

Critical Review

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## Pretreatment for Low Pressure Membranes in Water Treatment: A Review

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The application of low pressure membranes (LPMs) to drinking water treatment and wastewater reuse has undergone accelerated development in the past decade. Integration of pretreatment with LPM filtration has been widely employed at full scale to reduce membrane fouling and/or increase the removal of certain aquatic contaminants. In principle, pretreatment of source water can impact membrane filtration in three ways: altering contaminant size distributions, changing mutual affinities of contaminants or their affinities to membrane surfaces, and suppressing undesirable microbial growth or removing biodegradable contaminants. The literature shows that, compared to the well-demonstrated enhancement of contaminant removal, impact of pretreatment to membrane fouling is often small or even negative, which is further complicated by variations in source water quality and membrane properties. Coagulation has been the most successful pretreatment for fouling reduction. Novel technologies are in immediate need for fouling control; ones which rely on a better understanding of the mechanisms of pretreatment and LPM filtration are warranted. This article provides a critical review of the state-of-the-art of pretreatment for LPMs, and discusses potential areas for future technical development and scientific studies.

### 1. Introduction

Membrane filtration is widely used as an industrial separation technology in the filtration of aqueous mixtures. Its application to water treatment has increased dramatically in the past decade (1–4) with the improvement in membrane quality and the decrease in membrane costs. In particular, low pressure membrane (LPM) technology has experienced accelerated growth. As shown in Figure 1, the total installed capacity of LPM systems reached nearly 3,500 million gallons per day (MGD) by the end of 2006. Drinking water treatment and wastewater reuse accounted for 82% of the total capacity (4). As the sustainability of water supply is challenged worldwide, LPM filtration is becoming one of the most important technologies in this century for water treatment due to its superb efficacy in producing a high quality of water, its small footprint, and its relatively low costs (4–6). The overall goal of this paper is to summarize the state of the art with respect to the integration of pretreatment and LPM

filtration for water treatment (drinking water treatment and wastewater reuse). Pretreatment herein refers to different operations or processes that (1) are conducted prior to or upstream of membrane filtration, (2) effectively modify the feedwater quality and properties of certain aquatic constituents, and (3) improve the performance of membranes in filtering natural waters and wastewater effluents. Although mentioned in some cited studies, this review focuses on the impacts of pretreatment on feedwater quality, and does not attempt to systematically address the related impact of membrane materials, geometry, operational modes, and cleaning regimes.

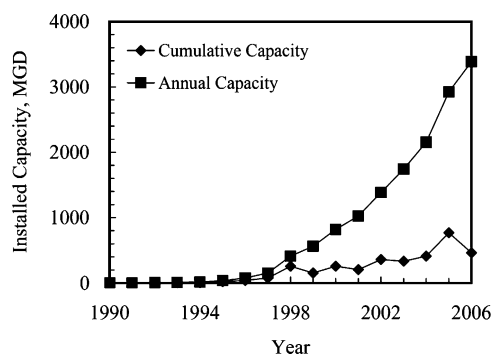
Membranes employed in water treatment are porous or nonporous water-permeable polymeric films or ceramic matrices that are designed to remove aquatic contaminants primarily through size exclusion. Based on the operating transmembrane pressure (TMP), membranes for water-treatment use can be broadly classified as high pressure and low pressure. LPMs are operated at relatively low TMPs (less than 1 to 2 bar, typically), and include microfiltration (MF) membranes and “loose” ultrafiltration (UF) membranes. With pore sizes ranging from approximately 10 to 100 nm, LPMs are effective in removing aquatic substances such as turbidity and pathogens, but not effective for substances such as precursors of disinfection byproduct (DBPs) and organic micropollutants. Upon filtration of natural waters or wastewater effluents, LPMs are subject to loss of membrane permeability as a result of the accumulation of aquatic substances on or inside membrane matrices (7). This phenomenon is termed membrane fouling. Contaminant removal efficiency and fouling resistance comprise the most important aspects of LPM performance; membrane fouling is usually considered the most challenging factor in LPM application.

A very important trend in the development of membrane filtration for water treatment is the integration of different pretreatment strategies to improve the performance of LPMs. When first employed for municipal drinking water in the late 1980s, LPMs were primarily stand-alone processes employed for turbidity and pathogen removal (2, 8, 9). However, pretreatment of the feedwater to LPMs has become more commonly used for two major reasons: (1) enhancement of the removal of aquatic contaminants, such as micropollutants and DBP precursors; and (2) reduction of membrane fouling. Both rationales, in turn, influence the cost and acceptability of membrane use. A 2005 survey of 64 drinking water treatment plants showed that 45 plants,

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**FIGURE 1. Global low pressure membrane installed capacity. Adapted from ref (4) with permission.**

i.e., 70% of the surveyed plants, employed selected types of pretreatment (10).

