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Pretreatment for membrane water treatment systems: a laboratory study

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Abstract

The goal of the work was to determine if biological treatment of water containing soil-derived humic substances has the potential for reducing the fouling of membranes used in water treatment. Laboratory scale biological filters containing biologically active carbon or iron oxide coated sand were fed humic-laden water with or without prechlorination. This stream was split, with half being further treated by microfiltration. Treated water was assessed for total organic carbon removal and biofouling potential using a glass bead assay and membrane assay for total cell counts, fouling layer thickness, and flux reduction. A combination of these assays provided more insight than any single measurement. Compared to untreated control water, biological treatment was capable of reducing downstream fouling of membrane systems. For example, fouling layer thickness was reduced by half after biological treatment, and cell counts were reduced four- to five-fold. Biological treatment coupled with microfiltration provided the best reduction of fouling, while prechlorination did not appear to impact the process. These results suggest that biological treatment may be valuable in reducing membrane fouling while reducing the amount of disinfectants used in pretreatment.
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1. Introduction

The material that fouls reverse osmosis membranes is diverse, and is composed of inorganic particles (precipitated metal oxides, colloids, etc.), natural organic matter (NOM), and bacterial, fungal, algal, and protozoan cells [1,2]. The rate and extent of fouling is a strong function of the quality of water applied to the membranes. It has traditionally been held that fouling material is the result of concentration and retention of constituents from the bulk. Another mechanism of fouling is the proliferation of organisms in biofilms on the membranes [3–5]. In fact, a combination of these effects most likely is responsible for the adverse influence on membrane production [6,7].

In response to these types of fouling, control has typically been attempted via (1) physical and/or chemical treatment of the water to remove or stabilize particulates and/or ions, (2) periodic direct cleaning of membranes, (3) development of membranes with reduced fouling potential or modification of the surface chemistry with chemical addition to reduce fouling and (4) application of biocides. As a consequence, there are a wide variety of potential "pretreatment" options for reverse osmosis including dual or single media filtration, softening and/or ion exchange, granular activated

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carbon filters, pH adjustment, etc. [1]. It is obvious that none of the above approaches for mitigating membrane fouling will always work by itself and that a combination of methods is optimal for increasing membrane productivity.

A potential process in the treatment train is biological pretreatment of the water to reduce the organic constituents that either contribute directly to organic fouling or provide carbon sources for the development of biofilms on the membrane surfaces. As noted by Flemming et al. [3] this would take the form of a ‘‘bioreactor in the right place’’ where biofilm growth is encouraged as opposed to having it occur in an undesirable location (the membrane). The approach is ecologically sound because it uses biological processes to control subsequent biological activity and reduces the dependence on disinfectants. This approach has also been advocated by Vrouwenvelder and van der Kooij [8] who have observed that lower concentrations of microbially available organic matter in the feed water are associated with reduced biofouling on membranes. These same investigators note that a reverse osmosis plant fed with water pretreated by slow sand filtration [5] had the lowest amount of fouling when compared to two other plants where no biologically active filtration was used in the treatment train.

There is a reasonable amount of information available on biological treatment of drinking water. Processes include bank filtration for river sources, soil passage, and slow/rapid sand filtration. A relatively modern approach is the use of biologically active carbon. This process was first implemented in France and other western European countries over 20 years ago [9–11]. In the most traditional form, separate granular activated carbon (GAC) filters are located downstream from conventional treatment. Biological filters are operated with exhausted carbon, that is, the chemisorptive capacity of the GAC has been exceeded. The surfaces of the filter media act as a support for microbial attachment and growth, resulting in a biofilm adapted to using the organic matter found in that particular water. Total organic carbon (TOC) removals in these filters range from 5% to 75% [12].

Even though the emphasis in drinking water has been on the use of GAC, there is other evidence to suggest that iron oxide coated media may be a better choice for removal of NOM that directly causes fouling [13,14] and/or subsequent biofouling at the expense of the immobilized organics on reverse osmosis membranes. Chang and Benjamin [15] demonstrated that addition of iron oxide particles to individual ultrafiltration hollow fibers greatly reduced fouling by organic matter. The organic matter was preferentially bound to the iron oxide particles which could then be removed by backwashing. Iron oxides have a large potential for the sorption of NOM [16–18]. Under abiotic conditions, humic material is irreversibly held on the surface of iron oxides [19,20]. In fact, this property has been used to develop a technique for the removal of NOM from water by coating sand particles used in slow sand filter beds with iron oxides [21]. Circumstantial evidence indicates that the bound organic matter is potentially available for biofilm bacteria when these same investigators mentioned that the iron oxide-coated olivine used in their filtration studies continued to remove NOM for a 16 month time period; they suggested that the adsorption sites were being ‘‘bioregenerated.’’

