DISSERTATION

UNDERSTANDING AND MITIGATING THE NEGATIVE IMPACT OF NATURAL ORGANIC MATTER ON FILTRATION PROCESSES

Submitted by

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WE HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER OUR SUPERVISION BY DEAN GREGORY, ENTITLED *UNDERSTANDING AND MITIGATING THE NEGATIVE IMPACTS OF NATURAL ORGANIC MATTER ON FILTRATION PROCESSES*, BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

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ABSTRACT OF DISSERTATION

UNDERSTANDING AND MITIGATING THE NEGATIVE IMPACT OF NATURAL ORGANIC MATTER ON FILTRATION PROCESSES

The overall objective of this project was to develop and understand effective coagulation processes for optimizing filtration performance during the treatment of high-TOC concentration raw waters. Specific objectives were to determine the impact of coagulation pH, ζ-potential, and alum addition mode (single vs. two-stage) on floc formation and filtration performance. Another goal was to evaluate a photometric dispersion analyzer (PDA) as an indicator of overall process performance. Two-stage coagulation processes were proposed as a means to mitigate restabilization of floc by natural organic matter, particularly for high-TOC concentration water.

Bench and pilot-scale experiments compared floc development, filtration performance, and ζ-potential distributions of post-rapid mix and settled water particles for single and two-stage coagulation processes over the pH range of 6.0 to 7.4.

Overall, in terms of filtration performance during the treatment of high-TOC concentration waters, single-stage high-pH and two-stage coagulation processes were most effective. The use of relatively high coagulation pH conditions (e.g. 7.5) along with alum doses optimized by ζ-potential optimized particle removal in the settling process and significantly increased the operating range, in terms of ζ-potential, for optimum filtration performance.

Two-stage coagulation processes also improved filtration performance, evidenced primarily by increased filter run lengths prior to particle breakthrough. Two-stage coagulant addition consistently increased turbidity removal during sedimentation, oftentimes dramatically when compared to single-stage processes using the same alum dose. This result correlated with the significant increase in floc formation rates and floc size consistently observed for the two-stage processes, particularly in high-TOC concentration waters. The fact that two-stage processes did not impact floc formation in low-TOC conditions supported the proposed mechanistic advantage of this process, i.e. mitigation of NOM-induced floc restabilization by allowing NOM-$Al(OH)_{3\ (S)}$ reactions to occur primarily in the first coagulation stage.

The photometric dispersion analyzer (PDA) appears to be a useful alternative to jar tests for determining optimum coagulant doses and quickly evaluating different coagulation scenarios. Overall, processes that the PDA indicated were optimum, in terms of the kinetics of floc development, were also optimum in terms of filtration performance.

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CHAPTER 1

INTRODUCTION

The ultimate purpose of the coagulation process in water treatment is to remove suspended particles and natural organic matter (NOM). Suspended particles, commonly measured as turbidity, may include inorganic compounds such as clays as well as microbiological constituents such as algae and protozoa. NOM consists primarily of humic substances, including humic and fulvic acids which result from the decomposition of terrestrial and aquatic biomass. Since promulgation of the Disinfectants/Disinfection By-products Rule in 1998 (USEPA, 1998), NOM removal has been emphasized to minimize the formation of compounds such as trihalomethanes (THMs) and haloacetic acids (HAAs), which can be formed upon the reaction between NOM and free chlorine.

However, from a public health and thus regulatory perspective, the removal of suspended particles—particularly pathogenic organisms such as the protozoa *Giardia* and *Cryptosporidium*—remains a treatment priority. In addition to the current USEPA performance standard that exists for turbidity removal under the Surface Water Treatment Rule (combined filter effluent turbidity < 0.3 NTU in 95 percent of samples), future regulations aimed specifically at *Cryptosporidium* may provide log credit for treatment facilities that meet filter effluent turbidity standards (Pontius, 2003). For example, a 0.5-log credit has been proposed under the removal Long-term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) when combined filter effluent is < 0.15 NTU in 95 percent of samples each month. The research presented here was focused on developing effective coagulation methods for optimizing particle removal during the treatment of waters containing moderate-high NOM levels, e.g. those with a TOC concentration greater than approximately 5 mg/L.

