



Making humic substances more biodegradable
by Judel Ann Buls

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Environmental Engineering - Civil
Montana State University
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Abstract:

Humic substances are complex, large molecules, which vary from water source to water source, and are related to a wide variety of water quality problems. They are related to a health risk because they react with chlorine to form chlorinated hydrocarbons, which are considered to be carcinogenic. Additionally, they can be available as a food source for microorganisms, which can lead to the development of biofilm on surfaces, causing a problem called biofouling. Therefore, researchers have attempted to eliminate humic substances using several different methods. One method involves removing the biodegradable fraction through a biofilter, which limits the use of the humic material by microbes downstream. Increasing the biodegradable fraction of humic material through the use of a pre-oxidant can optimize this process, which will allow for higher removal rates, thus decreasing the overall fraction of organic matter that may be available for use at some point in a treatment train.

In this study, four pre-oxidants were studied for their ability to increase the biodegradable fraction of humic substances, which include ozone, chlorine, monochloramine, and UV-light. These oxidants were applied to a humic solution with a 4 ppm TOC concentration, and the treated solution was fractionated based on molecular weight, hydrophobic character, biodegradability, and aromatic character. The results found that ozone was the most effective oxidant, although chlorine and UV-light also showed some ability to make humic substances more biodegradable. Ozone, however, was the only oxidant capable of increasing biodegradability at practical doses commonly used in water treatment facilities. Monochloramine did not show any increases in biodegradability making this oxidant the most stable oxidant used in the study, and useful for purposes where increasing the biodegradability of a humic substance can be detrimental to treatment goals.

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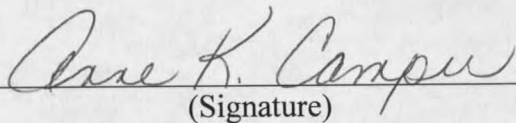
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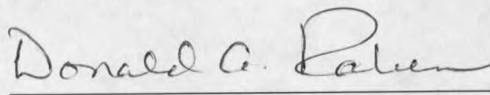
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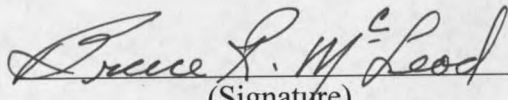
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ABSTRACT

Humic substances are complex, large molecules, which vary from water source to water source, and are related to a wide variety of water quality problems. They are related to a health risk because they react with chlorine to form chlorinated hydrocarbons, which are considered to be carcinogenic. Additionally, they can be available as a food source for microorganisms, which can lead to the development of biofilm on surfaces, causing a problem called biofouling. Therefore, researchers have attempted to eliminate humic substances using several different methods. One method involves removing the biodegradable fraction through a biofilter, which limits the use of the humic material by microbes downstream. Increasing the biodegradable fraction of humic material through the use of a pre-oxidant can optimize this process, which will allow for higher removal rates, thus decreasing the overall fraction of organic matter that may be available for use at some point in a treatment train.

In this study, four pre-oxidants were studied for their ability to increase the biodegradable fraction of humic substances, which include ozone, chlorine, monochloramine, and UV-light. These oxidants were applied to a humic solution with a 4 ppm TOC concentration, and the treated solution was fractionated based on molecular weight, hydrophobic character, biodegradability, and aromatic character. The results found that ozone was the most effective oxidant, although chlorine and UV-light also showed some ability to make humic substances more biodegradable. Ozone, however, was the only oxidant capable of increasing biodegradability at practical doses commonly used in water treatment facilities. Monochloramine did not show any increases in biodegradability making this oxidant the most stable oxidant used in the study, and useful for purposes where increasing the biodegradability of a humic substance can be detrimental to treatment goals.

CHAPTER 1

Introduction

As water treatment processes for supplying drinking water or providing ultrapure water for industrial purposes become better understood, the role that natural organic matter (NOM) plays in these processes has become increasingly important. For example, NOM has the potential to transport pollutants, such as metals, in natural water supplies (MacCarthy and Suffet, 1989). In drinking water treatment, NOM has been linked to several problems including foul taste and odor, displeasing color, increases in chemical disinfectant demand, increased organism counts, and the formation of chlorinated disinfection by-products (DBPs) (Amy, et al., 1987).

