

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/10773324>

# Fouling and Natural Organic Matter Removal in Adsorbent/Membrane Systems for Drinking Water Treatment

ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · MAY 2003

Impact Factor: 5.33 · DOI: 10.1021/es0260418 · Source: PubMed

---

CITATIONS

100

---

READS

147

4 AUTHORS, INCLUDING:



**Mark M. Benjamin**

University of Washington Seattle

100 PUBLICATIONS 4,256 CITATIONS

SEE PROFILE



**Yujung Chang**

University of Washington Seattle

8 PUBLICATIONS 204 CITATIONS

SEE PROFILE

# Fouling and Natural Organic Matter Removal in Adsorbent/Membrane Systems for Drinking Water Treatment

MIAOMIAO ZHANG,<sup>†</sup> CHUN LI,  
MARK M. BENJAMIN,\* AND  
YUJUNG CHANG<sup>‡</sup>

Department of Civil and Environmental Engineering,  
University of Washington, Seattle, Washington 98195-2700

Adsorbent particles added to ultrafiltration (UF) systems treating drinking water can remove natural organic matter (NOM) and some other contaminants from the water, but their effect on membrane fouling is inconsistent—in some cases, fouling is reduced, and in others, it is exacerbated. This research investigated the behavior of UF systems to which powdered activated carbon (PAC), heated iron oxide particles (HIOPs), or (nonadsorbent) SiO<sub>2</sub> particles were added. On a mass basis, the PAC removed the most NOM from solution, the HIOPs removed less, and the SiO<sub>2</sub> removed essentially none. However, in the case of both PAC and SiO<sub>2</sub>, increasing the dose of solids led to a steady increase in fouling, whereas the opposite trend applied when HIOPs were added. In the absence of NOM, none of the solids fouled the membrane significantly. Thus, even though NOM is a causative agent for fouling, removing it from solution does not necessarily reduce fouling; the mechanism of removal can be just as important as the absolute amount removed, if the removal occurs in a cake layer near the membrane surface. Scanning electron microscopy images of the cake layers formed in the three systems suggest that the NOM binds PAC or SiO<sub>2</sub> particles to one another and to the membrane surface, so that the particles become part of the foulant in the system. By contrast, the NOM appears to bind HIOPs to one another but not to the membrane. This process leaves enough pore space in the cake layer for water to reach the membrane with minimal resistance, and it reduces the tendency for either the NOM or the HIOPs to foul the membrane surface.

## Introduction

Microfiltration (MF) and ultrafiltration (UF) membranes can remove most particulate and colloidal matter (including microorganisms) from natural waters, but they are not very effective at removing natural organic matter (NOM). Furthermore, NOM is often implicated as a major foulant of membrane systems (1–3). Although such fouling is well-documented, the fouling mechanism is incompletely understood. Evidence for at least three mechanisms exists—the NOM might adsorb in the membrane pores and narrow or

block the passageways available to the water, it might block access to the pores by forming a separate gel layer on the membrane surface, or in cases where both NOM and particles are present, it might bind particles together to form a low permeability particle/NOM layer on the membrane surface.

Methods that have been used to reduce NOM fouling include frequent backwashing (4–7) and application of advanced pretreatment processes (2, 8–10). In some cases, fouling can be reduced by adding particles that remove the foulants upstream of or directly in the membrane system (11–16). For instance, Adham et al. (11) reported that addition of 25 mg/L powdered activated carbon (PAC) to systems treating a groundwater with ~3 mg/L DOC reduced the rate of membrane fouling by approximately one-third.

Although adsorption presumably reduces the potential for direct fouling of the membrane by NOM in all such systems, the overall effect on fouling cannot be predicted since the adsorbent particles with bound NOM might foul the membrane even more severely than the NOM alone. For instance, the presence of freshly precipitated aluminum hydroxide (Al(OH)<sub>3</sub>) or ferrihydrite (Fe(OH)<sub>3</sub>) in the feed to a membrane system can exacerbate fouling dramatically (8), whereas the presence of more crystalline materials often impedes fouling (16–19). One interpretation of these results is that the freshly precipitated hydroxides form gel layers at the membrane surface and that, when the membrane system is pressurized, the gels become compressed and distorted and thereby block the pores on the membrane surface.

However, even rigid particles can exacerbate fouling by NOM in some cases. For instance, in a pilot PAC/UF system treating a low-quality surface water, when the fouling rate in the system increased unexpectedly (apparently because of a change in influent water quality), increasing the PAC dose increased the fouling rate further (13). Similarly, the fouling of a UF membrane treating a synthetic water containing a commercial humic acid was exacerbated by the addition of PAC to the system even though the PAC removed a substantial fraction of the DOC (15). Scanning electron microscope (SEM) images of the fouling layer showed PAC particles embedded in a continuous film of the organics. Recently, Schäfer et al. (20) reported that addition of ferric chloride to solutions containing humic acids can dramatically increase the fouling of microfilters and ultrafilters.

