



Performance of PAC treatments on MF membrane fouling behavior and mechanism by various algogenic organic matter

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ABSTRACT

Algogenic organic matter (AOM) resulting from algal blooms in water can cause severe membrane fouling in water treatment. This paper investigated the performance of mesoporous and microporous carbon (CPAC) treatments on microfiltration (MF) membrane fouling behavior and mechanism of various AOMs. The results indicated that microporous activated carbon had limited effects on improving filtration flux, whereas the synthesis of mesoporous carbon (SOMC) exhibited a great ability to alleviate membrane fouling. When the SOMC was added in 100 mg/L doses, the filtration flux improved by 5%, 9.2%, 8.7%, and 33% for *Aphanizomenon flos-aquae* (APF), *Anabaena flos-aquae* (ANF), *Scenedesmus obliquus*, and *Cyclotella* (Cy) AOM, respectively. The molecular weight distributions, organic hydrophobicity demonstrated that the SOMC mainly removed macromolecules of the neutral hydrophilic (N-HPI) and hydrophobic (HPO) organics, such as polysaccharides and protein-like organic matter, whereas the CPAC mainly adsorbed humic-like substances organics. Linear regression analyses suggested that the content of biopolymers content in the AOM were highly correlated to membrane fouling, whereas humic-like organics had minor effects on MF membrane fouling. Diatoms of Cy-AOM with lower macro molecular biopolymers and higher HPO fraction can be better treated than cyanobacteria of APF- and ANF-AOM by SOMC. The SOMC of mesoporous-rich activated carbon was suggested as an appropriate pretreatment method in AOM-involving water treatment during MF compared to microporous carbon.

Keywords: Algogenic organic matter; Mesoporous carbon; Membrane fouling; Microfiltration

1. Introduction

Frequent outbreaks of algal blooms and associated algogenic organic matter (AOM) in lakes and reservoirs have posed serious challenges to water treatment [1]. Membrane filtration technology is a promising technology for the removal of microalgae due to its absolute removal of algal cells. Even in algae biomass harvesting, which usually includes centrifugation, flocculation, gravity sedimentation, and air flotation, membrane technology has

drawn increasing attention [2]. However, membrane fouling caused by AOM remains a challenge that restricts its extensive usage [3]. Fouling by algae in membrane systems is a topic that has come to the forefront of discussion in the field of membrane filtration in recent years. Many studies have focused on the AOM characteristics of membrane fouling, such as organic hydrophobicity/hydrophilicity and molecular weight (MW) distribution, and have found that charged (C-HPI) and neutral hydrophilic (N-HPI) fractions of AOM

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lead to greater flux decreases than those of hydrophobic (HPO) and transphilic (TPI) fractions [4]. Other studies have been devoted to understanding the effects of membrane foulants, such as polysaccharides, proteins, and humic substances [5].

To alleviate AOM-associated membrane fouling, many pretreatment processes have been employed for the treatment of AOM-involving water, such as coagulation by ferric chloride [6], peroxidation by ozone, ultraviolet (UV)/H₂O₂, manganese dioxides, and adsorption by mesoporous adsorbent resin [7–9]. Although many studies have found that pre-oxidation by ozone, potassium permanganate, and chlorine were efficient in inactivating microalgal cells, the high doses that are needed may give rise to cell lysis, thus leading to the release of undesirable compounds and the formation of harmful byproducts [10]. The glucose and aldonic acid secreted by algae cells might also be reported to form complicated colloids with coagulants, which may be not conducive to coagulation [11].

Powdered activated carbon (PAC) combined with membrane filtration might be a prospective water treatment option, particularly when hunting for the safe treatment of cyanobacteria and associated toxins. PAC is also generally considered to be a simpler approach to remove natural organic matter (NOM) and is proposed to be an available technology [12]. Although PAC pretreatment has been widely investigated in membrane filtration, to summarize prior studies, the influence of PAC treatment on membrane fouling is not consistent when treating the complicated and changeable nature of NOM. Many studies have indicated that PAC could reduce the amount of organic matter deposited on the membrane and efficiently mitigate membrane fouling [13]. Others have found that the addition of PAC could not improve the membrane's penetration, and sometimes, it even led to more severe membrane fouling [14]. The adsorption of NOM by activated carbon can be influenced by the characteristics of organic matters as well as carbon surface chemistry [15]. PAC pore structure is another important factor controlling organic adsorption. Kilduff et al. [16] investigated the humic acids adsorption from aqueous solutions on active carbon and activated charcoal cloths and found that a large portion of micropores (pore size <2 nm) in active carbon were inaccessible for the adsorption of macromolecular humic acids, whereas the mesopores (2–50 nm) played a crucial role in the enhancement adsorption of NOM [17].

For the purpose of understanding the pretreatment method or the NOM characteristics on membrane fouling, recent improvements in analytical techniques seem prospective. High-performance size-exclusion chromatography (HPSEC) combined with peak-fitting prediction is one of the most prospective approaches. This approach not only provides qualitative information based on the contrast between raw water and distinct treatments but also provides quantitative information on dissolved organic carbon (DOC) removal [18]. Xing et al. [19] predicted DOM removal using HPSEC combined with peak fitting and indicated that HPSEC combined with peak-fitting could effectively determine the removable DOC compositions. Lai et al. [20] found that this method could analyze NOM more efficiently. Our previous research has indicated that this

approach could better characterize NOM when analyzing ultrafiltration (UF) membrane-fouling mechanisms [21].

Considering that there are great discrepancies between NOM and AOM and that it is still unclear whether PAC pretreatment could alleviate membrane fouling no matter in separated PAC treatment or combined treatment, especially when treating AOM in algae-laden water treatment, the behavior, and mechanism of PAC to influence AOM membrane fouling must be elucidated. However, to the best of our knowledge, there have been few studies that systematically investigate the effects of AOM membrane fouling by PAC treatment. Therefore, the purpose of this research was to investigate the performance of PAC treatment on MF membrane fouling behavior and mechanism of AOM. HPSEC combined with peak-fitting technology was utilized to analyze the membrane fouling. This research supplies some important information for diagnosing membrane fouling and controls by PAC treatment during algal-rich water treatment or algae harvesting.

2. Materials and methods

2.1. Microalgae cultures and AOM extractions

Four kinds of algae including the cyanobacteria *Aphanizomenon flos-aquae*, *Anabaena flos-aquae*, the green algae *Scenedesmus obliquus*, and the diatoms *Cyclotella* (Cy) were used in this study, which were purchased from the Institute of Hydrobiology, Chinese Academy of Sciences, China. The four algae were selected in this research based on the premise that various AOMs that are generated from different blooming algae or algae biomass in real waters might have their own unique characteristics, and therefore, the PAC pretreatment method on changing water prior to filtration might also change. *Aphanizomenon flos-aquae* and *Anabaena flos-aquae* were cultivated under the control ambient conditions of 12 h fluorescent light followed by 12 h dark, with an irradiance of approximately 90 $\mu\text{mol}/\text{m}^2 \text{ s}$, in BG-11 medium at 20°C. *S. obliquus* was grown at 25°C and a 12–12 h light-dark cycle with an irradiance of approximately 120 $\mu\text{mol}/\text{m}^2 \text{ s}$ using SE medium. *Cyclotella* was grown at 20°C in a 12–12 h light-dark cycle of approximately 90 $\mu\text{mol}/\text{m}^2 \text{ s}$ using D1 medium.

AOM was extracted from algal solutions of stationary growth phase by centrifuging at 10,000 g for 15 min and subsequently filtering through a Millipore 0.45 μm filter. The maximum cell densities of *S. obliquus* and *Cyclotella* were 1.4×10^7 and 1.1×10^6 cell/mL, respectively, whereas the corresponding OD₆₈₀ for *Aphanizomenon flos-aquae* and *Anabaena flos-aquae* were 1.737 and 1.403, respectively [22]. AOM extracted from *A. flos-aquae*, *Anabaena flos-aquae*, *S. obliquus*, and *Cyclotella* was recorded as APF-AOM, ANF-AOM, SO-AOM, and Cy-AOM, respectively.

2.2. PAC, membrane, and MF experiment

Two types of carbon materials, a mesoporous and a microporous (CPAC, Shanghai Company) carbon, were used in this study, because it has been reported that membrane fouling is not only related to NOM characteristics but also to PAC properties [23]. A newly ordered mesoporous carbon (SOMC) was synthesized by means of a hard template

method at Nanjing University, which has been reported in previous research [24].