DBP formation is a public health risk since DBPs are considered to be carcinogenic (or cancer causing). Therefore, the EPA has recently adopted new regulations concerning their concentrations. The D/DBP Rule imposes stricter disinfection requirements, and also sets limits regulating the allowable concentration of DBPs released into a distribution system. As a result of this new rule, many municipal water treatment facilities are now out of compliance, increasing the need for alternative water treatment processes for NOM removal prior to the disinfection step.

In both drinking water and in industrial settings, another interest in NOM removal has evolved because NOM is the major food source for microorganisms. These organisms are usually found in the form of a biofilm on surfaces such as reverse osmosis (RO) membranes, pipes walls, and in holding tanks. If the purpose of water treatment is to produce ultrapure water, microbial growth on system elements can cause

contamination problems. Additionally, biofouling, or the buildup of biofilms on surfaces such as RO membranes, can occur. This raises pressure requirements making these units more costly to operate, and ultimately makes replacement necessary (Whittaker, 1984).

In response to these problems, researchers have begun to investigate NOM, its chemical makeup, characteristics that make it difficult to remove, and removal methods that are inexpensive, easy to implement, and effective. Identifying specific fractions of NOM has proven to be quite useful in understanding how and why it may or may not be easily removed. A major fraction of NOM is humic material, which is the constituent most commonly associated with the problems generated by NOM (Beckett, 1990). Researchers studying the removal of humic substances have considered a variety of methods such as enhanced coagulation, membrane processes, adding additional treatment steps, and biological removal (Pontius, 1990; Crozes, 1995; LeChevallier, et al., 1992; Wang, et al., 1995; Bouwer and Crowe, 1988). Biological methods have become quite promising since they are often less expensive, less chemically intensive, and more easily implemented than other methods. Biological treatment research has also recently shown that humic substances can be manipulated, through the use of ozone, to become more biodegradable (Owen, et al., 1993; Cipparone, 1997; LeChevallier, 1992; Goel et al., 1995; Langlais, 1991; Gilbert, 1987; Kruithof, et al., 1989). Ozonation increases the amount of NOM removed by biological treatment, making it an even more attractive technology.

Methods of oxidation other than ozonation are currently being used widely in water treatment. These include, but are not limited to, chlorine, monochloramine, and UV-light. Each of these methods can be a cheaper alternative to ozone, and may be