Chang and co-workers (17, 21) reported that, like PAC, heated iron oxide particles (HIOPs) can remove NOM from natural water, and they also reduce membrane fouling substantially in integrated HIOPs/UF systems. In those studies, SEM images before and after backwashing suggested that, in the absence of HIOPs, UF membranes were fouled by the formation of an NOM gel on the membrane surface. In the presence of HIOPs, the NOM gel layer was less likely to form (because some of the NOM sorbs), and when it did form, it formed on the surface of the HIOPs rather than on the membrane. Then, when the system was backwashed, the gel layer was flushed out of the system along with the HIOPs, leaving an essentially clean membrane for the next treatment cycle.

The studies cited above have shown that integrated adsorption/membrane processes are a promising technology for drinking water treatment. However, our understanding of the interactions among the various constituents (membrane, NOM, and adsorbent particles) in the complex system and of the effect of each constituent on system performance is very incomplete. The current research was undertaken to explore the performance of three adsorbent/membrane processes and the mechanisms of fouling in those systems.

\* Corresponding author phone: (206)543-7645; fax: (206)685-9185; e-mail: markbenj@u.washington.edu.

<sup>†</sup> CH2M-Hill, Bellevue, Washington 98004.

<sup>‡</sup> HDR Engineering, Inc., Bellevue, Washington, 98155.

TABLE 1. Some Physical/Chemical Characteristics of the Particles Used in This Study<sup>a</sup>

	particle size ( $\mu\text{m}$ )	density ( $\text{g}/\text{cm}^3$ )	specific surface area ( $\text{m}^2/\text{g}$ )	volume-avg diameter ( $\mu\text{m}$ )		$\zeta$ -potential (mV)	
				DI water	LW water	DI water	LW water
HIOPs	0.5–50; mostly 2–5	2.7	3.2	2.31	6.55	32.6	11.9
PAC	1–80	1.34	800	5.81	9.22	–31.8	–13.3
SiO <sub>2</sub>	0.5–10; mostly 1–5	2.27	2.02	2.74	2.9	–43.7	–24.5

<sup>a</sup> Complete particle size distributions for all the samples are provided in the Supporting Information.

## Materials and Methods

**Reagents.** All chemicals were of reagent quality. High-purity water was used to prepare stock solutions and as dilution water. Water samples were collected from Lake Washington (LW) at a dock adjacent to the University of Washington in Seattle, WA, and were filtered through a 75- $\mu\text{m}$  sieve and a 0.45- $\mu\text{m}$  membrane (Millipore) immediately after sampling. They were then stored at 4 °C. The water had a pH between 6.5 and 7.0 and contained approximately 15 mg/L Ca<sup>2+</sup>. The DOC concentration and UV absorbance at 254 nm (UV<sub>254</sub>) of the samples were in the ranges 3.5–5.5 mg/L and 0.07–0.13 cm<sup>–1</sup>, respectively, with typical values of 4.0 mg/L and 0.09 cm<sup>–1</sup>.

HIOPs were generated in the laboratory by neutralizing 3.9 M FeCl<sub>3</sub> to pH 7.0  $\pm$  0.1 with 10 N NaOH and then heating the resulting slurry of hydrous iron oxide particles at 110 °C for 1 h. The heating step generated a thick suspension of HIOPs beneath a crust of NaCl crystals. After the NaCl was scraped off, the HIOPs were diluted into clean water and used in experiments. PAC and amorphous silica (SiO<sub>2</sub>) solids were purchased and used without pretreatment. [PAC was from Integra Chemical Company (Renton, WA); SiO<sub>2</sub> was from Sigma Chemical Corporation (St. Louis MO).] Some properties of all the particles investigated are shown in Table 1.

The UF membranes used in the experiments were polysulfone hollow fibers (model PM 100-43, Koch Membrane Systems, Inc., Wilmington, MA) with an i.d. of 1.1 mm, a wall thickness of 0.4 mm, and a nominal molecular weight cutoff (MWCO) of 100 000.

**Adsorption Tests.** The kinetics of NOM sorption to HIOPs and the equilibrium adsorption of NOM by different solids were studied in batch experiments. In these tests, HIOPs, PAC, or SiO<sub>2</sub> particles were added to 45 mL of LW water adjusted to pH 7.0. The samples were mixed on a laboratory shaker for up to 24 h, filtered through 0.45- $\mu\text{m}$  membrane filters, and analyzed for UV<sub>254</sub> and DOC concentration.

**Membrane System Operation.** All tests of the UF system used a single-fiber membrane module with inside-to-outside flow, similar to those described by Chang and Benjamin (17). Each test consisted of a few dozen to several hundred three-step cycles, with each cycle consisting of a 2-min step during which a concentrated slurry of the particles was fed to the system, a 56-min step during which LW water was fed to the system, and a 2-min backwashing and flushing step. During the treatment step, the permeate flux was 100 L m<sup>–2</sup> h<sup>–1</sup>. The backwash pressure was 140 kPa, and the backwash water contained 5 mg/L free chlorine (as Cl<sub>2</sub>). Throughout the cycle, the cross-flow velocity was 1 m/s. The transmembrane pressure (TMP) required to maintain the desired flux was used as the indicator of system fouling. Dissolved organic

carbon (DOC) concentration and UV<sub>254</sub> were used as measures of NOM concentration. At preselected times during a test, a 2-cm length at the end of the membrane fiber was frozen and cut, and its surface (including any foulant or particles that had accumulated) was examined by SEM. The cut end of the module was then reconnected, and the operation was resumed.

