Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.21868

102 (2018) 16–37
January

Pretreatments to control low-pressure membrane fouling: a review on the coagulant/adsorbent applied and contact modes with the feed

Longfei Wang, Peisheng Zhang, Yi Li*

Key Laboratory of Integrated Regulation and Resource Development on Shallow Lakes, Ministry of Education, College of Environment, Hohai University, Nanjing, Jiangsu 210098, China, emails: envly@hhu.edu.cn (Y. Li), lfwang@hhu.edu.cn (L. Wang), 646128347@qq.com (P. Zhang)

Received 17 August 2017; Accepted 30 December 2017

ABSTRACT

The application of low-pressure membranes (LPMs) to drinking water treatment has undergone tremendous developments in the past decades. Integration of pretreatment approaches has been devoted in conjunction with LPMs in mitigating membrane fouling, among which coagulation/adsorption pretreatments are most frequently employed. However, the impact of coagulation/adsorption on fouling reduction is sometimes less pronounced and even adverse. The ability in mitigating membrane fouling varies significantly among various types of coagulants/adsorbents. The literature suggests that the contact modes between coagulants/adsorbents and the feed remarkably affect natural organic matter (NOM) removal and membrane behaviors. Compared with conventional approaches, for example, coagulation, coagulation + sedimentation, inline coagulation, adsorption + direct filtration, preadsorption or integrated adsorption treatments, which has limited effects to fouling control and occasionally even accelerate fouling, a novel approach named micrograular adsorptive filtration performs superior in NOM removal and fouling reduction. This article provides a critical review of the coagulation/adsorption pretreatments for LPMs using conventional coagulants/adsorbents and some novel solids. The difference and mechanism in the contact modes between adsorbents with the feed in NOM removal and fouling control are comprehensively discussed. Finally, it summarizes the results gathered here and emphasizes the need for further research.

Keywords: Low-pressure membrane filtration; Natural organic matter; Coagulation; Adsorption; Membrane fouling; Contact mode

1. Background and introduction

Low-pressure membrane (LPM) filtration includes microfiltration (MF) and loose ultrafiltration (UF), which is widely applied in drinking water treatment to remove suspended solids, bacteria and viruses, with a global installed capacity of 15 million m^3/d at the end of 2018 [1]. The researchers have witnessed an explosion in the number of studies aimed at revealing the fundamental aspects and improving the efficiencies of membrane processes [2–5]. Although the applications of LPMs as reliable approaches to obtain clean water is attractive, membrane fouling caused by natural organic matter (NOM), which result in the decline of membrane permeability, elevation of energy consumption and reduction of membrane lifetime, still remains the greatest impediment to improved performance and even wider adoption of LPM processes [6–11]. The fouling processes and mechanisms induced by NOM have been a continuing interest in the field of water treatment.

NOM molecules were widely identified as key components in the evolution of membrane fouling in LPMs and they also serve as the precursor of many disinfection by-products (DBPs) [12–14]. NOM molecules foul membranes by blocking pore openings, shrinking the effective pore diameter and/or forming foulant layers on the membrane surface [15–18]. The severity of such fouling depends on the properties of the NOM (e.g., chemical composition, molecular weight

---

* Corresponding author.

(MW) and hydrophobicity) [11,19], the characteristics of the membrane (e.g., hydrophobicity, roughness, surface charge and pore size) [14,20] and the operational parameters (e.g., flux, inorganic composition of the feed and temperature) [11,15,21,22]. To effectively control membrane fouling in LPMs, therefore, it is important to establish methods that can remove NOM with high efficient.

Numerous pretreatment strategies, including coagulation, adsorption, preoxidation and prefiltration, have been introduced to mitigate fouling in lab-scale and full-scale systems [23–25]. Since the applications of coagulation and adsorption are practicable and cost-effective, they have been the most successful treatment in fouling control [23]. Coagulation approach traditionally adds Al or Fe salts externally to the feedwater ahead of LPM [23,26]. Coagulation of feedwater with polyelectrolytes can remove a substantial fraction of the NOM from the feed [27–29], but deposition of metal–NOM complexes on the membrane can be problematic and the chemical sludge produced during treatment can even lead to secondary problems [29,30]. To minimize these problems, rigid adsorbents with low solubility, such as powdered activated carbon (PAC) [31], silica particles and polysulfone colloids [32], have been applied in place of conventional coagulants. However, these treatment approaches with absorbents did not always mitigate fouling, and even occasionally accelerates fouling processes [23]. The NOM removal and fouling control behaviors were also found significantly related to the types of adsorbents [23,24].

Operation mode and contact mode between coagulants/adsorbents and the feed, which has often been neglected in related studies, were another factor governing the NOM removal and fouling behaviors. Generally, three approaches could be introduced for combining coagulation with LPM filtration as shown in Fig. 1: (1) coagulation with/without sedimentation, in which substances adsorptive to coagulant precipitates are separated from the feedwater, followed by sedimentation or directly fed to membrane, (2) inline coagulation, in which the coagulated water will directly enter the membrane filtration system and (3) electrocoagulation, which will be discussed in the later sections. Similarly, three contact modes could be applied by using adsorbents: (1) direct filtration, in which the suspension of adsorbent and feed solution is mixed and then applied directly to the membrane; (2) preadsorption, in which the water is contacted with and then separated from the adsorbent before filtration and (3) predeposition, in which an adsorbent layer is deposited on the membrane surface prior to membrane filtration. Based on predeposition approach, a novel pretreatment process, referred to as microgranular adsorptive filtration (μGAF), has been developed which combines adsorption, granular media filtration and membrane filtration by Benjamin and co-workers [33–38].

The main goal of this review is to study coagulation/adsorption approaches in mitigating NOM-induced membrane fouling by using coagulants/absorbents in recent studies. The effects of contact modes between NOM and adsorbents in controlling fouling by using adsorbents were evaluated and compared. Specifically, the potentials of μGAF in water treatment applications were explored. Also, the major foulants in LPMs system were summarized and attempts were made to identify the superior fouling control mechanism in μGAF. Clarifying those aspects can help in evaluating the potential of coagulation/adsorption pretreatments from both fundamental and application perspectives and is ultimately beneficial for developing a better pretreatment process for the water treatment industry.

2. Coagulants/adsorbents used in pretreatment approaches

Coagulation is so far the most frequently used and successful approach for controlling the fouling of LPMs. Inorganic coagulants such as Al and Fe can react with water to form cationic hydrolytic species and precipitates. Then, the coagulation process of NOM could be achieved through charge neutralization, destabilization of particles and sweep flocculation [39]. While for organic coagulants, adsorption and bridging effects were mainly responsible for the effective coagulation and generally a lower dose is required compared with inorganic coagulants [40,41]. Adsorption pretreatment refers to the application of adsorbents prior to LPMs as

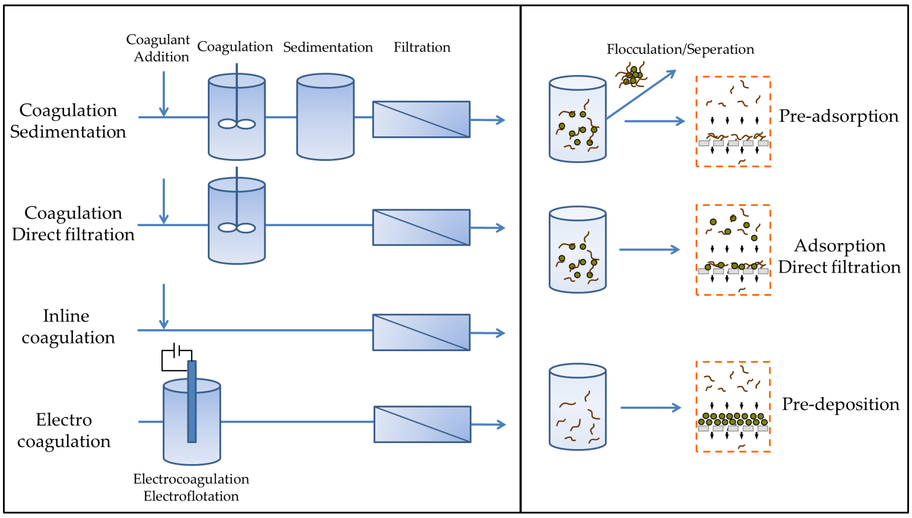

Fig. 1. Various approaches to control membrane fouling by using coagulants or adsorbents.

suspended powder solutions or fixed adsorbent contactors. The porous or non-porous adsorbents could provide interfaces to adsorb/accumulate substances detrimental to membrane behaviors [23,24,33]. Micropollutants including NOM are favorably adsorbed onto the thermodynamic unstable surfaces of adsorbents. Some major foulants could be effectively removed and the subsequent membrane fouling in LPMs could be mitigated. Conventional adsorbents include PAC, metal oxide particles or silica. In addition, some novel adsorbents have been introduced to remove foulants in recent studies.

2.1. Inorganic coagulants

Al or Fe salts are probably the most widely employed coagulants for pretreatments. Al or Fe salts, for example, $FeCl_3$ and $Al_2(SO_4)_2$, first react with water molecules to form cationic hydrolytic species and weakly charged or uncharged precipitates [39]. The formation of cationic hydrolytic species is highly pH dependent. At neutral pH, effective coagulation occurs through charge neutralization and sweep flocculation, meanwhile the coagulation of NOM molecules, virus, DBP precursors or antibiotic resistance genes could be achieved through the adsorption and capture to precipitates or complex [42,43]. Polyinorganic coagulants such as polyaluminum chloride (PACl) [44] and polyaluminum sulfate [45] exhibit slightly different coagulation behaviors due to the preformation of highly positively charged ion species [29,44,46,47]. Compared with Al and Fe salts, PACl selectively removes more proteinaceous fractions from feed [44]. However, no significant difference between fouling control could be observed by using traditional Al/Fe salts and polyinorganic coagulants [44,48].

The treatment with inorganic coagulants could results in several impacts on membrane fouling control. First, the particle size distribution is altered with the addition of inorganic coagulants. As larger particles are formed, they are less likely to penetrate into membrane pores and reduce fouling development [24,28,49]. Previous researches showed that large particles (>3 μm) had limited impacts on fouling while small particles (possibly <0.2 μm) could produce rapid fouling. Second, the coagulation process could reduce the hydraulic resistances of the cake layer which is formed on the surface of membrane. The formation of large particles resulted in loose cake layer with the lowest specific cake resistance, which is beneficial to fouling control [28,50]. However, there are still shortcomings of coagulation processes as an effective pretreatment approach, which will be discussed in section 3.

2.2. Organic coagulants

The employment of organic coagulants in membrane pretreatment processes is less extensively discussed. Organic coagulants such as poly(diallyldimethylammonium chloride) (PDMDAAC), dimethylamine polymers and cationic polyacrylamides (PAMs) are commonly used as coagulant aids in NOM removal and sludge thickening [40,41,51]. Due to the combination of adsorption and bridging effects of organic coagulants, a lower coagulant dose is required compared with inorganic coagulants. The organic coagulants are more efficient with little quantities and the formed flocs are bigger and stronger than those formed in the presence of inorganic salts. The addition of PAM could improve the coagulation performance and floc properties, simultaneously with a higher NOM removal efficiency [40,41,51]. Yu et al. [41] found that a PAM dose of 0.2 mg/L could effectively promote the alum coagulation behavior and contribute best in fouling control in UF filtration. However, a higher dose adversely led to worse membrane behaviors due to the formation of dense alum–PAM–NOM cake, which resulted in a higher residue PAM blocking the membrane surface.

2.3. Composite coagulants

Composite coagulants are comprised of both inorganic and organic coagulants in NOM removal and membrane fouling control. During production of drinking water, organic coagulants such as PDMDAAC and PAM could be used as alternative of metal salts as the coagulants due to higher sweeping flocculation efficiencies [41,52–54]. However, fewer examples were found using only organic coagulants due to the relatively high cost of these polymers. Some previous studies also reported that turbidity could not be totally removed by using inorganic coagulants especially for water with high suspended solids [51,53,55,56]. Thus, organic coagulants are more frequently used as aids in coagulating water in conjunction with metal salts, especially in treating water containing high concentrations of turbidity. Lee et al. [57] found that the use of dimethylamine of low MW (10–50 kDa) was more effective in treating raw waters with high turbidity after coagulation of Al or Fe salts. By using organic polymers after Al or Fe dosing, more effective filtration in LPM process could be achieved. For example, by adding 0.3 mg/L cationic polymers after ferric chloride dosing, an increased flow of 25% could be achieved in a pilot-scale plant [52,57].

2.4. Activated carbon

PAC is the most intensively studied adsorbent to LPM pretreatments. PAC adsorption was often applied in conjunction with additional approaches, for example, coagulation and sedimentation, in fouling control [58,59]. The efficiencies of NOM removal by PAC were significantly affected by the types applied, dose, NOM concentration, NOM properties and the competition between other contaminants [23,60]. Despite the overwhelming evidence supporting the positive influence of PAC pretreatment on membrane performance, the negative effects on fouling control were also widely reported [23,61,62]. Lin et al. [63] found that a high MW NOM fraction (6.5–22.2 kDa) that exerted the greatest fouling on a hydrophobic PS membrane was not removed by PAC adsorption. The addition of PAC might result in solids with similar sizes to the membrane pore sizes. As a result, the deposition of PAC–NOM mixture or residue NOM fraction (non-adsorbable components) may cause fouling [64].