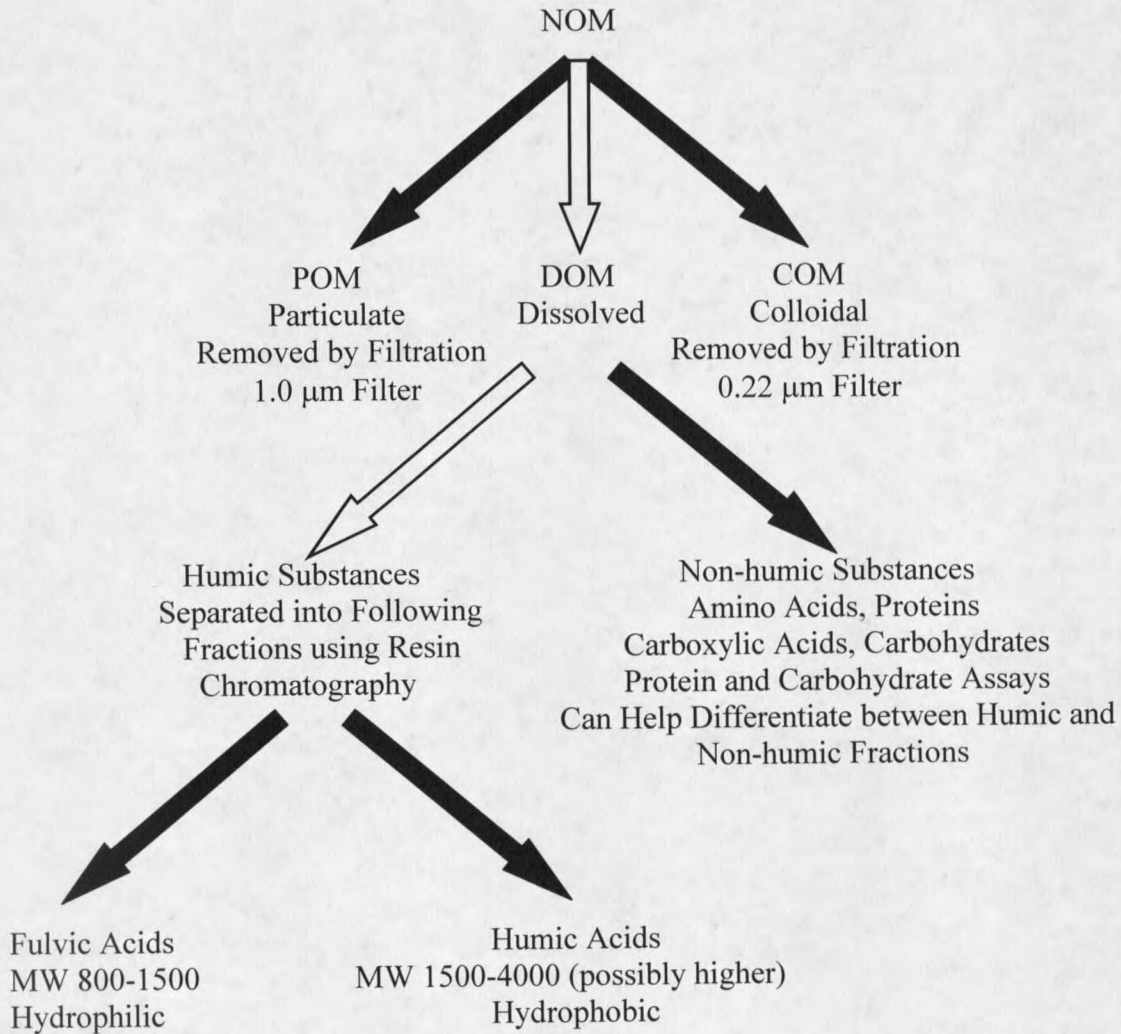
easier to implement. Additionally, most water treatment plant operators are more familiar with one or more of these alternatives, decreasing training requirements. However, limited research has been done regarding their ability to oxidize NOM. In this study, a comparison of oxidizing potential for increasing the biodegradability of NOM was drawn between ozone, chlorine, monochloramine, and UV-light. Ultimately, the most effective oxidant will be used in combination with a biofilter to optimize the process of biofiltration for TOC removal.

Humic Substances

Natural organic matter (NOM) is comprised of all organic material present in a natural water source, and is often the cause of color, taste, and odor properties. It appears to be derived mostly from decaying plant and animal matter; however, other sources such as human pollution may contribute (Bouwer and Crowe, 1988; MacCarthy, 1989). NOM can be dissolved (DOM), colloidal (COM), or particulate (POM) in nature. The particulate and colloidal fractions are seldom a problem in water treatment since removal is often easy to achieve through coagulation/flocculation/sedimentation/filtration (Owen et al., 1993, and 1995). NOM is so diverse in composition that it is defined based mostly on separation techniques used within a laboratory. Figure 1, developed in part by Owen et al. (1995), demonstrates the various major fractions of NOM, as well as the laboratory techniques for isolating these fractions. The white arrows represent fractions that can be further separated into other categories, while the black arrows represent fractions that may or may not be further separated depending on the direction of a study, or the detail required.

Since COM and POM can be removed by filtration, removal studies most often focus on DOM. DOM is commonly measured as dissolved organic carbon (DOC), ranging from low concentrations, of 0.1 mg/L (Pettersson, 1994) in aged groundwater sources, to as high as 50 mg/L in surface water sources affected by spring runoff events (Beckett, 1990). The majority of waters, however, fall between 2 and 10 mg/L DOC (Beckett, 1990; Pettersson, 1994; Owen et al., 1993).

