Application of immersed ultrafiltration membranes for organic removal and disinfection by-product reduction

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Abstract

Natural organic matter (NOM) present in raw water can not only impart color to water, but can also cause health risks associated with disinfection by-products (DBP). The most common DBPs found in drinking water are trihalomethanes (THMs) and haloacetic acids (HAAs), which are formed when NOM reacts with chlorine or chlorine based disinfectants. In order to prevent the formation of DBP’s, the US EPA has introduced a two stage Disinfectants-Disinfection Byproduct Rule (D/DBPR). Stage 1, finalized in November of 1998, established the maximum contaminant level (MCL) at 0.080 mg/L for total trihalomethanes (TTHMs) and 0.060 mg/L for five haloacetic acids (HAA5). This will be followed by Stage 2 (Final Rule due in 2002) of the D/DBPR, which may set lower contaminant levels at 0.040 mg/L and 0.030 mg/L for TTHM’s and HAA5, respectively. Enhanced coagulation has been identified as the best available technology for meeting the requirements of the D/DBP Stage 1 Rule for Total Organic Carbon (TOC) reduction and the removal of disinfection byproduct precursors. With enhanced coagulation, NOM, color and TOC reduction is achieved using a higher coagulant dosage than would be utilized for turbidity removal. The pH of the raw water is also commonly optimized to maximize process efficiency. The application of immersed ultrafiltration membranes using enhanced coagulation has been successfully applied for disinfection byproduct precursor (DBP), color and TOC removal for drinking water applications. With this process, a single tank coagulation-ultrafiltration process replaces the coagulation-flocculation-sedimentation-filtration stages of a conventional treatment plant. Enhanced coagulation ultrafiltration has three stages: 1) rapid mix, 2) coagulation/adsorption of NOM, and 3) ultrafiltration. A high solids concentration is maintained in the membrane tank to promote the adsorption of organics onto the small settling flocs. Subsequently, the barrier characteristics of the ultrafilter are used to separate flocculated particles, precipitates, and colloidal particles. Powdered activated carbon (PAC) can also be used in combination with enhanced coagulation, or alone to reduce disinfectant byproduct precursors by addition to the rapid mix stage upstream of the ultrafiltration membranes. Compared to conventional treatment, this novel method of water treatment results in higher color and TOC removal and requires less coagulant and PAC. The use of lower chemical dosage results in significantly less treatment residuals and reduced disposal costs. The system also has a small footprint since it is designed with a shorter hydraulic retention time as it is only necessary to form a floc that exceeds the membrane pore size. This paper presents the application of immersed ultrafiltration membranes using enhanced coagulation and PAC processes for color and TOC removal as well as the reduction of DBP precursors. It also presents pilot data on a number of applications where the process is being effectively used and compares it with performance data reported for conventional treatment facilities using enhanced coagulation.

Keywords DBP and THM reduction; enhanced coagulation; membranes; TOC removal; ultrafiltration

Introduction

Membrane filtration operates on the principles of particle separation based on a pore size and pore size distribution gradient. Microfiltration membranes have pore sizes that vary from 0.075 microns to 3.0 microns. Ultrafiltration membranes have smaller pore sizes typically in the range of 0.0015 microns to 0.2 microns. Depending on the membrane selected, it will allow a separation of suspended solids, bacteria, cysts and other parasites whose diameters are larger than the nominal pore size of the membrane (Jacangelo et al., 1995). This allows for production of treated water that is free of parasites and solids without the need for chemical addition.
Microfiltration (MF) and ultrafiltration (UF) processes have expanded rapidly as an alternative to conventional clarification and filtration to meet increasingly stringent regulations related to the Interim and Long Term Enhanced Surface Water Treatment Rule, as well as for removal of pathogens such as *Giardia* and *Cryptosporidium* (Yoo et al., 1995). This is assisted by the fact that MF and UF plants are becoming increasingly cost effective over a large range of plant sizes ranging from 100 gpm to 100 MGD.

Typically, membranes do not remove color or natural organic matter (NOM) when used alone (Scanlan et al., 1997). To remove these latter, microfiltration and ultrafiltration membrane processes must be combined with other conventional technologies, such as activated carbon adsorption and coagulation, to remove the organics from solution and allow for filtration separation (Lebeau et al., 1998). A sedimentation phase is also commonly required.