The characteristics of the two carbon materials are listed in Table 1. The respective surface areas of the CPAC and SOMC were 580.13 and 988 m²/g, whereas the respective pore sizes of the CPAC and SOMC were 1.86 and 3.7 nm, and the mesoporous volume of the SOMC was 1.29 cm³/g.

PAC adsorption was conducted at doses of 20, 50, and 100 mg/L before the AOM were filtrated. The specific steps were as follows: 30 min fast stirring at 100 rpm after PAC was added; 2 h slow stirring at 50 rpm; 45 min of precipitation; and then, the supernatant was filtrated through a Millipore 0.45 μm filter. The PAC adsorption ability was evaluated through the equilibrium experiment before performing the MF experiment.

Fig. 1 and Table 2 show the adsorption isotherm and kinetic data of the two PACs. As can be seen in Fig. 1, both of the carbons can be fitted using the Freundlich sorption model. K_a is the Freundlich affinity coefficient, representing the ratio of organic matter adsorbed on the adsorbent to the equilibrium solution concentration. K_a in SOMC was significantly higher than that of CPAC, indicating that SOMC had higher adsorption capacity than CPAC, which might due to its higher specific surface areas (988 m²/g) (Table 2). While for $1/n$, $1/n$ was higher for SOMC than that of CPAC, suggesting that SOMC was more suitable for high AOM concentrations.

Table 1
Characteristics of the two carbon used

	Mesoporous carbon	Microporous carbon
Carbon (%)	95.57	98.4
Surface area (m ² /g)	988	580.13
Pore size (nm)	3.7	1.86
Microporous volume (cm ³)	0.04	0.2015
Mesoporous volume (20–500 Å) (cm ³ /g)	1.29	/

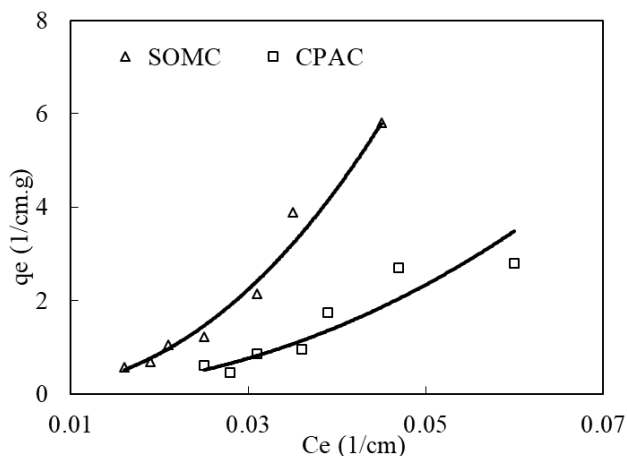


Fig. 1. Adsorption isotherm for two PACs: equilibrium time 3 d, temperature 25°C, and initial UV₂₅₄ absorbance 0.074.

PAC pretreatment for organic hydrophobicity was performed using a SOMC of 20 mg/L. Before adsorption, the AOM fractions were adjusted to the same DOC at 5 mg/L and neutralized to a pH of 7.0.

A microfiltration (MF) experiment was conducted on a flat filtration unit of a dead-end filtration unit. A flat, mixed-cellulose Millipore membrane (0.1 μm, 80%–100% of nitrate cellulose; 0%–20% acetate cellulose, hydrophilic, Millipore Corporation, US) was utilized. A schematic diagram of the experimental setup was described in our previous publication [22]. The filtration flux was calculated using the ratios of water filtration flux J (L/h m²) to the initial membrane flux J_0 (J/J_0).

All experiments were duplicated three times, and the errors between the filtration fluxes of duplicated experiments were <0.05.

2.3. Analytical methods

2.3.1. DOC and UV analysis

DOC and ultraviolet absorbance at a wavelength of 254 nm (UV₂₅₄) were determined using a total organic carbon analyzer (TOC-VCPH, Shimadzu, Japan) and a UV spectrophotometer (Hach-5000, USA), respectively.

2.3.2. MW distribution

The MW distribution was measured on a HPSEC (Waters e2695, USA) coupled with a UV/visible detector (Waters 2489, USA) and total organic carbon analyzer (Sievers 900 Turbo, USA) system, which we have described in a previous publication [22]. Before detection, the ionic concentrations of the solutions were adjusted to 0.1 mol/L in accordance with the ionic strength of the HPSEC mobile phase, and the samples were neutralized to a pH of 7.0. The chromatograms were examined using a peak-fitting technique, and the peak area was determined using the PeakFit software package (Version 4.12 Systat Software Inc., CA, USA) [19,25].

2.3.3. Organic hydrophobicity

Organic fractionation was performed by SUPELCO VISIPREPTM DL (USA). XAD-4, DAX-8, and IRA-958 resins were utilized to separate the organics into a HPO, a TPI, a C-HPI, and a N-HPI fraction [26].

2.3.4. Fluorescence excitation-emission matrix determination

Excitation-emission matrix (EEM) was determined on a fluorescence spectrometer (F-4500, Hitachi, Japan). The excitation and emission wavelengths were set in the range of 200–550 nm with 5 nm increments [22]. AOM fluorescent

Table 2
Fitting curve parameters by PAC adsorption

Type	Sorption isotherm	K	$1/n$	R^2
SOMC	$y = 8,340.8x^{2.3449}$	8,340	2.3449	0.9741
CPAC	$y = 1,654x^{2.1901}$	1,654	2.1901	0.8739

organic matter was quantified according to the EEM volume in each region using the fluorescence regional integration method [27].

2.3.5. Characterization of cake layer on the membrane surface

The cake layer on the membrane surface was analyzed using a scanning electron microscope (S4800, Hitachi, Japan).

3. Results and Discussion

3.1. Membrane fouling caused by various AOM solutions

Fig. 2 shows the variations of normalized filtration flux of AOM solutions without PAC pretreatment. The elevated flux decline was perhaps caused either by monolayer adsorption of various-sized foulants into membrane pores or the formation of a fouling layer on the membrane surface [28]. The APF-AOM had the most noticeable effects on membrane fouling, resulting in a flux decline of 9.7% over 800 mL of filtration. This value is slightly higher than the ANF-AOM driven flux decline (9.35%) and very different from the SO-AOM (25.2%) and Cy-AOM (31.08%) driven flux decreases. The higher fouling potential of hydrophilic AOM has already been mentioned by several studies [1,29]. However, the APF-AOM and ANF-AOM exert more serious membrane fouling than do SO- and Cy-AOM, which might be associated not only with the type of organics but also the associated fouling mechanisms. Our previous research indicated that for blooming cyanobacteria, including APF- and ANF-AOM, more negative cohesion and adhesion free energies with the membrane are exhibited, the attractive forces are stronger, and a thick cake layer forms on the membrane surface. Whereas the cohesion and adhesion free energy of bloom diatoms and green algae (SO- and Cy-AOM) are smaller and weaker than those of cyanobacteria, their associated membrane fouling potential is lower [22].

3.2. Membrane fouling control by PAC treatment

Fig. 3 shows the effects of PAC treatment on MF performance using various AOM solutions. The data demonstrated that CPAC alone had limited effects on the filtration flux of the MF membrane (the curves with and without PAC nearly overlap, and sometimes, the filtration flux decreased even more than that of the curves without PAC), as determined by many studies [14,30]. However, the MF performance was greatly improved after the SOMC treatment. In fact, after 100 mg/L SOMC treatment, Cy-AOM demonstrated the highest improvement of filtration flux with 33% compared to 9.1% for APF-AOM, 8.7% for SO-AOM, and 5% for ANF-AOM. PAC was prospectively to compete with the MF membrane for the adsorption of organic compounds that otherwise would adsorb on the membrane, causing fouling. However, when in the presence of NOM, PAC increased the fouling resistance [30]. Thus, to eliminate the PAC influence on MF performance, PAC was pre-filtrated using a 0.45 μm filter after adsorption. However, the discrepancy in improving filtration fluxes still existed among various AOM, which might be related to their AOM characteristics and also to their adsorption characteristics.