Lab-scale and pilot-scale tests were performed to test the effects of PAC and granular activated carbon in fouling control [65,66]. The particle size of PAC was found as one of the key factors controlling fouling processes. The results were inconsistent with research showing larger or smaller sizes of PAC were more effective in fouling control [67,68]. The dose of PAC also affected the removal efficiencies of contaminants. A relatively low PAC dose could effectively remove micropollutants such as geosmin, while a higher dose was required to remove humic substances [60].

2.5. Metal oxide particles

Adding metal oxide particles, such as aluminum oxide particles, iron oxide particles and ferrihydrite, to LPM systems can effectively control fouling [38,69–71]. Iron oxide particles (IOPs) could selectively remove NOM with MWs higher than 30 kDa and significantly reduce fouling. Kang and Choo [72] found that the same level of DOC removal was achieved by PAC and ferrihydrite (FH), the reduction in fouling by FH was more notable. The authors suggested that the attachment of NOM and FH particles led to a decrease in the cake layer resistance, which might be responsible for the superior performance of metal oxide particles. The major obstacle for the application of metal oxide particles is the poor settleability and separation efficiency. In order to solve the problem, immobilization of iron oxides on the surfaces of granular media has been attempted and effective fouling mitigation was also achieved by the coated particles [69,73,74]. Recently, other metal oxide particles such as MnO_2 [75] or $KMnO_4/MnO_2$ [49] were applied in pretreatments. However, the NOM removal and fouling reduction were limited using these particles than PAC or other metal oxide particles.

2.6. Heated metal oxide particles

Benjamin and co-workers synthesized another type of metal oxide particles, that is, heated aluminum oxide particles (HAOPs) and heated iron oxide particles (HIOPs), and evaluated their effects in adsorption and fouling control. Fig. 2 shows the NOM removal from typical natural water by sorption onto various solids. In adsorption tests, HAOPs could remove more NOM at equivalent molar doses than ferric or alum, especially at lower dosages [33]. It is worth mentioning that after HAOPs were deposited onto membrane or supporting materials ahead of UF filtration, the advantage of HAOPs in removing key foulants and fouling control was much more amplified than conventional absorbents [35]. The performance of HAOPs deposition in mitigating fouling will be discussed in detail in the later sections.

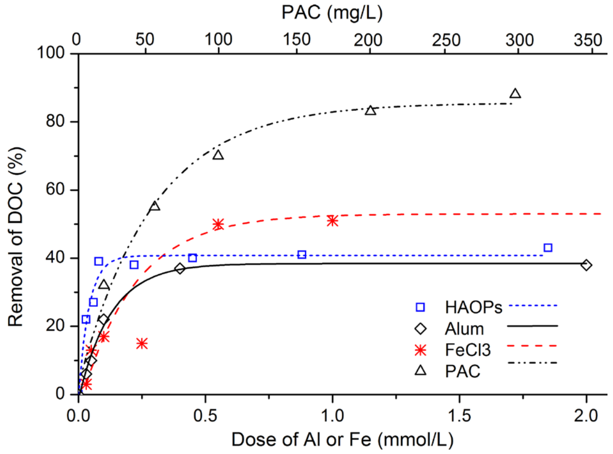

Fig. 2. NOM removal from Lake Washington water by sorption onto various solids, pH 7.0 ± 0.1 [33].

The superior performance of metal oxide particles and particle-coated polymer beads over PAC in removing NOM with high fouling capacity were confirmed in many reports [69,72,76]. Molecules to Al (and Fe) oxides are commonly attributed to surface complexation reactions, in which carboxyl and/or hydroxyl groups act as ligands that bind the metal ions at the solid surface. Metal (iron and aluminum) oxide surfaces become hydroxylated via sorption of a monolayer of water molecules [77]. The hydroxylated sites behave much like diprotic acids, with the three potential species commonly represented as $\equiv MeOH_2^+$, $\equiv MeOH$ and $\equiv MeO-$:

$$\equiv MeOH_2^+ \leftrightarrow \equiv MeOH + H^+ \ pK_{a1}$$

$$\equiv MeOH \leftrightarrow \equiv MeO^- + H^+ \ pK_{a2}$$

Adsorption of dissolved NOM on oxide surfaces is often attributed to replacement of surface-coordinated H_2O or OH^- groups by anionic functional groups of the organic ligand in the following reactions [78]:

$$RCOO^- + \equiv MeOH \leftrightarrow \equiv MeOOCR + OH^-$$

Due to the abundant complexation sites and functional groups in metal oxide particles, these solids have relatively higher affinity to the surface ions for aromatic carboxyl and hydroxyl groups [79]. As a result, a higher removal efficiency of UV_{254} and DOC could be achieved compared with other adsorbents. After HAOPs were deposited onto membrane or supporting materials, the attachment between HAOPs particles and membranes are much reduced, making backwashing of fouled layer cake more easily, thus enhancing their ability in NOM removal foulants and fouling control [35,69].

2.7. Other novel adsorbents

Some novel adsorbents/coagulants were synthesized or applied for adsorption pretreatments, including polysulfone colloids [80], magnetic ion exchange resin (MIEX) [66,81], mesoporous adsorbent resin [82], combination use of PDMDAAC/Fe_3O_4 [83], powdered zeolite [84], Ti- and Zr-based coagulants [85–87]. Su et al. [87] found the novel coagulant $ZrOCl_2$ could effectively alleviate irreversible fouling than conventional PACl or Al coagulants. $TiCl_4$ and polytitanium tetrachloride were applied to coagulate NOM in pretreating algal turbid water or seawater [85,86]. Koh et al. [32] observed remarkable fouling decline after application of polysulfone colloids prior to UF filtration. The polysulfone solids can specifically remove a fraction of NOM that had an apparent molecular size between 20 and 200 kDa, which might be important membrane foulants. MIEX and mesoporous adsorbent resin can remove a certain amount of NOM. However, they could not effectively mitigate fouling developments, indicating that the NOM fractions removed had less than average fouling potential [66,82]. With the application of powdered zeolites, the membrane fouling induced by secondary effluents was reduced and the permeate flux recovery was improved [84]. Generally, the novel adsorbents for the purpose of fouling control could not perform as effective as PAC or metal oxides.

3. Coagulation pretreatments in mitigating fouling

3.1. Impacts of coagulation in fouling control

Coagulation, being the most commonly used chemical pretreatment approach, incorporates physicochemical processes including rapid mixing, flocculation, sedimentation or inline flocculation. By destabilizing the contaminants, the NOM molecules could aggregate into larger flocs or adsorbed onto coagulant precipitates [23]. As a result, the sizes of aquatic substances increased and became large enough to settle or be removed by membrane. Substances responsible for membrane fouling could be partially removed through the process due to the combined mechanisms including double layer compression, charge neutralization, sweep coagulation and interparticle bridging [23,24,52]. In a systematical review on flocculants, Lee et al. [52] compared the engineering cases and effectiveness by using coagulation–flocculation and direct flocculation. In coagulation–flocculation process, metal salts such as Al and Fe are used as coagulants and organic polymers are served as flocculants. While in direct flocculation process, high MW organic polymers were added into feedwater and filtered. Direct flocculation generates less sludge compared with coagulation–flocculation because the formed flocs are dense and closely packed due to strong bridging forces.

Table 1 summarized the NOM removal and fouling control performances by using coagulation pretreatments including (1) coagulation + direct filtration, (2) coagulation + sedimentation, (3) inline coagulation and (4) electrocoagulation. Generally, coagulation treatments could work well in terms of mitigation of membrane fouling [47,88]. In coagulation–sedimentation approach, destabilized colloids and other substances adsorptive to coagulant precipitates are separated prior to membrane filtration. Since more foulants such as colloids are removed, coagulation–sedimentation usually performs better in fouling control [89]. However, some studies indicated that fouling reduction was similar with or without sedimentation [90]. Inline coagulation means the coagulant was applied to feedwater and the coagulated water will directly enter the membrane. Experimental results suggested that inline coagulation performed better than conventional coagulation especially at low coagulant dose [91–93]. At high coagulant dose, sweep floc conditions prevailed in all approaches, the NOM removal and fouling control was controlled by coagulant dose rather than coagulation mode [93]. Electrocoagulation could remove both hydrophobic and hydrophilic fractions, which are not easily removed in conventional coagulation processes [94]. The combination of coagulation, flotation and liquid–solid separation enabled electrocoagulation excellent performance in NOM removal and fouling mitigation, which has been attracting more attention in pretreatments [95–97].

3.2. Limitations of coagulation approach

Even though the positive influence of coagulation pretreatments on membrane performance was widely reported, several studies showed the contrary results [23,27,47,98,99]. For example, Schafer et al. [89] reported that coagulation of feedwater with $FeCl_3$ resulted in severe fouling of flat sheet MF membrane. Kimura et al. [46] found that in a series of bench-scale filtration tests, high dose of coagulant frequently caused more severe irreversible fouling. Based on the results, dose effect was found playing predominant role in governing the performance of coagulation. A proper dose of coagulant is highly required to achieve optimized NOM removal efficiency as well as excellent membrane behavior. With the increase in coagulant dosage, the NOM removal efficiency and settleability of flocs gradually increased. As the dosage increased to an optimal one, settable flocs sizes larger than membrane pore sizes are formed. At high coagulant dose, flocs with sizes similar to membrane pore sizes are usually formed and these flocs could cause physically irreversible fouling during the passage through membrane [46]. The contradictory results whether coagulation is beneficial or detrimental to fouling control also suggested that the influences of coagulation depended on the raw water properties, membrane materials and characteristics of coagulants [47,50].

Coagulation treatment might also result in the cake formation on the membrane surface [56], plugging of an inside-out UF [100] and severe trivalent ion fouling [24]. The effectiveness of coagulation is highly related to solution pH. A rise in pH might remarkably affect the solubility of ferric or aluminum, resulting in precipitates formed on membrane surfaces. In comparison, a decrease of pH to acidic condition might lead to higher Al or Fe ions in permeate. Meanwhile, smaller floc sizes were more easily formed and caused physically irreversible fouling by plugging or adsorption at acidic condition [46].

4. Effects of contact modes between coagulants/adsorbents and feedwater

4.1. Direct filtration/preadsorption using adsorbents

As mentioned above, the applications of adsorbent by combining adsorption and membrane filtration can be carried out in various forms [62,101]. Table S1 summarized NOM removal by adsorbents by using direct filtration or preadsorption treatments. The NOM removal efficiencies varied among adsorbents, types and the characteristics of feedwater. The applications of PAC, HAOPs and novel adsorbents, for example, MIEX can remove much of the UV_{254} from feedwater. For example, the UV_{254} removal efficiencies can reach higher than 90% by using 200 mg/L PAC when treating Lake Washington water [35]. While the DOC removal efficiencies were generally lower than the removal efficiencies of UV_{254} [62,66,101], suggesting some fractions selectively removed more UV-absorbing fractions.

The fouling control behaviors for combining adsorption and membrane filtration, using HAOPs as the adsorbent was shown in Fig. 3. Fig. 3(a) shows that direct filtration of suspended adsorbent solution and the feed almost contributed no fouling reduction compared with filtering raw water. While preadsorption treatment mitigated membrane fouling to some extent. In several studies, direct filtration occasionally enhanced fouling when using PAC or SiO_2 [64,91,101]. Fig. 3(b) indicates that the system in which alum or HAOPs were used for coagulants could effectively mitigate fouling developments compared with filtering raw water.

4.2. Integrated adsorption pretreatments

Since conventional treatments using adsorbents could preferably remove certain types of contaminants, it is reasonable

Table 1
Coagulation treatments in NOM removal and fouling control

Feedwater	Coagulant	Pretreatment approach	NOM removal efficiency	Fouling reduction	References
Surface water	PACl	C	DOC and UV removal efficiencies are related to hydraulic-irreversible fouling index (HIFI)	Coagulation mitigates membrane fouling in all cases The extent of fouling was correlated with biopolymer concentrations	[22]
Surface water	PACl	C	DOC removal efficiency: 38%–58% UV removal efficiency: 40%–75%	Almost all the tested condition worked well in terms of mitigation of irreversible fouling	[46]
Humic acid	Alum, PACl and aluminum chlorohydrate (ACH)	C	The UV removal efficiency could all reach 100% and inorganic polymer coagulants save dosage on conventional treatment process	Compared with coagulation by alum, more compact flocs were formed by ACH and PACl, resulting in a deteriorated fouling	[47]
Surface water	Aluminum sulfate	C and CS	At optimum dose of 3.2 mg/L Al, DOC and UV_{254} removal of 46% and 69%	Permeate flow rate declined by 50% after filtering 0.8 L of feed The fouling control behavior was similar with or without sedimentation	[112]
Surface water	Polysilicato-iron (PSI) Polysilicato-aluminum (PSA)	CS	Highest DOC removal efficiency could reach 82%–89% by PSI, compared with 67%–86% by alum	A relative flux of unity through the PVDF-2 membrane was achieved pretreated with PSI-1, compared with 0.7–0.8 for treatments with alum	[98]
Surface water	PACl	CS and ILC	Coagulation selectively removed high-MW fractions	Coagulation pretreatment provided stable membrane operation Inline coagulation performed better than coagulation in fouling control	[92]
Algal organic matter (AOM)	$FeCl_3$	CS and ILC	Inline coagulation performed best in biopolymer removal at dose from 0 to 10 mg/L Fe and the advantage became insignificant at higher dose	At low dose, inline coagulation was more effective in fouling control At high dose, fouling reduction was controlled by coagulant dose rather than coagulation mode	[93]
Treated domestic wastewater	$FeCl_3$, $AlCl_3$ and PACl	ILC	At 0.037 mmol Me^{3+}/L, $FeCl_3$ reduced 35% of biopolymer N content while $AlCl_3$ and PACl achieved only 20% and 25% removal	At a Me^{3+} of 0.148 mmol/L, the filterability increased from 0.24 to 0.39, 0.45 and 0.59 at the end of run for $FeCl_3$, $AlCl_3$ and PACl, respectively	[44]
Lake water	Electrochemical produced aluminum	EC	EC/MF removed ~40% DOC and 52% UV_{254} removal	A combination of lower pH, low pressure and intermediate Al concentrations were optimal for fouling mitigation	[96]
Surface water	Electrochemical produced aluminum	EC	Highest DOC removal: 63% at pH 6.4 Highest UV_{254} removal: 85% at pH 6.4	Fouling control ability: Electroflotation > Electrocoagulation > Raw water	[95]
MBR permeate	Electrochemical produced aluminum	EC	High NOM removal efficiencies achieved	The average fouling rate was substantially reduced 7.8-fold resulting in no chemical cleaning requirements during the entire operation	[97]

C: Coagulation + direct filtration; CS: Coagulation + sedimentation; ILC: Inline coagulation; EC: Electrocoagulation.