Innovative immersed membranes allow the combination of conventional coagulation or powdered activated carbon with the membrane system to achieve effective removal of dissolved organics. In these systems, shell-less, loosely packed hollow fiber membranes are directly immersed in a process tank and are operated under slight negative pressure. The low packing density allows the operator to build solids in the process tank and thus to operate the coagulation/adsorption process effectively, similar to a solids contact clarification process. The membranes represent a positive barrier between the “reaction zone” and the treated water.

The immersed membrane described within this paper is commercially called ZeeWeed®. This paper describes the integration of ZeeWeed® with coagulation/flocculation either alone or in combination with PAC to remove TOC and corresponding disinfection by-product precursors.

**The ZeeWeed® membrane – process description**

The ZeeWeed® based drinking water process is a low energy membrane process that consists of outside-in, hollow-fiber ultrafiltration modules immersed directly in the raw feed-water (Mourato et al., 1997). The ultrafilter has a 0.04 micron nominal and a 0.10 micron absolute pore size, ensuring that no particulate matter including *Cryptosporidium* oocysts, *Giardia* cysts, suspended solids or pin sized pollutants will escape to the treated water stream.

The membranes operate under a partial vacuum created within the hollow fibers by the operation of a centrifugal pump. The treated water passes through the membrane, enters the hollow fibers and is pumped to treated water storage by the permeate pumps. Air is introduced at the bottom of the membrane module to provide mixing and create turbulence, which scrubs and cleans the outside of the membrane fibers, allowing them to operate at a high flux. An immersed membrane plant consists of membranes for separation, submerged inside a process tank where raw water is fed either via pumps or under gravity. The clean permeate is extracted by means of a permeate pump. The low pressure air required to keep the membrane clean is generated by an air blower, which can be either a positive displacement or centrifugal type depending on the airflow requirements.

Without the contribution of a chemical to coagulate the organics, microfiltration and ultrafiltration are not effective processes to remove non-colloidal organics from the water. For such cases, aluminum or iron based coagulants are added upstream of the membranes. Coagulation destabilizes the dissolved organics and converts them into particulate forms, which are bigger than the pore size of the ultrafiltration membranes and hence easily removed.

**ZeeWeed® ultrafiltration enhanced coagulation process**

The proprietary ZeeWeed® ultrafiltration enhanced coagulation process consists of the integration of immersed membrane technology with the conventional coagulation/filtra-
tion. However, in this process, a three-stage process comprised of rapid-mix-coagulation-ultrafiltration replaces the conventional coagulation-flocculation-sedimentation-filtration steps. This is accomplished in a single process tank containing the membranes as shown in Figure 1.

The success of Immersed Ultrafiltration Enhanced Coagulation (IUEC) is based on the presence of a high concentration of pin sized iron or aluminum based flocs in the process tank. A high floc concentration is maintained by starting the plant in zero bleed mode, until the recovery reaches the desired level. Typical recoveries with the ZeeWeed® system can be anywhere between 90 to 99% and the solids concentration in the process tank corresponding to these recoveries can be anywhere between 0.5–2 g/L.

There are numerous advantages associated with the (IUEC) process some of which are listed below:

1. A high floc concentration in the process tank increases the surface area available for the solid concentration increases the floc retention time in the process tank. When adsorption of NOM and thus increases the TOC removal efficiency.

2. Increasing standard microfiltration and ultrafiltration membranes are combined with coagulation, it is very likely that some impurities do not have sufficient time to get adsorbed on to the floc surface and thus escape treatment. Increasing floc retention time enhances the removal of these particles.

3. A higher solid concentration translates into improved membrane performance as most of the impurities that would normally adsorb on the membrane surface and cause fouling will have more floc surface area and time available for adsorption, thereby eliminating their availability as a foulant.

4. Since settling is not an issue for membrane based separation, there is only the need to form micro-flocs of 0.1 microns and larger for the membrane to effectively separate the coagulated organic and colloidal particles. This is achieved by providing enough mixing to maintain G values greater than 80–100 sec\(^{-1}\) in the process tank. The small size of flocs further increases the surface area available for adsorption and thus improves the overall process efficiency.

5. Compared to conventional treatment, which typically requires 20–30 min of flocculation time and a sedimentation stage, IUEC requires a smaller building footprint area and thus reduces capital cost.

6. Based on the process efficiencies discussed above, lower coagulant dosages are required to achieve similar results which further decreases chemical and sludge disposal costs.

