Selected processes for removing NOM: an overview

GAC adsorption and membrane processes offer alternatives to enhanced coagulation for removing NOM.

Joseph G. Jacangelo, Jack DeMarco, Douglas M. Owen, and Stephen J. Randtke

As a result of the anticipated Disinfectants/Disinfection By-product Rule, there has been increasing emphasis by the water industry on the removal of natural organic matter (NOM) from raw-water supplies. Three important NOM removal options are coagulation, granular activated carbon (GAC) adsorption, and membrane filtration. Of these three processes, coagulation is the most widely used in the water industry. But when coagulation cannot remove adequate concentrations of NOM so that disinfection by-products can be controlled, other treatment technologies such as GAC and nanofiltration may need to be used. Various aspects of each of these technologies are discussed.

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classic studies by Packham and Black et al., focused on highly colored water supplies and on coagulation, an existing technology that was both effective and affordable.

In recent years, there has been an increase in both the number and the stringency of drinking water regulations. The current Surface Water Treatment Rule (SWTR) details the removal and inactivation requirements for Giardia and viruses for utilities supplied by surface waters. Some of these requirements may become more stringent under a future Enhanced SWTR. Although utilities provide better disinfection practices than in the past, they must also limit the concentrations of DBPs that are formed by the disinfection process. The anticipated Disinfectants/Disinfection By-Products (D/DBP) Rule will be promulgated in two stages. Under Stage 1, the maximum contaminant level (MCL) for trihalomethanes (THMs) will be reduced from 0.10 to 0.080 mg/L and the sum of haloacetic acids (HAA5) will have an MCL of 0.060 mg/L. There will also be MCLs for bromate and chlorite. In addition to regulations for DBPs, maximum residual disinfectant levels (MRDLs) will be set for chlorine, chloramines, and chlorine dioxide. Finally, an enhanced coagulation treatment technique for improving DBP precursor removal for utilities using conventional treatment has been proposed. As a result of the dilemma of providing better disinfection while reducing DBP formation, a great deal of interest has been generated in employing alternative treatment technologies such as adsorption by granular activated carbon (GAC) and pressure-driven membrane processes to remove DBP precursors before disinfectants are applied.

This article provides an overview of selected aspects of three physical–chemical processes for NOM removal: coagulation, GAC adsorption, and membrane technology (nanofiltration). The information provided is based on the papers presented at the American Water Works Association Research Foundation Workshop on NOM held in Chamonix, France.

Coagulation of NOM

Water utilities in the United States first began to practice coagulation to improve particle removal by sedimentation and filtration, which in turn improved postfiltration disinfection efficacy. When guidelines for color were adopted, some utilities found that an increase in the dosage of coagulant or an adjustment in pH was necessary for acceptable color removal. In 1979, regulations for THM control forced many water utilities to take a closer look at treatment, and interest in NOM removal, especially by means of coagulation, increased sharply. Since then, numerous studies and reports have focused on the use of coagulation for NOM and DBP precursor removal. Because of the concurrent economic crisis (high interest rates and oil prices), utilities were more interested in modifying existing facilities than in building new ones. At the time, there were strong persuasive and economic reasons for avoiding GAC and membranes, given the relative lack of information on these processes compared with coagulation. Ultimately, the overwhelming majority of utilities in the United States met the standard for THMs by modifying the chlorination process, e.g., reducing chlorine dosages, avoiding prechlorination, switching to another preoxidant, or converting free chlorine to combined chlorine after a short period of free chlorine contact time. Relatively few utilities found it cost-effective to modify their coagulation processes to achieve increased NOM removal. As stated previously, however, the D/DBP Rule will enact more stringent requirements, thus renewing the emphasis on coagulation. As such, recent studies have focused on the practice of enhanced coagulation.