Although the overall rate of membrane fouling should be significantly less than if no biological treatment was in place, there is concern from operators that filtration steps that result in bacterial activity are deleterious to membrane performance. For example, Collentro and Collentro [22] suggest that GAC has a low efficiency for organic carbon removal and that GAC filter effluent contains elevated nutrients and high organism counts that increase membrane fouling. This is probably because these GAC filters were not optimized for either chemisorption or biological activity. This philosophy has lead to reports that GAC should be used for RO feedwater pretreatment only if no other options exist [23]. This prejudice may be unfounded if the biological filter is operated optimally.

The approach of the work described here was to develop and test biological treatment processes that may be integrated in traditional pretreatment trains with the purpose of prolonging membrane performance. A favorable outcome would be a cost effective treatment method to reduce fouling and chemical use. As such, the goal of this work was to determine if biological pretreatment can reduce fouling in membrane systems. The work was performed in the laboratory with realistically scaled treatment options that included biological treatment of humic-laden water through exhausted granular activated carbon or iron oxide coated sand columns. In addition, the influence of upstream prechlorination of the water as typically practiced in the field was assessed. The additional benefit of a microfiltration step following biological treatment was also investigated. The influence of these treatment options on fouling was assessed using a suite of measurement techniques to ensure that relevant results were obtained.

2. Materials and methods

2.1. Experimental setup

This project examined the impacts of biological filtration using biologically active carbon and iron-oxide coated sand, chlorination of the feed water, and a microfiltration step on downstream fouling in a

laboratory system. To measure the influence of these variables, it was necessary to refine and test a number of assays including a membrane fouling apparatus. These components were assembled into a treatment train shown in Fig. 1. Two types of packing media for the biological pretreatment columns were used; iron-oxide coated sand and biologically activated carbon. These two packing types, along with a control that had no packing, represented three treatments. The effluent of each of these treatments was split and a 0.22 μm postfiltration (MSI #DCN0200006 Calyx Nylon, Osmonics) step was added on one of the streams from each treatment. The entire system, with the omission of the chlorination step, was duplicated. Thus, twelve treatments (two types of packing, controls, with and without chlorination, and with and without postfiltration) were constructed for sampling and evaluation. Flow configuration was in the upflow mode with the columns mounted vertically. The apparatus also included several assays that were placed in the effluent streams. One assay was a 4.93 mm inside diameter 316 stainless-steel tube, 25.4 mm in length packed with 0.5 mm glass spheres. The other assay was an in-line membrane holder that allowed for flux through a 47 mm diameter membrane swatch and flow across the membrane while the system was under pressure. Each of these assays is described in more detail below.

The choice of material for the system was based upon the need to limit the amount of leachable organic carbon

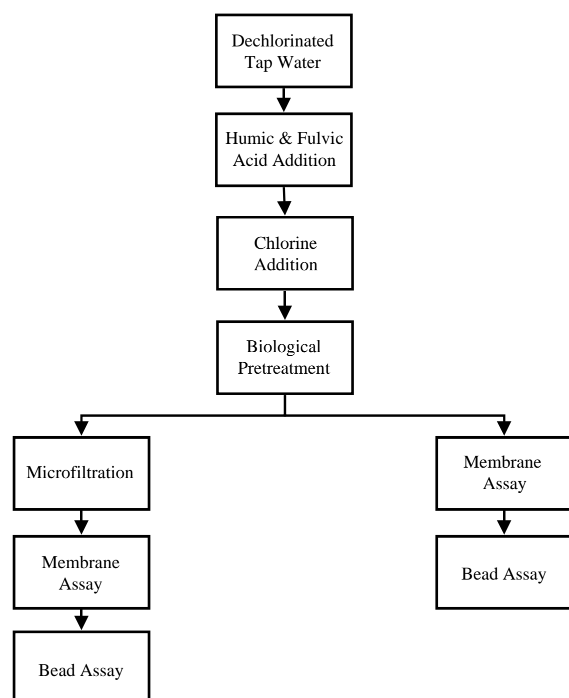

Fig. 1. Treatment train schematic.

and still provide sufficient strength for the pressures involved with the operation of the columns. Therefore, the apparatus was constructed using type 316 stainless steel (ASTM A-213/ASME SA-213 average wall; ASTM A-269, ASTM A-511). The columns for the biological filters were constructed with 316 stainless-steel tubing ordered from Marmon/Keystone Corporation. 25.4 mm tubing (internal diameter of 23.6 mm) was specified with a wall thickness of 0.89 mm. The column length was 229 mm and the resulting volume for the columns was approximately 100, 200 mm^3. All connecting tubing was 6.35 mm (4.93 mm internal diameter) and 12.7 mm (10.92 mm internal diameter) type 316 stainless steel.

Total system pressure was maintained at 207 kPa (30 psi) during the entire time the system was running (>12 months). During this time, the laboratory temperature was maintained at a constant 22°C (72°F). The flow rate through each treatment was maintained individually with a stainless-steel needle valve between 1 and 2 ml/min.

2.2. Feedwater

The organic carbon used in the study was humic/fulvic acids that were extracted from Elliot Silt Loam Soil. Elliot Silt Loam Soil is a standard soil used for laboratory work on humic/fulvic acids and is obtained from the International Humic Substances Society.

