Biological pretreatment for membrane water treatment sytems
by Christopher Francis Wend

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Engineering
Montana State University

Abstract:
Biological processes are often used in the drinking water industry to reduce the amount of organic carbon present in the source water. This reduction of organic carbon will limit the production of disinfection by-products and reduce regrowth events within the distribution system. The goal of this work was to determine if biological pretreatment will reduce fouling in membrane water treatment systems. Biological pretreatment for membrane water treatment processes were shown to reduce biofouling of membrane surfaces using membrane cell counts, glass bead cell counts, total organic carbon measurements, fouling layer thickness measured by light microscopy and scanning electron microscopy, and membrane flux reduction. The organic carbon source was humic and fulvic acids extracted from Elliot Silt Loam Soil obtained from the International Humic Substances Society. The biological processes used biological activated carbon and iron-oxide coated sand as support media for the biofilm. The experimental design also included prechlorination and post-filtration as additional factors to be considered. Results indicated that biological pretreatment was capable of reducing downstream fouling of membrane water treatment processes. The biological pretreatment process coupled with filtration resulted in the best reduction of downstream fouling as measured by the assays employed, while prechlorination did not appear to impact the biofouling reduction. Destructive column sampling yielded cell count data that was used in a biofilm model to show that first-order kinetics adequately accounted for the cell reduction in the columns and that the organic carbon pool was comprised of two pools of substrate where one pool is more usable by the microorganisms than the other pool.

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A dissertation submitted in partial fulfillment
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Christopher Francis Wend

This dissertation has been read by each member of the dissertation committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

Philip S. Stewart — Philip S. Stewart (Signature) — 11-27-2000 Date

Approved for the Department of Civil Engineering

Donald Rabern — Donald A. Rabern (Signature) — 11/27/00 Date

Approved for the College of Graduate Studies

Bruce McLeod — Bruce R. McLeod (Signature) — 12-4-00 Date

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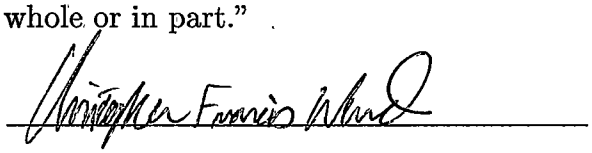
Signature 

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ABSTRACT

Biological processes are often used in the drinking water industry to reduce the amount of organic carbon present in the source water. This reduction of organic carbon will limit the production of disinfection by-products and reduce regrowth events within the distribution system. The goal of this work was to determine if biological pretreatment will reduce fouling in membrane water treatment systems. Biological pretreatment for membrane water treatment processes were shown to reduce biofouling of membrane surfaces using membrane cell counts, glass bead cell counts, total organic carbon measurements, fouling layer thickness measured by light microscopy and scanning electron microscopy, and membrane flux reduction. The organic carbon source was humic and fulvic acids extracted from Elliot Silt Loam Soil obtained from the International Humic Substances Society. The biological processes used biological activated carbon and iron-oxide coated sand as support media for the biofilm. The experimental design also included prechlorination and post-filtration as additional factors to be considered. Results indicated that biological pretreatment was capable of reducing downstream fouling of membrane water treatment processes. The biological pretreatment process coupled with filtration resulted in the best reduction of downstream fouling as measured by the assays employed, while prechlorination did not appear to impact the biofouling reduction. Destructive column sampling yielded cell count data that was used in a biofilm model to show that first-order kinetics adequately accounted for the cell reduction in the columns and that the organic carbon pool was comprised of two pools of substrate where one pool is more usable by the microorganisms than the other pool.

CHAPTER 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, and bacterial/fungal/algal/protozoan cells (DuPont, 1994; Al-Ahmad and Aleem, 1993). 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 simple concentration and retention of constituents from the bulk. Another mechanism of fouling is the proliferation of organisms in biofilms on the membranes. In fact, a combination of these effects most likely is responsible for the adverse influence on membrane production (Mallevialle et al., 1996; Chapman-Wilbert, 1997).

Current Methods of Fouling Control

The control of reverse osmosis (RO) membrane fouling 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) continuous upstream ap-

plication of biocides. In the first case, considerable effort has been expended by the industry to identify processes that decrease the load of particulates onto the membranes. As a consequence, there are a wide variety of "pretreatment" options found at locations using reverse osmosis including dual or single media filtration, softening and/or ion exchange, granular activated carbon filters, pH adjustment, etc. (DuPont, 1994). In practice, there is no one general process train; the treatment options are dependent on water quality and the preferences of the consulting company responsible for installation.

It is also possible for membranes to be cleaned directly with agents compatible with the membrane chemistry. Since many membranes are sensitive to oxidizing disinfectants (chlorine, for example) the choice of chemicals must be made judiciously. This aspect of membrane maintenance can be very frustrating to the process operators. In many cases, vendors prescribe a specific chemical and application regime without providing the operators with any information on their rationale, presumably because the cleaning process is proprietary.

The third point above is the search for membranes with reduced fouling potential. This could be achieved by either creating/modifying polymers that foul at a decreased rate or producing membranes that can be more easily disinfected or cleaned (Chapman-Wilbert, 1997). Experience suggests that neither of these approaches will eliminate fouling. During long term operation, the surface chemistry of membranes is modified by molecules and microorganisms found in the water, therefore masking

the designed or altered surface chemistry features. There have been improvements in surface modification techniques that reduce fouling by the addition of surfactants and work is continuing in this area (Ridgway, 1997).

The fourth point brings out the attempts by the membrane industry to control fouling through the use of biocides. This approach will produce a situation where the fouling may be controlled but not eliminated. There is ample evidence to indicate that biofilm communities are considerably less susceptible to disinfection than suspended cells and that long-term disinfection will not completely control fouling of surfaces. Continuous upstream disinfection, which is commonly practiced, also has limitations. Typically, oxidizing disinfectants are present until immediately before the membrane in an attempt to suppress biological activity in the pretreatment train. The end result is that the environmental pressures that have repressed biofilm growth are removed at the membrane, which creates the opportunity for microbial proliferation at precisely the point where it is least desired (Saeed et al., 1998). It is also possible that continuous biocide addition will select for resistant strains of bacteria that can then foul the membrane.

Biological Pretreatment

It is obvious that none of the above approaches for mitigating membrane fouling are singularly sound. It is most probable that a combination of methods will be required to increase membrane productivity. In light of the problems inherent in

suppressing biological activity and fouling of upstream processes and membranes, it was proposed to reduce membrane fouling by pretreating feed water using biological reactors to remove the organic nutrients that support formation of fouling biofilms. The process was designed to increase the biological stability of water to be further processed by reverse osmosis membranes and to improve membrane productivity by complementing existing processes in a pretreatment train while reducing dependence on extensive use of disinfectants. The approach is ecologically sound because it uses biological processes to control subsequent biological activity; the emphasis is on controlling biofouling in an engineered system rather than having it occur in undesirable locations. The process is based on the experiences of the drinking water industry where biological filtration is being used to reduce concentrations of natural organic matter, decrease disinfectant demand, and reduce downstream fouling of the distribution system.

Drinking Water Industry

There is a reasonable amount of information available on biological treatment of drinking water. The process was first implemented in France and other western European countries nearly 20 years ago (Sontheimer et al., 1978, 1979a,b). In the most traditional form, separate granular activated carbon (GAC) filters are located downstream from conventional treatment. In conventional treatment, particle removal is optimized through coagulation, flocculation, sedimentation, and filtration.

The biological filters are then optimized for microbial utilization of a portion of the natural organic matter remaining in the water. 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 removals in these filters range from 5% to 75% (Bouwer and Crowe, 1988).

One of the first observations in the full-scale use of biological filtration was that the type of filter media had a substantial influence on the net removal of organic carbon from the water. For instance, although rapid sand filters do have the capacity to biologically remove carbon (Eberhardt et al., 1977; Sontheimer et al., 1978; Borbiogot et al., 1982; van der Kooij and Hijnen, 1985) it has been found that GAC has superior performance (LeChevallier et al., 1992; comparison between DeWaters and DiGiano, 1990 and Hozalski et al., 1995). This is presumed to be the result of a higher amount of biomass that attaches to GAC vs anthracite (Niquette et al., 1998). LeChevallier et al. (1992) demonstrated that there were more bacteria per unit surface area on GAC than sand, and that the TOC removal rates were 51% vs 26%. Another advantage of GAC over other media is that the attached microbial population is less prone to shock from changes in water quality, down time, or accidental application of disinfectant (Bablon et al., 1988; Krasner et al., 1993). This knowledge of the performance of filter media was strongly considered in the experimental design.

In most cases, improved TOC removal in biological filters can be gained by increasing the empty bed contact time (EBCT). The EBCT is the residence time of the fluid in the filter calculated as though the entire volume occupied by the filter media is occupied by water. Because of the very large volumes of water that a drinking water plant treats, a small reduction in EBCT results in substantial savings in filter volume. Experimental EBCTs in biological filters have varied from two to 30 minutes. Sontheimer and Hubele (1987) demonstrated an increase in dissolved organic carbon removal from 27% to 41% when the EBCT increased from 5 to 20 minutes. LeChevallier et al. (1992) reported a 29% removal of TOC with a 5 minute EBCT and a 51.5% reduction at 20 minutes. Prevost et al. (1990) suggest that a 20 minute EBCT is required for 90% removal of biodegradable organic carbon. However, there are instances where increased EBCT is not beneficial, which is probably a result of the biodegradability of the organic matter present in the water (Hozalski et al., 1995). Certainly the EBCT required for biological removal of TOC will be temperature dependent. This has been demonstrated at a full-scale biological filtration plant, where 12 minutes of EBCT was required at 0.5° C for the same percent removal obtained in 6 minutes at 10 - 12° C (Niquette et al., 1998). Due to design constraints and stringent regulatory requirements for filtration to meet particle removal standards, most full scale biological filters operate with short (5 min) EBCTs. In instances where the technology can be applied for pretreatment of water for membrane processing, the EBCT can be optimized for organic removal.

A common treatment step before biological treatment is ozonation. Ozone may be applied to reduce taste and odor compounds, remove color, provide primary disinfection for protozoan cysts, or to reduce disinfection demand/disinfection by products by oxidizing some of the organic matter. Water that has been preozonated often has elevated levels of lower molecular weight organic compounds; these compounds have been associated with increased biofilm development downstream (van der Kooij et al., 1989; Price, 1994; LeChevallier et al., 1996). Goel et al. (1995) reported that the fraction of recalcitrant natural organic matter in water made available for microbial growth was increased after ozonation, but the numerical value varied from site to site. This has also been substantiated by van der Kooij et al. (1982), Werner and Hambsch (1986), Servais et al. (1987) and Speitel et al. (1993). Because biofilms can form either in controlled treatment processes (biological filters) or in uncontrolled deleterious locations (distribution systems), the drinking water industry strongly considers biological filtration after ozonation, regardless of the original intent of ozone application.

Interestingly, chlorination sometimes has the same effect on biodegradability of natural organic matter as ozonation. LeChevallier et al. (1992) showed that chlorination increased the biodegradable fraction of organic matter in water. In a survey of plants in the Netherlands, this increase was as high as 1.75 fold (Cooperative Report, 1988). Chlorine has been found to alter the structure of humic substances in water, which may render them more degradable (Hanna et al., 1991). Paul (1996)

reports not only an increase in degradable organic carbon after chlorination, but an increase in culturable cell counts as well. These observations show how the current practice of applying oxidizing disinfectants until immediately before a reverse osmosis membrane actually "pushes" biological activity and associated fouling onto the membrane. The use of preoxidation to improve the ability of biological pretreatment to remove organic matter from water is a key component of the work plan.

Even though the emphasis in drinking water has been on the use of GAC, there is other evidence to suggest that the iron oxide coated media may be a better choice for removal of natural organic matter that directly causes fouling (Jacangelo et al., 1995; Owen et al., 1995) and/or subsequent biofouling. Chang and Benjamin (1996) demonstrated that addition of iron oxide particles to individual ultrafiltration hollow fibers greatly reduced fouling by organic matter. Organic matter preferentially bound to the oxide particles which could then be removed by backwashing. Iron oxides have a large potential for the sorption of natural organic matter (McCarthy et al., 1993; Parfitt et al., 1977; Zhou et al., 1994). Under abiotic conditions, humic material is irreversibly held on the surface of iron oxides (Gu et al., 1994; Gu et al., 1996). 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 (McMeen and Benjamin, 1997). 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."

A classification of the constituents of NOM from surface waters (Malcolm, 1991; Kaplan, 1993) indicates that approximately 50-75% is humic substances. These concentrations are lower in groundwater. Humic substances are generally considered to be poorly biodegradable, because of their large molecular size. However, Namkung and Rittmann (1987) have shown that humic substances are in fact biodegradable. More recently, Volk et al.(1997) have shown that biofilm bacteria are capable of using humic materials. Because humic substances in the bulk water are poorly degraded, it is probable that bioavailability of the humic substances is enhanced when bound to surfaces. The humic molecules then undergo a conformational change and expose the utilizable functional groups (Beckett, 1990). Immobilization on the surface is also likely to permit the cells to use exoenzymes to attack the bonds between the bound amino acids, sugars, etc. and the backbone of the humic molecule (Wetzel et al., 1991; Jones and Lock, 1991; Munster, 1991). There is strong evidence to suggest that the sorption of humic substances allows them to become available for biofilm use. When an assessment of the growth rates of biofilm bacteria grown on humic materials was made in experiments at the Center for Biofilm Engineering, it was found that the growth rate was independent of the added humic carbon concentration (zero order kinetics). It is believed this may be caused by the large amount of humic materials bound to the biofilm (8.3 - 11 $\frac{\mu gC}{cm^2}$); supplementation of additional humic material

did not influence the growth rate. There was also visual evidence that the humic material was sorbed, as these biofilms were a characteristic brown color (AWWARF final report).

This mechanism has profound implications for the biological treatment of water as well as providing a potential explanation for observations of biofouling on membranes. Membrane autopsy data from a polyamide nanofiltration membrane showed that 73% of fouling deposit was organics, of which 34% was humic material. This same deposit also contained 16% iron oxide. In the same report, foulant from a polyamide RO membrane contained 62% organics and 6% iron oxides (Dudley and Fazel, 1997). Similarly, Butt et al. (1997) reported that RO desalination membrane foulant was primarily biomass with iron contributing appreciably to foulant mass.

It is probable that the choice of filter media (GAC vs iron coated sand) and whether or not to preoxidize prior to biological filtration will depend on the nature of the organic matter in the source water. Although NOM has a high affinity for iron oxides, high molecular weight fractions of NOM are also preferentially removed by GAC binding (Owen et al., 1995). Preoxidation can result in increased biodegradable fractions, but on occasion biofiltration following ozonation only reduces the biodegradable fraction to preozonation levels (LeChevallier et al., 1992). Since iron oxide coated media tend to remove reduced iron from solution, there may be further advantages for these media when the source water is high in dissolved iron. Therefore, it was proposed to investigate several potential combinations of filter media

and the presence/absence of prechlorination under controlled laboratory conditions to bracket ideal design parameters for biological pretreatment.

The premise of biological treatment as described above is to (1) immobilize organic matter that would otherwise accumulate on reverse osmosis membranes and (2) use indigenous organisms to metabolize the sorbed organics as well as other bulk phase carbon compounds. The end result will be the reproduction of bacterial cells within the filter. These organisms will be released from the filter and could then accumulate on the reverse osmosis membrane. Decay processes would then permit the dead microbial cells to become substrate for surviving bacteria. Although the overall rate of fouling from this process should be significantly less than if no biological treatment was in place, there is still concern from operators that bacterial accumulation is deleterious to membrane performance. For example, Collentro and Collentro (1997) 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 (Kucera, 1997). This prejudice may be unfounded if (1) the biological filter is operated properly and (2) adequate downstream removal techniques for minimizing bacterial and carbon fine particle release are in place.

To minimize the chance for transport of bacteria produced in the biological filter and released sand/GAC particles, it was proposed to use a low maintenance particle filter. Prior to performing this work, particle size distribution data on particles released from a biological filter were collected by Nick Krauss at the Center for Biofilm Engineering and it was decided that the best option will likely be a microfiltration unit. A microfilter downstream from a laboratory biological filter was installed and it operated extremely well. The microfilter was effective for removing the vast majority of the bacteria and shed filter fines. It should be noted, however, that microfiltration alone would not provide the same advantages for reducing reverse osmosis membrane fouling as microfiltration after biological pretreatment. Although MF has been shown to remove significant fractions of iron and reduce colloidal fouling of downstream nanofiltration membranes (Chellam et al., 1997), a portion of the humic substances found in typical surface waters will pass through MF membranes (Jacangelo et al., 1989). Laine et al. (1990, 1989) demonstrated that pretreatment is necessary to reduce the organic matter that may pass through UF membranes, and that activated carbon pretreatment shows the most promise.

The approach I adopted was to develop and test biological treatment processes to be integrated in traditional pretreatment trains with the purpose of prolonging membrane performance. It was believed that the deliberate encouragement of biological growth within a component of the pretreatment train that is under process control will substantially reduce the undesirable growth on reverse osmosis mem-

branes. Additionally, the biological filters may significantly reduce natural organic matter/humic fouling. Griebe and Flemming (1998) have produced work that supports these last two points. The design incorporated both a biological treatment step and a method to remove organisms and fines shed from the biological filter. A favorable outcome would be a cost effective treatment method to reduce fouling and chemical use.

Experimental Goals and Objectives

As set forth in the previous sections, it was proposed to reduce membrane fouling by pretreating feed water using biological reactors to remove the organic nutrients that support formation of fouling biofilms. To this end the following overall goal is stated here.

GOAL: Determine if biological pretreatment can reduce fouling in membrane systems.

Several objectives were set forth to test the feasibility of utilizing biological pretreatment as a membrane pretreatment step.

1. Determine if biological pretreatment using BAC and IOCS as support media will reduce downstream fouling.

2. Determine if chlorination as an oxidation step for feed water will reduce downstream fouling both by itself and in combination with biological pretreatment.

3. Determine if microfiltration of feed water will reduce downstream fouling both by itself and in combination with biological pretreatment.