Figure 1. Diagram of NOM Fractions



DOM is further characterized based on its humic fraction. This fraction is highly dependent on the water source, and can range from 40-90% of the total DOC. It is commonly estimated to be around 50% of the total DOC, with higher concentrations seen only in waters that are considerably colored. It can be separated from the total DOM concentration through a DAX-8 resin adsorption procedure (discussed in detail in Chapter 2). The remaining DOC is made up of amino acids, carboxylic acids, proteins, and carbohydrates (Amy, et al., 1987).

Humic substances can again be divided into three more fractions. Humin is considered the fraction that is not soluble at any pH, and is usually particulate in nature. Humic acids comprise the fraction that precipitates out of a water source at a pH below 2, and fulvic acids comprise the fraction that remains in solution at every pH (Beckett, 1990). Although the concentration of each fraction depends largely on the water source, it is often safe to assume that in highly colored waters, the dominant fraction is the humic acids, and in uncolored waters, the dominant fraction is the fulvic acids (Beckett, 1990).

Since humic substances contain several different functional groups such as carboxyls, phenols, hydroxyls, carbonyls, ethers, and esters, it is difficult, and most likely impossible, to establish a common molecular structure. Their molecular weight covers a wide range of sizes, differing both within and between water sources. Molecular weight ranges from 500 to 200,000 Da have been estimated (Thurman, 1985; Beckett, 1990). Other researchers have found that for fulvic acids, a common range is 800-1500 Da, and for humic acids, a reasonable range is from 1500-4000 Da (Beckett, et al., 1987; Beckett, 1989). Still others have found MW ranges through 30,000 Da and higher (Owen, et al., 1993). The methods used for this type of characterization, however, vary widely, and are

often quite expensive to do correctly. Additionally, it is a common belief that these fractions can change quite readily through water treatment processes where pH is often altered, oxidizing chemicals are added, and microorganisms degrade certain fractions. This only compounds the problem of accurately representing molecular weight fractions within a water source, let alone between water sources.

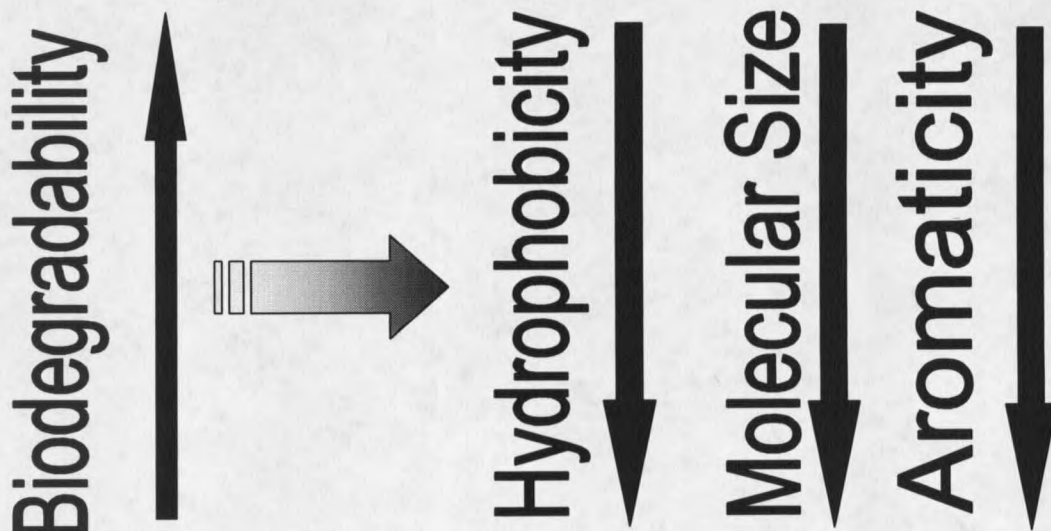
The conformational structure of humic substances has also been a subject of debate. Current beliefs are that humic substances are comprised of coiled, long-chained molecules, which may be cross-linked (Stevenson, 1994). These coils are most dense at high concentrations, low pH, and high ionic strength, and are much more flexible at neutral pH, low ionic strength, and low concentration. It has also been suggested that humic substances are comprised of low molecular weight molecules that are held together by hydrophobic forces, which are stronger at low pH and high ionic strength. This conformation is responsible for "apparently high-molecular weight" molecules (Conte and Piccolo, 1999).

