulation and oxidation have been studied.⁵ Although coagulation has been shown to be an effective and relatively low cost pretreatment to remove pollutants and alleviate membrane fouling,^{6–10} it has two clear drawbacks. First, during operation, quantities of poorly and nonsettling flocs, as well as microorganisms, attach and deposit on the membrane surface and gradually form a cake layer. As the cake layer becomes thicker, the membrane fouling is more serious, and the efficiency of membrane separation decreases. Second, coagulation is only effective for removing colloids and high molecular weight (MW) substances but is less effective for low-

to-medium MW organic substances.^{6,7} Unremoved organic matter will accumulate on, and within, the membrane. These organic substances of low-to-medium MW may block the membrane pores, inducing internal fouling. Overall, the application of coagulation alone as pretreatment is not enough to relieve the extent of membrane fouling, and other methods are required, in combination with it, to mitigate fouling and enhance the treatment.

Anion exchange for separating organic substances has been studied and received considerable attention in recent years,¹¹ and commercial technologies based on anion exchange have been developed, such as the Suspended Ion eXchange (SIX) process¹² and the magnetic ion exchange, MIEX, resin process.¹³ MIEX has a strong base functionality capable of exchanging weak organic acid ions and can be effective for the removal of a wide range of natural organic matter (NOM)

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Table 1. Principal Quality Parameters for Model Raw Water and UF Systems^a

Parameter	Raw water	CUF Tank	MIEX-CUF tank	CUF filtrate	MIEX-CUF filtrate
UV ₂₅₄ (cm ⁻¹)	0.114 ± 0.015	0.042 ± 0.003	0.025 ± 0.003	0.024 ± 0.002	0.017 ± 0.002
DOC (mg/L)	4.04 ± 0.28	2.83 ± 0.11	2.20 ± 0.14	2.69 ± 0.12	2.01 ± 0.11
Turbidity (NTU)	3.13 ± 0.56	4.47 ± 0.18	4.83 ± 0.23	0.08 ± 0.02	0.07 ± 0.02
P (mg/L)	0.325 ± 0.013	0.088 ± 0.005	0.047 ± 0.003	0.049 ± 0.003	0.031 ± 0.002
Al (mg/L)	0.021 ± 0.003	0.042 ± 0.012	0.035 ± 0.008	0.029 ± 0.008	0.027 ± 0.005
NO ₃ ⁻ -N (mg/L)	5.63 ± 0.49	5.88 ± 0.38	5.90 ± 0.26	6.06 ± 0.23	6.11 ± 0.18
NH ₄ ⁺ -N (mg/L)	0.441 ± 0.112	0.210 ± 0.027	0.165 ± 0.021	0.074 ± 0.017	0.059 ± 0.013
pH	7.90 ± 0.08	7.18 ± 0.05	7.17 ± 0.05	7.14 ± 0.03	7.13 ± 0.04

^aThe values in Table 1 are averages for all the measurements every 7 days (8 times). CUF, alum coagulation alone; MIEX-CUF, alum coagulation with MIEX and sand.

constituents, particularly those of mid-to-low MW,^{13,14} high charge density, and high aromaticity.¹⁵ As an alternative to conventional coagulation, MIEX treatment was reported in one study to achieve a greater reduction in trihalomethane (THM) and haloacetic acid (HAA) formation potentials.¹⁶ As such, MIEX can assist in controlling disinfection byproduct formation and reducing chemical requirements (e.g., coagulants, oxidants, and disinfectants) in downstream treatment processes.^{17,18}

As mentioned above, MIEX can remove NOM of mid-to-low MW that is unable to be removed by coagulation, while coagulation can treat colloids and high MW dissolved organic matter (DOM) that are not adsorbed by MIEX.¹⁹ Thus, combining MIEX and coagulation can maximize the removal of organic matter and represent an optimal approach to avoid membrane fouling. Previous studies have reported that the use of MIEX before coagulation can not only significantly reduce the dose of coagulant but can also achieve an improvement in the overall dissolved organic matter (DOC) and ultraviolet (UV) removals²⁰ and a significant decrease in the amount of trihalomethane (THM) and haloacetic acid (HAA) precursors in the final water.^{13,21} Furthermore, the combination of MIEX and coagulation appears to be superior to using anion exchange resins alone for the removal of high MW organic compounds (MW > 20 kDa), attributed to biopolymers (proteins and polysaccharides), which were found to be responsible for reversible fouling of UF membranes.²²

In addition to the decreasing of organic matter, another issue of using coagulation alone is the presence of unseparated or slowly forming flocs from the coagulation process that can approach the surface of the membrane and form the cake layer, causing membrane fouling.^{23–25} Furthermore, the microorganisms associated with flocs also accumulate on the membrane surface, producing extracellular polymeric substances (EPS) that have a high affinity with flocs, leading to more binding of flocs to the membrane surface and the development of membrane fouling.²⁶ Therefore, it is necessary to decrease the quantity of flocs approaching the membrane surface.