Background

This project grew out of preliminary experiments, conducted in the pilot laboratory at the Fort Collins Water Treatment Facility, that attempted to identify effective processes for treating the challenging spring runoff water from the Cache la Poudre River.This water was characterized by low alkalinity (generally less than 10 mg/L as $CaCO_3$) and a high TOC concentration (often greater than 10 mg/L). Historically, the city had relied upon blending this water with a low-TOC source (Horsetooth Reservoir) in order to meet its particle removal goals during the runoff period. However, due to water rights issues (i.e. the city's decree for river water is essentially lifted during spring runoff) the goal of the city was to use river runoff water to meet 100 percent of its demand during the runoff period, which typically extends from mid-May through the end of June. Initial experiments examined the impact of coagulation variables such as pH, alkalinity concentration, alum dose, and alum addition mode (single and two-stage coagulant addition).

The two-stage coagulation process was initially conceived as a method to mitigate the restabilizing effect of NOM on floc particles. It was more closely examined after preliminary bench-scale experiments showed that it significantly increased particle removal in the sedimentation process. The two-stage process entailed simply splitting the total dose of metal salt coagulant between two distinct addition points, with adequate time (approximately 30 seconds) provided between the two points for coagulant-NOM reactions to occur.

During the treatment of these waters particle removal is complicated by the adsorption of hydrophobic, high molecular weight organic molecules to metal hydroxide surfaces during coagulation. When aluminum sulfate (alum) is used as the primary coagulant, these surfaces are provided by i) poorly-soluble, positively-charged aluminum hydroxide sols formed within a few seconds after alum addition (Licsko, 1997; Letterman et al, 1999), and ii) charge-neutralized $Al(OH)_{3\,(S)}$-colloid complexes (microfloc). In the latter case, the microfloc aggregate can be effectively restabilized by the NOM, potentially hindering the formation of larger aggregates (Carlson et al, 2000). Although the adsorption/precipitation of NOM on aluminum hydroxide surfaces is desirable as a primary removal mechanism (Edwards, 1997; Croue et al, 1993; Randtke, 1988), it has been demonstrated that turbidity removal is adversely affected by this process, even for relatively low-TOC (2 mg/L C) waters (Exall et al, 2000; Tseng et al, 2000; Van Benschoten et al, 1990).

A factor that can further complicate particle removal during the treatment of high-TOC concentration water is controlling the coagulation pH while meeting the relatively high alum demand exerted by the NOM. Due to its acidity, alum consumes naturally occurring alkalinity (generally HCO_3^-) and depresses the pH of water. In raw waters lacking sufficient buffering capacity, particularly runoff from snowmelt or thunderstorms and those waters associated with reduced or low-pH environments, the use of alum requires alkalinity addition for pH control. Because runoff waters often contain relatively high concentrations of NOM, the alum demand in these waters is proportionally high, further emphasizing the need for pH control.

In treatment conditions that require alkalinity addition, the chemical doses and resulting coagulation pH levels are often determined by jar tests and settled water data. The target coagulation pH (for non-softening plants) is usually between 6.0 and 7.5. Within this range it is possible to minimize the concentration of soluble aluminum in finished water and effectively remove organic and particulate matter, as demonstrated by Edzwald and Tobiason (1999). However, within this pH range the overall effectiveness of the treatment process, particularly filtration performance, can also vary significantly. The sequence in which coagulation chemicals, including those used for acid/base adjustment, are added will determine coagulation pH and may significantly impact the filtration process.