4. Develop evaluation methods for objectives 1-3 by developing and testing the following assays.

   (a) Membrane flux measurements

   (b) Membrane fouling layer cell counts

   (c) Membrane fouling layer thickness measured with SEM

   (d) Membrane fouling layer thickness measured with DAPI stained thin sections.

   (e) TOC removal from the system.

   (f) Bead assay biofilm cell counts.

CHAPTER 2

MATERIALS AND METHODS

Experimental Setup

The tasks set forth for this work proposed to investigate biological filtration using biologically active carbon and iron-oxide coated sand, examine the impact of chlorination of the feed water on downstream fouling, and refine and test a membrane fouling assay and a post biological treatment microfiltration step. Combining the factors of chlorination, different packing media, and post filtration resulted in an experimental design that consisted of 12 separate treatments.

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 determination after treatment and flux measurements through a diagnostic membrane assay were taken and at the end of each run, destructive biofilm assays were performed. Figure (1) outlines the order in a treatment where additions and assays were placed. Note that the treatment splits after the biological pretreatment step with one stream going through a microfilter and the other

not going through a microfilter. Control treatments did not have a biological pretreatment step and the nonchlorinated treatments did not have a chlorination step. The test filtration apparatus for this study was constructed using type 316 stainless steel (ASTM A- 213/ASME SA-213 average wall; ASTM A-269,ASTM A-511). The choice of material was based upon the need to limit the amount of leachable organic carbon and still provide sufficient strength for the pressures involved with the operation of the columns. All connecting tubing was either 6.35 *mm* (0.25 *in*) or 12.7 *mm* (0.5 *in*) outside diameter of type 316 stainless steel. The inside diameter of the 6.35 *mm* (0.25 *in*) tubing was 4.93 *mm* (0.194 *in*) and the inside diameter of the 12.7 *mm* (0.5 *in*) tubing was 10.92 *mm* (0.430 *in*).

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 an empty control, represented three treatments. The effluent of each of these treatments was split and a 0.22 μm ($8.66 \times 10^{-6} in$) post filtration step was added on one of the streams from each treatment. To assess the effects of chlorination on the system the entire system was duplicated. One side was prechlorinated and the other side was not. Thus, twelve treatment systems were constructed for sampling and evaluation.

The setup also contained several biofilm assays that were placed in the effluent streams. One assay was a 4.93 *mm* (0.194 *in*) inside diameter tube of 316 stainless steel, 25.4 *mm* (1 *in*) in length that was packed with 0.5 *mm* (0.0197 *in*) glass spheres.

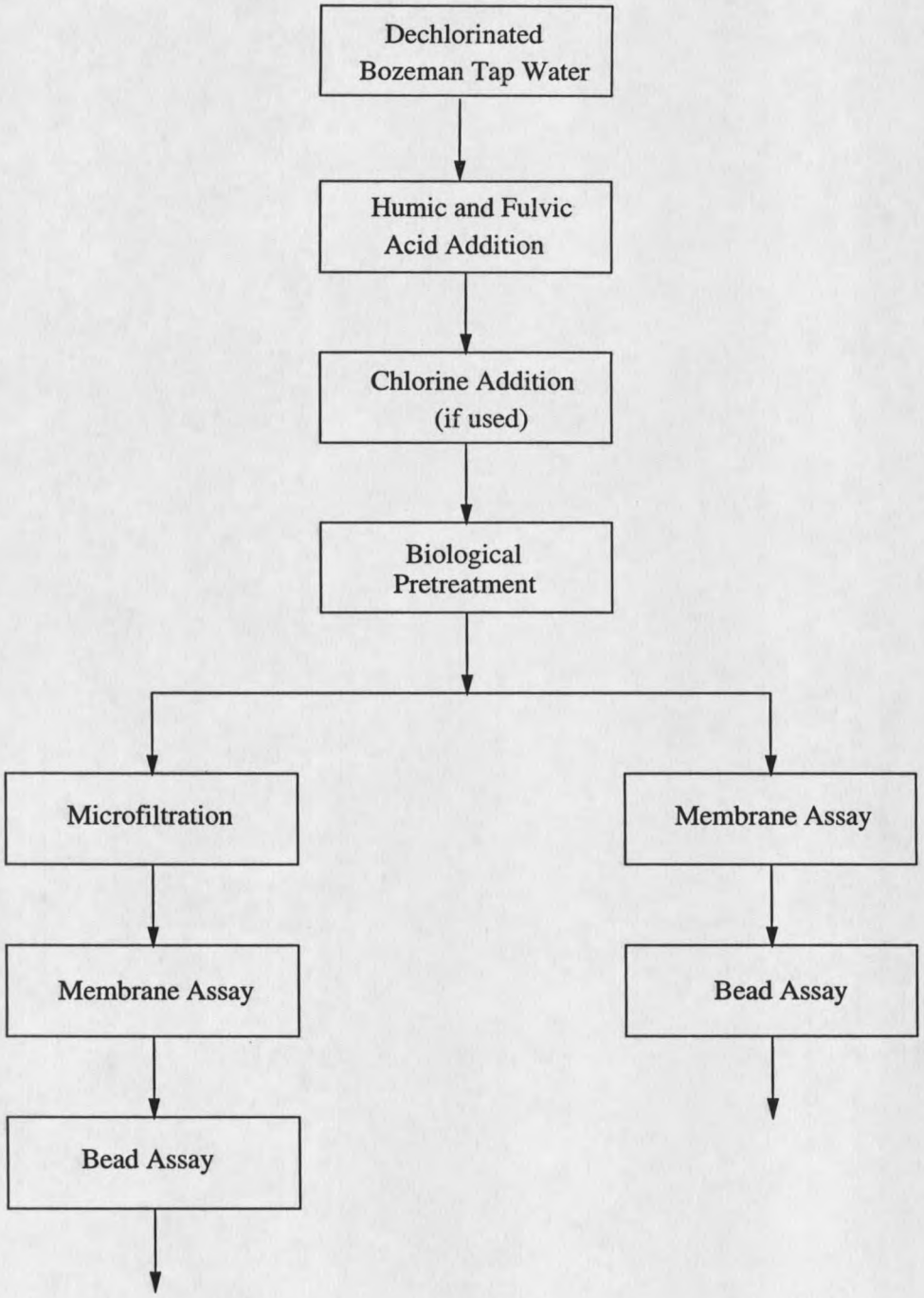


Figure 1: Treatment train schematic. Schematic of a treatment train used during this study.

The other assay was an in-line membrane holder that allowed for flux through a 47 *mm* (1.85 *in*) diameter membrane swatch and flow across the membrane while the system was under pressure.

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 72° F. The flow rate through each set of assay devices was maintained individually with a stainless steel needle valve. Flows were maintained between 1-1.2 $\frac{ml}{min}$.

Biological Pretreatment Columns

Using information from the drinking water industry, a minimum of 20 minutes empty bed contact time was desired. Studies have shown that a 20 minute empty bed contact time is sufficient to remove the majority of easily assimilable organic compounds commonly found in surface waters.

To assure that this situation was met, the columns were designed to have an empty bed contact time that was at least 30 minutes.

The columns were constructed with 316 stainless steel tubing that was ordered from Marmon/Keystone Corporation. 25.4 *mm* (1 *in*) tubing was specified with a wall thickness of 0.889 *mm* (0.035 *in*). The inside diameter was 23.62 *mm* (0.930 *in*). The column length was 228.6 *mm* (9*in*) and the resulting volume for the columns was 100167 mm^3 (6.1136 in^3).

During the three experiments,the flow rate through the columns was 2-2.4 $\frac{ml}{min}$ which resulted in an empty bed contact time of 41-50 minutes. Note that this flow rate is twice the flow rate through the assay devices since the stream was split after the biological pretreatment step and the range accounts for the flow change through the membrane assay as the flux declined.

Support screening was 100 mesh 316 stainless steel. All end caps were Swagelock 316 stainless steel compression tube fittings.

Flow configuration was in the upflow mode with the columns mounted vertically.

Column Packing Media

The support packing for the biological pretreatment columns were iron-oxide coated sand and biologically active carbon.

Biological Activated Carbon

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 due mainly 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.

Iron-Oxide Coated Sand

Iron-oxide coated sand was produced using the method outlined in "NOM Adsorption Onto Iron-Oxide-Coated Sand", AWWARF, 1993. This stable coating was developed so that it could be regenerated in a full scale operation and retain good NOM (natural organic matter) adsorption.

Industrial quartz sand manufactured by Unmin corporation, Emmett, Idaho, was screened to between 30-40 mesh. The effective size in this range is 0.45 *mm*. This sand was soaked in 50% sulfuric acid solution for 24 hours, then rinsed with deionized water, and dried at 110° C for 20 hours in accordance with the method of Chang and Benjamin, 1996.

An iron oxide solution was prepared with 1 g of ferric chloride per milliliter of deionized water. A 10M solution of NaOH was added to this solution until the OH:Fe molar ratio was 2.5. This material was then dried in a pan at 110° C for 14 hours. 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 hours, 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.

Total Organic Carbon Amendment

Bozeman tap water was used as the source water. This water is typically low in total organic carbon and was not considered to be representative of a typical source water for a membrane water treatment plant. To simulate the natural organic carbon found in many surface waters, Bozeman tap water was amended with organic carbon. The organic carbon 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 were extracted from the soil by mixing 75 g of soil in 750 ml of 6N NaOH solution for 24-48 hours. After mixing, the slurry was centrifuged for 20 minutes at 16,300g at 4° C. The supernatant was decanted and used as a stock solution to prepare a feed solution of humic/fulvic acids. This solution was fed into the influent of the experimental setup at a 500ppb to 2ppm carbon level. Due to the variability of the influent water carbon content and the feed solution input control, the final level of organic carbon fed to the reactors was not constant. The amount of organic carbon entering the columns was measured routinely.

The feed water was Bozeman tap water that was passed through a column packed with biological activated carbon (BAC). The BAC column was used to dechlorinate the tap water and remove a portion of the readily assimilable organic carbon. Therefore, the carbon amendment represents the major carbon source introduced into the system. Nitrogen and phosphorus were added to ensure that the limiting nutrient would be carbon. The maximum carbon input from the carbon amendment was 2 $\frac{mg}{l}$ and the maximum amount from the tap water after dechlorination was estimated to be around 2 $\frac{mg}{l}$. Adding these two concentrations yielded an upper bound on the carbon concentration of 4 $\frac{mg}{l}$ of carbon. Based upon the 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. The stock carbon amendment solution contained 2.5 $\frac{mmoleC}{l}$. Twice the necessary nitrogen and phosphorus amounts were determined to be 0.5 $\frac{mmoleN}{l}$ and 0.05 $\frac{mmoleP}{l}$, respectively. The nitrogen and phosphorus were then added to the stock amendment solution in the form of ammonium nitrate and potassium phosphate when it was prepared. This allowed the nitrogen and phosphorus to be mixed with the carbon source just prior to injection into the test apparatus.

Chlorination

A stock solution of chlorine was prepared from bleach and deionized water at pH 7 and was injected into the chlorinated treatment train after addition and mixing of the TOC amendment. The chlorine and TOC amended source water were mixed

with a static mixer for an initial concentration of 1 $\frac{mgCl}{l}$ and a 30 minute contact time with the TOC was allowed prior to application to any columns. 30 minutes was found to be sufficient time for the chlorine to react with the TOC and not be present in the biological pretreatment columns. However, the design of the test equipment did not allow for chlorine measurement just prior to application to the biological pretreatment columns. The contact time was achieved by building a longer inlet tube to the treatment columns than the inlet tube for the non-chlorinated treatment columns.

Postfiltration

Microfiltration was chosen to provide postfiltration of the biological pretreatment process. A 0.22 μm cartridge microfilter was placed in-line before the biofilm assays. These filters never plugged and were left in place during the entire project.

Experimental Assays

Two experimental assays were developed to examine the biofilm and the biofilm's impact on the system. The membrane assay provided a measure of the biofilm thickness and membrane flux reduction with active transport of water through the biofilm and membrane while at the same time having flow across the biofilm. The

bead assay measured only the in-line biofilm growth potential of the water without the added factor of flux through a membrane.

Membrane Assay

The membrane assay device was constructed out of two plates of aluminum block (Figure 2). The blocks measured 25.4 mm x 76.2 mm x 76.2 mm (1 in x 3 in x 3 in). Two blocks are sandwiched together with four bolts. A membrane, silicon gasket, polycarbonate screen, and filter paper support for the membrane are placed between the blocks. One block allows the effluent to enter and leave while crossing the membrane swatch. The other block allows for flux through the membrane by providing an outlet for the permeate to atmospheric pressure.

The polycarbonate screen was placed over the holes of the block that provide 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. The four bolts were then torqued down to 10 $N \cdot m$ (7.38 $ft \cdot lbs$) in a cross hole pattern.

The silicon gasket forms the flow channel for the cross flow of the test stream. With the design flow of the system, the Reynold's number is at least 450 and is probably higher due to the reduced cross- sectional area produced from compression of the gasket.

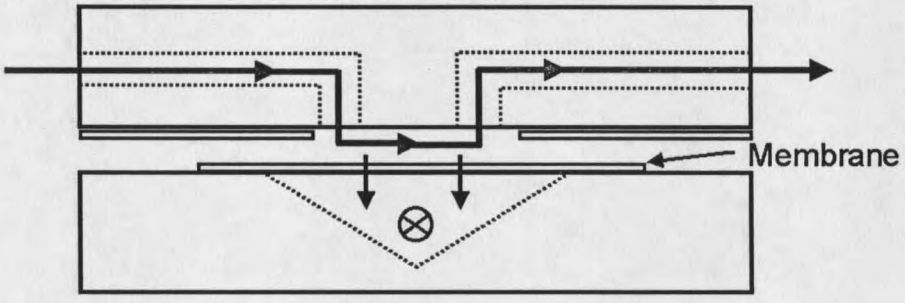


Figure 2: Side view of the membrane assay holder.

During the experimental run, the flux through the membrane was measured periodically to determine the flux reduction as the fouling layer was developing. Flux measurement was determined 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 assays 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.

Bead Assay

The bead assay was put in-line with the effluent stream. Its purpose was to provide an assessment of the biofilm growth potential after each of the treatments.

The apparatus consisted of a short 316 stainless steel tube. The assay column was a 4.93 *mm* (0.194 *in*) inside diameter tube of 316 stainless steel, 25.4 *mm* (1 *in*) in length that was packed with 0.5 *mm* (0.0197 *in*) 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 dilution water. This mixture of beads, biofilm, and water was vortexed for 30 seconds and the appropriate dilution series performed to enumerate the bacteria.

Analytical Methods

Cell Enumeration

The bacteria were counted using direct count epifluorescent microscopy on a Nikon 8100 microscope at 1000x. 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 minute at a concentration of 10 $\frac{mg}{l}$.

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.

SEM Fouling Layer Thickness:

Scanning electron microscopy was utilized to assess the membrane fouling layer thickness. The scanning electron microscope 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. The SEM was purchased with a grant from the Murdock Charitable Trust and MSU and is located in the Image and Chemical Analysis Laboratory at MSU-Bozeman.

To determine the thickness of the fouling layer, a small portion of the fouled layer and membrane was cut from the membrane. This sample was then mounted vertically in a special stage. The stage is mounted on a post that allows insertion into a flash freezer that utilizes liquid nitrogen and vacuum to quickly freeze the sample. The sample is then introduced into the cryostage where the pressure is reduced to $1x10^{-4}$ *torr* and the stage is further cooled to around $-190°$ C. At this point tools within the microscope sample preparation area are used to cut across the membrane and fouling layer 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 2 nm gold prior to moving the sample into the SEM chamber.

Once in the SEM chamber, the pressure is further reduced to $1x10^{-6}$ $torr$ and the chamber is 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 low nutrient conditions of the experimental system.

DAPI Fouling Layer Thickness

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 (VWR Scientific Products part no. 25608-930). This compound is an embedding medium for frozen tissue specimens. The specimen was frozen in a pool of OCT 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.

The slices were then stained with DAPI. The staining procedure consisted of immersion of the slide in 100 $\frac{mg}{l}$ DAPI solution for 20 seconds and then drying before placing on the microscope for analysis.

The thickness of the fouling layer could then be estimated through several measurements of the fouling layer. 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 could be estimated 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).

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 into 10 *ml* of dilution water and homogenized. The appropriate dilution was made and a direct count as described earlier was performed.

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. The results were then reported as the number of cells per square centimeter of membrane surface.

Total Organic Carbon Analysis

To determine the amount of carbon that was removed by each treatment, a sample of each treatment effluent was collected daily during the experimental runs. These samples were then tested for carbon content.

To prevent outside carbon contamination, all glassware was acid washed for 8 hours, triple rinsed with deionized water, triple rinsed with ultrapure water, and baked in an oven at 300° C.

The samples were tested for nonpurgeable organic carbon. First the samples were acidified to a pH below 2 with 2N HCl. The samples were 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 nonpurgeable organic carbon to carbon dioxide and the carbon dioxide was detected with an infrared detector.

The Shimadzu TOC-5000A was calibrated using NIST traceable potassium hydrogen phthalate standards obtained from Fisher Scientific.

Chlorine Measurement

Chlorine Measurements were taken using Iodometric method 1 from AWWA Standard Methods (section 408A, AWWA, 1980).

Destructive Column Sampling

The columns were destructively sampled at the end of the experimental runs. Cell numbers in the column were collected to aid in modeling TOC removal.

Samples of the packing were taken at 0, 76 *mm*, 152 *mm*, and 228 *mm*, from the influent end of the column. A known volume of packing was obtained from each sample and placed in 10 *ml* of filtered ultrapure water. The packing and water were

vortexed for 30 seconds and allowed to settle. An aqueous sample was obtained, filtered, and stained with DAPI for total direct cell counts. The method used here was identical to that described in the cell enumeration section.

CHAPTER 3

RESULTS

From objectives 1-3 that support the goal of determining if biological pretreatment can reduce fouling in membrane systems, 3 null hypotheses can be stated for statistical testing. They are:

1. The treatment means for the biological treatments are equal to their corresponding control (no biological treatment) treatment means.

2. The treatment means for chlorinated treatments are equal to their corresponding non-chlorinated treatment means.

3. The treatment means for the microfiltered treatments are equal to their corresponding non-filtered treatment means.

Evaluation methods for objectives 1-3 were developed and the following assays were used for measurement.