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Variability of NOM. Before considering coagulation of NOM or any other NOM removal process, it is important to recognize its temporal variability. The NOM in the surface water sources of many utilities can vary in type and concentration throughout the year. Seasonal data have shown that the amount of precursor or the type of precursor that can react with disinfectants can vary significantly over short time periods. An example of the variation in influent conditions that poses a challenge for adsorption or any other NOM removal process is shown in Table 1. The yearly average dissolved organic carbon (DOC) and maximum trihalomethane formation potential (max-THMFP) vary only slightly from year to year. For this study, the max-THMFP represented a measure of precursors that form THMs at a pH of 9.5, a storage time of seven days, and a temperature of about 30°C, while maintaining a chlorine residual. However, the minimum and maximum concentrations show a much greater variation. Evaluation of monthly minimum, maximum, and average variations did not show any seasonal trends for either DOC or max-THMFP.

Removal mechanisms. Coagulation, broadly defined as a treatment process that includes chemical addition, rapid mixing, and flocculation, can remove NOM by three mechanisms: (1) colloid destabilization, accomplished by electrical double-layer compression, charge neutralization, enmeshment, or bridging; (2) precipitation; and (3) coprecipitation, primarily by occlusion or surface adsorption but conceivably by nonisomorphous inclusion. NOM comprises particulate matter (e.g., plant debris and microorganisms) and DOC. By definition, coagulation can remove particulate NOM only by colloid destabilization (a particle removal mechanism) and can remove truly dissolved NOM only by precipitation or coprecipitation. A variety of other separation processes, such as sedimentation and filtration, are used in conjunction with coagulation for NOM removal.

A significant fraction of NOM comprises aquatic humic substances (AHSs), which exhibit colloidal properties but are considered by some scientists to exist in true solution. Because of uncertainty regarding the physical state of AHSs, all three mechanisms are often considered by scientists studying their removal by coagulation.

A conceptual model of NOM coagulation helps to organize information regarding the typical behavior of NOM during coagulation, including the influence of process operating variables and variations in NOM characteristics, as well as interactions among treatment processes. The model, described in Table 2, considers NOM to be a complex mixture of polyprotic anions that vary in molecular weight, functionality, and hydrophobicity. These molecules interact with protons, metal hydrolysis products, and cations; these interactions are influenced by interactions of metal hydrolysis products (soluble and insoluble) and precipitated metal hydroxides.

A significant fraction of NOM comprises aquatic humic substances (AHSs), which exhibit colloidal properties but are considered by some scientists to exist in true solution. Most surface waters contain much more fulvic acid than humic acid. Fulvic acid does not precipitate at pH 1 (by definition) nor does it precipitate at its isoelectric point. Because it cannot be effectively destabilized by simple charge neutralization, but is hydrophobic enough to be removed by metal–salt coagulants, it is reasonable to consider it dissolved.

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A conceptual model of NOM coagulation. A conceptual model of NOM coagulation helps to organize information regarding the typical behavior of NOM during coagulation, including the influence of process operating variables and variations in NOM characteristics, as well as interactions among treatment processes. The model, described in Table 2, considers NOM to be a complex mixture of polyprotic anions that vary in molecular weight, functionality, and hydrophobicity. These molecules interact with protons, metal hydrolysis products, and cations; these interactions are influenced by interactions of metal hydrolysis products (soluble and insoluble) and precipitated metal hydroxides.

Before the 1970s, research into the nature of natural organic matter in drinking water and into methods for its removal was driven primarily by the desire to remove color from public water supplies.
with protons and anions (especially hydroxyl ions and sulfate).

**Operational factors influencing NOM removal.**

Removal of NOM can be influenced by the type of coagulant used, the coagulant dosage, pH, mixing, changes in water quality, the order of chemical addition, and other factors. The following general observations can be made:

- One coagulant may be significantly more effective than another for a given water. No clear pattern emerged in a 1988 literature review, but there have been several recent reports of iron salts outperforming alum. In one study involving waters from 14 different water treatment facilities, high dosages of ferric sulfate or ferric chloride removed significantly more NOM than alum in 13 of the waters. However, at the lower dosages commonly used in water treatment practice, the differences were not as great, especially in relation to the influence of other factors, such as pH.

- When used as primary coagulants, polymers are not expected to perform as well as metal–salt coagulants. Although polymers can remove some NOM, including particulate NOM and relatively high-molecular-weight NOM, they are generally not effective for removing truly dissolved matter from solution. Nevertheless, when used as coagulant aids, they may increase TOC removal by improving liquid–solid separation.

