

**COLLOID FORMATION  
FOR THE REMOVAL OF NATURAL ORGANIC MATTER  
DURING IRON SULFATE COAGULATION**

by

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**(ABSTRACT)**

Removal of organic matter is increasingly important to drinking water utilities and consumers. Organic matter is a significant precursor in the formation of disinfection by-products (DBPs). The maximum contaminant levels for (DBPs) are decreasing and more DBPs are believed carcinogenic. Traditional coagulation focuses on the removal of particulate matter and in the last decade soluble species have also been targeted with high coagulant doses. However, colloidal matter is smaller than particulate matter and therefore not easily removed by conventional drinking water treatment. This research focused on the conversion of soluble organic matter to colloids using relatively low doses of ferric sulfate coagulant and the subsequent removal of the colloids by filtration during drinking water treatment. The goal is to achieve enhanced removal of soluble organic matter with minimal chemical costs and residual formation.

This study investigated the effects of pH, iron coagulant dose, turbidity, organic matter concentration, and temperature on colloid formation. Characterization of the colloidal organic matter was attempted using zeta potential and sizing analyses. Cationic low molecular weight, nonionic high molecular weight, and cationic medium molecular weight polymers were evaluated on their removal of colloidal organic matter.

Colloidal organic matter formation was affected by changes in coagulation pH, coagulant dose, and organic matter concentration, whereas turbidity and temperature did not significantly impact colloid formation. Decreased coagulation pH caused increased organic carbon removal. As coagulant dose was increased, colloid formation initially increased to maximum and subsequently rapidly decreased. Colloid formation was increased as the organic matter concentration increased. Due to low sample signal, the colloids could not be characterized using zeta potential and sizing analyses. In addition, polymers were ineffective for aggregating colloidal organic matter when used as flocculant aids.

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## Chapter I

### INTRODUCTION

Natural organic matter (NOM) is considered problematic in drinking water treatment because it is a significant precursor in the formation of disinfection by-products (DBPs). The significance of NOM in DBP formation has been studied since 1974. Furthermore, in 1998 the U.S. Environmental Protection Agency (EPA) promulgated the Disinfectants/Disinfection By-products Rule, which regulated the concentrations of two prominent DBPs, trihalomethanes and haloacetic acids, in drinking waters.

Coagulation is an easily amenable strategy for NOM removal that would lead to DBP reduction in drinking water treatment. Conventional coagulation focuses on forming particulate sized organic matter that is easily removed during sedimentation and filtration. Under certain coagulation conditions, colloidal sized organic matter is also formed. However during conventional treatment, colloidal matter is challenging to remove due to its small size, high stability, and slow settling rates.

The utilization of polymers during water treatment could increase colloidal organic matter removal. Polymers can be used as primary coagulants or as coagulant aids or flocculants. The use of polymers for enhanced organic matter removal reduces DBP formation and decreases coagulant dosage, thereby reducing carcinogenic chemical concentrations, reducing residual metal concentrations, and lessening treatment chemical costs.

The water treatment conditions that produce colloidal organic matter are not well defined. Further study of drinking water coagulation has been suggested to determine the water quality parameters and coagulation conditions that result in colloidal organic matter formation (Knocke et al. 1994; Tadanier et al. 1997). Various chemical and physical parameters can potentially influence formation of colloidal organic matter during drinking water treatment. This study investigated the effects of pH, coagulant dose, initial turbidity, organic matter concentration, and temperature on colloid formation during coagulation of drinking water with ferric sulfate, and evaluated the effect of selected polymers on subsequent removal of colloidal organic matter.

## **Chapter II**

### **LITERATURE REVIEW**

Natural organic matter (NOM) is considered problematic in drinking water treatment because it provides the precursor material that reacts with halogenated disinfectants to form disinfection by-products (DBPs), including haloacetic acids (HAAs) and trihalomethanes (THMs) (Singer 1994; Singer 1999; States et al. 2002). Coagulation of colloidal organic matter is a practical strategy for NOM reduction in drinking water treatment. The advantages of coagulation amendments to remove DBP precursors include little or no required capital investment, minimal increase in unit operating costs, and use of well-known technology (Kavanaugh 1978).

#### **Disinfection By-Products**

In 1974, it was reported that THMs were formed from the reaction of chlorine with NOM in drinking water treatment systems (Rook 1974). The U.S. EPA conducted the National Organics Reconnaissance Survey in 1975 and found that chloroform was ubiquitous in chlorinated drinking waters, thereby linking chloroform formation to water chlorination (Rook 1974; Symons et al. 1975). Also from the National Organics Reconnaissance Survey, THM concentrations in treated water were shown to be related to total organic carbon (TOC) concentration in untreated drinking water (Stevens et al. 1976; Babcock et al. 1979). At neutral pH values, approximately 50 to 100  $\mu\text{g}$  THM was formed per mg TOC and 50 to 100  $\mu\text{g}$  HAA was formed per mg TOC (Edzwald 1994). Organic carbon in natural waters is due to the presence of NOM which is a heterogeneous mixture of plant and animal materials (Krasner et al. 1995; Vickers et al. 1995). NOM is measured indirectly based on the amount of carbon through TOC analysis (Vickers et al. 1995). Using TOC analysis, DBP formation is therefore directly proportional to NOM concentration (Singer 1994; Singer 1999; Marhaba et al. 2000). NOM is considered the most significant organic precursor with which halogenated disinfectants react to form DBPs (Singer 1994; States et al. 2002).

In 1976, the National Cancer Institute identified chloroform as a carcinogen (NTIS 1976); people who drank chlorinated water appeared to contract cancers of the urinary and digestive tracts slightly more than people who drank non-chlorinated water

(Singer 1994; Singer 1999). This finding led to the regulation of THMs by the EPA (U.S. 1979).

In 1998, the Disinfectants/Disinfection By-products (D/DBP) Rule set the THM maximum contaminant level (MCL) to 0.080 mg/L and the HAA MCL to 0.060 mg/L (U.S. 1998). Because NOM is a DBP precursor and NOM is measured using TOC, TOC removal was the best conservative surrogate for determining DBP reduction (Bell-Ajy et al. 2000). Under the D/DBP Rule, drinking water utilities are required to remove TOC based on untreated water TOC concentration and alkalinity (Bell-Ajy et al. 2000). Utilities do not have to further remove TOC if the untreated water TOC concentration is less than or equal to 2 mg/L. Higher TOC removal percentages are required for untreated waters with increased TOC and decreased alkalinity (Table 1) (Edzwald 1994).

Enhanced coagulation is employed to achieve the percent TOC removal regulated by the D/DBP rule. Before the D/DBP rule, traditional coagulation methods focused on turbidity removal. Under the D/DBP rule, enhanced coagulation focuses on TOC removal thereby removing NOM and decreasing DBPs (Vickers et al. 1995; Edzwald et al. 1999). Enhanced coagulation involves altering the coagulant type, coagulant dose, and coagulation pH to achieve improved TOC removal (Krasner et al. 1995; Edwards 1997; Tadanier et al. 1997; Edzwald et al. 1998; Ruehl 1999). Typically, the coagulant dose is increased to increase organic matter removal. One obstacle with changing from traditional coagulation to enhanced coagulation was that the optimum conditions for turbidity removal are not always the same as the optimum conditions for organic matter removal. For instance, effective organic matter removal typically occurs at lower pH conditions than those optimum for turbidity removal (Kavanaugh 1978; Gianatasio et al. 1995; Dennett et al. 1996). The optimum pH range for turbidity removal is 6.0 to 6.5, whereas the optimal operating pH range for organic matter removal is 5.3 to 5.7 (Licskó 1993). However, it has been found that effective organic matter removal always coincides with sufficient turbidity removal (Semmens et al. 1980).

Enhanced coagulation can increase DOC removal by 32% over conventional treatment (Volk et al. 2000). Using ferric sulfate, enhanced coagulation has been shown to significantly increase THM precursor removal (Gianatasio et al. 1995). Ferric sulfate is an ideal coagulant for enhanced coagulation. This coagulant has demonstrated

Table 1

D/DBP Rule: Step 1 Enhanced coagulation TOC percent removal requirements

Raw Water TOC (mg/L)	Raw Water Alkalinity (mg/L CaCO <sub>3</sub> )		
	< 60	60-120	> 120
≤ 2	no removal required		
2 – 4	35	25	10
4 - 8	45	35	25
> 8	50	40	30

(Krasner et al. 1995)

excellent operational versatility with respect to effective coagulation over a wide pH range and a wide coagulant dose range (Gianatasio et al. 1995). Enhanced coagulation is an economically feasible means of controlling DBP formation without requiring significant capital investments because it amends existing coagulation technology (Crozes et al. 1995).

An advanced strategy over enhanced coagulation for organic matter removal is optimized coagulation. Optimized coagulation is first optimizing the pH before optimizing the coagulant dosage for optimal organic matter removal. Optimized coagulation can avoid increased coagulant dosage. Once optimal pH was achieved, the coagulant dosage was similar to that for turbidity removal (Bell-Ajy et al. 2000). Optimum coagulation is defined as coagulation pH and coagulant dosage that achieve maximum TOC removal, DBP precursor removal, and pathogen removal and minimum residual turbidity and residual coagulant metal and minimum operating costs (Edzwald et al. 1998; Edzwald et al. 1999). The method of optimized coagulation was utilized in this thesis study.

If a water utility cannot meet its Step 1 TOC removal percentage requirement (Table 1), then Step 2 of the D/DBP Rule is enforced. To achieve Step 2 TOC removal requirements, the point of diminishing returns (PODR) is calculated. The PODR is the required coagulant dose where for a certain increase in coagulant dose yields a specified decrease in TOC. For a water utility using ferric sulfate, the PODR is achieved when an increase by 7.8 mg/L ferric sulfate yields a decrease of less 0.3 mg/L TOC (Krasner et al. 1995; White et al. 1997; Edzwald et al. 1998; States et al. 2002). It is important to note that D/DBP rule Step 1 is based on untreated water TOC and Step 2 is determined by treated water TOC (White et al. 1997).

### **Colloidal Organic Matter**

Colloidal matter is challenging to remove using conventional drinking water treatment. Colloidal matter has very small settling velocities in water of only a few meters per year and high stability in water due to small size, large surface area, and relatively high electric charge (Liciskó 1997). Because of their high stability and slow settling rates, colloidal matter can pass through a water-treatment system and must be

coagulated or otherwise entrained to be removed by sedimentation or filtration (Chowdhury et al. 1991).

A universally accepted size for colloidal organic matter does not exist; colloidal size is operationally defined within each study. In general, matter that is smaller than 1  $\mu\text{m}$  in diameter is considered colloidal. The size of colloidal organic matter formed during chemical coagulation has been defined in previous studies: 5  $\mu\text{m}$  to 0.1  $\mu\text{m}$  (Chowdhury et al. 1991), 4  $\mu\text{m}$  to 0.004  $\mu\text{m}$  (Millipore 1996), 1  $\mu\text{m}$  to 100 KDa (Tadanier et al. 1997), 0.7  $\mu\text{m}$  to 100,000 amu (100 KDa) (Bose et al. 1998), and 0.2  $\mu\text{m}$  to 100 KDa (Knocke et al. 1994). Colloidal organic matter has been documented and examined in additional studies (Tadanier et al.; Stumm et al. 1962; Perdue 1976; Beckett et al. 1990; Knocke et al. 1994; Licskó 1997; Tadanier et al. 1997).

Typically, the upper boundary of colloidal size is defined using glass fiber vacuum filtration and the lower boundary is defined using ultrafiltration. While the size associated with glass fiber filters is considered an absolute size, the size defined by ultrafiltration is considered a nominal molecular weight limit (Collins et al. 1986). The molecular weight of an ultrafiltration membrane is 80 to 95% of the pore size distribution. Therefore, ultrafiltration membranes retain molecules of different sizes at different percentages. The manufacturers of the ultrafiltration membranes used in this study defined the nominal molecular weight limit of 30,000 amu (30 KDa) as equivalent to 40Å or 0.004 $\mu\text{m}$  (Millipore 1996).

In addition, glass fiber filtration is a physical separation method, whereas membrane ultrafiltration is a physical and chemical permeation method. With ultrafiltration, molecule retention depends on the Stokes radius and shape of the molecule, the amount of polarization during ultrafiltration, the pH, ionic strength, and composition of the solution, and the amount of fouling or rejection during ultrafiltration (Millipore 1996). Membrane properties including molecular weight limit, hydrophobicity, and surface or pore charge also affect membrane interaction with molecules. Rejection or fouling of NOM with ultrafiltration membranes can occur due to steric exclusion (rejection), electrostatic exclusion (rejection), and adsorption (fouling). (Amy et al. 1999). Physical fouling occurs when molecule transport from the membrane surface by Brownian diffusion, shear-induced diffusion, and later migration is less than

the advective transport of molecules up to membrane surface. Fouling due to adsorption and pore blockage is increased as molecular size approaches the effective membrane pore size (Wiesner et al. 1990).

### **Removal of Natural Organic Matter by Coagulation**

One of the primary objectives of water treatment is the removal of organic matter because it is precursory to DBP formation (Polasek et al. 2002). Traditionally, coagulation is the formation of particulate matter so that it is removed by sedimentation and/or filtration. Particulate matter formation during coagulation is accomplished through the precipitation of dissolved matter and the destabilization of colloidal matter (Hannah et al. 1967; Edzwald 1993; Edzwald 1994).

The effectiveness of coagulation is affected by process variables and by untreated water quality conditions. These physical and chemical parameters include coagulant type and dosage, coagulation pH, NOM type and concentration, turbidity, alkalinity, hardness, and temperature (Kavanaugh 1978; Chadik et al. 1983; Sinsabaugh et al. 1986; Chowdhury et al. 1991; Dennett et al. 1996; Amy et al. 1999; O'Melia et al. 1999).

In general metal-salt coagulants are effective for NOM removal and therefore reduce DBP formation (Kavanaugh 1978; Babcock et al. 1979; Semmens et al. 1980). Iron salts typically result in greater DOC removal over aluminum salts because iron salts function better at decreased pH where more DOC is removed (Volk et al. 2000). DOC removal with ferric sulfate (72%) was consistently better than with alum (59%) (Gianatasio et al. 1995). Organic carbon removal is also affected by coagulant dose. With increased coagulant dosage, TOC and DBP concentrations were decreased. THM reductions with ferric chloride ranged from 33 to 77 percent using up to 20 mg/L iron. Also, coagulation with ferric salts is a practical method of DBP reduction that does not sacrifice turbidity removal (Chadik et al. 1983).

The effective coagulant dose for DOC removal strongly depends on pH; at lower pH values, less coagulant is required for DOC removal (Edzwald 1994). Coagulant dose and coagulation pH are considered the most important conditions for organic matter removal (Semmens et al. 1980). Ferric sulfate coagulation was sensitive to pH changes (Knocke et al. 1986). Chemically, the influence of pH is a balance between the competition of hydrogen ions and metal hydrolysis products for organic ligands and

between hydroxyl ions and organic anions for metal hydrolysis products (Randtke 1988). The optimum coagulation pH is defined as “the pH condition with the minimum coagulant requirement to convert dissolved organic matter into particulate organic matter.” The optimum coagulation pH range for ferric coagulants is considered pH 3 to pH 5 (Edzwald 1994) (Kavanaugh 1978) (Volk et al. 2000) and the operating coagulation pH is recommended pH 5.5 to 6 (Edzwald 1994; Volk et al. 2000). Each water utility must consider the practical combination of coagulant type, coagulant dosage, and coagulation pH for organic matter removal (Bell-Ajy et al. 2000).

Coagulant dose is also related to the concentration and type of NOM present in untreated water. An effective coagulant dose is proportional to the DOM concentration with increased DOM requiring increased coagulant dose for effective coagulation (Kavanaugh 1978; Semmens et al. 1980; Dennett et al. 1996). Also increased TOC removal is found with samples with moderate to high DOC concentrations (Volk et al. 2000). This occurs because coagulation efficiency increases as the number of molecules, or concentration, increases. A stoichiometric relationship exists between required coagulant dosage and TOC concentration.

The concentration of NOM controls coagulant dose demand due to the high negative charge density of NOM (Semmens et al. 1980; Edwards 1997; Carlson et al. 2000). NOM is negatively charged at neutral pH values due to carboxyl (-COOH) and phenolic (ar-OH) functional groups (Polasek et al. 2002) and depending on pH, NOM has a charge density of 5 to 15  $\mu\text{eq}/\text{mg}$  (Edzwald 1993; Edzwald 1994). Even in waters with low TOC values, the negative charge associated with NOM is much greater than the negative charge associated with turbidity. Water with 3 mg/L DOC has a negative charge of 15 to 22.5  $\mu\text{eq}/\text{L}$ , whereas the same water with 10 mg/L clay only has a negative charge of approximately 5  $\mu\text{eq}/\text{L}$ . In other words, a turbidity of 10 NTU or 20 mg/L clay has a similar coagulant demand as approximately 1 mg of DOC (Edzwald 1999). Therefore NOM, not turbidity, typically controls the coagulant demand required to neutralize the negative charge of most waters (Edzwald 1993; Edzwald 1994; Edzwald et al. 1999). This is supported in that optimum organics removal requires higher coagulant doses than optimum turbidity removal (Semmens et al. 1980). In addition,

turbidity does not significantly effect coagulation effectiveness in the presence of NOM (Randtke 1988).

The type of NOM also affects coagulation. NOM type determines how amenable the NOM is to coagulation and determines the NOM potential for DBP formation. Coagulation preferentially removes more hydrophobic, higher molecular weight, and more aromatic NOM (Collins et al. 1986; Edzwald 1993; Edzwald 1994; Krasner et al. 1995; White et al. 1997; Bose et al. 1998). DBP formation is most affected by the aromatic carbon content of NOM. NOM with high levels of aromatic carbon cause greater levels of DBPs (Singer 1999). Ultraviolet light absorbance is a surrogate measure for aromatic carbon (Chadik et al. 1983; Singer 1999). The specific ultraviolet absorbance (SUVA) is the UV absorbance per meter per mg/L of TOC (Edzwald 1993). Higher aromatic content gives higher SUVA values and causes greater levels of DBPs (Singer 1999). The SUVA for Suwannee River NOM was measured at 3.8, which implies that this NOM is composed mostly of hydrophobic, aromatic, and higher molecular weight organic matter with a high negative charge density (Edzwald 1993; Edzwald 1994; Edwards 1997; Carlson et al. 2000). Therefore, Suwannee River NOM has increased DBP formation potential and is amenable to coagulation with ferric sulfate.

Solution chemistry parameters such as alkalinity, hardness, and ionic strength can also influence coagulation. Alkalinity buffers against the acidic effect of metal-salt coagulants (Stumm et al. 1962) and determines the amount of acid or base necessary to adjust the pH (Randtke 1988). The main components are carbonate, bicarbonate, and hydroxide. Alkalinity is added during coagulation in the form of sodium hydroxide or bicarbonate. Hardness is a measure of polyvalent cations present in water. Calcium concentration influences coagulation processes because coagulation efficiency increases with increasing calcium concentration (Pizarro et al. 1995). Due to increased coagulation efficiency, divalent cations widen the pH range and lower the required coagulant dose for effective organic matter removal. The lowered coagulant dose is possibly due to complexation of divalent cations with functional groups on the organic material that would otherwise be complexed by metal hydrolysis products. (Randtke 1988; Beckett et al. 1990). Ionic strength includes monovalent and polyvalent ions and is a measure of total ions in solution. Increased levels of sulfate, a divalent anion and the anion in alum

and ferric sulfate coagulants, was found not to affect organic matter removal (Hardin 2002). Chloride at high concentrations can displace hydroxide from ferric hydroxide. The pH of optimum coagulation will usually be higher in the presence of complexing anions (Stumm et al. 1962).

Decreased temperature can potentially affect the coagulation process, as well as flocculation and sedimentation, due to increased water density or viscosity (Morris et al. 1984; Viraraghavan et al. 1988). The density of water increases with decreases in temperature from 0.99823 to 0.99862 to 1.00000 g/mL at 20, 18, and 4°C, respectively. Increased density of water can cause decreased coagulation effectiveness, flocculation efficiency, and settling rate. Mixing power from the water is also increased due to the increased water viscosity. When the temperature is decreased from 27°C to 4°C, the water horsepower is almost doubled from 2.2 to 4.3 (Viraraghavan et al. 1988). Temperatures below 20°C shift the minimum solubility of metal to higher pH conditions and so optimum coagulation pH is greater at colder temperatures (Edzwald 1993; Edzwald 1994). The increased optimum pH could also be due to the decreased hydroxide concentration due to decreased water dissociation at colder temperatures. At 25°C, the dissociation constant of water,  $K_w$ , is  $1.01 \times 10^{-14}$ ; however, the dissociation constant decreases at 4°C to  $1.83 \times 10^{-15}$ . To have an equivalent hydroxide concentration at 25°C and 4°C, the pH of water must be increased from pH 5.80 to pH 6.54. Flocculation is hypothesized to decrease at colder temperatures. This is because smaller floc are produced during treatment at colder temperatures (Morris et al. 1984). Sedimentation also decreases at colder temperatures. The settling velocity of particles is decreased by increased density and viscosity of cold waters. Smaller floc size and increased water viscosity could lead to decreased settling and turbidity removal.