1. Membrane flux measurements $\left(\frac{ml}{mm^2 \cdot min}\right)$

2. Membrane fouling layer cell counts $\left(\frac{cells}{mm^2}\right)$

3. Membrane fouling layer thickness measured with SEM (μm)

4. Membrane fouling layer thickness measured with DAPI stained thin sections (μm)

5. TOC removal from the system $\left(\frac{mg}{l}\right)$

6. Bead assay biofilm cell counts $\left(\frac{cells}{cm^2}\right)$

Throughout the results and discussion, the following abbreviations will be used.

- 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
- CL - Treatments with chlorine only (includes controls)
- PF - Treatments with postfiltration only (includes controls)
- PFCL - Treatments with chlorination and post microfiltration (includes controls)
- NPFCL - Treatments with no chlorination and no post microfiltration (includes controls)

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

Flux

All flux results for each of the three experiments were fit to the model $y = ax^b$ where y = flux $\left(\frac{ml}{mm^2 \cdot min}\right)$ and x = time (hrs). Table 1 contains the fitted model parameters (a,b) for each treatment. Included in the table are the R^2 values which indicate the amount of variability explained by the model and the F-statistic with its corresponding P-value.

Plots of the curve fits are in Appendix A, Figures 26-37. The inside confidence intervals are a point-wise 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.

Table 1: Flux prediction model parameters

Treatment	a	b	R^2	F-statistic	P-value	Flux at 120 Hrs.
BAC	$4.88\text{x}10^{-3}$	-0.4757	0.7203	41.21	$8.482\text{x}10^{-6}$	$5.0\text{x}10^{-4}$
BACPF	$7.33\text{x}10^{-2}$	-0.7323	0.7764	55.56	$1.371\text{x}10^{-6}$	$2.2\text{x}10^{-3}$
IOCSPF	$2.84\text{x}10^{-2}$	-0.6901	0.8522	92.24	$4.80\text{x}105^{-8}$	$1.0\text{x}10^{-3}$
IOCS	$1.18\text{x}10^{-2}$	-0.6859	0.7317	43.63	$6.048\text{x}10^{-6}$	$4.4\text{x}10^{-4}$
CTRL	$2.94\text{x}10^{-3}$	-0.3869	0.6662	31.93	$3.613\text{x}10^{-5}$	$4.6\text{x}10^{-4}$
CTRLPF	$9.56\text{x}10^{-3}$	-0.5006	0.6917	35.89	$1.883\text{x}10^{-5}$	$8.7\text{x}10^{-4}$
BACCL	$6.39\text{x}10^{-3}$	-0.4539	0.6261	26.79	$9.193\text{x}10^{-5}$	$7.3\text{x}10^{-4}$
BACPFCL	$2.69\text{x}10^{-2}$	-0.557	0.5809	22.17	$2.365\text{x}10^{-4}$	$1.9\text{x}10^{-3}$
IOCSPFCL	$2.15\text{x}10^{-2}$	-0.6273	0.6072	24.73	$1.382\text{x}10^{-4}$	$1.1\text{x}10^{-3}$
IOCSCL	$7.66\text{x}10^{-3}$	-0.5004	0.5529	19.78	$4.051\text{x}10^{-4}$	$6.9\text{x}10^{-4}$
CTRLCL	$8.41\text{x}10^{-3}$	-0.5571	0.5278	17.88	$6.387\text{x}10^{-4}$	$5.8\text{x}10^{-4}$
CTRLPFCL	$2.83\text{x}10^{-2}$	-0.6765	0.768	52.95	$1.853\text{x}10^{-6}$	$1.1\text{x}10^{-3}$

The simultaneous confidence intervals were used to generate the upper and lower flux values at 120 hours for use in the multiple comparison tests across experiments used to assess the three hypotheses. These values cover 95% of the predicted values and are considered conservative. The flux results were analyzed using a Monte Carlo based simulation multiple comparison with a control test. The simulation size was 12616 and the simultaneous confidence interval was 95%.

The flux data were collected during the 5 day runs and hence the times of collection do not all coincide. As a result, the time of 120 hours was chosen to compare all of the flux data at a common point in time. Since the simultaneous confidence intervals were used to generate the range of data found for the flux at 120 hours, the observed differences were difficult to detect statistically. Hence, any differences that were detected are noteworthy.

Figure 3 shows that the chlorinated treatments had a greater flux value for all treatments except the BACPF treatment. However, the flux did not change with chlorination between treatments in a manner that was statistically significant.

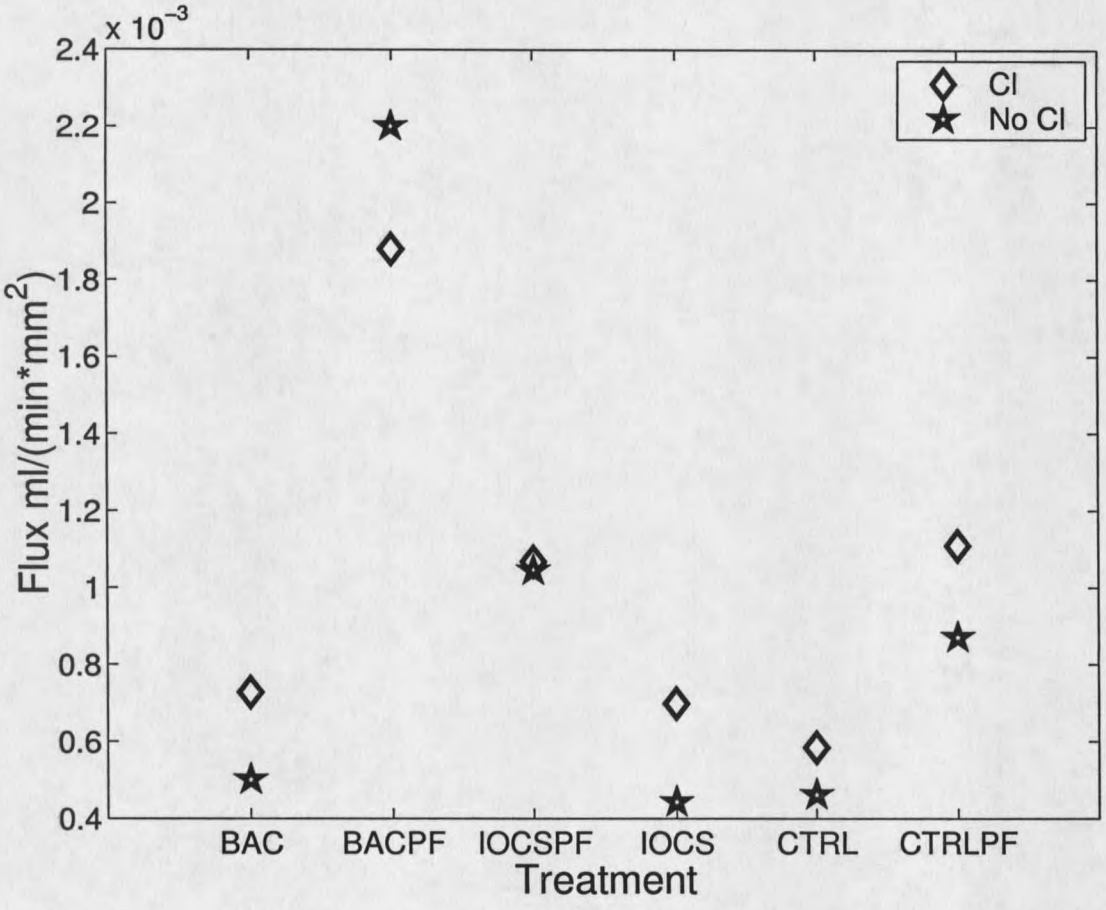


Figure 3: Chlorine comparison of treatment flux at 120 hours. Statistical comparison of chlorination using the flux assay.

Figure 4 shows there was a significant difference between post-filtration and no post-filtration for both BAC and BACCL biological treatments. In all the treatments, the general trend showed that the flux was greater for the treatments that were post-filtered.

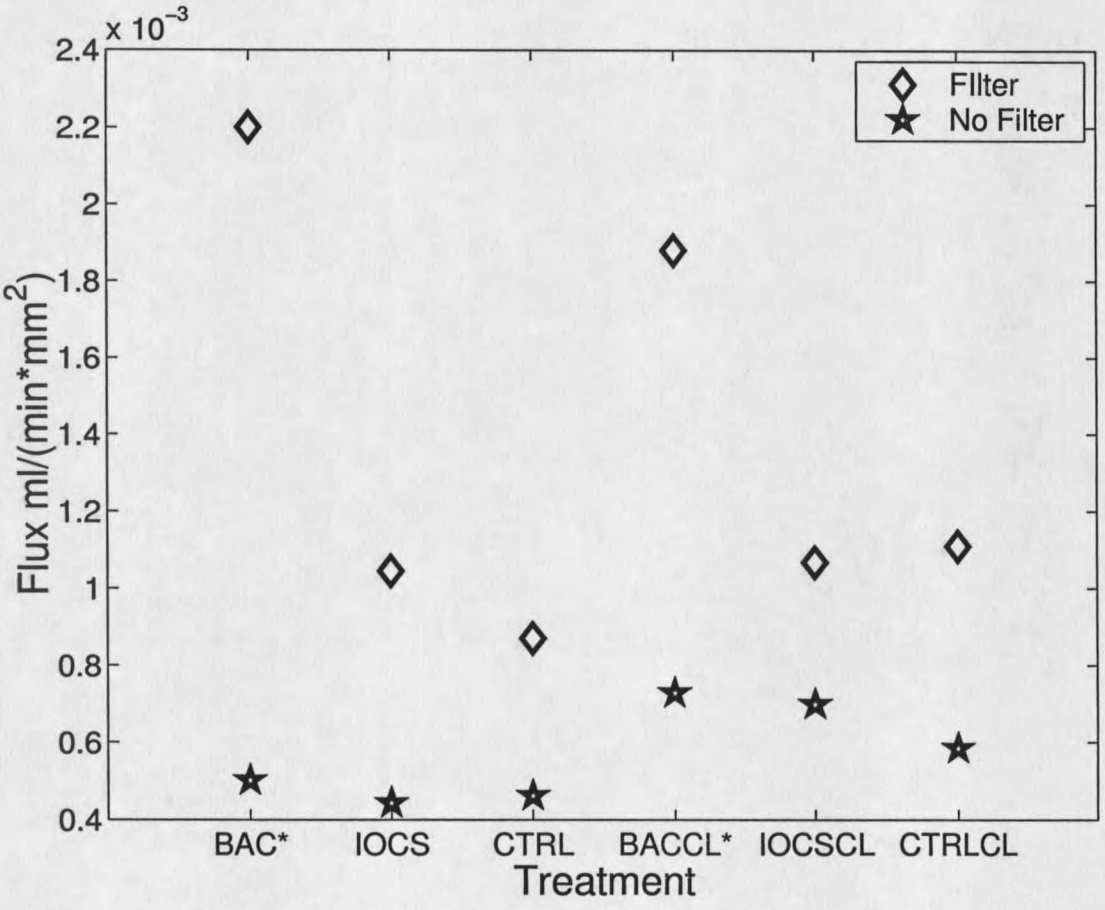


Figure 4: Filtration comparison of treatment flux at 120 hours. Statistical comparison of post-filtration using the flux assay.

For the biological treatment process, Figure 5 shows that only BAC was significantly better for flux improvement, and only in combination with post-filtration. In both post-filtered treatments, the BAC had a greater flux.

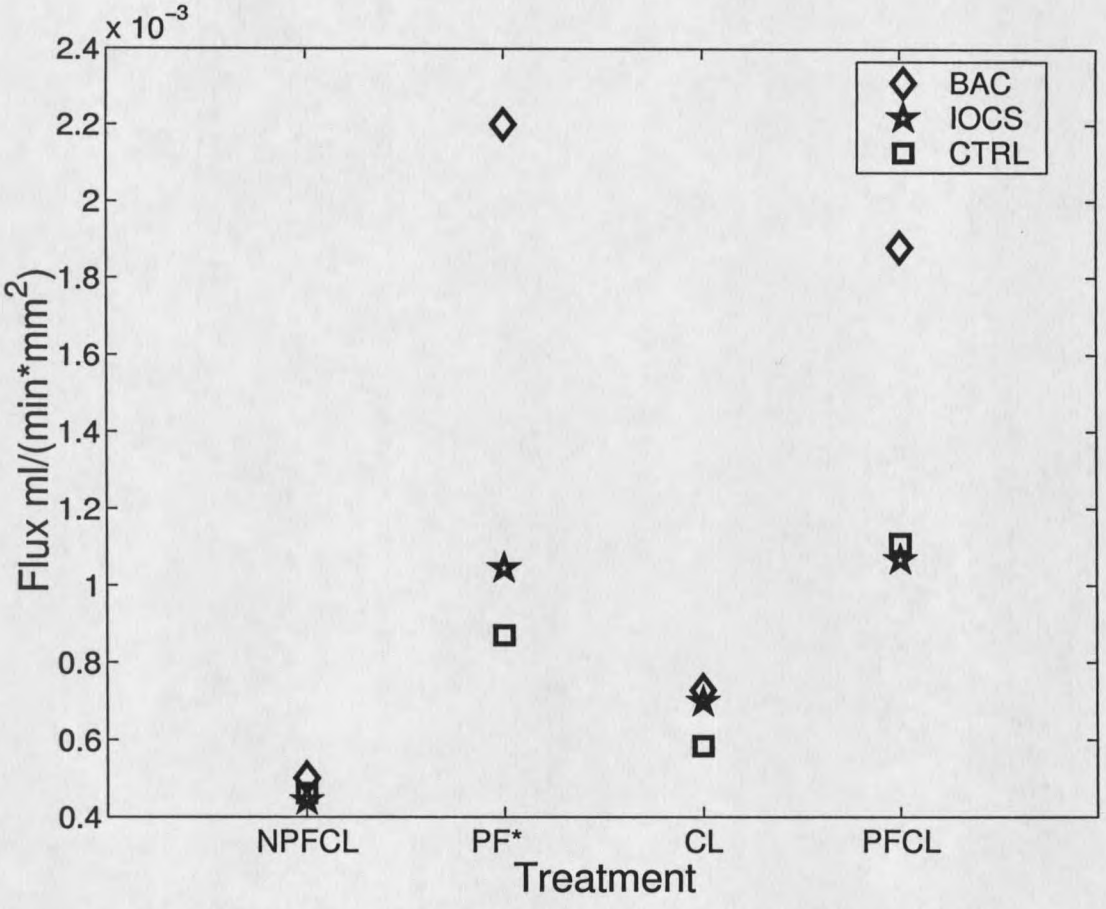


Figure 5: Biological pretreatment comparison of treatment flux at 120 hours. Statistical comparison of biological pretreatment using the flux assay.

Total Organic Carbon Removal

The percent TOC removal versus amount of TOC added to the system was plotted for each treatment. A linear model ($y = mx + b$) where x = the amount of TOC going into the system and y = the percent of TOC removed was then fit to the data (Table 2). The resulting plots of the data and the curve fit are presented in Appendix B Figures 38-47. As in the flux data, the inside confidence bands represent a single point-wise standard error and the outside confidence band represents a simultaneous confidence interval generated with an F-distribution and a confidence interval of 95%.

Table 2: TOC prediction model parameters

Treatment	m	b	R^2	F-statistic	P-value	Removal
BAC	0.0283	−0.1600	0.894	194.1	$1.066\text{x}10^{-12}$	22.5%
BACPF	0.0386	7.0781	0.9566	485.1	$2.22\text{x}10^{-16}$	37.9%
IOCSPF	0.0344	3.2004	0.8859	170.8	$7.578\text{x}10^{-12}$	30.7%
IOCS	0.0306	−5.4254	0.8736	170.8	$2.348\text{x}10^{-11}$	19.0%
CTRLPF	0.0155	10.3283	0.8995	196.9	$1.862\text{x}10^{-12}$	22.7%
CTRLPFCL	0.0309	−3.5511	0.9567	486.1	$2.22\text{x}10^{-16}$	21.2%
BACCL	0.0104	8.1912	0.6014	33.19	$8.538\text{x}10^{-6}$	16.5%
BACPFCL	0.0310	11.3549	0.9539	454.9	$3.331\text{x}10^{-16}$	36.2%
IOCSPFCL	0.0309	0.4006	0.944	371	$2.887\text{x}10^{-15}$	25.1%
IOCSCL	0.0005	3.5192	0.01242	0.2767	0.6041	3.9%

Using the same approach as the flux data, the simultaneous confidence intervals were used to generate upper and lower values for percent TOC removal at 800 *ppb*. The choice of 800 *ppb* (measured humics addition and background tap water carbon) allowed the experiments to be compared on a common basis. These numbers were

then used for the multiple comparison tests of the hypotheses. The TOC results were analyzed using a Monte Carlo based simulation multiple comparison with a control test. The simulation size was 12616 and the simultaneous confidence interval was 95%.

TOC removal was significantly different when prechlorination was used for the BAC, IOCS, and IOCSPF treatments. In all of these cases, the removal was greater for the treatments where chlorine was not applied. Figure 6 shows the results of this comparison.