Due to the above complexities of humic substances, researchers have undertaken considerable efforts to develop universal methods for measuring them. Currently, TOC measurements seem to be the general consensus, however, other researchers use the absorbance of UV-light at a wavelength of 254 nm as an alternative (Dobbs, et al., 1972). This method has one major advantage over TOC measurements because it only takes a few seconds to perform a measurement. However, its major drawback is that the only material absorbing UV-light at this wavelength is the aromatic fraction of a sample. This may or may not be related to the TOC of a sample because aromatic character is highly dependent on a water source (Owen, et al, 1993; Dobbs, et al., 1972). In fact, many water

sources do not exhibit a large aromatic character, unless it is highly colored, which is commonly caused by a very high fraction of organic matter derived from soil and plant debris, such as a swamp (Beckett, 1990). UV-254 can also be a valuable measurement when it is done in conjunction with TOC. The comparison of the two measurements provides knowledge of how aromaticity and organic carbon content are related (Dobbs, et al., 1972).

Although the characteristics of humic substances are far from being completely understood, the research that has been done regarding these characteristics has given researchers some insight into the relationship between them and the biodegradability of humic substances. Figure 2 shows general relationships between hydrophobicity, aromaticity, and molecular weight. Additionally, it is believed that tightly coiled, highly complex, large molecular weight humic material is the most difficult to break down (Owen et al., 1993; Conte and Piccolo, 1999).

Figure 2. Relationship between Biodegradability and Humic Properties



Owen, et al. (1993), used laboratory methods based on the characteristics shown in Figure 2, to develop a reliable protocol for analyzing the biodegradability of humic substances. The combination of protocols is necessary because simply measuring biodegradability has proven to be difficult.

Researchers (Servais, et al., 1989; Block, et al., 1992; Volk, et al., 1997, and 1993; Goel, et al., 1995) have attempted to develop standard methods for determining biodegradable dissolved organic carbon (BDOC). However, since these tests are largely dependent on the water source being studied, as well as the organisms doing the degradation, the water quality community has been hesitant to adopt a standard method (Gjessing, et al., 1999). This is largely due to the fact that the BDOC methods may be difficult to duplicate both between and within laboratories at confidence intervals reliable enough to be considered standard protocol.

At this time, most BDOC methods being employed involve sampling a water source, measuring the initial DOC, allowing the sample to incubate for a set period of time, and then measuring the remaining DOC. This process produces somewhere between 11-35% DOC reduction (Bouwer and Crowe, et al., 1988; Martin-Mousset, et al., 1997). This fraction, termed the BDOC, depends on the length of time the test is run, which varies from a few days to a month, or until a steady DOC concentration is reached. It also depends on the type of inoculation utilized. If a biomass support medium is used, it is important to note that different media exhibit different adsorption properties and biomass support capabilities. Therefore, researchers commonly develop BDOC protocol based on the following principles. Sand that has been inoculated with indigenous microorganisms should be used for the media. This media should preferably be low in

organic carbon content to limit contamination of a sample. The organisms should be capable of degrading similar concentrations and types of NOM. Additionally, initial tests should be done to establish the effluent DOC concentration over time. This will establish the amount of time that is necessary to meet a constant DOC concentration. Finally, all samples should be filtered to prevent biological contamination (Servais, et al., 1989; Block, et al., 1992; Volk, et al., 1997, and 1993; Goel, et al., 1995).

Since BDOC measurements are difficult to quantify, the ability to correlate an increase in biodegradability of humic substances to the humic properties discussed above, may provide supporting evidence that biodegradation of the NOM is occurring.

Methods for Removing Humic Substances

There are a variety of alternative water treatment options available to municipalities and industry. The best choice for each facility, however, is likely to be different and depends on several parameters. First, the level of removal that has to be met may require more than one method to be employed. Additionally, the space available at the facility for implementing new treatment steps should be considered. Other water quality parameters must be considered to ensure that they will not interfere with the treatment option chosen, and most importantly, the cost of implementation should be considered. Since there is a wide range of treatment trains used today, it is first necessary to analyze each process, and find an effective alternative that will fit the specific facility. If the facility in question is planned from scratch, with the primary treatment goal being the removal of humic substances, a combination of alternatives would be very advantageous, and conducive to process optimization. The following

discussion explores the advantages and disadvantages of the alternatives currently available.