In traditional water treatment processes, higher settling rates of flocs allow for substantially smaller sedimentation units and lower capital costs for the sedimentation tank. While in the membrane separation process, the improvement in settling ability can reduce the particles/flocs deposited on the membrane surface, and then, the membrane fouling is relieved. The settleability of flocs is dependent on the floc/particle sizes and density,²⁷ so for a given floc diameter, the settling velocities will rise as the floc density increases.²⁸ Adding microsand to a coagulating suspension enhances the formation

of strong flocs while maintaining their size²⁹ and provides ballast (increased density), thereby significantly increasing their settling velocity.^{30,31} Hence, the addition of microsand before coagulation is an effective way to lower the quantity of flocs approaching the membrane surface.

Previous studies concerning the combination of MIEX and coagulation have been based only on short-duration tests using plate membranes. In this study, the comparative performance of membranes in continuous operation with coagulation and preaddition of MIEX/microsand before UF membrane filtration was evaluated. In particular, the effect of MIEX and microsand before coagulation on the variation of bacteria and EPS has been explored, and their role in terms of the nature and extent of membrane fouling has been examined in this paper. Both MIEX and microsand can be recycled within the proposed process by simple methods, and previous studies have shown no difference in the performance (impact on membrane fouling) of regenerated MIEX compared to a single use of virgin MIEX.³² Therefore, this study was undertaken to demonstrate an improved pretreatment arrangement for mitigating UF membrane fouling.

MATERIALS AND METHODS

Synthetic Raw Water and Jar Test. Domestic effluent from a sewage treatment plant and tap water at South Kensington, London, United Kingdom were mixed (the volumetric ratio of domestic effluent to tap water was 1 to 50), and 5 mg/L of humic acid (IHSS, USA) was added to prepare the synthetic raw water that represented a typical micropolluted surface water.⁵ MIEX was purchased from ORICA (Pty) Ltd., Australia, and it contains a magnetized component within its structure which allows the beads to act as weak individual magnets. Cl on the surface of MIEX could exchange the organic matter in the water, and its particle size is between 160 to 180 μm. Other information can be found by previous research.³³ The very small size of the resin beads provides a high surface area, allowing rapid exchange kinetics of organic matter.³⁴ The principal characteristics of the synthetic raw water are listed in Table 1.

A jar test was used to investigate the adsorption and coagulation processes for the removal of organic matter from synthetic raw water. An optimal MIEX dose of 10 mg/L together with different concentrations of microsand were added in the raw water and reacted for 10 min; after that, 0.15 mM alum (Al₂SO₄·18H₂O, calculated as Al³⁺, Aldrich, USA) was added for 15 min coagulation at a speed of 50 rpm (23 s⁻¹) with Flocculator 2000 (Kemira Kemi, Helsingborg, Sweden). Finally, flocs were settled for 20 min, and samples were collected for turbidity and total organic matter/dissolved organic matter (TOC/DOC) measurement.

Membrane Filtration Test System. Two parallel, mini-pilot-scale ultrafiltration processes with different pretreatments were operated simultaneously. The first pretreatment was a conventional coagulation process (CUF), and in the second one, MIEX (10 mg/L) and microsand (5 mg/L; with size and specific gravity of 100–180

Table 2. Specific Analytical Methods and Instrumentation

Parameter	Conditions of analysis/Remarks	Analytical method/Device	Others
UV ₂₅₄ (cm ⁻¹)	After 0.45 μm membrane filtration	Ultraviolet spectrophotometer (U-3010, Hitachi High Technologies Co., Japan)	
DOC (mg/L)	After 0.45 μm membrane filtration	Total organic carbon (TOC) analyzer (TOC-VCPH, Shimadzu, Japan)	
Turbidity (NTU)		Turbidity meter (TL23, Hach, USA)	
P (mg/L)	After 0.45 μm membrane filtration	Inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 7300 DV, PerkinElmer, USA)	
Al (mg/L)	After 0.45 μm membrane filtration		
NO ₃ ⁻ -N (mg/L)	Water sample was precoagulated, filtrated, and then measured at 420 nm	Colorimetric methods	According to APHA Standard Methods ⁴⁰
NH ₄ ⁺ -N (mg/L)	Water sample was precoagulated and adsorbed by XAD-2, filtrated, and then measured at 220 and 275 nm		
SS(mg/L)	Filtrated by 0.45 μm membrane, dried at 105 °C for 2 h, and then weighed		

μm, and 2.65, respectively) were added into the coagulation tank (MS-CUF). The characteristics of the membrane and other aspects of the process operation were mentioned in our previous paper,³⁵ and further details of the membrane systems, including the experimental setup, are provided in the Supporting Information (Figure S1).