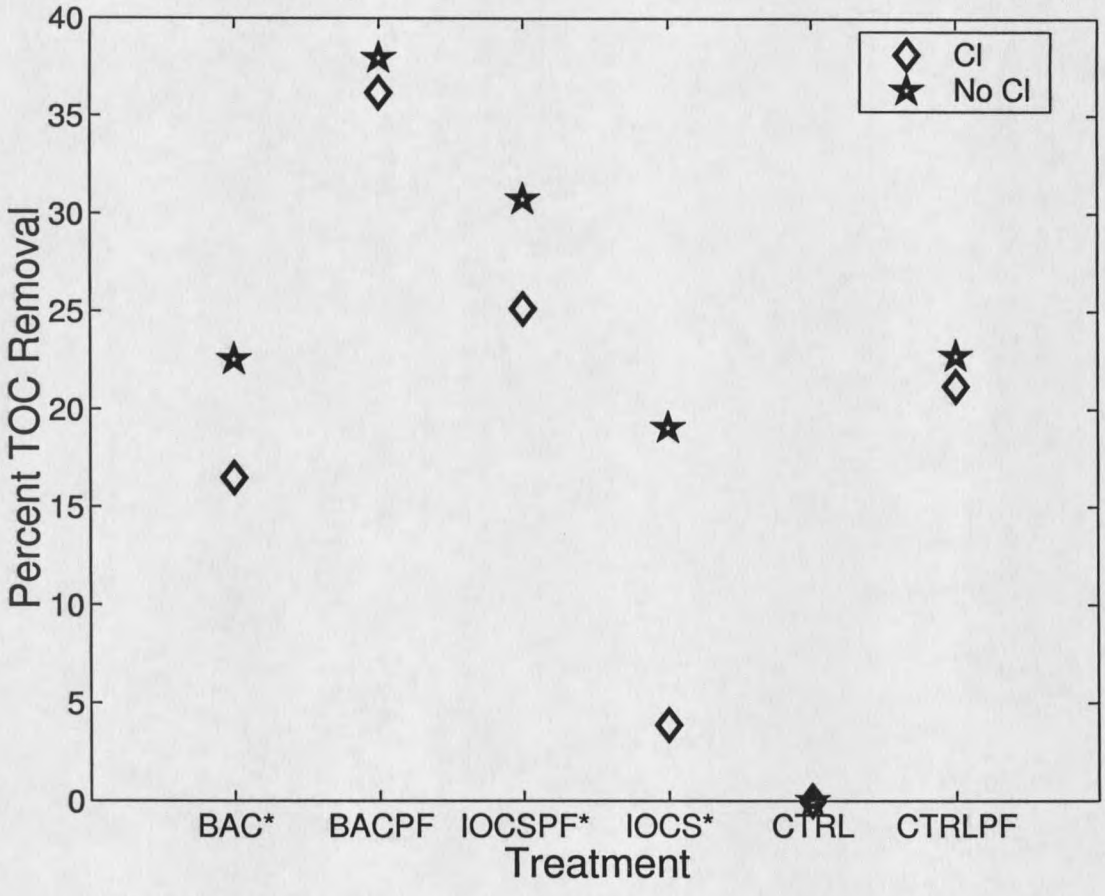


Figure 6: Chlorine comparison of TOC removal. Statistical comparison of chlorination using the TOC removal assay.

TOC removal was significantly different for all treatments that were post-filtered from those that were not post-filtered. Figure 7 shows that the post-filtered treatments removed twice as TOC as the non-filtered treatments.

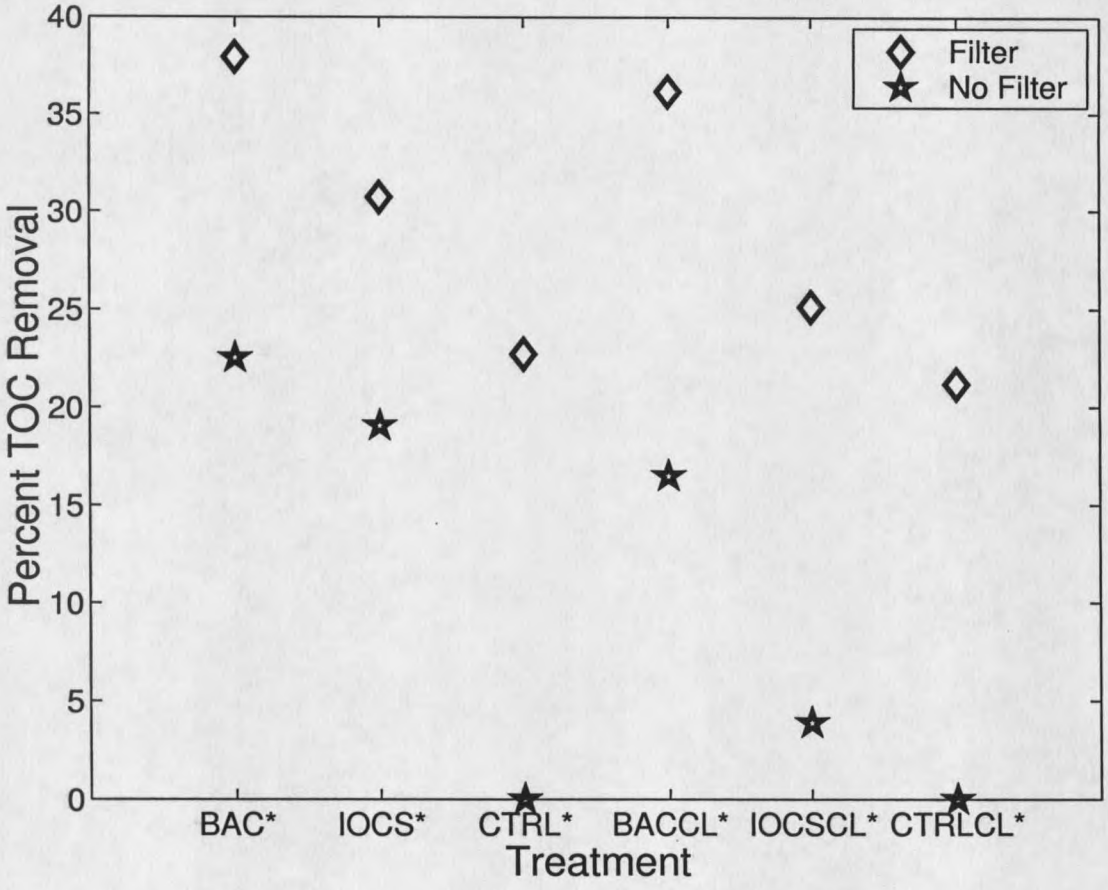


Figure 7: Filtration comparison of TOC removal. Statistical comparison of post-filtration using the TOC removal assay.

The ability of biological treatment to remove TOC was significant for all BAC treatments with respect to the control treatment. The IOCS treatment was significant only for the non-chlorinated and post-filtered treatments. Figure 8 shows that the BAC and IOCS removal trends were consistently greater than the control and that the BAC was consistently greater than the IOCS for all of the treatments.

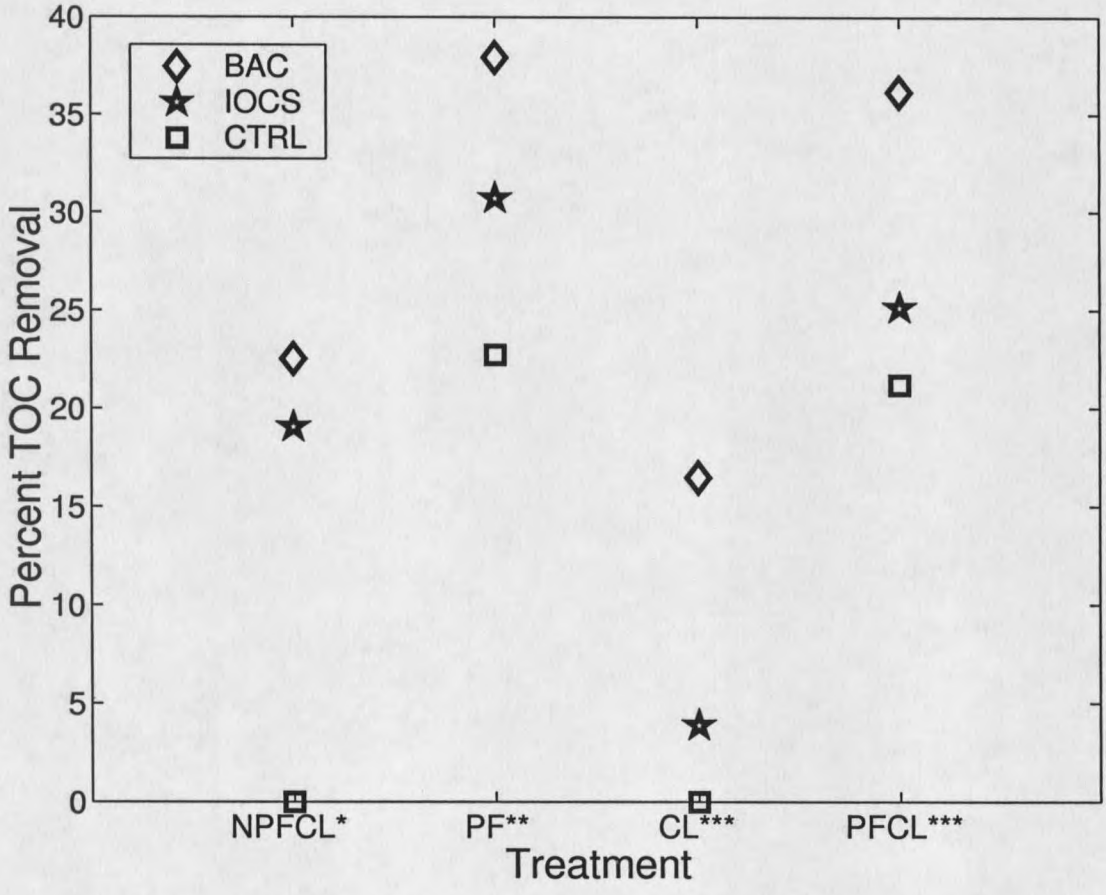


Figure 8: Biological pretreatment comparison of TOC removal. Statistical comparison of biological pretreatment using the TOC removal assay.

Membrane Cell Counts

The membrane cell counts were analyzed using a Monte Carlo based simulation multiple comparison with a control test. The simulation size was 12616 and the simultaneous confidence interval was 95%.

The impact of chlorination on the concentration of cells on the membrane was not significant for any of the treatments. Figure 9 shows the trends in the data were mixed.

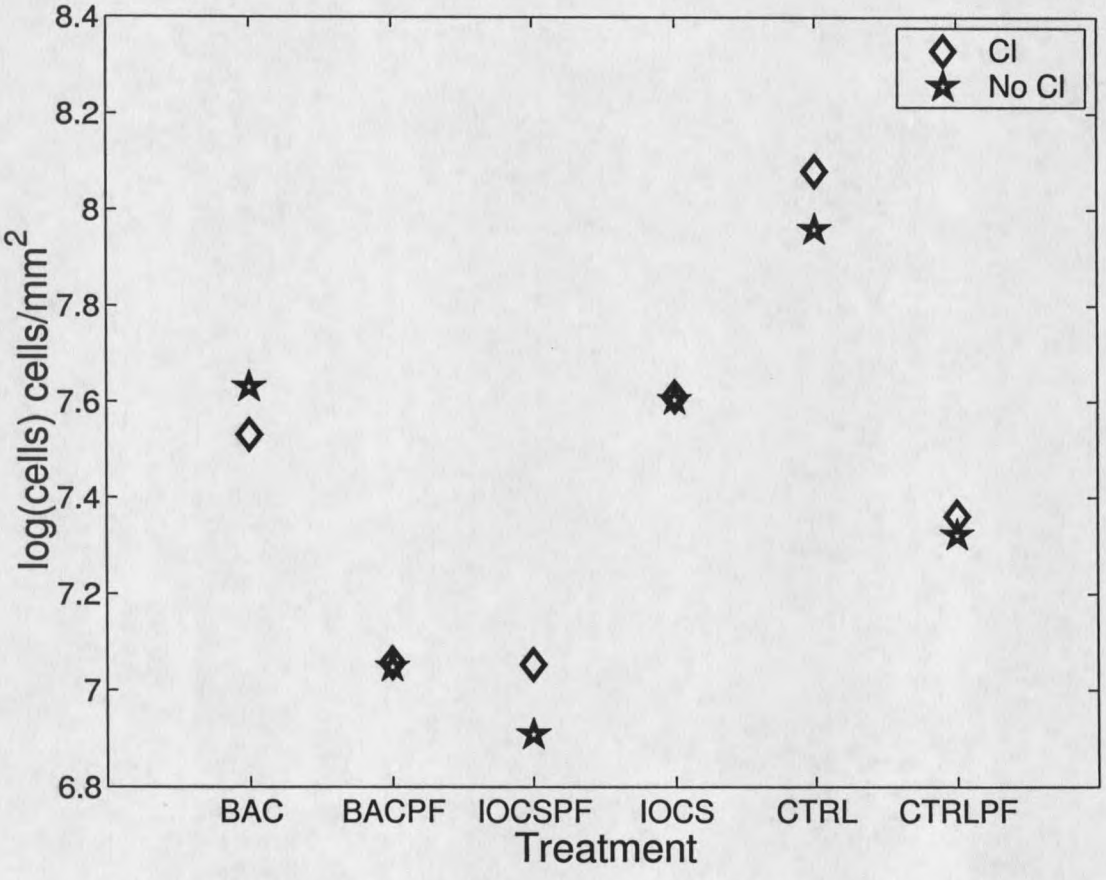


Figure 9: Chlorine comparison of membrane cells. Statistical comparison of chlorination using the membrane biofilm cell count assay.

Post-filtration was found to significantly change the cell counts for all treatments. Figure 10 shows that all post-filtered treatments had at least a one-half log lower cell count on the membrane.

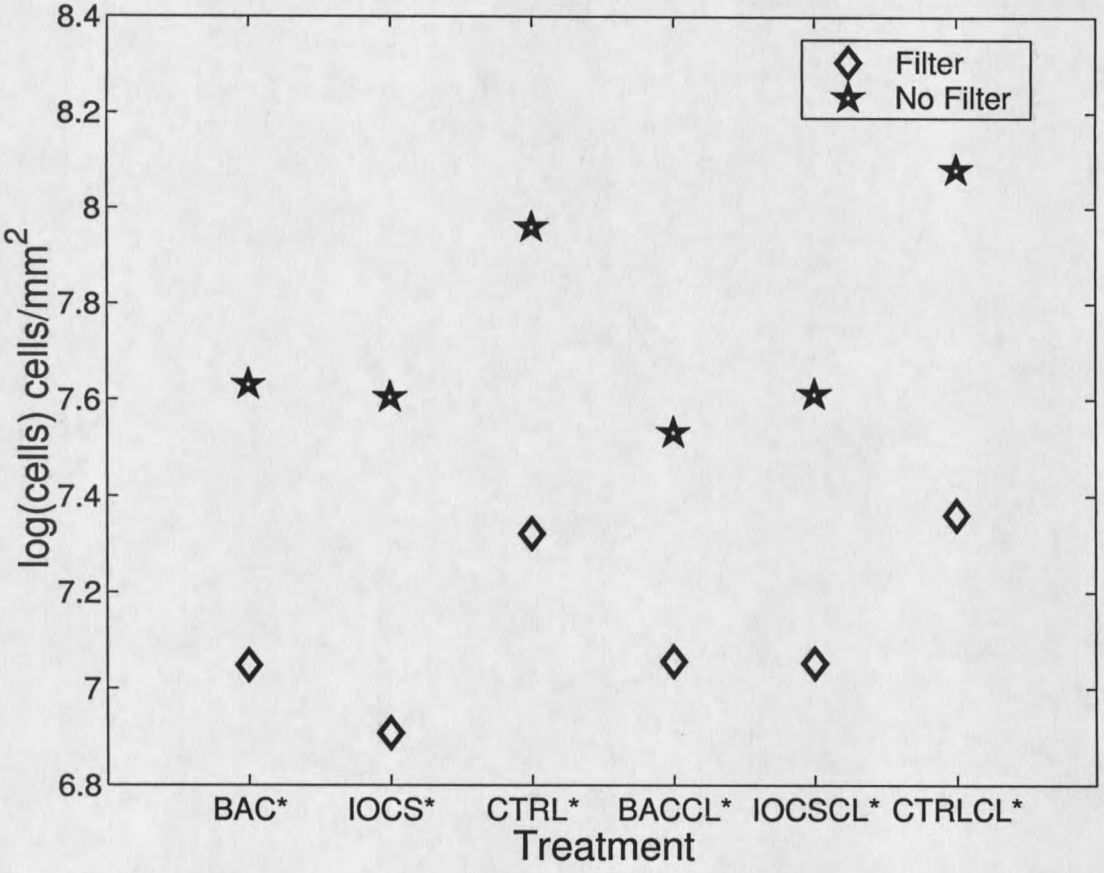


Figure 10: Filtration comparison of membrane cells. Statistical comparison of post-filtration using the membrane biofilm cell count assay.

The impact of the different biological treatments on the cell counts was found to be significant for all treatments. The biological treatments showed a reduction of at least 0.3 log with no difference between the biological treatments. Figure 11 summarizes these results.

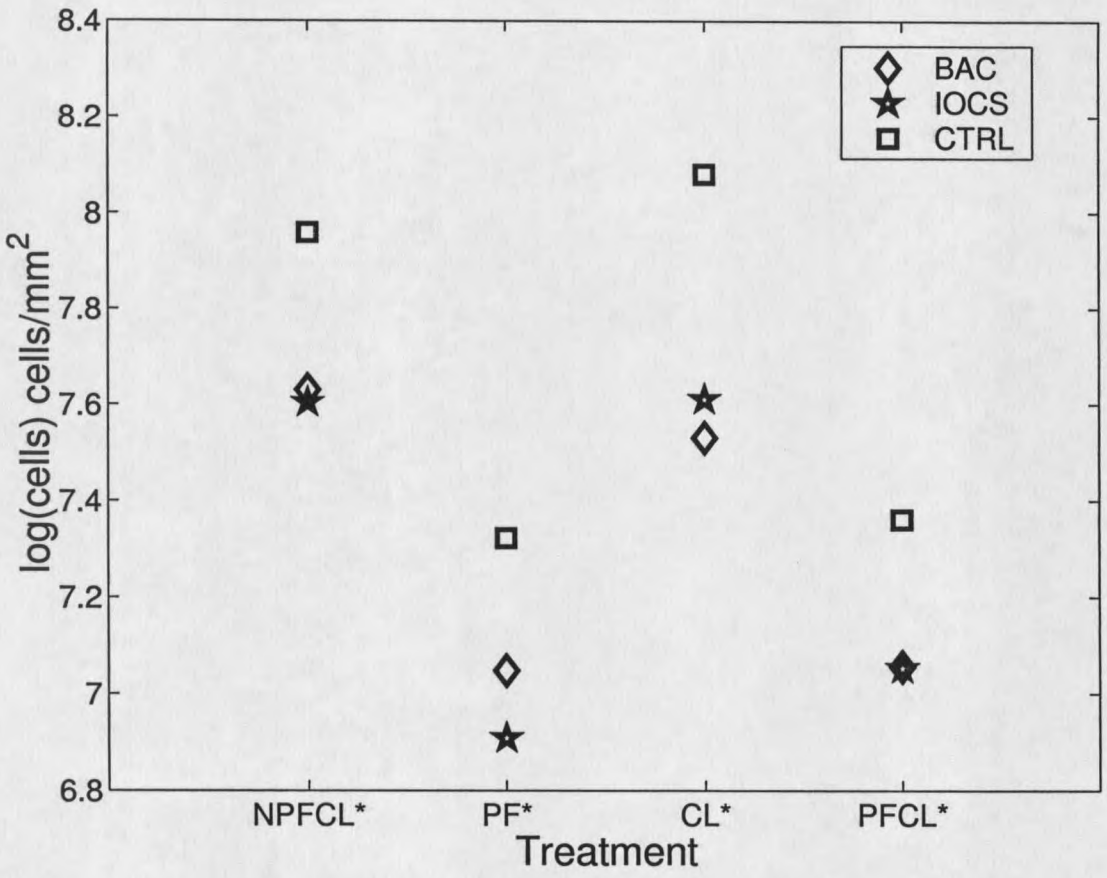


Figure 11: Biological pretreatment comparison of membrane cells. Statistical comparison of biological pretreatment using the membrane biofilm cell count assay.