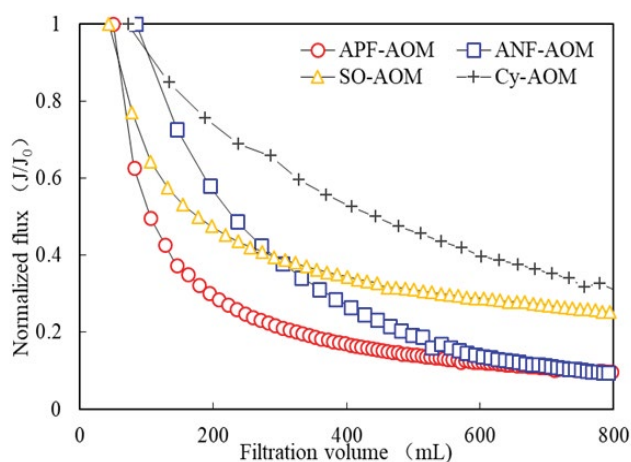


Fig. 2. Variation in normalized filtration fluxes of AOM solutions without PAC pretreatment.

As is already known, the pore size of mesoporous carbon is mainly concentrated at 3.7 nm, whereas most microporous carbon has a pore size of less than 1.8 nm (Table 1). In the adsorption of macromolecular AOM, the presence of steric effects might prevent some of the AOM macromolecules from entering the pores of microporous carbon. Even when some portion of the macro-MW organics can be adsorbed by CPAC, the pore size of microporous carbon might be further blocked, whereas the SOMC could overcome the disadvantage of these characteristics and improve filtration fluxes. To further analyze the discrepancy of membrane filtration fluxes, the AOM characteristics and membrane fouling are discussed below.

3.3. Influence of PAC treatment on membrane fouling alleviation

3.3.1. Influence of PAC treatment on membrane fouling alleviation by membrane morphological analysis

Fig. 4 shows the surface morphology of the clean and fouled membranes with and without PAC treatment. The surface of the virgin membrane is very clean and smooth, with multiple uniform membrane pores. In contrast, the membrane surface was seriously fouled after filtering various AOM solutions, with dense cake layers formed by foulants attached to the membrane surface and abundant macromolecular organics accumulated on the membrane surface. These organics were speculated to be proteins, polysaccharides, or humic-like organics [31].

After CPAC pretreatment, it was found that thinner cake layers and a large amount of organic matter still existed, although many narrowed pores and a small amount of organic complexes were found after CPAC pretreatment. Specifically, after SO-AOM filtration, the membrane fouling remained serious (Fig. 3). This phenomenon may be because the organic matter that was not absorbed by CPAC might still foul the membrane. Comparatively, after 100 mg/L SOMC treatment, the membrane that was fouled by SO-AOM had many clearly visible pores on the membrane surface. The degree of organic complexation was also significantly

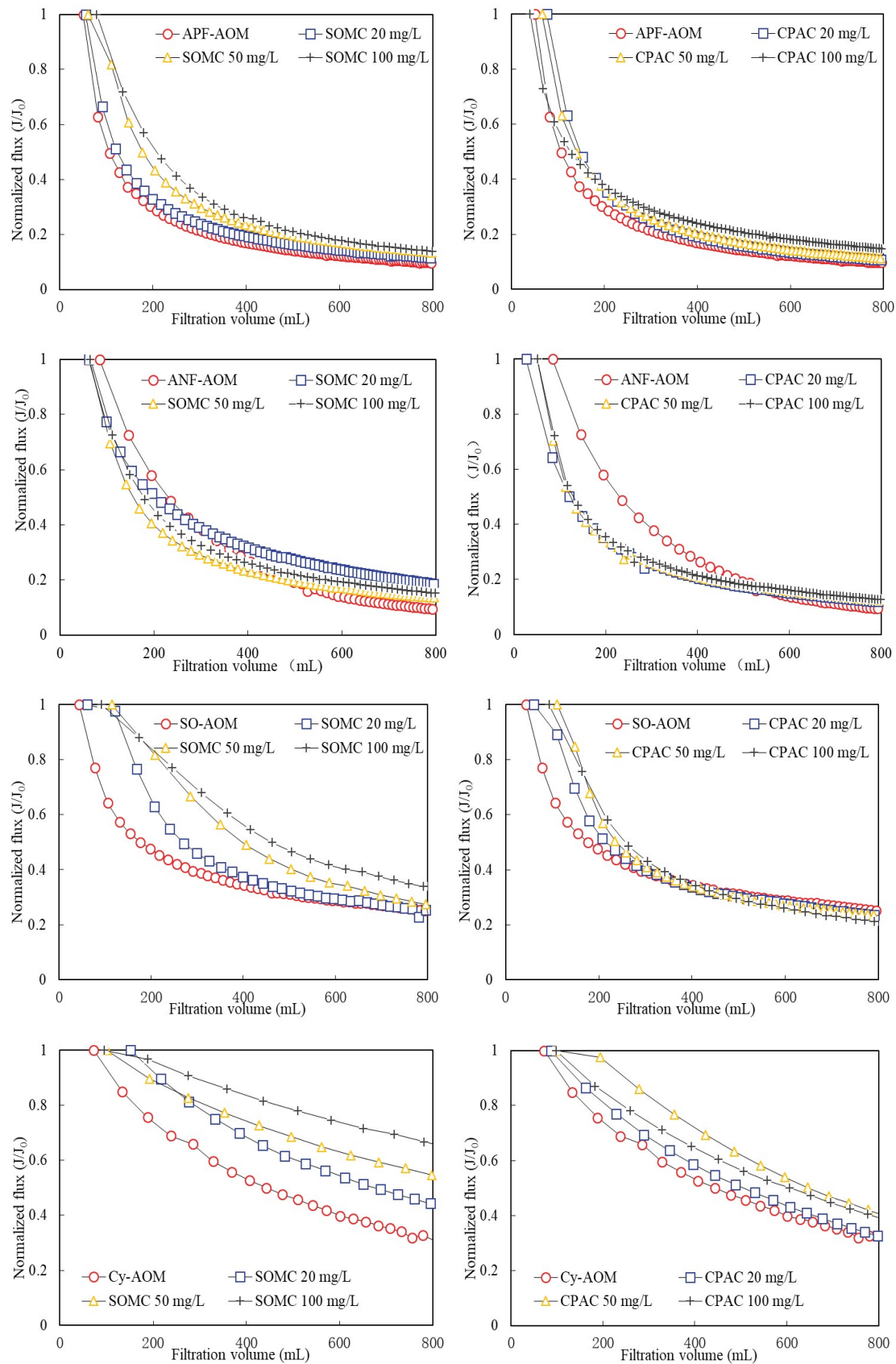


Fig. 3. Normalized filtration fluxes of AOM solutions after PAC pretreatment.