TOC removal can also be achieved and/or enhanced by the addition of PAC to the rapid mix stage of the IUEC process. Aeration provided in the solids contact zone and membrane

![Figure 1 Immersed ultrafiltration enhanced coagulation – PFD](image-url)
tank maintains the PAC in suspension. Similar to the immersed enhanced coagulation process, a high solids concentration is maintained in the process tank to enhance the adsorption of dissolved organic carbon, particularly low molecular weight organics, which may not be amenable to coagulation and can exhibit rapid DBP formation kinetics.

Similar advantages are achieved when PAC is used with immersed membranes either alone, or in combination with the IUEC process as follows:

1. The increased retention time and high solids concentration in the process tank contributes to an increased adsorption of organics onto the PAC.
2. The high solids concentration of PAC may result in improved membrane performance as organics are preferentially adsorbed onto the PAC rather than on the membrane. The PAC may also provide a dynamic barrier on the surface of the membrane, which contributes to improved treated water quality and membrane performance.
3. PAC particles are unable to pass through the membrane; thereby eliminating the potential for high turbidity or color in the treated water in the event of a process upset.

Results of ultrafiltration enhanced coagulation

Numerous pilot studies were conducted with a wide range of water qualities to demonstrate the improved membrane and process performance as a result of IUEC process. The studies were all conducted with ZeeWeed Ultrafiltration modules. A variety of coagulants have been used in the pilots, including aluminum sulfate (alum), ferric chloride, ferric sulfate, aluminum chlorohydrate (ACH) and polyhydroxy aluminum chloride (PACl). The feed water characteristics for each of the pilot studies are shown in Table 1. The results from each of the pilots are discussed in the following sections.

Arkansas pilot

The pilot study in Arkansas, which lasted for 15 weeks, was performed to demonstrate the treatability of a creek water and a lake water using the ZeeWeed® UF system with enhanced coagulation. The study was started without any coagulant addition but alum dosage at 15 mg/L was started after the first week of operation. The alum dosage was increased to 25 mg/L on February 2nd and remained at that dose for the remainder of the study. From February 24th to March 28th, powdered activated carbon (PAC) was also dosed at 10 mg/L. The final phase of the study included the addition of potassium permanganate (KMnO₄) at dosages between 0.2 and 1 mg/L for manganese removal.

Table 2 shows the feed and the permeate TOC concentrations, the percent removal, and the conditions under which the results were obtained for creek water. Table 3 presents the corresponding data for lake water. The maximum TOC removals were 66% and 70% for creek water and lake water, respectively. Both of these results were achieved with 25 mg/L alum and 10 ppm PAC.

Table 1 Feed water quality of various pilot studies
It can be seen from Tables 2 and 3 that the addition of powdered activated carbon resulted in a significant improvement in TOC removal efficiency. On average the TOC removal increased by almost 20% after adding 10 mg/L PAC. These results suggest that PAC and coagulant can be used simultaneously without significantly affecting the adsorption capacity of PAC.

Figure 2 compares the simulated distribution system (SDS) trihalomethane (THM) and haloacetic acid (HAA) of the existing water treatment plant water to the permeate produced in the ZENON Pilot system while dosing 25 mg/L alum for creek water. The SDS tests were conducted using 1.7 to 2 mg/l of chlorine dose. The ZENON permeate had lower SDS THM and SDS HAA values over the entire range of retention times. Figure 3 shows a similar comparison between the two systems for lake water, with the ZENON pilot dosing alum at 15 mg/L.

Table 2 TOC data for Creek water Arkansas pilot

<table>
<thead>
<tr>
<th>Raw water TOC (mg/L)</th>
<th>Permeate TOC (mg/L)</th>
<th>Percent removal (%)</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.8</td>
<td>10%</td>
<td>No coagulant</td>
</tr>
<tr>
<td>1.9</td>
<td>1</td>
<td>47%</td>
<td>25 mg/L alum</td>
</tr>
<tr>
<td>2</td>
<td>1.1</td>
<td>45%</td>
<td>25 mg/L alum</td>
</tr>
<tr>
<td>1.75</td>
<td>1.0</td>
<td>43%</td>
<td>25 mg/L alum</td>
</tr>
<tr>
<td>4.5</td>
<td>1.75</td>
<td>61%</td>
<td>25 mg/L alum, 10 ppm PAC</td>
</tr>
<tr>
<td>3.95</td>
<td>1.35</td>
<td>66%</td>
<td>25 mg/L alum, 10 ppm PAC</td>
</tr>
<tr>
<td>3.05</td>
<td>1.05</td>
<td>66%</td>
<td>25 mg/L alum, 10 ppm PAC</td>
</tr>
<tr>
<td>3.3</td>
<td>1.5</td>
<td>55%</td>
<td>25 mg/L alum, 0.2 ppm KMnO₄</td>
</tr>
<tr>
<td>2.35</td>
<td>1.05</td>
<td>55%</td>
<td>25 mg/L alum, 0.2 ppm KMnO₄</td>
</tr>
<tr>
<td>2.1</td>
<td>1.24</td>
<td>3%</td>
<td>25 mg/L alum, 0.2 ppm KMnO₄</td>
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</tbody>
</table>