With alum and ferric chloride coagulation, residual turbidity has been found to be a function of solution temperature with increased residual turbidity in colder waters (Morris et al. 1984). However, water temperature did not seem to significantly effect the removal of TOC during iron salt coagulation in subsequent studies (Knocke et al. 1986; Edzwald 1993; Edzwald 1994). Better turbidity removal with iron is found over alum at colder temperatures. Turbidity removal relates to precipitation rates and iron precipitates faster. This is supported by reduced levels of iron associated with reduced levels of

turbidity (Morris et al. 1984). Jar test studies have also shown that although decreased temperature affects residual turbidity and metal concentration, TOC removal is not affected by decreased temperature (Braul et al. 2001). Overall, the effects from decreasing temperature are significantly less for coagulation with ferric salts than for coagulation with alum (Morris et al. 1984; Edzwald 1993; Edzwald 1994).

### **Removal of Colloidal Organic Matter Using Polymers**

The use of polymers to enhance colloidal organic matter removal has important health and economic implications. Polymer addition increases NOM removal thereby reducing DBP formation and decreases coagulant dosage thereby reducing residual metal concentrations and saving on chemical costs. Cationic polymers are usually used as primary coagulants, whereas anionic and nonionic polymers are used as coagulant aids or flocculants (Lee et al. 1998). Coagulant aids try to improve the coagulation efficiency and form stronger or denser floc (Randtke 1988; Lee et al. 1998). Flocculant aid polymers increase adsorptive flocculation by bridging floc to create larger floc (Narkis et al. 1991). By enhancing coagulation or flocculation, coagulant and flocculant aid polymers improve organic matter removal and reduce the coagulant dose required for organic matter removal.

There are many advantages of polymer utilization. These include a lack of metal solids from metal hydroxides, less dependency of performance on pH, lower level of dissolved ions in treated water, and decreased consumption of alkalinity during treatment (Bolto et al. 1999). Lower residual metal concentrations could allow for land application of residuals. Polymers do not dissociate like metal coagulants, so their mechanisms do not depend on pH, do not add as many ions to the water, and do not consume alkalinity. Because there is minimal impact to pH and alkalinity, less lime or other alkalinity addition is required and so there is decreased residual production (Edzwald 1994). Decreased coagulant dose and decreased lime dose results in decreased chemical costs and decreased residual production results in decreased disposal costs. Overall, the cost of drinking water treatment could be decreased with the use of polymers.

A pilot scale treatment of Lake Gaillard (a supply for the South Central Connecticut Regional Water Authority of New Haven) in a direct filtration mode with 7.5 mg/L alum in combination with 3.1 mg/L cationic polymer led to less than 2 mg/L DOC

in treated waters with no significant effect on pH. The cationic polymer reduced the alum dosage required for DOC removal from 20 mg/L to 7.5 mg/L. This decreased the pH dependency of TOC removal and decreased the production of metal solids. The best pH condition occurred at pH 6.3 which was higher than conventional operating pH of 5.5 and which required no acid or base addition to adjust raw water pH (Edzwald 1994).

In contrast, synthetic organic polymers are limited in their use for drinking water treatment. Impurities and by-products from organic polymers can have negative health effects. Because these polymers contain organic carbon, they can react with hypochlorite and form DBPs (Lee et al. 1998). Therefore, polymer addition can improve organic matter removal and decrease chemical costs; however, the use of polymers in drinking water treatment must be evaluated thoroughly.

## **Chapter III**

### **METHODS AND MATERIALS**

This chapter describes all the laboratory experiments performed during this research study. The main sections are: 1) General Laboratory Procedures, which explains the general experimental methods, 2) Specific Experiments, which describes the procedures specific to each type of experiment, and 3) Physical and Chemical Analyses, which explains the analytical methods.

#### **Experimental Methods Development**

The first issue was to define a colloidal size region. In order to follow previous studies, coagulated samples were passed through 1  $\mu\text{m}$  glass fiber filters prior to DOC measurement (Siczka). It has been found that significant residual DOC can exist between 1  $\mu\text{m}$  filtrate and 100,000 amu (100 KDa) permeate (Knocke et al. 1994). The differences in DOC between the 1 $\mu\text{m}$  filtrate and 100 KDa permeate were attributed to the formation of iron colloids which contained significant amounts of adsorbed DOC. In a previous study, Siczka defined the colloidal region using 1 $\mu\text{m}$  filtrate for the particulate-colloid boundary and 100 KDa permeate and 30,000 amu (30 KDa) permeate for the colloidal-dissolved boundary. Since there was no significant difference between the 100 KDa and 30 KDa DOC, the 30 KDa membrane was chosen for this research to define the lower boundary of the colloid region.

The second issue was to select an organic matter source. Suwanee River natural organic matter was chosen because it was readily available from the International Humic Substances Society. Since a 30 KDa membrane was used to determine the lower colloidal boundary, the DOC in the test water was ultrafiltered to be less than 30 KDa. The dissolved natural organic matter was permeated through a 10 KDa membrane and a 30 KDa membrane. There was no significant difference between the permeate DOC from the 10 KDa and 30 KDa membrane. Because the 10 KDa ultrafiltration was significantly more time intensive, the 30 KDa membrane was used to ultrafilter the organic matter stock solutions.

The final issue was to determine which water parameters to study. Studies were performed to determine the effect of coagulation pH, coagulant dose, initial turbidity,

initial organic matter concentration, and temperature on colloid formation. All jar tests were performed using less 30 KDa Suwanee River natural organic matter. Residual turbidity, residual DOC, and residual total iron were analyzed for each jar test.

The pH study was performed to investigate the phase-change behavior of DOC as a function of pH. The ferric sulfate dose was set to 22 mg/L iron over the pH range 4.5-7.0. The dose was the metal molar equivalent to 25 mg/L alum which was used in a complimentary colloid study with alum coagulation (Hardin 2003). The untreated waters contained 5.5 mg/L DOC and no added turbidity ( $\leq 0.5$  NTU). The 1  $\mu\text{m}$  filtrates and 30 KDa permeates of the treated waters were measured for residual DOC and residual iron. The results were used to determine the test water pH values for the subsequent research.

The coagulant dose study was performed to investigate the phase-change behavior of DOC as a function of coagulant dose. The experiments in this study were performed at pH 5.80 and at pH 6.80 with coagulant doses up to 17 mg/L ferric iron at pH 5.80 and up to 27 mg/L ferric iron at pH 6.80. A higher dose range was chosen for the pH 6.80 jar tests because at more neutral pH values, ferric sulfate requires higher doses to be an effective coagulant. The untreated waters contained 6 mg/L DOC and no added turbidity ( $\leq 0.5$  NTU). The 1  $\mu\text{m}$  filtrates and 30 KDa permeates of the treated waters were measured for residual DOC and residual iron. The results were used to demonstrate colloidal formation reproducibility.

The turbidity study was performed to investigate the phase-change behavior of DOC as a function of initial turbidity level. The experiments in this study were performed at pH 5.80 and at pH 6.80 with added bentonite to produced turbidity levels of 10 NTU and 40 NTU. The results were used to establish a standard turbidity level that produced significant colloidal matter for the subsequent research.

The organic matter study was performed to investigate the phase-change behavior of DOC as a function of initial organic matter concentration. The experiments in this study were performed at pH 5.80 and at pH 6.80 with initial organic carbon concentrations of 2.5 mg/L and 8 mg/L DOC. The results from this study were used to establish initial organic matter concentrations for the temperature study.

The temperature study was performed to investigate the phase-change behavior of DOC as a function of temperature. The experiments in this study were performed at 4°C

with initial organic carbon concentrations of 2.5 mg/L, 5 mg/L, and 10 mg/L DOC. The experiments were performed at both pH 6.54 and pH 7.54. For the decreased temperature studies, the pH values were increased to maintain the equivalent hydroxide concentration from room temperature.

### **General Laboratory Procedures**

#### *Glassware Preparation*

All of the glassware used in the experimental studies was washed using Fisherbrand (Pittsburgh, PA) Sparkleen 1 detergent (04-320-4), rinsed with tap water three times, and rinsed with ultrapure water (deionized, low-organic Millipore) three times. Because the jar testing jars and amber jars held treated water containing iron, these jars were soaked in a 10% nitric acid bath for a minimum of thirty minutes after the tap water rinse. The acid bath procedure was followed by rinsing with deionized water three times and then rinsing with Ultrapure water three times.

#### *Chemicals and Solutions*

Ultrapure water was used to make all of the dilutions and solutions. Dilution water was used to make the organic matter stock and the waters used for treatment. The waters used for treatment consisted of 2 meq/L as CaCO<sub>3</sub> alkalinity, 0.5 meq/L hardness, and 10 meq/L ionic strength. The chemicals used in this research are summarized in Table 2.

#### *Definition of Dissolved, Colloidal, and Particulate Matter*

For this study, the resulting iron precipitates found during treatment as well as any iron-bound organic material was operationally defined and physically separated into three size classifications: particulate, colloidal, and dissolved. Particulate material was defined based upon being retained by a Pall Gelman (Ann Arbor, MI) 1 µm glass fiber filter (A/E 47 mm diameter). Colloidal matter was the fraction that passed through a 1 µm filter and was retained by a Amicon (Beverly, MA) 30 KDa membrane (model YM-30 63.5mm diameter). Dissolved iron and/or organic matter was represented by the fraction that permeated through the 30 KDa membrane. A schematic example of this classification system is shown in Figure 1.

#### *Ultrafiltration Process*

Before ultrafiltration, the ultrafiltration membranes were cleaned to remove the

Table 2  
Chemicals used in this research

Chemical	Supplier and Stock No.	Purity or Strength	Grade
Sodium Bicarbonate	Fisher (S233-500)	99.70%	Certified A..C.S.
Calcium Chloride Dihydrate	Fisher (C79-500)	100.60%	Certified A.C.S.
Sodium Chloride	Fisher (S271-50)		Certified A.C.S.
Buffer Soution pH 4.00	Fisher (SB98-10)		Certified
Bentonite (Montmorillonite)	Adrich (1302-78-9)		
Suwannee River NOM	IHSS (1R101N)		
Buffer solution pH 7.00	Fisher (SB108-10)		Certified
Hydrochloric Acid	Fisher (SA54-1)	0.1 N	Certified
Hydrochloric Acid	Fisher (SA48-4)	1 N	Certified
Sodium Hydroxide	Fisher (SS266-4)	1 N	Certified
Sodium Hydroxide	Fisher (SS276-1)	0.1 N	Certified
Iron (III) Sulfate Hydrate	Aldrich (307718-500G)	97%	
Superfloc® C-572	Cytec Industries, Inc.		
Superfloc® N-1986	Cytec Industries, Inc.		
Superfloc® C-581	Cytec Industries, Inc.		
2000 mg/L DOC standard			
Nitric Acid	Fisher (A200 <sup>S</sup> -212)	69.50%	Certified A.C.S. <i>PLUS</i>

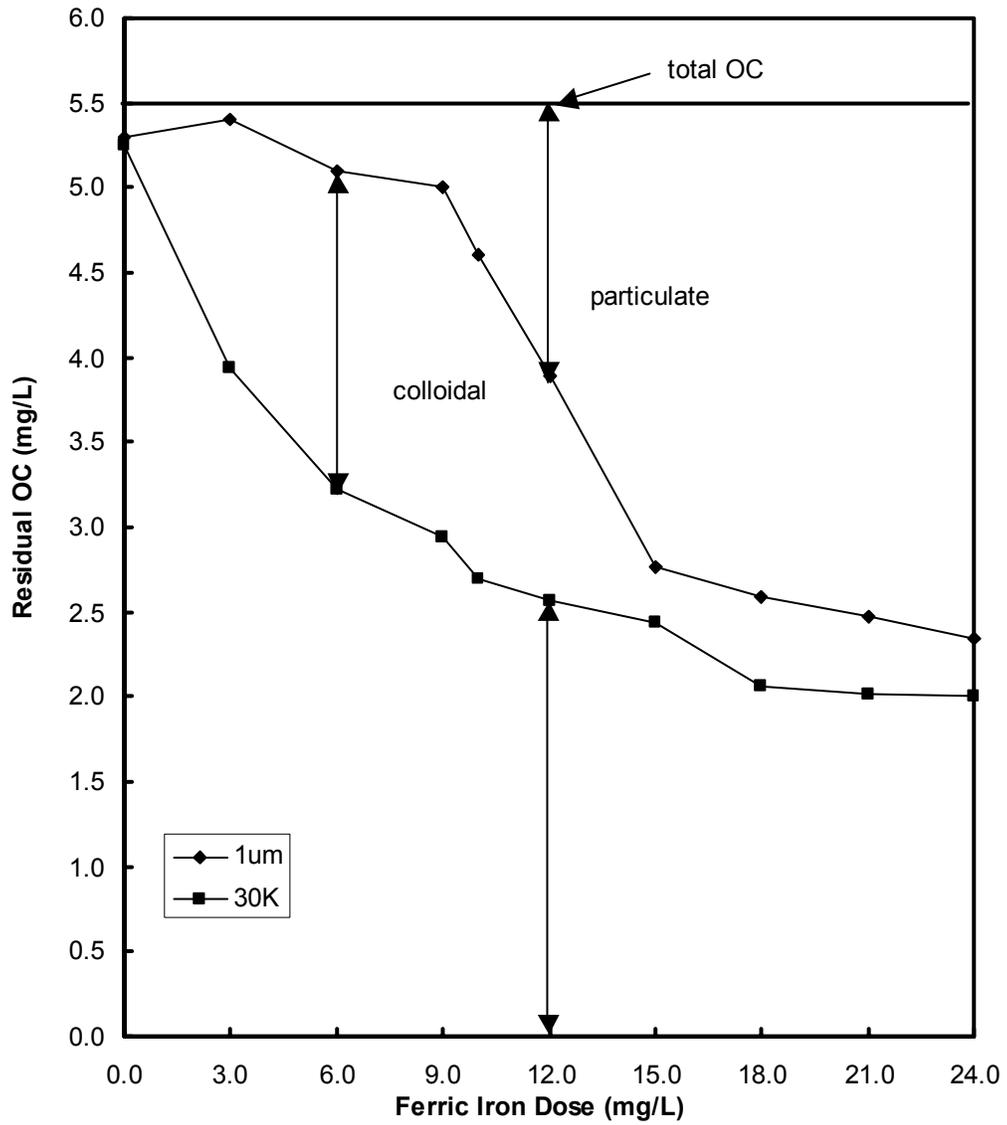


Figure 1. An illustration of particle, colloidal, and dissolved OC classifications based on 1µm filtration and 30KDa ultrafiltration

glycerol coating, as the organic carbon from glycerol would contaminate the DOC samples. The membranes were prepared by soaking them (emulsion side down) in 200 mL of ultrapure water for at least one hour; the soaking water was changed every twenty minutes. Then, the membranes were stored (emulsion side up) in the 200 mL Amicon (W.R. Grace & Co., Danvers, MA) ultrafiltration cell apparatus (model 8200) in 200 mL of ultrapure water overnight. The membranes were ready for use when permeated ultrapure water contained 400  $\mu\text{g/L}$  or less DOC.

Before each use, each ultrafiltration membrane was flushed by permeating one cell with ultrapure water under 55 pounds per square inch of nitrogen gas pressure while stirring on a Corning (Corning, NY) pulse motor magnetic stir plate (model PC-131). The water was permeated down to 40 – 50 mL. The samples were permeated following the same conditions.

After each sample, the membranes were cleaned by permeating 180 mL of ultrapure water with 5 mL of 0.1 N sodium hydroxide, then 180 mL of ultrapure water with 5 mL of 0.1 N hydrochloric acid, then 180 mL of ultrapure water with 5 mL of pH 7.00 buffer, and finally 180 mL of ultrapure water. The membranes were stored in 100 mL of ultrapure water inside the ultrafiltration cells in the 4°C refrigerator for up to one week.

#### *Preparation of Organic Matter Stock Solutions*

To represent organic carbon in natural waters, a surrogate of natural organic matter was added to the waters used for treatment. The reference natural organic matter was ordered from the International Humic Substances Society (1R101N). It was isolated from the Suwannee River using reverse osmosis and then preserved through freeze-drying.

The organic matter was diluted by dissolving 1000 mg of solid organic matter up to 1 L in dilution water. This dissolved organic matter was divided using ultrafiltration. Dissolved material was operationally defined to be less than 30 KDa and so to ensure colloidal DOC was not present in the untreated waters and that measured colloidal DOC was formed during treatment, NOM larger than the dissolved cut off was removed by ultrafiltering the organic matter through 30 KDa membranes. After the initial flush, each cell was then filled (200 mL) with whole organic matter solution and permeated down to

50 mL. This supernatant was resuspended up to 200 mL with dilution water (2 meq/L as CaCO<sub>3</sub> alkalinity, 0.5 meq/L hardness, and 10 meq/L additional ionic strength) and re-permeated down to 50 mL twice. All of the less than 30,000 amu permeate was combined into a Nalgene (Rochester, NY) nine liter rectangular HDPE carboy.

The permeate was then concentrated by pouring 500 mL aliquots into a Büchi Rotovapor (Brinkmann Instruments, Switzerland; model R110) and evaporating the sample down to a volume of approximately 100 mL. These concentrated organic matter samples were combined and subsequently stored in an amber-colored jar at 4°C for future use.

The specific ultraviolet absorbance (SUVA) of the organic matter stock solutions was quantified to ensure that the organic matter in the stock solutions were chemically similar. The SUVAs were calculated using the DOC and the Abs<sub>254nm</sub> in the following equation:

$$SUVA \left( L * cm^{-1} / mg - C \right) = \frac{Abs_{254nm} (cm^{-1}) * 100}{DOC (mg / L)}$$

The ultraviolet absorbance of the organic matter stock solutions was measured at 254 nm using a Beckman DU 640 Spectrophotometer (Irvine, CA). Also, the amounts of iron in the organic matter stock solution and the bentonite slurry suspension were quantified using atomic adsorption spectrometry.

#### *Preparation of Bentonite Slurry Suspensions*

Bentonite clay was added to the waters used for treatment to represent turbidity in natural waters. The bentonite was converted from a powder into a slurry to facilitate better mixing of bentonite in the waters used for treatment.

The bentonite clay was suspended in ultrapure water by weighing 10 g into a 600 mL beaker and adding 200 mL of ultrapure water and forcibly suspending the bentonite against the side of the beaker with a spatula. When a significant amount of bentonite was suspended, it was decanted and another 200 mL of ultrapure water was added to the rest of the bentonite. The dissolution and decantation was repeated until 1 L of water had suspended all of the bentonite. To ensure thorough suspension, the bentonite slurry was sonicated using a Branson Ultrasonics sonicator (Danbury, CT) model 250 with macrotip

(duty cycle 1/second and power 40 KHz) for three five-minute intervals. The bentonite slurry was stored in an amber-colored jar in a cabinet.

#### *Preparation of Ferric Sulfate Coagulant Stock Solutions*

The 3.0 mg/mL iron(III) stock coagulant solution was prepared by dissolving 1.500g of ferric sulfate hydrate ( $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$ ) up to 100 mL in ultrapure water. Each coagulant stock solution was analyzed using atomic adsorption spectrometry to verify the stock concentration. The solution pH was very acidic, pH 2, so it was not acidified for storage. The coagulant stock solution was prepared at least every month.

#### *Preparation of Polymer Working Solutions*

Three polymers were chosen to coagulate or flocculate the iron-bound organic matter colloids formed during coagulation. Low molecular weight polymers are typically coagulant aids and high molecular weight polymers are typically flocculant aids. Cationic and nonionic polymers are used to attract the oppositely charged particles and enmesh them, while nonionic polymers work solely by enmeshment.

The Superfloc® C-572 (Cytex Industries, Inc., West Paterson, NJ) polymer was chosen because it was a cationic, low molecular weight polyquaternary amine polymer in water. Because of its low molecular weight, it was considered a primary coagulant or a possible coagulant aid. The Superfloc® N-1986 polymer was a nonionic, high molecular weight polyacrylamide in water-in-oil emulsion polymer and the Superfloc® C-581 polymer was a cationic, high molecular weight polyquaternary amine polymer. Due to their high molecular weights, N-1986 and C-581 were classified as flocculant aids.

Each polymer was serially diluted from concentrated product to 1% dilution and ultimately down to an actual working solution that was approximately 0.012% weight-by-weight (120 mg/L polymer). The 1% stock solutions were prepared gravimetrically by weighing the concentrated polymer into a 10 mL plastic Teflon® sealed syringe. A GE (Bentonville, AR) hand blender (model 1106757) was inserted into the water and turned on to high speed. The syringe was held over the vortex in the water and the plunger was inserted into the syringe. The Teflon® tape was removed and then the polymer was injected into the vortex. The polymer was injected continuously for twelve seconds. The 1% polymer dilutions were allowed to age at least overnight. The 0.1% dilution and the 0.012% working solutions were prepared the day of the jar test.

### *Preparation of Test Water Solutions*

The water used in the jar test experiments was prepared at least twelve hours, but no more than 24 hours, prior to treatment to allow for equilibration. The test waters were stored in a Nalgene (Rochester, NY) nine liter rectangular HDPE carboy (NNI 22110020). All of the test waters consisted of ultrapure water, 2 meq/L as CaCO<sub>3</sub> alkalinity, 0.5 meq/L hardness, and 10 meq/L additional ionic strength. The raw water turbidity, total organic carbon (TOC), temperature, and pH were varied among jar tests. The turbidity, TOC, and temperature were determined prior to equilibration. The pH of the test water was adjusted just prior to the jar test experiment.