EPS Extraction and Measurement. A heating and extraction method³⁶ was used to extract the EPS from the sludge and cake layers that were carefully scraped off the membrane surface at the middle and end of the test period (days 32 and 59, respectively). More details of the method can be found in our previous paper.³⁵ The extracted internal foulants were obtained by soaking the membrane fibers in an alkaline solution (0.01 mol/L NaOH) for 24 h at 20 °C after being wiped with a sponge and cut into small pieces.^{37,38}

Size exclusion chromatography (SEC) with UV absorption detection was used to analyze EPS/organic matter to determine the apparent molecular weight (MW) distribution of substances, and further details can be found elsewhere.^{5,39} The absolute concentration of polysaccharide and proteins were measured by a phenol–sulfuric acid method and the Coomassie procedure, respectively.⁴⁰

Other Analytical Methods. Other specific analytical methods and instrumentation used are listed in Table 2. In addition to these, the Heterotrophic Plate Count (HPC) procedure with yeast extract agar was used for determining the bacterial concentrations in the two membrane systems.⁴¹

At the end of the operation, the membrane modules were taken out from the tank. Membrane samples were cut from the two membrane modules, broken directly after being freeze-dried with liquid N₂, and then gold-coated and imaged by scanning electron microscopy (FEGSEM, LEO Gemini 1525, Germany), as well as in cross section. Organic matter in the solution was analyzed by Fourier transform infrared spectroscopy (FTIR, Spectrum 400, PerkinElmer, USA) after being freeze-dried.

The analyses of hydrophilic and hydrophobic organic components were carried out using resins of Superlite DAX-8 (Supelco, USA) and Amberlite XAD-4 (Rohm and Hass, Germany), and the full process can be found in our previous paper.^{5,39}

RESULTS AND DISCUSSION

Jar Tests for DOC and Turbidity Removal. A series of jar tests were conducted to determine the dose of MIEX and microsand in the subsequent continuous membrane filtration evaluation. First, the effect of MIEX dose on the removal of organic matter was considered. As shown in Figure 1, TOC concentration decreased as MIEX dose increased. Alum coagulation alone was able to decrease the TOC concentration from 3.72 to 2.67 mg/L (28.2% reduction), and the preaddition of MIEX enhanced the removal of TOC to 1.92 mg/L (48.4% reduction overall) when the MIEX dose was 10 mg/L. A further increase in MIEX dose presented little improvement in TOC removal. With the addition of 10 mg/L as the optimal MIEX dose, the addition of different doses of

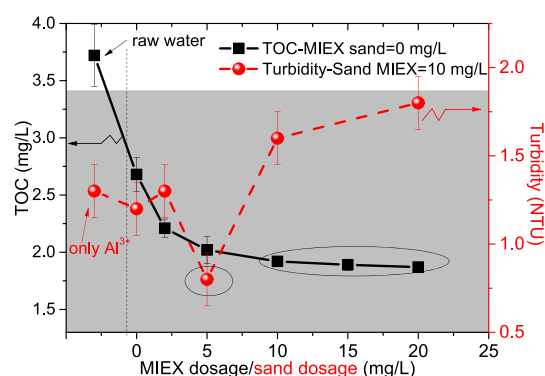


Figure 1. Effect of MIEX and microsand dose on the removal of TOC and turbidity in the jar test. Different doses of MIEX were mixed with raw water for 10 min, and then, 0.15 mM Al was added for 15 min coagulation.

microsand was investigated. The addition of microsand improved the density of flocs at low dose and did not change the size of flocs below a certain sand concentration,²⁹ while higher doses of microsand resulted in greater residual turbidity because of insufficient coagulant dose. A dose of 5 mg/L was found to produce the lowest turbidity for the synthetic raw water (Figure 1). Therefore, the optimum doses of MIEX and microsand were 10 and 5 mg/L respectively.