A new membrane was used for each test (i.e., each dose of each adsorbent). Prior tests (17) demonstrated the reproducibility of experimental results with different membrane fibers and before and after sections of the membrane were cut from a single fiber. The consistent trends that were obtained in experiments with different adsorbent doses reinforce the reliability of the observations.

**Analyses.** DOC concentrations were analyzed using an OI model 700 carbon analyzer, and UV<sub>254</sub> was measured with a Hach DR/4000U spectrophotometer with a 1-cm quartz cell. A Horiba model CAPA-500 centrifugal particle size analyzer was used to characterize particle size distributions, and a Rank Brothers Mark II microelectrophoresis apparatus was used to evaluate the  $\zeta$ -potential of the test particles.

The material accumulated on the membrane surfaces was prepared for SEM analysis using procedures described by Kim et al. (22). After being rinsed with deionized water, samples were immersed in 3% glutaraldehyde and 25 mM sodium phosphate buffer (pH 7.2) for 15 min. This fixation process minimizes deformation of the organics during the subsequent drying process. The samples were then cut into smaller pieces, immobilized on Al specimen mounts using Ag paste, and dried under ambient conditions for 24 h. Finally, they were coated with 2 nm of Au/Pd alloy using a Hummer II sputter coater operating at a current of 20 mA for 2 min, before being observed through a high-resolution, low-damage field emission scanning electron microscope (JSM 6300 F).

## Results and Discussion

**Sorption of NOM onto the Test Solids.** Sorption of NOM onto HIOPs in a batch system reached equilibrium within 15 min, suggesting that the NOM binding is almost entirely on the exterior surface of the particles. In the membrane systems investigated subsequently, the liquid residence time was ~13 min. The influent and a portion of the HIOPs circulated through the system on the feed side of the membrane, and this suspension was presumably mixed well enough to avoid any significant limitations on transport of NOM molecules to the surface of the particles. The remaining HIOPs formed a cake layer on the membrane surface, and the solution had to pass through that cake layer to reach the membrane. Given the close packing of the particles in the cake layer, molecules would have to travel only a very short distance to come into contact with a particle, so a transport limitation in that part of the system is considered unlikely as well. As a result, sorption was expected to closely approach equilibrium in all of the systems investigated.

In batch experiments with a 24-h equilibration time, NOM sorption onto the HIOPs and PAC increased significantly as the adsorbent dose was increased from 0 to 50 mg/L (Figure 1). PAC consistently removed more NOM than did HIOPs at comparable mass doses, and it also reached a higher maximum NOM removal efficiency. SiO<sub>2</sub> had almost no NOM removal capacity, even at very high doses of SiO<sub>2</sub> particles.

**Fouling and NOM Removal in Particle/UF Systems.** Prior research (17, 21) had indicated that the addition of HIOPs to a cellulose acetate UF membrane can reduce fouling dramatically. To assess whether a similar phenomenon applied to the polysulfone membrane and to distinguish the physical effects of particle addition from the effect of removing NOM from the solution contacting the membrane,

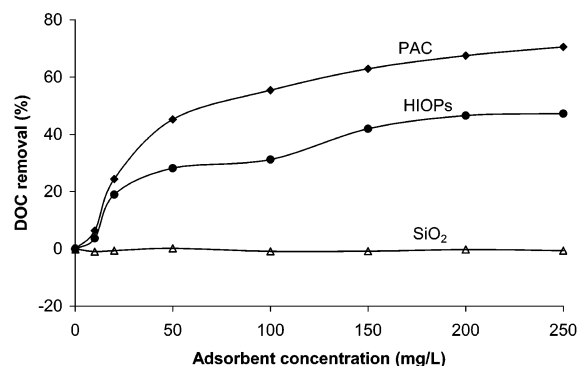


FIGURE 1. Sorption of NOM from Lake Washington (LW) onto HIOPs, PAC, and  $\text{SiO}_2$  in batch tests. HIOPs concentration expressed as Fe. Initial DOC = 5.9 mg/L, initial  $\text{UV}_{254}$  = 0.12  $\text{cm}^{-1}$ . Samples were prefiltered (0.22  $\mu\text{m}$ ) prior to the tests.

experiments were conducted in which HIOPs, PAC, or  $\text{SiO}_2$  particles were introduced into the hollow fiber prior to the feed solution. The TMP profiles for systems with a range of particle doses are shown in Figure 2, and the corresponding data for NOM removal are summarized in Table 2.

The different particles had dramatically different effects on membrane fouling: whereas the HIOPs delayed the onset of fouling substantially, as it had in previous studies; PAC or  $\text{SiO}_2$  particles accelerated membrane fouling. Furthermore, in each case, the magnitude of the effect increased steadily as the particle dose increased. Taken together, these results strongly suggest that the interaction of HIOPs with foulants and/or the membranes in these systems is fundamentally different from and more favorable than that of PAC or of nonadsorbent particles such as  $\text{SiO}_2$ .

Although the TMP results reinforce the previous findings regarding the anti-fouling benefits of HIOPs, fouling nevertheless became very severe after relatively short operational times in all the tests. This phenomenon was unexpected because many membrane systems have been tested without HIOPs addition under field conditions and have performed better for far longer than the time-to-failure in our tests. Therefore, results obtained with the single fiber modules cannot be extrapolated directly to predict run time or TMPs in pilot- or full-scale systems. That caveat notwithstanding, the results are internally consistent and were reproducible in multiple runs. As a result, systems operated under different conditions in this research can be reliably compared with one another, and the trends they display might be expected to apply in at least some larger systems.