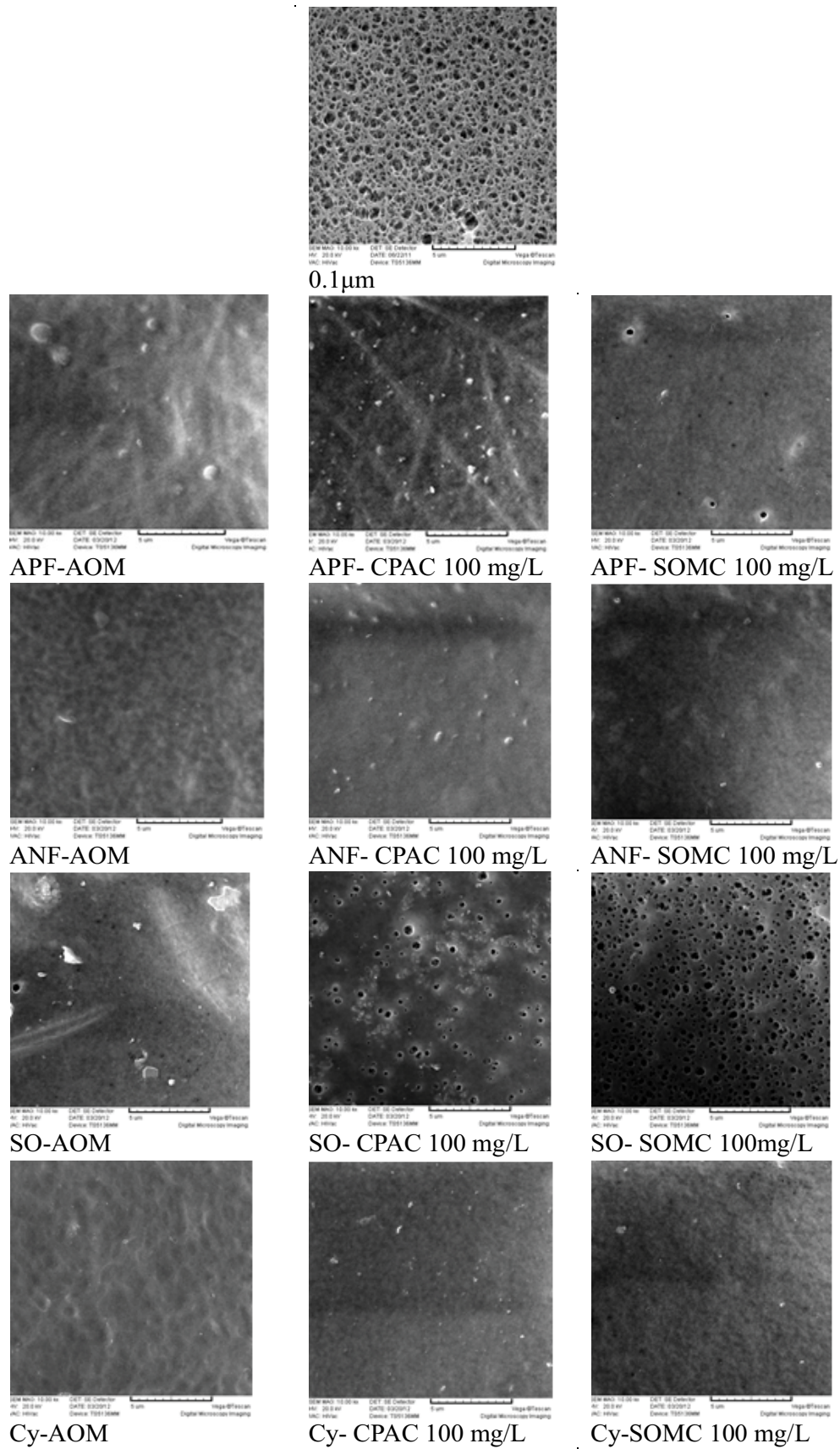


Fig. 4. SEM images (bar = 5 µm) of a clean membrane and fouled membrane following filtration of AOM solutions with and without PAC treatments.

reduced compared to the case of the CPAC treatment, which might be one of its causes of increased filtration fluxes by SOMC.

3.3.2. Influence of PAC treatment on membrane fouling alleviation by MW distribution

The decreased resistance of the cake/gel layer after PAC pretreatment most likely originated from both quality and component alteration of AOM that are shown as changes in MW distribution and hydrophobicity.

Fig. 5 shows the MW distribution of various AOM solutions by PAC treatment. The fraction of peak areas in raw water, PAC-treated water, and MF permeate was further analyzed using peak-fitting technology, the results of which are displayed in Table 3. As shown in Fig. 5, all the AOM samples can be separated into four peaks. Peak A has a MW of 1,000 kDa, which is considered to represent macro-MW biopolymers (BP) of polysaccharides and proteins. Peak B has a MW of 6,500 Da and is considered to represent medium-MW humic-like substances (HS). Peak C has a MW of 1,200 Da made up of small-MW building blocks of low-MW acids and humics (LMWA&BB). Peak D has a MW of 440 Da composed of low-MW neutrals (LMWN) [4].

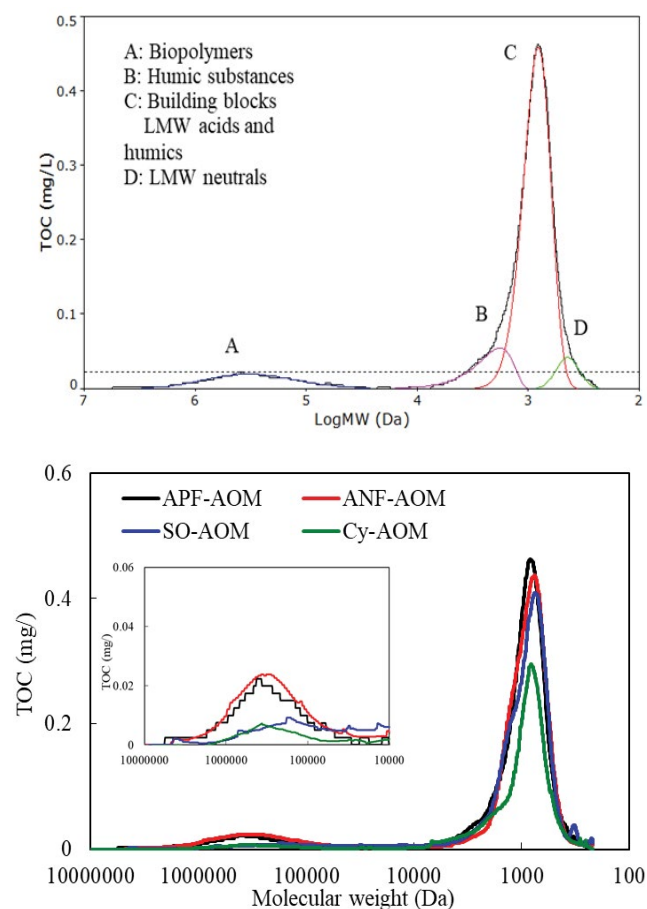


Fig. 5. Molecular weight distribution of various AOM solutions by HPSEC-peak fitting.

Compared to the peak areas of the AOM solutions (Table 3), the peak A areas of BP followed the order ANF-AOM > APF-AOM > SO-AOM > Cy-AOM. Considering HS, the peak area was the highest in APF-AOM, followed by Cy-AOM, ANF-AOM, and SO-AOM. The peak C area of LMWA&BB followed the order of APF-AOM > ANF-AOM > SO-AOM > Cy-AOM. After the CPAC treatment, CPAC had limited effects on reducing the areas of peak A, C, and D. In contrast, CPAC resulted in a greater decrease in peak B areas, illustrating that medium-MW fractions of HS could be better adsorbed by CPAC, which was consistent with previous studies that have shown that activated carbon exhibited greater adsorption for the small molecules (e.g., humic acid) than for those with large molecules [32].

Comparing the effects of the SOMC treatments (Table 3), the peak areas of MWs between the raw water and water after the SOMC treatment changed significantly after various SOMC doses. Macro-MW biopolymers gradually decreased by increasing the SOMC doses. The percent reduction of the peak A area between the raw water and water after the 50 mg/L SOMC pretreatment was 63% for Cy-AOM, 45.9% for SO-AOM, 36% for ANF-AOM, and 8% for APF-AOM. In contrast, the peak A area percent reduction increased to 100% for Cy-AOM, 100% for SO-AOM, 49% for ANF-AOM, and 46.7% for APF-AOM at SOMC 100 mg/L, indicating that the SOMC had excellent effects on the removal of high-MW BP. Prior research determined that PAC could control membrane fouling by removing a certain proportion of NOM [33]. The higher BP reduction by the SOMC might cause fewer substances to be intercepted on the membrane surface, thereby decreasing the resistance of the gel layer and increasing the filtration fluxes. In addition to the large reduction in the peak A area, the peak B area was also reduced by the SOMC, illustrating that SOMC could also remove a portion of HS organics. We note that the removal efficiency of HS decreased as the PAC doses increased. This phenomenon may be because as the SOMC doses increase, more macro-MW organics can be adsorbed by the SOMC due to its ordered mesoporous structure, which might cause fewer medium-MW organics to be adsorbed. For peak C, the removal efficiency was limited. Despite the adsorbing effects, peak D was significantly lower than that of BP and HS. The percentage reduction was also enhanced as the SOMC doses increased, indicating that the SOMC pretreatment can remove high-MW BP as well as medium- and low-MW organics, which might alleviate membrane fouling.