The humic/fulvic acids are extracted from the soil by mixing 75 g of soil in 750 ml of 6 N NaOH solution for 24–48 h. After the mixing is done, the slurry is centrifuged for 20 min at 5000*g* and 4°C. The supernatant is decanted and used as a stock solution to prepare a feed solution of humic/fulvic acids. The humic substances were mixed with Bozeman tap water that was dechlorinated by passing the water through a column packed with biological activated carbon. The BAC column used to dechlorinate the tap water also removes any readily assimilable organic carbon. Therefore, the carbon amendment represents the major carbon source introduced into the system. The maximum carbon input from the carbon amendment was 2 mg/L and the maximum amount from the tap water after dechlorination was approximately 2 mg/L, giving an upper bound on the carbon concentration of 4 mg/L of carbon. To ascertain the actual influent carbon concentration, a TOC measurement of the influent was taken and paired with effluent TOC measurements.

Nitrogen and phosphorus were added to ensure that the limiting nutrient would be carbon. Based upon this concentration and using the common 100:10:1 C:N:P ratio for microbial growth, the amount of nitrogen and phosphorus to be added to the amendment solution was calculated and determined to be 7.5 and 0.75 mmole, respectively, provided as ammonium nitrate and potassium phosphate. These compounds were

mixed with the carbon source prior to injection into the test apparatus.

Half of the treatment systems received water that was prechlorinated. A stock solution of 1 mg/L chlorine was mixed with a static mixer and a 30 min contact time with the TOC prior to application to any columns to simulate conditions likely to occur in actual field situations. The contact time was achieved by building a longer inlet tube to the columns receiving chlorinated water. This procedure resulted in a depletion of the chlorine residual, and measurements after the contact time were typically at or below the level of detection.

The experimental setup was run continuously for 10 months. During the first six months, experimental protocols and operational experience were developed. The results presented were obtained from three experimental runs performed after this 6 month break in period. Each run was performed over a period of five days. During each five day run, TOC and flux measurements were taken and at the end of each run, the destructive assays were performed.

2.3. Biological pretreatment columns

Using information from the drinking water industry [24–26], a minimum of 20 min empty bed contact time was desired to provide optimal removal of organic carbon. To assure that this situation was met, the columns were designed to have an empty bed contact time that was approximately 30 min. The average flow rate through the columns was 1.7 ml/min resulting in an empty bed contact time of 29.5 min.

The columns were packed with either iron-oxide coated sand or biologically active carbon. Support screening was 100 mesh 316 stainless steel. All end caps were Swagelock 316 stainless-steel compression tube fittings.

The biologically active carbon was PICA brand activated carbon that had been operating in a biological filtration process at a drinking water plant in Laval, Quebec, Canada. The plant was treating surface water and the filtration process was operated to promote biological growth on the activated carbon. The activated carbon had been on line for several years and was never regenerated. The sorptive capacity of the media is mainly due to the microbial activity on the medium. To acclimate the microbial community to the organic carbon present in Bozeman tap water, the packing material was placed online with Bozeman tap water for more than one year. The material was then used to pack the columns that were used in this study, and was acclimated in these columns for several months prior to initiation of the experiments.

Iron-oxide coated sand was produced using the method outlined in Benjamin et al. [27]. This coating was developed to be a stable sand coating that could be regenerated in a full scale operation and provide good NOM adsorption. Support sand was industrial quartz sand manufactured by Unmin Corporation, Emmett, Idaho screened to between 30 and 40 mesh giving an effective size of 0.45 mm. This sand was soaked in 50% sulfuric acid solution for 24 h, then rinsed with deionized water, and dried at 110°C for 20 h in accordance with the method of Chang and Benjamin [15].

An iron oxide solution was prepared with 1 g of ferric chloride per ml of deionized water. A 10 M solution of NaOH was added to this solution until the hydroxide to iron molar ratio was 2.5. This material was then dried in a pan at 110°C for 14 h. The top crust of salts was scraped off and the iron oxide sludge underneath was used to coat the sand. The iron oxide sludge and the sand were mixed in a ratio of 0.1 g iron oxide sludge per 1 g of sand. The sand was dried at 110°C for 20 h. The sand was rinsed and the process repeated two more times to obtain a good coating. Once the sand was coated, it was used to pack two columns; one for the non-chlorinated treatment and one for the chlorinated treatment. All column dimensions and materials were the same as for the biological activated carbon columns described previously.

2.4. Fouling assays

2.4.1. Bead assay

The bead assay was put in-line with the effluent stream of each treatment to provide an assessment of the biofilm growth potential of the treated water. The apparatus consisted of a short 316 stainless-steel tube 4.93 mm inside diameter, 25.4 mm in length that was packed with 0.5 mm glass spheres.

At the end of each experimental run (5 days), the assay column was removed and the glass beads extracted into 10 ml of sterile dilution water. This mixture of beads, biofilm, and water was vortexed for 30 s and the appropriate dilution series performed to enumerate the bacteria. A time of 30 s was chosen because increased vortexing did not result in higher counts (data not shown).