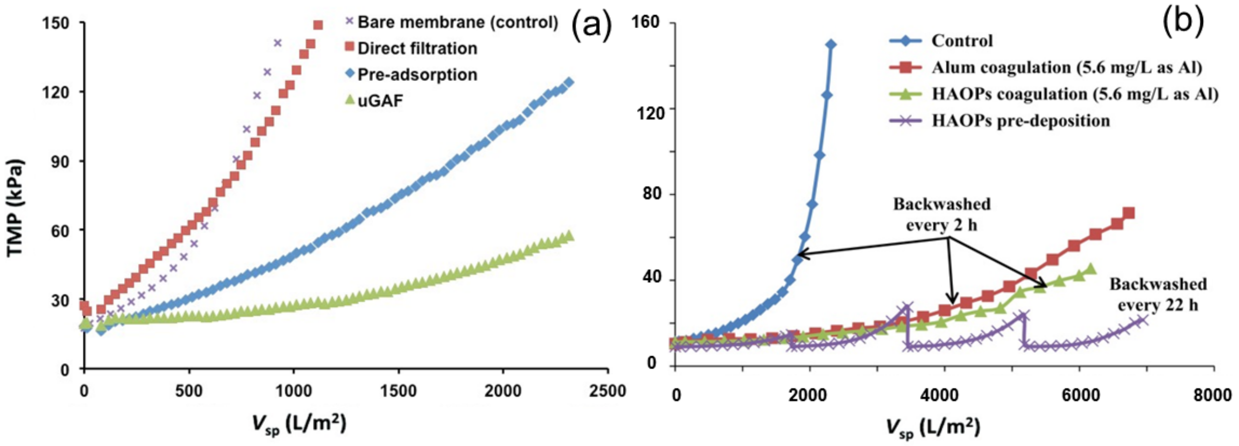

Fig. 3. (a) Membrane fouling using three different approaches of integrating HAOPs adsorption into the process; equivalent dose = 4 mg/L, flux = 100 LMH [108]. (b) TMP in experiments exploring effects of coagulant identity (none, alum or HAOPs) and contacting mode (well-mixed in feed vs. predeposited layer on membrane) on membrane fouling and NOM removal. Ceramic membrane, 75 LMH [110].

to consider integration of multiple approaches for NOM removal and fouling control. The conventional pretreatments using adsorbents can be classified into (1) precoagulation/preadsorption and direct filtration [65,102], (2) precoagulation/preadsorption, settling and filtration [93,103] or (3) precoagulation/preadsorption, filtering with 0.45 μm filters [104]. In some works, coagulation/adsorption was integrated with other pretreatment approaches, which was summarized in Table 2. The common hybrid approaches include coagulation/adsorbent adsorption/filtration [66,105], magnetic enhanced flocculation/membrane filtration [106], coagulant aid/oxidant pretreatment [53], coagulation/adsorption/sedimentation/in situ chlorination/filtration [59], chemically enhanced primary treatment (CEPT) + trickling filter (TF) [107].

The integration of various treatments usually performed better than single treatment. For example, Fabris et al. [66] found that MIEX and PAC treatment were unable to prevent fouling in a hollow fiber submerged membrane system. While the additional treatment of alum coagulation could reduce the majority of DOC of all MW ranges, including colloidal materials, thus successfully prevented short-term fouling of MF. Wang et al. [59] introduced in situ chlorination into pretreatment processes, which alleviated both irreversible and reversible fouling due to small modifications to NOM. The addition of PAC during flocculation after coagulation led to a greater removal of NOM. Zhao et al. [107] found that the combination of CEPT and TF could serve as a highly efficient and effective process in pretreatment before UF. In a hybrid approach using both adsorption and coagulation, the order of treatments was also important. The treatment of MIEX resin prior to coagulation could achieve a higher NOM removal and fouling control efficiency [50].

4.3. Microgranular adsorptive filtration system

Predeposition mode shifts the adsorption pretreatment step from a separate process upstream of the membrane to an integrated part of the membrane filtration step [108]. Predeposition of adsorbents altered the role of membrane from an agent of contaminant removal to a support layer of adsorbents for most of the NOM removal, which is referred to μGAF. Fig. S1 shows the typical cartridge and tubular membrane filtration setups for predeposition treatments [37,109].

4.3.1. NOM removal in μGAF system

Regardless of the membrane types, bare membrane could hardly remove NOM. The removal efficiencies of both DOC and UV_{254} were less than 10% through most of the run [37]. In comparison, NOM removal in μGAF system was significantly enhanced. Generally, DOC removal was lower than UV_{254} removal and HAOPs performed best in removing NOM from feedwater [34,36]. The removal efficiencies differed by absorbents, hydrodynamic conditions as well as NOM properties, which were summarized in Table S2. Fig. 4(a) shows UV_{254} removal was much greater in the systems with HAOPs and IX resin. In comparison, by using PAC as adsorbents, UV_{254} removal was somewhat less early in the run, but comparable later [37]. Fig. 4(b) suggested that HAOPs predeposition outperformed HAOPs coagulation and alum coagulation in removing UV_{254} fractions in a tubular system [110].

The characteristics of NOM removed by absorbents in μGAF also differed to those removed by conventional adsorption. Even though both preadsorption and predeposition can effectively remove high-MW fractions, UV-absorbing fractions and fluorophores [37,109], predeposited adsorbent layer could remove more low-MW weight and non-UV-absorbing fractions than preadsorption does [37,111]. The higher removal of these fractions in μGAF might be responsible for its superior fouling control behavior, since the importance of the low-MW neutral fractions in governing membrane fouling was widely reported [11,90,112]. For example, Lee et al. [90] reported that hydrophilic macromolecules with apparent MW between 10 and 100 kDa (most likely natural polysaccharides) caused significant flux decline in LPM filtration. Carroll et al. [112] reported that in a combined coagulation–MF process, the neutral hydrophilic substances were mainly responsible for irreversible fouling.

Table 2
Hybrid use of adsorption with other approaches and fouling control

Feedwater	Absorbent/coagulant	Pretreatment approach	NOM removal efficiency	Fouling reduction	References
Humic acid solution	Single walled carbon nanotubes (SWNTs)	Preadsorption + direct filtration	NOM removal efficiency increased as a result of SWNT binding site adsorption of humic acid (HA)	The addition of SWNTs to the UF process did not significantly exacerbate the permeate flux decline	[102]
Algal extracellular organic matter	Mesoporous adsorbent resin PAC	Preadsorption followed by filtering with 0.45 mixed cellulose filters	MAR mainly removed high-MW fraction of EOM, while PAC primarily adsorbed low-MW fraction Both particles removed more hydrophobic fraction than hydrophilic fraction	MAR pretreatment significantly reduced the reversible fouling With respect to EOM fouling control, MAR was much more efficient than PAC	[104]
Secondary domestic wastewater	$FeCl_3$ PAC	Coagulation/MF and PAC/MF	Maximum removal efficiency: Coagulation/MF: 80% By PAC/MF: 90%	Precoagulation/MF resulted in a significant reduction of the flux decline ratio	[105]
Natural water from a reservoir	Alum/PAC/ Magnetic ion exchange resin (MIEX)	MIEX treated + Alum coagulation MIEX treated + PAC treated + Alum coagulation	MIEX + PAC removed most of the DOC but not the colloidal components MIEX + PAC + Alum reduced the majority of DOC, including colloidal materials	MIEX + PAC were unable to prevent fouling MIEX + PAC + Alum successfully prevented short-term fouling of MF	[66]
Surface water	PACl PAC Magnetic ion exchange resin (MIEX)	Coagulation + adsorption (PAC or MIEX) Adsorption (PAC or MIEX) + coagulation Coagulant dosed with PAC or MIEX	Highest biopolymer removal efficiency achieved by combination of MIEX and coagulation	MIEX + coagulation was effective in mitigating fouling and MIEX adsorption should be conducted first PAC + coagulation sometimes caused more rapid evolution of fouling	[50]
Surface water	MIEX resin Aluminum potassium sulfate	MIEX resin adsorption Coagulation MIEX adsorption + coagulation	MIEX adsorption + coagulation approach removed more DOC and more colloidal fractions compared with single treatment	Integrated MIEX and coagulation pretreatment performed better in fouling control	[126]
River water	A novel coagulant prepared by mixing ferromagnetic seeds in ferric chloride (FC)	Coagulation/flocculation-membrane filtration (CF-MF) Magnetic enhanced flocculation-membrane filtration (MEF-MF)	Ferromagnetic seeds selectively removed more high-MW biopolymers Low- and mid-MW organic structures, that is, humics were partially removed by MEF pretreatment	MEF-MF had a palpable superiority on mitigating membrane fouling than CF-MF process	[106]
Water from a reservoir	Polyaluminum chloride PAC NaClO	CUF: coagulation (C) + sedimentation (S) + ultrafiltration (UF); CCUF: C + S + in situ chlorination + UF; CAUF: C + PAC adsorption + S + UF; CACUF: C + PAC adsorption + S + in situ chlorination + UF	DOC and UV_{254} removal efficiencies: CACUF > CAUF > CA > CUF > CCUF	In the CUF system, in situ chlorination alleviated both irreversible and reversible fouling In the system combining coagulation–PAC adsorption pretreatment with chlorination and UF, the membrane performance was even improved	[59]
Synthetic raw water	Alum PAC	Coagulation + UF Coagulation + PAC + UF (CAUF)	Coagulation removed 75% of UV_{254} and 43% of DOC from feedwater The addition of PAC removed more organic matter	A low dosage of PAC with alum coagulation can effectively mitigate both irreversible and reversible fouling The presence of PAC in the CAUF system could prevent DOM from reaching the membrane surface and contributing to internal membrane fouling	[103]
Domestic wastewater	A complex coagulant produced from fly ash	Chemically enhanced primary treatment (CEPT) + trickling filter (TF) + UF	95% and 88% removal of COD and ammonium were achieved, while TP and SS were found to be removed completely at a coagulant dosage of 2.5 mL/L	CEPT–TF–UF system was a highly efficient and effective process for water reclamation	[107]

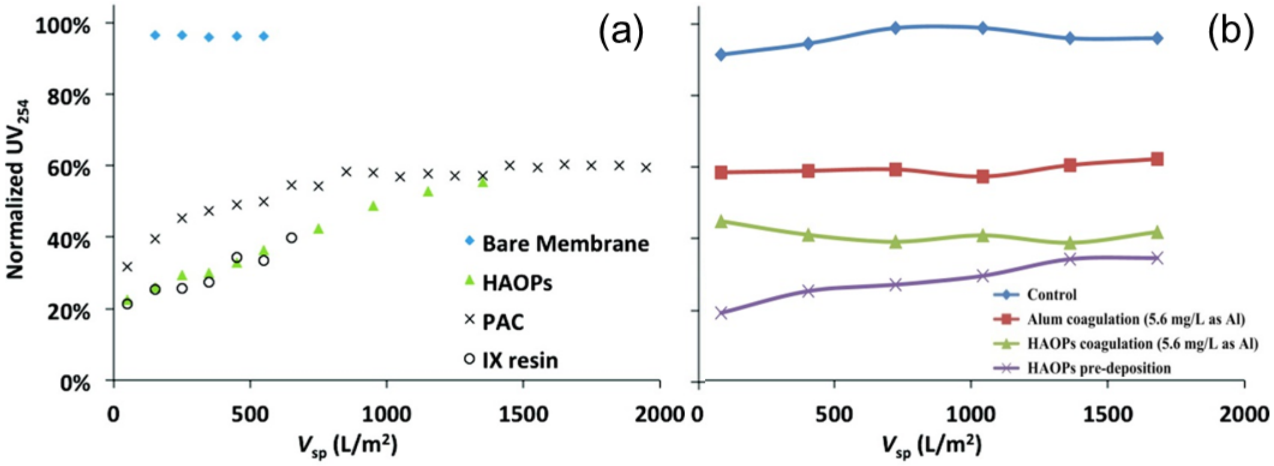

Fig. 4. (a) Breakthrough of UV_{254} and with various adsorbents in a cartridge system. Absorbent dose 40 g/m^2 and flux = 100 LMH [37]. (b) Fractional breakthrough (permeate/feed) of UV_{254} in experiments exploring effects of coagulant identity (none, alum or HAOPs) and contacting mode (well-mixed in feed vs. predeposited layer on membrane) on membrane fouling and NOM removal. Ceramic membrane, 75 LMH [110].