The major pretreatments employed at full-scale LPM filtration facilities include coagulation, adsorption, oxidation, and media filtration. The impact of coagulation and oxidation, as well as clarification and softening, on LPMs was reviewed by Farahbakhsh et al. in 2004 (11). Since then, important progress has been made in the mechanistic understanding of these processes due to the advances of analytical technology, such as size exclusion chromatography coupled with organic carbon detector (SEC-OCD). Moreover, various chemical and biological processes have emerged as novel pretreatment technologies, and as such, are discussed in this paper.

Three specific objectives of this paper are to (1) introduce the major pretreatment approaches that have been used in conjunction with membrane filtration for full-scale water treatment; (2) discuss current mechanistic findings related to these pretreatments; and (3) describe novel pretreatments currently being studied and their potential application to membrane filtration. This review is organized in four sequential sections: (1) principles of membrane filtration, (2) mechanisms and effects of major pretreatments that have been employed in full-scale applications, (3) advances in other pretreatment processes, and (4) needs for future research.

## 2. Principles of Membrane Filtration

In principle, LPM filtration of natural waters and wastewater effluents may be influenced by different physical, chemical, and biological processes. These processes are often associated with each other, and therefore, have synergetic effects on the performance of membranes used in water treatment.

**2.1. Contaminant Removal.** LPMs may be considered as physical “sieves” with submicron-sized “meshes” for contaminant removal (12). Contaminants are rejected by the membrane if they are too large to enter membrane pores. Additionally, aquatic particles may also be removed by the membrane through repulsive colloidal interactions (13); organic contaminants, such as extracellular cyanotoxins (14) and humic substances (15) can be removed through adsorption to membrane surfaces. However, removals of contaminants smaller than membrane pores are variable depending on membrane properties (e.g., hydrophobicity and surface charge density) and water chemistry, and are less reliable for water treatment than physical sieving.

**2.2. Membrane Fouling.** LPMs may be considered as chemical absorbers for aquatic contaminants of various sizes (16). The identification of organic colloids as major foulants to LPMs (17–23) has been an important advance in the use of LPMs for water treatment. A colloid is conventionally described as “an entity having at least in one direction a dimension of between 1 nm and 1  $\mu$ m” (24); an organic colloid

is thereby referred to as any aquatic organic particles in this size range, including organic macromolecules (e.g., polysaccharide, peptidoglycans, proteins, humic aggregates) and their clusters (e.g., cellular debris) (25, 26).

Organic colloids and other particles removed by LPMs alter membrane pore structure through pore blocking (sealing membrane pore entrances), pore constriction (narrowing membrane pore channels), and/or cake layer formation (buildup of deposit layers outside membrane surfaces) (16, 23, 27), resulting in a decrease in membrane permeability (fouling) and variations in membrane removal efficacy for other aquatic constituents, e.g., viruses (28). The occurrence of different modes of fouling is related to colloid size relative to membrane pore size (16). Colloids close to the size of membrane pores can cause pore blocking, the most severe mode of fouling; those much larger than membrane pores lead to cake formation that is more readily removed.

Colloidal and particulate foulants without affinity to the membrane surface can be removed by hydraulically flushing/backwashing the fouled membranes or scouring membrane fibers with air bubbles; the corresponding fouling removed is termed physically reversible fouling. Foulants with affinity to the membrane surface remain and contribute to physically irreversible fouling that needs to be removed by chemical cleaning; it involves mitigation of the foulant’s affinity through chemical reactions and subsequent release of colloids from the membrane surface (29). Some organic colloids appear to have strong affinities to membrane surfaces, regardless of solution chemistry (23); this makes them particularly important to physically irreversible fouling. Related chemical interactions need to be investigated and identified in order to effectively control fouling. Besides the universal van der Waals interactions and electrostatic interactions, the contributions from other aqueous interactions (e.g., “hydrophobic” interaction and hydration forces) may be important (30).