Fouling Layer Thickness (SEM)

The fouling layer thickness as measured by the SEM method was analyzed using the Dunnett method of multiple comparison with a control and a 95% confidence interval. See Figure 12 for an example image.

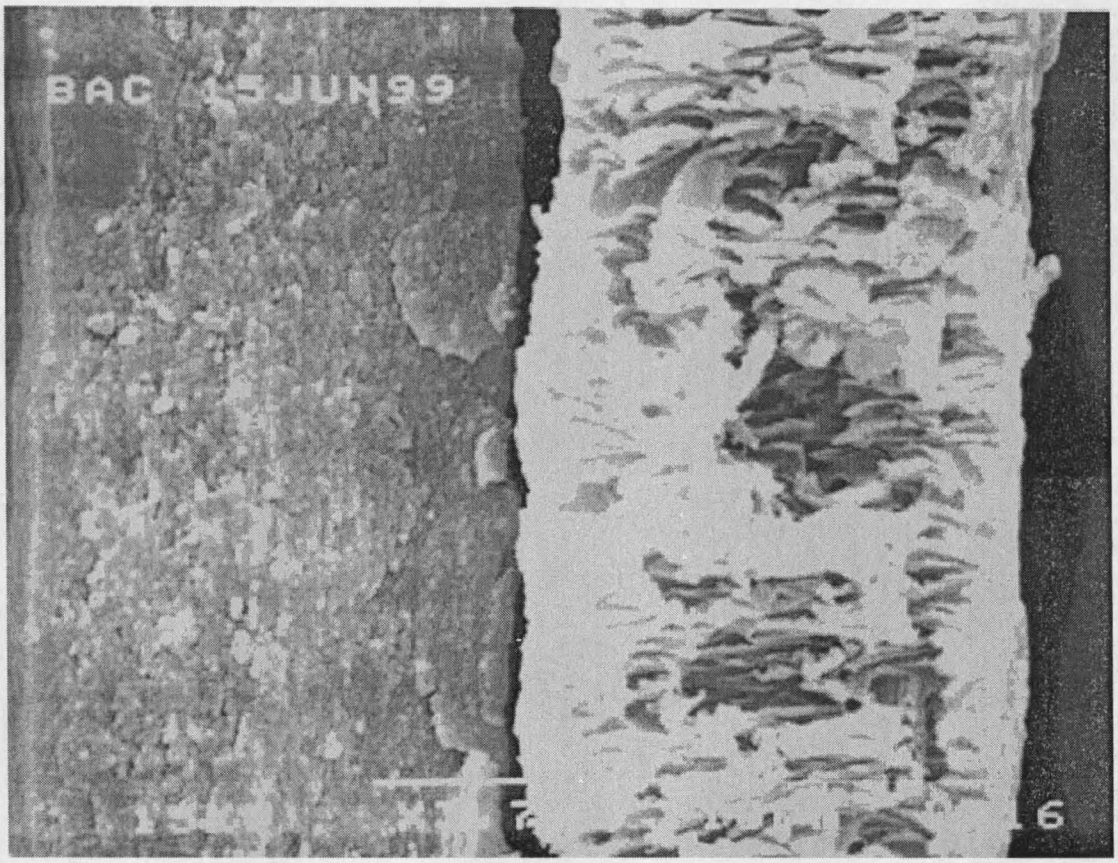


Figure 12: Fouling layer thickness (SEM) assay. Biofilm is on the left and the membrane is on the right. The membrane is $\simeq 10\mu m$ thick. Separation of fouling layer from membrane is due to sample preparation.

Chlorination had an impact on the BAC and CTRL treatments only. Figure 13 shows that in the two cases where there was a statistical difference the fouling layer was thicker for the chlorinated treatment. In all other treatments, the difference in fouling layer thickness was less than 5 μm between the chlorinated and non-chlorinated treatments.

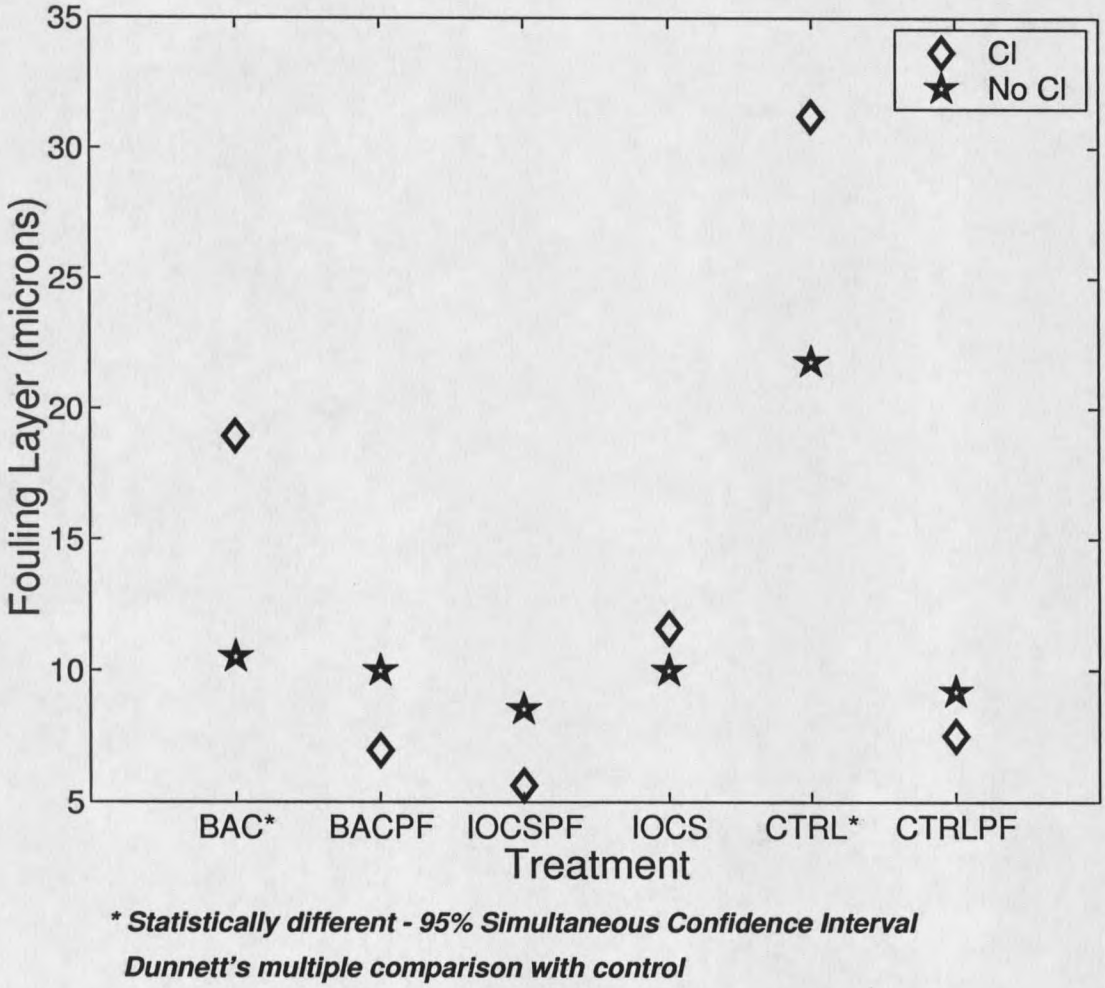


Figure 13: Chlorine comparison of thickness (SEM). Statistical comparison of chlorination using the fouling layer thickness (SEM) assay.

When post-filtration was applied, the treatments were significantly different for all treatments except BAC and IOCS, which were within 2 μm of each other. Figure 14 shows that the non-post-filtered treatments had greater fouling layer thicknesses than the post-filtered treatments. The difference in these thicknesses ranged from 5 μm to greater than 20 μm.

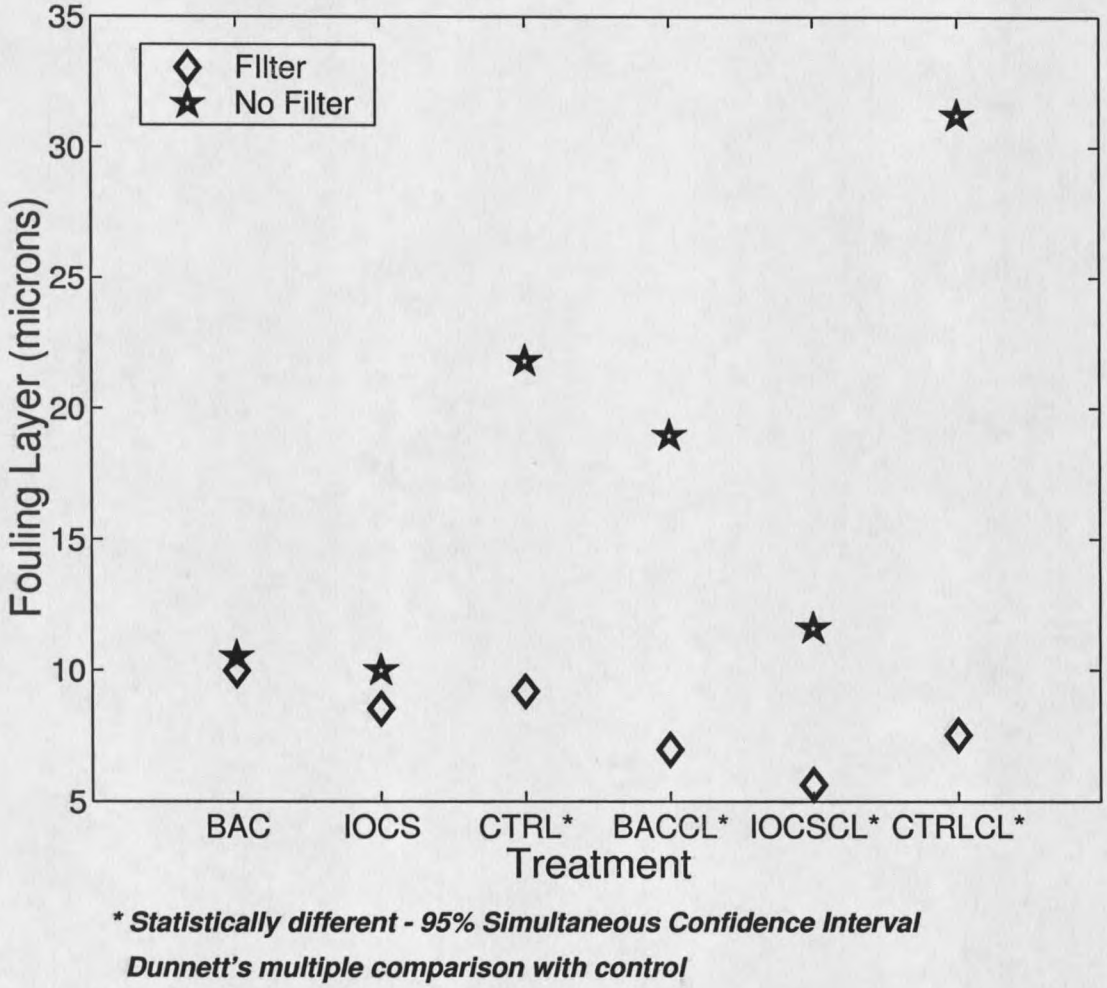
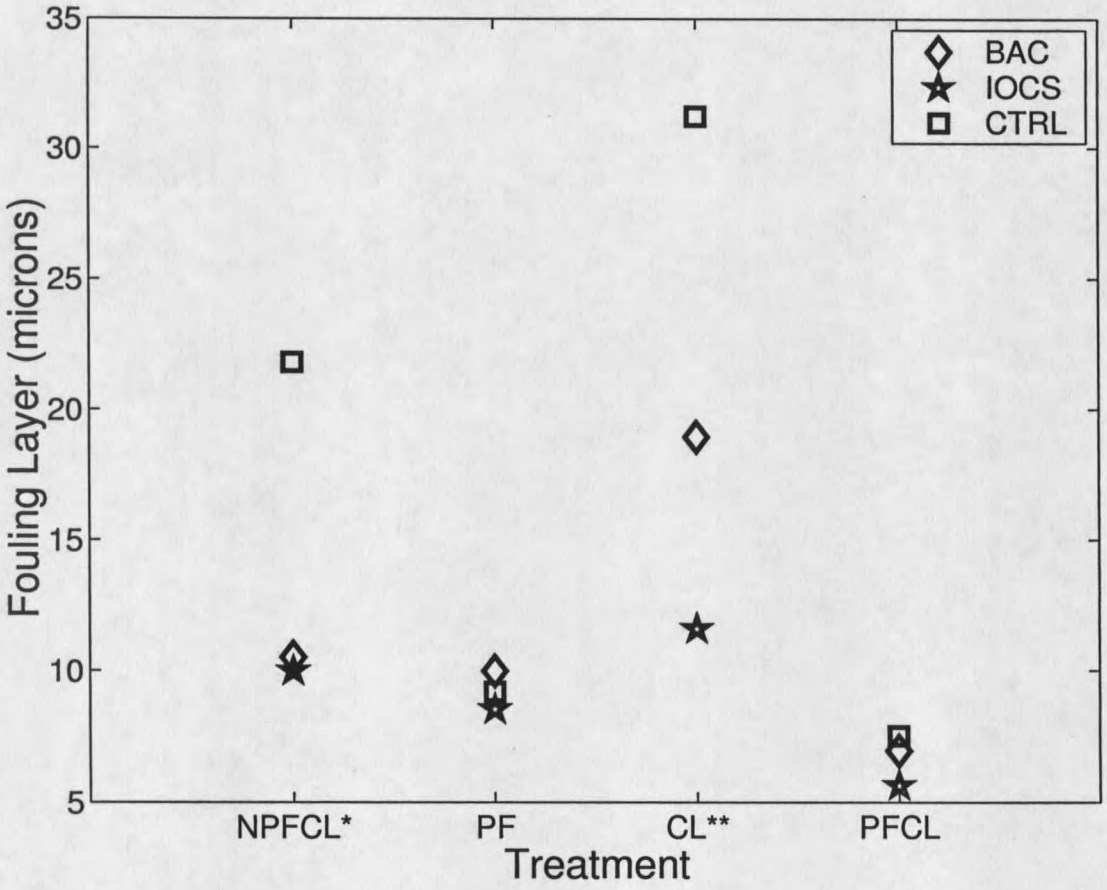


Figure 14: Filtration comparison of thickness (SEM). Statistical comparison of post-filtration using the fouling layer thickness (SEM) assay.

The impact of biological treatment on fouling layer thickness was significant in the absence of post-filtration. Figure 15 shows that the non-post-filtered biological treatments showed a thinner fouling layer ($> 10\mu m$) than the control, while both biological treatments with post-filtration treatments were the same as the control.



**** Statistically different from control - 95% Simultaneous Confidence Interval***

***** BAC and IOCS are statistically different from each other and control***

Dunnett's multiple comparison with control

Figure 15: Biological pretreatment comparison of thickness (SEM). Statistical comparison of biological pretreatment using the fouling layer thickness (SEM) assay.

Fouling Layer Thickness (DAPI)

The fouling layer thickness as measured by DAPI stained thin sections under a microscope provided another measure for comparison. See Figure 16 for an example image. These results were analyzed using a Monte Carlo based simulation multiple comparison with a control test. The simulation size was 12616 and the simultaneous confidence interval was 95%.