4.3.2. DBP precursor and TEP control results

Predeposition mode performed better than preadsorption in respect of DBP precursor and transparent exopolymer particle (TEP) removal. The potentials for brominated trihalomethanes (THM) formation from chlorination of HAOPs-pretreated water from a tubular system are analyzed, with an efficiency between 53% and 76% in removing DBP precursors [109]. A layer of HAOPs in a cartridge system dramatically reduced the THM formation by up to 72% at an HAOPs dose of 100 mg Al/L [111]. TEP have received increased attention in membrane research since they can cause membrane fouling not just by forming a sticky gel layer on the membrane surface, but also by initiating membrane biofouling [113–116]. The average TEP removal by HAOPs can achieve as high as 64% in a tubular system, much higher than other adsorption approaches did [109]. Lowering the pH of the feed enhanced NOM (and TEP) removal by μGAF, higher fluxes led to increased NOM and TEP removal and increased resistance across the HAOPs layer [117]. Cai and Benjamin [37] observed a higher removal efficiency of alginate in both adsorption tests and μGAF system, which was possibly another key point responsible for the superior performance of predeposition mode in fouling mitigation.

4.3.3. Membrane fouling control by μGAF system

A predeposited layer of adsorbent provides a surface for NOM molecules to transform into a condensed gel phase, which enhances NOM removal and fouling reduction. Fig. 3(a) shows the predeposited HAOPs layer could dramatically mitigated fouling than other treatments even though the effective HAOPs dose was the same. The average fouling rate in μGAF system was approximately reduced two and five folds compared with preadsorption and direct adsorption modes, respectively, treating the same amount of feed. Fig. 3(b) suggests that predeposition mode removed more NOM and mitigated fouling with more efficiency than systems where either alum or HAOPs were added to the bulk feed, even though the system with predeposition was backwashed only one-eleventh as frequently as the other systems. [110] The membranes receiving HAOPs-treated lake water as feed were operated at conventional fluxes for almost 2 weeks without backwashing and with no significant fouling [109,110]. Table S3 summarizes the membrane fouling control behaviors in μGAF system and the results highly indicated that the trans-membrane pressure (TMP) increase was much retarded when μGAF was used as pretreatment and HAOPs were the best in fouling mitigation among absorbents.

4.3.4. Main factors affecting fouling in μGAF system

The performance of μGAF was remarkably affected by absorbents used, feedwater properties and membrane characteristics. The performance of heated metal oxides, for example, HAOPs and HIOPs, was much better than commercial PAC, IX resin, SiO_2 and alum. The superior performance of HAOPs over PAC in fouling control was highly related to their foulant removal behaviors. Even though PAC performed better in DOC removal, however, the majority of the foulants could not be accumulated on PAC [33,35]. Similarly, IX resins could remove most of the UV and high-MW fractions, but fouling reduction was limited [37]. The fouling control was also related to absorbent combination. When using both HAOPs and PAC, the fouling reduction efficiency follows the order: HAOPs over PAC ≈ PAC over HAOPs ≈ mixture ≈ HAOPs + PAC > HAOPs > PAC, possibly because of overlap between the pools of NOM that could be removed by each adsorbent; that is, some of the same NOM molecules could be removed by either adsorbent alone [33].

Fouling in the μGAF unit became progressively more severe as the feed solution pH decreased from 9 to 5, especially when it was lowered to 3 [117]. Increasing flux led to an increase in fouling of the μGAF unit, while the resistance across the downstream membrane decreased as the flux through the μGAF unit increased [117]. Fouling in μGAF was also highly related to the characteristics of feedwater applied.

When the feed contains mixtures of various NOM fractions, it fouls the membrane more than any of the individual components do at the same DOC concentration. In addition, unaltered raw water fouls the membrane more severely than reconstituted raw water generated by fractionating the source water and then recombining the fractions. These findings indicate that the fouling contributions of different fractions are not simply additive, but rather interactions among the fractions exacerbate the fouling [118].

5. Foulant identifications in LPM systems

For mitigation of membrane fouling and optimization of membrane pretreatment processes, identification of major foulants is indispensable. Researchers have not researched consensus regarding the importance of foulants in feedwater. The particulate and colloidal matters were commonly found to be the primary foulants during membrane filtration, which can decrease the permeability of LPMs through pore blockage or cake layer formation [38,119–121]. Hydrophobic humic substances account for large fraction of NOM and have been attributed to key foulants in LPM system [9,10]. However, more recent studies indicated that hydrophilic fractions, including proteins and polysaccharides can be major foulants [11,22,122]. Yamamura et al. [123] observed that low-MW hydrophobic fractions first adsorbed on membrane and then hydrophilic NOM with high MW accumulates on/in the membrane. The importance of high-MW fractions in fouling developments was pointed out in earlier reports [9,17]. While in recent studies, hydrophilic fractions with low-MW were considered major foulants in LPM systems [22,37,111,122]. With the help of advanced analytical techniques such as high performance liquid chromatography with online organic carbon detection, NOM could be fractionated into biopolymers, humic substances, building blocks, low-MW acids and neutrals [124]. The biopolymer fractions [121,125] or colloidal fractions [126] were generally observed correlated with fouling developments.

With the application of adsorbent layer in μGAF system, NOM fractions could be separated by the adsorbent media and new insights could be shed into the key foulants in LPM system. Particulate and colloidal matters were inferred to be the dominant foulants in predeposited adsorbent layer [38,117], as shown in Fig. 5. Chemical analysis including C/Al atomic ratio and energy dispersive spectrometer spectra all supported that almost all NOM molecules were accumulated on the layer surface [36,38,117,127]. Most of the humic substances, UV-absorbing NOM and high-MW fractions are retained within the cake layer. Compared with other adsorption treatments, the adsorbent layer could remove more low-MW organics and polysaccharides/TEP fractions, among which HAOPs could generate the best removal efficiency [38,117,127]. The higher removal of low-MW and polysaccharides/TEP fractions might be responsible for the superior performance of μGAF system. Finally, after NOM broke through the cake layer, their accumulation onto membrane surface resulted in membrane fouling. The chemical analysis of NOM accumulated on fouled membrane indicated that these NOM moieties were enriched in non-fluorescent material, possibly polysaccharides. The fouling was attributed to a very small fraction with no UV absorbance and fluorescence [111]. The fouling process was also dependent on the characteristics of the feed. Small amounts of hydrophobic but non-fluorescent (i.e., non-humic) NOM have disproportionately high fouling potentials and can be responsible for a substantial portion of membrane fouling [37,109,117]. The interactions among different fractions are important contributors to fouling, since filtering raw water and reconstituted raw water caused higher fouling than filtering individual fraction at the same DOC level [117].

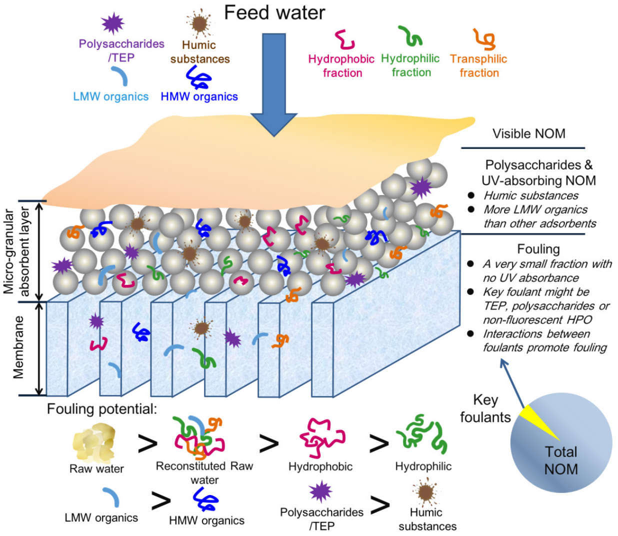

Fig. 5. Foulants removal in μGAF system.

6. Fouling control mechanisms in conventional approach and in μGAF system

6.1. Conventional coagulation/adsorption treatments

The schematic of fouling mechanisms by using coagulation/adsorption processes is shown in Fig. 6. As discussed above, the fouling control behaviors are highly related to the coagulants and adsorbents applied as well as the contact mode between coagulant/adsorbent and the feed [23,44,88]. Coagulation treatments could usually mitigate membrane fouling by removing more NOM. The NOM removal efficiency and fouling control behavior are affected by the mode of operation. In coagulation + direct filtration mode, cake layer was easily formed on the surface of membrane, possibly resulting in worse membrane permeability and more severe irreversible fouling [22,46]. In inline coagulation process, the mixing condition usually leads to a less dense cake layer structure and better membrane performance compared with conventional coagulation [44,93]. Coagulation–sedimentation approach provided the separation process prior to membrane filtration and it usually causes less fouling than other coagulation processes. Generally, the efficiencies of coagulation are highly related to the coagulation conditions such as reaction time, coagulant dose and stirring strength. Since coagulation treatment selectively removed more high-MW fractions from feed, which were widely reported in previous works [49,88,92], some key foulants such as low-MW neutral fractions could not be sufficiently removed by coagulation approach.

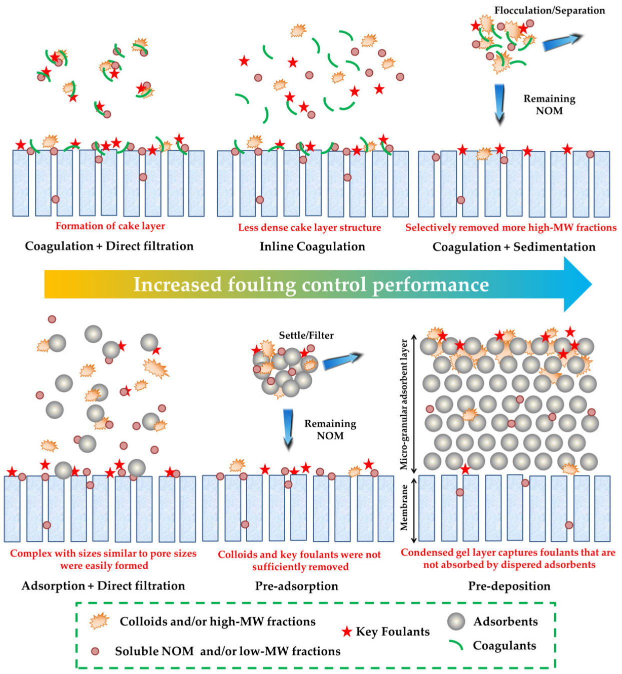

Fig. 6. Schematic of fouling mechanisms by using coagulation/adsorption approaches.

The mechanism of adsorption approaches in mitigating membrane fouling is possibly due to the new interfaces provided by adsorbents to adsorb/accumulate substances contributing to membrane performance. Studies were performed to discuss how to supply enough surface areas or interfaces for adsorbing NOM. Some researchers found that at certain NOM removal rate and pH condition, PAC adsorbents might be glued to the membrane surface to form a cake layer and avoided the approaching of foulants onto surfaces. Thus, a slight increase in fouling control could be achieved. However, although conventional adsorbents such as PAC can efficiently remove various types of organic matter, its effectiveness in mitigate membrane fouling is still in debate. There are two possible reasons for the lacked efficiency in fouling control by using PAC. First, PAC only selectively removes more UV-absorbing fractions but could not effectively remove small particles [23,64]. Based on the discussion in section 5, these small particles might play key role in membrane fouling development. Second, the formation of NOM–PAC complexes with similar sizes to the membrane pore sizes might easily penetrate into membrane pores and cause irreversible fouling. As a result, the direct filtration of these mixture or residue NOM fractions usually causes severe membrane fouling [64,128]. Preadsorption treatment might alleviate the problem by separating NOM-adsorbent mixture ahead of membrane filtration. However, preadsorption could not effectively remove some colloids and key foulants such as polysaccharides in a dispersed system [24,34,72]. The fouling control was not sufficient by using preadsorption approach. The difficulty in removing adsorbent particles from treatment facilities might also impede the wider applications of adsorbent treatments.

6.2. Superior fouling control behaviors in µGAF system

The superior fouling control behaviors of µGAF than conventional approaches using absorbents can be attributed to three main reasons. First, in a well-mixed system, all the adsorbent particles are in contact with a solution from which some of the NOM has already been removed. However, feedwater with full NOM concentration enters the adsorbent layer in the predeposition process. As a result, the driving force for adsorption is higher at that location than it is anywhere in the preadsorption system [111]. Second, the micron-sized adsorbents can form a predeposited layer which provides a surface for individual NOM molecules to transform into a condensed gel phase. As discussed above, the water treated in the mode of preadsorption could always result in higher membrane fouling than that passed through a layer of adsorbent such as HAOPs and PAC. The results highly suggested that the adsorbent layer plays key role in capturing foulants molecules that could not be effectively adsorbed by dispersed adsorbents [33,36]. A similar interaction might account for the selective removal of THM precursors relative to other NOM in the predeposition systems. Finally, predeposition mode can more effectively remove low-MW (~30 Da), non-UV-absorbing fractions, as well as more neutral organics such as polysaccharides, which are probably key foulants in fouling developments [37,111].