- Removal of NOM generally follows one of two patterns (Figure 1) as the coagulant dosage increases: a sharp increase in removal at a particular dosage stoichiometrically related to the concentration of NOM (type I) or a relatively gradual increase in removal (type II). Type I is indicative of precipitation (the pattern being the same as that produced by precipitation of a polymeric ligand) and is associated with lower pH values, more removable

### TABLE 2  Conceptual model of NOM coagulation

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Results</th>
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</thead>
<tbody>
<tr>
<td>Interactions</td>
<td></td>
</tr>
<tr>
<td>NOM + H⁺</td>
<td>Precipitation of HA if pH = 1; enhanced coagulation of removable NOM up to an optimum point, beyond which protons inhibit interactions between NOM and metal hydrolysis products; renders NOM molecules smaller in size and more hydrophobic, enhancing GAC adsorption</td>
</tr>
<tr>
<td>NOM + metal hydrolysis products</td>
<td>Precipitation of NOM molecules whose solubility is exceeded; adsorption of NOM on metal hydroxide solids; some anions (e.g., OH⁻ and SO₄²⁻) interfere by competing with NOM for adsorption sites; cations able to bind to NOM can replace some metal hydrolysis products, reducing coagulant demand</td>
</tr>
<tr>
<td>NOM + cations</td>
<td>Precipitation of NOM molecules whose solubility is exceeded; reduction in the concentration of metal hydrolysis products needed for precipitation, coagulation, or adsorption of NOM</td>
</tr>
<tr>
<td>NOM characteristic*</td>
<td>Increased hydrophobicity, increased number of binding sites per molecule, increased heterogeneity</td>
</tr>
<tr>
<td>Increased hydrophobicity</td>
<td>Increased removal</td>
</tr>
<tr>
<td>More binding sites per molecule</td>
<td>Increased removal, greater coagulant demand, and a sharper increase in removal as coagulant dosage increases (but increased solubility can override)</td>
</tr>
<tr>
<td>Higher molecular weight</td>
<td>Increased removal (as a result of increased hydrophobicity and more binding sites per molecule)</td>
</tr>
<tr>
<td>Increased heterogeneity</td>
<td>A more gradual increase in removal as dosage increases</td>
</tr>
<tr>
<td>Treatment</td>
<td></td>
</tr>
<tr>
<td>Coagulation</td>
<td>Removes larger MW and more hydrophobic NOM; remaining NOM molecules adsorb more rapidly on GAC and go deeper into GAC pores, so a net increase in adsorption is possible; bed life can be greatly extended because of the decreased NOM loading; reduced concentration polarization (gel formation) on membranes; reduced oxidant demand</td>
</tr>
<tr>
<td>Ozonation–oxidation</td>
<td>Decreased hydrophobicity, decreased MW, but possibly increased number of binding sites per molecule; could help or hinder coagulation</td>
</tr>
<tr>
<td>Softening</td>
<td>Removes much of the coagulable NOM by precipitation and coprecipitation</td>
</tr>
</tbody>
</table>

*Assuming that all other characteristics remain unchanged

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NOM, AHSs, and increased homogeneity. Type II is attributable to adsorption and is associated with higher pH values and less coagulable, less humic, and more heterogeneous NOM.

- Plants experiencing type I behavior are, in many cases, in compliance with the enhanced coagulation requirements of the proposed D/DBP Rule because floc formation is generally inadequate at low coagulant dosages and the percent removal of TOC tends to be higher at higher coagulant dosages. Plants experiencing type II behavior may be less likely to meet the TOC removal requirements of the proposed rule, but are also more likely to be deemed “nonamenable” to enhanced coagulation.

- Maximum removal of NOM generally occurs at pH values between 5 and 6.7. Low-alkalinity waters may require addition of lime to maintain the pH in this range. For high-alkalinity waters, the pH may need to be lowered to this range by coagulant or acid addition. As shown in Figure 2, supplemental acid addition lowers the amount of coagulant required to achieve a given TOC concentration. For a given pH value, acid addition (accompanied by decreased coagulant addition) mildly inhibits TOC removal because smaller amounts of metal hydroxide precipitates are produced. Because sulfuric acid is less costly than coagulants, many utilities are exploring acid addition as a promising means of complying with the enhanced coagulation requirements of the proposed D/DBP Rule. However, a number of related issues—control of coagulant residuals, settled- and finished-water turbidity counts, manganese concentrations, finished-water sulfate concentrations, corrosion—cause concerns that remain to be adequately addressed.