Organic Matter and Bacteria Concentration. An improvement in organic matter removal was found with the MIEX-CUF system as shown in Table 1, with approximately 45.5% DOC removal overall (cf., 31.0% for CUF). The small difference in the DOC of the membrane feed and permeate waters was expected due to the large pore size of the UF membrane. However, significant differences could be seen between the CUF and MIEX-CUF water samples in terms of the MW distributions of the organic fractions (Figure 2a). MIEX-CUF enhanced the removal of molecules with MW in the range of 1000–10000, which broadly corresponded to humic substances; these results were consistent with those of other researchers.⁴²

The hydrophobicity and hydrophilicity of the influent water also influence the treatment performance. Since the hydrophobic organic matter is adsorbed more easily on to the similar hydrophobic PVDF membrane surface, it is believed that decreasing the hydrophobic component in the feedwater can mitigate the membrane fouling. From the results in Figure 2b, both coagulation and MIEX/microsand/coagulation pretreatment significantly decreased the proportion of hydrophobic and weakly hydrophobic organic matter, and the adsorption by

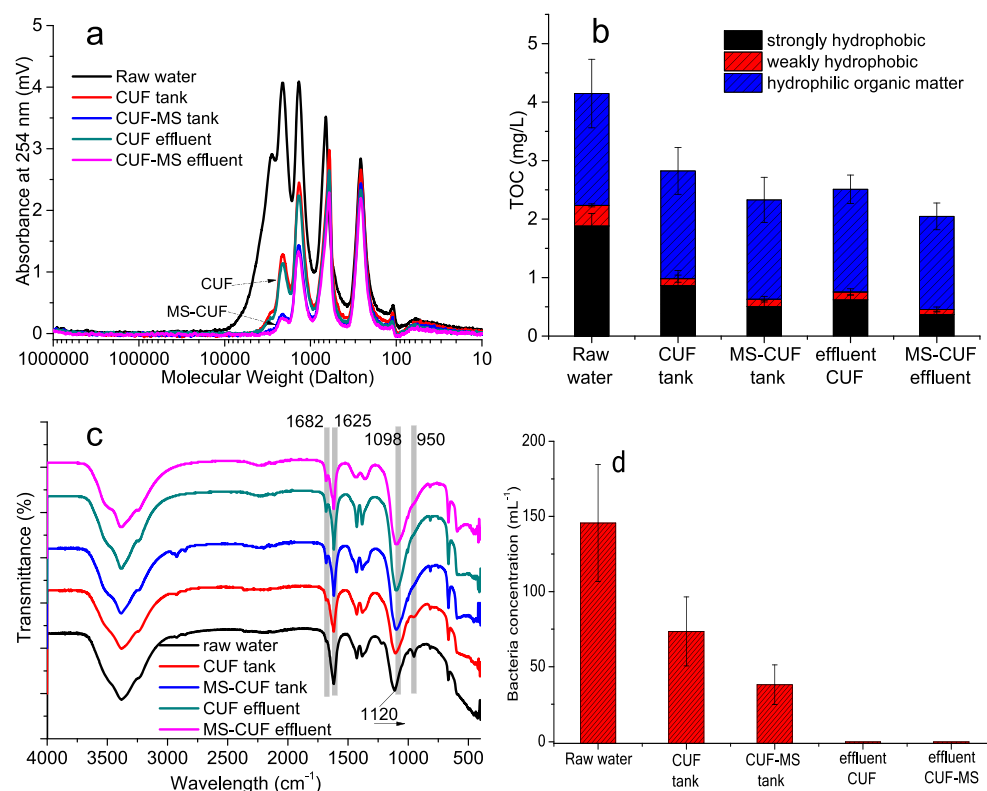


Figure 2. Comparison of organic matter and bacteria in the two membrane systems at day 50: (a) MW distributions, (b) hydrophilic and hydrophobic components, (c) FTIR spectra, and (d) bacteria concentrations.

MIEX resin enhanced the removal, especially for the strongly hydrophobic organic matter. Similar results were also found by other researchers, who, for example in one study, found that the very hydrophobic acid fraction (VHA) was the dominant NOM component in the raw water and was best removed by MIEX pretreatment, regardless of the raw water VHA concentration.⁴²

In addition, the FTIR spectra of the organic matter in the feedwater, membrane tank, and permeate were determined (Figure 2c). Carboxylic bonds C=O at around 1625 cm⁻¹ could be seen, and the peaks in the 1000–1200 cm⁻¹ region corresponded to C–O bond from alcohols and esters in polysaccharides.⁴³ The C–H deformation of aliphatic and CH₃ groups was suggested by the band at 1470–1390 cm⁻¹. The peak at 950 cm⁻¹, believed to be related to >C=N–OH, was probably a constituent of the waste effluent in the synthetic raw water. This peak (950 cm⁻¹) decreased in the treatment process, indicating that some organic nitrogen was removed during the treatment, especially in the MIEX-CUF system. Also, the movement of the peak at 1120 cm⁻¹ to 1098 cm⁻¹ meant that some polysaccharides were removed during the treatment, particularly for the MIEX-CUF effluent. Overall, the results of MW and FTIR analyses were consistent in showing the impact of MIEX (and microsand) in altering the nature of the organic matter in the water.