**Structure of the Cake Layer and Possible Mechanisms for Fouling Reduction by HIOPs.** The different effects of HIOPs, PAC, and  $\text{SiO}_2$  particles on membrane fouling might, in theory, be driven by differences in membrane/NOM, membrane/particle, or particle/NOM interactions in the different systems, or they might depend on three-way interactions among all three system components. If the different rates of fouling were caused primarily by differences in membrane/NOM interactions, then decreasing the NOM concentration in the solution contacting and passing through the membranes would be expected to decrease fouling consistently. However, in the PAC/UF systems, increasing the PAC concentration and thereby decreasing the dissolved NOM concentration led to an increase in the fouling rate. Furthermore, the NOM concentration was approximately equal in the experiments with 150 mg/L HIOPs and 40 mg/L PAC, and in both those systems it was substantially lower than in the systems with  $\text{SiO}_2$ , yet the relative degrees of fouling did not correspond to these differences at all. Therefore, several lines of reasoning lead to the conclusion that the different behaviors of the particles tested cannot be

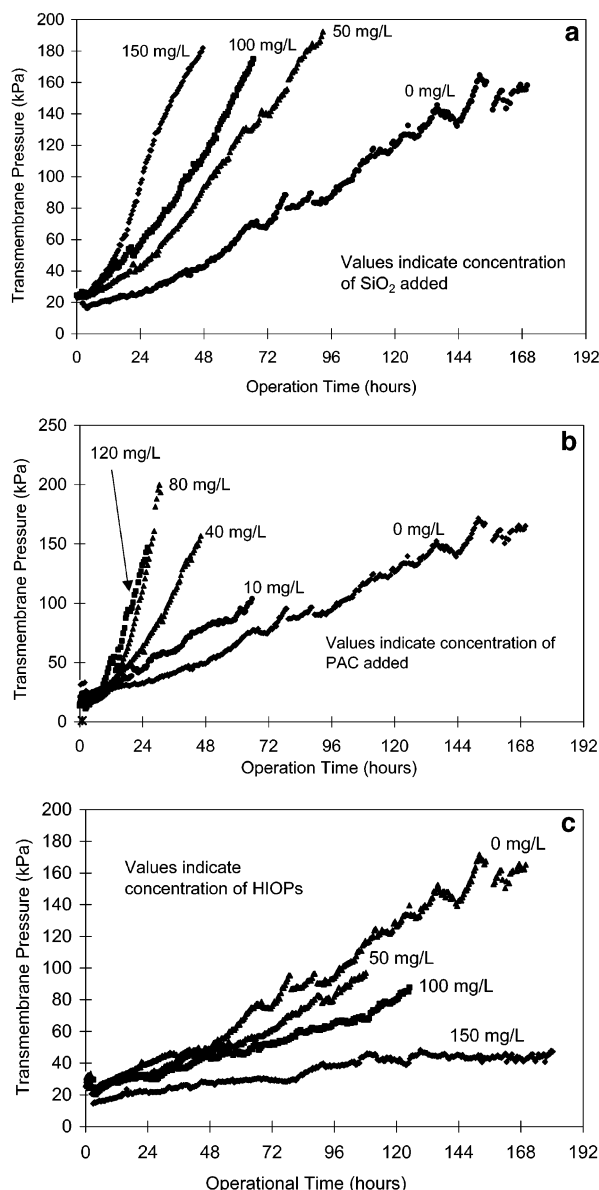


FIGURE 2. TMP profiles in systems dosed with various doses of (a)  $\text{SiO}_2$ , (b) PAC, and (c) HIOPs.

attributed directly or primarily to different NOM/membrane interactions in the systems.

A second possible explanation for the different fouling rates is that the PAC and  $\text{SiO}_2$  particles themselves fouled the membranes, while the HIOPs did not. To evaluate this possibility, NOM-free systems were dosed with each type of particle. The same experimental conditions were used as in the previous experiments, except that the influent was high-purity water. The TMP versus time profiles differed in the three systems (Figure 3), but in all cases, the fouling was much less than in the systems containing particles and NOM together.

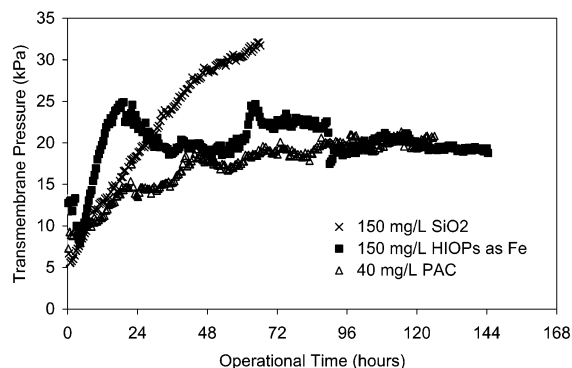
The results of this experiment discount the possibility that direct particle/membrane interactions caused the differences in fouling when the systems contained NOM. However, some key properties of the particles (e.g., the particle size distribution [PSD] and the surface charge) change when they contact natural water, so that experiments in NOM-free water do not completely capture the particles' behavior in the systems of interest. Therefore, those parameters were investigated in batch systems with both LW and high-purity water. The particle concentrations used in