2.4.2. Membrane assay

The membrane assay holder (Fig. 2) was constructed out of two plates of aluminum block 25.4 mm × 76.2 mm × 76.2 mm. A polycarbonate screen was placed over the holes of the block that provides an outlet for the flux through the membrane. Next, an ashless filter paper (47 mm) was placed over the screen to protect the membrane. A polycarbonate, 0.22 μm, 47 mm membrane (Poretics) was placed on top of the filter paper. To seal and create a flow channel, a silicon gasket with the flow area cut out was placed over the screen, filter paper, membrane stack and the other membrane assay block was placed on top. With the design flow of the system,

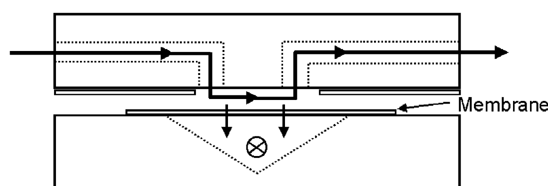

Fig. 2. Membrane assay holder. The horizontal arrow represents the direction of fluid flow under normal operation and the vertical arrows illustrate flow when flux measurements were taken.

the Reynold's number is at least 450 and is probably more due to the reduced cross-sectional area produced from compression of the gasket. Following assembly, the four bolts were then torqued down to 10 N-m in a cross-hole pattern.

During the experimental run, flux reduction was assessed by collecting the flux effluent from the membrane assay for a known time and then measuring the collected volume. After the final day of the experimental run, the blocks were dismantled and the membrane removed for analysis. Immediately, the membrane was photographed for digital analysis of the fouling area for use in the flux calculations. In addition, the fouling layer color could be recorded.

2.4.3. *Scanning electron microscopy fouling layer assessment*

Scanning electron microscopy (SEM) was utilized to assess the membrane fouling layer thickness. The SEM used in this work was a JEOL Model 6100/NORAN SEM equipped with an Oxford cryostage and cryoprep chamber. The cryostage allows an environmental sample to be frozen quickly to preserve the original structure and then placed under a vacuum for manipulation prior to sputter coating for the SEM. The sample is never removed from vacuum so that it remains intact.

To determine the thickness of the fouling layer, a small portion of the fouled layer was cut from the membrane. This sample was then mounted vertically on the cryostage mounted on a post that allows insertion into a flash freezer that utilizes liquid nitrogen and vacuum. The sample is then introduced into a chamber where the pressure is reduced to 10^{-4} Torr and further cooled to around $-190°C$. Tools within the microscope sample preparation area were used to cut across the frozen sample to expose a cross section of the membrane and the fouling layer.

After the fouling layer cross section is exposed, the sample can be sputter coated with gold (2 nm) before moving the sample into the SEM chamber. Once in the SEM chamber, the pressure is further reduced to 10^{-6} Torr and the temperature held at $-195°C$. Images of the cross section were taken so that an estimate of the fouling layer thickness could be made using the scale bar from the instrument. In addition, bacteria in the fouling layer could be seen. These bacteria were often small ($<1\,\mu m$) due to the oligotrophic conditions of the experimental system.

2.4.4. *4′,6-diamidino-2-phenylindole, dihydrochloride (DAPI) fouling layer assessment*

Another section of the membrane fouling layer, similar in size to that used for the SEM analysis, was cut out and embedded in TISSUE-Tek™ OCT 4583 compound, an embedding medium for frozen tissue specimen, and frozen on a block of solid carbon dioxide. The specimen was then mounted on a stage in a Leica CM 1800 Cryostat. This machine enables 5 and 10 μm slices to be made of the cross section of the membrane and fouling layer. These slices were then transferred onto a microscope slide.

Frozen sections were then stained with DAPI. The staining procedure consisted of immersion of the slide in 100 mg/L DAPI solution for 20 s and then drying before placing on the microscope for analysis as described below.

The thickness of the fouling layer could then be estimated. To obtain this measurement, the microscope counting grid in the ocular eye piece was first calibrated using a micrometer slide. Then the thickness of the observed fouling layer was evaluated directly in several places. In addition, images were obtained for some samples and the thickness measurements were performed using ImageTool (http://www.ddsdx.uthscsa.edu/dig/itdesc.html).

2.4.5. *Fouling layer cell counts*

To estimate the number of cells per area that were in the fouling layer, a specific area of the polycarbonate membrane from the membrane assay was scraped with a scalpel, placed in 10 ml of sterile dilution water and homogenized. The appropriate dilution was made and a direct count performed according to the procedure outlined below.

To normalize the counts to a specific surface area, a photograph of the membrane was taken with a calibration scale. The photograph was then electronically scanned and the scraped area determined digitally using ImageTool.

2.5. *Analytical assays*

2.5.1. *Chlorine*

Chlorine measurements were taken using Iodometric method (4500-Cl B) from Standard Methods [28].

