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Fouling mechanisms in low-pressure membrane filtration in the presence of an adsorbent cake layer

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A B S T R A C T

Fouling of low-pressure membranes treating natural waters can be substantially mitigated by pre-depositing a thin layer of micron-size adsorbent particles on the membrane, a process we refer to as microgranular adsorptive filtration (μGAF). The role of adsorbent particle size, adsorbent surface loading, and membrane pore size in fouling of μGAF systems by natural surface water has been investigated. μGAF tests using heated aluminum oxide particles (HAOPs) and powdered activated carbon (PAC) reveal that fouling in such systems occurs both on the membrane and in the cake layer. Fouling on the membrane is primarily caused by soluble NOM and is exacerbated by the use of larger adsorbent particles and smaller-pore membranes. Such fouling is mitigated by removal of foulants in the pre-deposited layers, so the extent of mitigation is proportional to the adsorbent surface loading (i.e., the thickness of the cake layer). By contrast, fouling in the cake layer is caused by larger foulants such as colloids and particulate matter. Such fouling is insensitive to the layer's thickness. Use of smaller adsorbent particles improves the capture of colloids and particles but also exacerbates such fouling. In these cases, increasing the membrane pore size decreases the rate of fouling on the membrane, but does not affect the cake layer fouling.

1. Introduction

Membrane fouling presents the greatest impediment to improved performance of low-pressure membrane systems for drinking water treatment [1–7]. The primary foulants in such systems are thought to include colloids and fine particles, which can block or become trapped inside membrane pores, and natural organic matter (NOM) molecules, which can coagulate to form a gel on the membrane surface or adsorb inside the pores [8,9]. These two groups of foulants can act synergistically, generating a fouling layer that often causes more severe fouling than would be expected based on additivity of the individual foulants [5,10]. However, even if the particulate matter is largely removed by pre-filtration, the membranes typically become fouled very rapidly. In these cases, the membranes remove a negligible fraction of the dissolved organic carbon (DOC) or UV absorbance at 254 nm (UV_{254}), indicating that the key organic foulants comprise a very small portion of the NOM that absorbs little UV light [11].

A variety of physical and chemical pretreatments have been employed in efforts to control membrane fouling. Coagulation, adsorption, oxidation, and granular media filtration all remove some contaminants from the feed [12–15], and they often reduce fouling [12,13,16,17]. However, in other cases, these processes have little or no effect on fouling, and occasionally they even exacerbate the problem [18,19].

At least three approaches have been investigated for combining pretreatment by adsorption with low-pressure membrane filtration: (1) pre-adsorption, in which the water is contacted with and then separated from the adsorbent before the water is applied to the membrane; (2) direct filtration, in which the suspension of adsorbent and feed solution is mixed and then applied directly to the membrane; and (3) pre-deposition, in which an adsorbent layer is deposited on the membrane surface prior to application of the feed solution. The first two of these processes have been used in full-scale treatment systems, while the last has been tested only at laboratory-scale [16,20–24]. These tests have generally shown that pre-deposition can yield excellent results, often out-performing the other options with respect to both organic removal and fouling reduction [25,26]. We refer to this process as microgranular adsorptive filtration (μGAF).

In the μGAF tests conducted previously in our laboratory, the treatment system has typically comprised a thin ($<300\,\mu m$) layer of heated aluminum oxide particles (HAOPs) pre-deposited on a microfiltration (MF) membrane. The amounts of NOM and foulant removed in those tests were approximately proportional to the mass of pre-deposited adsorbent, suggesting that the

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adsorbent layer could be treated as a microscale, packed adsorption bed, and that fouling was caused by foulants that penetrated through the layer and reached the membrane surface [27]. According to this conceptual picture of the process, most of the benefits of the hybrid adsorption/membrane process are provided by the adsorbent, and the primary role of the membrane is not contaminant removal, but simply supporting the adsorbent particles.

We have also investigated μGAF systems using an ion exchange (IX) resin or powdered activated carbon (PAC) as the adsorbent [28]. The ion exchange resin removed UV_{254} almost identically to HAOPs, both overall and with respect to the different NOM size fractions (based on size exclusion chromatography). Nevertheless, the μGAF systems with pre-deposited resin fouled as rapidly as the control systems without any adsorbent, reinforcing the idea that UV_{254} is a very poor indicator of the foulant concentration in the water. The μGAF systems with PAC selectively removed different size fractions of the NOM (when compared to HAOPs) and did reduce fouling compared to the control systems, but less effectively than the systems with HAOPs.