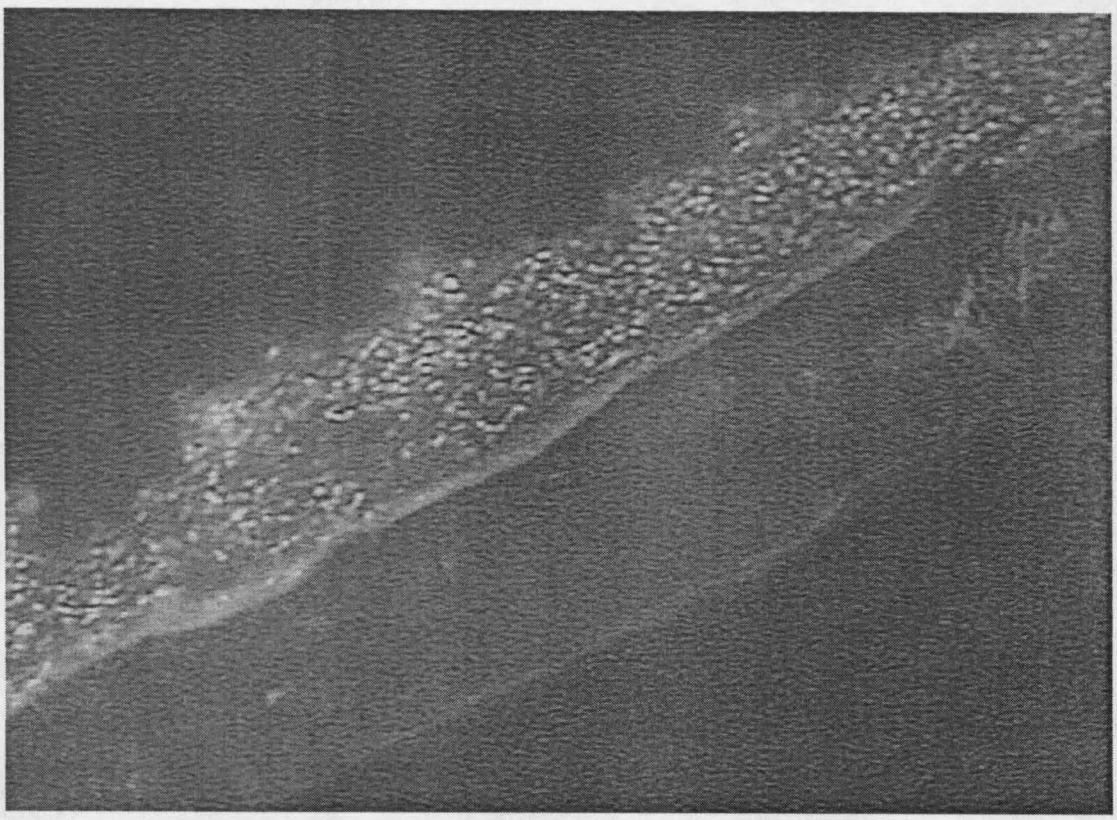


Figure 16: Fouling layer thickness (DAPI) assay. Membrane is on the bottom and the cells are stained with DAPI in the biofilm on top. The membrane is $\simeq 10\mu m$ thick.

The fouling layer thickness was not significantly different for the prechlorinated versus unchlorinated treatments. Figure 17 shows that the trends were mixed.

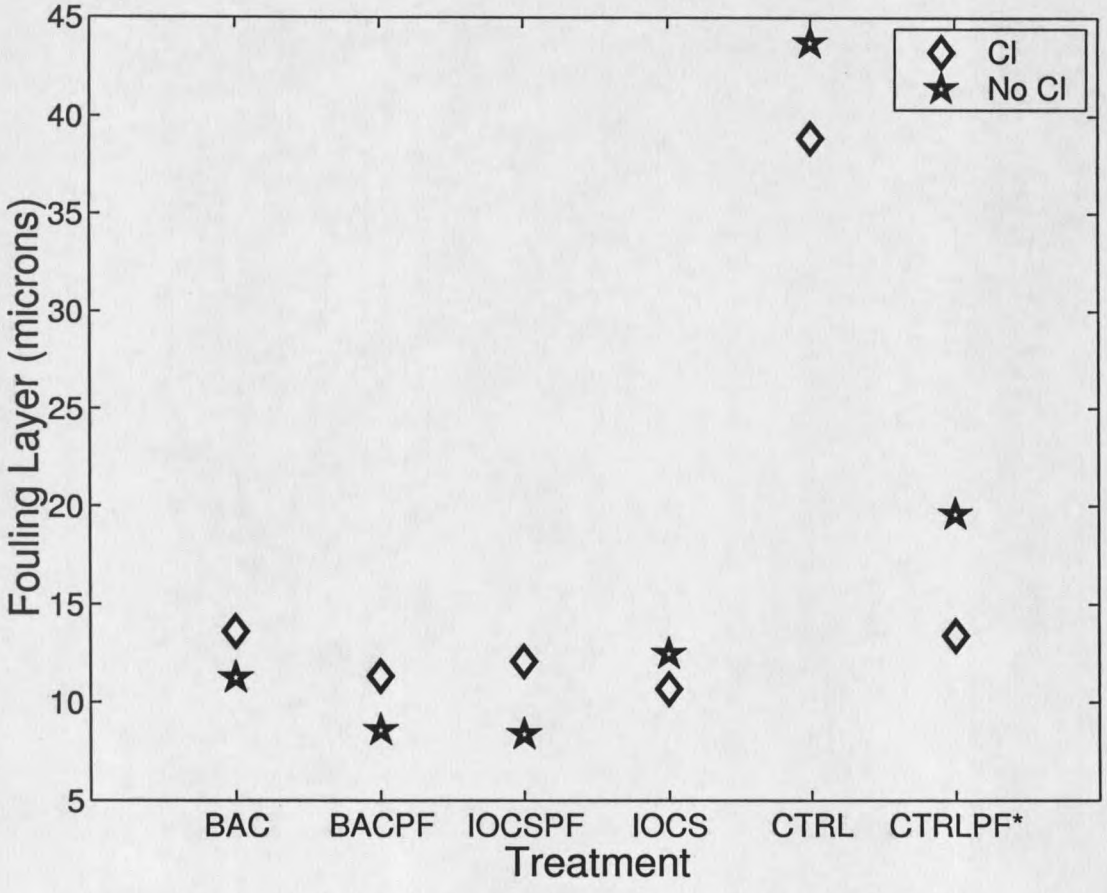


Figure 17: Chlorine comparison of thickness (DAPI). Statistical comparison of chlorination using the fouling layer thickness (DAPI) assay.

Post-filtration reduced the fouling layer thickness for CTRL and CTRLCL only. Figure 18 shows that with the other treatments the impact of post-filtration on the fouling layer thickness was not significant.

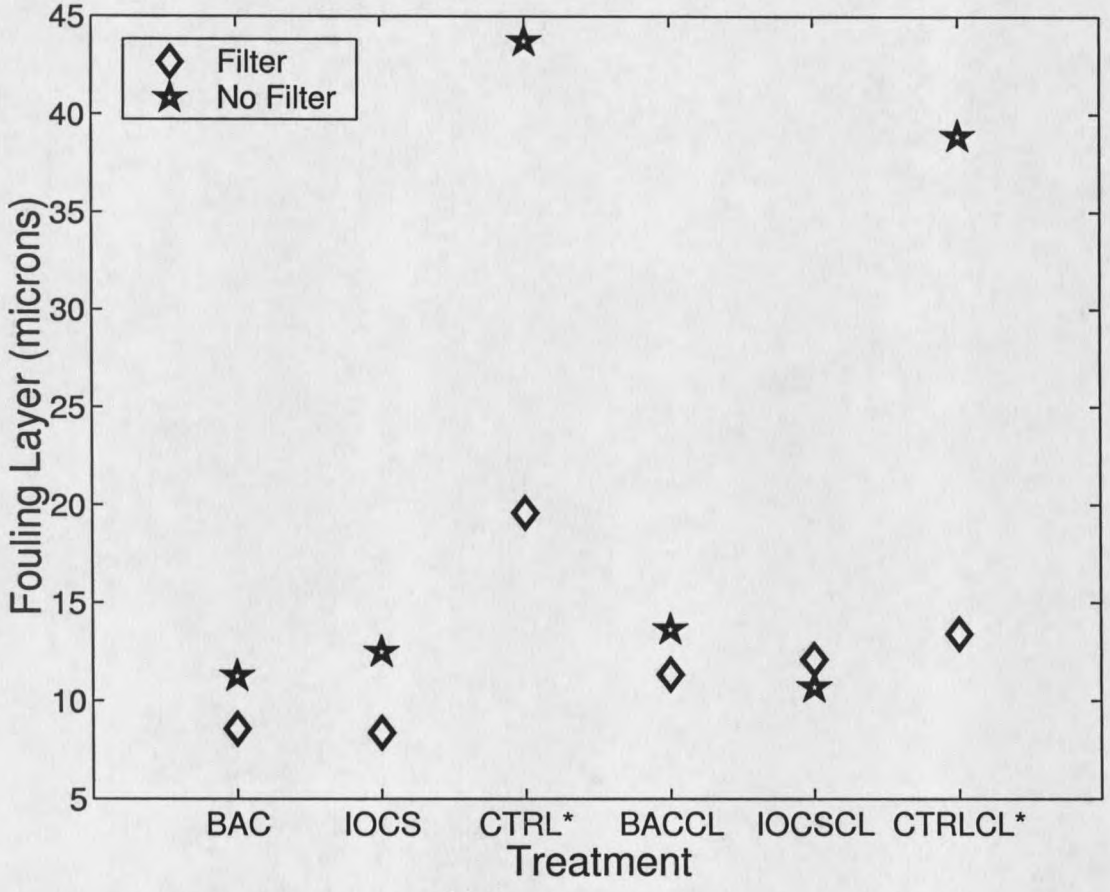


Figure 18: Filtration comparison of thickness (DAPI). Statistical comparison of post-filtration using the fouling layer thickness (DAPI) assay.

Biological treatment produced a significant reduction in fouling layer thickness as compared to the control for all treatments except the post-filtered treatments that were prechlorinated. Figure 19 shows as much as 30 μm (74% reduction of thickness) difference from the control.

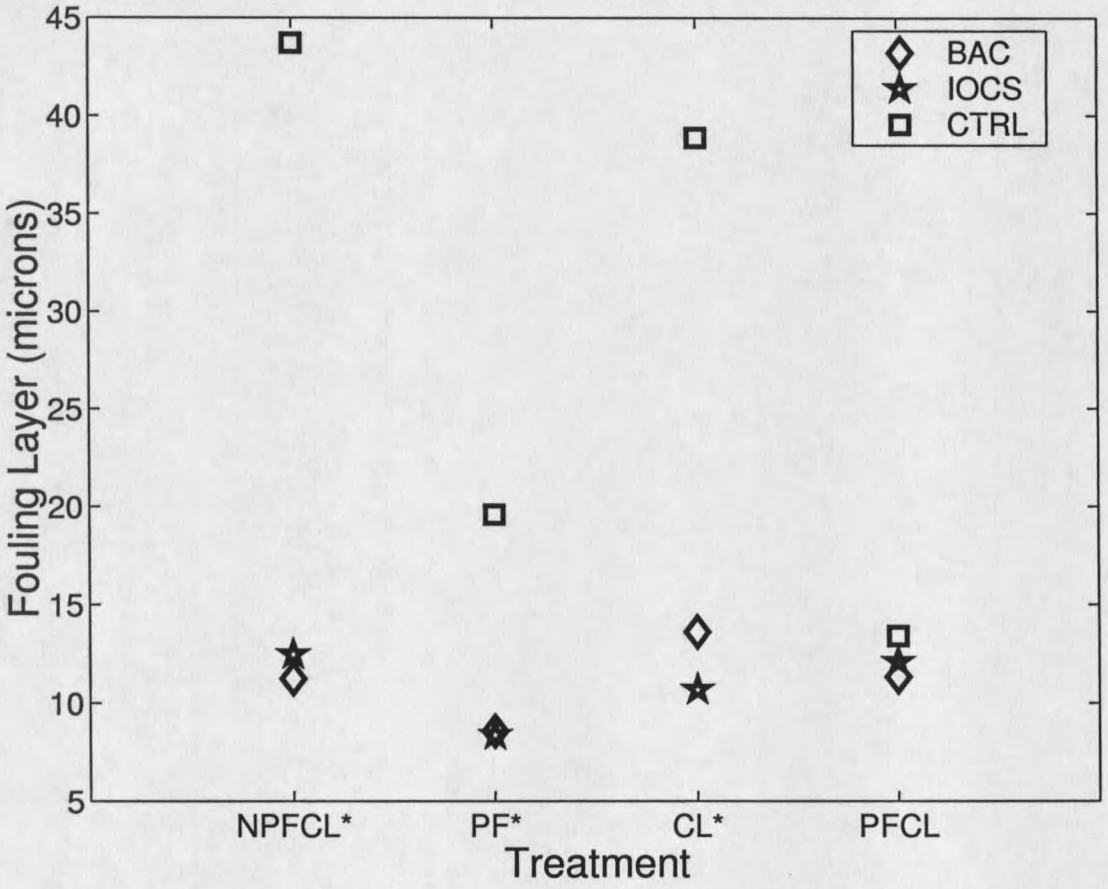


Figure 19: Biological pretreatment comparison of thickness (DAPI). Statistical comparison of biological pretreatment using the fouling layer thickness (DAPI) assay.

Bead Assay

The bead assay cell counts were analyzed with a Monte Carlo based simulation multiple comparison with a control test. The simulation size was 12616 and the simultaneous confidence interval was 95%.

Prechlorination reduced the bead assay cell counts significantly for BAC, IOCS, and CTRL. Figure 20 shows that in the cases where there was a statistical difference there was close to a one log reduction for the prechlorinated treatments. It should be noted that there is no chlorine residual carried through the system.

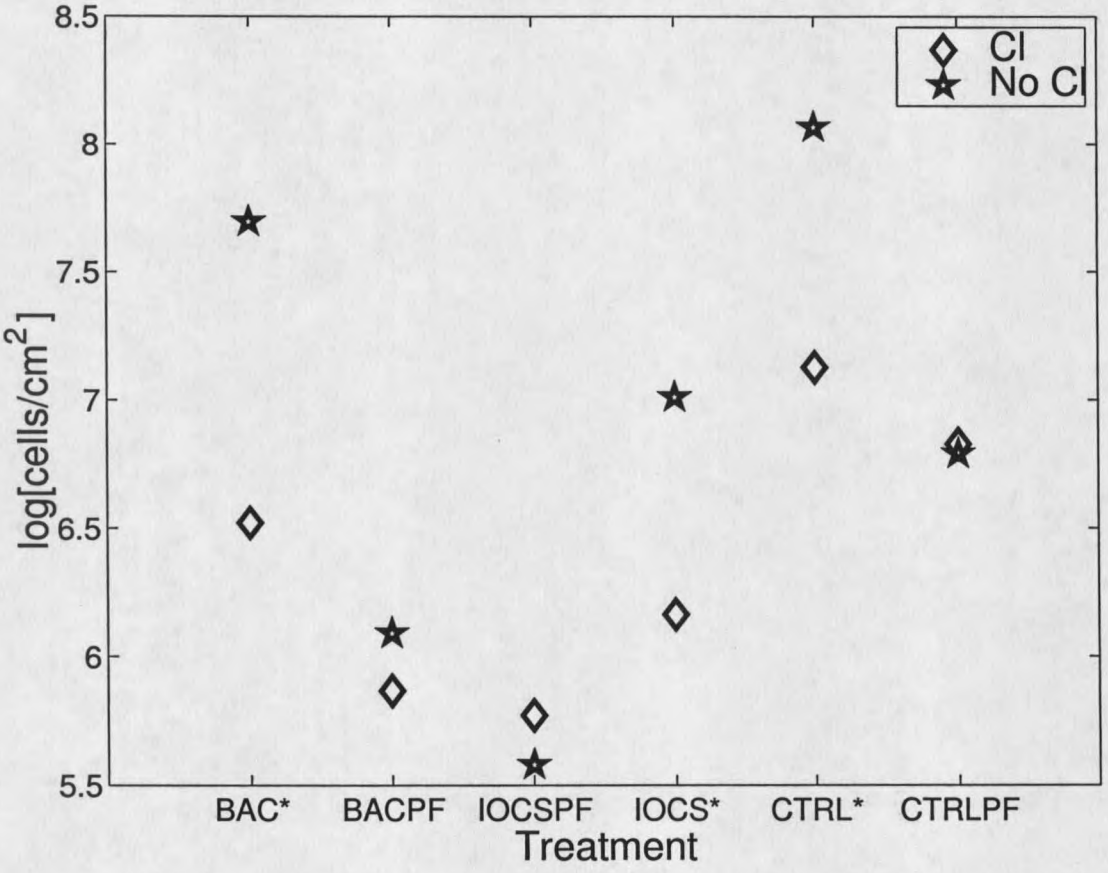


Figure 20: Chlorine comparison of bead assay. Statistical comparison of chlorination using the bead assay biofilm cell count assay.

Figure 21 shows that the bead assay cell counts were all higher for the non-post-filtered treatments; this difference was significant for all but the CTRLCL treatment.

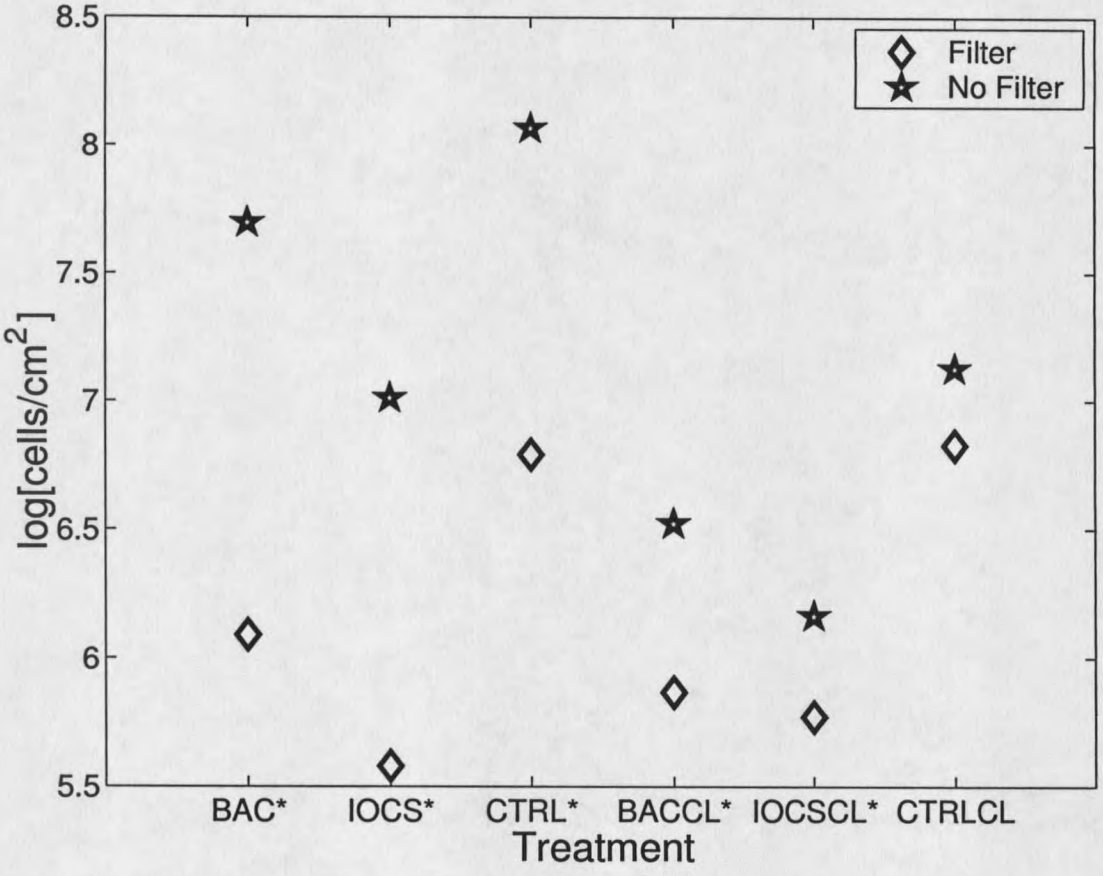


Figure 21: Filtration comparison of bead assay. Statistical comparison of post-filtration using the bead assay biofilm cell count assay.