**TABLE 2. Water Quality of Influent and Permeate from System Using Different Kind of Particles**

	pH	UV <sub>254</sub> (cm <sup>-1</sup> )	DOC (mg/L)	UV removal (%)	DOC removal (%)
<b>PAC</b>					
influent	6.69	0.079	4.2		
10 mg/L <sup>a</sup>		0.050	2.9	39	26
40 mg/L		0.038	2.3	52	45
80 mg/L		0.033	2.2	58	48
120 mg/L		0.029	1.7	63	60
<b>HIOPs</b>					
influent	6.25	0.084	4.5		
50 mg/L		0.035	2.2	58	52
100 mg/L		0.030	2.0	64	55
150 mg/L		0.026	1.9	69	58
<b>SiO<sub>2</sub></b>					
influent	6.98	0.082	4.0		
50 mg/L		0.065	3.3	21	17
100 mg/L		0.064	3.4	22	15
150 mg/L		0.062	3.4	24	13

<sup>a</sup> For the test with 10 mg/L PAC, the influent was the influent used for the SiO<sub>2</sub> tests.



**FIGURE 3. Transmembrane pressure curves for Milli-Q water filtration with HIOPs, PAC, and SiO<sub>2</sub>.**

the tests was double the dosage used in the membrane tests (300 mg Fe/L HIOPs as Fe, 300 mg/L SiO<sub>2</sub>, and 80 mg/L PAC). The key outcomes are summarized in Table 1.

The PSD data do not demonstrate any obvious trends that would link them to the effects of the particles on membrane fouling. The  $\zeta$ -potential data do indicate a difference between the positively charged HIOPs and the negatively charged PAC and SiO<sub>2</sub>, but no causative linkage between the sign of the particle surface charge and the membrane fouling is obvious. Although both parameters changed when the particles were suspended in lake water instead of DI water, those changes were not so dramatic as to suggest that the trends of membrane fouling by the particles themselves would be different in lake water from those observed in NOM-free water. It is therefore concluded that direct particle/membrane interactions were not responsible for most of the fouling in the experimental systems and that the different effects of the particles on membrane fouling must be attributed to other factors.

The third pairwise interaction that might explain the different behaviors of the experimental systems is between NOM and the particles. The exploration of these types of interactions and the interactions between the NOM/particle aggregates and the membrane was qualitative and relied on SEM examination of the deposited particles after various periods of use in the membrane module. All the SEM images presented here are for membrane samples taken at the end of a treatment cycle and before a backwashing step.

Figure 4 shows images of the membrane and cake layer in the test system fed 150 mg/L HIOPs (as Fe). After 1 h of filtration, a thin, slightly bumpy layer of NOM covered the membrane surface (Figure 4a), but no cake layer could be seen. A mass balance on the solids indicated that, at that time, more than 96% of the HIOPs that had been added could be accounted for in the circulating suspension.

After 55 h of operation, a cake layer with a thickness of ~300 nm was evident on the membrane surface (Figure 4b), and by  $t = 75$  h, that layer had grown much thicker (~5  $\mu$ m) (Figure 4c). In the latter image, the layer appears as cleanly broken fragments, but no individual particles are identifiable in the structure. The breakage of the layer presumably occurred during desiccation and does not reflect the structure during operation. The extensive fragmentation of the entire cake can be seen clearly in Figure 4d, which was taken at  $t = 170$  h.

In the system dosed with 150 mg/L SiO<sub>2</sub>, the membrane was almost completely covered by SiO<sub>2</sub> particles after only 1 h of operation (Figure 5a). Thus, the rate of particle deposition was apparently much higher in this system than in the system with HIOPs. After another 19 h of operation, more particles were clumped together on the surface, forming a continuous layer approximately 8–9  $\mu$ m thick (Figure 5b). After 48 h of operation, the thickness of the cake layer had increased to approximately 15  $\mu$ m, but no change was apparent in the composition or structure of the cake surface (Figure 5c).

After 1 h in the test using 40 mg/L PAC, some PAC particles were collected by the membrane, and a discontinuous film of organic matter linked some of those particles together (Figure 6a). By  $t = 26$  h (Figure 6b), the particles had formed a virtually continuous layer on the membrane surface, and after 60 h of operation, particles can be seen to be aggregated into larger colonies linked by organic matter (Figure 6c).

Images of the cake layers after backwashing (not shown) did not look different from those before backwashing for any of the particles tested (i.e., backwashing did not seem to remove or even dramatically disrupt the cake layers once they had formed). Thus, in all the systems, the cake layer grew thicker with time. However, even though all the samples shown in the SEM images were prepared in the same way, only the HIOPs formed a cake layer that broke into chunks and separated cleanly from membrane surface upon desiccation. Desiccation, of course, never occurs during normal membrane operation. Nevertheless, we believe that the different responses of the cake layers to desiccation reflect real differences in their structures prior to desiccation and in the strength of the bonds between those layers and the membrane.