Table 3 TOC data for Lake water Arkansas pilot

<table>
<thead>
<tr>
<th>Raw water TOC (mg/L)</th>
<th>Permeate TOC (mg/L)</th>
<th>Percent removal (%)</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7</td>
<td>2.4</td>
<td>11%</td>
<td>No coagulant</td>
</tr>
<tr>
<td>2.6</td>
<td>1.5</td>
<td>42%</td>
<td>15 mg/L alum</td>
</tr>
<tr>
<td>2.65</td>
<td>1.5</td>
<td>43%</td>
<td>5 mg/L alum</td>
</tr>
<tr>
<td>2.8</td>
<td>0.85</td>
<td>70%</td>
<td>25 mg/L alum, 10 ppm PAC</td>
</tr>
<tr>
<td>2.8</td>
<td>0.9</td>
<td>68%</td>
<td>25 mg/L alum, 10 ppm PAC</td>
</tr>
<tr>
<td>2.75</td>
<td>1.35</td>
<td>51%</td>
<td>25 mg/L alum, 0.5 ppm KMnO₄</td>
</tr>
<tr>
<td>2.6</td>
<td>1.3</td>
<td>50%</td>
<td>25 mg/L alum, 0.5 ppm KMnO₄</td>
</tr>
<tr>
<td>2.5</td>
<td>1.3</td>
<td>48%</td>
<td>25 mg/L alum, 0.5 ppm KMnO₄</td>
</tr>
</tbody>
</table>
The entire pilot testing was conducted at 30 gfd flux and 90% recovery. Figure 4 shows the vacuum profile throughout the study, with the corresponding phase of the study shown along the top of the graph. As shown in Figure 4, there were a few instances during the pilot study during which a sudden increase in vacuum was observed. These spikes in vacuum were due to either an under dose of coagulant or due to a sudden change in the feed water pH. These sudden increases in vacuum indicated that the raw water without coagulant addition was very fouling to the membrane. However, through optimization of the coagulant addition and pH control using an on-line controller, stable operation, resulting in a 4–6 week cleaning interval could be achieved.

Alberta pilot
The pilot study in Alberta, which ran from April to July 1999, was performed to demonstrate that the ZeeWeed® Enhanced Coagulation Process could achieve the desired objectives of TOC less than 5 mg/L and color less than 5 PCU. The full-scale conventional plant running in the city was adding approximately 18 mg/L of NIAD® 1–8 (polyhydroxy aluminum chloride) during the pilot study, while the ZeeWeed® Ultrafiltration pilot unit was tested at an average coagulant dose of 12 mg/L NIAD® 1–8.

Table 4 shows the measured quantities of various water quality parameters in both the feed and the permeate for the ZeeWeed® UF pilot unit. The corresponding values for the existing full scale conventional plant are shown in Table 5. The percent removals of each parameter are also presented. As anticipated, with the exception of color, the ZeeWeed®
UF pilot achieved a higher percent removal for all of the parameters measured. It should be noted that the color values below 5 are less than the accurate detection limit of the spectrophotometer used. While removals of color and TOC were achieved using enhanced coagulation, manganese and iron were likely removed as a result of oxidation using ZeeWeed® air and/or size exclusion by the membrane.

Figure 5 shows the permeability profile of the membrane throughout the study in Alberta. The pilot was operated at 35 gfd flux and 95% recovery without a chemical clean for approximately 7 weeks, indicating a very stable membrane performance. The increase in permeability on June 9th was due to the chemical cleaning of membranes.

Florida pilot A
The pilot study in Florida started in October of 1999 and lasted for approximately 10 weeks. Both ferric sulfate and powdered activated carbon (PAC) were used for enhanced coagulation in this study, at concentrations of 40–200 ppm ferric sulfate and 0–30 ppm PAC. Figure 6 shows the variation of the ferric sulfate and PAC doses throughout the study.
Figure 7 shows the feed and permeate TOC throughout this study. The maximum TOC removal achieved using only ferric sulfate was 84%, which was achieved while dosing 200 mg/L. Dosing 30 ppm of PAC along with the 200 mg/L of ferric sulfate resulted in an additional 8% removal, for a maximum TOC removal of 92%.