Both types of biological treatment reduced the bead assay cell counts significantly for all treatments. The biological treatments resulted in as much as a full log reduction in biofilm cells on the beads. In addition, as seen in Figure 22, the difference between the BAC and IOCS treatments was significant (> 0.5 log) except for the filtered treatments that were prechlorinated.

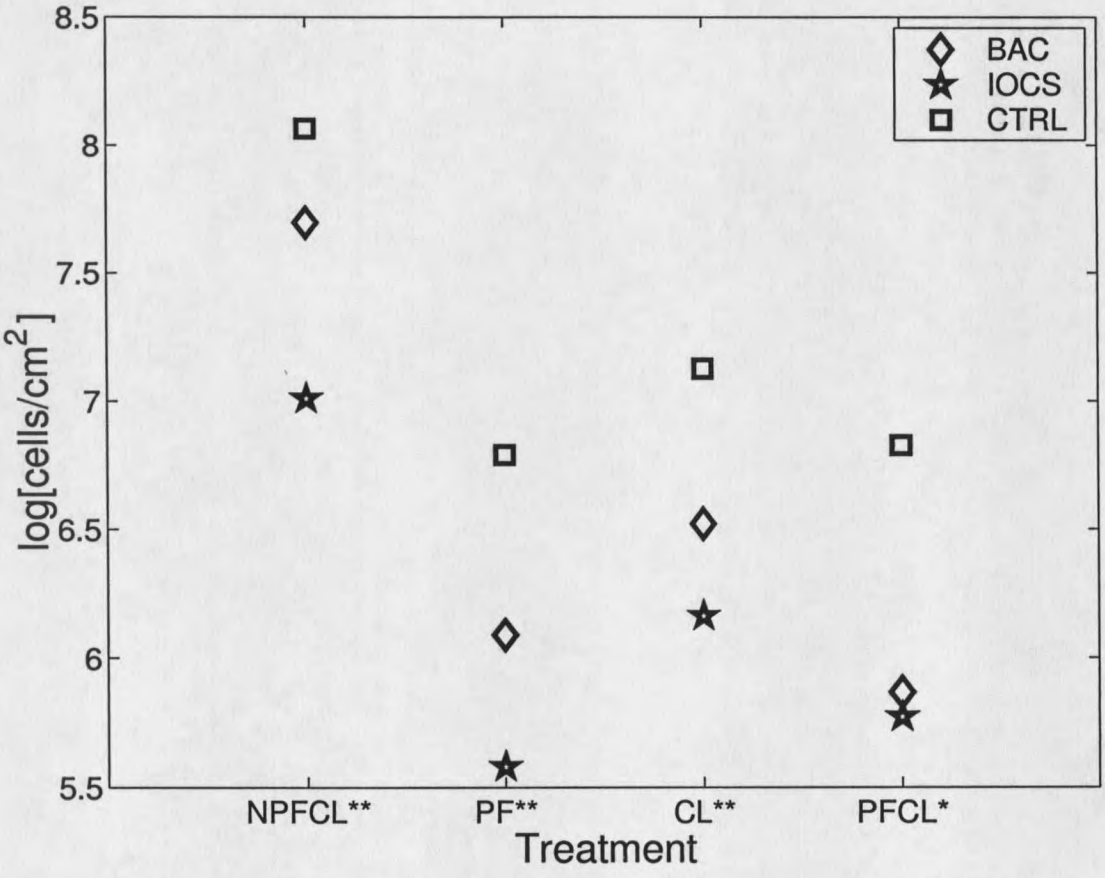


Figure 22: Biological pretreatment comparison of bead assay. Statistical comparison of biological pretreatment using the bead assay biofilm cell count assay.

Biofilm Modeling

The biological pretreatment reactors had been on line for more than one year when the final experimental run was completed. At the end of the experiments, the columns were torn down, samples of the packing were taken and cell counts were performed.

For the purposes of modeling, the columns that had the chlorine pretreatment as an oxidation step will not be discussed due to the scattered nature of the TOC data for those treatments. In addition, the organic carbon removal data will only be from the non-filtered treatments so that the effects of post microfiltration will not need to be accounted for in the model. The results from the enumeration of the cells in the columns are shown in Figure 23. Results from the bottom of the column ($0m$) represent the influent end since the columns were operated in an upflow mode.

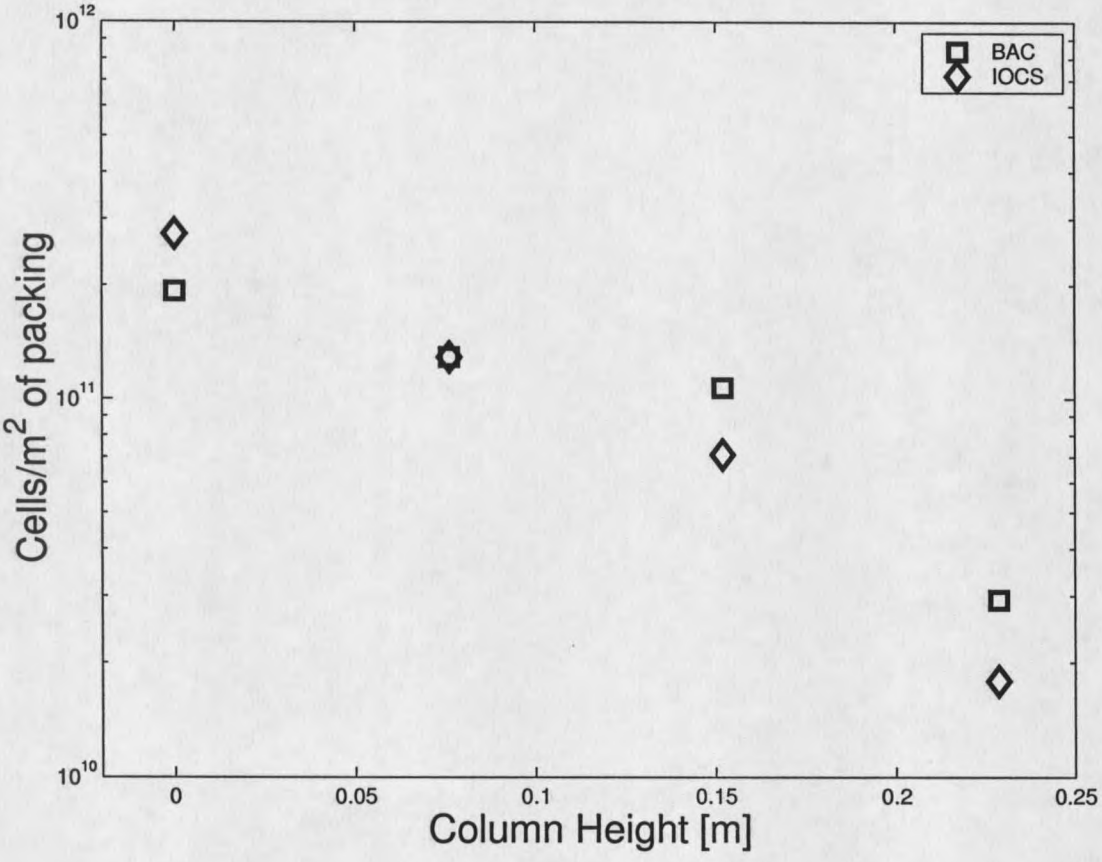


Figure 23: Total direct cell counts from column packing.

The experiments performed were not specifically designed to obtain kinetic parameters for the organisms in the columns. However, some modeling of the process is possible without this information.

Using a standard modeling approach, the rate of cell growth, detachment, and substrate uptake were employed (Characklis and Marshall, 1990).

Let the rate of growth of cells be given by

$$r_g = \frac{\mu_m S X}{K_s + S} \tag{1}$$

and the rate of cell detachment be given as

$$r_d = -k_d X^2 \tag{2}$$

where

μ_{max} = maximum specific cell growth rate (constant) $[=] \frac{1}{day}$

K_s = substrate half-saturation coefficient (constant) $[=] \frac{kg}{m^3}$

k_d = cell detachment coefficient (constant) $[=] \frac{m^2}{(cells)(day)}$

S = substrate concentration $[=] \frac{kg}{m^3}$

X = cells per area of column packing $[=] \frac{cells}{m^2}$

The rate of change of cells with respect to time may described by combining equations (1) and (2) to obtain

$$\frac{dX}{dt} = r_g + r_d = \frac{\mu_m S X}{K_s + S} - k_d X^2 \tag{3}$$

At steady state $\frac{dX}{dt} = 0$ and (3) reduces to

$$\frac{\mu_m S X}{K_s + S} = k_d X^2 \tag{4}$$

Solving (4) for X yields

$$X = \frac{\mu_m S}{k_d(K_s + S)} \tag{5}$$

Now introduce the dimensionless variables

$$b = \frac{X}{X_0} \tag{6}$$

$$C = \frac{S}{S_0} \tag{7}$$

substitute into (5), and solve for b.

$$b = \frac{\alpha C}{\beta + C} \tag{8}$$

Where

$$\alpha = \frac{\mu_m}{k_d X_0} \tag{9}$$

$$\beta = \frac{K_s}{S_0} \tag{10}$$

From (5), evaluated near the influent end of the columns,

$$k_d = \frac{\mu_m S_0}{X_0(K_s + S_0)} \tag{11}$$

Where S_0 = influent concentration of substrate and X_0 = cells per area of packing at the influent end of the column. Note that the assumption here is that k_d = *constant* for the system.

Now combine (5), (6), (7), and (11) and solve for b.

$$b = (\beta + 1)\frac{C}{\beta + C} \tag{12}$$

For zero-order kinetics, $K_s \ll S \Longrightarrow \beta = 0$.

$$b = \lim_{\beta \to 0}\left[(\beta + 1)\frac{C}{\beta + C}\right] = 1 \tag{13}$$

The implication of equation (13) is that there is no change in cell counts throughout the length of the column. As can be seen from Figure 23, there was not a constant cell population through out the columns.

For first-order kinetics, $K_s \gg S \Longrightarrow \beta \to \infty$.

$$\lim_{\beta \to \infty}(b) = \lim_{\beta \to \infty}\left[(\beta + 1)\frac{C}{\beta + C}\right] = \frac{\infty}{\infty} \tag{14}$$

Apply L'Hopital's Rule

$$\lim_{\beta \to \infty}(b) = \frac{\lim_{\beta \to \infty}\left(\frac{d}{d\beta}[(\beta + 1)C]\right)}{\lim_{\beta \to \infty}\left(\frac{d}{d\beta}[\beta + C]\right)} \tag{15}$$

$$\lim_{\beta \to \infty}(b) = \frac{\lim_{\beta \to \infty}(C)}{\lim_{\beta \to \infty}(1)} = C \tag{16}$$

$$b = C \tag{17}$$

Equation (17) shows that for first-order kinetics the cell counts throughout the column will vary directly with the substrate concentration in the column.

Figure 24 shows a plot of the dimensionless substrate concentration with dimensionless cell counts. Equation (12) was used with the labeled values for β to generate

the curves. The lab data was plotted assuming first-order kinetics (equation (17)) with plug flow to determine the column interior substrate concentrations while the influent and effluent numbers are direct observations of the substrate concentration and cell counts.

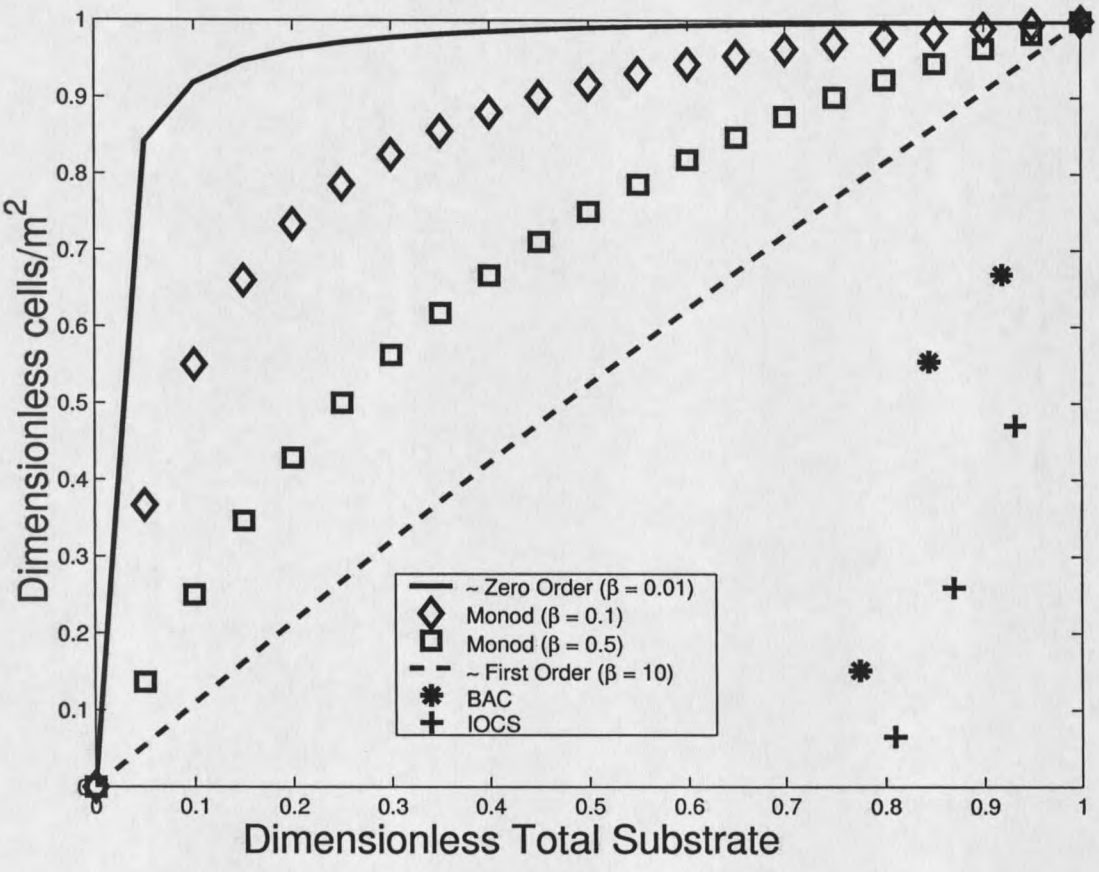


Figure 24: Zero to first-order kinetics (single substrate pool). Comparison of the observed cell counts in the column with the predicted model results using the total DOC as a single pool of substrate.

By assuming that the total organic carbon pool has two parts, one utilized by the organisms (f_u) and one not used (f_r), Figure 25 was constructed using first-order kinetics as the lower bound on substrate utilization. The data points now represent the amount of f_u utilized as observed by the cell count data.

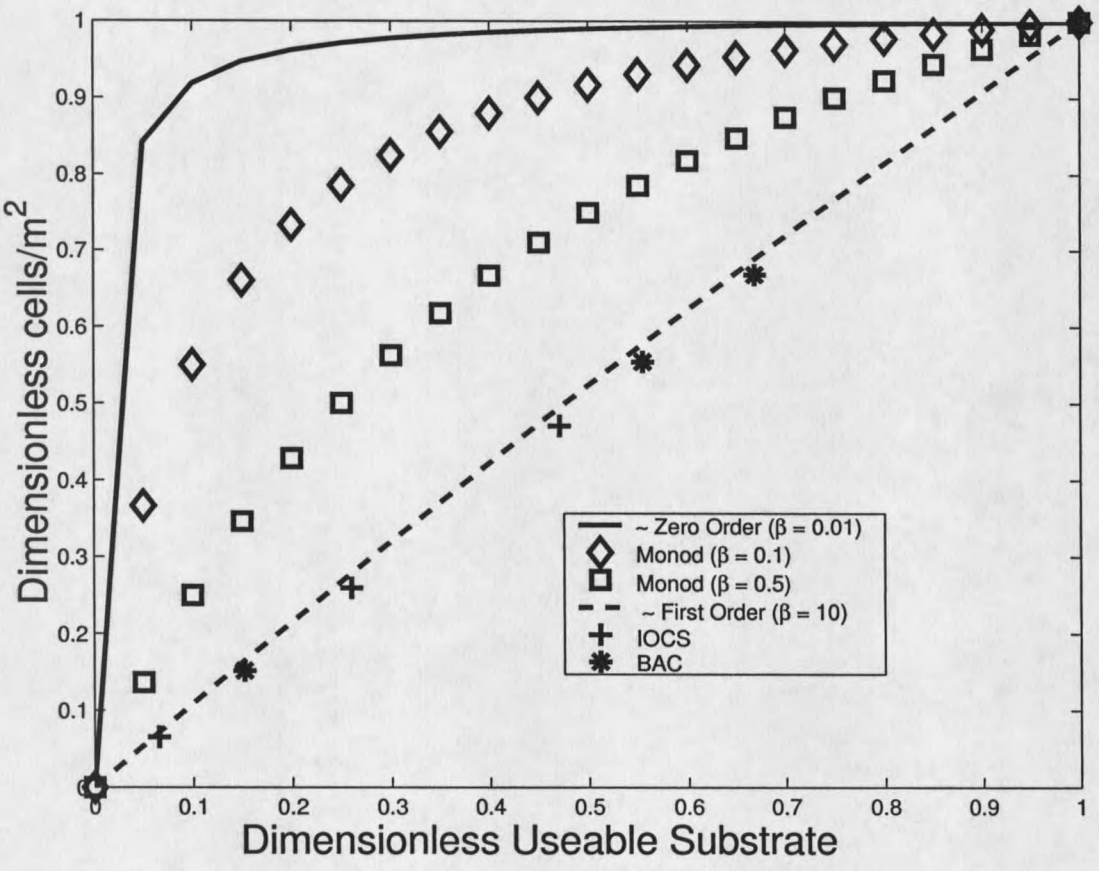


Figure 25: Zero to first-order kinetics (dual substrate pool). Comparison of the observed cell counts in the column with the predicted model results using the total DOC divided into two pools of substrate.