- Inorganic ions can influence the coagulation of NOM. Cations, especially divalent cations, may reduce the required coagulant dose by binding to specific functional groups on NOM molecules. Hydroxide and sulfate anions can inhibit removal, presumably by competing with anionic organic molecules for adsorption sites or by forming complexes with cationic metal hydrolysis products. Other ions, notably bromide and ammonium, influence DBP formation and thus may influence the degree of precursor removal required. More detailed discussions of these and other factors are presented elsewhere.
Coagulation as a pre-treatment. Some utilities may find that coagulation achieves insufficient precursor removal for the purpose of meeting the MCLs specified in the proposed D/DBP Rule. Nevertheless, coagulation may play a key role in pre-treating water prior to subsequent treatment using GAC or membranes. Not only does coagulation remove particles that might clog GAC beds or membranes, it also removes NOM, which reduces the loading on GAC columns. Previous studies have shown that coagulation can significantly increase both the bed life and the adsorptive capacity of GAC. Most studies that used coagulant addition as a pretreatment for membrane filtration have focused on the use of aluminum sulfate or ferric sulfate at concentrations ranging from 5 to 50 mg/L. It appears that the coagulation of smaller particles into larger ones reduces the penetration of various materials, including colloidal and large organic macromolecules, into pores of the membrane. Coagulation may also increase the size of the particles composing the cake layer on the membrane, increasing its porosity and, as a consequence, enhancing the feedwater flux through the membrane.

Adsorption by GAC

Adsorption is a treatment technology often considered when dissolved organics must be removed. Many of the US Environmental Protection Agency’s current and proposed regulations for synthetic organic chemicals, THMs, and HAAs cite GAC as a best available technology. Both GAC and powdered activated carbon (PAC) are widely used in the United States for taste and odor control and thus are technologies familiar to utility managers. Most pesticides are readily adsorbed by GAC or PAC. Either type of activated carbon adsorbs NOM to some degree. The discussion here is limited to the use of GAC in a post-filter adsorption mode.

Jefferson Parish, La., and Cincinnati, Ohio, provide the most comprehensive data available for evaluating continuous performance for precursor removal. Both cities have surface water sources. These locations have also been the subject of studies of large-scale, long-term, continuous operation of GAC at empty-bed contact times (EBCTs) longer than those achieved by sand replacement systems. Both locations also investigated precursor removal by GAC at EBCTs typical of sand replacement systems in conventional filtration. DBP precursor removal by GAC generally requires at least a 10–15-min EBCT to achieve DBP reductions of any magnitude over a reasonable time period. During the conceptual phase of a project to consider the use of GAC, key design parameters must be carefully evaluated and optimized. Research is needed to understand the basic characteristics of NOM and the treatment technology changes required to remove the

<table>
<thead>
<tr>
<th>Year</th>
<th>DOC</th>
<th>Max-THMFP*</th>
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<tbody>
<tr>
<td>1978</td>
<td>38</td>
<td>48</td>
</tr>
<tr>
<td>1979</td>
<td>48</td>
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<td>56</td>
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<td>1992</td>
<td>24</td>
<td>48</td>
</tr>
<tr>
<td>Range</td>
<td>8-48</td>
<td>29-56</td>
</tr>
</tbody>
</table>

*Max-THMFP conditions—pH 9.5, 30°C, seven days of holding time, presence of free chlorine residual after seven days

FIGURE 4

Removal of selected DBP precursor materials at Cincinnati Water Works by GAC over time

TABLE 3

Variability in removal of DOC and max-THMFP through conventional treatment at Cincinnati Water Works

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fractions of NOM responsible for water quality degradation (e.g., DBP formation).

Removal of NOM by adsorption. Precursor removal by unit processes can vary widely over time. Table 3 shows that for conventional treatment at the Cincinnati Water Works, the DOC yearly average removal has varied from 8 to 48 percent and the max-THMFP removal has varied from 29 to 56 percent. DOC removal, by conventional treatment at Jefferson Parish from 1978 to 1982, varied from 4 to 27 percent and max-THMFP varied from 14 to 29 percent.