2.5.2. TOC analysis

To determine influent carbon levels and the amount that was removed by each treatment, a sample of the influent and each treatment effluent was collected daily during the experimental runs in glass vials. These vials and all glassware for the analyses were acid washed for 8 h, triple rinsed with deionized water, triple rinsed with ultrapure water, and baked in an oven at 300°C prior to use.

The water samples were acidified to a pH below 2 with 2 N HCl and then sparged with medical grade oxygen to remove the dissolved carbon dioxide. A Shimadzu TOC-5000A carbon analyzer with a high sensitivity platinum–palladium catalyst operating at 680°C was used to oxidize the non-purgeable organic carbon to carbon dioxide and the carbon dioxide was detected with an infrared detector. The Shimadzu was calibrated using NIST traceable potassium hydrogen phthalate standards obtained from Fisher Scientific.

2.5.3. Cell enumeration

Bacteria were counted using direct count epifluorescent microscopy on a Nikon 8100 at 1000 ×. The cells were filtered onto a 0.22 μm filter (25 mm black polycarbonate—Poretics) and stained using 4′,6-diamidino-2-phenylindole, dihydrochloride (DAPI) obtained from Molecular Probes (catalog number D-1306). 1 ml of the stain was placed on the membrane for 1 min at a concentration of 10 mg/L.

Ten fields were randomly selected and counted. The appropriate magnification and dilution were then applied to the numbers to arrive at the total cell count per ml. This number was then applied to the appropriate surface area (either total bead area or membrane scrape area) to arrive at the biofilm cells per area number.

2.6. Statistical analyses

Results were analyzed using a Monte Carlo-based simulation multiple comparison with a control test or a simulation-based multiple comparison test without a control. The simulation size was 12616 and the simultaneous confidence interval was 95%. All statistical analyses were performed using SPLUS version 5.1 release 1 for LINUX 2.0.31: 1999, MathSoft, Inc., Seattle, WA, http://www.mathsoft.com. For comparisons between treatments, a statistically significant difference was determined to be at the level of 95%.

3. Results

The fouling potential of water, after various treatments (Table 1), was investigated with six assays that measured different aspects such as flow through a microporous membrane, surface-associated bacterial cell counts, and fouling layer thickness. This section presents the results of these measurements.

The first assay involved measuring the flux of water through a microfiltration membrane over time. Biofouling of microfiltration membranes was evidenced by a reduction in the flux of water through the membrane with time (Fig. 3). Flux reduction was initially rapid, and after a period of approximately 120 h, change was minimal. Based on these results, all destructive analyses were also done at 120 h (5 days) to provide a direct basis for comparison. To interpolate the flux at 120 h, a

Table 1
Treatments evaluated

Treatment	Description
BAC	Biological activated carbon
BACCL	Biological activated carbon and prechlorination of the influent stream
BACPF	Biological activated carbon and post-microfiltration
BACPFCL	Biological activated carbon, post-microfiltration and prechlorination
IOCS	Iron-oxide coated sand
IOCSCL	Iron-oxide coated sand and prechlorination
IOCSPF	Iron-oxide coated sand and post-microfiltration
IOCSPFCL	Iron-oxide coated sand, post-microfiltration and prechlorination
CTRL	Control, no treatment
CTRLCL	Control, prechlorination
CTRLPF	Control, post-microfiltration
CTRLPFCL	Control, post-microfiltration, prechlorination

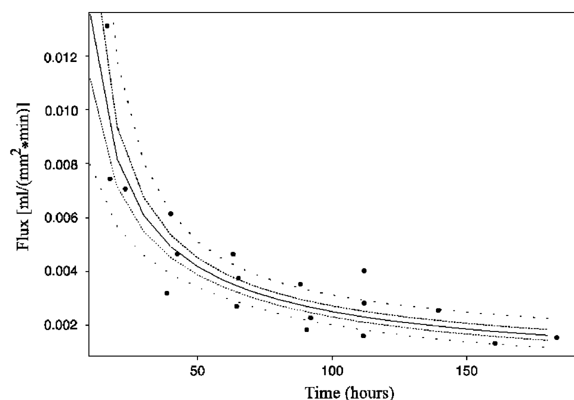

Fig. 3. Typical decrease in membrane permeability with time. Filled circles represent experimental measurements and the solid line represents a curve fit as described in Section 2. The inside confidence intervals are a pointwise standard error and the outside confidence intervals are a simultaneous confidence interval generated for the whole range using an *F*-distribution and a 95% confidence interval.

Monte Carlo based multiple comparison simulation model fit to data of this type was used and this value (Table 2) was used for statistical comparisons of treatments. The simultaneous confidence intervals generated upper and lower flux values covering 95% of the predicted values. The lowest fluxes, or worst fouling, were measured in treatment options that did not include a postfiltration step. The highest fluxes were measured in options combining biologically activated carbon pretreatment with postfiltration. Chlorination had no discernable effect on membrane permeability by this assay.