The feed and permeate true color results presented in Figure 8 show that the ZeeWeed® UF system consistently achieved 85% removal of color, with a maximum removal efficiency of 97%.

During the pilot testing, simulated distribution system (SDS) THMs and HAAs were measured and were reported to be 39 and 23.7 µg/L respectively, which are well below the current regulations of 80 and 60 µg/L. The SDSTHM and SDSHAA tests were conducted with 2 ppm chlorine concentration and 4 day retention time. The maximum reduction of UV$_{254}$ was 99%, which was achieved while dosing 180 mg/L ferric sulfate.

Figure 6 Florida pilot A chemical dosage profile

Figure 7 Florida pilot A: feed and permeate TOC profiles

Figure 8 Florida pilot A: feed and permeate true color profiles
Figure 9 displays the important operating parameters of the pilot throughout the study. The water temperature varied between 16°C and 26°C, while the flux varied between 35 and 43 gfd.

As seen from the permeability curve, there were two process upsets during the study. The drop in permeability around October 13th was caused by the underdosing of ferric sulfate, which resulted in organic fouling of the membrane. However, Figure 9 shows that the membrane permeability recovered once the coagulant dosage was corrected and the membrane did not require cleaning for 32 days despite the upset. The second upset occurred after the chemical clean on November 9th. When the system was started up after the clean, the process tank pH was too low (<5), which caused the permeability to drop rapidly.

**Florida pilot B**

A pilot study was conducted from July to September of 1998 at another location in Florida. The system began operation without the addition of any coagulant, but fouled after only five days. The system was restarted with the addition of alum as a coagulant and did not require cleaning for over 7 weeks.

The membrane permeability during each phase of the study is shown in Figure 10. A constant flux of 30 gfd was maintained for the duration of the study. The recovery was started at 95% but increased to 98.5% after 4 weeks of operation. The average TOC removal increased from 55% with 1 meq/L (100 mg/L) of alum to 70% with 3 meq/L (300 mg/L) of alum. Color removal also increased from 77% to 93% when the alum dose was increased from 1 to 3 meq/L. The feed and permeate TOC and color values are shown in Figure 11 and

![Figure 9](image-url)  
**Figure 9** Florida pilot A: flux, permeability and temperature profiles

![Figure 10](image-url)  
**Figure 10** Florida pilot B: permeability profile
Figure 12 respectively. It is likely that the treated water TOC values achieved at this location could be decreased to the 3–5 range after adjusting the pH to an optimum value of 6.2.

**Conclusions**

Microfiltration and ultrafiltration membranes are being used frequently to treat Cryptosporidium and Giardia contaminated or suspected waters. However, typical pressure driven membranes are limited in their capability to treat highly colored and TOC rich waters since the use of high dosages of coagulants and/or PAC is often fouling and/or adversely affects system performance. These systems are restricted to operation using a direct coagulation or PAC addition process at low concentrations and/or require the use of a sedimentation stage. As such, the benefits of operating at a high reactor solids concentration are not realized.

The particular design of immersed membranes allows their use in solids rich environments. Thus, they can operate well in an enhanced coagulation mode or using PAC at high concentrations in the process tank. Pilot studies conducted with a wide range of raw water qualities demonstrated that the ZeeWeed® immersed membranes can successfully handle high dosages of coagulants and powdered activated carbons to treat highly colored and organic laden waters.

These studies also demonstrated that, depending upon the raw water quality, up to 90% reduction in TOC could be achieved using the IUEC process. Along with TOC reduction, the IUEC process also demonstrated up to 99% reduction in UV254 absorbance and up to 95% reduction in raw water color. Because of the excellent TOC removals achieved, the
treated water THMs and HAAs were typically decreased to below 40 and 30 µg/L even though the feed water had TOCs up to 20 mg/L.

The results also demonstrated that powdered activated carbon could be used in conjunction with coagulant addition to improve the TOC removal efficiency of the process. Various pilot studies demonstrated that the organic removal efficiency of the IUEC process was improved by up to 20% as a result of PAC addition. In spite of adding large amounts of coagulants, the membrane performance was stable with cleaning frequencies of between 4 to 6 weeks corresponding to fluxes in the range of 30 to 45 gfd.

References