The operation of LPMs is influenced by algae and bacteria in source waters. Algae and cyanobacteria are important sources of membrane foulants, including organic colloids (20). Babel et al. (31) found membrane fouling varied for algae growing in different seasons under various nutrient and radiation conditions. Spinette (32) found that the fouling of a PVDF membrane varied with algal species and growth phases; for single species, the most severe fouling occurred when algal growth was in the decline phase. Meanwhile, bacteria can adhere and grow on membrane surfaces, which leads to the formation of biologically active, but hydraulically poorly permeable biofilms (33, 34). Biofilm formation on LPMs has rarely been reported for full-scale systems possibly because of the frequent use of chlorine backwash/cleaning. Limited bench-scale studies showed that extracellular products (EPS) released by bacteria governed their adhesion to membrane surfaces and the fouling of LPMs (33, 35).

**2.3. Mechanisms of Pretreatment.** Pretreatments can alter the physical, chemical, and/or biological properties of feedwater and improve the performance of LPMs.

- Physical mechanisms: Pretreatment can increase the size of aquatic substances to the level separable by the LPM or other upstream solid/liquid separation processes (e.g., sedimentation and filtration), thereby enhancing their removals by the integrated membrane system. Size increase also shifts membrane fouling from pore constriction or blocking to cake filtration that is usually less severe and more reversible.
- Chemical mechanisms: Different chemicals (e.g., coagulants, oxidants, and adsorbents) can be added to the feedwater to alter water chemistry and reduce the affinity of foulants to membrane surfaces, thereby alleviating irreversible membrane fouling.
- Biological mechanisms: Pretreatment can remove bio-

**TABLE 1. List of the mechanisms, effects, and applications of major pretreatments for membrane filtration**

pretreatment	coagulation	adsorption	preoxidation	prefiltration
chemicals applied	coagulants (or flocculants) at proper dose	porous or nonporous adsorbents in suspension or fixed contactor	gaseous or liquid oxidants	granular media with/without coagulants, membranes
dose effects	under-, optimal, or overdose (optimal for enhanced coagulation)	minimal effective dose if used as suspended particles	minimal effective dose	none
physical mechanisms	increases the size of aquatic contaminants to filterable level	binds small contaminants to adsorbents much larger than membrane pores	may cause dissociation of organic colloids into smaller sizes or the release of EPS by aquatic organisms	removes coarse materials that may cause cake/gel layer formation on downstream membranes
chemical mechanisms	destabilizes contaminants to cause aggregation or adsorption on coagulant precipitates or membrane surfaces	provides new interfaces to adsorb/accumulate substances detrimental to membrane performance	oxidizes and/or partially decomposes NOM, possible mineralization if VUV used	selectively removes contaminants or other particles that are sticky to filter media and downstream membranes
biological mechanisms	partially removes autochthonous NOM and hinder bacterial growth in feedwater or on membrane	may adsorb organic contaminants relevant to biofouling	suppresses microbial growth	partially removes microorganisms that can cause biofouling
targeted contaminants	viruses, humic/fulvic acids, proteins, polysaccharides with acidic groups, colloids smaller than membrane pores	humic/fulvic acids, small natural organic acids, some DBPs, pesticides and other synthetic organic compounds	viruses and organic contaminants with ozonation	particulate and colloidal organic/inorganic substances, microbiota
effects on membrane fouling	reduces colloidal fouling and NOM fouling	may increase or decrease membrane fouling	may reduce biofouling and NOM fouling	may reduce fouling to different extents
advantages	significantly improves LPM performance (less fouling and greater rejection)	increases the removal of DBPs and DBP precursors	reduces the occurrence of biofouling; increases organic removal (ozonation)	may reduce biofouling, colloidal fouling, and/or solids loading
disadvantages	(i) requires proper dose that can be difficult to meet if feedwater quality varies rapidly/significantly, (ii) may exacerbate fouling, (iii) produce solid wastes, (iv) ineffective in mitigating the fouling by hydrophilic neutral organics	(i) possible exacerbation of LPM fouling, (ii) difficulty in removing PAC powders from treatment facilities	(i) formation of DBPs; (ii) may damage membranes incompatible with oxidants; (iii) may be ineffective in suppressing the growth of some microbiota resistant to oxidation	(i) performance of prefilters may deteriorate and be difficult to recover, (ii) may require pretreatment (e.g., coagulation or preoxidation) to enhance the efficacy

degradable contaminants relevant to membrane fouling or treated-water quality, or disinfect feedwater to reduce biofilm formation.

### 3. Major Pretreatments for Full-Scale Membrane Filtration

In this section, results from bench-scale, pilot-scale, and full-scale studies are presented in order to further elucidate the impacts and implications of major pretreatment processes on LPMs employed in full-scale water treatment. Major mechanisms and effects of these pretreatments are summarized in Table 1, together with the advantages and disadvantages.