7. Conclusion and outlook

In this study, the recent applications of coagulation/adsorption pretreatments on LPM fouling control were summarized. The review highlights the effects of coagulant/adsorbent types and their contact mode with the feed on NOM removal and fouling control behaviors. The main conclusions are summarized as follows:

- Coagulation–sedimentation and inline coagulation usually perform better than conventional process at low coagulant dose. At high coagulant dose, the NOM removal and fouling control are controlled by coagulant dose rather than coagulation mode.
- The effects of adsorption pretreatments are highly related to adsorbents applied. Even though PAC is the most frequently used, the fouling reduction is limited and sometimes even adverse. Metal oxide particles can control NOM-induced membrane fouling. Heated metal oxide particles could perform even better due to the abundant surface complexation sites and higher rigidity of particles.
- Integrated approach of coagulation, adsorption, sedimentation, oxidation, chlorination and TF could always result in promoted fouling control behaviors.
- The deposition of an adsorbent layer on the membrane surface exhibits the best performance in mitigating fouling. The superior performance can be attributed to the higher driving force for adsorption, the formation of gel layer by NOM molecules and the capture of more foulants.
- The fouling at the surface of adsorbent layer in µGAF system is attributed to larger foulants such as colloids and particulate matter. While after feedwater broke through the cake layer, key foulants appear to include, but not be limited to, hydrophilic NOM such as polysaccharides and proteins [38].

Although coagulation and adsorption approaches by coagulants and solids have long been applied as pretreatments prior to LPM processes, the present review suggests that the contact mode between coagulants/adsorbents and feedwater could remarkably affect the NOM removal efficiency and subsequent membrane fouling control behaviors. In a lab-scale, the predeposition of adsorbents such as HAOPs performed than any other modes in removing NOM and mitigating membrane fouling. However, whether the application of μGAF systems was feasible in a pilot or larger scale remains unknown. Due to the relatively low predictability of membrane fouling, assessment is of great importance to the wider applications of pretreatments. Future studies are needed to assess the feasibility of superior pretreatment approaches, for example, μGAF in mitigating fouling. The application of μGAF in a larger scale should be tested and it is interesting to examine whether the deposition of adsorbents could also effectively alleviate fouling in an industrial-scale system when receiving a larger amount of feedwater.

To offer a better insight into the coagulation/adsorption pretreatment processes, scientific researchers are required to explore the mitigation and transformation of foulants during pretreatments. On one hand, novel adsorbents with high NOM removal and high recovery efficiencies are still required to be synthesized. It is essential to develop novel coagulants and adsorbents with high foulant removal efficiency, outstanding recycling property as well as system applicability. The potential applications of these novel adsorbents in pilot and large-scale system should also be tested. On the other hand, advanced analytical approaches allow us to unravel the mechanism of fouling in μGAF systems. For example, by using atomic force microscopy or surface plasma resonance, the foulant–adsorbent, foulant–foulant and foulant–membrane interactions could be analyzed at the molecular level to unravel the mechanisms of excellent membrane behaviors in μGAF system [129].

Acknowledgments

We thank Professor Mark M. Benjamin from Department of Civil and Environmental Engineering, University of Washington for his great support and valuable review comments on the manuscript. We also wish to thank Priority Academic Program Development of Jiangsu Higher Education Institutions, the China Postdoctoral Science Foundation (grant 2017M610293) and the Open Research Fund of the Ministry of Education Key Laboratory of Integrated Regulation and Resource Development on Shallow Lakes (grant 2013B1602020401) for the partial support of this work.

References

[1] GWI, Low Pressure: High Expectations. Opportunities and Dynamic in the MF/UF Membrane Market, Global Water Intelligence, 2014.
[2] P.E. Odendaal, Water Treatment Membrane Processes, McGraw-Hill, New York, 1996.
[3] L.J. Zeman, A.L. Zydney, Microfiltration and Ultrafiltration: Principles and Applications, CRC Press, Boca Raton, 1996.
[4] E.M.V. Hoek, V.V. Tarabara, Encyclopedia of Membrane Science and Technology, John Wiley & Sons, New York, 2013.
[5] M.R. Wiesner, S. Chellam, The promise of membrane technologies, Environ. Sci. Technol., 33 (1999) 360–366.
[6] A.S. Al-Amoudi, Factors affecting natural organic matter (NOM) and scaling fouling in NF membranes: a review, Desalination, 259 (2010) 1–10.
[7] D. Jermann, W. Pronk, S. Meylan, M. Boller, Interplay of different NOM fouling mechanisms during ultrafiltration for drinking water production, Water Res., 41 (2007) 1713–1722.
[8] S. Lee, J.W. Cho, M. Elimelech, Combined influence of natural organic matter (NOM) and colloidal particles on nanofiltration membrane fouling, J. Membr. Sci., 262 (2005) 27–41.
[9] W. Yuan, A.L. Zydney, Humic acid fouling during ultrafiltration, Environ. Sci. Technol., 34 (2000) 5043–5050.
[10] D. Jermann, W. Pronk, R. Kagi, M. Halbeisen, M. Boller, Influence of interactions between NOM and particles on UF fouling mechanisms, Water Res., 42 (2008) 3870–3878.
[11] H. Yamamura, K. Okimoto, K. Kimura, Y. Watanabe, Hydrophilic fraction of natural organic matter causing irreversible fouling of microfiltration and ultrafiltration membranes, Water Res., 54 (2014) 123–136.
[12] N. Lee, G. Amy, J.-P. Croué, Low-pressure membrane (MF/UF) fouling associated with allochthonous versus autochthonous natural organic matter, Water Res., 40 (2006) 2357–2368.
[13] X. Zheng, M. Ernst, M. Jekel, Identification and quantification of major organic foulants in treated domestic wastewater affecting filterability in dead-end ultrafiltration, Water Res., 43 (2009) 238–244.
[14] S.K. Hong, M. Elimelech, Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes, J. Membr. Sci., 132 (1997) 159–181.
[15] I. Sutzkover-Gutman, D. Hasson, R. Semiat, Humic substances fouling in ultrafiltration processes, Desalination, 261 (2010) 218–231.
[16] X. Zheng, M.T. Khan, J.-P. Croué, Contribution of effluent organic matter (EfOM) to ultrafiltration (UF) membrane fouling: Isolation, characterization, and fouling effect of EfOM fractions, Water Res., 65 (2014) 414–424.
[17] K.J. Howe, M.M. Clark, Fouling of microfiltration and ultrafiltration membranes by natural waters, Environ. Sci. Technol., 36 (2002) 3571–3576.
[18] F. Xiao, P. Xiao, W.J. Zhang, D.S. Wang, Identification of key factors affecting the organic fouling on low-pressure ultrafiltration membranes, J. Membr. Sci., 447 (2013) 144–152.
[19] Y. Gao, D. Chen, L.K. Weavers, H.W. Walker, Ultrasonic control of UF membrane fouling by natural waters: effects of calcium, pH, and fractionated natural organic matter, J. Membr. Sci., 401 (2012) 232–240.
[20] C. Jucker, M.M. Clark, Adsorption of aquatic humic substances on hydrophobic ultrafiltration membranes, J. Membr. Sci., 97 (1994) 37–52.
[21] W.Y. Ahn, A.G. Kalinichev, M.M. Clark, Effects of background cations on the fouling of polyethersulfone membranes by natural organic matter: experimental and molecular modeling study, J. Membr. Sci., 309 (2008) 128–140.
[22] K. Kimura, K. Tanaka, Y. Watanabe, Microfiltration of different surface waters with/without coagulation: clear correlations between membrane fouling and hydrophilic biopolymers, Water Res., 49 (2014) 434–443.
[23] H. Huang, K. Schwab, J.G. Jacangelo, Pretreatment for low pressure membranes in water treatment: a review, Environ. Sci. Technol., 43 (2009) 3011–3019.
[24] K. Farahbakhsh, C. Svrcek, R.K. Guest, D.W. Smith, A review of the impact of chemical pretreatment on low-pressure water treatment membranes, J. Environ. Eng. Sci., 3 (2004) 237–253.
[25] C. Thamaraiselvan, M. Noel, Membrane processes for dye wastewater treatment: recent progress in fouling control, Crit. Rev. Environ. Sci. Technol., 45 (2015) 1007–1040.
[26] M.R. Wiesner, J.M. Laine, Coagulation and Membrane Separation in Water Treatment Membrane Processes, McGraw Hill, New York, 1996.
[27] K.J. Howe, A. Marwah, K.P. Chiu, S.S. Adham, Effect of coagulation on the size of MF and UF membrane foulants, Environ. Sci. Technol., 40 (2006) 7908–7913.

[28] J.D. Lee, S.H. Lee, M.H. Jo, P.K. Park, C.H. Lee, J.W. Kwak, Effect of coagulation conditions on membrane filtration characteristics in coagulation-microfiltration process for water treatment, Environ. Sci. Technol., 34 (2000) 3780–3788.

[29] M.Q. Yan, D.S. Wang, J.R. Ni, J.H. Qu, C.W.K. Chow, H.L. Liu, Mechanism of natural organic matter removal by polyaluminum chloride: effect of coagulant particle size and hydrolysis kinetics, Water Res., 42 (2008) 3361–3370.

[30] A. Maartens, P. Swart, E.P. Jacobs, Feed-water pretreatment: methods to reduce membrane fouling by natural organic matter, J. Membr. Sci., 163 (1999) 51–62.

[31] C. Stoquart, P. Servais, P.R. Berube, B. Barbeau, Hybrid membrane processes using activated carbon treatment for drinking water: a review, J. Membr. Sci., 411 (2012) 1–12.

[32] L.C. Koh, W.-Y. Ahn, M.M. Clark, Selective adsorption of natural organic foulants by polysulfone colloids: effect on ultrafiltration fouling, J. Membr. Sci., 281 (2006) 472–479.

[33] Z.X. Cai, J.S. Kim, M.M. Benjamin, NOM removal by adsorption and membrane filtration using heated aluminum oxide particles, Environ. Sci. Technol., 42 (2008) 619–623.

[34] J. Kim, Q.R. Deng, M.M. Benjamin, Simultaneous removal of phosphorus and foulants in a hybrid coagulation/membrane filtration system, Water Res., 42 (2008) 2017–2024.

[35] J.S. Kim, Z.X. Cai, M.M. Benjamin, Effects of adsorbents on membrane fouling by natural organic matter, J. Membr. Sci., 310 (2008) 356–364.

[36] J. Kim, Z.X. Cai, M.M. Benjamin, NOM fouling mechanisms in a hybrid adsorption/membrane system, J. Membr. Sci., 349 (2010) 35–43.

[37] Z.X. Cai, M.M. Benjamin, NOM fractionation and fouling of low-pressure membranes in microgranular adsorptive filtration, Environ. Sci. Technol., 45 (2011) 8935–8940.

[38] Z.X. Cai, C. Wee, M.M. Benjamin, Fouling mechanisms in low-pressure membrane filtration in the presence of an adsorbent cake layer, J. Membr. Sci., 433 (2013) 32–38.

[39] W. Stumm, J.J. Morgan, Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, John Wiley & Sons, New York, 1996.

[40] B. Bolto, J. Gregory, Organic polyelectrolytes in water treatment, Water Res., 41 (2007) 2301–2324.

[41] W.Z. Yu, H.J. Liu, L. Xu, J.H. Qu, N. Graham, The pre-treatment of submerged ultrafiltration membrane by coagulation—effect of polyacrylamide as a coagulant aid, J. Membr. Sci., 446 (2013) 50–58.

[42] N. Li, G.P. Sheng, Y.Z. Lu, R.J. Zeng, H.Q. Yu, Removal of antibiotic resistance genes from wastewater treatment plant effluent by coagulation, Water Res., 111 (2017) 204–212.

[43] B.T. Zhu, D.A. Clifford, S. Chellam, Virus removal by iron coagulation-microfiltration, Water Res., 39 (2005) 5153–5161.

[44] X. Zheng, S. Plume, M. Ernst, J.P. Croue, M. Jekel, In-line coagulation prior to UF of treated domestic wastewater – foulants removal, fouling control and phosphorus removal, J. Membr. Sci., 403 (2012) 129–139.

[45] M. Kimura, Y. Matsui, S. Saito, T. Takahashi, M. Nakagawa, N. Shirasaki, T. Matsushita, Hydraulically irreversible membrane fouling during coagulation-microfiltration and its control by using high-basicity polyaluminum chloride, J. Membr. Sci., 477 (2015) 115–122.

[46] K. Kimura, T. Maeda, H. Yamamura, Y. Watanabe, Irreversible membrane fouling in microfiltration membranes filtering coagulated surface water, J. Membr. Sci., 320 (2008) 356–362.

[47] J. Wang, J. Guan, S.R. Santiwong, T.D. Waite, Characterization of floc size and structure under different monomer and polymer coagulants on microfiltration membrane fouling, J. Membr. Sci., 321 (2008) 132–138.

[48] A.K. Verma, R.R. Dash, P. Bhunia, A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters, J. Environ. Manage., 93 (2012) 154–168.

[49] Z. Yan, B. Liu, F. Qu, A. Ding, H. Liang, Y. Zhao, G. Li, Control of ultrafiltration membrane fouling caused by algal extracellular organic matter (EOM) using enhanced Al coagulation with permanganate, Sep. Sci. Technol., 172 (2017) 51–58.

[50] K. Kimura, Y. Oki, Efficient control of membrane fouling in MF by removal of biopolymers: comparison of various pretreatments, Water Res., 115 (2017) 172–179.