Table 4 lists the peaks area reductions of HPSEC chromatograms for the raw water and water after MF. The differences in peak areas between the raw water and the water without the PAC treatment indicated that the peak A area was greatly reduced after MF (Table 4). The removal efficiency was 65.4% for APF-AOM, 51% for ANF-AOM, 52.8% for SO-AOM, and 40.8% for Cy-AOM, which was consistent with their filtration fluxes that are shown in Fig. 2. This result indicated that the MF membrane mainly intercepted this portion of organics, which is in line with previous studies of macro-MW biopolymers such as polysaccharides and proteins resulted in severe fouling of the polymeric MF membrane [34]. In addition, a fraction of medium-MW components of HS and low-MW neutrals were rejected by MF

Table 3
Peak areas reductions of the four AOMs by CPAC and SOMC treatments using HPSEC combined with peak-fitting prediction

Samples	CPAC				SOMC			
	Peak A	Peak B	Peak C	Peak D	Peak A	Peak B	Peak C	Peak D
APF–	0.201**	0.0239**	0.1438**	0.1438**				
20	37.92*	9.28*	–1.06*	6.45*	–1.1*	7.66*	–6.18*	–47.89*
50	7.09*	3.67*	–11.3*	–2.57*	8.07*	17.19*	–8.1*	–27.99*
100	–6.15*	–31.93*	15.7*	–56.8*	46.97*	41.8*	15.7*	5.86*
ANF–	0.0247**	0.0068**	0.1590**	0.008**				
20	–1.17*	–73.6*	–3.5*	5.46*	10.62*	–30.00*	0.07*	12.42*
50	–5.44*	–26.4*	1.45*	–18.3*	36.00*	–41.3*	0*	24.49*
100	–23.2*	–7.97*	–2.47*	–0.75*	49.19*	0.007*	0*	62.44*
Cy–	0.0056**	0.0346**	0.0702**	0.0056**				
20	22.55*	65.32*	–19.5*	–19.5*	20.06*	70.64*	–25.78*	–16.62*
50	–6.99*	53.51*	5.85*	5.85*	63.52*	72.24*	–22.13*	–40.85*
100	4.26*	76.62*	–5.24*	–5.24*	100*	34.38*	–14.89*	23.43*
SO–	0.0061**	0.0196**	0.1392**	0.0056**				
20	–8.76*	22.68*	–0.57*	–51.3*	46.13*	–4.45*	–0.45*	16.94*
50	–41.79*	34.17*	–6.9*	12.65*	45.96*	2.23*	0.22*	–47.79*
100	20.19*	51.67*	3.72*	–41.48*	100*	5.72*	0.57*	51.50*

*Percentage reduction in peak area between source water and water after CPAC treatment.

**Peak areas of the four AOM solutions by peak-fitting.

Table 4
Areas of Peaks A–D for the feed and permeate of MF membrane filtration by SOMC and CPAC treatment using peak-fitting

Samples	Parts of the HPSEC-OCD chromatogram by SOMC				Parts of the HPSEC-OCD chromatogram by CPAC			
	Peak A	Peak B	Peak C	Peak D	Peak A	Peak B	Peak C	Peak D
APF–	65.38*	–33.8*	–5.88*	–13.2*				
20	75.65*	10.32*	–1.86*	13.45*	64.21*	79.43*	86.72*	–14.3*
50	61.41*	–27.8*	–2.27*	30.78*	100*	–6.53*	3.02*	–29.1*
100	62.96*	0.82*	–22.3*	–32.4*	100*	7.37*	1.48*	33.62*
ANF–	51.07**	–9.28*	–5.85*	38.19*				
20	100**	–30.5*	0.87*	8.42*	83.93*	57.42*	–3.14*	–31.2*
50	83.02**	18.52*	0.003*	65.65*	100*	–3.03*	1.3*	12.51*
100	100**	8.73*	3.19*	–47.9*	100*	–17.4*	10.85*	2.61*
Cy–	40.86*	15.45*	–22.5*	0.406*				
20	100*	15.93*	–2.06*	–47.6*	30.73*	–56.5*	12.59*	26.64*
50	100*	–6.15*	–1.37*	34.70*	45.42*	39.42*	–32.88*	–26.6*
100	100*	24.65*	–4.97*	–1.13*	61.63*	–9.0*	–16.67*	42.44*
SO–	52.82*	–2.84*	1.69*	–22.8*				
20	100*	–48.9*	3.09*	50.17*	100*	–4.0*	–1.79*	18.26*
50	43.47*	–11.3*	3.54*	–2.01*	100*	–41.9*	–0.95*	6.93*
100	100*	–36*	6.01*	–7.07*	100*	–86.1*	–6.8*	50.88*

** Percentage reduction in peak area between source water and water after MF;

* Percentage reduction in peak area between water after PAC treatment and MF;

during the ANF- and Cy-AOM filtrations, illustrating that the cake/gel layer formed by ANF- and Cy-AOM was not only composed of polysaccharides and proteins but also contained humic-like substances and low-MW neutrals.

After the SOMC treatment, the Table 4 clearly shows that the organics rejected by the MF were macro-MW BP. Despite

the increase in the removal efficiency of BP compared to that without PAC treatment, the filtration flux increased, which might due to the adsorbed organics introduced by the SOMC treatment. In addition to the higher rejection of the peak A area, MF also improved rejections of the peak area of HS, LMWA&BB, and low-MW neutrals during the CPAC

treatment, illustrating that the membrane fouling caused by the AOM after CPAC included not only macro-MW of BP but also medium- and low-MW organics.

3.3.3. Effect of SOMC treatment on membrane fouling mitigation by organic hydrophobicity

Organic hydrophobicity has also been reported to have great influence on membrane fouling [35]. Fig. 6 shows the SOMC treatment on ANF- and Cy-AOM organic hydrophobicity. ANF- and Cy-AOM were investigated in this part considering that there had the greatest discrepancies between the filtration fluxes of ANF- and SO-AOM by SOMC treatment. As can be seen, without PAC treatment, the N-HPI fraction in the feed water accounted for 68.1% and 64.85% of ANF- and Cy-AOM, whereas the percentages of HPO, TPI, and C-HPI were 17.22%, 8.25%, and 17.22% for APF-AOM, respectively, and 18.52% (HPO), 12.07% (TPI), and 17.1% (C-HPI) for Cy-AOM. After MF, N-HPI (9.2%), and HPO (7.9%) fractions were greatly reduced after ANF-AOM filtration. The organic removal of HPO, TPI, C-TPI, and N-HP was 8.4%, 10.4%, 8%, and 4.12% for Cy-AOM, respectively, indicating that N-HPI and HPO were the main components that caused membrane fouling during MF of APF-AOM, whereas the MF membrane mainly intercepted the

hydrophobic fraction of Cy-AOM. Previous research indicated that HPO organics accounted for most of the formation of the gel layer, and those HPO substances might aggregate on the membrane surface by hydrophobic interactions between the organic matter and membrane materials during UF. The N-HPI fraction of macro-MW organics mainly foul the membrane by fully obstructing the membrane pores or densely forming the cake layer [3,31]. Although both processes could cause membrane fouling, the membrane fouling caused by N-HPI might be more serious due to direct pore blockage or cake layer formation [36], which might be one of the explanations for less fouling observed with Cy-AOM than ANF-AOM in Fig. 2.

After the SOMC treatment, the HPO, TPI, and N-HPI were significantly removed, and the organic reduction that was reached for HPO and TPI was as high as 48%–50% for ANF- and Cy-AOM, whereas the N-HPI removed was 44%–60% by SOMC. The SOMC had higher removal efficiencies of HPO and N-HPI during Cy-AOM treatment than those of ANP-AOM, which might cause fewer organics to be intercepted on the membrane surface, therefore alleviating the gel/cake layer fouling.

3.3.4. Influence of PAC treatment on membrane fouling mitigation by EEM organics

Fig. 7 show the EEM volumes of APF-AOM and the other three AOM solutions before and after the PAC treatment. Three-dimensional fluorescence EEM spectroscopy has been widely used to recognize the chemical components of both NOM and NOM foulants in membrane bioreactors due to its capability of differentiating certain classes of organic matter. According to previous studies, the EEM spectra of AOM samples can be divided into five regions (Fig. 8) [27]. Region I (Ex: 220–270 nm/Em: 280–330 nm) and region II (Ex: 220–270 nm/Em: 330–380 nm) represent aromatic proteins. Region III (220–270 nm/380–540 nm) and region V (270–440 nm/380–540 nm) correspond to fulvic acid-like (FA) and humic acid-like substances (HA), respectively. Region IV (Ex/Em: 270–440 nm/280–380 nm) represents soluble microbial products (SMPs). Despite the fact that all the AOM extracted from the four algae exhibited the same EEM spectra at the aromatic protein-like and humic-like fluorescence regions, when comparing the EEM volumes among the various AOM solutions, the EEM spectral features were extremely different. The highest EEM volumes occurred in ANF-AOM, followed by APF-AOM, SO-AOM, and Cy-AOM.

After the SOMC treatment (Fig. 8), there were greater decreases in EEM volumes in regions III, IV, and V for the four AOMs than for the reductions in regions I and II, indicating that HS-like and SMP-like organic matter were the main components that were reduced by the SOMC, which was consistent with the MW distribution results (Table 3). However, when comparing the treatment effects of the SOMC and CPAC, the reduction in EEM volume in all of the regions was markedly lower for the CPAC treatment than for the SOMC treatment, suggesting that fewer substances associated with those regions were adsorbed by the CPAC. The lower rejection of the fluorescence organic matter could be ascribed to the relatively small pore size of the CPAC that is displayed in Table 1.