**3.1. Coagulation.** Precoagulation is so far the most successful treatment for controlling the fouling of LPMs employed in full-scale water treatment. Two types of coagulants are available in the commercial market: inorganic metal salts and organic macromolecules. Al or Fe salts are probably the most widely employed coagulants for pretreatment. Al and Fe salts, upon addition to water, first react with water to form a series of cationic hydrolytic species and weakly charged or uncharged precipitates (36, 37). Their speciation is strongly pH-dependent. If the coagulation is controlled at neutral pH, effective coagulation of particles occurs through the combination of charge neutralization and “sweep-flocculation”, while the coagulation of negatively charged NOM moieties and viruses (38) is possibly achieved through their adsorption to Al or Fe precipitates or metal-NOM

complexation and precipitation. For drinking water treatment, the optimal dose of Al coagulants required for coagulation of natural waters is often driven by the NOM concentration measured as total organic carbon (39). Poly-aluminium chloride (PACl) and other polymeric inorganic coagulants have slightly different coagulation behavior in water treatment due to the preformation of highly positively charged ion species (40). In comparison, organic macromolecule coagulants/flocculants (mostly polyelectrolytes) are different from inorganic coagulants due to their adsorption behaviors and bridging effects. Related topics have been extensively reviewed by Bolto and Gregory (41). However, the use of organic coagulants in pretreatment for membrane filtration has been less frequently reported in the literature and, therefore, is not discussed here.

**Coagulation–Sedimentation.** Precoagulation for membrane filtration may be operated with or without sedimentation. In the presence of sedimentation, destabilized aquatic colloids and other substances adsorptive to coagulant precipitates are separated from the feedwater prior to membrane filtration. At the so-called “optimal” coagulant dose, most aquatic particles related to water turbidity are effectively removed. These particles include some organic and inorganic colloids that contribute to membrane fouling (42). Therefore, the feedwater after coagulation–sedimentation usually causes less fouling than raw waters. However, the fouling, especially irreversible fouling, may or may not be completely eliminated due to the presence of aquatic

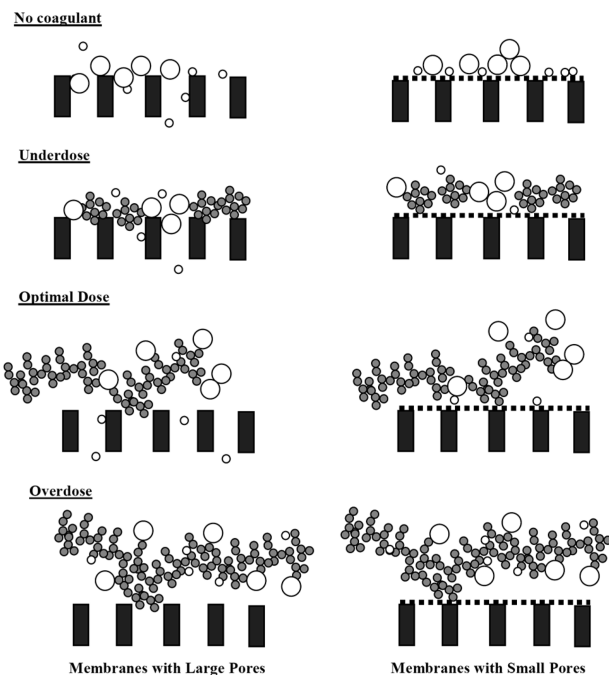
foulants that are not reactive or adsorptive to hydrolytic species formed by coagulants. The nature of these persistent foulants has not been identified yet, but a previous study (43) showed that the operationally defined hydrophilic neutral fraction of an aquatic NOM caused significant fouling on a polypropylene (PP) MF membrane after coagulation pretreatment. This fraction consists of uncharged polymeric substances.

**Inline Coagulation.** Coagulants may be applied “in-line” or in the absence of flocculation/sedimentation in order to reduce the footprint of the entire LPM filtration facility (44). In this case, the coagulated water will directly enter the membrane filtration system. Not only destabilized contaminants or their aggregates, but also coagulant hydrolytes/precipitates may accumulate on the membrane surface. Similar to model particles (16), fouling is expected to be important if these materials have strong affinity to the membrane surface and are of a size suitable to block membrane pores. This adverse impact may be alleviated by decreasing the membrane pore size to increase cake formation or selecting membrane materials to reduce particle affinity to the membrane surface. The decreased fouling of UF membranes as compared to MF membranes was observed by Howe et al. (42) after pre-coagulation. Tran et al. (45) found that alum added at a dose for effective DOC removal reduced the fouling of a PVDF MF membrane by a high-DOC water, while a slight increase in fouling was observed for a PP MF membrane; the results are indicative of the impact of membrane material on the fouling effect of inline coagulation.