Enhanced Coagulation

Enhanced coagulation is the addition of excess or alternative coagulants for the increased removal of DBP precursors (mostly NOM). This process can be a fast, cheap alternative for facilities already doing coagulation/flocculation. In order to implement this process effectively, simple jar tests investigating a range of pH values, a variety of coagulants, and a range of coagulant doses must be done. These tests can evaluate the most effective coagulation process for a specific water source, thus optimizing coagulation and flocculation for a given water (Pontius, 1990; Tambo, et al., 1989).

However, this alternative is not possible in all water treatment facilities. For example, facilities that operate by direct in-line filtration often skip flocculation and sedimentation steps, and may even limit coagulation processes. Additionally, facilities that are treating water for industrial purposes may not use coagulation at all, or may not want the chemicals in their water stream. Therefore, these facilities have very limited options regarding enhanced coagulation, and other alternatives will be better (Crozes, 1995).

Rapid Rate Filters

For treatment facilities that require additional removal beyond enhanced coagulation, or treatment facilities that operate with direct in-line filtration, an option might be to change the media used during the filtration step. Media such as granular activated carbon (GAC) may be more effective since it can adsorb a fraction of NOM.

This provides for both filtration of particulate matter, and adsorption of dissolved organic matter, thus reducing taste and odor problems as well as organic compound concentrations. However, some precautions must be taken when using GAC. Very high organic carbon waters can exhaust the GAC much faster than a sand/anthracite combination. This could be costly because the GAC would have to be replaced much more frequently. Therefore, it is important to note that GAC used in this manner requires substantial control measures for limiting biological activity, in order to enhance adsorption properties. Also, an additional pre-disinfection step may be necessary to control microbial growth within the filter, and/or increased disinfection may be required after filtration to combat sloughed organisms. Some facilities may have to be concerned about backwashing, as well, because GAC has a lower density than anthracite (Pontius, 1990).

Ion Exchange

Ion exchange has also been used for TOC removal; however, this process requires a macroporous resin specifically designed to attract polyvalent humate and fulvate anions. The resin can be expensive, is very weak since it consists of large molecules, and can be difficult to regenerate due to a strong attraction of the NOM for the aromatic resin matrix. Additionally, ion exchange may require space within the treatment facility that is not available.

Ion exchange has shown promise by significantly decreasing chlorine demand during the disinfection process. However, long-term operation can be a problem due to fouling and resin losses caused by the problems associated with regeneration.

Additionally, Fu and Symons (1988) measured the effectiveness of ion exchange on different molecular weight fractions of humic substances and found that limited adsorption was achieved in MW fractions below 5000 Da. Another problem is waste disposal of the regenerant, which may add to shipping and disposal requirements (Pontius, 1990).

Membrane Processes

Membrane processes have also been used for NOM removal, and are very effective for preventing downstream biofouling, and removing DBP precursors (Thorsen, 1999). There are many different membrane processes. One option is reverse osmosis, which is a pressure-driven process that removes virtually everything within a water sample. The membrane modules for this process are very expensive and sensitive, making this process less practical for the removal of NOM than other options since high molecular weights can cause fouling due to buildup on the membrane surface. Electrodialysis involves the transfer of ions through membranes via a direct electric current. This method is not commonly used for NOM removal since it is based on charged particles, and humic substances and other organic matter are usually weak in charge (Pontius, 1990).

A much more effective membrane process for NOM removal is ultrafiltration (UF). This is another pressure driven process, but is much more applicable for NOM removal since the membrane's molecular weight cutoff (MWC) ranges from 10,000 to 300,000 Da. This range is much larger than an RO membrane, and can be adjusted according to the purpose of treatment. Particulate and colloidal material,

microorganisms, and organic constituents larger than the MWC of the membrane are removed (Dietrich, 1995). This option may not always be the best one, however, since the membranes have additional pressure requirements within the plant, and must be replaced or cleaned routinely due to fouling. This fouling could be caused by scale, colloidal deposition, silt layer formation, metal oxide and silica buildup, and microbial buildup (biofouling) (Conlon, 1990; Thorsen, 1999). Additionally, the filtration apparatuses usually have considerable space requirements. Waste disposal of the concentrated water stream can be a concern as well.