The bacteria concentration (HPC) was quantified for the two membrane systems (Figure 2d) to further investigate the membrane fouling mechanism. The presence of viable bacteria (HPC) decreased from 145 mL⁻¹ in the raw water to 72 mL⁻¹ in the CUF membrane tank and 38 mL⁻¹ in the MIEX-CUF tank. It was clear that MIEX-CUF reduced the bacteria concentration more than CUF, which could be explained in

terms of two aspects: First, the adsorption by MIEX reduced the quantity of organic matter and thus decreased the “food” for the bacteria. Second, microsand enhanced the settleability of flocs, leaving a lower level of bacteria in the membrane tanks due to the incorporation/association of the microorganisms with the coagulated flocs. It was expected that lower concentrations of EPS would be present; this was confirmed and is discussed subsequently.

Fouling Development: Variation of Trans-Membrane Pressure (TMP). The development of TMP provided a measure of the extent of membrane fouling when the membrane flux in the two systems was maintained at a constant value (20 L m⁻² h⁻¹). In Figure 3, it can be seen that TMP of the CUF system started to increase at day 5, while TMP of the MIEX-CUF system changed little in the first 15 days. Comparing the two systems, the membrane fouling rate for CUF (Δ TMP of 5.7 kPa after 32 days) was substantially greater (double) than that for MIEX-CUF (Δ TMP of 2.7 kPa after 32 days). After physical cleaning of the membranes (sponge washing) at day 32, it was evident that TMP of the MIEX-CUF membrane (1.2 kPa) was nearly the same as that of a new UF membrane (1.0 kPa), with little irreversible fouling (0.2 kPa), but TMP of the CUF membrane after washing (2.0 kPa) was an evidence of slightly higher irreversible fouling (1.0 kPa). These results indicated that the addition of MIEX and microsand eliminated the irreversible fouling that occurred on the CUF membrane. In the second stage of operation, the initial rate of TMP increase of the CUF membrane was nearly four times that of MIEX-CUF, and the TMP value of CUF and MIEX-CUF reached 9 and 4 kPa respectively, at the end of the test period at day 60.

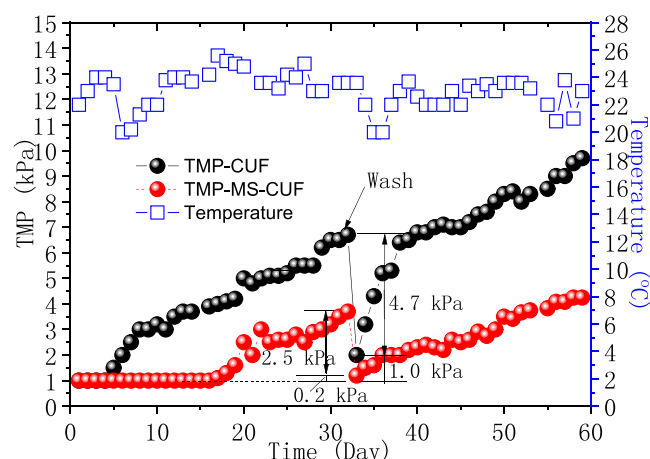


Figure 3. Temporal variations of TMP in the membrane systems over a period of approximately 59 days. In the UF filtration experiments, the membrane flux of CUF and MIEX-CUF streams were both set at a constant value of $20 \text{ L m}^{-2} \text{ h}^{-1}$ in a cycle of 30 min filtration/1 min water backwash ($40 \text{ L m}^{-2} \text{ h}^{-1}$).

From these results, it is concluded that the enhanced removal of organic matter and flocs before membrane filtration by MIEX and microsand considerably improved the filtration performance (reduced rate of fouling). The cake layer is the main contribution to TMP increase for both membrane systems (reversible fouling) as the external membrane fouling. The addition of MIEX decreased the mid-to-small MW organic matter, which caused lower adsorption of these parts of organic matter in the membrane pores, and consequently decreased the inner membrane fouling (irreversible fouling). For the microsand, it will improve the settlement ability of flocs and reduce particles/flocs concentration, and thus, less cake layer was formed, inducing lower external fouling (reversible fouling).