Test water solutions were prepared as follows:

1. The background ions were added to ultrapure water: sodium bicarbonate for 2 meq/L as CaCO<sub>3</sub> alkalinity, calcium dichloride dihydrate for 0.5 meq/L hardness, and sodium chloride for 10 meq/L ionic strength.
2. The bentonite slurry was shaken to resuspend the settled bentonite and then sonicated (duty cycle 1/sec and power 40 KHz) for five minutes to ensure thorough suspension. The aliquot of bentonite slurry to produce the corresponding raw water turbidity was measured and added to ultrapure water.
3. The current organic matter stock solution was gently inverted. The aliquot of organic matter stock solution to produce the corresponding raw water DOC was measured and added to the ultrapure water containing bentonite. The bentonite and organic matter was then combined with the background water.
4. The remaining ultrapure water was added to make the total volume of test water.
5. The prepared test water was shaken vigorously for two minutes and stored overnight in a dark cabinet at room temperature or in a refrigerator at 4°C (for the studies evaluating temperature effects).

### *Jar Testing*

The same jar testing procedure was followed regardless of the experimental parameters being evaluated in a given study. All jar tests were performed to analyze the removal of DOC and turbidity as a function of coagulation pH, coagulant dose, initial DOC concentration, and/or temperature.

Before each jar test, the raw water was vigorously shaken for two minutes and sampled for turbidity, DOC, and iron. Then, the temperature of the test water was measured using a Fisher Scientific (Springfield, NJ) Red-Spirit No-Roll thermometer (model 14-997). Next, the pH of the test water was adjusted to pH 5.80 or pH 6.80 using hydrochloric acid and/or sodium hydroxide as necessary. For each jar test, 900 mL or 600mL aliquots of test water were treated in six to ten 1000-mL Nalgene square PETG topless media bottles (NNI 2019-1000). For the pH, coagulant dose, and temperature studies, the test water pH was adjusted in each jar. After many experiments, it was found that the test water could be adjusted as a whole in the carboy; thus for the turbidity and organic matter studies, the test water pH was adjusted in the carboy.

The coagulant doses were measured from the 3 mg/mL as iron (III) ferric sulfate stock solution. The stoichiometric doses of 0.1 N sodium hydroxide were used to neutralize the acidic effect of the coagulant dose added to each jar. The coagulant and base dose volumes were less than three percent of the raw water volume to minimize dilution effects. The coagulant and base doses were delivered simultaneously using Fisher Scientific (Springfield, NJ) Polystyrene weigh dish pour boat (1 5/8" x 1 1/4" x 5/16"; model PB 316).

Two Phipps and Bird (Richmond, VA) six-paddle stirrers (models 300 and PB-700) were used for treatment. The paddles were turned at 100 revolutions per minute (rpm) for the rapid mix phase of treatment. Treatment was begun by simultaneously adding the corresponding coagulant and base doses. This began the rapid mix phase of treatment which was 100 rpm for two minutes. After rapid mix, tapered flocculation was performed. The paddle speed was decreased in three ten-minute intervals from 40 rpm to 30 rpm to 20 rpm. At the beginning of tapered flocculation, the water pH was measured and, if necessary, adjusted to within 0.1 pH units of the initial raw water pH value using 0.1 N hydrochloric acid and/or 0.1 N sodium hydroxide. After flocculation, the treated water was allowed to undergo sedimentation for one hour. After sedimentation, turbidity samples were taken and analyzed. Then, approximately 300 mL sample of each treated water was carefully poured (to not disturb the settled floc) into 1L amber glass jar. The pH of this sample was measured. This sample was ultimately filtered to determine the amounts of particulate, colloidal, and dissolved organic carbon in the treated waters

After residual turbidity and pH analyses, filtration was performed to separate the particulate and colloidal fractions. Prior to sample filtration, the glass fiber filters were cleaned with three flushes of 250 mL of distilled water and one flush of 250 mL of ultrapure water. The samples were pulled through the 1  $\mu\text{m}$  glass fiber filters using a GE Motors (Fort Wayne, IN) vacuum pump. The filters were held in a Nalgene (Rochester, NY) reusable 250 mL filter holder with funnel (NNI 310-4000), which was placed in a 500 mL filter flask. The 1 $\mu\text{m}$  filtrate was sampled for DOC and iron analyses. The filter flask was rinsed three times with ultrapure water between samples.

After 1  $\mu\text{m}$  filtration, the samples were permeated through the 30 KDa ultrafiltration membranes. Twenty milliliter of permeate was wasted, the next forty milliliters was collected for DOC analysis, and the next fifty milliliters was collected for iron analysis.

### **Specific Experiments**

Jar tests were performed that tested the effect of test water pH, coagulant dose, initial turbidity, initial organic matter concentration, and temperature on colloid formation. The pH, dose, turbidity, and organic matter studies were performed at 25°C and the temperature study was performed at 4°C.

#### *pH Optimization*

The pH study was performed to determine the optimal coagulation pH for removal of DOC using ferric sulfate. Each jar was given the same ferric sulfate dose of 22 mg/L as iron. The initial DOC concentration for this study was 5.5 mg/L.

#### *Phase-Change Behavior of DOC and Iron*

The coagulant dose study was performed to determine the range of coagulant doses that encompassed the colloid formation range at 6 mg/L DOC at both pH values. At pH 5.80, coagulation was performed with doses up to 17 mg/L ferric iron and at pH 6.80, coagulation was performed with doses up to 27 mg/L ferric iron.

The turbidity study was performed to determine if increased turbidity significantly affected colloid formation. Jar tests were performed at both pH values in which there was 6 mg/L DOC and no added turbidity so the initial turbidity was less than 1 NTU. For the turbidity studies, the initial turbidity was increased to 10 NTU and to 40 NTU using added bentonite slurry.

The organic matter study was performed to determine if the level of organic carbon significantly affected colloid formation. Jar tests were performed at both pH values with 10 NTU of turbidity. Initial DOC concentrations of 2.5 mg/L and 8 mg/L were studied.

The temperature study was performed to determine if a decreased temperature, to simulate coagulation during winter, significantly affected colloid formation. The test water was equilibrated overnight and the jar tests were performed at 4°C using a chiller and an ice water bath.

#### *Colloidal Iron-Bound Organic Matter Characterization*

The zeta potentials of selected water samples were determined using laser Doppler velocimetry with a Malvern Instruments Zetasizer (Malvern, Worcestershire, UK; model 3000 HS). The instrument was calibrated with a certified -50 mV standard and the measured values fell within the range specified by the manufacturer. The effect of coagulation pH on the zeta potential of colloidal DOC was determined by analyzing water samples before and after treatment with 5 mg/L iron at pH 5.80 and pH 6.80. The effect of added turbidity on zeta potential at the same coagulant dose was determined by analyzing samples before and after treatment with 5 mg/L iron at pH 6.80 without added turbidity and with 10 NTU added turbidity. The effect of added organic matter was determined by analyzing samples before and after treatment with 5 mg/L iron at pH 6.80 without added organic matter and with 5 mg/L added DOC. The water samples were treated following the standard jar test procedure. These zeta potential samples were drawn up with a 25 mL wide-opening pipette and filtered using 1 µm glass fiber filters.

Differences in zeta potential during each treatment stage at a colloidal coagulant dose (5 mg/L iron) and an effective coagulant dose (15 mg/L iron) were determined by analyzing test and treated waters with 4 – 5mg/L DOC and 10 NTU turbidity. The difference in zeta potential due to the presence of organic matter during effective coagulation (15 mg/L iron) was also determined by analyzing test and treated waters with 10 NTU turbidity and no added organic matter.

To determine background zeta potential values, an organic matter stock solution and a bentonite slurry were analyzed. Separately in the dilution water, 5 mg/L DOC and 10 NTU turbidity were measured.

The Zetasizer was used to quantify the size of the bentonite particles using photon correlation spectroscopy. The bentonite slurry was filtered through a 0.45  $\mu\text{m}$  filter to prevent the bentonite particles from settling during the analysis. The filtration removed any particulate bentonite so that only the colloidal bentonite was analyzed. The Zetasizer was also used in an attempt to quantify the size of colloids formed with test waters containing 5 mg/L DOC and 10 NTU turbidity during coagulation with 5 mg/L iron.

#### *Removal of Colloidal Iron-Bound Organic Matter Using Polymer Addition*

A polymer was utilized to evaluate the effects of polymer addition. The goal was to achieve the 40% TOC removal obtained with 15 mg/L ferric iron by using one-third of the iron dose and a polymer aid. Waters with initial DOC of 5 mg/L and initial turbidity of 10 NTU were treated at pH 6.80 and 25°C with 5 mg/L ferric iron and up to 1.20 mg/L polymer. When the jar tests involved polymer addition, the selected polymer was added after the coagulant. The coagulant aid polymer, C-572, was dosed simultaneously after ninety seconds of rapid mix using the weigh dish pour boats. The flocculant aid polymers, N-1986 and C-581, were dosed after three minutes of the third flocculation stage using a wide-opening pipette.

### **Physical and Chemical Analyses**

#### *pH Measurement*

The pH of all raw waters and treated water samples was measured using a Fisher Scientific (Springfield, NJ) Accumet pH meter (model 910). The meter was calibrated with pH 7.00 and pH 4.00 buffer solutions.

#### *Turbidity Measurement*

The turbidity of the treated, settled water samples was measured by first withdrawing aliquots using Fisherbrand (Springfield, NJ) wide-opening 25 mL pipettes (13-671-108E). The turbidity of the samples was measured using a Orbeco-Hellige (Farmingdale, NY) Digital-Reading Turbidimeter (model 965-10A). The meter was calibrated using a blank solution (0 nephelometric turbidity units (NTU)) and a 40 NTU standard.

#### *Organic Carbon Determinations*

Dissolved organic carbon (DOC) concentrations were measured using a Sievers Portable Total Organic Carbon Analyzer (model 800) with autosampler (Ionics

Instruments, Watertown, MA) or a Dohrmann Carbon Analyzer model DC-80 (Xertex Corporation, Santa Clara, CA).

All samples were collected in 40 mL glass vials and sealed with Teflon lined caps or septa. Samples analyzed using the Sievers analyzer were loaded into the autosampler. Samples analyzed using the Dohrmann analyzer were acidified at the time of collection with 85% phosphoric acid and sparged with oxygen to remove any inorganic carbon present. If the samples were at room temperature, then they were sparged for five minutes; if the samples were 4°C, then they were sparged for ten minutes. Sparging is performed to drive off carbon dioxide from the sample. Because gases are more soluble in colder solutions, the sparging time for the 4°C samples was increased. The 2000 mg/L DOC phthalic acid standard was prepared using dried potassium hydrogen phthalate and the 10 mg/L DOC standard was prepared by diluting the 2000 mg/L standard with ultrapure water. Duplicate injections per sample were analyzed. DOC measurements were made following the manufacturers' procedures.

### *Iron*

The residual iron concentration was measured for selected jar tests. Samples for iron analysis were collected in 25 mL HDPE bottles and acidified with 1 to 2 drops of concentrated nitric acid prior to analysis. The iron analysis was performed using a Perkin-Elmer (Norwalk, CT) model 5100 PC flame atomic absorption spectrophotometer. Instruments setting included a wavelength of 248.3 nanometers and a slit width of 0.3 millimeters. The detection limit for iron was 0.1 mg/L. The iron calibration standards were 0.1 mg/L, 5.0 mg/L, 1.0 mg/L, 5.0 mg/L, and 10.0 mg/L. The instrument response was based on the concentration of iron in the samples. It utilized a flame to excite the iron atoms in the sample and these excited iron atoms absorb light at a specific wavelength. The decrease in light at that wavelength is detected.

## Chapter IV

### EXPERIMENTAL RESULTS AND DISCUSSION

#### Phase-Change Behavior of Organic Matter

Colloidal organic matter was defined for this study as organic matter less than 1  $\mu\text{m}$  and greater than 30 KDa in size. The colloidal envelope was the area enclosed by the 1  $\mu\text{m}$  and the 30 KDa concentrations. The 1  $\mu\text{m}$  concentrations had an initial plateau and a subsequent shoulder, whereas the 30 KDa concentrations steadily decreased. The tail of the colloidal envelope occurred where the 1  $\mu\text{m}$  values decreased to the 30 KDa values or where the 1  $\mu\text{m}$  and 30 KDa values reached constant values. A schematic example of the colloidal envelope is shown in Figure 2.

#### *Effect of pH on Colloid Formation*

Colloid formation, as determined by residual organic carbon (OC) concentration, depended on the coagulation pH such that residual OC decreased with decreasing pH, as shown in Figure 3. Also, the colloid formation region (defined by the 1  $\mu\text{m}$  and 30 KDa residual organic matter data) decreased with decreasing pH. The trend of increasing organic matter removal with decreasing pH has been commonly observed in previous studies that found coagulation pH to be an important factor in OC removal (Kavanaugh 1978; Chadik et al. 1983; Sinsabaugh et al. 1986; Gray 1988; Chowdhury et al. 1991; Crozes et al. 1995; Edzwald et al. 1998). The optimum pH range for organic removal by coagulation with ferric salts has been found to be between pH 3 and pH 5 (Kavanaugh 1978).

For the remainder of this study, pH values of 5.8 and 6.8 were chosen for coagulation. The lower value is in the recommended operating pH range for ferric iron coagulants (pH 5.5 to 6.0) (Edzwald 1994), and the higher value is representative of coagulation pH for many natural waters used as drinking water sources. These pH values also correspond with a companion coagulation study utilizing alum (Hardin 2003).

#### *Effect of Coagulant Dose on Colloid Formation*

Coagulant dose dramatically affected residual OC and colloidal OC formation. The height of the colloidal matter envelope varied with coagulant dose as shown in

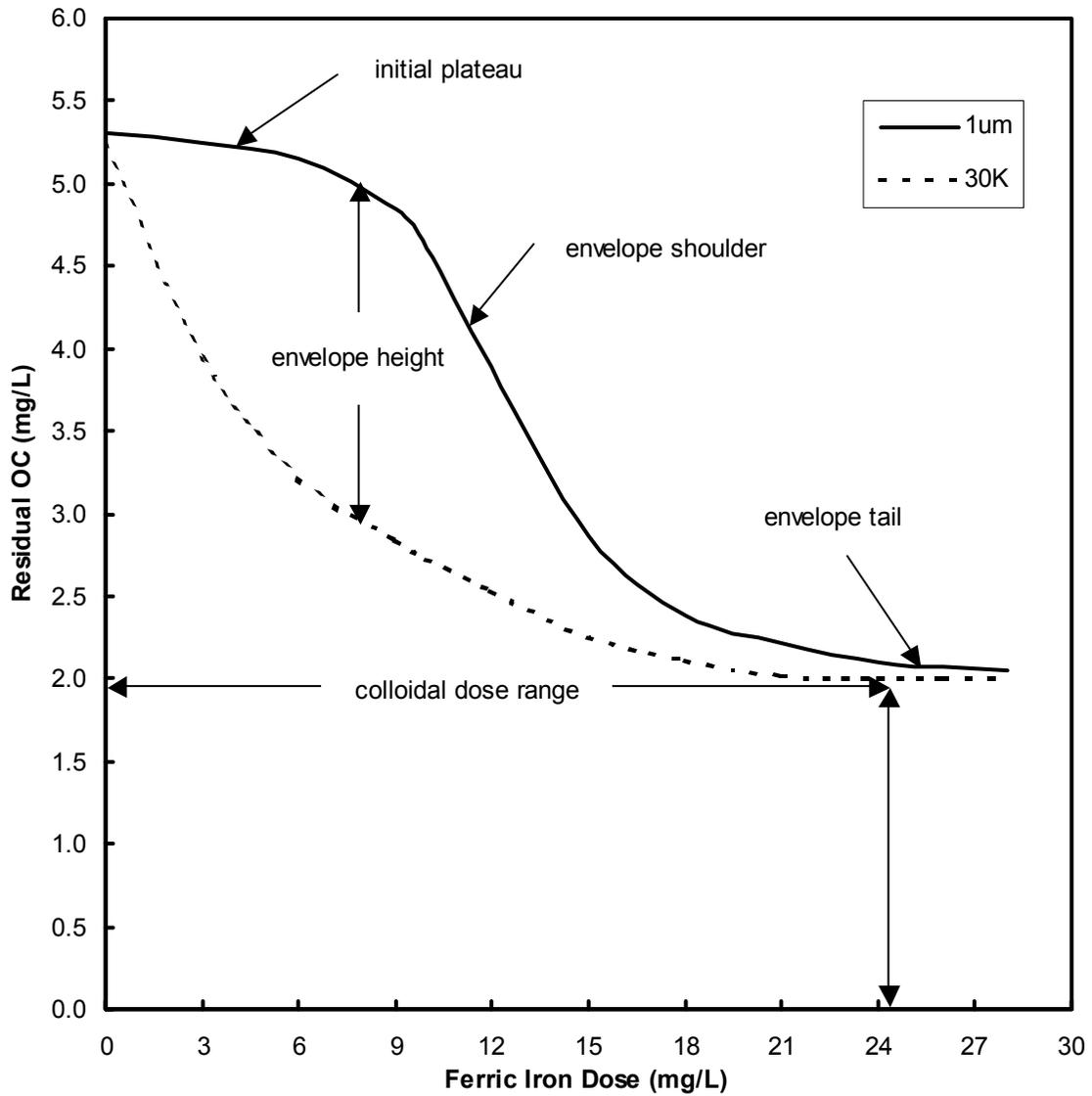


Figure 2. Conceptual colloidal matter envelope formed by coagulation with ferric sulfate.

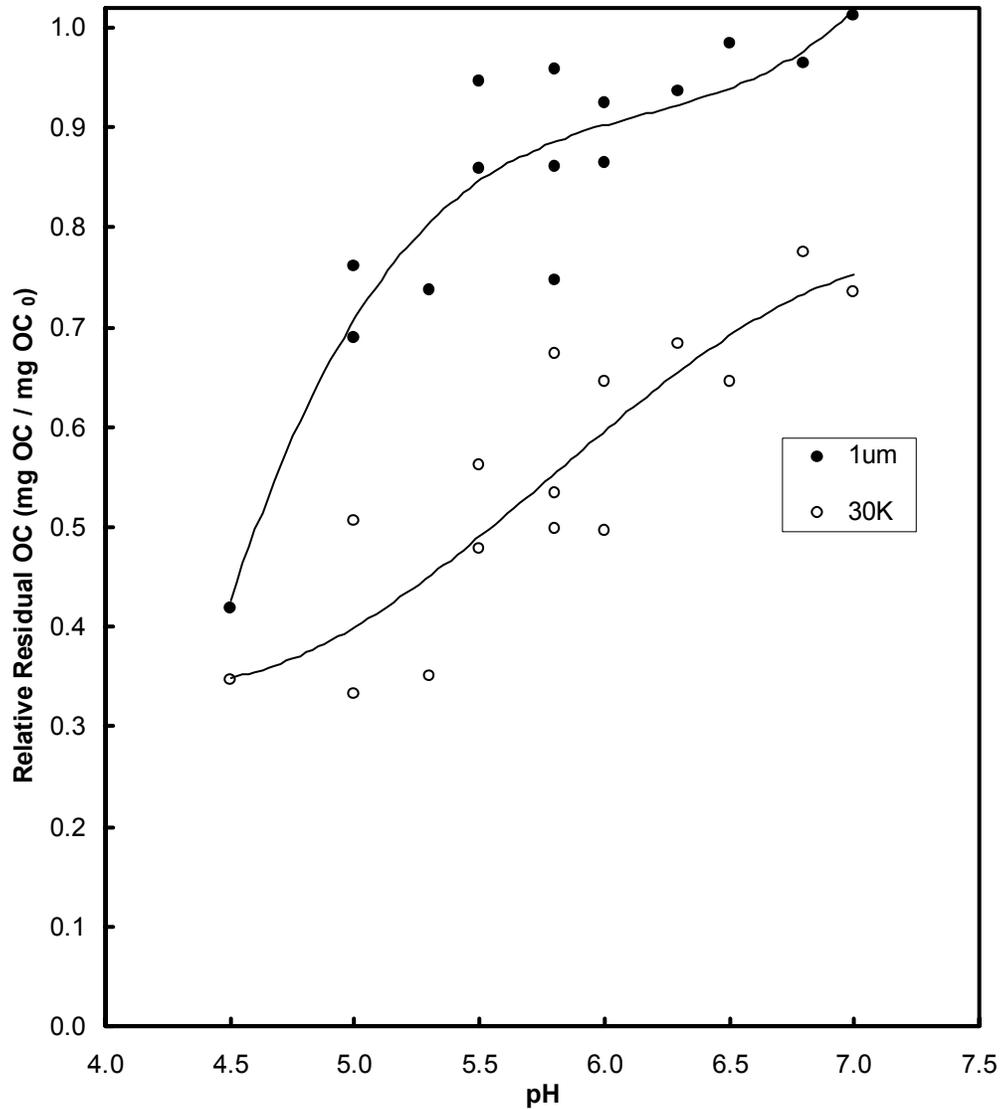


Figure 3. Relative residual OC as a function of pH (ferric iron coagulant = 5 mg/L as Fe). Untreated waters contained 5.5 mg/L DOC and no added turbidity ( $\leq 0.5$  NTU). Replicate values for several pH values are shown.

Figure 4. The maximum envelope height occurred at 6 mg/L iron for pH 5.8 and at 9 mg/L iron for pH 6.8. At both pH values, increasing coagulant dose above the dose at the maximum envelope height caused the 1  $\mu\text{m}$  OC to decrease rapidly.

Residual turbidity was strongly related to colloidal OC formation. The maximum residual turbidity corresponded with the maximum colloidal envelope height (Figure 5). For pH 5.8, the maximum residual turbidity occurred at 6 mg/L iron as did the maximum colloidal envelope height and for pH 6.8, the maximum residual turbidity and the maximum colloid formation occurred at 9 mg/L iron. Also, the subsequent sharp decrease in turbidity corresponded to the rapid decrease in residual colloidal OC.