Reducing adsorbent particle size is a well-established strategy for improving adsorption capacity and kinetics. For example, Matsui and co-workers [29,30] reported that, in batch adsorption tests, submicron-size powdered activated carbon (PAC) prepared by crushing larger particles removed more NOM and reached adsorptive equilibrium faster than the original-size PAC. All of our prior work with HAOPs utilized particles prepared in the same way and therefore with a similar particle size distribution. The current study was initiated to investigate whether a reduction in the HAOPs size could improve their performance in μGAF systems. However, the experiments suggested that the effects of particle size were more complex than just altering the adsorption capacity and kinetics, and extended to a change in the fouling mechanism. To explore the basis for these changes, the effects of adsorbent dose and membrane pore size were explored along with the effects of particle size. This paper describes those investigations and presents a comprehensive, integrated conceptual model for fouling in μGAF using low-pressure membranes, applicable to a broad range of sizes of the adsorbent particles, the foulants, and the membrane pores.

2. Materials and methods

2.1. Source water, adsorbents, and membranes

Water used in this study was collected from Lake Union (LU) at Portage Bay, adjacent to the University of Washington, in Seattle, WA. Samples were stored at 4 °C and were brought to room temperature (around 20 °C) immediately before the tests. The DOC concentration of the water was 2.4–3.1 mg/L, and the UV_{254} was 0.053–0.066 cm^{-1}. In some tests, the LU water was passed through a 0.45-μm cartridge filter (Polycap AS, Whatman) before being fed to the μGAF system.

Two adsorbents were investigated: HAOPs and PAC. The HAOPs were synthesized as described previously [25,26], and the PAC was a wood-based, commercial product (PICAPURE L, PICA USA Inc.). Throughout this paper, HAOPs doses are expressed in terms of their aluminum (Al) content. Samples of these adsorbents were slurried in deionized (DI) water (Millipore Milli-Q, Billerica, MA) and pulverized in an agitator bead mill with no dispersant added (LabStar, NETZSCH, Exton, PA). The particle size distributions of original and pulverized adsorbent were analyzed by laser light-scattering (Horiba model LA-95), and the surface area was determined by the multipoint BET method using a NOVA 4200e surface area analyzer (Quantachrome Instruments, Boynton Beach, FL). The meso- and macro-pore properties were explored by nitrogen adsorption (Quantachrome Instruments NOVA 4200e) and mercury intrusion (Micromeritics AutoPore IV 9500), respectively.

Table 1
Characteristics of various membranes.

Name	Pore size (μm)	Material	Manufacturer
CA0.025	0.025	Cellulose acetate	Millipore
PES0.05	0.05	Polyethersulfone	Microndyn-Nadir
PC1.2	1.2	Polycarbonate	Millipore
PC3	3	Polycarbonate	Millipore
PC5	5	Polycarbonate	Millipore

All the membranes tested were 47-mm-diameter flat discs. Polyethersulfone membranes with a nominal pore size of 0.05 μm and an effective surface area of 9.62 cm^2 (Mirodyn-Nadir MP005) were used in most of the μGAF tests, but a few other membranes were also investigated. Some key characteristics of all the membranes are provided in Table 1. All membranes were pre-conditioned by soaking and rinsing in DI water prior to their use in tests.

2.2. Batch adsorption tests

Adsorption of LU NOM onto HAOPs and PAC was studied over an adsorbent dose range of 0–500 mg/L at room temperature. After the adsorbents were added to 100 mL of LU water, the pH was adjusted to 7.1 ± 0.2 with 0.1 M NaOH or HCl, and the flasks were placed on a rotary shaker operating at 200 rpm for 24 h. The samples were then passed through a 0.45-μm syringe filter to separate the solid from solution prior to chemical analysis. Adsorption kinetics was studied by mixing 100 mg/L of the adsorbent with 500 mL lake water. The mixture was continuously stirred using a magnetic stirring plate, and the pH was maintained at 7.0 ± 0.2 by an automatic pH controller. Samples were collected intermittently over the course of 24 h and were filtered with a 0.45-μm filter.

2.3. Membrane filtration tests

In μGAF tests, after the adsorbent was deposited on the membrane, DI water was fed to the system in dead-end mode at a constant flux of 100 L/m^2 h (LMH) for 30 min to obtain a stable baseline. Then, the feed was switched to lake water, and permeate samples were collected at pre-selected intervals for analysis of UV_{254} and DOC. Transmembrane pressure (TMP) was recorded online with a pressure transducer. Runs were terminated when the TMP reached ~80 kPa. Similar runs were conducted without any adsorbent, as controls. Many μGAF tests and control tests were conducted in duplicate and yielded consistent results.

2.4. Chemical analyses

UV_{254} and DOC were determined on filtered samples using a dual-beam Lambda-18 spectrophotometer (Perkin-Elmer) with a 5-cm cell and a TOC analyzer (Shimadzu TOC-V_{CSH}), respectively. The DOC data followed the same trends as UV_{254} but, due to frequent instrumental malfunction, the DOC data had more scatter. We demonstrated a strong correlation between UV_{254} and the DOC concentration in both feed and permeate samples treated with various adsorbents in a previous publication [28], so UV_{254} is presented here as the primary indicator of NOM concentration.