In the system dosed with HIOPs, it appears that the NOM bonded HIOPs to one another but not to the membrane, leaving the pore spaces between the HIOPs in the cake large enough so that water flow was not impeded significantly. The NOM removed from solution by adsorption was prevented from forming a gel layer on the membrane surface, so fouling was reduced.

By contrast, the ability of the NOM to bind PAC or SiO<sub>2</sub> particles together was apparently similar to or weaker than its ability to bind the particles to the membrane or to bind to the membrane itself. As a result, in systems with all three components (PAC or SiO<sub>2</sub> particles, NOM, and membrane), the NOM and particles together formed a continuous layer on the membrane with the NOM filling in spaces between the particles. Note that, according to this hypothesis, the strength of the adsorptive bond between individual molecules and PAC surfaces is not an issue; that bonding might be stronger or weaker than the comparable bonds of NOM molecules to HIOPs.

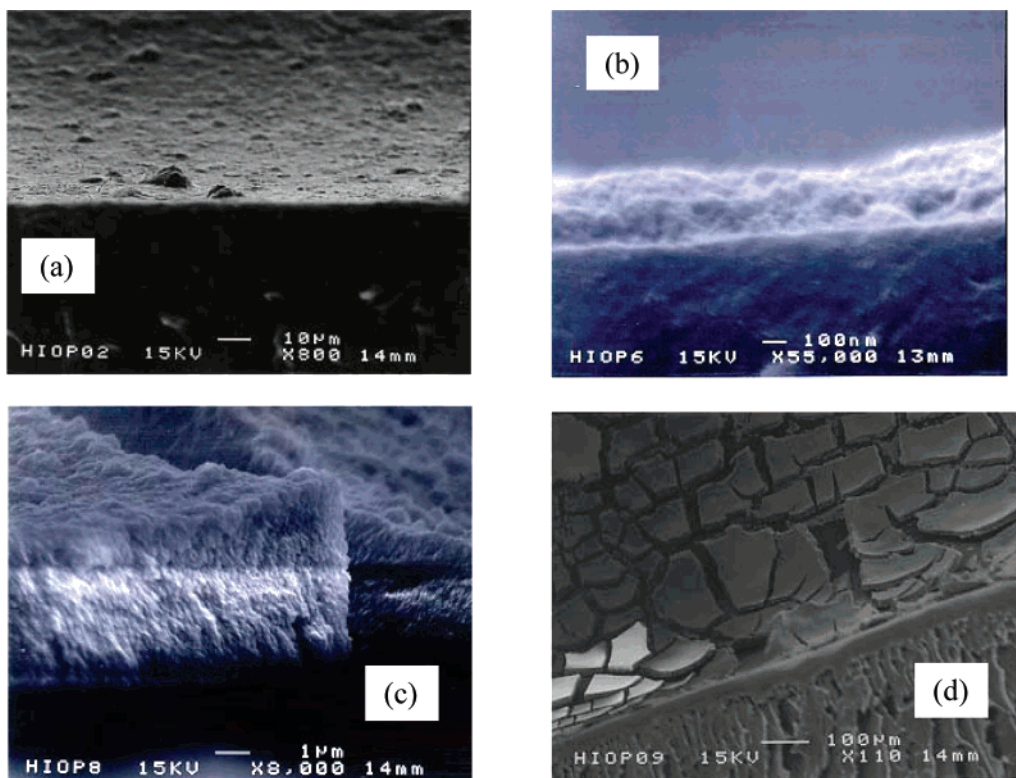


FIGURE 4. HIOPs layer on membrane surface at different times of operation: (a) 1, (b) 55, (c) 75, and (d) 170 h. HIOPs dose = 150 mg/L as Fe; feed was 0.45  $\mu$ m of prefiltered LW water.