[51] Y.X. Zhao, B.Y. Gao, Q.B. Qi, Y. Wang, S. Phuntsho, J.H. Kim, Q.Y. Yue, Q. Li, H.K. Shon, Cationic polyacrylamide as coagulant aid with titanium tetrachloride for low molecule organic matter removal, J. Hazard. Mater., 258 (2013) 84–92.

[52] C.S. Lee, J. Robinson, M.F. Chong, A review on application of flocculants in wastewater treatment, Process Saf. Environ. Prot., 92 (2014) 489–508.

[53] W. Yu, Y. Yang, N. Graham, Evaluation of ferrate as a coagulant aid/oxidant pretreatment for mitigating submerged ultrafiltration membrane fouling in drinking water treatment, Chem. Eng. J., 298 (2016) 234–242.

[54] C.H. Wu, Y. Wang, B.Y. Gao, Y.X. Zhao, Q.Y. Yue, Coagulation performance and floc characteristics of aluminum sulfate using sodium alginate as coagulant aid for synthetic dying wastewater treatment, Sep. Sci. Technol., 95 (2012) 180–187.

[55] G.S. Logsdon, D.G. Neden, A.M.D. Ferguson, S.D. Labonde, Testing direct-filtration for the treatment of high-turbidity water, J. Am. Water Works Assoc., 85 (1993) 39–46.

[56] K.J. Howe, M.M. Clark, Effect of coagulation pretreatment on membrane filtration performance, J. Am. Water Works Assoc., 98 (2006) 133–146.

[57] S.H. Lee, W.S. Shin, M.C. Shin, S.J. Choi, L.S. Park, Improvement of water treatment performance by using polyamine flocculants, Environ. Technol., 22 (2001) 653–659.

[58] J. Haberkamp, A.S. Ruhl, M. Ernst, M. Jekel, Impact of coagulation and adsorption on DOC fractions of secondary effluent and resulting fouling behaviour in ultrafiltration, Water Res., 41 (2007) 3794–3802.

[59] H. Wang, F.S. Qu, A. Ding, H. Liang, R.B. Jia, K. Li, L.M. Bai, H.Q. Chang, G.B. Li, Combined effects of PAC adsorption and in situ chlorination on membrane fouling in a pilot-scale coagulation and ultrafiltration process, Chem. Eng. J., 283 (2016) 1374–1383.

[60] I.N. Najm, V.L. Snoeyink, B.W. Lykins, J.Q. Adams, Using Powdered Activated Carbon – A Critical Review, Workshop on Influence and Removal of Orgaincs in Drinking Water, 1992.

[61] B.W. Ma, W.Z. Yu, H.J. Liu, J.B. Yao, J.H. Qu, Effect of iron/aluminum hydrolyzed precipitate layer on ultrafiltration membrane, Desalination, 330 (2013) 16–21.

[62] H.K. Shon, S. Vigneswaran, I.S. Kim, J. Cho, H.H. Ngo, The effect of pretreatment to ultrafiltration of biologically treated sewage effluent: a detailed effluent organic matter (EfOM) characterization, Water Res., 38 (2004) 1933–1939.

[63] C.F. Lin, Y.J. Huang, I.J. Hao, Ultrafiltration processes for removing humic substances: effect of molecular weight fractions and PAC treatment, Water Res., 33 (1999) 1252–1264.

[64] P. Zhao, S. Takizawa, H. Katayama, S. Ohgaki, Factors causing PAC cake fouling in PAC-MF (powdered activated carbon-microfiltration) water treatment systems, Water Sci. Technol., 51 (2005) 231–240.

[65] C. Tansakul, S. Laborie, C. Cabassud, Adsorption combined with ultrafiltration to remove organic matter from seawater, Water Res., 45 (2011) 6362–6370.

[66] R. Fabris, E.K. Lee, C.W.K. Chow, V. Chen, M. Drikas, Pre-treatments to reduce fouling of low pressure micro-filtration (MF) membranes, J. Membr. Sci., 289 (2007) 231–240.

[67] L.C. Schideman, B.J. Marinas, V.L. Snoeyink, S.Y. Qi, C. Campos, Three-component adsorption modeling to evaluate and improve integrated sorption-membrane processes, Environ. Sci. Technol., 41 (2007) 6547–6553.

[68] Y. Matsui, R. Murase, T. Sanogawa, H. Aoki, S. Mima, T. Inoue, T. Matsushita, Rapid adsorption pretreatment with submicrometre powdered activated carbon particles before microfiltration, Water Sci. Technol., 51 (2005) 249–256.

[69] X. Cui, K.H. Choo, Granular iron oxide adsorbents to control natural organic matter and membrane fouling in ultrafiltration water treatment, Water Res., 47 (2013) 4227–4237.

[70] Y.J. Chang, K.H. Choo, M.M. Benjamin, S. Reiber, Combined adsorption – UF process increases TOC removal, J. Am. Water Works Assoc., 90 (1998) 90–102.

[71] P. Yao, K.H. Choo, M.H. Kim, A hybridized photocatalysis-microfiltration system with iron oxide-coated membranes for the removal of natural organic matter in water treatment: effects of iron oxide layers and colloids, Water Res., 43 (2009) 4238–4248.

[72] S.K. Kang, K.H. Choo, Why does a mineral oxide adsorbent control fouling better than powdered activated carbon in hybrid ultrafiltration water treatment? J. Membr. Sci., 355 (2010) 69–77.

[73] Y.J. Chang, M.M. Benjamin, Iron oxide adsorption and UF to remove NOM and control fouling, J. Am. Water Works Assoc., 88 (1996) 74–88.

[74] C.L. Ding, X. Yang, W. Liu, Y.J. Chang, C.I. Shang, Removal of natural organic matter using surfactant-modified iron oxide-coated sand, J. Hazard. Mater., 174 (2010) 567–572.

[75] F. Qu, Z. Yan, W. Liu, S. Shao, X. Ren, N. Ren, G. Li, H. Liang, Effects of manganese dioxides on the ultrafiltration membrane fouling by algal extracellular organic matter, Sep. Sci. Technol., 153 (2015) 29–36.

[76] Y.J. Chang, C.W. Li, M.M. Benjamin, Iron oxide-coated media for NOM sorption and particulate filtration, J. Am. Water Works Assoc., 89 (1997) 100–113.

[77] W. Stumm, Chemistry of the Solid-Water Interface, Wiley Interscience, New York, 1992.

[78] B. Gu, J. Schmitt, Z. Chen, L. Liang, J.F. McCarthy, Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models, Environ. Sci. Technol., 28 (1994) 38–46.

[79] J.K. Edzwald, Coagulation in drinking-water treatment-particles, organics and coagulants, Water Sci. Technol., 27 (1993) 21–35.

[80] M.M. Clark, W.Y. Ahn, X. Li, N. Sternisha, R.L. Riley, Formation of polysulfone colloids for adsorption of natural organic foulants, Langmuir, 21 (2005) 7207–7213.

[81] D.T. Myat, M. Mergen, O. Zhao, M.B. Stewart, J.D. Orbell, T. Merle, J.-P. Croue, S. Gray, Effect of IX dosing on polypropylene and PVDF membrane fouling control, Water Res., 47 (2013) 3827–3834.

[82] K. Li, H. Liang, F.S. Qu, S.L. Shao, H.R. Yu, Z.S. Han, X. Du, G.B. Li, Control of natural organic matter fouling of ultrafiltration membrane by adsorption pretreatment: comparison of mesoporous adsorbent resin and powdered activated carbon, J. Membr. Sci., 471 (2014) 94–102.

[83] H. Wang, Z. Chen, J. Miao, Y. Li, A novel approach for mitigation of membrane fouling: concomitant use of flocculant and magnetic powder, Bioresour. Technol., 209 (2016) 318–325.

[84] Y. Chen, Y. Tu, Y. Bai, M. Tang, W. Liu, H. Wu, Combined adsorption/ultrafiltration of secondary effluents using powdered zeolites, Chem. Eng. Technol., 39 (2016) 285–292.

[85] L. Chekli, E. Corjon, S.A.A. Tabatabai, G. Naidu, B. Tamburic, S.H. Park, H.K. Shon, Performance of titanium salts compared to conventional $FeCl_3$ for the removal of algal organic matter (AOM) in synthetic seawater: coagulation performance, organic fraction removal and floc characteristics, J. Environ. Manage., 201 (2017) 28–36.

[86] L. Chekli, C. Eripret, S.H. Park, S.A.A. Tabatabai, O. Vronska, B. Tamburic, J.H. Kim, H.K. Shon, Coagulation performance and floc characteristics of polytitanium tetrachloride (PTC) compared with titanium tetrachloride ($TiCl_4$) and ferric chloride ($FeCl_3$) in algal turbid water, Sep. Sci. Technol., 175 (2017) 99–106.

[87] Z. Su, X. Li, Y. Yang, Y. Fan, Probing the application of a zirconium coagulant in a coagulation-ultrafiltration process: observations on organics removal and membrane fouling, RSC Adv., 7 (2017) 42329–42338.

[88] A. Matilainen, M. Vepsalainen, M. Sillanpaa, Natural organic matter removal by coagulation during drinking water treatment: a review, Adv. Colloid Interface Sci., 159 (2010) 189–197.

[89] A.I. Schafer, A.G. Fane, T.D. Waite, Cost factors and chemical pretreatment effects in the membrane filtration of waters containing natural organic matter, Water Res., 35 (2001) 1509–1517.

[90] N.H. Lee, G. Amy, J.P. Croue, H. Buisson, Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM), Water Res., 38 (2004) 4511–4523.

[91] S. Mozia, M. Tomaszewska, A.W. Morawski, Application of an ozonation-adsorption-ultrafiltration system for surface water treatment, Desalination, 190 (2006) 308–314.

[92] D. Metcalfe, P. Jarvis, C. Rockey, S. Judd, Pre-treatment of surface waters for ceramic microfiltration, Sep. Sci. Technol., 163 (2016) 173–180.

[93] S.A. Alizadeh Tabatabai, J.C. Schippers, M.D. Kennedy, Effect of coagulation on fouling potential and removal of algal organic matter in ultrafiltration pretreatment to seawater reverse osmosis, Water Res., 59 (2014) 283–294.

[94] M. Vepsalainen, M. Ghiasvand, J. Selin, J. Pienimaa, E. Repo, M. Pulliainen, M. Sillanpaa, Investigations of the effects of temperature and initial sample pH on natural organic matter (NOM) removal with electrocoagulation using response surface method (RSM), Sep. Sci. Technol., 69 (2009) 255–261.

[95] S. Chellam, M.A. Sari, Aluminum electrocoagulation as pretreatment during microfiltration of surface water containing NOM: a review of fouling, NOM, DBP, and virus control, J. Hazard. Mater., 304 (2016) 490–501.

[96] N.P. Gamage, S. Chellam, Aluminum electrocoagulation pretreatment reduces fouling during surface water microfiltration, J. Membr. Sci., 379 (2011) 97–105.

[97] L.C. Hua, C. Huang, Y.C. Su, N. TranNgocPhu, P.C. Chen, Effects of electro-coagulation on fouling mitigation and sludge characteristics in a coagulation-assisted membrane bioreactor, J. Membr. Sci., 495 (2015) 29–36.

[98] T. Tran, S. Gray, R. Naughton, B. Bolto, Polysilicato-iron for improved NOM removal and membrane performance, J. Membr. Sci., 280 (2006) 560–571.

[99] K.Y.J. Choi, B.A. Dempsey, In-line coagulation with low-pressure membrane filtration, Water Res., 38 (2004) 4271–4281.

[100] C. Guiguia, P. Manno, P. Moulin, M.J. Clifton, J.C. Rouch, P. Aptel, J.M. Laine, The use of Dean vortices in coiled hollow-fibre ultrafiltration membranes for water and wastewater treatment, Desalination, 118 (1998) 73–79.

[101] M.M. Zhang, C. Li, M.M. Benjamin, Y.J. Chang, Fouling and natural organic matter removal in adsorbent/membrane systems for drinking water treatment, Environ. Sci. Technol., 37 (2003) 1663–1669.

[102] J. Heo, J.R.V. Flora, N. Her, Y.G. Park, J. Cho, A. Son, Y. Yoon, Removal of bisphenol A and 17 beta-estradiol in single walled carbon nanotubes-ultrafiltration (SWNTs-UF) membrane systems, Sep. Sci. Technol., 90 (2012) 39–52.

[103] W. Yu, L. Xu, J. Qu, N. Graham, Investigation of pre-coagulation and powder activate carbon adsorption on ultrafiltration membrane fouling, J. Membr. Sci., 459 (2014) 157–168.

[104] K. Li, F. Qu, H. Liang, S. Shao, Z.-S. Han, H. Chang, X. Du, G. Li, Performance of mesoporous adsorbent resin and powdered activated carbon in mitigating ultrafiltration membrane fouling caused by algal extracellular organic matter, Desalination, 336 (2014) 129–137.

[105] J.W. Lee, J.I. Chun, H.J. Jung, D.H. Kwak, T. Ramesh, W.G. Shim, H. Moon, Comparative studies on coagulation and adsorption as a pretreatment method for the performance improvement of submerged MF membrane for secondary domestic wastewater treatment, Sep. Sci. Technol., 40 (2005) 2613–2632.

[106] J. Wang, J. Yang, H. Zhang, W. Guo, H.-H. Ngo, Feasibility study on magnetic enhanced flocculation for mitigating membrane fouling, Ind. Eng. Chem. Res., 26 (2015) 37–45.