Research Objectives/Approach

The overall objective of this project was to develop and understand effective coagulation processes for optimizing filtration performance during the treatment of moderate to high-TOC concentration raw waters. The general approach was to evaluate single and two-stage alum addition processes over the pH range of 6.0 to 7.4. This range was chosen to represent relatively low and high coagulation pH conditions (for non-softening plants). The specific objectives of the bench-scale experiments were to determine the impact of coagulation pH, ζ-potential, coagulant dose, and coagulant addition mode (single or two-stage coagulant addition) on turbidity removal, floc size and floc formation kinetics. Another goal during this phase of the project was to evaluate the photometric dispersion analyzer (PDA) as an indicator of overall process performance. The PDA was the optical particle aggregation monitor used to assess floc formation kinetics. It was developed in conjunction with Hach Co. (Loveland, CO) for this project.

The pilot-scale experiments were conducted to correlate bench-scale findings with filtration performance. Although settled water particle removal data were collected and provided useful information on the effectiveness of different processes, the focus of this project was the impact of coagulation variables on filtration performance. The filtration experiments were performed using 1) a river source during spring runoff, characterized by high turbidity, low alkalinity, and relatively high NOM levels, and 2) a typical reservoir surface water of constant quality and containing moderate NOM levels (approximately 3.5 mg/L TOC). Filter effluent particle counts and TOC removal were used to determine the overall effectiveness of three different single-stage coagulation scenarios (pH=6.0, 6.7, and 7.5) as well as two-stage processes.

Dissertation Overview

A literature review for this project is presented in Chapter 2. The focus of this section is research related to i) the chemistry of alum coagulation, particularly the species most important for particle destabilization, ii) the effect of coagulation pH on particle removal/floc development , iii) the impact of coagulation pH/ζ-potential on filtration , iv) NOM removal mechanisms, and v) two-stage coagulation processes. In Chapter 3 an overall Materials and Methods section is provided.

The main body of the dissertation is contained in Chapters 4, 5, and 6. Each of these chapters is a complete, stand-alone paper that has been published previously

(Chapter 4 and 5) or has been submitted for publication (Chapter 6). Although an overview is provided in Chapter 3, more detailed information concerning experimental materials and methods can be found in these chapters. Chapter 4 describes preliminary bench and pilot-scale experiments in which single and two-stage processes were compared. This research represented the early stages of the project. In Chapter 5 the impact of pH and ζ-potential, for single-stage coagulant addition only, on floc formation kinetics was examined and related to filtration performance. Chapter 6 specifically examines the impact of two-stage coagulation on floc formation kinetics, the surface charge of post-rapid mix and settled water particles, and filtration performance in terms of particle breakthrough.

Chapter 7 presents a summary of the findings of this project and describes potential impacts for full-scale treatment processes. Chapter 8 provides references for Chapters 1 – 3 of the dissertation. In the Appendices following Chapter 8, raw data from all filtration experiments (spring runoff and reservoir water) is provided along with a description of the coagulation conditions. Examples of the ζ-potential raw data and output from the photometric dispersion analyzer are also provided.

CHAPTER 2

LITERATURE REVIEW

The subject of alum coagulation has been extensively researched and discussed in the literature. Numerous studies have documented 1) the role and relative concentration of various aluminum hydrolysis products in the pH range to be discussed here (6.0 – 7.5), and 2) the impact of dose, pH and ζ-potential on settled water quality. A majority of the filtration research has focused on developing theoretical models to predict particle removal. In general, these models have illustrated the relative importance of various physical and chemical filtration variables. Their correlation with laboratory filtration results, however, has been mixed.

The intent of this research was to understand some important chemical factors that influence coagulation and to extend these findings to filtration. It is hoped that the combination of laboratory and pilot-scale results will further the understanding of mechanisms that affect coagulation and filtration of high-TOC concentration raw water. In the sections to follow, discussion will focus on previous studies that have: 1) clarified the role of different alum species in coagulation, particularly the importance of aluminum hydroxide sols ("sols" are defined as the sub-colloidal, poorly water-soluble, positively-charged aluminum hydroxide solids which form within 1-2 seconds following alum addition), 2) examined the effect of pH, coagulant dose, and ζ-potential on sedimentation processes, 3) theoretically explored chemical and physical factors that influence filtration processes (primarily laboratory-scale studies), and 4) investigated the coagulation mechanisms that control NOM removal.