The second assay measured the removal of TOC from the water by the treatment option. Greater TOC removal is expected to correlate with reduced potential of the treated water to support microbial growth and fouling. TOC removal ranged from approximately 4% to 38% for the various treatment options (Table 2). TOC removal was consistently slightly higher for treatments operated without chlorination compared to those that were chlorinated. TOC removal was highest for options combining biologically activated carbon pretreatment with a postfiltration step.

The third assay involved enumerating microorganisms scraped from a known area of the membrane used in the permeability assay. This measurement provides one way of determining the amount of bacterial biofilm that had accumulated on the membrane. Membrane cell areal densities ranged from $\log_{10} 6.9$–8.1 cells mm^{-2} (Table 2). The highest accumulation occurred in the control. Chlorination had little effect on the number of cells accumulating on the membrane but postfiltration clearly reduced membrane cell counts. The lowest cell counts were measured on treatments combining either biologically activated carbon or iron oxide coated sand pretreatments with postfiltration.

The fourth assay enumerated bacteria that attached to glass beads placed in the effluent stream of a treatment train. This assay presumably reflects the potential of the water to promote biofilm formation. Areal cell densities measured in this assay ranged from $\log_{10} 5.6$ to $\log_{10} 8.9$ cells mm^{-2} (Table 2). Both postfiltration and biological pretreatment reduced cell counts in this assay. Cell counts were in most, but not all, cases higher in the non-chlorinated systems.

The fifth and sixth assays measured the thickness of the fouling layer that developed on the membrane used in the permeability assay. Thickness was measured by either SEM (Fig. 4) or by light microscopic examination of frozen sections stained with a nucleic acid dye. Fouling layer thicknesses ranged from about 5 to 45 μm. Chlorination had little effect on fouling layer thickness by either assay. Postfiltration consistently reduced fouling layer thickness. Biological pretreatment, by either biologically activated carbon or iron oxide coated sand, also reduced fouling layer thickness.

The impacts of chlorination on the downstream fouling potential of water are summarized in Table 3. In this table, the assays were scored with a +1 if the treatment with chlorine showed statistically less (at the 95% confidence level) fouling potential than the same treatment without chlorine and were scored with a –1 if the fouling was statistically worse (95% level) with chlorine than without chlorine. A zero was entered if no statistically significant difference between the chlorinated and unchlorinated treatments could be detected. Overall, the results indicated little effect of prechlorination on the fouling potential of the water.

The impacts of postfiltration are summarized in Table 4. If postfiltration was statistically better (95% level) than the parallel treatment without filtration, it scored a +1 and if was statistically worse (95% level) it scored a –1. A score of zero was used if postfiltration was not statistically significantly different from the treatment without filtration. Overall, these results show that postfiltration consistently contributed to a reduction in fouling potential.

The effectiveness of biological treatment, with respect to the six experimental assays, is summarized in Table 5. Here the biological treatment scores a +1 if it was statistically significantly better (95% level) than the control and a −1 if it was worse than the control. A zero was entered if the treatment was not statistically significantly different from the control. Note that only one of the biological treatments (IOCS or BAC) must work for the score to be +1, but both must fail for a score of zero. The results show that biological pretreatment clearly reduces the downstream fouling potential of the water.

An analysis similar to that contained in Tables 3–5 was performed to discriminate differences between the two biological pretreatments, IOCS and BAC. The results were mixed with neither treatment standing out as superior (data not shown). BAC removed more TOC than IOCS, while IOCS reduced the biofilm accumulation on glass beads more than BAC.

4. Discussion

Microorganisms are widely regarded as an anathema in the water treatment systems that deliver water to reverse osmosis or ultrafiltration membranes. The conventional view is that proliferation of bacteria or fungi in the water treatment system spells certain fouling for the downstream membranes. This perception is manifested in the common use of biocides, such as chlorine, to attempt to control microbial activity in the treatment system. In many industrial water treatment systems, a chlorine residual is maintained through part of the system and neutralized immediately upstream of the membranes to prevent damage to the polymers of