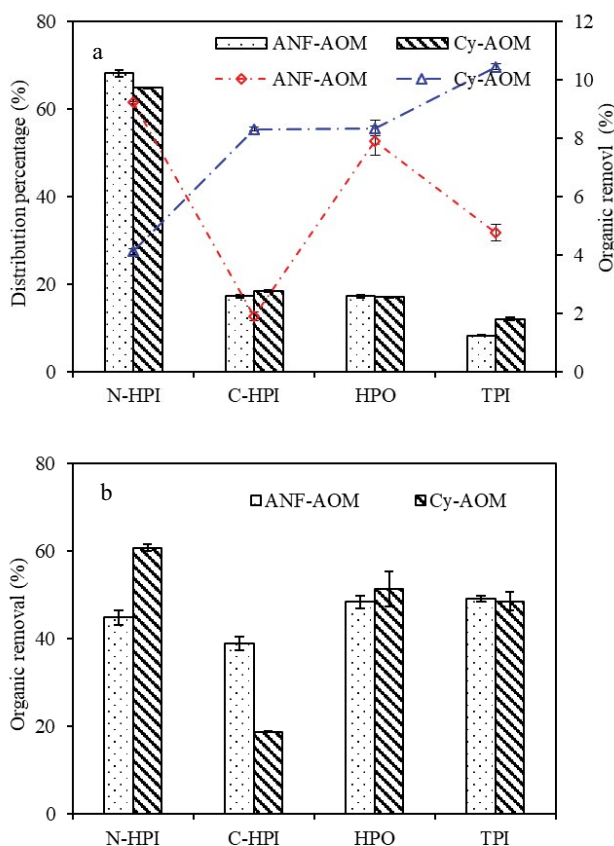


Fig. 6. Organic hydrophobicity of ANF- and Cy-AOM solutions and organic removal of fractional components by direct MF and SOMC treatments. (a) by direct MF and (b) by SOMC treatment. Error bars indicate the standard deviation ($n = 3$).

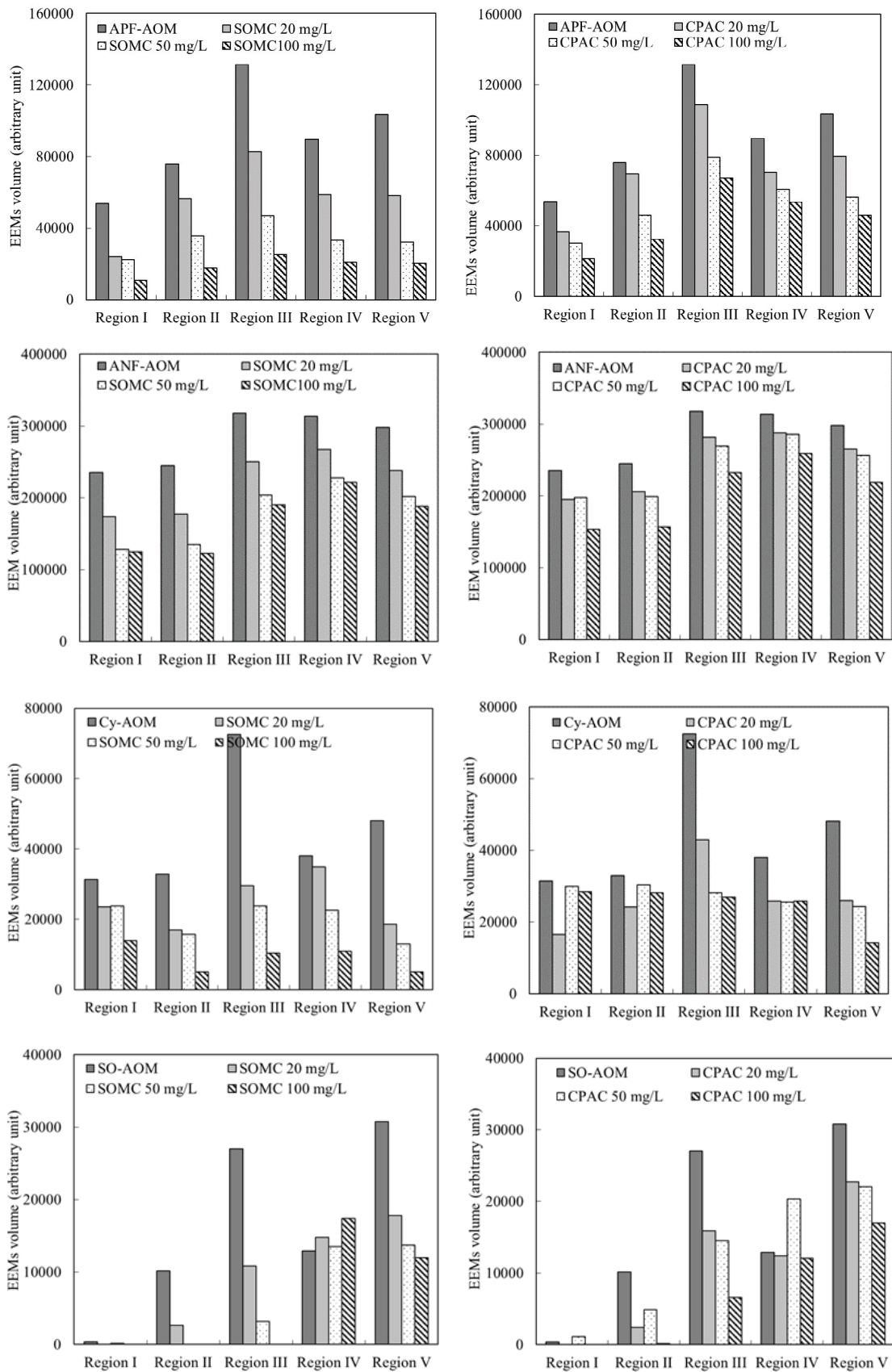


Fig. 7. EEM spectral volumes for various AOMs after SOMC and CPAC treatment.

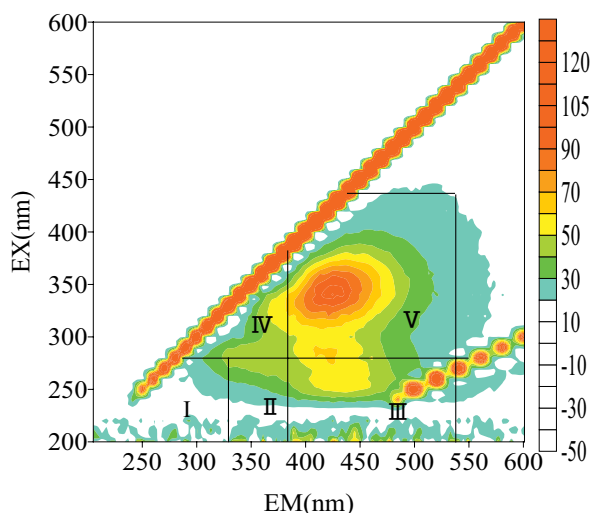


Fig. 8. EEM spectra of AOM solution.

After MF (Fig. 9), considerably greater amounts of protein-like (region I and II) and SMP (region IV) organics were retained by the membrane, which suggested that although PAC treatment could remove a part of the organics, the remaining substances associated with these regions could still be rejected by the membrane and result in membrane fouling. The volume of the AOM after MF was lower after the SOMC treatment than after the CPAC treatment, which might be due to the high adsorption potential of the SOMC, thus leading to less membrane fouling.

3.4. Analysis of fouling resistance with AOM characteristics by the PAC treatment

To determine the complex relationships between various AOM characteristics and membrane fouling by the PAC treatments, the MW distribution, DOC, and UV_{254} were correlated with the total fouling resistance (R) using a linear regression (Figs. 10 and 11).