Aluminum Species Formed During Coagulation

The aluminum species formed upon the addition of alum to water are classified as monomers (e.g. Al^{3+}, $Al[OH]^{2+}$), polymers ($Al_2[OH]_2^{4+}$, $Al_{13}O_4[OH]_{24}^{7+}$), and the poorly-soluble precipitate, $Al(OH)_{3\,(S)}$ (Baes and Mesmer, 1976). The monomeric and polymeric species are thought to be relatively short-lived (<1 sec) intermediates formed during the stepwise hydrolysis of aluminum ion (Al^{3+}) (Hahn and Stumm, 1968; Letterman et al., 1973). The term *hydrolysis* describes the general reaction in which a proton is transferred from an acid to water. The equilibrium species formed by aluminum hydrolysis reactions are pH-dependent and are comprised of one or more of the following hydroxoaluminum complexes: $Al(OH)^{2+}$, $Al(OH)_2^{+}$, $Al(OH)_3$, $Al(OH)_4^{-}$. As demonstrated previously (Hundt and O'Melia, 1988), in the pH and alum dose range of interest to this study, 6.0 – 7.5 and 15 – 100 mg/L, respectively, virtually all the aluminum is present as the solid precipitate $Al(OH)_{3\,(S)}$ at equilibrium. It was also shown in the same study that the presence of sulfate catalyzes the rapid formation of $Al(OH)_{3\,(S)}$ at pH > 4.6.

Role of highly-charged polymeric species. In the pH range of 6.0 – 7.5, the two Al species that appear to control coagulation processes are the short-lived highly positively-charged polymeric intermediates and the poorly water soluble aluminum hydroxide sols that are formed within a few seconds after alum addition. Of these two species, there is substantial evidence that the positively-charged aluminum hydroxide sols, which themselves will aggregate into aluminum hydroxide microflocs after several seconds if not adsorbed to a solid surface, appear to be the most realistic species responsible for the destabilization of natural particles (Licskó, 1997; Dentel and Gossett, 1988). Although the existence of the highly-charged polynuclear complexes has been shown (Akitt and Farthing, 1978), their actual contribution to coagulation processes appears to be minor. In an attempt to determine the influence of these species, Klute (1990) performed bench-scale experiments, using a specialized mixing device, which demonstrated that the aluminum hydrolysis products formed within approximately 0.1 seconds after alum addition—presumably highly positively-charged polymers--were more effective at changing the surface charge of silica particles than the aluminum hydroxide precipitate formed after a few seconds of hydrolysis. These experimental data supported the coagulation mechanisms proposed by previous researchers (Amirtharajah and Mills, 1982; Hahn and Stumm, 1968). In this work, it was shown that the formation of polymeric hydrolysis species took place within 0.1 seconds and that, ideally, coagulants should be homogeneously dispersed within this timeframe. However, in the same study the authors compared five full-scale rapid mix systems and found that homogeneous dispersion of coagulant within 0.1 seconds was not realistic, an observation made by other researchers (Dittman et al., 1989). Therefore, the conclusion was that the highly positively-charged polymeric species played a minor role in the charge neutralization of natural particles.

Role of aluminum hydroxide sols. A majority of the evidence in the literature, however, suggests that, under water treatment conditions, the positively-charged, insoluble aluminum hydroxide sols are primarily responsible for particle destabilization during coagulation by adsorbing to the surface of the oppositely-charged, much larger natural colloids and entering into an electrical bond. Licskó (1997) showed that, for alum doses $>10^{-2}$ M and in the pH range of 4.0-5.0, where the stability of positvely-charged polynuclear species is high, the alum dose required to change the ζ-potential of natural particles from a river source was significantly greater than in the pH range 6.0-6.5, where aluminum hydroxide sols are formed within 1-2 seconds. In the pH range 6.6 – 7.8, it was shown that greater than 98 percent of the applied alum was present as insoluble hydroxide within approximately 10 seconds. The author emphasized that the positively-charged sols themselves are relatively short-lived species (1-10 seconds) that readily aggregate into $Al(OH)_{3\,(S)}$ microfloc. This sol-sol interaction was viewed as an ineffective use of coagulant.