Significance of Nonsettleable Particles in the Membrane Tanks. During the membrane operation, suspensions/flocs either settle to form sludge or accumulate on the membrane surface and gradually develop a cake layer. Therefore, the concentration of suspensions and their settleability affect the formation of the cake layer. Figure 4a demonstrates the variation of particle concentration (as turbidity) in the two membrane tanks during one cycle (30 min). Initially, after the preceding backwash, the turbidity was much higher in the MIEX-CUF tank, indicating that more cake layer material was (easier to be) removed from the MIEX-CUF membrane surface; this indicates that the connection strength between particles in the cake layer was lower than in the CUF cake layer, which is most probably related to the lower EPS concentration on the MIEX-CUF membrane and its cake layer.^{44,45} Subsequently, it was found that the turbidity decreased approximately linearly with time during the operation cycle, and the reduction was greater in the MIEX-CUF tank (around 55%), confirming that the addition of microsand increased the settling velocity of flocs.

As shown in Figure 2d, the two pretreatments decreased the bacteria concentration in the membrane tanks, but the suspended solids (SS) concentration was much greater in the membrane tanks than that in the raw water, probably owing to the presence of unsettled Al-hydrolysis floc (Figure 4b). Comparing the two membrane tanks, the SS concentration in the MIEX-CUF tank was greater than that in the CUF tank,

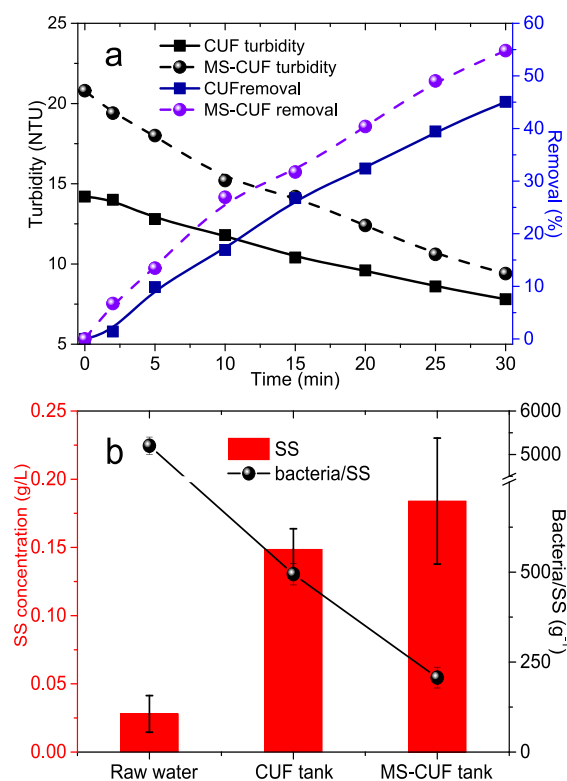


Figure 4. (a) Temporal variation of turbidity during one cycle of membrane filtration (30 min). (b) Comparative values of suspended solids (SS) and bacteria/SS ratio (six samples were taken during the whole operation process, and an SS sample was taken in the middle of the 30 min cycle) for the two membrane systems.

which is consistent with the turbidity results (Figure 4a). However, when expressed as bacteria number per SS concentration, the value was much lower in the MIEX-CUF tank (half of that in the CUF tank), which probably induced a poorer connection ability of particles (suspension) to the membrane surface and thus reduced the formation of a cake layer. As the EPS concentration is believed to significantly influence the connection between particles on the membrane surface, its concentration was also considered and is discussed in the following section.

EPS Concentration in Membrane Tanks. The EPS content was measured in terms of proteins and polysaccharides. Figure 5a and b shows the EPS content of sludge and cake layer in the two membrane systems. For the CUF membrane tank, the EPS concentration was higher in the cake layer than that in the sludge, confirming the accumulation of EPS and production of EPS by bacteria in the membrane tank throughout the operating period. As for the MIEX-CUF membrane system, less EPS accumulated on the membrane surface; thus, the amounts of total protein and polysaccharide in the CUF cake layer were moderately greater than that in the MIEX-CUF system, which explained the significantly lower membrane fouling observed in Figure 3.