At lower coagulant doses where the colloidal envelope was increasing, OC was converted to colloidal matter. Increasing turbidity supported this conversion. At higher coagulant doses, the colloidal envelope decreased as colloidal matter was converted to particulate matter. Likewise, decreasing turbidity was due to the resulting particulate matter settling from the treated water.

#### *Effect of Turbidity on Colloid Formation*

Initial turbidity did not significantly affect incorporation of OC in colloidal matter formed by ferric sulfate coagulation. For added turbidity levels of 0 NTU, 10 NTU, and 40 NTU, the 1  $\mu\text{m}$  and 30 KDa residual OC data defined very similar colloidal envelopes at each pH, as shown in Figure 6. The effects of pH on colloid formation are also evident in the colloidal OC envelopes in Figure 6, as the coagulant dose at maximum envelope height, coagulant dose range, and minimum residual organic matter fraction increased with pH. These pH effects on OC incorporation in colloidal matter were previously noted in Figures 3 and 4. The relative insensitivity of OC incorporation in colloidal matter on initial turbidity level implies that organic matter dominated coagulant demand for the waters treated here, which is consistent with the findings of previous coagulation studies (Edwards 1997; O'Melia et al. 1999; Carlson et al. 2000).

There was a slight trend in OC removal with increased turbidity. As the turbidity increased, OC removal at the envelope tail decreased (Figure 6). OC removal can decrease with increasing turbidity because some portion of the coagulant must satisfy the coagulant demand of the bentonite that causes the turbidity.

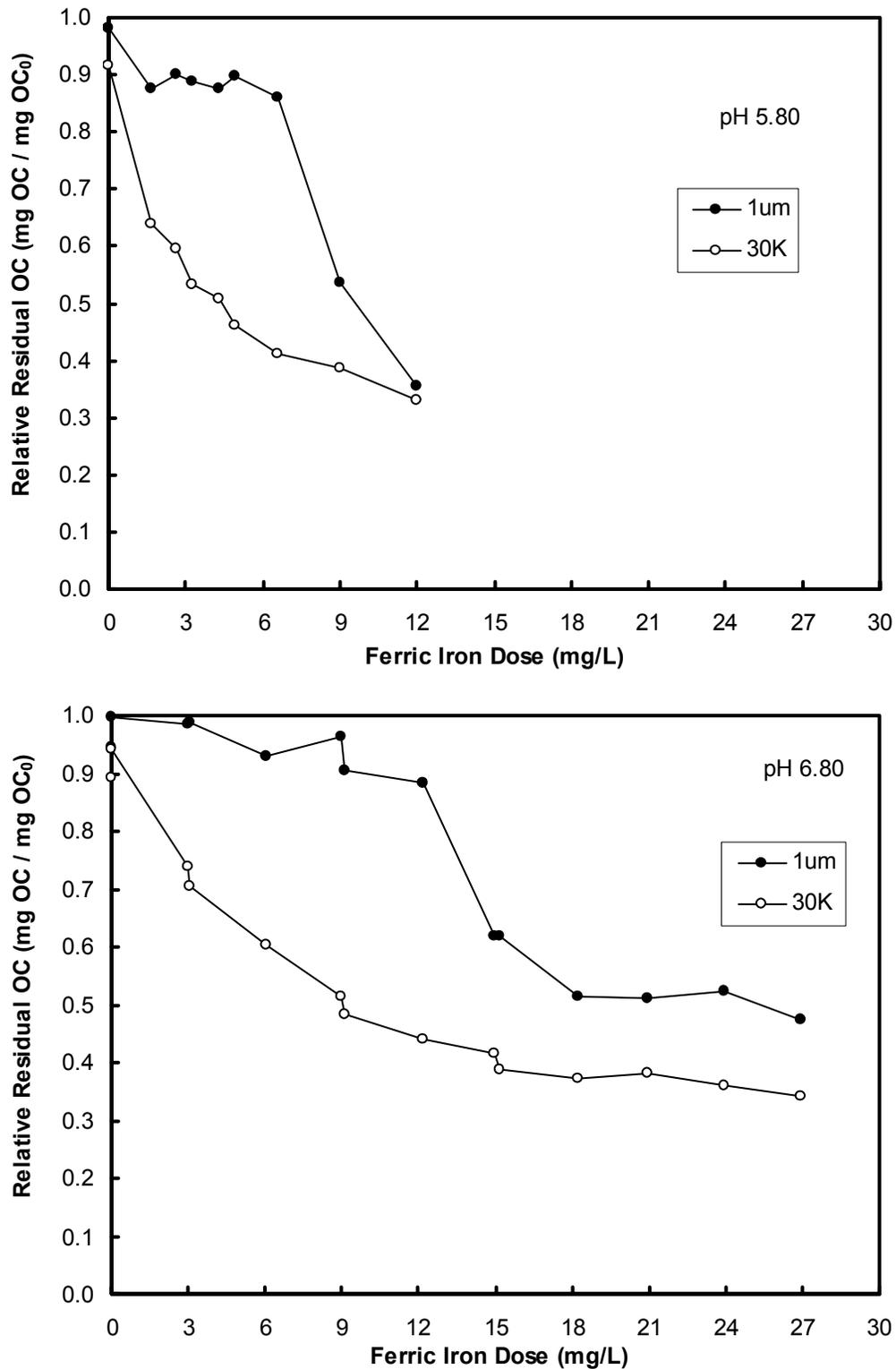


Figure 4. Colloidal OC formation as a function of ferric iron coagulant dose. Untreated waters contained 6 mg/L DOC and no added turbidity ( $\leq 0.5$  NTU). Replicate values for several doses are shown for pH 6.8.

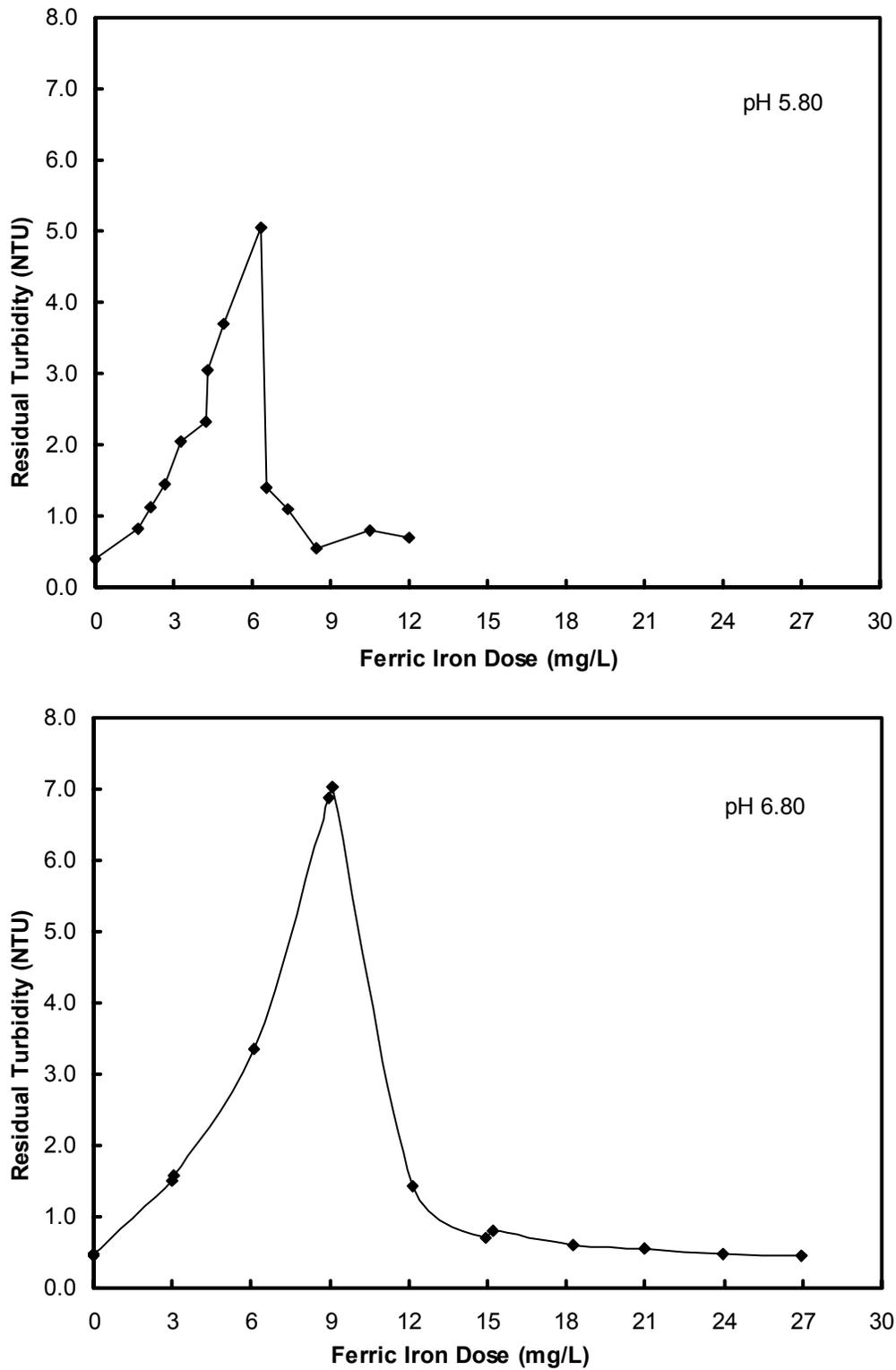


Figure 5. Residual turbidity as a function of ferric iron coagulant dose. Untreated waters contained 6 mg/L DOC and no added turbidity ( $\leq 0.5$  NTU). Replicate values for several doses are shown for pH 6.8.

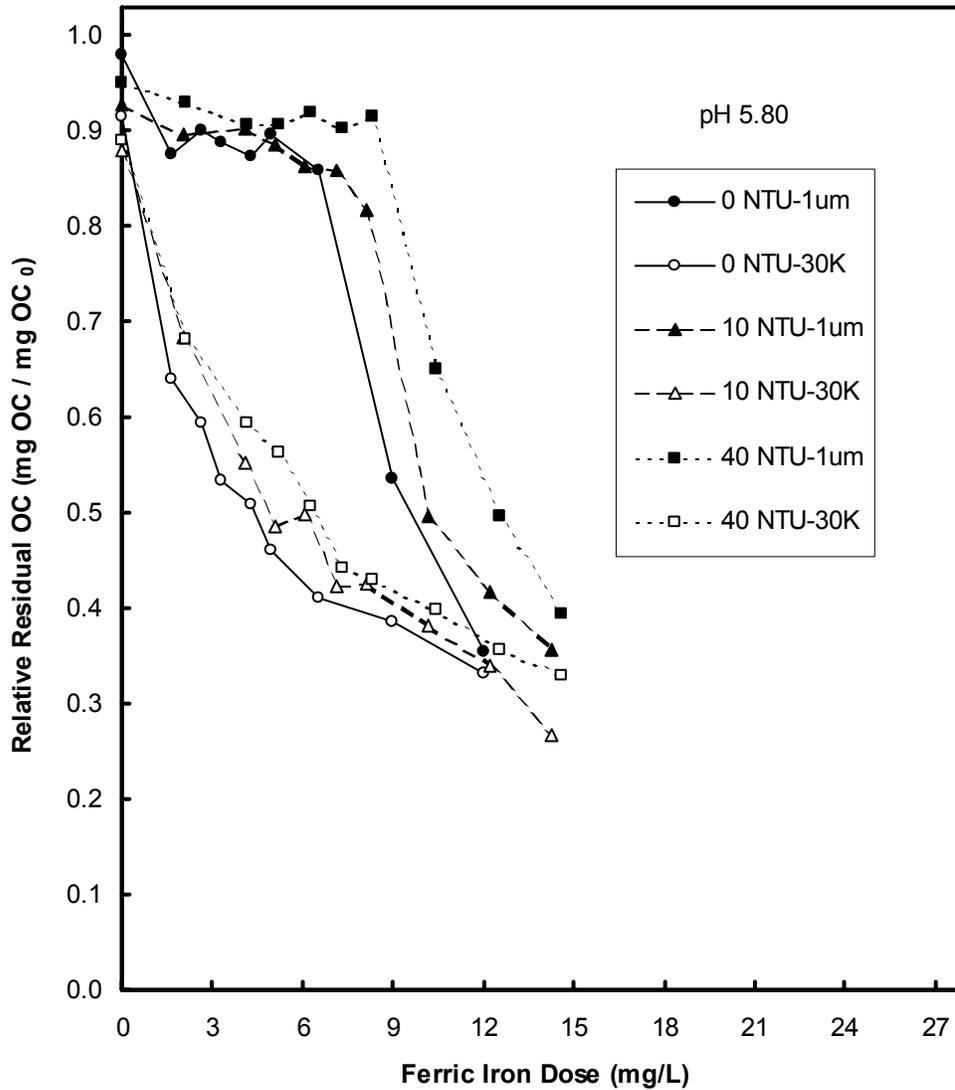


Figure 6a. Colloidal OC formation as a function of ferric iron coagulant dose and added turbidity. Untreated waters contained 5 mg/L DOC.

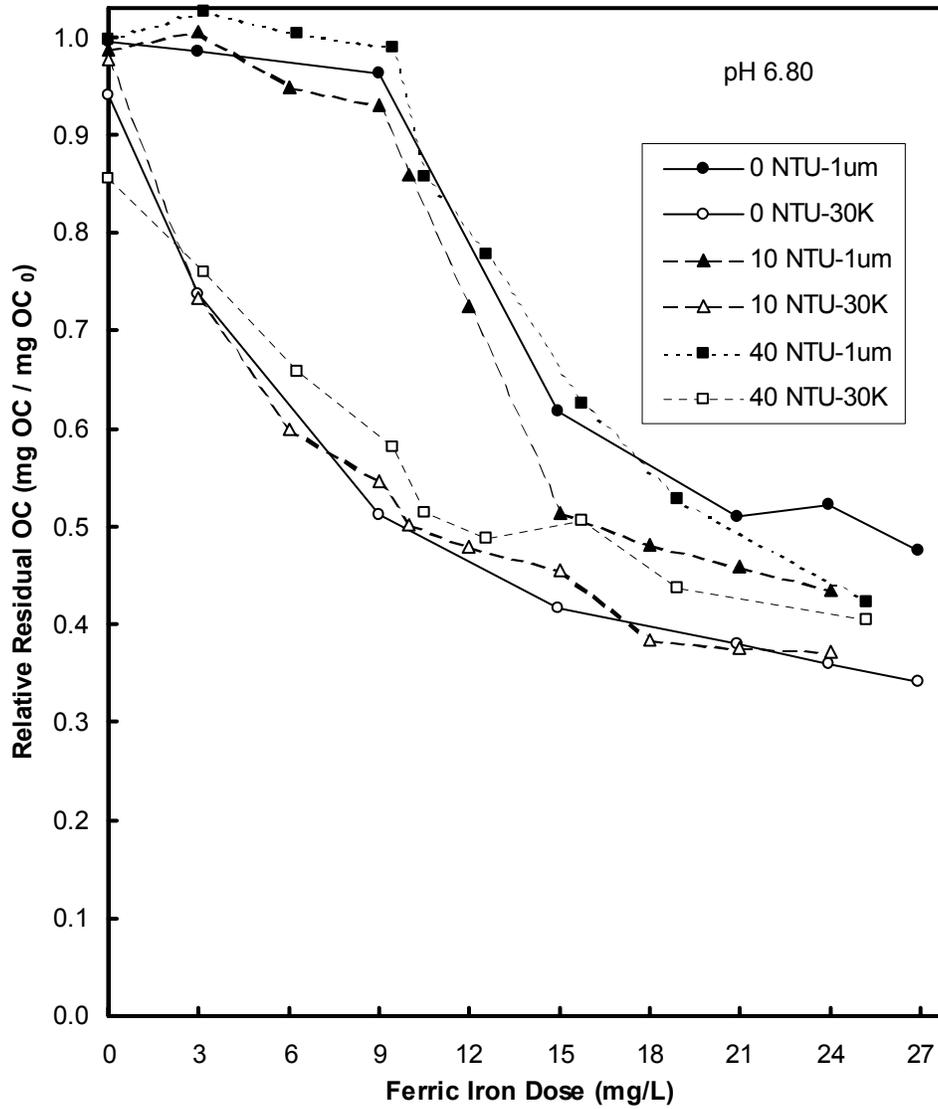


Figure 6b. Colloidal OC formation as a function of ferric iron coagulant dose and added turbidity. Untreated waters contained 5 mg/L DOC.

The initial turbidity level strongly influenced residual turbidity in settled waters, with residual turbidity increasing as bentonite added to untreated waters increased. Due to slight settling of the added bentonite clay, residual turbidity in the control jars (0 mg/L ferric iron dose) was slightly lower than before treatment, as shown in Figure 7. Colloidal matter formation was also evident in the residual turbidity data as seen by the initial increase in residual turbidity up to a coagulant dose of 6 to 9 mg/L iron. This initial increase in turbidity reflects incorporation of organic matter and coagulant metal in colloidal material, as well as potential incorporation of bentonite. However, colloid formation displayed different trends with pH in the presence and absence of bentonite: when no bentonite was added to the untreated water residual turbidity and hence colloid formation was higher at pH 6.8, whereas if bentonite was added to the untreated water residual turbidity and colloid formation were enhanced at pH 5.8.

Formation of colloidal matter was also evident from residual iron analyses; however, the observed amount of colloidal iron present was essentially unaffected by initial turbidity level (Figure 8). As expected for the pH range used here, very low soluble iron concentrations ( $< 0.1$  mg/L Fe) were observed for all initial turbidity conditions. The maximum residual iron for all initial turbidity conditions occurred at a ferric iron dose in the range of 6 to 9 mg/L. Incorporation of coagulant iron into colloidal matter was therefore maximized in this dose range. Often as much as 80 to 90% of the iron added as a coagulant was found to reside in this colloidal region.

Collectively, the residual organic matter, turbidity, and coagulant iron data shown in Figures 6 to 8 demonstrate the influence of coagulant dose on colloid formation. In each case, colloid formation increased up to a ferric iron coagulant dose of 6 to 9 mg/L, and then dramatically decreased at higher doses. This phenomenon implies that organic matter, coagulant metal, and bentonite were all simultaneously incorporated in the colloidal fraction at coagulant doses below the envelope shoulder, and then progressively shifted to the particulate fraction at higher coagulant doses. However, the exact mechanism of colloid formation and sequence of organic matter, coagulant, and bentonite incorporation in colloidal matter cannot be unambiguously determined from these data.

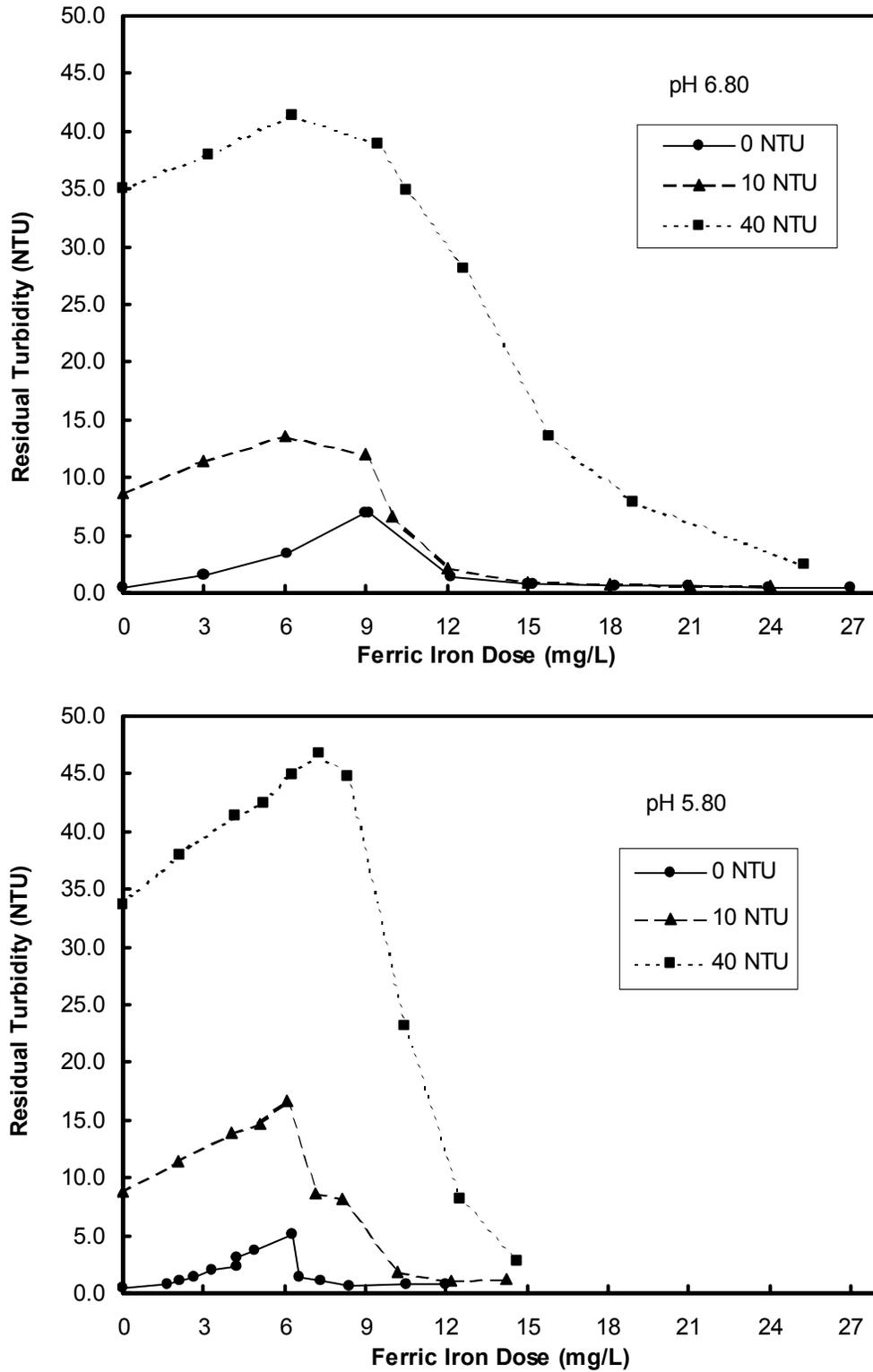


Figure 7. Residual turbidity as a function of ferric iron coagulant dose and added turbidity. Untreated waters contained 5 mg/L DOC.