Dentel and Gossett (1988) also concluded that the formation and adsorption of positively charged precipitates (sols) to suspended particles achieves charge neutralization. They supported this conclusion by comparing experimental electrophoretic mobility data to aluminum solubility diagrams and showed that charge neutralization did not take place until aluminum hydroxide solubility limits were exceeded, a mechanism that had been suggested by prior researchers (Mackrle, 1962; Hall, 1966). Likewise, DiTommaso and Van Benshcoten (1996) showed that providing a brief period of low-pH contact time between the more positively-charged soluble aluminum species and suspended particles, before increasing the pH to the near-neutral range, did not appear to enhance particle removal.

Effect of Coagulation pH on Sedimentation and Floc Development

In terms of the impact of pH and alum dose on coagulation and solid-liquid separation processes, a majority of research has focused on settled water data. These results have shown that particle removal through the sedimentation process improves significantly as pH is increased. Tseng et al. (2000) observed that turbidity removal in jar tests improved directly as pH was increased incrementally from 5.7 to 7.2. In this work alum doses were increased with pH to maintain a constant ζ-potential. Although a definitive explanation for the increased turbidity removal with increasing pH was not provided, the authors noted that the logarithm of percentage turbidity reduction exhibited a rough linear correlation to the mass of $Al(OH)_{3\,(S)}$ formed. Likewise, in the bench-scale alum coagulation experiments conducted by DiTomasso and van Benschoten (1996), the most effective turbidity removal was achieved at the highest alum dose and pH levels (6.9 – 7.4). Budd et al. (1996) also observed in jar test experiments that the optimum pH range for particle removal when using alum was 7.2 – 7.6 for cold water.

Matsui et al. (1998), used a photometric dispersion analyzer (PDA) to perform a dynamic analysis of coagulation mechanisms during bench-scale experiments. They reported that the time required for particle destabilization and the onset of floc formation increased as pH and alum dose decreased. The output from the PDA, called the flocculation index (FI), is a sensitive indicator of the state of aggregation of a suspension (Gregory, 1985) and has been directly related to particle size (Ohto et al., 1993). A rapidly increasing FI following alum addition, which was observed by Matsui et al at higher pH levels, is indicative of optimum particle destabilization conditions. In another study, in which the PDA output was used to control microfloc size and thus settled water quality in a pilot plant, coagulation was optimized at pH = 7.4 (Tambo et al., 1997).

Particle destabilization mechanisms. At higher pH levels (e.g. 7.5) and coagulant doses, the interaction between voluminous aluminum hydroxide precipitates and natural colloids is known as sweep coagulation (Amirtharaja et al, 1982; Amirtharaja et al, 1990). In this mode, particles are destabilized by adsorption of aluminum hydroxide sols and are enmeshed in sol aggregates, promoting the formation of relatively large, settleable floc. At pH=6.0, particles are also destabilized primarily by aluminum hydroxide sols, which are more positively-charged (compared to pH=7.5). However, at lower pH levels and thus lower alum doses, the physical enmeshment mechanism is less significant and smaller, lighter flocs develop. It should be noted that large aluminum hydroxide aggregates (formed after approximately 60 sec., for example) are by themselves ineffective for destabilizing natural colloids and removing turbidity (Licsko, 1997). The adsorption of newly-formed, positively charged $Al(OH)_{3\,(s)}$ to colloid surfaces is critical at both pH levels.