The apparent MW distributions of EPS were determined by SEC and given in terms of UV absorbance at 254 nm (Figure 5c). As a consequence of the addition of MIEX and sand, the amount of EPS associated with the MIEX-CUF cake layer was substantially less than that of the CUF cake layer over the entire MW range, especially for the large molecular weight components ($\text{MW} > 10^5$), which were most likely attributable

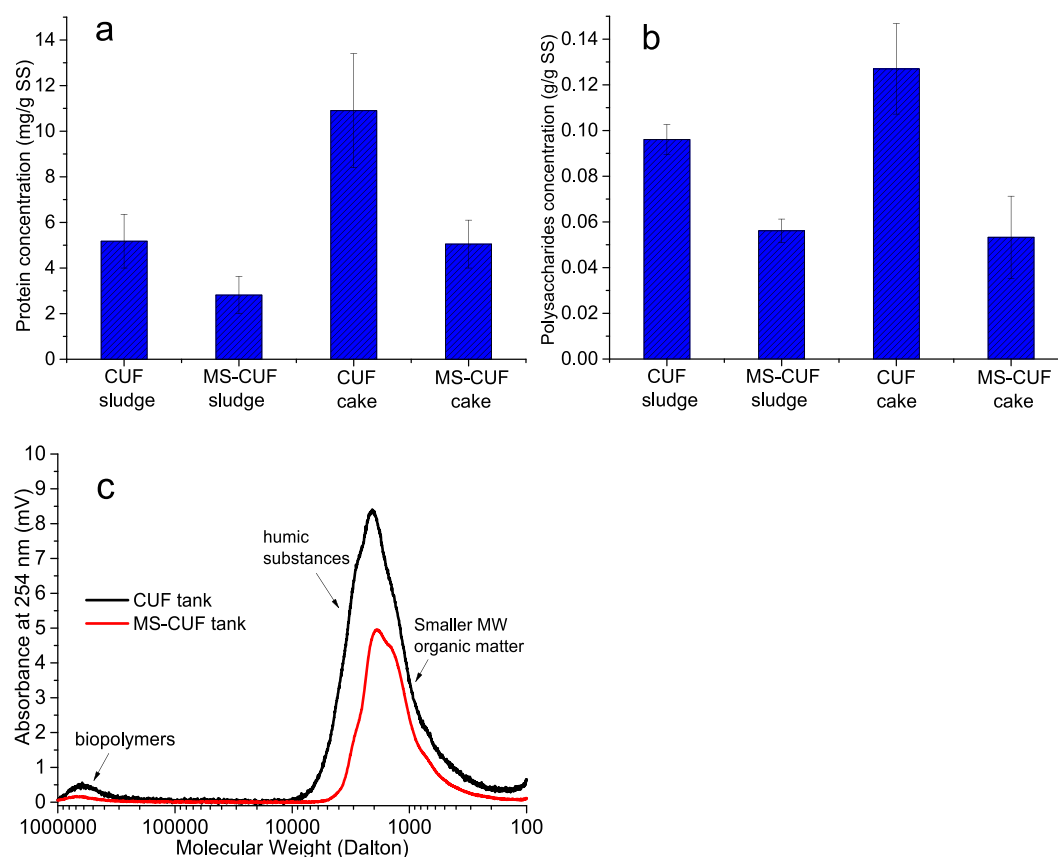


Figure 5. Comparative EPS concentrations in the cake layers and sludges for the two membrane systems: (a) protein and (b) polysaccharide concentration. (c) MW distributions from cake layers at day 32 (first wash).

to biopolymers (polysaccharide-like and protein-like substances).⁴⁶ These results provide further evidence for the removal of organic matter by MIEX and the enhanced settleability of flocs associated with microsand. Hence, by limiting the concentration of EPS in this way (by MIEX adsorption, controlling bacteria and rapidly settling flocs), the organic matter in the cake layer was reduced, and the connection strength between particles and membrane surface was weakened.

Inner Membrane Fouling. In addition to the cake formation and external membrane fouling, the material accumulated within the membrane pores was extracted and characterized to evaluate the extent of inner membrane fouling.⁴⁷ Figure 6 shows the MW distributions of extracted material from the two membranes. A variety of organic matter was deposited or adsorbed in the pores of both membranes, but the quantity of organic matter was much less for the MIEX-CUF membrane, in particular, of the large MW organic substances such as biopolymers and humic-like materials. This is attributed to the adsorption of organic substances by MIEX, reducing the quantity of humic-like materials (Figure 2a), and the lower levels of bacteria, secreting less biopolymer (Figure 5). These results are consistent with the degree of irreversible membrane fouling after the sponge washing observed in Figure 3.