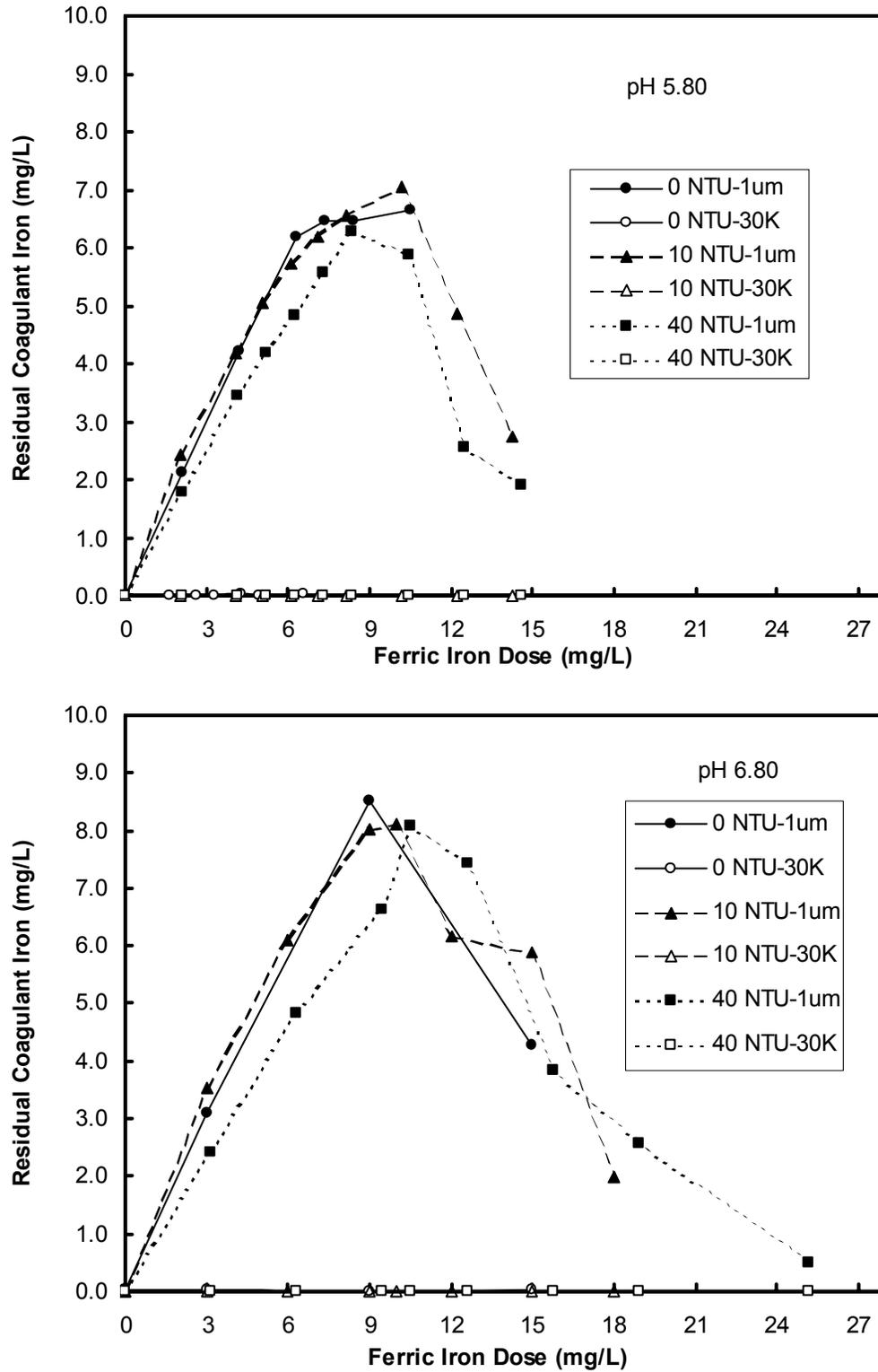


Figure 8. Residual iron as a function of ferric iron coagulant dose and added turbidity. Untreated waters contained 5 mg/L DOC.

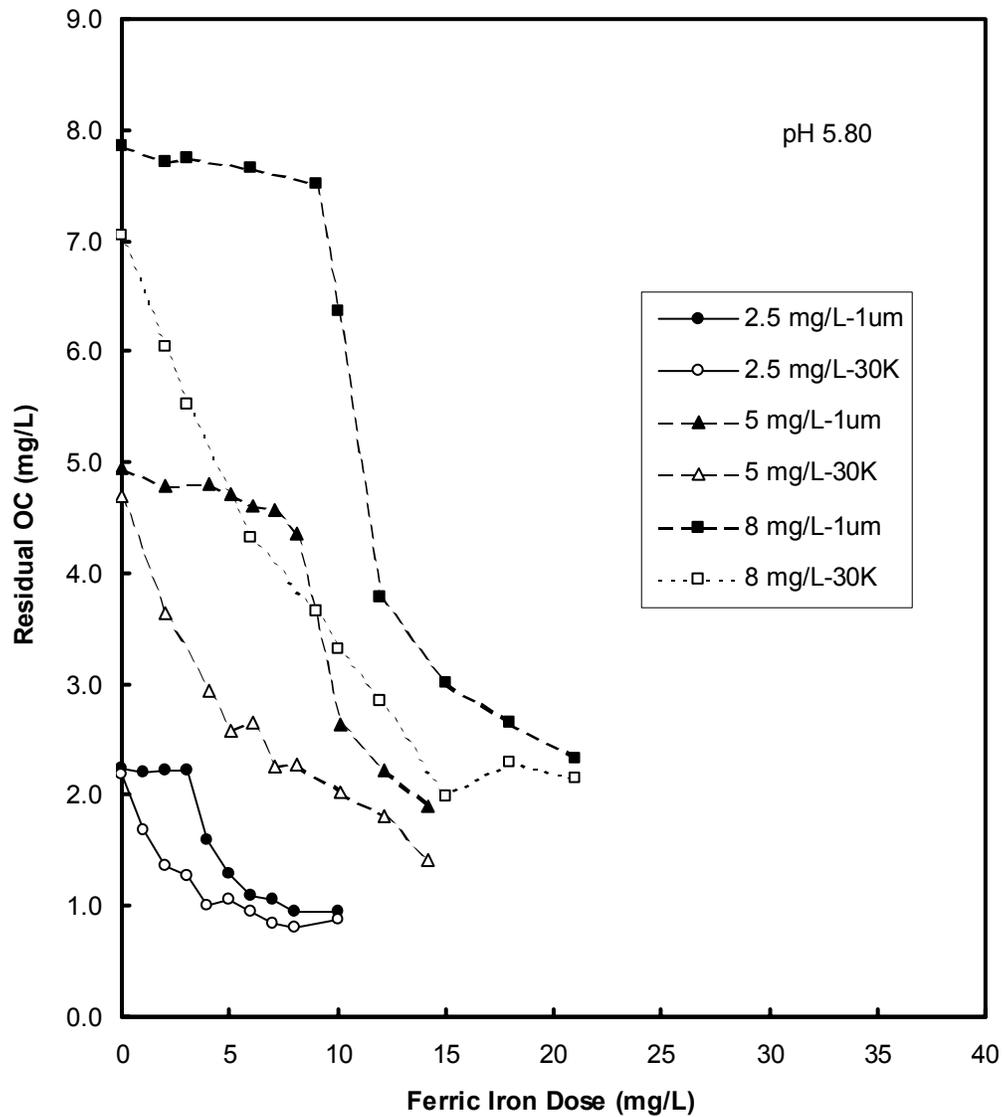


Figure 9a. Colloidal OC formation as a function of ferric iron coagulant dose and organic matter concentration. Untreated waters contained 10 NTU turbidity and DOC concentration as indicated in legend.

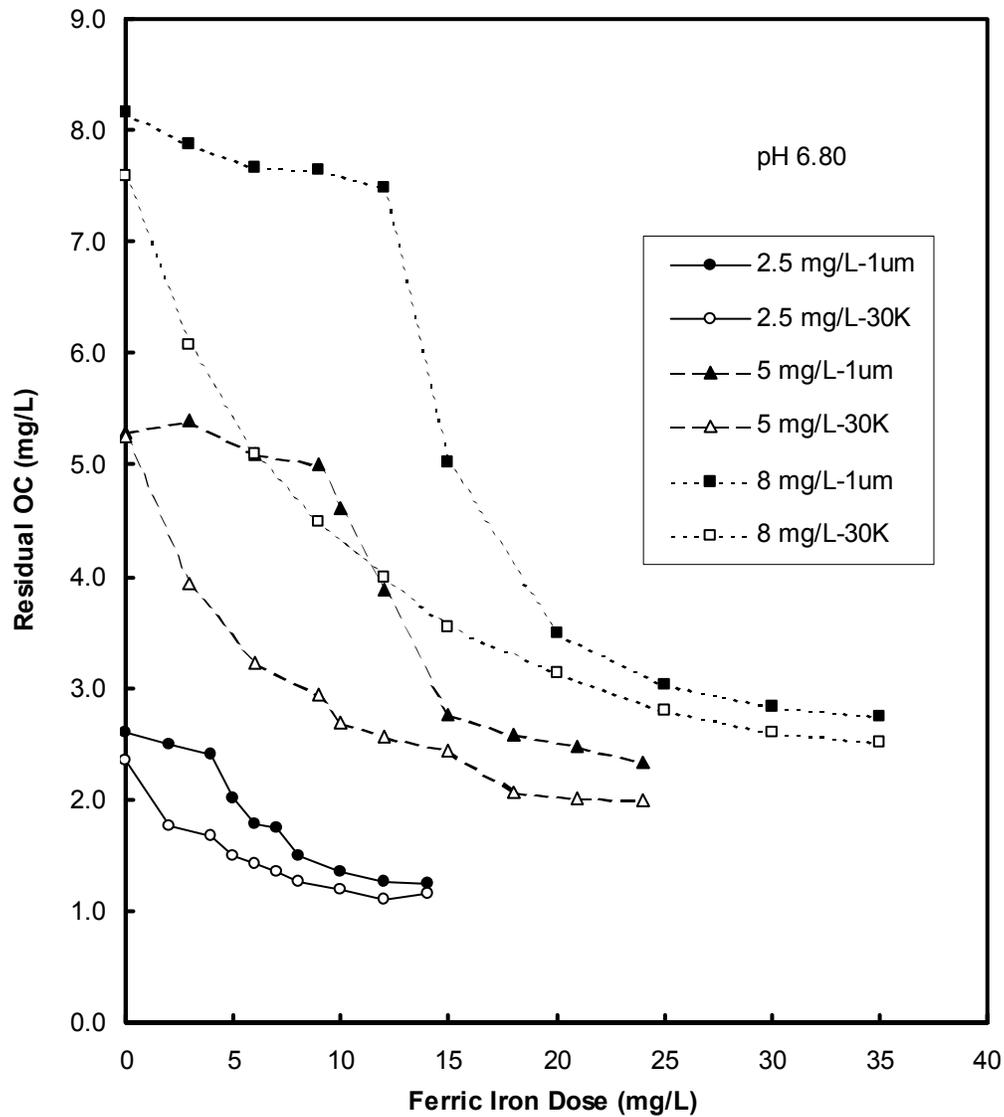


Figure 9b. Colloidal OC formation as a function of ferric iron coagulant dose and organic matter concentration. Untreated waters contained 10 NTU turbidity and DOC concentration as indicated in legend.

*Effect of Organic Matter Concentration on Colloid Formation*

The SUVA of the organic matter stock solutions was quantified to ensure that the organic matter stock solutions were chemically similar. The mean SUVA values for the three stock solution was 3.79 L/mg\*min (standard deviation 0.06). For waters with SUVA of 4 or higher at pH 5.5 to 6, approximately 2 mg iron per mg DOC has been found to be the requirement for effective coagulation (Edzwald 1994). This thesis study found consistent results, as at pH 5.8, 2 mg ferric iron per mg DOC was required to remove the percentage TOC, 40%, regulated by the D/DBP rule (Figure 10a).

The amount of OC incorporated in colloidal matter was significantly impacted by the initial DOC concentration of untreated waters. The colloidal envelope height and the colloidal dose range increased with increasing OC concentration at both pH values studies, as shown in Figure 9. However, the shape of the envelopes was not affected by the OC concentration, which suggests a similar mechanism of OC incorporation in colloidal matter for the untreated DOC concentration range studied. The trend of enhanced OC removal at lower pH was again observed, as the minimum residual organic fractions were slightly lower at pH 5.8 compared to pH 6.8.

When normalized to the initial DOC, coagulant performance with respect to residual OC phase shift was only minimally affected by untreated water DOC concentration as shown in Figure 10. For all of the initial DOC concentrations, the maximum colloidal envelope height for pH 5.8 occurred at approximately 1.0 mg iron / mg initial DOC and for pH 6.8, the maximum occurred at approximately 1.5 mg iron / mg initial DOC. This phenomenon suggests that the OC controlled coagulant demand for the waters treated here, as proportional increases in DOC and coagulant dose resulted in very similar OC phase change behavior. A slight trend toward enhanced coagulant performance (lower minimum residual organic carbon fraction with increasing initial DOC) was observed at both pH values studied. This enhancement in coagulant performance may be related to increased flocculation of colloids with increasing colloidal matter concentration, rather than a fundamental difference in the mechanism or extent of DOC incorporation in these colloids.

Residual turbidity data also demonstrate the increased incorporation of organic carbon into colloidal matter with increased DOC concentration (Figure 11). At each pH

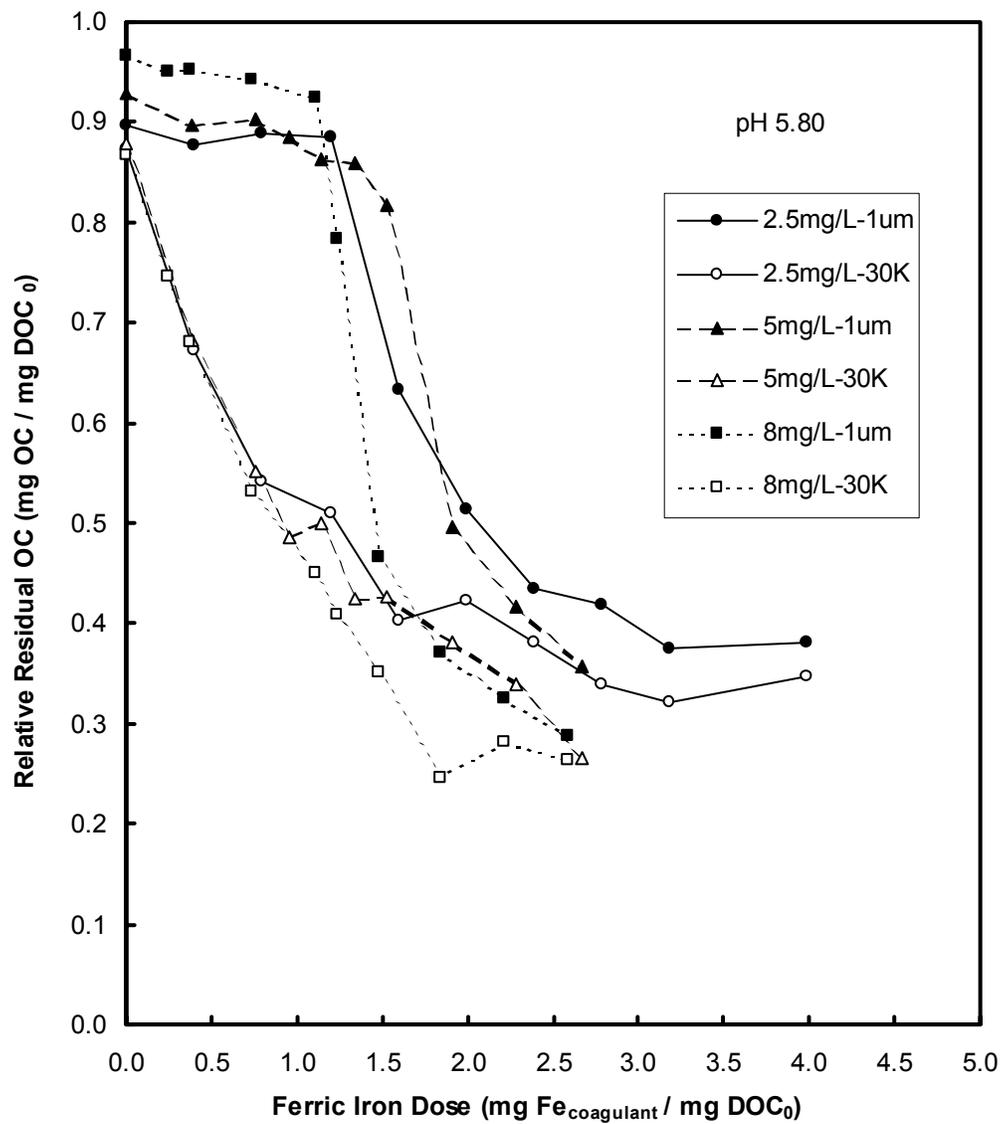


Figure 10a. Colloidal OC formation as a function of normalized ferric iron coagulant dose and organic matter concentration. Untreated waters contained 10 NTU turbidity and DOC concentration as indicated in legend.

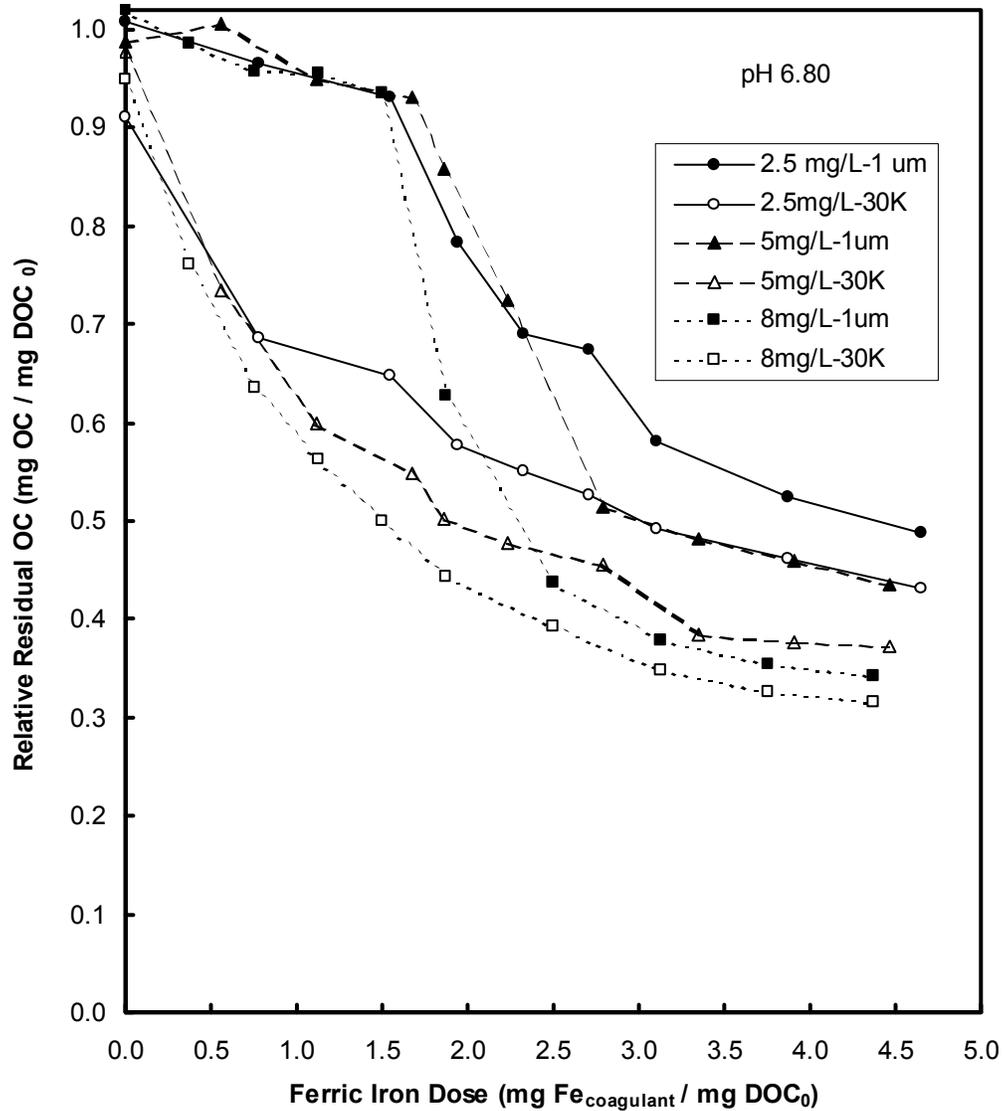


Figure 10b. Colloidal OC formation as a function of normalized ferric iron coagulant dose and organic matter concentration. Untreated waters contained 10 NTU turbidity and DOC concentration as indicated in legend.