Table 2
Membrane fouling parameters

Treatment	Flux at 120 h mL/(mm^2 min)	C.I. 95% $n=$ 16 each	TOC removal	C.I. 95% $n=23$ each	Cell count $\log_{10}$(cells) cells/mm^2	C.I. 95% $n=350$	Bead assay $\log_{10}$(cells) cells/mm^2	C.I. 95% $n=350$	SEM thickness (μm)	C.I. 95% $n=114$	DAPI thickness (μm)	C.I. 95% $n=188$
BAC	5.0×10^{-4}	$+1.0\times10^{-4}$ -8.5×10^{-5}	22.5%	±2.0%	7.6	±0.2	7.7	±0.27	10.5	±3.9	11.2	±4.9
BACPF	2.2×10^{-3}	$+6.2\times10^{-4}$ -4.8×10^{-4}	37.9%	±1.7%	7.0	±0.2	6.1	±0.27	10.0	±3.9	8.6	±4.9
IOCSPF	1.0×10^{-3}	$+2.1\times10^{-4}$ -1.7×10^{-4}	30.7%	±2.6%	6.9	±0.2	5.6	±0.27	8.5	±3.9	8.4	±4.9
IOCS	4.4×10^{-4}	$+1.3\times10^{-4}$ -1.0×10^{-4}	19.0%	±2.4%	7.6	±0.2	7.0	±0.27	10.0	±3.9	12.5	±4.9
CTRL	4.6×10^{-4}	$+8.7\times10^{-5}$ -7.3×10^{-5}	0.0%	±0.0%	8.0	±0.2	8.1	±0.27	21.8	±3.9	43.7	±4.9
CTRLPF	8.7×10^{-4}	$+2.0\times10^{-4}$ -1.6×10^{-4}	22.7%	±1.1%	7.3	±0.2	6.8	±0.27	9.2	±3.9	19.6	±4.9
BACCL	7.3×10^{-4}	$+1.8\times10^{-4}$ -1.4×10^{-4}	16.5%	±2.2%	7.5	±0.2	6.5	±0.27	18.9	±3.9	13.6	±4.9
BACPFCL	1.9×10^{-3}	$+6.5\times10^{-4}$ -4.8×10^{-4}	36.2%	±1.75%	7.1	±0.2	5.9	±0.27	7.0	±3.9	11.3	±4.9
IOCSPFCL	1.1×10^{-3}	$+4.0\times10^{-4}$ -2.9×10^{-4}	25.1%	±1.9%	7.0	±0.2	5.8	±0.27	5.6	±3.9	12.1	±4.9
IOCSCL	6.9×10^{-4}	$+2.3\times10^{-4}$ -1.7×10^{-4}	3.9%	±1.0%	7.6	±0.2	6.2	±0.27	11.6	±3.9	10.7	±4.9
CTRLCL	5.8×10^{-4}	$+2.3\times10^{-4}$ -1.6×10^{-4}	0.0%	±0.0	8.1	±0.2	7.1	±0.27	31.2	±3.9	38.9	±4.9
CTRLPFCL	1.1×10^{-3}	$+2.9\times10^{-4}$ -2.3×10^{-4}	21.2%	±1.7%	7.4	±0.2	6.8	±0.27	7.5	±3.9	13.4	±4.9

the membrane. By suppressing microbial growth upstream of the membranes this approach may simply displace biofouling from the treatment system to the membranes themselves. An alternative viewpoint of deliberately promoting microbial growth in a biological pretreatment unit operation included in the treatment train has been proposed by others [8,29,30] and is supported by the data reported in this article.

Fig. 4. SEM image of fouling layer. The fouling layer is on the left and membrane on the right.

A comparison of the numbers of bacteria on these laboratory membranes was made with available literature values. Vrouwenvelder and van der Kooij [8] reported an average of $\log_{10} 7$–$9.3\,\text{cm}^{-2}$ total cells in 30 RO membranes from 13 pilot plants. In pilot studies where RO membranes were exposed for ten days, the total bacterial counts were $\log_{10} 8.0$ before the biological filter and $\log_{10} 6.7$ after treatment [29]. The numbers in the current study were somewhat higher than the second study but similar to those of the first at approximately $\log_{10} 9$–$10\,\text{cm}^{-2}$. It is important to note that these studies were not designed to duplicate all phenomena leading to biofouling on membranes in field systems, but rather were developed to provide a mechanism for evaluating the relative efficacy of upstream treatments on biofouling potential. Therefore, it is not unexpected that these laboratory systems do not produce bacterial numbers identical to those found in the field.

Table 3
Summary of chlorination impacts

Assay	Prechlorination treatment					
	BAC	BACPF	IOCSPF	IOCS	CTRL	CTRLPF
Flux	0	0	0	0	0	0
Cells	0	0	0	0	0	0
SEM	−1	0	0	0	−1	0
DAPI	0	0	0	0	0	+1
TOC	−1	0	−1	−1	0	0
Bead	+1	0	0	+1	+1	0
Total	−1	0	−1	0	0	+1

Values of ± 1 were assigned if the test process was found to be statistically different (better performance = +1, worse performance = −1) than the control at the 95% confidence level using a multiple comparison testing. No significant difference between the test process and the control resulted in a 0 score.

Table 4
Summary of filtration impacts

Assay	Post-filtration treatment					
	BAC	IOCS	CTRL	BACCL	IOCSCL	CTRLCL
Flux	+1	0	0	+1	0	0
Cells	+1	+1	+1	+1	+1	+1
SEM	0	0	+1	+1	+1	+1
DAPI	0	0	+1	0	0	+1
TOC	+1	+1	+1	+1	+1	+1
Bead	+1	+1	+1	+1	+1	+1
Total	+4	+3	+5	+5	+4	+5

Values of ± 1 were assigned if the test process was found to be statistically different (better performance = +1, worse performance = −1) than the control at the 95% confidence level using a multiple comparison testing. No significant difference between the test process and the control resulted in a 0 score.