However, as research in the area of UF continues, the process has become more and more economical, and process control has improved (Conlon, 1990; Thorsen, 1999). This method will likely become a very popular method for NOM removal in the future (Pontius, 1990), especially as research redirects itself to combine it with additional processes, such as upstream biological pretreatment. This combination has the potential to optimize membrane life, decrease additional power requirements, and improve the overall stability of water source (Conlon, 1990; Dietrich, 1995; Pontius, 1990; Thorsen, 1999).

Oxidation/Disinfection Alternatives

Several chemicals used in water treatment, commonly employed for disinfection purposes, can act as oxidizing chemicals, which can influence and possibly even cause the removal of NOM concentrations. If NOM removal to prevent downstream biofouling is the main objective of treatment, specific primary disinfection processes may be implemented, which usually involves the addition of a disinfection chemical prior to the

filtration step. If this method is used, the chemical can actually act much more like an oxidizer, as opposed to a disinfectant. As an oxidizer, the chemical can alter the makeup of NOM and make it more biodegradable for organisms in the filter. Additionally, primary disinfectants can be removed within the filter, along with their reaction byproducts to eliminate adverse effects later in the treatment process (Crozes, 1995; Pontius, 1990):

If preventing disinfection by-product formation is the goal, changing disinfectants can be effective. At this stage of treatment, NOM removal is probably not happening, and oxidation is not advisable. It is more productive to maintain the stability of the NOM by apply a disinfectant chemical that does not react with humic substances. Chloramines, most commonly monochloramine, offer a great advantage over chlorine, since they do not react with humic substances as readily, virtually eliminating the formation of DBPs, and maintaining a residual much longer. However, it is not as effective a disinfectant as chlorine, and contact times, for specific disinfection criteria are impossible to meet (Crozes, 1995; Pontius, 1990).

Ozonation is another alternative, and can be quite effective since ozone is capable of providing fast and efficient kills, while considerably decreasing the DBP formation in most waters. However, in highly brominated waters, hypobromous acid formation may actually compromise ozone's effectiveness. Additionally, cost and space requirements may make ozonation an unfeasible option (Crozes, 1995).

Although there are other disinfection chemicals available, the ones mentioned above are most applicable for the majority of water treatment facilities with regards to potential NOM removal or chemical modification. Each of the disinfection alternatives

will decrease the concentration of chlorine required for post filtration disinfection, thus decreasing the formation of DBPs. However, chlorine continues to be the most widely used disinfection chemical. Although changing disinfection chemicals may be cheap and easy to implement, optimizing preceding steps within the treatment process for the removal of DBP precursors prior to disinfection (such as doing enhanced coagulation) is a much more attractive option. It will allow for much better process control and performance because it not only removes known DBP precursors, but can also remove unknown precursors. This is a big advantage because little is known about DBPs formed during chlorination, and even less is known about potential DBPs formed during other disinfection processes such as ozonation (Crozes, 1995, Pontius, 1990). Therefore, if oxidation/disinfection processes are to be implemented, primary disinfection processes, as discussed above, likely provide the most effective option for oxidant application to enhance NOM removal because the formation of DBPs is limited.

Biofiltration

The final method for discussion, and the method being studied in this project is biofiltration. This process involves the use of a biofilter, which is comprised of a porous medium that has become colonized with a biofilm. Sand is commonly employed as the medium, and more recently, biologically activated carbon (BAC), or GAC that has become biologically spent during the filtration step of water treatment, has been used. The media are continuously colonized with organisms that are indigenous to the treated water supply. These organisms will then biodegrade a fraction of the NOM, thus

lowering the total concentration available to react with disinfectants during the final or secondary disinfection process.