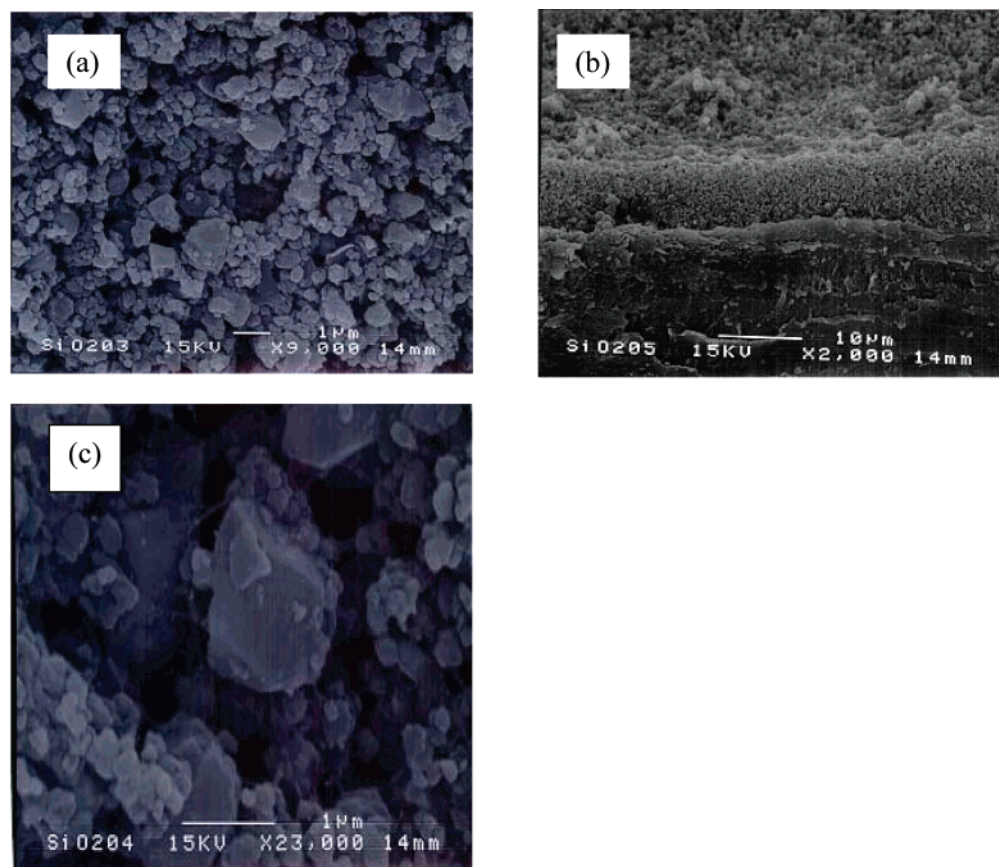


FIGURE 5. SiO<sub>2</sub> layer on membrane surface at different times of operation: (a) 1, (b) 19, and (c) 48 h. SiO<sub>2</sub> dose = 150 mg/L; feed was 0.45  $\mu$ m of prefiltered LW water.

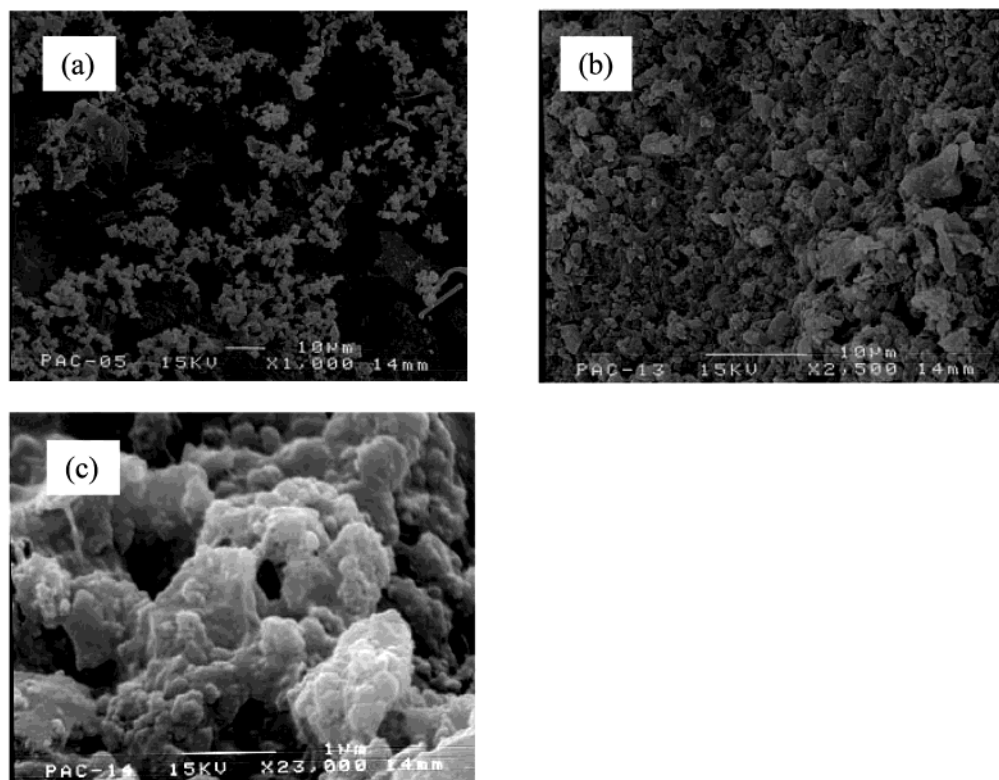


FIGURE 6. PAC layer on membrane surface at different times of operation: (a) 1, (b) 26, and (c) 60 h. PAC dose = 40 mg/L; feed was 0.45  $\mu\text{m}$  of prefiltered LW water.

Since the amount of membrane surface that must be covered by the NOM itself was less in the systems with PAC or  $\text{SiO}_2$  than in systems with no particles present (because some of the surface area was covered by the particles), fouling occurred more quickly. Sorption of NOM by PAC particles that were in the recirculating suspension or the outer portion of the cake layer might have mitigated fouling, but the formation of the nearly continuous NOM/PAC layer adjacent to the membrane appears to have dominated the system behavior.

To summarize, the hypothesis for the beneficial effects of HIOPs in UF systems is that the HIOPs form a cake layer on, but only weakly attached to, the membrane surface. That cake layer is relatively porous, so it contributes only slightly to fouling. Over time, the pores in the cake layer gradually fill with coagulated or precipitated NOM, as (perhaps) the pores in the membrane do, and fouling increases. For the range of HIOPs doses studied in this research, injecting more HIOPs into the system had a beneficial effect, indicating that the benefit of spreading the NOM over a larger number of adsorbent particles outweighed any adverse effect associated with increased fouling by the particles themselves.