The ineffectiveness of "aged" floc in charge neutralizing natural colloids indicates that the conventional notion of the "sweep" coagulation mechanism at higher alum doses, i.e. simple enmeshment of particles within relatively large aluminum hydroxide flocs, may not be conceptually accurate. Assuming that the destabilization of suspended particles is accomplished through adsorption of positively-charged aluminum hydroxide sols, a more realistic mechanistic explanation may be that higher alum doses enhance particle removal by more uniformly distributing positive charges on particle surfaces. In the pH range of 6.0 – 8.0, dissolved organic molecules adsorb rapidly to newly-formed aluminum hydroxide sols, essentially restabilizing them and preventing their adsorption to particles in solution. Therefore, a certain fraction of the sols are used to meet the coagulant "demand" exerted by NOM. The remaining fraction is available for destabilization of particles as well as sol-NOM complexes. At low pH, this fraction is relatively low and particles are destabilized by fewer but more highly-charged sols. While the net surface charge is zero, distribution of that charge may be less consistent than at higher pH levels. When the pH is raised, the sol demand from the hydrophobic NOM fraction will increase somewhat due to increased negative charge density, but a higher concentration of aluminum hydroxide is available for adsorption and charge neutralization, resulting in a more even distribution of charge.

Ultimately, an uneven surface charge distribution may reduce the probability of successful collisions (Amal et al., 1992), hindering the development of floc suitable to solid-liquid separation, i.e. large floc. Elimelech and O'Melia (1990) also discussed distribution of surface charge as a possible explanation for discrepancies between theoretical and experimentally observed attachment coefficients, but no experiments were conducted to directly examine it.

Impact of Coagulation pH and ζ-Potential on Filtration

Although it seems clear from the literature, as well as from bench and pilot-scale data to be presented here, that coagulation at relatively high pH and alum dose conditions enhances turbidity removal in the sedimentation process, regardless of ζ-potential, it is less clear whether these benefits extend to filtration. Although several excellent studies have focused on modeling the theory of deep-bed filtration using controlled laboratory systems, filtration research focusing specifically on pH and ζ-potential effects is not well represented. Edzwald and Tobiason (1999) presented jar test results and pilot-scale filtration data in a study that examined the effect of pH on multiple objective coagulation processes (i.e. balancing coagulation pH and dose with particle, DOC, and TTHMFP removal). This work focused on low-alkalinity waters that require base/alkalinity addition for pH control during coagulation. The authors emphasized the need for strict pH control to achieve optimum coagulation. For colder waters, a coagulation pH near 7 was recommended in order to maximize particle removal without compromising NOM removal. Although it was shown, for example, that less alum is required to remove similar amounts of DOC at pH =5.5 vs. 6.1, at optimized doses there was little difference in DOC removal over the pH range of 5.5 – 6.6.

In most cases authors have optimized filtration conditions based on surface charge (electrophoretic mobility or ζ-potential) and not necessarily pH. O'Melia and Stumm (1967) concluded that "no unique relationship exists between pH and filtration efficiency." In other words, there is not one pH level that will produce optimum filtration results for all coagulation conditions. In laboratory-scale filtration experiments conducted with Fe^{3+} dispersions the authors showed that the optimum pH for filtration varied with several variables, including the age of the dispersion, the presence of complex-forming ligands other than OH^-, and ionic strength. Overall, filtration efficiency was greatest at pH=7.0 (compared to pH =5.0 and 9.5), which is near the isoelectric point of Fe_2O_3, but the authors emphasized that these results applied only to the specific type of particle dispersion examined. Darby and Lawler (1990) modeled the removal of different size particles, filter ripening, and head loss accumulation at pH = 2, conditions that were optimized for filtration on the basis of electrophoretic mobility (e.m.) measurements. The e.m. range used was -1.1 - +1.3 (μm/s)/(V/cm). Elimelech and O'Melia (1990) performed laboratory-scale filtration experiments at a constant pH of 6.7, a typical level used in water treatment. Surface electric potential, particle removal, and filter attachment efficiency (α) were found to vary directly with electrolyte concentration, which was essentially the coagulation chemical. For the small particle sizes examined (< 1 μm), removal and α increased as surface potential decreased (became less negative). Although constant pH conditions were used in this study, the changes in surface potential observed over a range of electrolyte concentrations are analogous to surface chemistry changes during coagulation. In both cases, the repulsive energy barrier of a suspended particle is reduced, increasing attachment efficiency to filter media.