**Dosing Effects.** Proper dosing of coagulant needs to be determined for optimized operation of coagulation–membrane filtration systems. From the standpoint of enhancing removal of DBP precursors, the optimal dose for DOC removal or “overdose” for turbidity removal is usually favorable. The proper dosing for fouling reduction is, however, more complex. As illustrated in Figure 2, underdosing of coagulant results in the formation of fine flocs that are poorly settleable. These flocs have sizes close to the pore sizes of MF membranes, but much greater than those of UF membranes. If the affinity of the flocs to the membrane surface is similar, then these flocs are more effective in causing pore blocking on MF membranes than on UF membranes. In comparison, under an optimal dose scenario, settleable flocs are formed, and their sizes are much greater than the pores of MF and UF membranes. If inline coagulation is adopted, cake layer formation becomes the dominant mode of membrane fouling. This results in significant decrease in the fouling of LPMs due to the elimination of the pore blocking mode of fouling. For inorganic coagulant applied under controlled pH conditions, overdosing of coagulant usually improves the removal of aquatic NOM and, to a minor extent, settleability of flocs (indicative of floc sizes), further reducing the occurrence of pore-blocking/constriction. Howe et al. (42) found that an overdose condition persistently resulted in less fouling of MF membranes by natural waters, while coagulant dose did not affect the fouling of UF membranes employed in the study.

The effects of coagulant dose on membrane fouling are related to the properties of coagulants (45–47) and the type of LPM (45, 48). The cost-effective coagulant doses reported in the literature for membrane fouling reduction can be different from the optimal doses for conventional water treatment. Therefore, bench-scale or pilot-scale tests are often necessary in order to determine the effects of coagulant dose on a particular source water and membrane of interest.

**3.2. Adsorption.** Adsorption herein refers specifically to the use of adsorbents prior to LPMs as suspended powders or fixed adsorbent contactors. These adsorbents have relatively large specific surface areas due to their high dispersity or porosity. As a result, the surfaces of adsorbents



**FIGURE 2.** Diagram of the mechanisms of inline pre-coagulation–membrane filtration of natural waters. Small and large open circles represent small and large aquatic contaminants, respectively, filled circles represent coagulant precipitates, and black rectangles and dotted lines represent membrane structures. A diagram for coagulation–sedimentation pretreatment would be similar except that contaminants attaching to each other or to coagulant precipitates to form settleable flocs at optimal or overdoses are removed prior to membrane filtration.

are thermodynamically unstable and have a tendency to uptake certain substances (including humic substances and micropollutants with sizes not more than a few nm) from water. This is favorable to LPMs as they poorly remove these small substances (49). Some novel adsorbents have also been prepared to remove foulants to LPMs.

**Activated Carbon.** The most intensively studied adsorbent for LPM filtration is powdered activated carbon (PAC). The efficacy of PAC in removing organic contaminants is strongly dependent on PAC type (50), dose, properties of the organics (51), and the competition of other aquatic constituents (52). PAC may also remove inorganic contaminants, such as arsenic (53). However, Lin et al. (54) found that a high molecular weight NOM fraction (6.5 to 22.2 kDa) that exerted the greatest fouling on a hydrophobic PS membrane was not removed by PAC adsorption. Overall, the impact of PAC on membrane fouling is less pronounced and sometimes adverse. Mozia et al. (55) reported that the addition of PAC increased the fouling of a regenerated cellulose UF membrane with and without preozonation. Zhao et al. (56) had a similar observation in a study of a ceramic MF membrane; they speculated that the increase in membrane fouling was due to association and plugging of aquatic colloids in PAC cakes. Therefore, under certain conditions, PAC pretreatment may not be a suitable measure for fouling control in full-scale LPM systems.