Table 5
Summary of biological pretreatment impacts

Assay	Biological pretreatment			
	No post-filtration no prechlorination	Post-filtration only	Prechlorination only	Post-filtration prechlorination
Flux	0	+1	0	0
Cells	+1	+1	+1	+1
SEM	+1	0	+1	0
DAPI	+1	+1	+1	0
TOC	+1	+1	+1	+1
Bead	+1	+1	+1	+1
Total	+5	+5	+5	+3

Values of ± 1 were assigned if the test process was found to be statistically different (better performance = +1, worse performance = −1) than the control at the 95% confidence level using a multiple comparison testing. No significant difference between the test process and the control resulted in a 0 score.

Table 6
Qualitative ranking of treatments

Treatment	Assay						
	Flux	Cells	SEM	DAPI	TOC	Bead	Average
IOCSPF	3	1	4	1	3	1	2.2
BACPF	1	2	7	2	1	4	2.8
BACPFCL	2	4	2	5	2	3	3
IOCSPFCL	4	3	1	6	4	2	3.3
CTRLPF	5	5	5	10	5	7	6.2
CTRLPFCL	7	6	3	8	7	7	6.5
BAC	6	10	8	4	6	11	7.5
IOCS	8	8	6	7	8	9	7.7
IOCSCL	10	9	9	3	10	5	7.7
BACCL	9	7	10	9	9	6	8.3
CTRLCL	11	12	12	11	12	10	11.3
CTRL	12	11	11	12	11	12	11.5

Biological pretreatment reduced downstream fouling of membranes as measured by the suite of assays employed in this work. A biological pretreatment step reduced the number of biofilm cells in both the membrane and bead assays. There was also a significant reduction in TOC. Biologically activated carbon and microbially colonized iron oxide coated sand exhibited similar efficacy as biological pretreatment options. Microfiltration, after biological treatment, further reduced downstream fouling of membranes. It appears that the use of biological treatment coupled with microfiltration had the most significant impact on reducing the downstream fouling potential of membrane feed water.

The success of combining biological pretreatment and microfiltration is apparent in an overall ranking of the different treatment options (Table 6). To qualitatively rank all of the treatments, the treatments were scored from 1 to 12 (1 being the best performance and 12 being the worst) without regard to statistical differences according to the mean values of the results obtained for each assay. Many scores could differ by more than one and still be statistically the same. This analysis provides, however, another view of the overall trends of the experimental results. Table 6 shows how the treatments ranked in order from the most effective treatment (lowest total score) to the least effective treatment (highest total score). This ranking indicates that the combination of biological pretreatment and postfiltration is the most effective way to reduce downstream biofouling. This table also suggests that filtration alone is more effective than biological treatment alone. We hypothesize that the biological pretreatment step converts soluble carbon in the raw water to biomass and carbon dioxide and that the biomass is subsequently removed by the postfiltration step. In this way the fouling potential of the water is irreversibly reduced.

None of our measurements or analyses indicates an advantage to prechlorination. There was little effect of chlorination on any of the six assays we used. From the overall ranking of treatments (Table 6) there is also no discernable effect of chlorination. Chlorination might be hypothesized to have multiple effects in a biological pretreatment process. The antimicrobial effects of the chlorine could suppress microbial activity, reducing the efficacy of the biological step. On the other hand, an oxidant like chlorine could potentially partially oxidize complex organics in the water making them more available to microorganisms and actually promote growth. In any case, the results from our experimental system provide no support for including chlorination in the treatment train.

Our results are in general agreement with other published studies that examined biological pretreatment processes and their impact on membrane fouling. Griebe and Flemming [29] reported a 1.5 log-reduction in total

cell counts on a reverse osmosis membrane treating water from a sand biofilter. The biofilter also reduced by 70% the quantity of humic substances on the membrane. The flux through a reverse osmosis membrane was maintained unchanged for 200 h using biologically pretreated water whereas it was reduced by 20% in the control membrane. van der Hoek and colleagues [30] found that biologically activated carbon filtration followed by slow sand filtration produced reverse osmosis feedwater that met their requirements. They concluded that not only did biological pretreatment reduce the organic carbon content of the feedwater, but that synthetic organics were effectively removed in these biofilters and the reverse osmosis retentate was better quality resulting in lower disposal costs.

Biological treatment is universally employed in the treatment of wastewater and of drinking water. We suggest that biological unit operations, coupled with postfiltration, may be a viable unit operation in treatment systems that provide the feed water to membranes. Use of this technology has the potential to reduce both biofouling and NOM fouling of these membranes.

5. Conclusions

- Biological treatment of humic substances reduced TOC reaching downstream membranes.
- Biological treatment with biologically active carbon and iron oxide coated sand reduced fouling of downstream membranes.
- Microfiltration after biological treatment further reduced downstream membrane fouling. Microfiltration alone is also beneficial.
- Chlorination of the water prior to biological treatment had no effect on the process.
- A combination of assays to determine the effect of processes on membrane fouling provided a more comprehensive body of evidence than any single assay.
- The results presented here are likely to be conservative since humic substances are believed to be a reasonably recalcitrant form of dissolved organic matter.

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