[107] Q.L. Zhao, H.Y. Zhong, J.L. Liu, Y. Liu, Integrated coagulation-trickling filter-ultrafiltration processes for domestic wastewater treatment and reclamation, Water Sci. Technol., 65 (2012) 1599–1605.

[108] Z.X. Cai, Investigation of Microgranular Adsorptive Filtration System, Doctoral Thesis, Department of Civil and Environmental Engineering, University of Washington, Seattle, 2011.

[109] B. Malczewska, M.M. Benjamin, Efficacy of hybrid adsorption/membrane pretreatment for low pressure membrane, Water Res., 99 (2016) 263–271.

[110] B. Malczewska, J. Liu, M.M. Benjamin, Virtual elimination of MF and UF fouling by adsorptive pre-coat filtration, J. Membr. Sci., 479 (2015) 159–164.

[111] L.F. Wang, M.M. Benjamin, A multi-spectral approach to differentiate the effects of adsorbent pretreatments on the characteristics of NOM and membrane fouling, Water Res., 98 (2016) 56–63.

[112] T. Carroll, S. King, S.R. Gray, B.A. Bolto, N.A. Booker, The fouling of microfiltration membranes by NOM after coagulation treatment, Water Res., 34 (2000) 2861–2868.

[113] T. Berman, R. Mizrahi, C.G. Dosoretz, Transparent exopolymer particles (TEP): a critical factor in aquatic biofilm initiation and fouling on filtration membranes, Desalination, 276 (2011) 184–190.

[114] E. Bar-Zeev, U. Passow, S.R.-V. Castrillon, M. Elimelech, Transparent exopolymer particles: from aquatic environments and engineered systems to membrane biofouling, Environ. Sci. Technol., 49 (2015) 691–707.

[115] L.O. Villacorte, M.D. Kennedy, G.L. Amy, J.C. Schippers, The fate of Transparent Exopolymer Particles (TEP) in integrated membrane systems: removal through pre-treatment processes and deposition on reverse osmosis membranes, Water Res., 45 (2011) 960–960.

[116] U. Passow, Transparent exopolymer particles (TEP) in aquatic environments, Prog. Oceanogr., 55 (2002) 287–333.

[117] J. Liu, M.M. Benjamin, Effect of water chemistry and operational conditions on mu GAF process performance, Water Res., 105 (2016) 76–84.

[118] L.-F. Wang, M.M. Benjamin, HAOPs pretreatment to reduce membrane fouling: foulant identification, removal, and interactions, J. Membr. Sci., 515 (2016) 219–229.

[119] H.O. Huang, C.R. O'Melia, Direct-flow microfiltration of aquasols II. On the role of colloidal natural organic matter, J. Membr. Sci., 325 (2008) 903–913.

[120] R.H. Peiris, C. Halle, H. Budman, C. Moresoli, S. Peldszus, P.M. Huck, R.L. Legge, Identifying fouling events in a membrane-based drinking water treatment process using principal component analysis of fluorescence excitation-emission matrices, Water Res., 44 (2010) 185–194.

[121] J.Y. Tian, M. Ernst, F. Cui, M. Jekel, Correlations of relevant membrane foulants with UF membrane fouling in different waters, Water Res., 47 (2013) 1218–1228.

[122] N.P. Gamage, S. Chellam, Mechanisms of physically irreversible fouling during surface water microfiltration and mitigation by aluminum electroflotation pretreatment, Environ. Sci. Technol., 48 (2014) 1148–1157.

[123] H. Yamamura, K. Kimura, Y. Watanabe, Mechanism involved in the evolution of physically irreversible fouling in microfiltration and ultrafiltration membranes used for drinking water treatment, Environ. Sci. Technol., 41 (2007) 6789–6794.

[124] S.A. Huber, A. Balz, M. Abert, W. Pronk, Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography – organic carbon detection – organic nitrogen detection (LC-OCD-OND), Water Res., 45 (2011) 879–885.

[125] C. Halle, P.M. Huck, S. Peldszus, J. Haberkamp, M. Jekel, Assessing the performance of biological filtration as pretreatment to low pressure membranes for drinking water, Environ. Sci. Technol., 43 (2009) 3878–3884.

[126] H. Huang, H.-H. Cho, J.G. Jacangelo, K.J. Schwab, Mechanisms of membrane fouling control by integrated magnetic ion exchange and coagulation, Environ. Sci. Technol., 46 (2012) 10711–10717.

[127] D.C. Sioutopoulos, A.J. Karabelas, The effect of permeation flux on the specific resistance of polysaccharide fouling layers developing during dead-end ultrafiltration, J. Membr. Sci., 473 (2015) 292–301.

[128] Y. Liu, X. Li, Y. Yang, S. Liang, L. Liu, J. Ren, Treatment of micro-polluted alga-rich water with PAC and ultrafiltration integrated process, J. Cent. South Univ. Sci. Technol., 45 (2014) 2928–2933.

[129] Q.L. Li, M. Elimelech, Organic fouling and chemical cleaning of nanofiltration membranes: measurements and mechanisms, Environ. Sci. Technol., 38 (2004) 4683–4693.

Supplementary material

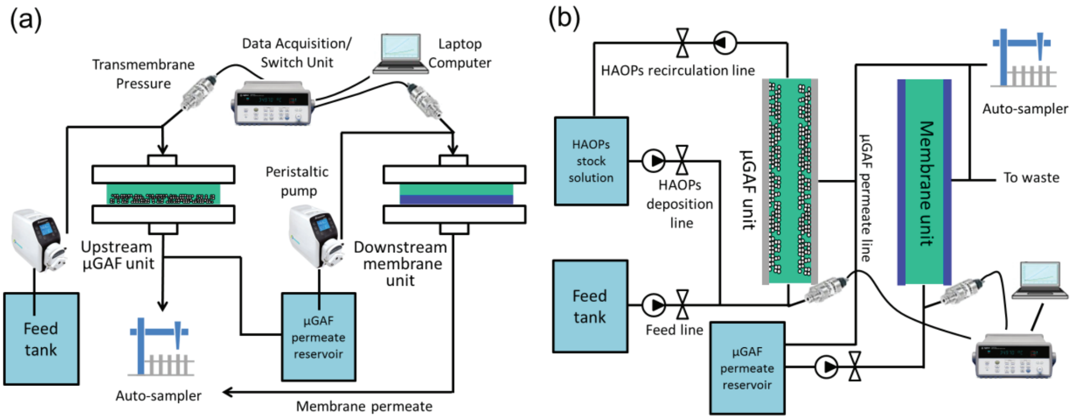

Fig. S1. Schematic of (a) the cartridge and (b) the tubular membrane filtration experimental setup.

Table S1
NOM removal by adsorption pretreatments

Absorbent applied	Dose	Feedwater	NOM removal (%)		References
			DOC removal	UV_{254} removal	
PAC	250 mg/L	Lake Washington water	71		[1]
HIOPs	250 mg/L		43		
SiO_2	250 mg/L		~0		
PAC	300 mg/L	Lake Washington water	90	73	[2]
HAOPs	0.1 mmol Al		41	79	
$Al(OH)_3$	1 mM Al^{3+}	Permeate from a pilot-scale MBR	30	38	[3]
HAOPs	1 mM Al^{3+}		29	44	
Silica	300 mg/L	Lake Washington water	~2	~2	[4]
HAOPs	150 mg/L		40	75	
HIOPs	200 mg/L		42	70	
PAC	200 mg/L		82	90	
HAOPs (0.5 µm)	100 mg/L	Lake Union water		60	[5]
HAOPs (7.5 µm)	100 mg/L			60	
PAC (1 µm)	100 mg/L			60	
PAC (80 µm)	100 mg/L			40	
HAOPs	5 mg/L as Al	1:3 dilute Lake Pleasant water	25	46	[6]
	20 mg/L as Al		50	77	
	100 mg/L as Al		49	80	
PAC adsorption	1 g/L	Biologically treated sewage effluent	66	91	[7]
Polysulfone colloids	5 mg/L	Surface waters from Lake Decatur, Illinois and Lake Michigan		14	[8]
	30 mg/L			13	
	100 mg/L			13	
PACs adsorption	75 mg/L	Secondary domestic wastewater treatment		72–75	[9]
Granular activated carbon	20 g	Biotreated sewage effluent	64		[10]
PAC	1 g/L		63		
$FeCl_3$ flocculation + PAC adsorption			90		

(continued)

Table S1 *(Continued)*

Absorbent applied	Dose	Feedwater	NOM removal (%)		References
			DOC removal	UV_{254} removal	
Magnetic ion exchange resin (MIEX)	MIEX 10 mL/L	Myponga reservoir in Australia	71	88	[11]
MIEX/Alum	Alum coagulation 40 mg/L		76	91	
MIEX/PAC			91	97	
MIEX/PAC/Alum	PAC adsorption 40 mg/L		92	98	
MIEX		Woronora reservoir	45	63	
MIEX/Alum			50	40	
MIEX/PAC			82	86	
MIEX/PAC/Alum			82	86	
Granular activated carbon	Pilot-scale columns	Domestic wastewater effluent	80%–90% DOM removal		[12]
Fine iron oxide particles (IOPs)	40 mg/L as Fe	Surface water in Daegu, Korea	10	38	[13]
	200 mg/L as Fe		21	62	
	1,000 mg/L as Fe		23	70	
Iron oxide coated polymer (IOCP) beads	40 mg/L as Fe		10	30	
	200 mg/L as Fe		18	54	
	1,000 mg/L as Fe		20	60	
Magnetic ion-exchange resin (MIEX)	1 mL/L	Secondary wastewater effluent	27	28	[14]
	5 mL/L		57	69	
	10 mL/L		64	77	
Mesoporous adsorbent resin (MAR)	50 mg/L	30 mg/L HA	46		[15]
	50 mg/L	30 mg/L BSA	29		
	50 mg/L	30 mg/L sodium alginate (SA)	4		
PAC	50 mg/L	30 mg/L HA	17		
	50 mg/L	30 mg/L BSA	23		
	50 mg/L	30 mg/L SA	4		
Commercial and prepared MnO_2	2 mg/L	Algal extracellular organic matter (EOM)	5–16	7–12	[16]
	4 mg/L		7–17	8–14	
	10 mg/L		8–25	8–18	
Powdered zeolite (PZ) adsorption		Effluents from industrial wastewater treatment plants	Removal of aromatic proteins, fulvic acid-like materials, soluble microbial by-product-like materials and humic acid-like organics increased by 28.1%, 16.1%, 18.9% and 37.1%		[17]
Suspended ion exchange (SIX) and PACl coagulation		Three raw waters from reservoir and rivers	SIX resin removed predominantly low-MW organic matter whereas coagulation removed the high-MW fractions LMW organics were not retained when coagulation was optimized		[18]

(continued)

Table S1 *(Continued)*

Absorbent applied	Dose	Feedwater	NOM removal (%)		References
			DOC removal	UV_{254} removal	
PDMDAAC and Fe_3O_4		Effluent from MBR	Addition of 120 mg/L magnetic powder improved the dehydrogenase activity and stimulated microbes to produce less SMPc and EPSp high COD removal efficiency of over 94% was observed in all MBRs		[19]
PACl + $KMnO_4$/MnO_2	PACl 0.4 mg Al/mg DOC	Algal extracellular organic matter (EOM)	18	12	[20]
	PACl 0.4 mg Al/mg DOC + $KMnO_4$ 0.3 mg Mn/mg DOC		21	18	
	PACl 0.4 mg Al/mg DOC + $KMnO_4$ 0.6 mg Mn/mg DOC		25	23	
	PACl 0.4 mg Al/mg DOC + MnO_2 0.3 mg Mn/mg DOC		24	15	
	PACl 0.4 mg Al/mg DOC + MnO_2 0.6 mg Mn/mg DOC		31	20	

Table S2
NOM removal efficiencies in μGAF systems

Adsorbent applied	Dose	Feedwater	V_{sp} (L/m^2)	DOC removal (%)	UV removal (%)	Reference
Cartridge system						
HAOPs	0.052 mmol/cm^2 as Al	Lake Washington water	1,000	62		[2]
Al(OH)$_3$	0.052 mmol/cm^2 as Al			17		
PAC	3.1 mg/cm^2			29		
PAC over HAOPs				66		
HAOPs over PAC				84		
HAOPs and PAC (two cartridges)				78		
Alum, no HAOPs		Permeate from a pilot-scale MBR	1,000	~0		[3]
No Alum, HAOPs				11	19	
Alum, HAOPs				13	30	
Alum + settling, HAOPs	29 mmol Al/cm^2			22	34	
HAOPs	60.3 g/m^2	Lake Washington water	350	75	81	[4]
HIOPs	60.3 g/m^2			50	56	
PAC	60.3 g/m^2			81	87	
HAOPs	0 g Al/m^2	Lake Washington water	1,000	~5	5	[21]
HAOPs	4.5 g Al/m^2			25	50	
HAOPs	9 g Al/m^2			40	62	
HAOPs	18 g Al/m^2			50	69	
IX resin	40 g/m^2	Lake Washington water	1,000		54	[22]
PAC	40 g/m^2				42	
HAOPs	40 g/m^2				55	
Bare		Lake Union water	1,000		5	[5]
HAOPs size: 7.5 μm	10 g/m^2				60	
HAOPs size: 0.5 μm	10 g/m^2				50	
PAC size: 80 μm	10 g/m^2				28	
PAC size: 1 μm	10 g/m^2				40	
HAOPs size: 0.5 μm	20 g/m^2				60	
HAOPs size: 0.5 μm	40 g/m^2				68	
PAC size: 1 μm	40 g/m^2				50	
PAC size: 1 μm	160 g/m^2				65	
HAOPs at a constant flux of 400 L/h (LMH)	10 g/m^2 as Al	1:2 Lake Pleasant water	900		48	[23]
HAOPs 250 LMH					39	
HAOPs 100 LMH					23	
pH 3					58	
pH 5					60	
pH 7					45	
pH 9					32	
HAOPs	5 mg Al/L	1:3 Lake Pleasant water	1,000	23	UV$_{254}$ 43 UV$_{210}$ 38	[6]
	20 mg Al/L			58	UV$_{254}$ 76 UV$_{210}$ 55	
	100 mg Al/L			55	UV$_{254}$ 85 UV$_{210}$ 77	