Variations in precursor removal by GAC at a single location are shown in Figure 3. GAC operations at Cincinnati show that when the treatment objective is to meet a given regulatory THM limit, the useful life of a GAC bed (before reactivation or replacement) varies considerably. At a THM requirement of 40 µg/L, GAC adsorption capacity could be exhausted after a period as short as 41 days or as long as 182 days. There are no assurances as to which conditions will be present at any time. Based on 22 separate, large field-scale breakthrough trials, a 15-min EBCT and an operation time of about 60 days resulted in an average of 30 percent breakthrough (70 percent removal) of DOC. Similarly, 110 days of operation resulted in an average of 50 percent breakthrough (50 percent removal) of DOC. (The time to reach a 30 percent breakthrough of DOC varied from 40 to 110 days, and for 50 percent breakthrough from 80 to more than 200 days). Table 4 shows the variation in DOC removal achieved at three locations.

The same brand of 12 ~ 40-mesh GAC was used for a field trial at each location. These results are evidence of the site-specific nature of DOC removal by GAC. Thus, the concerns regarding reliability of treatment practices to meet the new DBP regulations have a sound basis.

Figure 4 shows an example of precursor removal expressed as a percentage of the influent concentration of various parameters commonly investigated. The figure shows the precursor removal efficiency of a 21-min EBCT, postfilter GAC contactor operated continuously. After six months of operation, the GAC removed more than 40 percent of the haloacetonitriles (HANs) precursors, 55 percent of the TOC, 60 percent of the THM precursors, and more than 80 percent of the precursors to HAAs. Percent removal of individual DBP precursors, e.g., dichloroacetic acid, cannot be accurately predicted from the percent removal of its group of DBP precursors, e.g., HAAs. Thus, caution must be exercised in expecting the removal efficiency of a specific compound to correlate satisfactorily with a multicomponent parameter that includes it.

### Table 4

<table>
<thead>
<tr>
<th>Location</th>
<th>EBCT min</th>
<th>50 Percent Removal</th>
<th>70 Percent Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cincinnati, Ohio</td>
<td>15</td>
<td>10,600</td>
<td>5,800</td>
</tr>
<tr>
<td>Jefferson Parish, La.</td>
<td>18.8</td>
<td>7,400</td>
<td>4,800</td>
</tr>
<tr>
<td>Miami, Fla.</td>
<td>18.6</td>
<td>2,900</td>
<td>1,300</td>
</tr>
</tbody>
</table>
The occurrence of proportionately higher concentrations of brominated species in GAC effluent waters than in their corresponding influents has been observed for a number of years. Table 5 shows the results from one of the twelve 16-mgd post-sand-filter GAC adsorbers placed into service at Cincinnati Oct. 8, 1992. The effluent-to-influent-concentration ratio appears to increase with the bromine content of the species. This occurs whether precursors are removed by coagulation, membranes, or by GAC. The same phenomenon occurs for HAA5. This phenomenon is a result of two mechanisms. Because bromide is not removed to any extent by GAC, there is a higher bromide-to-TOC ratio in the GAC effluent than in the GAC influent. An increase in this ratio favors the formation of brominated DBPs after chlorination. The brominated DBP species will form unless the reactive TOC fraction is removed. Also, there is a higher bromide-to-chlorine-dose ratio in subsequent chlorination of GAC-treated water, because chlorine dosages decrease as a result of the TOC removal by GAC. An increase in the bromide-to-chlorine-dose ratio favors the formation of brominated organics.

Research also has been performed on the removal of fractions of NOM by the GAC process. Figure 5 presents data derived from pilot-scale treatment (ozonation, alum coagulation and filtration, and GAC treatment) for water obtained from the Ohio River. These figures portray bulk NOM as well as nonhumic and low-apparent-molecular-weight (AMW) fractions; these fractions are highlighted because overall they are the most difficult to remove. The GAC1 sample was collected near the beginning of the GAC column operation \((C/C_0 = 0.14)\), and GAC2 was collected at approximately a 50 percent breakthrough of TOC \((C/C_0 = 0.43)\).