SEM Images of Membrane. Scanning electron microscopy (SEM) was conducted to provide additional, supportive information concerning the membrane fouling mechanism (Figure 7 and Figure S2). The SEM images showed that there was a thick cake layer on the membranes composed of

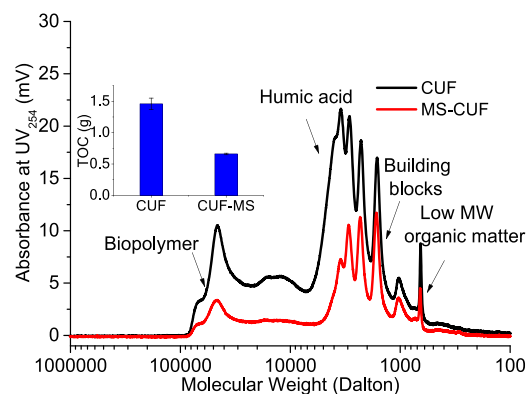


Figure 6. MW distribution of inner organic matter washed from membrane at day 59.

thousands of nanoscale primary particles with an average size of around 50 nm (statistics by SmileView software, version 2.1). However, the thickness of the cake layer on the MIEX-CUF membrane was only one-third of that on the CUF membrane (Figure 7c and d) because of the lower level of EPS and associated floc deposits. Microorganisms (most likely bacteria) could be seen in the CUF cake layer (circled in Figure 7c), which, as described, secrete EPS and thus increase the connection extent and strength between the membrane and cake layer/flocs and thereby form a thicker cake layer. Moreover, the produced EPS induces greater membrane fouling by blocking the membrane pores or pores between the nanoparticles in the cake layer.

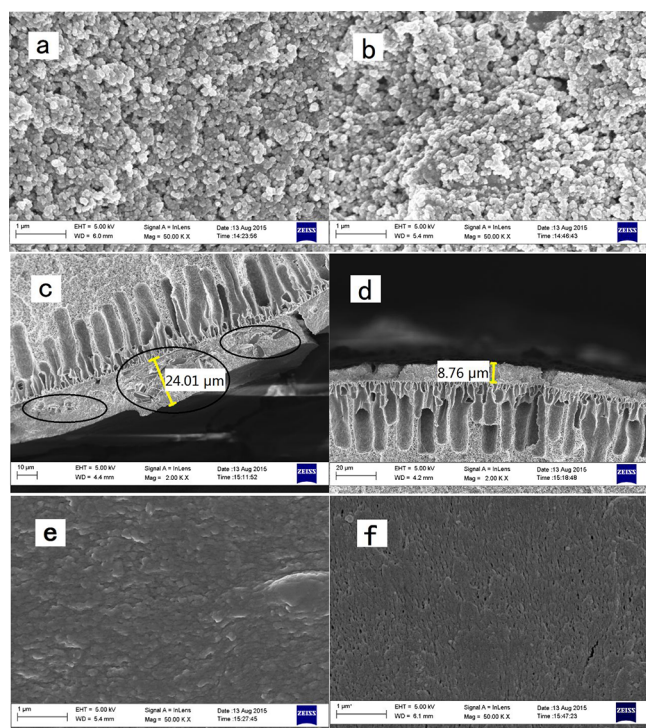


Figure 7. SEM images of membrane samples: CUF (a) and MIEX-CUF (b) membranes with cake layer, cross sections of CUF (c) and MIEX-CUF (d) membranes with cake layer, and CUF (e) and MIEX-CUF (f) membranes after being washed by sponges (microorganisms apparent in the cake layer highlighted in panel c).

SEM images of the membrane cleaned by sponges (Figure 7e and f) at day 32 confirmed the internal fouling and pore blockage for both membranes. As these images indicate, more pores were blocked in the case of the CUF membrane than the MIEX-CUF membrane, which is consistent with the results discussed previously.

CONCLUSIONS

A substantially reduced membrane fouling (50% less TMP development over 60 days of operation) was observed when adding optimal doses of MIEX and microsand prior to coagulation. Adsorption by MIEX was able to enhance the removal of organic matter and bacteria, while microsand increased the settling velocity of flocs. These two effects resulted in the reduction of bacteria within the membrane tank and cake layer, inducing less production of EPS that is believed to enhance the development and strength of the cake layer. Since both the MIEX and microsand can be recycled in full-scale processes, the inclusion of these in combination with conventional alum coagulation can provide an improved, and potentially cost-effective, pretreatment method for mitigating UF membrane fouling and improving treated water quality.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b04678.

Schematic diagram of the experimental setup (Figure S1) and SEM image of pristine PVDF membrane (Figure S2). (PDF)

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Notes

The authors declare no competing financial interest.

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