Two opposite measures have been conducted to improve the performance of integrated PAC adsorption–LPM filtration systems. An increase of activated carbon size to granular levels was found in a model study to provide better system economy by more efficiently utilizing the adsorption capacity of activated carbon (57). Granular activated carbon (GAC) filters have been integrated with LPM filtration in pilot-scale testing (58, 59). Tsujimoto et al. (58) found that GAC prefiltration/adsorption effectively reduced irreversible foul-

ing of some UF membranes treating a natural surface water. This may have been related to biological processes that occurred in GAC filters and the resulting degradation of organic foulants (60). Additional studies are needed to validate the effects of GAC pretreatment on membrane fouling and investigate the related mechanisms. In comparison, Matsui and co-workers developed submicron-size PAC for LPM filtration (61–63). The decrease in adsorbent size enhanced the adsorption kinetics of dissolved organics, thereby eliminating the need for an inline contactor in the integrated system; a reduction in PAC dose was also observed.

**Adsorbents for Fouling Reduction.** Different types of adsorbents for LPMs have been synthesized for the purpose of fouling control and tested at bench scale. Benjamin and co-workers (64–68) evaluated heated aluminum oxide particles (HAOPs) and heated iron oxide particles (HIOPs) and found that HIOPs and HAOPs reduced NOM fouling of a flat-sheet LPM. Due to the lack of data with respect to size fractionation of the feedwater NOM, it is unclear if the decrease in membrane fouling was related to the removal of organic colloids. Inspection of the cake layers formed on the surface of a PS UF membrane showed that PAC or silica particles were linked to each other and the membrane surface to form less permeable cakes, while HIOPs were linked to each other but only weakly to the membrane surface. These phenomena were considered to result in decreased fouling with HIOPs and increased fouling with PAC and silica (65). Practically, HAOPs can be predeposited on the membrane surface to form a fouling-resistant layer (66) or combined with precoagulation to simultaneously reduce fouling and remove ortho-phosphate for LPMs employed in wastewater reclamation (68).

Clark et al. synthesized PS colloids for membrane fouling control (69). Koh et al. (70) studied the fouling of a 20 kDa UF membrane by two natural lake waters with the addition of 5–100 mg/L of the PS colloids. The results showed significant decrease in membrane fouling after the addition of the PS colloids. Size fractionation of the feedwater NOM revealed that PS colloids specifically removed a fraction of NOM that had an apparent molecular size of 20–200 kDa. In this case, PS particles themselves appeared not to cause noticeable fouling at concentrations as high as 100 mg/L.

**3.3. Preoxidation.** At oxidant doses practical for pretreatment, previous studies of conventional water treatment have demonstrated that chlorine and permanganate can be added to the feedwater to suppress the growth of microorganisms and maintain oxidative conditions in the water; ozone can partially oxidize NOM and increase assimilable organic carbon (AOC) that may be removed by downstream biological filters (71). The presence of low levels of ozone may also improve the removal of organic or organic-coated particles by coagulation and filtration, which indicates a change to the stability or reactivity of aquatic particles with respect to coagulation or deposition (72, 73). Preoxidation using low doses of ozone has also been found to alter the size distribution of effluent organic matter, and hence, their contribution to membrane fouling (74). Chemical compatibility of some commercially available polymeric LPMs with various oxidants was summarized by Farahbakhsh et al. (11). Most polymeric LPMs are not compatible with ozone, which explains why ceramic membranes were often used in the cited studies.

**Contaminant Removal.** Preoxidation can enhance the removal of aquatic contaminants by membrane filtration. Vos et al. (75) found that, with the addition of  $\text{KMnO}_4$ , the concentration of manganese in the permeate of a pilot-scale UF system decreased from 0.16–0.19 mg/L to below the targeted 0.05 mg/L, as a result of oxidation and precipitation of soluble Mn species. The corresponding effects on membrane fouling were not reported. Schlichter et al. (76) found

that preoxidation lowered the TOC in the permeate of ceramic membranes to below detectable levels during treatment of a river water. Mozia et al. (55) also reported that preoxidation resulted in 96% removal of TOC and complete removal of  $\text{UV}_{254}$  absorbance. However, a disadvantage of preoxidation is the formation of oxidation byproduct that cannot be removed by the membrane. Karnik et al. (77) proposed the use of iron oxide nanoparticles to coat ceramic membranes in order to increase the removal of NOM and decrease the formation of aldehydes, ketones, and ketoacids formed by preoxidation. More than 50% reductions of these compounds were obtained.