The data in the figure illustrate that the DOC was reduced by 80 percent in GAC1 and that the

### TABLE 5

<table>
<thead>
<tr>
<th>Month</th>
<th>CHCl₃</th>
<th>CHCl₂Br</th>
<th>CHClBr₂</th>
<th>CHBr₃</th>
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<tr>
<td>October</td>
<td>0.001</td>
<td>0.41</td>
<td>0.93</td>
<td>4.69</td>
</tr>
<tr>
<td>November</td>
<td>0.24</td>
<td>0.61</td>
<td>1.18</td>
<td>5.00</td>
</tr>
<tr>
<td>December</td>
<td>0.36</td>
<td>0.73</td>
<td>1.15</td>
<td>2.41</td>
</tr>
<tr>
<td>January</td>
<td>0.41</td>
<td>0.84</td>
<td>1.25</td>
<td>1.00</td>
</tr>
<tr>
<td>February</td>
<td>0.50</td>
<td>0.88</td>
<td>1.40</td>
<td>5.00</td>
</tr>
<tr>
<td>March</td>
<td>0.28</td>
<td>0.69</td>
<td>1.13</td>
<td>3.00</td>
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<td>April</td>
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<td>May</td>
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<tr>
<td>June</td>
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effluent was composed almost entirely of nonhumic and low-AMW (<1K) DOC. It is noteworthy that GAC provided some reduction of nonhumic and lower-AMW DOC from the conventional treatment effluent. For GAC2, a higher concentration of DOC was observed in the effluent. Although nonhumic and lower-AMW DOC predominated, some humic and higher-AMW (>1K) DOC was observed in the GAC effluent. The THMFP trends are somewhat comparable (THMFP measured as a 3:1 chlorine-to-DOC ratio, 96 hours contact time, pH = 7.0, temperature = 20°C).

Samples were also collected from the Salt River Project in Phoenix, Ariz, at several points along the breakthrough curve for a rapid small-scale column test following conventional, full-scale treatment (coagulation, flocculation, sedimentation, and filtration). These data are shown in Figure 6. The first sample ($C/C_0 = 0.10$ based on DOC) is representative of nonadsorbable NOM. Subsequent samples reflect progressive changes along the breakthrough curve. As bulk DOC (or bulk UV absorbance) breaks through, NOM constituents follow slightly different patterns, reflecting the heterogeneous nature of NOM. Initially, the little DOC that breaks through is of nonhumic and lower-AMW character; subsequently humic and higher-AMW material appears in the GAC column effluent.

**NOM removal by membrane processes**

Membrane processes used for NOM removal are a relatively new innovation of a technology that has been used for several decades. Membranes can be described by a variety of criteria, including:

- membrane pore size,
- molecular weight cutoff (MWCO),
- membrane material and geometry,
- targeted materials to be removed,
- type of water quality to be treated, and
- treated water quality.

Although utilities provide better disinfection practices than in the past, they must also limit the concentrations of disinfection by-products that are formed by the disinfection process.

Along with the preceding criteria, membrane processes can also be categorized broadly into pressure-driven and electrically driven processes. The latter, which consist primarily of electrodialysis and electrodeposition reversal, are not normally used for the removal of NOM. Thus, the subsequent discussion is limited to pressure-driven membrane processes.

**Pressure-driven processes.** Figure 7 summarizes the various pressure-driven membrane processes and selected materials removed by each.
Reverse osmosis (RO). This process has traditionally been used for the removal of salts from brackish water and seawater. It depends on applying high pressures across the membrane (in the range of 150 to 1,200 psi) in order to overcome the osmotic pressure differential between the saline feedwaters and product waters.

Nanofiltration (NF). This process, also called membrane softening, lies between RO and ultrafiltration (UF) in terms of MWCO (200–1,000 daltons; NF membranes for potable water applications have MWCOs of 200–400 daltons). NF operates at pressures between 75 and 150 psi. Lime-softening has been the traditional technology of choice for softening. However, many raw waters, especially those in Florida, are characterized not only by high hardness but also by high concentrations of NOM. The advantage of NF over lime-softening is that it is more effective as a multi-contaminant removal technology. Although it provides removal of ions contributing to hardness, i.e., calcium and magnesium,36,37 the technology is also very effective for removal of color and DBP precursors.32,38–42 Consequently, NF can be cost-competitive when treating waters that would otherwise require several treatment processes to produce a similar finished-water quality.