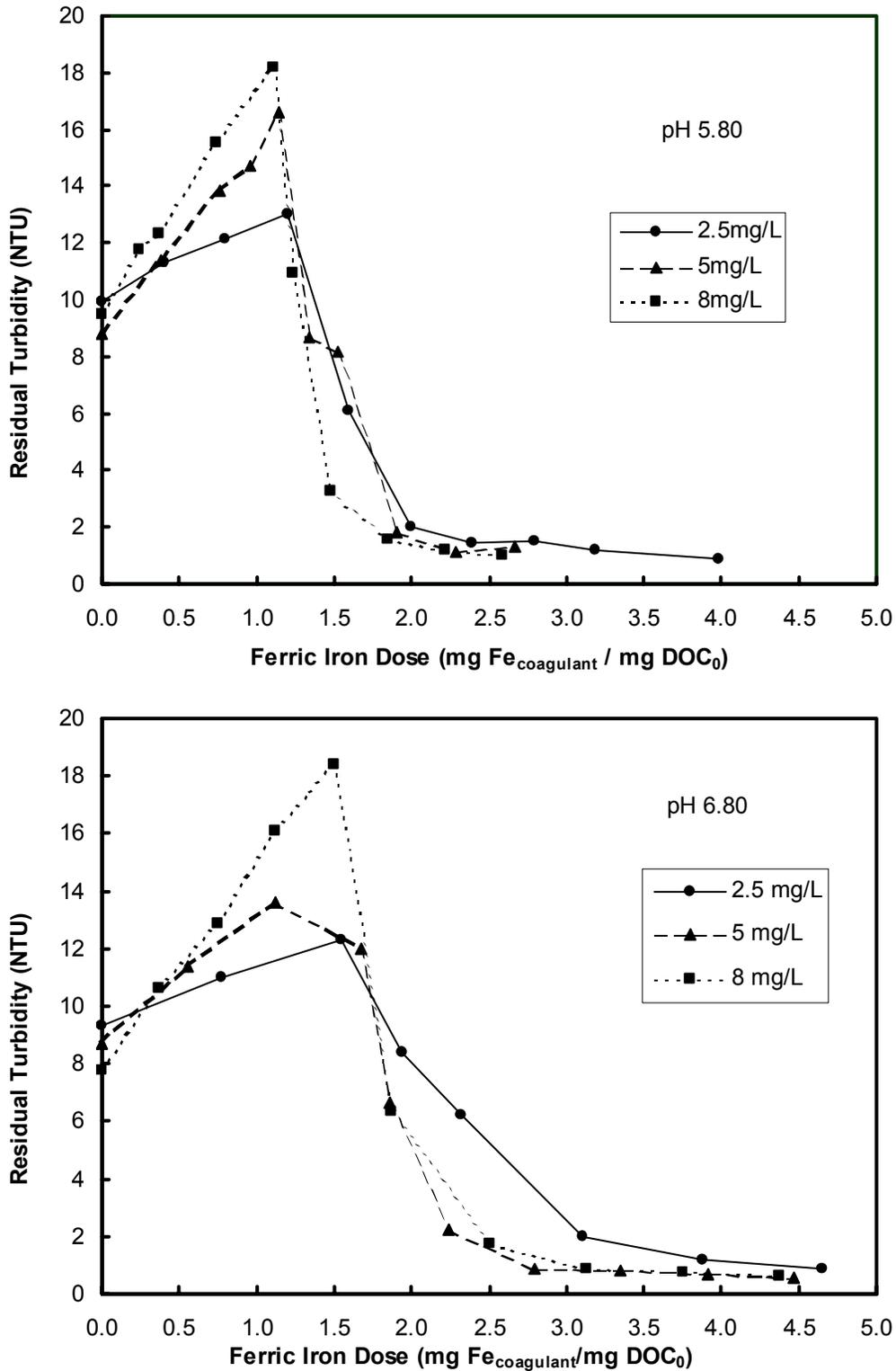


Figure 11. Residual turbidity as a function of normalized ferric iron coagulant dose and organic matter concentration. Untreated waters contained 10 NTU turbidity and DOC concentration as indicated in legend.

examined, the maximum residual turbidity observed corresponded to the maximum colloidal envelope height and the subsequent rapid drop in turbidity corresponded to the shoulder of colloidal matter envelope, illustrating the phase change of organic carbon between colloidal and particulate fractions.

As the pH was increased, the coagulant demand, and therefore the colloidal dose range, increased (Figure 10). The maximum colloidal envelope and the maximum residual turbidity were shifted to higher coagulant doses for pH 6.8 over pH 5.8. This increased coagulant demand at a higher coagulation pH was consistent with the results from the coagulation pH, coagulant dose, and initial turbidity studies.

#### *Effect of Temperature on Colloid Formation*

Temperature did not have a significant effect on colloidal matter formation, as the residual organic carbon envelopes were very similar at 25°C and 4°C, as seen by comparison of data presented in Figures 9 and 12. When normalized to untreated water DOC, the 4°C colloidal matter envelopes were nearly identical at each pH (Figure 13) and very similar to that at 25°C (Figure 10). Comparing the 25°C (Figure 11) and 4°C (Figure 14) residual turbidity data also showed little impact of temperature on colloid formation. In order to more directly compare the effect of temperature on colloid formation, the colloidal envelopes were replotted in pairs for each organic matter concentration and pOH as given in Figures 15, 16, and 17. No systematic differences in shape of colloidal envelope were seen versus temperature when ferric sulfate used as coagulant. This finding was consistent with previous research that found decreasing temperature did not significantly affect ferric coagulation (Morris et al. 1984; Edzwald 1993; Edzwald 1994). Because colder temperatures did not significantly affect ferric coagulants, the suggested operating pH range of 5.6 to 6 was applicable for ferric coagulation in warm and cold waters (Edzwald 1993).

The effect of increased coagulant demand from increasing pH was also found at 4°C coagulation. The maximum colloidal envelope heights and the maximum turbidity levels were shifted to higher coagulant doses for pH 7.54 relative to pH 6.54 (Figures 13 and 14). This increased coagulant demand at a higher coagulation pH was consistent with the results from the coagulation pH, coagulant dose, the initial turbidity, and the initial organic matter concentration studies.

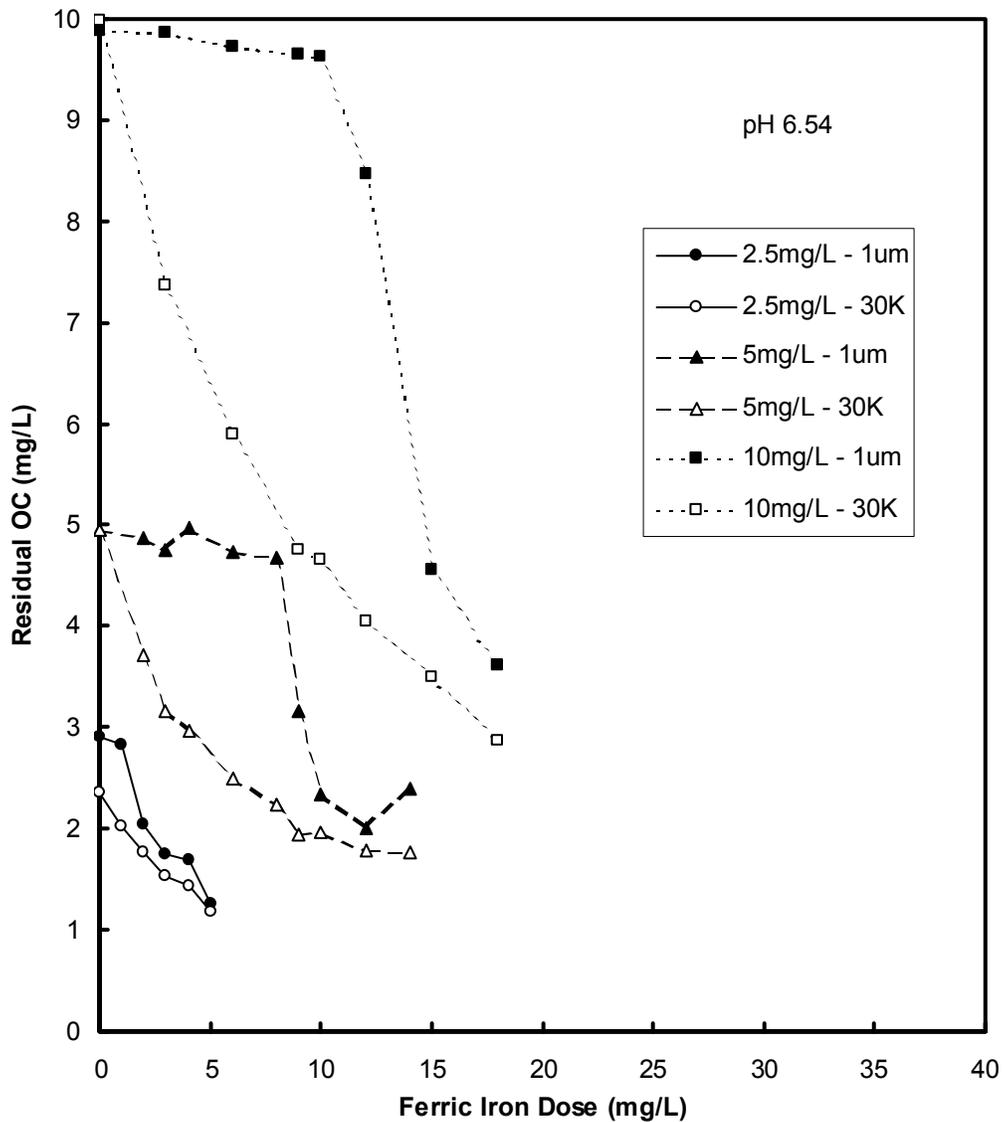


Figure 12a. Colloidal OC formation as a function of ferric iron coagulant dose and organic matter concentration at pH 6.54 and 4°C (same pOH as pH 5.80 at 25°C). Untreated waters contained 10 NTU turbidity and DOC concentration as indicated in legend.

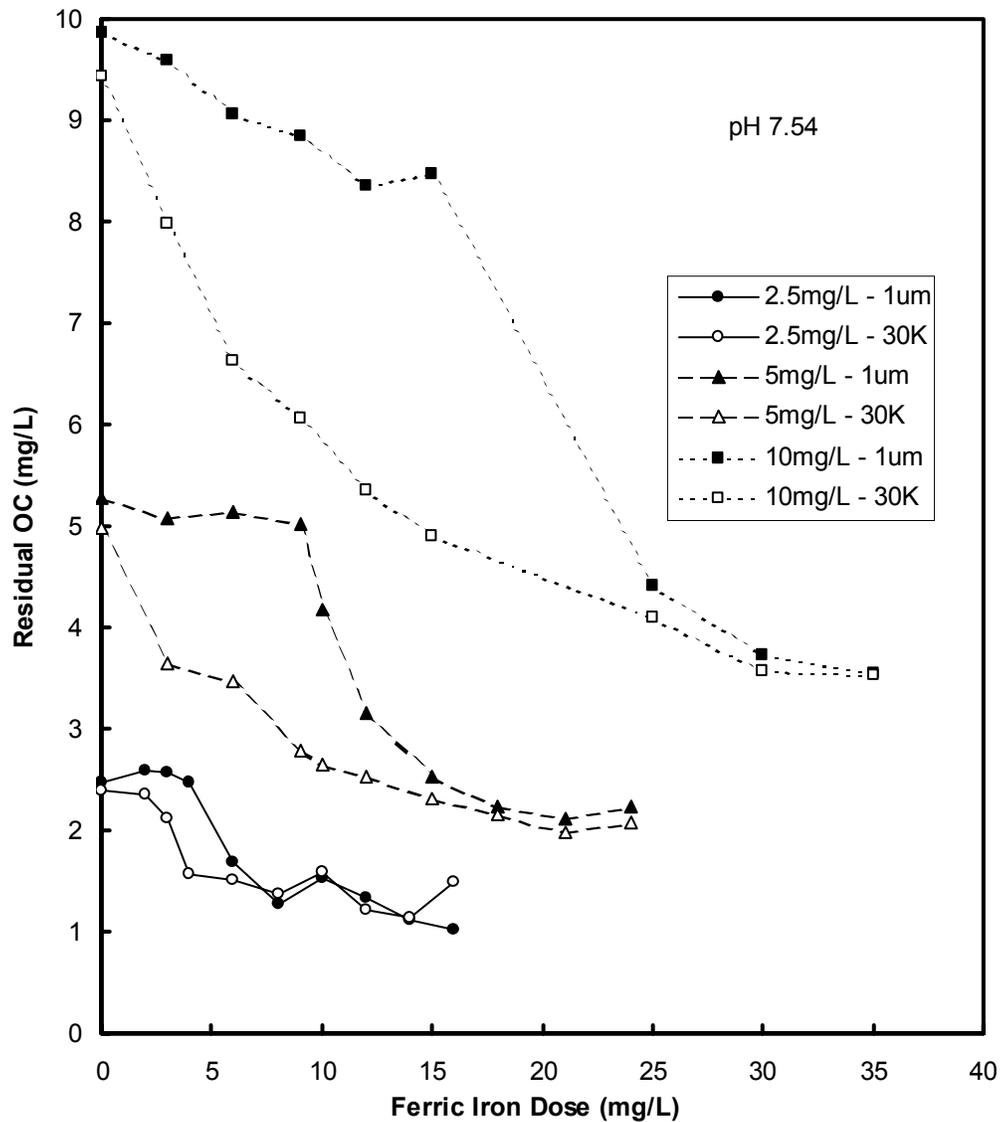


Figure 12b. Colloidal OC formation as a function of ferric iron coagulant dose and organic matter concentration at pH 7.54 and 4°C (same pOH as pH 6.80 at 25°C). Untreated waters contained 10 NTU turbidity and DOC concentration as indicated in legend.

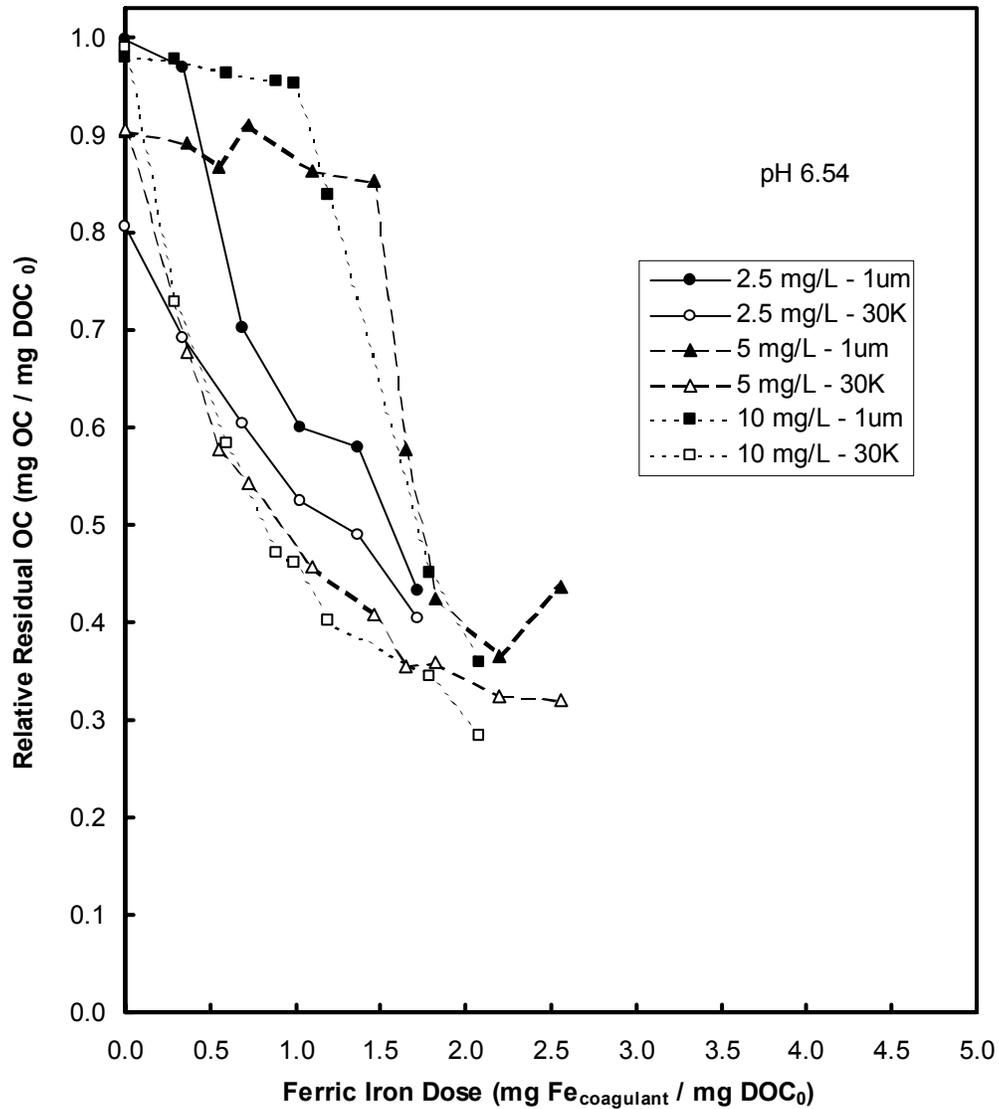


Figure 13a. Colloidal OC formation as a function of normalized ferric iron dose and organic matter concentration at pH 6.54 and 4°C (same pOH as pH 5.80 at 25°C). Untreated waters contained 10 NTU turbidity and DOC concentration as indicated in legend.

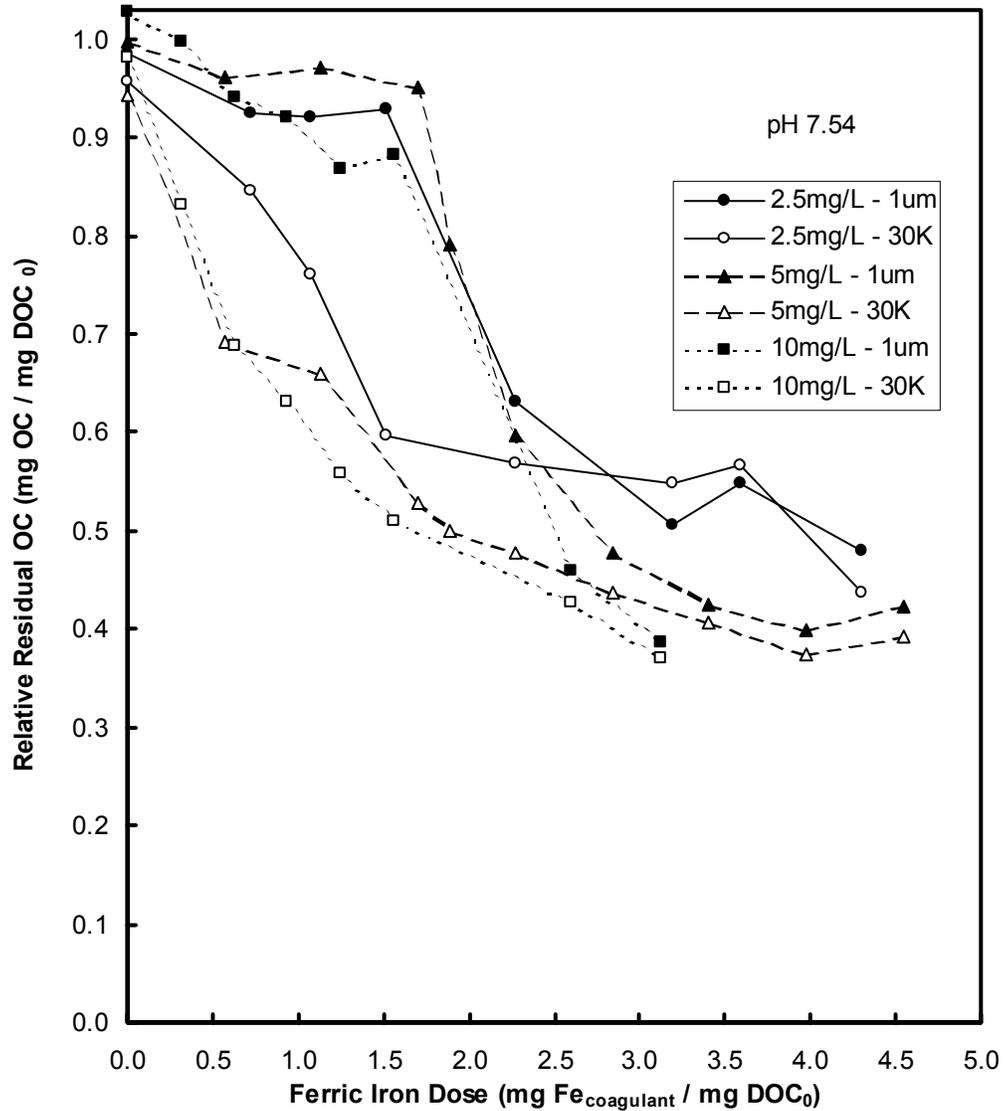


Figure 13b. Colloidal OC formation as a function of normalized ferric iron dose and organic matter concentration at pH 7.54 and 4°C (same pOH as pH 6.80 at 25°C). Untreated waters contained 10 NTU turbidity and DOC concentration as indicated in legend.