**Fouling Reduction.** Preoxidation has been found to be effective in reducing organic fouling of LPMs; ozone seems to be a promising preoxidant for this purpose as found in several studies (76, 78, 79). A recent pilot-scale study also showed that a combination of 0.5 mg/L of permanganate and 1 mg/L of chlorine significantly reduced the fouling of a UF membrane in an integrated coagulation–UF system during the treatment of a reservoir water impaired by algae (80). Ozone can be further combined with biological activated carbon filter as pretreatment for LPM systems. A full-scale system employing this process has been under construction as an expansion of an existing conventional water treatment facility that will have a capacity of 363 ML/d (81). The presence of inorganic metal species in the feedwater may adversely influence the efficacy of preoxidation. Schlichter et al. (82) found that preoxidation did not reduce the fouling of ceramic membranes by clay minerals. Chae et al. (83) found that prechlorination caused precipitation of Fe and Mn species on the surface of two PVDF LPMs; this precipitation was possibly related to more severe fouling observed in the study.

**3.4. Prefiltration.** As a pretreatment technology, prefiltration involves the use of packed bed filters or other membranes as preliminary barriers to remove feedwater particles that are detrimental to the performance of the primary LPM filtration. In principle, the mechanism of the removal can be either physical sieving or chemical adsorption/deposition. Compared to adsorption pretreatment, prefiltration targets aquatic particles that are relevant to water quality. Strainers with pore size ratings on the order of dozens of microns are sometimes employed prior to LPMs in pilot-scale or household LPM filters to reduce membrane solid loadings. However, application of prefiltration is not limited to these strainers and regeneration capability is important to practice.

**Membrane Prefiltration.** Due to the presence of favorable interactions, hydrophobic LPMs with coarse pore matrices are effective chemical “adsorbers” of organic foulants (23); this makes it possible to adopt these membranes to remove potential foulants to the primary LPMs. Koh et al. studied the effects of prefiltration by a PP MF membrane on the fouling of a PES UF membrane (84). The fouling of the UF membrane was significantly reduced after the prefiltration as a result of adsorption of a small fraction of NOM. To use hydrophobic membrane prefiltration to control the fouling of primary membranes for water treatment, cost-effective measures need to be developed to restore their removal capacities. A similar problem exists for strainer-type prefiltration commonly adopted in LPM systems.

**Granular Media Prefiltration.** Conventional packed-bed filters employed in water treatment are advantageous from the standpoint of regeneration because hydraulic backwashing has proven in conventional water treatment to be effective in restoring their capacity. Given proper physicochemical conditions, granular media filters are effective in capturing particles much greater than a few  $\mu\text{m}$  or smaller than 0.1  $\mu\text{m}$  (85). The removal of particles larger than membrane pore sizes can reduce the surface fouling of LPMs (86), and thereby extend their filtration cycle. The removal of small particles

may reduce internal membrane fouling. However, due to the difference in the surface composition of media filters (e.g., silica) and polymeric membranes, aquatic materials adherent to membrane surfaces may pass through media prefiltration and cause irreversible membrane fouling. This possibly explains why a secondary effluent employed in a previous study (22, 87) caused significant fouling on several PES and PVDF membranes after pretreatment with sand filters.

**Other Prefiltration.** Other materials have also been employed as filter media to pretreat the feedwater for LPMs as reported in the literature, e.g., fabric cloth (88), stainless steel, carbon steel, and string-wound polyester (89). A more perspicuous understanding of the interactions between aquatic particles and these materials is warranted in order to optimize the selection and operation of prefiltration for LPMs. This need represents a new frontier for the application of colloid and interface science to environmental engineering.

## 4. Development of Pretreatment for Membrane Filtration

**4.1. Feedwater Pretreatment.** In addition to coagulation, adsorption, prefiltration, and oxidation, other pretreatments have also been studied. Some have been employed in limited full-scale applications. For example, Braghetta et al. studied the effect of dissolved air flotation (DAF) on the performance of MF membranes (90); it was found that DAF pretreatment resulted in longer MF runs, possibly due to the reduction in membrane pore blocking. Meanwhile, the addition of metal oxides to the feedwater during DAF pretreatment may enhance the removal of aquatic contaminants through the integrated adsorptive flotation and membrane filtration process (91).

Integration of biological pretreatment and LPM filtration has drawn increasing attention in the past few years but mostly for wastewater treatment instead of drinking water treatment. Wend et al. (60) found that the fouling of a MF membrane was significantly reduced when the humic-laden feedwater was pretreated through biological filters (GAC or iron oxide coated sand). Tian et al. (92) used biological treatment prior to a polyvinyl chloride (PVC) UF membrane to treat a simulated sewage-contaminated surface water. Addition of PACl coagulant to the bioreactor resulted in greater removals of TOC, UV<sub>254</sub> absorbance, and phosphorus while assimilable organics were mostly removed by biodegradation. Additional studies in this regard are necessary to better assess the physical and chemical effects of biological pretreatment on membrane performance. Investigations of biological pretreatment to reduce the use of chemical reagents for feedwater pretreatment are also warranted.