Ultrafiltration (UF). UF membranes cover a wide range of MWCOs and pore sizes. Operational pressures range from 10 to 100 psi, depending on the application. “Tight” UF membranes (MWCO 1,000 daltons) may be used for removal of some organic materials from freshwater, whereas “loose” membranes (MWCO > 50,000 daltons, 10–30 psi) are primarily used for liquid-solid separation, i.e., particle and microbial removal.

Microfiltration (MF). A major difference between MF and loose UF is membrane pore size; the pore sizes (0.1 µm or greater) of MF units are approximately an order of magnitude greater than those of UF. The primary application for this membrane process is particulate and microbial removal.

Removal of NOM by NF. The original concept of NF was based on using a modified RO membrane as an alternative to lime-softening for hardness removal.36,37 NF has emerged as a viable alternative to conventional treatment processes, primarily because plants can operate at lower pressures (75–150 psi) and higher permeate recoveries (80–90 percent) than RO.40,41 The membranes used in this process are designed to reduce total dissolved solids (50–70 percent) to acceptable levels while removing a significant fraction (as high as 95 percent) of the divalent ions, primarily magnesium and calcium, that contribute to hardness. A recent study that used membranes with reduced inorganic ion rejection characteristics compared traditional NF membranes.43 These membranes may have important applications for water with low hardness and alkalinity, but high TOC concentrations. Such membranes would increase
feedwater recoveries, decrease the chemical requirements for stabilization of the product water, and allow more flexibility in process waste disposal because a less concentrated brine is produced.

To date, NF has primarily been used to treat groundwaters that contain relatively low total dissolved solids but that have high total hardness, color, THM, and other DBP precursors. Although most of the research and application of this membrane process has occurred in the United States (especially in Florida), there is increasing activity occurring in Europe. A large water treatment company in Europe is anticipating the design and construction of a 50-mgd NF facility to replace its existing ozonation and GAC treatment processes.

Removal of TOC, UV, and DBP precursors. Figure 8 gives an example of the removal of TOC and ultraviolet (UV) absorbance at 254 nm (UV-254) from two waters in northern California (Mokelumne River and the San Joaquin River–Sacramento Delta) and one in eastern Canada (Ottawa River). Ninety-five percent confidence intervals are also shown. The membranes ranged in MWCOs from 200 to 100,000 daltons. UF alone removed less than 22 percent of the TOC and UV-254, regardless of the source water tested. Hollow-fiber NF membranes removed considerably more TOC (55–83 percent) and UV-254 (71–97 percent). However, these NF membranes removed 16–21 percent less TOC and UV-254 from delta water than from the other two waters tested. For example, the hollow-fiber transverse-flow membrane with a 400–600 MWCO removed only 62 percent of the TOC and 79 percent of the UV-254 from delta water, whereas removals ranged from 78 to 83 percent for TOC and 90 to 97 percent for UV-254 in Mokelumne River and Ottawa River waters, respectively. These differences, which were the result of differences in the AMW distributions, were statistically significant at a 95 percent confidence level.