Fig. 10 shows a strong correlation between BP and total fouling resistance (R), with $r^2 = 0.8943$ for the SOMC and 0.8115 for the CPAC (Fig. 11), indicating that BP was highly correlated to total membrane fouling irrespective of treatment by the SOMC or CPAC. This result was consistent with our HPSEC data that showed that BP was the major component that resulted in membrane fouling, suggesting that the content of BP in various AOM solutions and the associated removal efficiency might be a good indicator of membrane fouling during MF and PAC treatments. Similar to those for the observed BP, LMWA&BB yielded high correlation values with R , suggesting that LMWA&BB was also strongly related to the fouling potential. This phenomenon may have occurred because the LMWA&BB organics may be important in the evolution of irreversible membrane fouling. Liu et al. [25] investigated fouling behaviors correlated to water characteristics with and without PAC treatments and found that LMWA&BB mainly induced the constriction of membrane inner pores and played an important role in the evolution of membrane fouling. Unlike BP and LMWA&BB, HS had

a low correlation with R . HS was reported to be one of the main components in UF fouling [37], yet there was no clear correlation between HS and R , suggesting that HS played a small role in the evolution of membrane fouling during MF of AOMs by PAC treatment. In addition, low-MW neutrals contributed minimally to membrane fouling, which was supported by the correlations between R and low-MW neutrals during both the SOMC and CPAC treatments. From the correlations between DOC/UV_{254} and R , there was a weak correlation with R and UV_{254}/DOC . This finding may be because the DOC content is only a measurement of the total amount of dissolved organic matter and cannot supply any quantitative or qualitative information regarding its various components [25].

3.5. Membrane fouling mechanisms

Previous studies indicated that BP contributed greatly to the reversible and irreversible fouling of low-pressure membranes and that pore narrowing played an important role in hydraulically irreversible fouling [25,28]. According to the above results, macro MW organics were the main components that caused membrane fouling during MF by AOM solutions. After the SOMC treatment, macro-MW BP can be significantly removed by the SOMC. Due to the decreased BP, HS, and low MW organic matter, the SOMC-pretreated water might exhibit a loose cake layer, thus alleviating reversible and irreversible fouling. Although the CPAC could adsorb more HS than the SOMC, as HS substances exerted little influence on MF membrane fouling, the remaining macro-MW BP and low-MW neutrals could still foul the membrane, making a dense cake layer or seriously obstructing the membrane pores. Furthermore, although the SOMC could remove a part of the macro-MW organics as well as the medium- and small-MW organics, because the AOM have different content of organic matters, the membrane fouling was ultimately determined by the residual AOM in the feed water. Therefore, the filtration flux increases of ANF-AOM and APF-AOM after the SOMC treatment were not as high as those of Cy-AOM and SO-AOM (Fig. 12).

4. Conclusions

This study investigated the performance of mesoporous and microporous carbon treatments for MF membrane fouling mitigation using various AOM. The following conclusions are drawn.

- Microporous activated carbon had limited effects on membrane filtration flux improvement, whereas the filtration fluxes could be improved by synthesized ordered mesoporous carbon. The filtration fluxes increased were 5%, 9.2%, 8.7%, and 33% for APF-, ANF-, SO-, and Cy-AOM, respectively, when the SOMC was added in 100 mg/L doses.
- MW distribution and organic hydrophobicity indicated that the SOMC mainly adsorbed macromolecules of N-HPI and HPO organics, such as BP of polysaccharides, protein-like organics, and HS, whereas the CPAC mainly adsorbed HS organics.

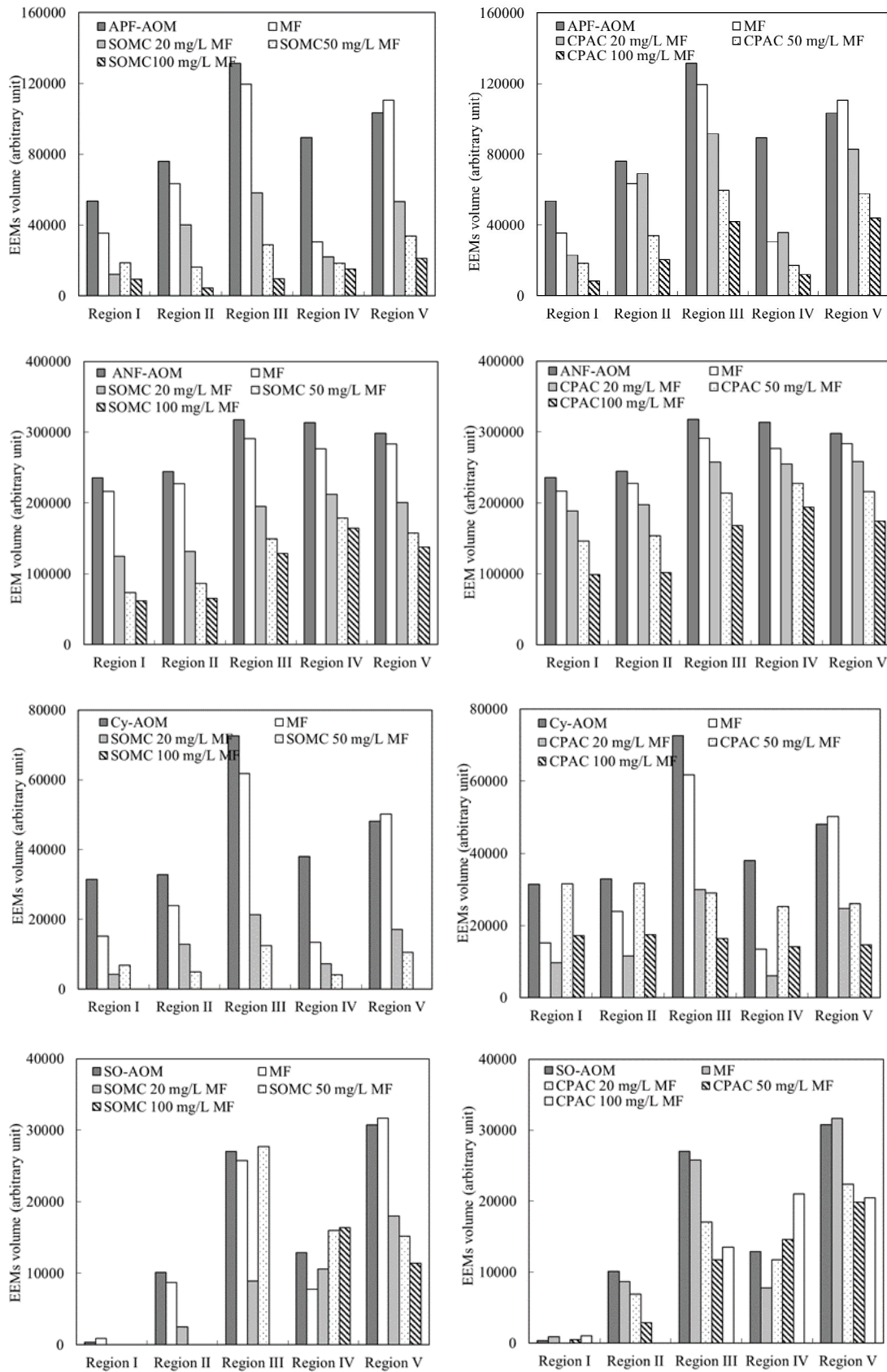


Fig. 9. EEM spectral volumes for various AOMs after MF.