Application of magnetic ion-exchange resin (MIEX) resin to membrane filtration has been studied at different scales in the past few years (93–95). This magnetic resin has a polyacrylic structure and is very effective in uptaking anionic substances in natural waters through anion exchange (96). The subsequent removal of the magnetically agglomerated resin beads provides effective separation of the adsorbed contaminants from the treated water. Therefore, substantial amounts of negatively charged inorganic substances and natural organic matter in the feedwater, including bromide, small acids, and humic/fulvic acids can be removed by this process (93, 94, 97–99). The removal of bromide is an advantage of MIEX pretreatment over aforementioned other techniques; as such, it is plausible for the control of the formation of brominated DBPs. The effects of MIEX resin on membrane fouling are still undetermined. For example, increased NOM removal and decreased fouling of UF membranes were observed by Kabsch-Korbutowicz et al. (100). A recent study showed that pretreatment (including MIEX) that removes organic colloids reduced the fouling of a LPM, while pretreatment that removed most DOC but not

organic colloids did not (101). However, a bench-scale study of different natural waters showed that MIEX was able to remove organic colloids in some but not all waters; this variability probably resulted in variations of membrane fouling reduction observed for these waters (18). Additional LPM fouling studies are necessary to obtain a comprehensive understanding of the interactions between MIEX resin and aquatic contaminants.

The integration of photocatalytic oxidation (PCO) is another option to improve the removal of organic contaminants by membrane filtration. For example, Fu et al. (102) developed a submerged membrane photocatalysis reactor (SMPR) that was effective in removing fulvic acids with TiO<sub>2</sub> as the catalyst. A recent study (103) also showed that, by pretreating a synthetic water containing Suwannee River NOM with 0.5 g/L of TiO<sub>2</sub> under UV light for 20 min, the fouling of a MF and a UF membrane was reduced significantly. The decrease in membrane fouling was coincident with the decrease in a high molecular weight NOM fraction. Application of this technology to full-scale water treatment is still premature due to insufficient knowledge with respect to the oxidation of organic contaminants in their natural states as well as due to other related technical issues.

### 4.2. Integration of Multiple Pretreatment Technologies.

As discussed previously, different pretreatment technologies often preferentially remove certain types of aquatic contaminants or have different effects on membrane fouling. It is, therefore, reasonable to consider proper integration of multiple pretreatments and combine the benefits of each separate pretreatment. Major pretreatments employed by large-scale LPM systems often involve multiple upstream treatment processes, e.g., coagulation–filtration. There has been recent increased interest in this area. Related pretreatments include adsorption–flocculation (104, 105), ozonation–GAC filtration (106), electrocoagulation–flotation (107), and ion exchange–coagulation (108). In general, integration of multiple pretreatments may increase the capital costs of the system, but the operational costs may decrease if membrane fouling can be effectively reduced by the integration. If the total costs increase, it may still be acceptable for agencies that have source waters with very poor qualities, as it may be otherwise impossible to effectively control membrane fouling and meet the desired effluent quality.

## 5. Research Needs

Despite the encouraging bench-scale results and promising full-scale data discussed above, additional studies are needed to address pretreatment technologies for LPMs employed in water treatment. This research may be broadly classified in three major areas: prediction, assessment, and new technology.

Prediction is based upon a high-level understanding of the outcomes of each pretreatment for individual membrane filtration systems. It relies on sufficient knowledge of the mechanisms of membrane filtration and the properties of aquatic contaminants. Considerable research is still needed to achieve this goal, particularly from the perspective of membrane fouling. However, identification of the role of organic colloids has shed light on the mechanistic aspects of LPM filtration and pretreatment technologies. From the standpoint of full-scale application, coagulation has yielded the most predictable and promising results as compared to the others.

Due to the insufficient predictability of membrane fouling, assessment is important to the development and application of pretreatment for LPMs. Research is needed in this aspect to link bench- and large-scale assessment of LPMs. As such, less field work will be needed to evaluate the performance of integrated LPM systems.

Finally, future research is needed to pursue new pretreatment technologies that can improve the quality of treated

water from membrane filtration, and more importantly, that can control membrane fouling in a cost-effective and environmentally friendly (e.g., few or reusable chemicals, less secondary pollution) manner. This is important to the viability of LPMs employed in municipal water treatment and water supply for individual households and small communities.

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