By contrast, in systems containing PAC or  $\text{SiO}_2$  particles, the coagulated or precipitated NOM bonds strongly and simultaneously with the particles and the membrane surface and can thereby form a layer with high resistance to water flow. PAC particles circulating in the bulk solution reduce the NOM concentration reaching the membrane and thereby interfere with fouling, but this effect can be overwhelmed by the increase in fouling associated with the PAC particles that accumulate at the surface and form part of the fouling layer.

The beneficial effects of HIOPs with respect to both fouling reduction and NOM removal in membrane systems have now been demonstrated in laboratory tests of 15 different water sources with three different membrane systems (21, 23); in no case did HIOPs addition ever exacerbate fouling. Although similar beneficial effects have been reported for

addition of PAC or amorphous oxides to membrane and systems, adverse effects have also been reported, both in this research and in the studies cited previously (8, 13, 15, 20). These results indicate that the use of adsorbent particles in conjunction with UF or other membrane processes can potentially provide benefits in terms of both NOM removal and fouling reduction but that the effect of such particles depends strongly on the structure of the cake layer and its interaction with both NOM and the membrane surface.

### Acknowledgments

The authors express their appreciation to Koch Membrane Systems, Inc. (Wilmington, MA) for providing membranes for this research and to the AwwaRF for funding. The views expressed are those of the authors and not necessarily those of the funding agency.

### Supporting Information Available

Complete particle size distributions for all the samples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

### Literature Cited

- (1) Lainé, J.-M.; Hagstrom, J. P.; Clark, M.; Mallevialle, J. *J. Am. Water Works Assoc.* **1989**, *81* (11), 61–67.
- (2) Lahoussine-Turcaud, V.; Wiesner, M. R.; Bottero, J. Y. *J. Membr. Sci.* **1990**, *52*, 173.
- (3) Nyström, M.; Ruohomäki, K.; Kaipia, L. *Desalination* **1996**, *106*, 79–87.
- (4) Matsumoto, K.; Kawahara, M.; Ohya, H. *J. Ferment. Technol.* **1988**, *66* (2), 199–205.
- (5) Rodgers, V. G. J.; Sparks, R. E. *J. Membr. Sci.* **1992**, *68*, 149–168.
- (6) Chellam, S.; Jacangelo, J. G. *J. Environ. Eng.* **1998**, *124* (12), 1211–1219.
- (7) Ahn, K. H.; Song, K. G. *Desalination* **2000**, *129*, 207–216.
- (8) Chellam, S.; Jacangelo, J. G.; Bonacquisti, T. P.; Long, B. W. *J. Am. Water Works Assoc.* **1997**, *89* (10), 77.
- (9) Jacangelo, J. G.; Lainé, J. M.; Cummings, E. W.; Adham, S. S. *J. Am. Water Works Assoc.* **1995**, *87* (3), 100–112.



- (10) AlMalack, M. H.; Anderson, G. K. *J. Membr. Sci.* **1996**, *112* (2), 287–296.
- (11) Adham, S. S.; Snoeyink, V. L.; Clark, M. M.; Bersillon, J. L. *J. Am. Water Works Assoc.* **1991**, *83* (12), 81–91.
- (12) Adham, S. S.; Snoeyink, V. L.; Clark, M. M.; Anselme, C. *J. Am. Water Works Assoc.* **1993**, *85* (12), 58–68.
- (13) Jack, A. M.; Clark, M. M. *J. Am. Water Works Assoc.* **1998**, *90* (11), 83–95.
- (14) Campos, C.; Marinas, B. J.; Snoeyink, V. L.; Baudin, I.; Lainé, J.-M. *Desalination* **1998**, *117* (1–3), 265–271.
- (15) Lin, C.-F.; Lin, T.-Y.; Hao, O. J. *Water Res.* **2000**, *34*, 1097–1106.
- (16) Pirbazari, M.; Badriyha, B. N.; Ravindran, V. *J. Am. Water Works Assoc.* **1992**, *84* (12), 95–103.
- (17) Chang, Y.-J.; Benjamin, M. M. *J. Am. Water Works Assoc.* **1996**, *88* (12), 74–88.
- (18) Murase, T.; Ohn, T.; Kimata, K. *J. Membr. Sci.* **1995**, *108* (1–2), 121.
- (19) McCarthy, A.; Walsh, P. K.; Foley, G. *Sep. Sci. Technol.* **1996**, *31* (11), 1615.
- (20) Schäfer, A. I.; Schwicker, U.; Fischer, M. M.; Fane, A. G.; Waite, T. D. *J. Membr. Sci.* **2000**, *171*, 151–172.
- (21) Chang, Y.-J.; Choo, K.-H.; Benjamin, M. M.; Reiber, S. A. *J. Am. Water Works Assoc.* **1998**, *90* (5), 57–71.
- (22) Kim, K. J.; Fane, A. G.; Fell, C. J. D.; Joy, D. C. *J. Membr. Sci.* **1992**, *68*, 79–91.
- (23) Benjamin, M. M.; Zhang, M.; Li, C.; Chang, Y. *Combining Adsorbents with Membranes for Water Treatment*; Awwa Research Foundation: Denver, CO, 2002.

*Received for review August 9, 2002. Revised manuscript received January 17, 2003. Accepted February 10, 2003.*

ES0260418