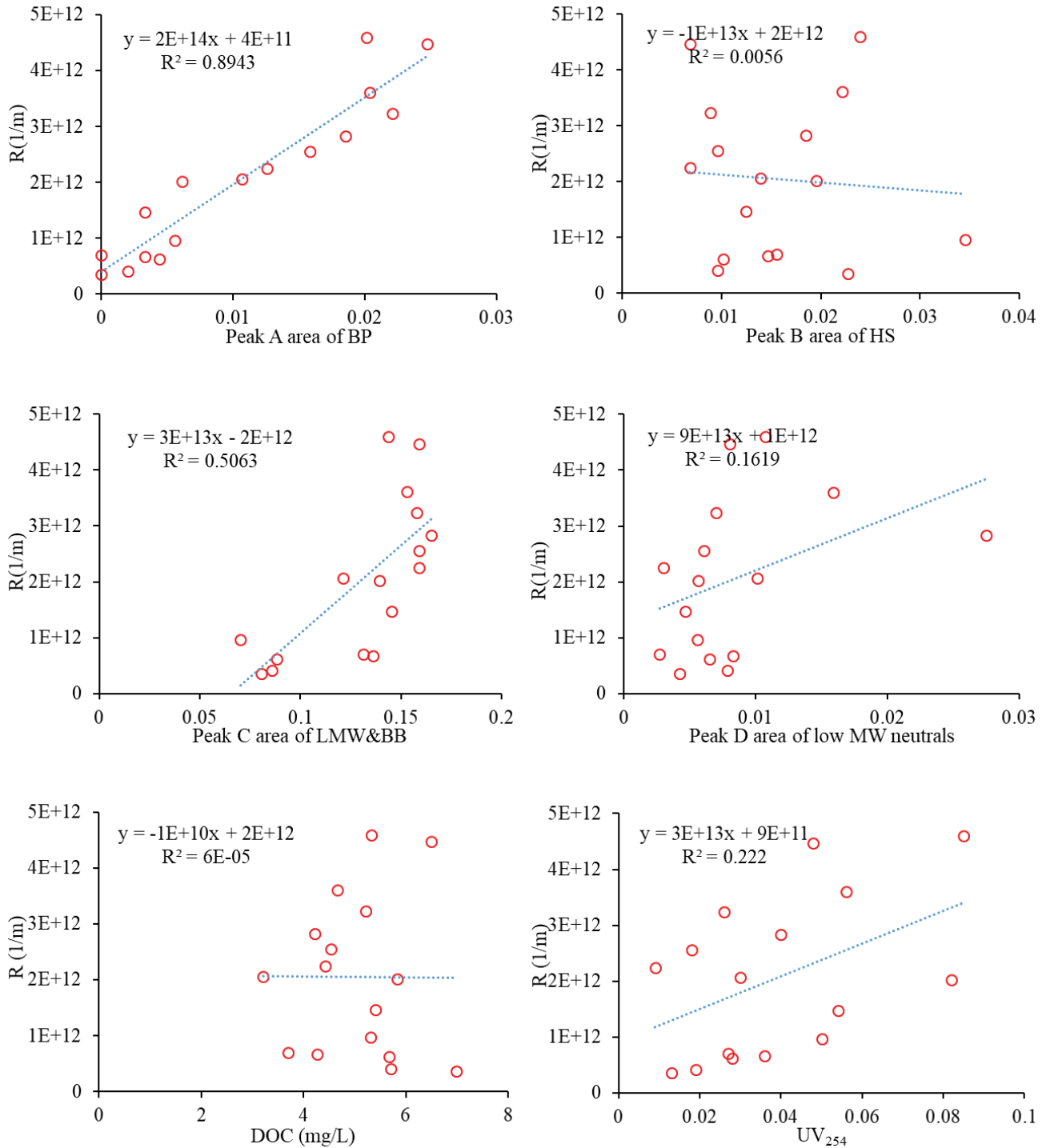


Fig. 10. Correlation between different MW distributions of peak areas, DOC, UV_{254} and total fouling resistance after SOMC treatment.

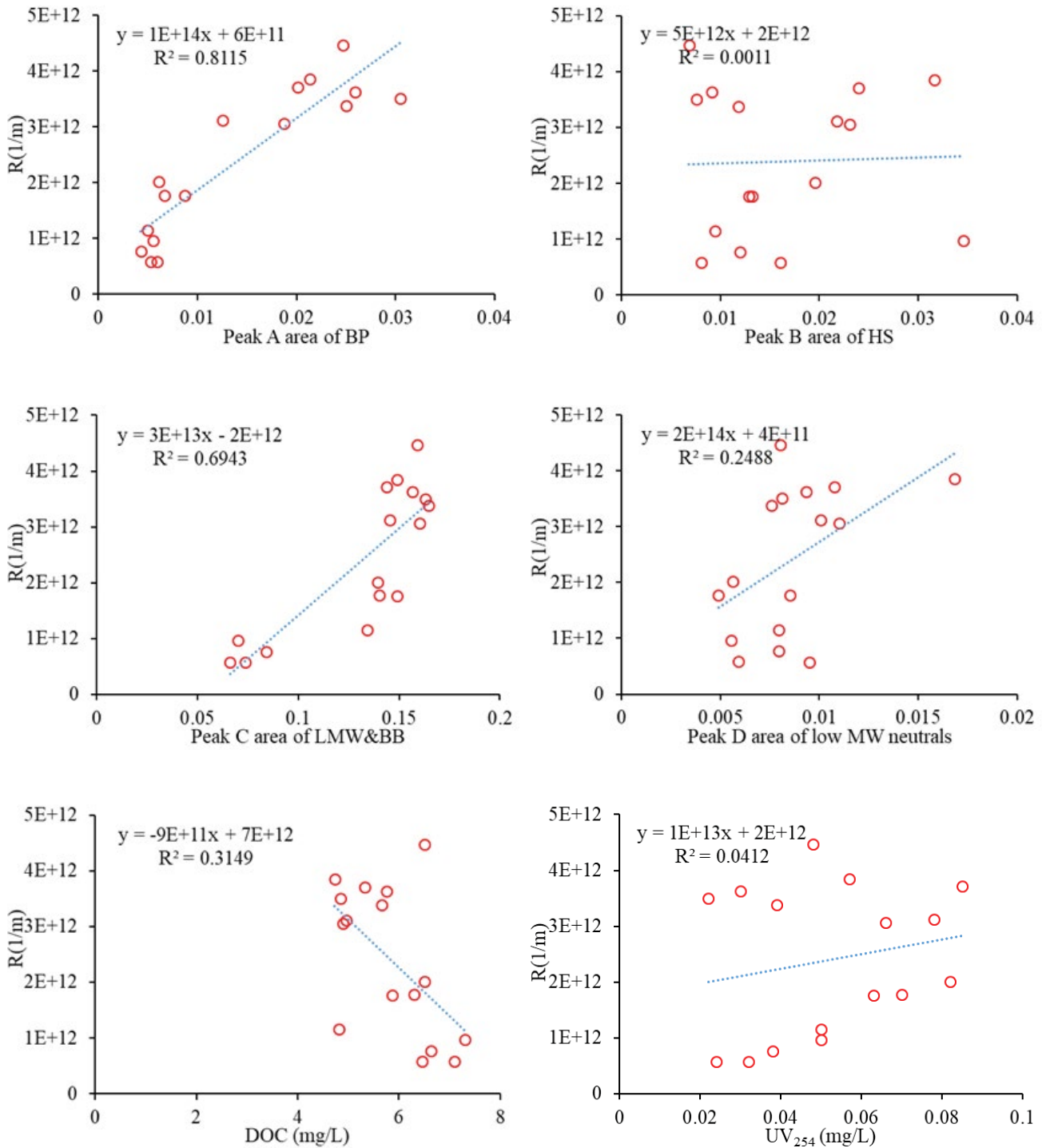


Fig. 11. Correlation between different MW distribution of peak areas, DOC, UV_{254} and total fouling resistance by CPAC treatment.

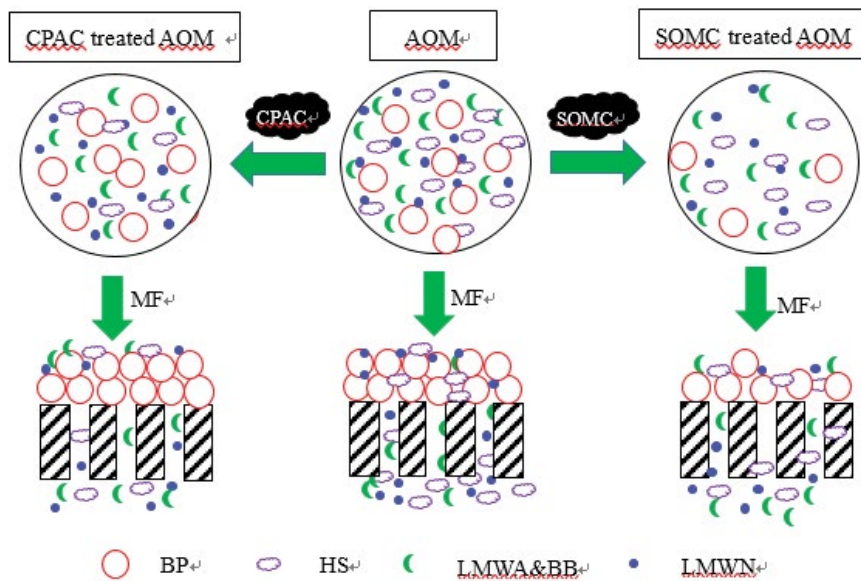


Fig. 12. MF membrane fouling mechanism associated with the AOM solution after CPAC and SOMC treatment.

- Linear regression analyses suggested that the BP content in the AOM samples by PAC treatment was highly correlated to membrane fouling. The SOMC of mesoporous-rich activated carbon is suggested as an appropriate pretreatment method in AOM-involving water treatment compared to the use microporous carbon during MF.

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