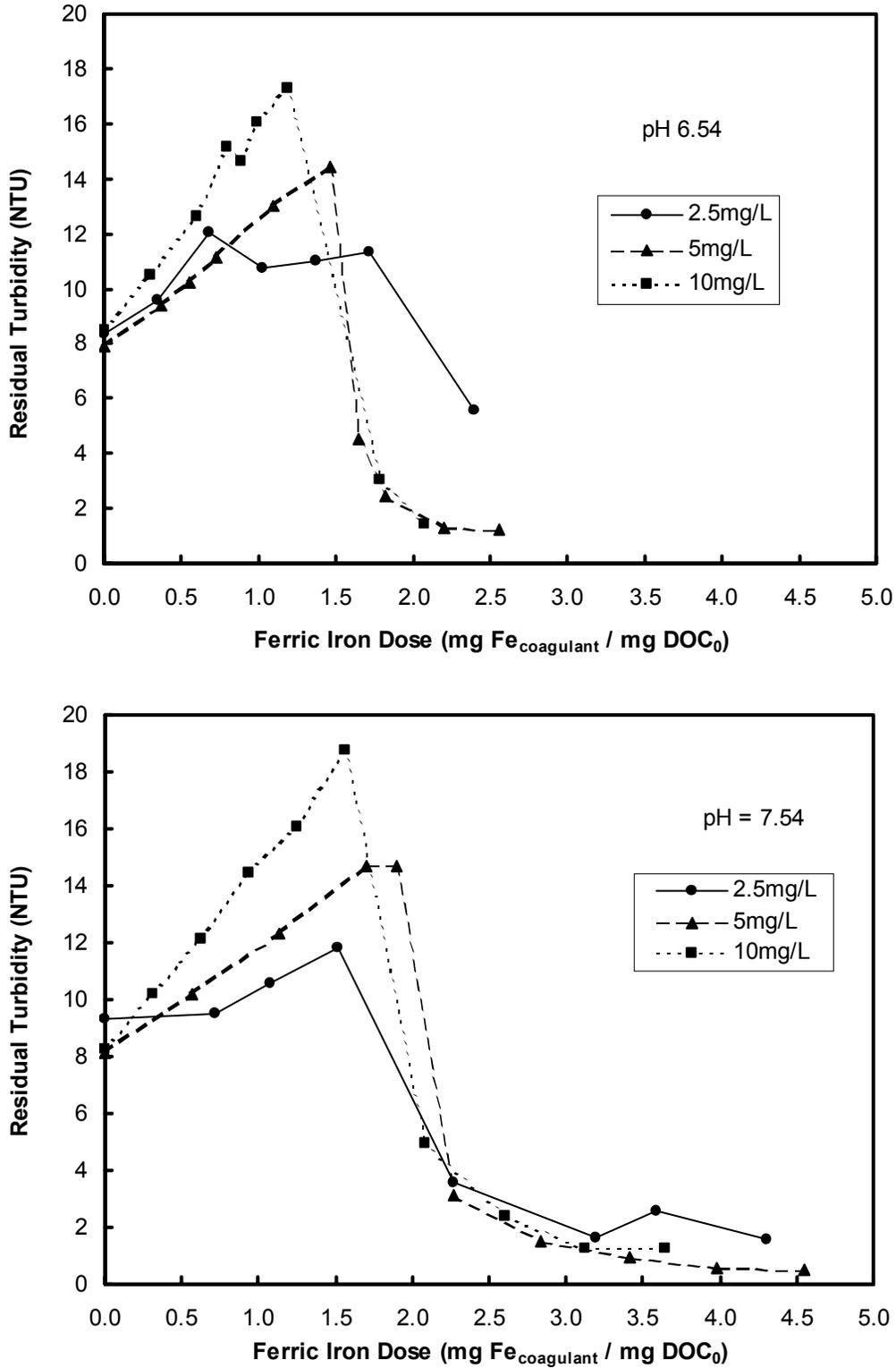


Figure 14. Residual turbidity as a function of normalized ferric iron coagulant dose and organic matter concentration at 4°C (pH 6.54 same pOH as pH 5.80 at 25°C and pH 7.54 same pOH as pH 6.80 at 25°C). Untreated waters contained 10 NTU turbidity and DOC concentration as indicated in legend.

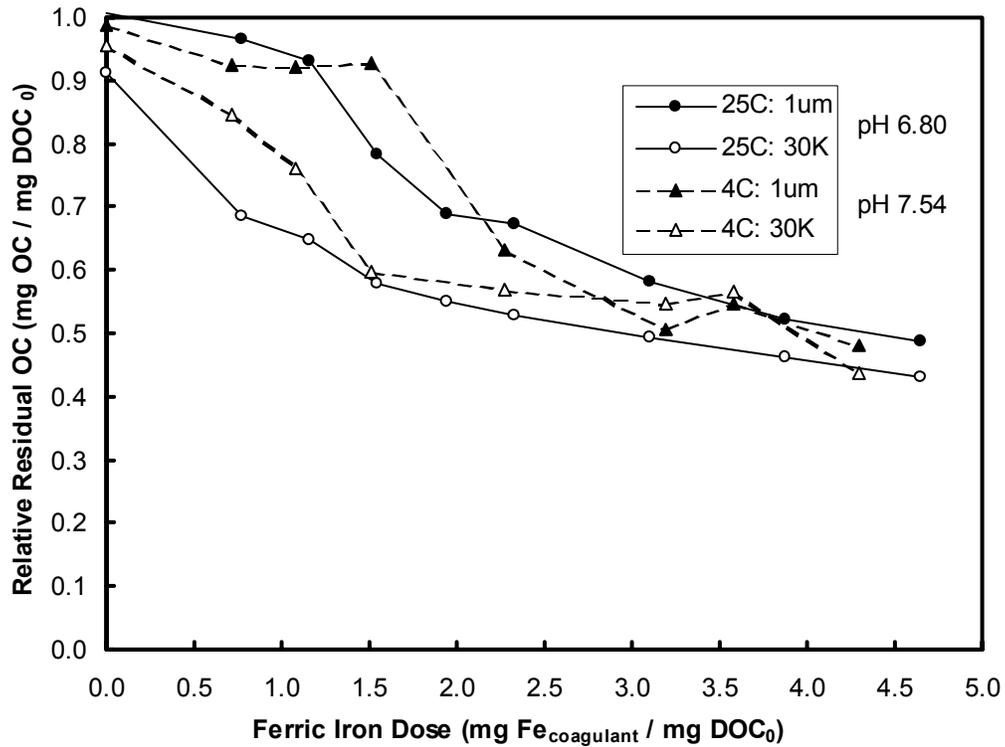
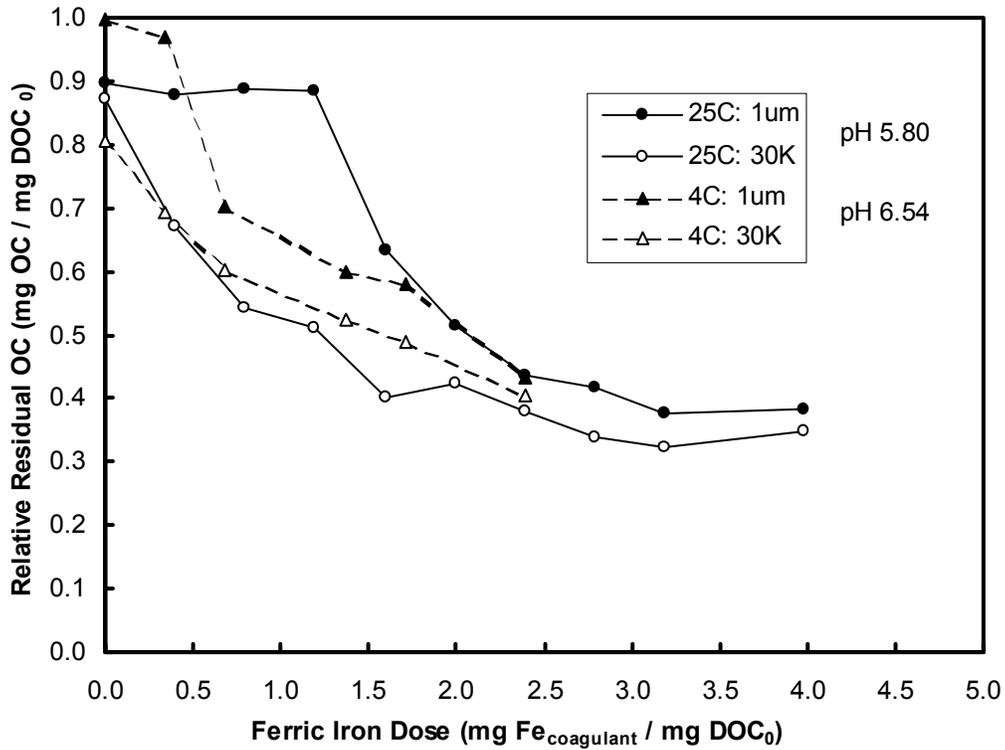


Figure 15. Colloidal OC formation as a function of normalized ferric iron coagulant dose and temperature (pH 6.54 same pOH as pH 5.80 at 25°C and pH 7.54 same pOH as pH 6.80 at 25°C). Untreated waters contained 2.5 mg/L DOC and 10 NTU turbidity.

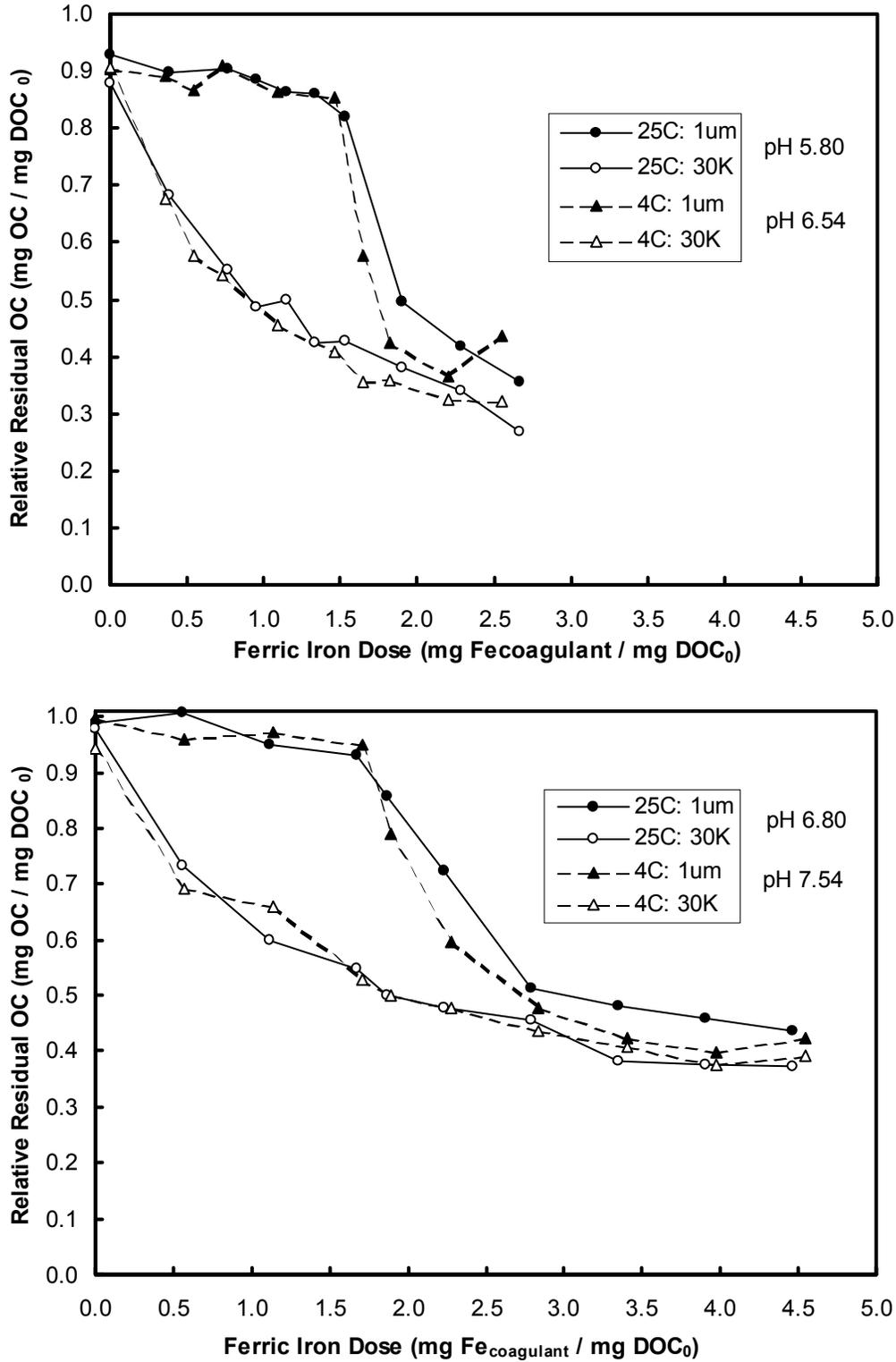


Figure 16. Colloidal OC formation as a function of normalized ferric iron coagulant dose and temperature (pH 6.54 same pOH as pH 5.80 at 25°C and pH 7.54 same pOH as pH 6.80 at 25°C). Untreated waters contained 5 mg/L DOC and 10 NTU turbidity.

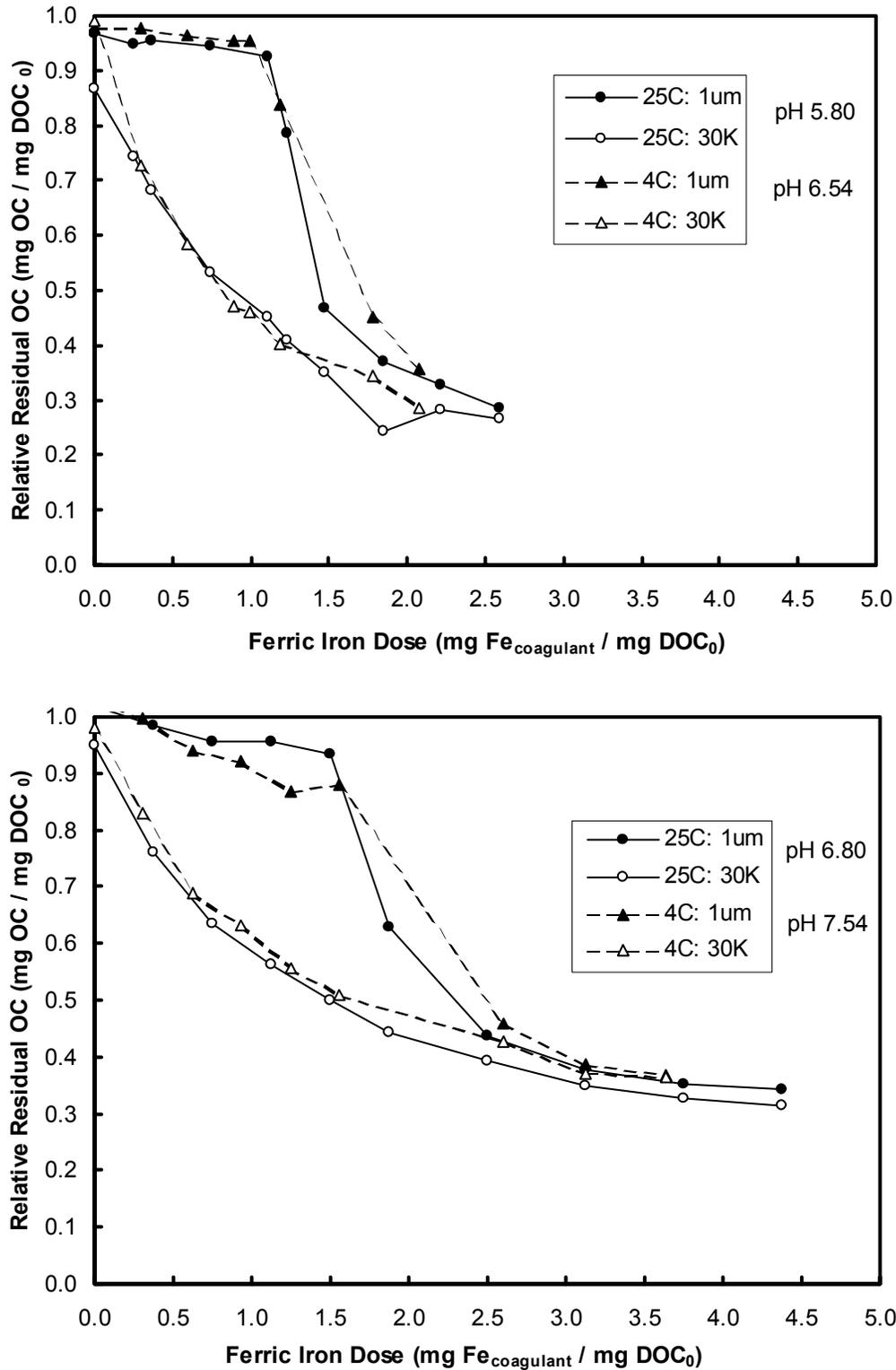


Figure 17. Colloidal OC formation as a function of normalized ferric iron coagulant dose and temperature (pH 6.54 same pOH as pH 5.80 at 25°C and pH 7.54 same pOH as pH 6.80 at 25°C). Untreated waters contained 10 mg/L DOC and 10 NTU turbidity.

### **Colloidal Iron-Bound Organic Matter Characterization**

Attempts to characterize the colloidal OC formed during iron sulfate coagulation were made to gain information relevant for colloidal OC removal. Surface charge data regarding the colloids were attempted from zeta potential analyses using capillary electrophoresis and laser Doppler velocimetry. Size of the colloids was assessed using dynamic light scattering and photon correlation spectroscopy. Together, the zeta potential and size could aid in the selection of an effective polymer.

#### *Zeta Potential*

The zeta potential of the colloids was determined as a function of water treatment stage and DOC concentration; data are listed in Table 3. In the presence of dissolved organic matter, zeta potential did not change significantly during treatment. However, in the absence of dissolved organic matter, zeta potential became measurably more positive within the first minute of coagulation. The differences in zeta potential could be due to shearing of the organic matter containing colloids. It is unknown whether the colloidal organic matter was tightly bound or loosely associated with coagulant metal and clay colloids. The sample injection syringe and the zeta potential and size analyses capillary tube were both very narrow. These narrow channels caused an increase in the velocity of the colloidal samples. This increased velocity could have been great enough to shear loosely associated colloidal organic matter.

#### *Size Analysis*

Sizing analysis was performed on the bentonite used to adjust turbidity of untreated waters. Because settling of bentonite particles larger than approximately 1  $\mu\text{m}$  may interfere with sizing by photon correlation spectroscopy, the stock suspension was prefiltered through a 0.45  $\mu\text{m}$  glass fiber filter. Approximately, 53% of the turbidity remained after filtration. The sizing analysis indicated an average size of colloidal bentonite particles in the bentonite slurry of 0.4  $\mu\text{m}$ .

Colloidal matter in untreated and treated waters were also analyzed for size. Samples were analyzed from test waters containing 5 mg/L DOC and 10 NTU turbidity subjected to coagulation with 5 mg/L iron. These sizing analyses were not conclusive because the signal from the colloidal matter below the detection limit ( $< 2100$  kilocounts per second). The low signal level indicated that there were not enough particles in the

Table 3  
Zeta Potential as a function of water treatment stage,  
iron sulfate coagulant dose, and organic matter concentration

Test Water		Average Zeta Potential (mV)						
Ferric Iron Dose (mg/L)	Added DOC (mg/L)	untreated	coagulation (1 min.)	coagulated	1st stage flocculation (5 min.)	2nd stage flocculation (5 min.)	flocculated	settled
5	5	-37.1	---	-37.1	---	---	-37.1	-37.4
15	4	-37.9	-38.4	-37.1	-38.3	-37.9	-36.4	-36.9
15	0	-35.3	-27.5	-28.1	-28.2	-29.0	-27.3	-26.6

Test waters contained 10 NTU turbidity and were coagulated at pH 6.8 and 25°C.

sample or that there was inadequate light reflection of the organic matter to measure colloid size accurately.

The inability to obtain an accurate colloidal zeta potential and colloidal size could have been due to shearing of the colloids. If the colloidal organic matter was loosely associated with coagulant metal and clay colloids, then the increased velocity due to the sample injection into narrow capillary tubes could have been great enough to shear loosely associated colloidal organic matter.

#### **Enhanced Removal of Colloidal Matter through Polymer Addition**

The impact of polymer addition for enhanced organic matter removal was evaluated using coagulant and flocculant aid polymers. Waters containing 5 mg/L initial DOC and 10 NTU initial turbidity at 25°C were chosen for coagulation at pH 6.8 to produce colloids (Figures 6b and 7). The goal of polymer addition was to achieve the 40% organic carbon removal regulated by the D/DBP rule for these untreated water conditions (U.S. 1998). A 40% organic carbon removal was achieved for these conditions with 15 mg/L ferric iron. The objective of this study was to coagulate with one-third of the iron dose along with a polymeric coagulant or flocculant aid in order to achieve the 40% organic carbon removal.