Biofiltration has significant advantages over the treatment methods discussed above. First, it is more desirable than disinfection alternatives because instead of simply avoiding the formation of disinfection by-products, biofiltration provides removal of NOM, therefore making it applicable for both biofouling prevention and DBP precursor removal. The advantage over membrane processes and ion-exchange is that biofiltration is usually cheaper to implement, does not require as much maintenance, and does not produce a waste stream that must be disposed of. In many cases, implementing biofiltration does not even require replacement of media due to the low carbon concentrations being treated in water treatment facilities thus minimizing operating and maintenance costs. In water treatment facilities that do not practice coagulation, or that do minimal coagulation, biofiltration is often much easier, and cheaper to implement than an advanced coagulation process due to space requirements for coag/floc/sed chambers. Overall, biofilters are relatively inexpensive, do not require much space for operation (depths of less than 1 meter are usually sufficient), require minimal chemical use, and are simple to operate (Bouwer and Crowe, 1988).

BAC is currently considered to be one of the best media for biofiltration. This is because BAC has a larger surface area and better surface texture than most other media, therefore having the potential to hold a greater amount of biomass. Many researchers have shown that during similar empty bed contact times (EBCT), BAC filters performed better for NOM removal than sand or sand-anthracite dual-media filters (Wang, 1995).

Additionally, LeChevallier, et al (1988), showed that as EBCT in BAC filters increased from 5 to 20 minutes, TOC removal increased from 29.0% to 51.2%.

Another medium that has gained positive recognition is iron-oxide coated sand. The basis for the development of this medium stems from relationships between cast iron pipe used in distribution systems, and natural organic matter. This relationship provides a favorable environment for biofilm growth, therefore increasing microbial activity within a distribution system. Several findings in research, including the following, provide evidence for this fact.

A survey conducted by LeChevallier et al., in 1996, suggested that distribution systems with over 1000 miles of unlined cast iron pipe had coliform levels three times greater than systems with less than 200 miles of unlined cast iron pipe. Additionally, long-term studies on bacterial growth vs. substratum material showed that exposed iron sustained more growth than cement, glass, and other materials (Delanoue et al., 1997). Another study conducted by Martin, et al., 1982, and further substantiated by LeChevallier, et al., in 1990, provides indirect evidence that using corrosion inhibitors, for reducing corrosion of iron pipes in a distribution system can provide for reduction or control of bacterial regrowth.

This research has culminated in the belief that corrosion events in iron pipes (providing for the formation of iron-oxides) are related to biological regrowth problems. The exact phenomenon responsible for this relationship has been questioned. Initially, researchers attributed it to the chlorine demand of iron and its corrosion products, believing that this lowered the chlorine residual within a distribution system allowing for less disinfectant efficiency (LeChevallier et al., 1990, 1993; Chen et al., 1993). However,

later research has shown that in a system where corrosion control was employed, and chlorine residuals were maintained at a consistent concentration, iron pipe surfaces allowed for faster biofilm development, as well as a more diverse population than PVC (Camper, 1997; LeChevallier, 1997). Therefore, another mechanism may be responsible. This mechanism, in fact, is related to corrosion products of iron, which provide significant surface area for colonization by bacteria, provide protection for cells from mechanical detachment (scrubbing), provide some disinfectant neutralization, and collect nutrients on the surface utilizable by biofilms (Qi, 1999).

Further studies of the relationship between iron-oxide and NOM have shown that iron-oxide coated materials have increased adsorptive capabilities regarding humic substances (Qi, 1999; Chang, 1992; Benjamin, et al., 1997). This adsorptive capability makes iron-oxide coated materials ideal as biofilter media because improved adsorption allows for increased exposure for biofilms to biodegradable NOM. This can then provide for an increase in biomass, therefore improving biofilter performance.

Since biomass accumulation is directly related to filter effectiveness, other pretreatment steps can have a large effect on the efficiency of a biofilter. Research suggests that substrate loading rate effects biomass accumulation significantly (Wang, 1995). Therefore, any pretreatment process that alters the loading rate to a biofilter can affect the biofilter performance. Even more importantly, any pretreatment process that alters the fraction of biodegradable substrate can significantly impact biofilter performance. One optional pretreatment method that has been shown to improve biofilter performance is the application of a preoxidant (LeChevallier, et. al., 1992). Initially, preoxidation of a water source was done to provide increased disinfection, for the control