Impact of bromide on controlling DBPs. Bromide has a significant impact on the formation of DBPs after chlorination of membrane permeates. For one water studied (San Joaquin River–Sacramento Delta water), the raw bromide concentration was approximately 0.6 mg/L. The simulated distribution system trihalomethane (SDSTHM) speciation for this bromide level after UF and NF treatment is shown in Figure 10. The data are presented relative to the individual raw-water SDSTHMs observed after chlorination. Thus, ratios less than 1 indicate that individual SDSTHM concentrations were reduced after treatment. At ratios above 1, higher concentrations of individual SDSTHMs were detected relative to the individual raw-water SDSTHMs. The results show that a ratio of approximately 1 was found for the four THM species measured after UF of delta water, indicating that UF...
removed little SDSTHM precursor material. The NF membranes in the 400–800 dalton range (hollow-fiber membranes) primarily reduced the concentrations of chloroform and bromodichloromethane, with ratios of 0.1 and 0.3, respectively. In absolute concentrations, chloroform was decreased from 49 to 5 µg/L with the 600–800 MWCO membrane and from 39 to 4 µg/L with the 400–600 MWCO membrane. However, increases in the bromoform ratios between 2.5 and 3.2 were observed using these membranes. The bromoform concentration after chlorination of the NF permeate was 70 µg/L with the 600–800 MWCO membrane and 56 µg/L with the 400–600 MWCO membrane, compared with the raw-water bromoform concentrations that ranged from 22 to 23 µg/L. A change in speciation toward the more brominated compounds was consistent with the decrease in MWCO. This was primarily a result of the increase in the bromide-to-TOC ratio, which favors the formation of brominated DBPs after chlorination.

The 200–300 MWCO spiral-wound NF membranes were the most effective for removing DBP precursor materials from delta water. TOC was reduced to approximately 0.3–0.4 mg/L. Although these membranes did not remove high levels of bromide (17 to 35 percent), it appears that the removals of organic precursor materials were great enough to control the formation of elevated levels of THMs (individual SDSTHM ratios ranged from 0.02 to 0.13). Among the total SDSTHM’s, which ranged from 15 to 16 µg/L, no chloroform was detected in the permeate (minimum reporting level = 0.5 µg/L) and only 8 µg/L of bromoform were produced after chlorination. The data suggest that if enough TOC is removed by the membrane, the absolute concentrations of DBPs will be limited, regardless of conditions such as high bromide levels.

Summary
As a result of the anticipated regulations on DBPs, but also because of other NOM-related concerns, interest in NOM removal is increasing dramatically among water treatment professionals in the United States. Many utilities are starting to measure the concentration of TOC in their raw and finished waters, to conduct jar tests to determine the extent to which they can increase TOC removal, and to explore other treatment options. Promulgation of the D/DBP Rule and the Information Collection Rule will substantially increase these efforts.

The three predominant precursor removal options for meeting the requirements of the proposed D/DBP Rule are those discussed here—coagulation, GAC adsorption, and membrane filtration (nanofiltration). Table 6 gives a qualitative summary of the three treatment options in terms of the efficiency of each process in removing NOM, the complexity of the process in relation to operation and maintenance, and total annualized cost of the technology. Coagulation is the least costly option. Many utilities hope to comply with the new regulations by using exist-
ing facilities and enhancing the coagulation process. In light of the uncertainty of the Stage 2 D/DBP regulations, modifying existing facilities and avoiding the construction of new facilities is attractive to utilities that hesitate to make large capital investments at this time. For some waters, however, enhanced coagulation may not be sufficient for adequate NOM removal to meet the regulations. In such cases, other options will need to be investigated. Planning and constructing GAC and membrane facilities take considerable time, so many utilities are beginning to evaluate these options in preparation for Stage 2 requirements.

GAC adsorption can remove high levels of NOM, but the associated costs are greater than using an enhanced coagulation process. A key to effective use of GAC is process optimization, which relies on developing a better knowledge about the specific NOM and GAC characteristics responsible for effective removal. Pretreatment techniques to reduce or modify NOM improve the cost-effectiveness of GAC for NOM removal. The ability of GAC to provide reductions in a wide spectrum of naturally occurring and synthetic organic substances places GAC among the technologies that deserve major research efforts for optimization.

Membrane filtration has the potential to achieve the highest removal of NOM and DBP precursors. The costs of the process have been higher than those of coagulation and GAC adsorption; however, the rate of decrease in costs over the past five years has been greater than those associated with other treatments. Because the process is not extremely complex in terms of operation and maintenance, it is a particularly attractive alternative for small systems. To date, membrane filtration for NOM removal has been limited to groundwaters because of the high pretreatment requirements for its use with surface water. Consequently, much research is focused on a greater understanding of the membrane fouling potential of surface water constituents and better pretreatment techniques. One of the most promising innovations for waters without existing treatment or plants requiring increased capacity is a total membrane system that involves the use of microfiltration or ultrafiltration as a pretreatment for nanofiltration.

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