Colloidal organic matter was formed during coagulation with 5 mg/L ferric iron as seen by the separation in 1  $\mu\text{m}$  OC and the 30 KDa OC data with no added polymer (Figures 18 and 20). Colloidal formation was supported by the increased turbidity level above the initial 10 NTU turbidity (Figures 19 and 21). In addition, the relative residual 1  $\mu\text{m}$  and 30 KDa organic carbon concentrations and the residual turbidity level without polymer were very similar to the previous jar test at pH 6.8 and 25°C with 5 mg/L DOC and 10 NTU turbidity coagulated with 5 mg/L ferric iron (Figures 6b and 7).

The three polymers chosen to remove the colloidal organic matter differed by charge and molecular weight. The Superfloc® C-572 polymer was a cationic, low molecular weight (30,000 amu) polyquaternary amine polymer in water. Because of its low molecular weight, C-572 was considered a coagulant aid and was added ninety seconds into rapid mix. The bentonite and DOC in the untreated waters were known to be negatively charged and so, it was hypothesized that the colloids were also negatively charged. The effective polymer dose to achieve 40% organic carbon removal was

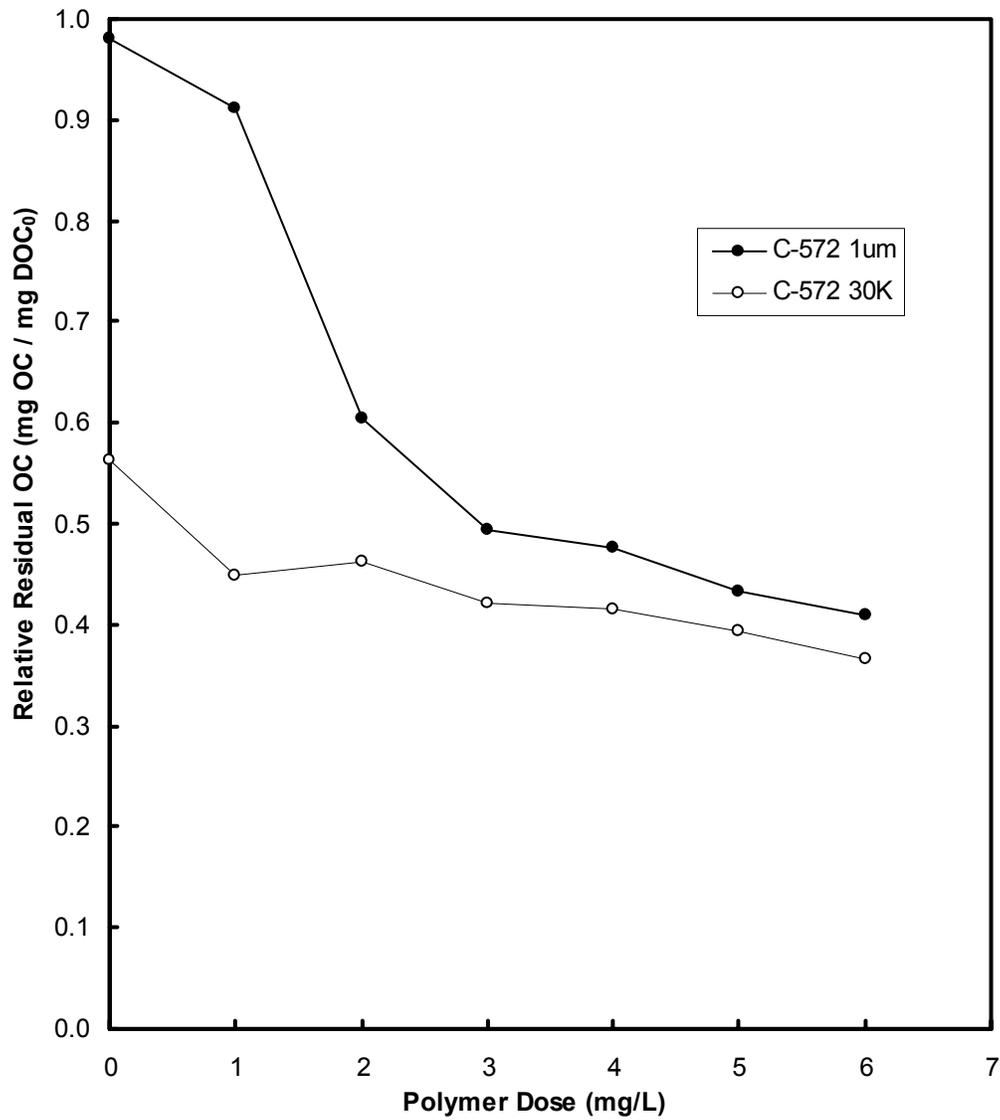


Figure 18. Colloidal OC formation as a function of polymer dose. Untreated waters contained 5mg/L TOC and 10 NTU turbidity. Coagulation at pH 6.80 with 5 mg/L ferric iron coagulant.

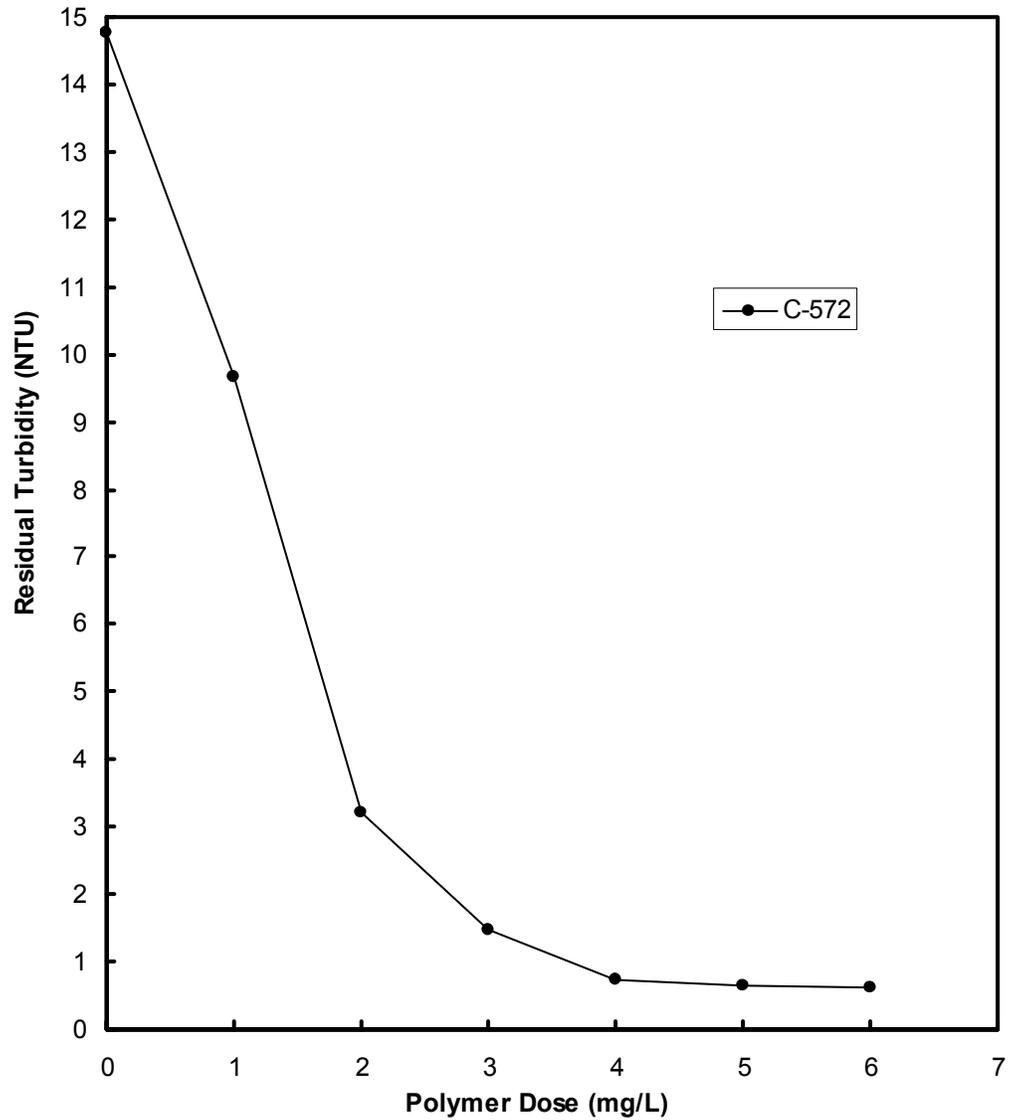


Figure 19. Residual turbidity as a function of polymer dose. Untreated waters contained 5mg/L TOC and 10 NTU turbidity. Coagulation at pH 6.80 with 5 mg/L ferric iron coagulant.

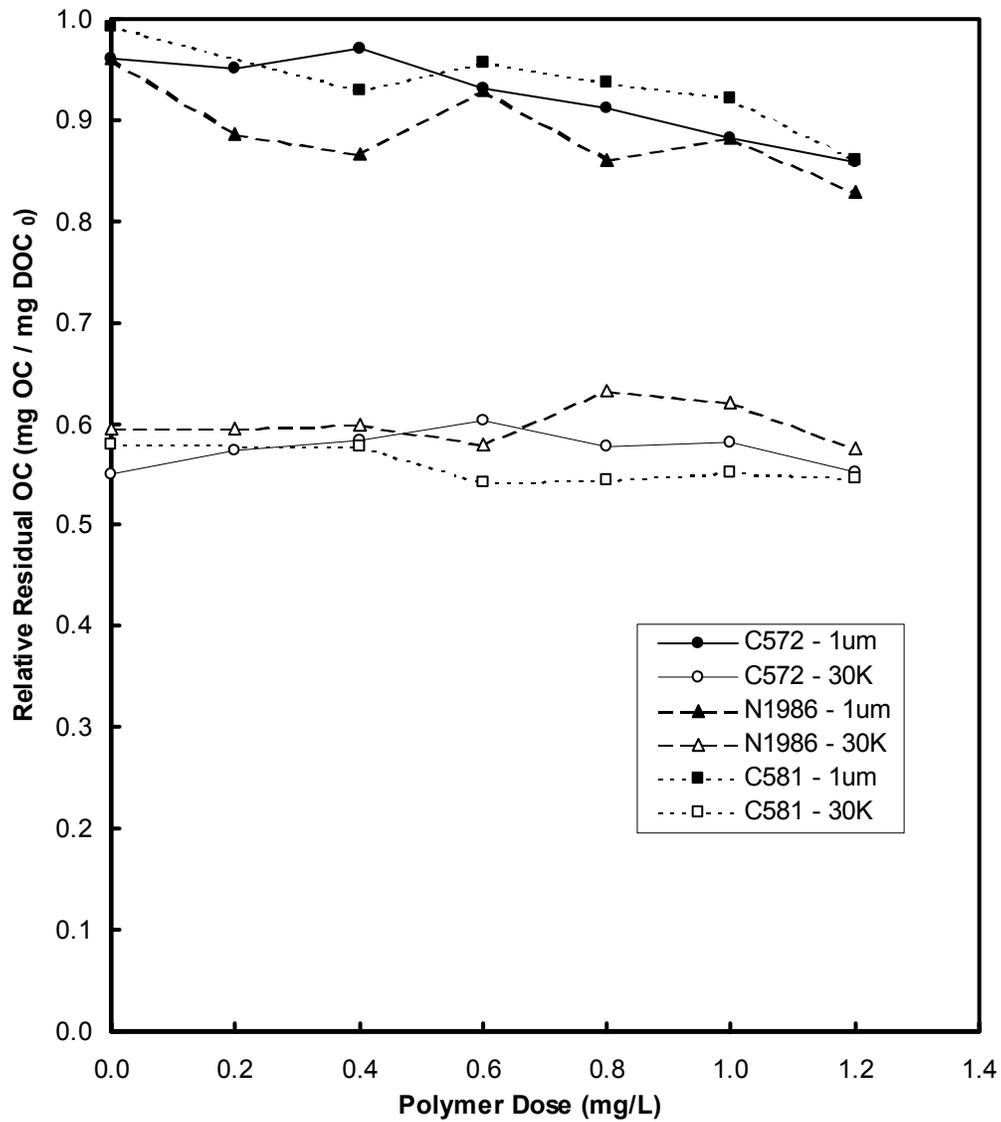


Figure 20. Colloidal OC formation as function of polymer dose.

Untreated waters contained 5mg/L TOC and 10 NTU turbidity.

Coagulation at pH 6.80 with 5 mg/L ferric iron coagulant.

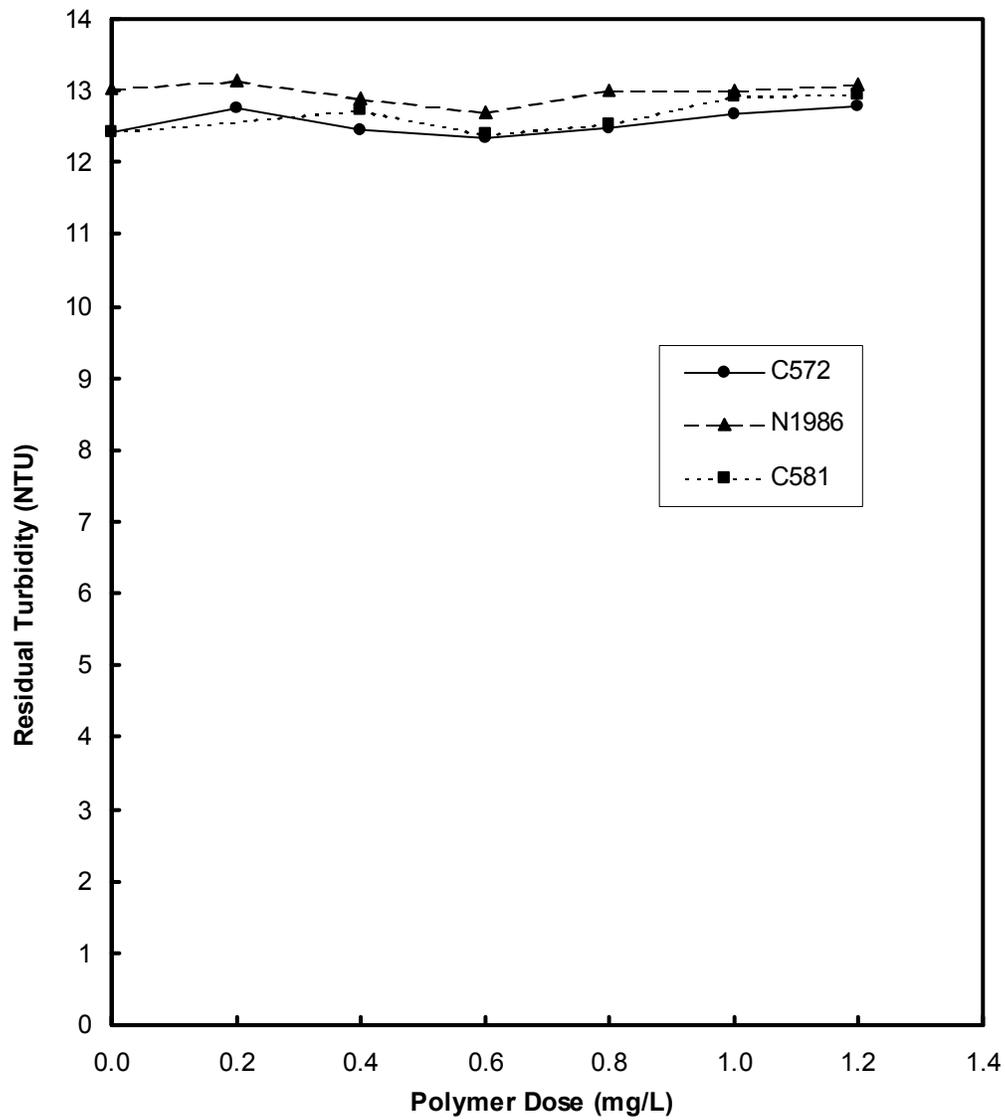


Figure 21. Residual turbidity as a function of polymer dose. Untreated waters contained 5mg/L TOC and 10 NTU turbidity. Coagulation at pH 6.80 with 5 mg/L ferric iron coagulant.

2 mg/L polymer; as illustrated in Figure 18. However, a dose of 4 mg/L polymer was required to achieve the less than 1 NTU turbidity maximum regulated National Primary Drinking Water Regulations (U.S. 2002) (Figure 19). Although acceptable OC removal and residual turbidity were achieved using C-572, the required polymer doses were considered to be greater than polymer doses typically used for drinking water treatment. As such, these doses would appear to be somewhat impractical due to expected cost considerations.

Higher molecular weight polymers were also utilized as flocculant aids in an attempt to meet enhanced DBP rule mandated DOC removal at lower primary coagulant doses. Two higher molecular weight polymers with differing charge characteristics were tested; nonionic Superfloc<sup>®</sup> N-1986 (polyacrylamide in water-in-oil emulsion polymer, 16,000,000 amu), and cationic Superfloc<sup>®</sup> C-581 (polyquaternary amine polymer, 250,000 amu). Both polymers were added three minutes into third stage flocculation at doses between 0 and 1.2 mg/L. These polymers did not achieve the target OC concentration or turbidity level in this dose range (Figures 20 and 21). For the purpose of comparison, the C-572 coagulant aid polymer results are also plotted in Figure 20 and 21. Both the coagulant aid and flocculant aid polymers exhibited similar residual OC and residual turbidity levels up to 1.2 mg/L polymer.

There are several possible explanations as to the lack of success with the cationic low molecular weight, nonionic high molecular weight, and cationic high molecular weight polymers. These involve polymer characteristics and polymer delivery techniques. The cationic polymers could have not been charged enough to neutralize the charge on the colloids, they could have been overly charged so that the colloids were restabilized, or the polymers could have been the same charge as the colloids. Also, the high molecular weight polymers could have been not large enough to convert the colloidal matter to particulate matter.

Notably, the polymers did not appear to remain suspended in the treated waters. All of the polymers contained significant amounts of OC. The 0.012% w/w (120 mg/L polymer) working solution of C-572 contained 24.5 mg/L OC, the N-1986 contained 31.4 mg/L OC, and the C-581 contained 25.3 mg/L OC. At the highest polymer dose, the organic carbon concentrations were 5 to 6% of the 5 mg/L initial DOC concentration.

Because they contained DOC, if the polymers had remained in solution, then the OC would have been increased above the initial DOC and the relative residual OC would have been greater than one.

Due to the lack of increased OC, the ineffectiveness of the polymers could also be due to their incorrect delivery. The polymers were large enough and their doses were small that if they were delivered incorrectly, then they would not remain in solution. A significant change in ionic strength can deactivate the polymers. The polymers were prepared with ultrapure water, so the ionic strength of the polymer solutions was close to 0 meq/L. However, the waters used for treatment contained 10 meq/L of added ionic strength. This significant increase in ionic strength from polymer solution to the test water could have deactivated the polymers.

Interestingly, the polymers intended as coagulant or flocculant aids appeared to be effective in organic carbon removal through an alternate means. As the polymer doses increased, the residual turbidity remained constant (Figure 21), but the residual organic carbon was removed (Figure 20). Residual turbidity was measured from the settled water, while residual organic carbon was measured after the settled water was filtered. Thus, it appeared that organic carbon was removed during filtration. Notably after waters treated with the polymers were filtered, smooth, opaque residues were retained on the filters. Without polymer, the filter cakes were a light grey color and were significantly less. Therefore, the polymers intended as coagulant or flocculant aids appeared to act as filtration aids. It is hypothetically possible that the filters trapped the polymers and then the polymers removed colloidal organic carbon as the treated waters passed through the filters.

## **Chapter V**

### **CONCLUSIONS**

This research study determined the effects of selected chemical and physical parameters on colloidal organic matter formation during ferric sulfate coagulation of drinking water. Attempts were made to characterize the colloidal organic matter using zeta potential and size. In addition, the impacts of selected polymers were evaluated on their removal of colloidal organic matter.

After investigating the phase-change behavior of organic matter, it was found that coagulation pH, coagulant dose, and organic matter concentration influenced colloid formation. Decreased pH led to increased organic carbon removal and increased pH led to an extended colloidal dose range. Increased ferric iron coagulant dose led to increased colloid formation up to a maximum colloidal envelope height and then colloid formation dramatically decreased at higher doses. Organic matter concentration controlled coagulant demand for treated waters. Increased concentrations of organic matter led to increased colloid formation. The coagulant performance was the same regardless of the organic matter concentration. In addition, there was slight trend toward enhanced coagulant performance with increased initial organic matter concentration. While the coagulation pH, coagulant dose, and initial DOC concentration affected colloid formation, turbidity and temperature did not influence colloid formation.

Collectively, the residual organic carbon, turbidity, and coagulant iron results demonstrated colloid formation. At lower coagulant doses, increased colloidal organic carbon coincided with increased residual turbidity and residual iron and at higher doses the subsequent decreased colloidal organic carbon coincided with decreased residual turbidity and residual iron. This phenomenon implied that organic matter, bentonite, and coagulant metal were all simultaneously incorporated in the colloidal matter at coagulant doses up to the maximum colloidal formation, and then progressively shifted to the particulate fraction at higher coagulant doses.

The colloidal organic matter characterization was inconclusive. The colloidal organic matter formed during ferric sulfate coagulation could not be analyzed for zeta

potential or size due to low signal from the colloids and possible shearing of the colloids during the analyses.

At typical treatment doses, the cationic low molecular weight, nonionic high molecular weight and cationic medium molecular weight polymers were ineffective at coagulating or flocculating the colloidal organic matter. Further study of polymeric coagulant and flocculant aids is warranted to determine their applicability as filtration aids for conventional and direct filtration drinking water treatment systems.

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