CHAPTER 4

DISCUSSION

Summary

The goal of this study was to determine if biological pretreatment could reduce the downstream fouling potential of feed water in membrane systems. In support of this goal, 4 objectives were stated.

1. Determine if chlorination as an oxidation step for feed water will reduce downstream fouling.

2. Determine if filtration of feed water will reduce downstream fouling.

3. Determine if biological pretreatment using BAC and IOCS as support media will reduce downstream fouling.

4. Develop evaluation methods for objectives 1-3 by developing and testing the following assays.

   (a) Membrane flux measurements

   (b) Membrane fouling layer cell counts

   (c) Membrane fouling layer thickness measured with SEM

(d) Membrane fouling layer thickness measured with DAPI stained thin sections

(e) TOC removal from the system

(f) Bead assay biofilm cell counts

The first three objectives represent the hypotheses to be tested while the fourth objective outlines the assays employed to test the hypotheses. Flux measurement are used as an indicator of membrane fouling in industrial settings while TOC measurement is sometimes used to assess the biological fouling potential in drinking water systems. The other assays were developed to measure the cell numbers and fouling layer thickness present after the treatments used in objectives 1-3.

Prechlorination

Use of chlorination as an oxidation step was examined to determine the impact on the biological pretreatment process and the downstream fouling potential of the feedwater. Figures 3, 6, 9, 13, 17, and 20 summarize the statistical analyses of the assays with respect to chlorination.

The flux and membrane biofilm cell count assays showed no significant differences between chlorinated and unchlorinated treatments. Fouling layer thickness as measured by DAPI stained thin sections and cell counts from the bead assay had a few treatments that demonstrated a reduction in fouling potential while the remaining assays (TOC removal and fouling layer thickness as measured by SEM) showed an

increase in fouling potential for a few treatments. None of the assays provided any consensus and seemed to contradict each other when there was a statistical difference.

Since the chlorine levels were held at a level that would not exceed the demand from the organic carbon present in the water, there may not have been enough oxidation present to alter the pools of substrate in a manner that could be assessed by the assays. In fact, Buls (2000) showed that chlorination of the same organic carbon source at similar concentrations used in this work did not increase the useable carbon pool.

To pool the results of the various assays, the assays were scored with a +1 if the treatment was statistically better than the control treatment and a -1 if it was statistically worse than the control treatment. If the treatment was not statistically different than the control treatment, then it received a score of zero. For the flux, a higher number means a greater flux and hence, better performance. Therefore, a statistically higher flux would score a +1. For membrane cells, a lower cell number is considered a reduction in fouling and hence a lower number would score +1. For both fouling layer thickness measurements, a thinner thickness is considered a reduction in fouling and would receive a +1. Similarly, a greater TOC removal is considered a +1 and a lower cell count on the bead assay is considered good and receives a +1.

The assay scores were then added together to obtain an overall score for the treatments. These summaries are then used to determine if the hypothesis in question is accepted.

The impacts of prechlorination 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 was statistically better than no chlorine and a -1 if it was statistically worse than no chlorine. In most cases, we fail to reject the null hypothesis that the chlorinated treatment means were equal to the treatment means without chlorination. Overall, the results were minimal and mixed. As a result, prechlorination did not appear to be a factor influencing down stream fouling.

Table 3: Summary of chlorination impacts on assay measurements.

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

Post-filtration

The effects of post-filtration on the downstream fouling potential are summarized in figures 4, 7, 10, 14, 18, and 21. Three of the six assays, TOC removal and bead and membrane cell counts, were in complete agreement that post-filtration reduced downstream fouling. The other three assays, flux and the fouling layer thickness measurements, showed reduced fouling when the results were significant.

This result is consistent with literature reports where microfiltration is being used as the primary pretreatment for reverse osmosis systems. The overall operating and maintenance costs are greatly reduced when using microfiltration instead of conventional pretreatment technologies. The primary savings has been reported as fewer cleaning cycles, lower chemical usage, and longer membrane replacement intervals, all of which result when fouling potential is reduced (Dawes, et al, 2000, Deshmukh, et al, 1999).

The impacts of post-filtration are summarized in Table 4. If post-filtration was statistically better it scored a +1 and if it was statistically worse it scored a -1. A score of zero was used if post-filtration was not statistically different from the non-post-filtration treatment. Overall, we failed to accept the null hypothesis that the post-filtered treatment means were equal to the treatment means without post-filtration in at least three, and often five, of the assays. This implies that post-filtration reduces the downstream fouling potential of the water.

Table 4: Summary of filtration impacts on assay measurements.

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

Biological Pretreatment

The effects of biological pretreatment on the downstream fouling potential are summarized in figures 5, 8, 11, 15, 19, and 22. Biological pretreatment demonstrated a statistically significant reduction in fouling potential as measured by three of the assays. The remaining three assays, flux and the two fouling layer thickness measurements, showed a strong trend towards fouling reduction.

These results are consistent with those from Griebe and Flemming (1998) who demonstrated use of a sand biological pretreatment process to reduce fouling on a downstream RO membrane. Griebe and Flemming observed no flux reduction for the RO membrane that had biological pretreatment while the control RO membrane demonstrated a 20% decline in flux. There was also a 1.5 log reduction in membrane cell counts for the system that had biological pretreatment and the biofilm thickness was reduced from $27\mu m$ to $3\mu m$.

The effectiveness of biological treatment with respect to the assays is summarized in Table 5. Here the biological treatment scores a +1 if it was statistically better than the control and a -1 if it is statistically worse than the control. The treatment will score a zero if it is not statistically 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. In this case, we fail to accept the null hypothesis that the biological treatment means were equal to the non-biological treatment means in at least three assays for the prechlorinated/post-filter treatment and in five

assays for the other combinations. This implies that biological treatment reduces the downstream fouling potential of the water.

Table 5: Summary of biological pretreatment impacts on assay measurements.

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

The membrane biofilm cell assay, the bead cell assay, and TOC removal were found to consistently indicate that the fouling potential of the feedwater had been reduced. Examination of Figures 8, 11, and 22 for the biological pretreatment process without prechlorination and post-filtration, shows that when there was a reduction in TOC, there was also a reduction in cell counts. In addition, the cell counts from the column packing demonstrate the reduction in cells as TOC is removed from the system. These comparisons indicate that reducing TOC will reduce cell numbers in the downstream processes.

BAC Versus IOCS

To pick out the difference between the IOCS and BAC, the rankings for the biological treatment were changed to +1 if BAC was statistically "better" than IOCS, zero if there was no difference and -1 if IOCS was statistically "better" than BAC. Table

6 shows that the results were mixed with BAC performing better than IOCS for the post-filtered treatments, IOCS performing "better" than BAC for the prechlorinated treatment and no difference for the non-post-filtered, non-prechlorinated treatment. The two assays that showed a preferential trend were TOC and Bead; BAC removed more TOC than IOCS, and IOCS reduced the biofilm cells on the glass beads more than the BAC.

Table 6: Summary of BAC versus IOCS biological treatments.

Assay	Biological Pretreatment			
	No Post-filtration No Prechlorination	Post-filtration Only	Prechlorination Only	Post-filtration Prechlorination
Flux	0	+1	0	0
Cells	0	0	0	0
SEM	0	0	-1	0
DAPI	0	0	0	0
TOC	+1	+1	+1	+1
Bead	-1	-1	-1	0
Total	0	+1	-1	+1

Treatment Combination

While not part of the original objectives, it was useful to compare the treatments to each other with respect to their overall trends in fouling reduction performance.

To qualitatively rank the treatments, the treatments were scored from 1 to 12 without regard to statistical differences according to the results obtained for each assay. Many scores could differ by more than one and still be statistically the same. However, this provides another view of the overall trends of the results of the experiments.

Table 7 shows how the treatments ranked in order from the most effective treatment (lowest score) to the least effective treatment (highest score) without regard to statistical differences. This provides a qualitative measure of the overall effectiveness of each treatment.

Table 7: Qualitative ranking of assay measurements.

Treatment	Assay						
	Flux	Cells	SEM	DAPI	TOC	Bead	Ave
IOCSPF	3	1	4	1	3	1	2.17
BACPF	1	2	7	2	1	4	2.83
BACPFCL	2	4	2	5	2	3	3
IOCSPFCL	4	3	1	6	4	2	3.33
CTRLPF	5	5	5	10	5	7	6.17
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	7.67
IOCSCL	10	9	9	3	10	5	7.67
BACCL	9	7	10	9	9	6	8.33
CTRLCL	11	12	12	11	12	10	11.33
CTRL	12	11	11	12	11	12	11.5

The ranking in Table 7 reveals that the combination of biological treatment and post-filtration proved to be the most effective in reducing the effects as measured by the assays. Filtration alone appears to do better than biological treatment alone and any treatment appears to reduce downstream fouling except for prechlorination.

Biofilm Model

The TOC removal rates found in this study are consistent with the removal rates found in drinking water biological treatment processes. The amount of TOC removal, typically less than 30%, could lead to the conclusion that to get a greater removal

rate, the columns would need to be greatly increased in size; this would be in error. The destructive sampling cell counts show that there is evidence of two pools of substrate that make up the total TOC component of the water. One pool is useable and the other is more recalcitrant. In addition, TOC removal is associated with reduced cell counts within the biological pretreatment columns indicating the removal of the useable pool of TOC will reduce downstream fouling.

The concept of two or more pools of dissolved organic matter in the water has been proposed before. For example, modeling the removal of biodegradable organic matter in biological filters using the CHABROL model was reported by Laurent et al. (1999). The CHABROL model incorporates the concept of two classes of the dissolved organic matter which is subject to exoenzymatic hydrolysis, H_1 which is rapidly hydrolyzed and H_2 which is slowly hydrolyzed.

The design of the biological pretreatment process depends upon knowledge of the useable portion of the TOC. With influent concentrations and the fraction of TOC that is useable, the biological pretreatment process may be properly sized. The modeling demonstrates the existence of two pools of substrate, f_u the useable portion and f_r the recalcitrant portion.

Biological pretreatment in the water treatment industry is a method used to reduce disinfection by-products and reduce regrowth events in drinking water distribution systems. In an effort to understand, predict, and model this process, a variety of tests have been developed to characterize the carbon sources in the feedwater.

These tests may be grouped into two categories, those that directly assess the carbon reduction as a result of biological activity and those that address the carbon directly utilized by the organisms and incorporated into the biomass. The former category is known as biodegradable organic carbon (BDOC) tests and the latter category is assimilable organic carbon (AOC) tests. Both measurements attempt to assess the amount of biodegradable or assimilable organic carbon in a water source (Geldreich, 1996).

The AOC tests represent the easily assimilable portion of the substrate pool while BDOC attempts to measure the entire pool of biodegradable organic matter. For this reason, AOC is usually less than the BDOC value and overall they are usually less than the total pool of organic carbon. A recent study presented results of BDOC values taken at 31 water treatment plants. The BDOC varied from 30 $\frac{\mu g}{L}$ to 1.03 $\frac{mg}{L}$ and represented 5-21% of the dissolved organic carbon (Volk and LeChevallier, 2000). The reported percent removal was comparable to the 30% removal observed in this work.

While there was ample evidence from the literature that only a portion of the influent organic carbon is removed by the biological pretreatment process, it was important to investigate this phenomenon for this work so that TOC removal could be better associated with fouling reduction. The experimental design was not set up to test this hypothesis, however there was enough information from this research

to provide provide some evidence that only part of the pool of organic carbon was usable by the resident biota.

There does not appear to be a single pool of substrate that is utilizable by the microorganisms colonizing the columns. The results in Figure 24 show that the lab data is not well represented through a single pool of substrate. By considering the pool of substrate as being comprised of two pools of substrate, and using first-order kinetics, the cell data can be better represented as seen in Figure 25.

Even with two pools of substrate, the results of this analysis suggest that cell growth and substrate utilization is not modeled well with zero-order kinetics. If the cell growth was zero-order, there should be a relatively constant concentration of cells throughout the column. Since the cell counts decreased by an order of magnitude, this claim is not supported.

First-order kinetics results in a reasonable representation of cell counts in the column. With first-order kinetics, the useable substrate pool, f_u, was depleted by about 90% based on the cell data. Using the mean percent removal of BAC and IOCS from Figure 8 yields $f_u = 0.23$. Monod kinetics are also a possibility in the system with the cell data showing a higher percent removal of the usable substrate pool.

Comparison to Literature Reports of Biological Pretreatment

The results presented here in this study show general agreement with other published studies that examined biological pretreatment processes and their impact on membrane fouling.

Biological pretreatment has been utilized in drinking water treatment to reduce the organic carbon levels which are often precursors of disinfection by-products and can support regrowth events within the distribution system. The use of biological pretreatment in membrane water treatment has been investigated by Griebe and Flemming (1998) and van der Hoek et al. (1999) and implemented in rinse water reclamation in some Japanese semiconductor manufacturing plants. The Japanese applications are proprietary and there is little information available on these processes (personal communication with Deb Mukhopadhyay).

Griebe and Flemming (1998) reported a 1.5 log reduction in total cell counts on a reverse osmosis membrane treating water from a sand biofilter. In addition the process reduced 70% of the humic substances found on the membrane. After 200 hours of flux through a flat plate reverse osmosis membrane there was no flux reduction for the biologically pretreated feedwater while the control membrane had a flux reduction of 20%. These results indicate that a reduction in humic substances reduced the cell numbers and that both of these are indicators of reduced fouling of the membrane.

van der Hoek et al. (1999) found that biological activated carbon filtration (BACF) followed by slow sand filtration successfully produced reverse osmosis feedwater that met their feedwater requirements. They concluded that not only did the BACF reduce the organic carbon content of the feedwater, but that synthetic organics were effectively removed in these filters and the reverse osmosis retentate was better quality resulting in reduced disposal costs.

The results from the literature support the evidence gathered in this study that a reduction of humic substances results in a reduction in cell numbers on downstream processes and that biological pretreatment produces reverse osmosis feedwater quality that is less likely to foul the downstream processes.

Post-filtration during this study represents microfiltration as a pretreatment for reverse osmosis in practice. During the last few years, microfiltration has emerged as an economically viable pretreatment technology for reverse osmosis water treatment. The operation and maintenance costs during wastewater reclamation pilot scale studies at Orange County Water District, CA, were reduced by approximately a factor of two over the conventional pretreatment technologies using microfiltration (Dawes et al. 2000). The results of the work presented in this document demonstrate that not only does microfiltration result in reduced downstream fouling, but that using biological activated carbon filtration before microfiltration provides a further improvement in the quality of the feedwater as measured by cell counts and TOC removal.

Conclusions

Biological pretreatment reduces downstream fouling of membranes as measured by the assays employed in this work. The biological pretreatment step reduced the number of biofilm cells in both the membrane and bead assays. In addition, there was a reduction in TOC which was consistent with both the reduced cell counts in the assays and reduced cell counts within the columns.

Chlorination, as an oxidation step, had no impact on downstream fouling potential of the feed water. The results indicated little or no difference as a result of chlorination. Chlorine may have a more definitive impact if used in greater concentrations, however those concentration levels may be unrealistic in a production operation. It is possible that long contact times and carrying a residual into the system may promote more changes in the nature of the organic carbon than was observed in this study.

Microfiltration, after biological treatment, further reduces downstream fouling of membranes. Postfiltration reduced the number of biofilm cells in both the membrane and bead assays. 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.

All assays were used to assess the fouling potential of a particular treatment. The combination of assays provided a much more comprehensive body of evidence that fouling potential had been reduced than any single assay. Therefore a variety

of assays may be necessary to determine the downstream fouling potential of feed water. The assays developed during this study that consistently revealed a reduction of fouling were the membrane biofilm enumeration, bead assay biofilm enumeration, and TOC removal. The TOC removed appeared to be from a portion of the TOC that is more useable by the microorganisms. This portion is the critical part of the TOC that must be removed to reduce downstream fouling.

Cell growth modeling within the columns indicated that there are at least two portions of the organic carbon pool to consider. The kinetics were shown to not follow zero-order and therefore first-order kinetics were used to estimate the fraction of the two pools of substrate. The column cell count data along with TOC removal for the biological pretreatment process alone were adequately modeled with first-order kinetics.

Biological pretreatment appears to be a promising technology for reducing the downstream fouling of membrane water treatment units. Fouling reduction will reduce cleaning intervals, which in turn will reduce chemical usage and increase membrane replacement intervals all of which will decrease overall maintenance and operation costs in membrane water treatment plants.

Recommendations

The results presented here are considered to be conservative, since the organic carbon amendment of humic and fulvic acids is believed to be a very recalcitrant

form of dissolved organic material typically found in feed water. In a real situation, the improvements may be greater.

Recalcitrant organic material may be converted to a more useable form using an oxidation step such as ozonation. Ozonation has been shown to increase the AOC content of water (Hu, et.,al.,1999, Siddiqui, et al., 1997) and should be carefully examined in the context of biological pretreatment and the assays used for this work. Continued work with biological pretreatment using different oxidation steps and different oxidation levels is necessary to determine the design impact of these unit processes on the overall system.

Of the assays performed, TOC reduction, membrane biofilm cell counts, and in stream biofilm cell counts were good indicators of the level of fouling found in the system. These assays consistently revealed evidence that fouling had been reduced in the system and therefore would be considered useful assays for assessment of system fouling.

Application of the assays developed here, along with modern optical and acoustical sensing capability, may help prove the usefulness of this technology in predicting the reduction of membrane biofouling.

Knowledge of the portion of the TOC that is useable by the microorganisms should prevent over design of a biological pretreatment reactor. However, appropriate reactor models and further kinetics analysis will need to be developed and tested for design purposes.

Finally, the next step will be to perform pilot scale studies using reverse osmosis as the final membrane step. The reverse osmosis membranes can then serve as the membrane assay.

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