(continued)

Table S2 *(Continued)*

Adsorbent applied	Dose	Feedwater	V_{sp} (L/m^2)	DOC removal (%)	UV removal (%)	Reference
HAOPs	10 mg Al	5 mg/L 1:3 dilute LP	600	83	50	[24]
		5 mg/L reconstituted water		81	62	
		5 mg/L HPO		86	57	
		5 mg/L HPI		84	38	
Tubular system						
Raw		Lake Union water	1,000		5	[25]
Alum coagulation	5.6 mg/L Al				45	
HAOPs coagulation	5.6 mg/L Al				60	
HAOPs predeposition					72	
150 LMH to HAOPs unit and 87 LMH to UF					~70	
210 LMH to HAOPs unit and 261 LMH to UF					~70	
210 LMH to HAOPs unit and 400 LMH to UF					~50	

Table S3
Summary of membrane fouling in μGAF processes

Absorbent applied	Dose	Feedwater	Membrane applied	TMP development		Reference
No absorbent		Lake Washington Water	Polyethersulfone membrane nominal pore size of 0.05 μm	Specific volume filtered when TMP reaching 55 kPa, V_{sp} (L/m^2)	1,800	[2]
HAOPs	0.052 mmol/cm^2 as Al^{3+}				4,900	
Al(OH)3	0.052 mmol/cm^2 as Al^{3+}				2,700	
PAC	3.1 mg/cm^2				2,100	
PAC over HAOPs					4,500	
HAOPs over PAC					4,650	
HAOPs + PAC (two cartridges)					4,850	
No Alum, no HAOPs	Alum: 0.3 mM as Al added to MBR permeate HAOPs: 3 mg/cm^2	Permeate from a pilot-scale membrane bioreactor (MBR)	Mixed cellulose esters membrane with a nominal pore size of 0.025 mm	Specific volume filtered when TMP reaching 150 kPa, V_{sp} (L/m^2)	200	[3]
Alum, No HAOPs					220	
No Alum, HAOPs					600	
Alum, HAOPs					1,200	
Alum + settling, HAOPs					1,550	
No absorbent		Lake Washington water	Mixed cellulose esters membrane with a nominal pore size of 0.025 mm	Specific volume filtered when TMP reaching 100 kPa, V_{sp} (L/m^2)	120	[3]
Preadsorbed HAOPs	Absorbent dose: 200 mg/L				Almost no fouling	
Preadsorbed HIOPs					Almost no fouling	
Preadsorbed PAC					400	
No absorbent		Lake Washington water	PES, MP005	Specific volume filtered when TMP reaching 100 kPa, V_{sp} (L/m^2)	1,100	[21]
HAOPs	4.5 g Al/m^2				2,000	
HAOPs	9 g Al/m^2				3,000	
HAOPs	18 g Al/m^2				4,400	

(continued)

Table S3 *(Continued)*

Absorbent applied	Dose	Feedwater	Membrane applied	TMP development		Reference
Bare		Lake Washington water	PES, MP005	Specific volume filtered when TMP reaching 100 kPa, V_{sp} (L/m^2)	550	[22]
IX resin	40 g/m^2				550	
PAC	40 g/m^2				1,800	
HAOPs	40 g/m^2				2,000	
Bare		Lake Union water	PES, MP005	Specific volume filtered when TMP reaching 80 kPa, V_{sp} (L/m^2)	480	[5]
HAOPs 7.5 μm	10 g/m^2				1,600	
HAOPs 0.5 μm	10 g/m^2				1,250	
PAC 80 μm	10 g/m^2				550	
PAC 1 μm	10 g/m^2				1,700	
HAOPs 0.5 μm	20 g/m^2				1,600	
HAOPs 0.5 μm	40 g/m^2				1,800	
PAC 1 μm	40 g/m^2				1,200	
PAC 1 μm	160 g/m^2				2,300	
HAOPs 7.5 μm	10 g/m^2		CA 0.025 μm	Specific volume filtered when TMP reaching 30 kPa, V_{sp} (L/m^2)	550	
HAOPs 7.5 μm	10 g/m^2		PES 0.05 μm		1,280	
HAOPs 7.5 μm	10 g/m^2		Polycarbonate (PC) 1.2 μm		1,220	
HAOPs 7.5 μm	10 g/m^2		PC 3 μm		1,500	
HAOPs 7.5 μm	10 g/m^2		PC 5 μm		2,000	
HAOPs 0.5 μm	10 g/m^2		PES 0.05 μm		980	
HAOPs 0.5 μm	10 g/m^2		PC 5 μm		1,000	
PAC 1 μm	10 g/m^2		PES 0.05 μm		750	
PAC 1 μm	10 g/m^2		PC 5 μm		850	
HAOPs 400 LMH	10 g/m^2 as Al	1:2 Lake Pleasant water	PES, MP005	Specific volume filtered when TMP reaching 50 kPa, V_{sp} (L/m^2)	840	[23]
HAOPs 250 LMH					720	
HAOPs 100 LMH					630	
pH 3				Specific volume filtered when TMP reaching 20 kPa, V_{sp} (L/m^2)	Almost no fouling	
pH 5					1,200	
pH 7					620	
pH 9					440	
HAOPs	10 mg Al	5 mg/L 1:3 dilute LP water	PES, MP005	Specific volume filtered when TMP reaching 20 kPa, V_{sp} (L/m^2)	740	[24]
		5 mg/L reconstituted water			1,240	
		5 mg/L HPO			Almost no fouling	
		5 mg/L HPI				
		5 mg/L TPI				
Tubular system						
Raw		Lake Union water	HAOPs deposited onto 0.2-μm cellular ceramic membranes, then passing through 8-nm PES hollow fibers	Specific volume filtered when TMP reaching 40 kPa, V_{sp} (L/m^2)	1,800	[25]
Alum coagulation	(5.6 mg/L Al)				5,300	
HAOPs coagulation	(5.6 mg/L Al)				6,200	
HAOPs predeposition					20 kPa increase per 22 h	

(continued)

Table S3 *(Continued)*

Absorbent applied	Dose	Feedwater	Membrane applied	TMP development	Reference
HAOPs predeposition	During 11 d of filtration	Lake Union water	HAOPs deposited on the stainless steel mesh, then passing through 8-nm PES hollow fibers	The average TMP increase across the HAOPs unit during a single (1-d) cycle was 5.3 kPa, and was almost fully reversed by hydraulic cleaning. The TMP increase across the downstream UF module was only 7.0 kPa during the entire 11-d experiment	[26]

References

[1] M.M. Zhang, C. Li, M.M. Benjamin, Y.J. Chang, Fouling and natural organic matter removal in adsorben/membrane systems for drinking water treatment, Environ. Sci. Technol., 37 (2003) 1663–1669.

[2] Z.X. Cai, J.S. Kim, M.M. Benjamin, NOM removal by adsorption and membrane filtration using heated aluminum oxide particles, Environ. Sci. Technol., 42 (2008) 619–623.

[3] J. Kim, Q.R. Deng, M.M. Benjamin, Simultaneous removal of phosphorus and foulants in a hybrid coagulation/membrane filtration system, Water Res., 42 (2008) 2017–2024.

[4] J.S. Kim, Z.X. Cai, M.M. Benjamin, Effects of adsorbents on membrane fouling by natural organic matter, J. Membr. Sci., 310 (2008) 356–364.

[5] Z.X. Cai, C. Wee, M.M. Benjamin, Fouling mechanisms in low-pressure membrane filtration in the presence of an adsorbent cake layer, J. Membr. Sci., 433 (2013) 32–38.

[6] L.-F. Wang, M.M. Benjamin, A multi-spectral approach to differentiate the effects of adsorbent pretreatments on the characteristics of NOM and membrane fouling, Water Res., 98 (2016) 56–63.

[7] H.K. Shon, S. Vigneswaran, I.S. Kim, J. Cho, H.H. Ngo, The effect of pretreatment to ultrafiltration of biologically treated sewage effluent: a detailed effluent organic matter (EfOM) characterization, Water Res., 38 (2004) 1933–1939.

[8] M.M. Clark, W.Y. Ahn, X. Li, N. Sternisha, R.L. Riley, Formation of polysulfone colloids for adsorption of natural organic foulants, Langmuir, 21 (2005) 7207–7213.

[9] J.W. Lee, J.I. Chun, H.J. Jung, D.H. Kwak, T. Ramesh, W.G. Shim, H. Moon, Comparative studies on coagulation and adsorption as a pretreatment method for the performance improvement of submerged MF membrane for secondary domestic wastewater treatment, Sep. Sci. Technol., 40 (2005) 2613–2632.

[10] H.K. Shon, S. Vigneswaran, R. Ben Aim, H.H. Ngo, I.S. Kim, J. Cho, Influence of flocculation and adsorption as pretreatment on the fouling of ultrafiltration and nanofiltration membranes: application with biologically treated sewage effluent, Environ. Sci. Technol., 39 (2005) 3864–3871.

[11] R. Fabris, E.K. Lee, C.W.K. Chow, V. Chen, M. Drikas, Pre-treatments to reduce fouling of low pressure micro-filtration (MF) membranes, J. Membr. Sci., 289 (2007) 231–240.

[12] S. Gur-Reznik, I. Katz, C.G. Dosoretz, Removal of dissolved organic matter by granular-activated carbon adsorption as a pretreatment to reverse osmosis of membrane bioreactor effluents, Water Res., 42 (2008) 1595–1605.

[13] X. Cui, K.H. Choo, Granular iron oxide adsorbents to control natural organic matter and membrane fouling in ultrafiltration water treatment, Water Res., 47 (2013) 4227–4237.

[14] D.T. Myat, M. Mergen, O. Zhao, M.B. Stewart, J.D. Orbell, T. Merle, J.-P. Croue, S. Gray, Effect of IX dosing on polypropylene and PVDF membrane fouling control, Water Res., 47 (2013) 3827–3834.

[15] K. Li, F. Qu, H. Liang, S. Shao, Z.-S. Han, H. Chang, X. Du, G. Li, Performance of mesoporous adsorbent resin and powdered activated carbon in mitigating ultrafiltration membrane fouling caused by algal extracellular organic matter, Desalination, 336 (2014) 129–137.

[16] F. Qu, Z. Yan, W. Liu, S. Shao, X. Ren, N. Ren, G. Li, H. Liang, Effects of manganese dioxides on the ultrafiltration membrane fouling by algal extracellular organic matter, Sep. Sci. Technol., 153 (2015) 29–36.

[17] Y. Chen, Y. Tu, Y. Bai, M. Tang, W. Liu, H. Wu, Combined adsorption/ultrafiltration of secondary effluents using powdered zeolites, Chem. Eng. Technol., 39 (2016) 285–292.

[18] D. Metcalfe, P. Jarvis, C. Rockey, S. Judd, Pre-treatment of surface waters for ceramic microfiltration, Sep. Sci. Technol., 163 (2016) 173–180.

[19] H. Wang, Z. Chen, J. Miao, Y. Li, A novel approach for mitigation of membrane fouling: concomitant use of flocculant and magnetic powder, Bioresour. Technol., 209 (2016) 318–325.

[20] Z. Yan, B. Liu, F. Qu, A. Ding, H. Liang, Y. Zhao, G. Li, Control of ultrafiltration membrane fouling caused by algal extracellular organic matter (EOM) using enhanced Al coagulation with permanganate, Sep. Sci. Technol., 172 (2017) 51–58.

[21] J. Kim, Z.X. Cai, M.M. Benjamin, NOM fouling mechanisms in a hybrid adsorption/membrane system, J. Membr. Sci., 349 (2010) 35–43.

[22] Z.X. Cai, M.M. Benjamin, NOM fractionation and fouling of low-pressure membranes in microgranular adsorptive filtration, Environ. Sci. Technol., 45 (2011) 8935–8940.

[23] J. Liu, M.M. Benjamin, Effect of water chemistry and operational conditions on mu GAF process performance, Water Res., 105 (2016) 76–84.

[24] L.-F. Wang, M.M. Benjamin, HAOPs pretreatment to reduce membrane fouling: foulant identification, removal, and interactions, J. Membr. Sci., 515 (2016) 219–229.

[25] B. Malczewska, J. Liu, M.M. Benjamin, Virtual elimination of MF and UF fouling by adsorptive pre-coat filtration, J. Membr. Sci., 479 (2015) 159–164.

[26] B. Malczewska, M.M. Benjamin, Efficacy of hybrid adsorption/membrane pretreatment for low pressure membrane, Water Res., 99 (2016) 263–271.