It appears that discussions of the impact of pH on filtration should focus on its effect on suspended particle surface chemistry, the most dominant variable affecting the attachment of particles to filter media (O'Melia, 1985). Surface chemistry is usually characterized by the effective net surface charge, or ζ-potential, of particles. Changes in coagulation pH, for a constant coagulant dose, are accompanied by changes ζ-potential, i.e. ζ-potential becomes more positive as pH decreases and more negative as it increases. To achieve effective removal in filtration it is essential to charge neutralize, or destabilize, the particles in suspension through optimized pre-treatment processes (Chipps et al., 2001; Benjamin et al, 2003). In doing so, the attachment of suspended particles to filter media upon collisions between the two is maximized.

The importance of this attachment mechanism and proper particle destabilization, as well as the relative unimportance of the straining mechanism in filtration, has been demonstrated in several studies (e.g. Habibian and O'Melia, 1975; Cleasby et al., 1992). In their classic filtration theory describing the relative importance of different particle-to-media grain transport mechanisms and subsequent removal efficiencies, Yao et al. (1971) concluded that there are many opportunities for particle-media grain collisions and that a high removal percentage should be achieved as long as proper destabilization conditions are maintained. In their equation describing particle removal, the attachment coefficient,

α, was used. A value of $\alpha = 1$ implies complete destabilization while $\alpha = 0.1$, for example, indicates poor particle destabilization. Figure 2.1 illustrates the dramatic impact of attachment efficiency on clean bed particle removal for the Yao et al. model. The removal of smaller particles (< 1 μm diameter), in particular, is extremely negatively impacted by poor destabilization conditions. Although this model appears to predict inadequate particle removal for a water treatment plant, it should be noted that clean bed conditions are assumed, i.e. no ripening has occurred. Elimelech and O'Melia (1990) showed that α was directly related to the concentration of a destabilizing electrolyte and electrokinetic potential, which was calculated from electrophoretic mobility.

The overall effect of changes in pH, for a constant alum dose, is to change the surface charge or ζ-potential of suspended particles, therefore changing α. To maintain a relatively constant ζ-potential, and α, alum doses must be adjusted with pH. Coagulation

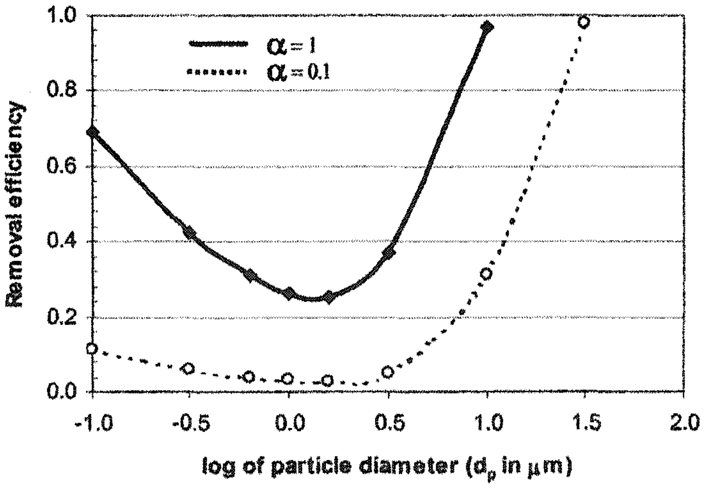

Figure 2.1 Effect of attachment efficiency on overall filter removal efficiency (adapted from Benjamin and Lawler, 2003).

at relatively high pH levels, for example, requires correspondingly high alum doses due to the increase in the charge density of natural organic matter (NOM) present as well as the decrease in positive charge of the aluminum hydroxide sols formed within seconds of alum addition (Edzwald and Van Benschoten, 1997).

Influence of Coagulation pH on NOM Removal

A few general conclusions can be drawn from previous research that has examined NOM removal during alum coagulation: 1) there is a sorbable fraction of NOM, generally characterized by higher molecular weight and hydrophobic tendencies, that is amenable to removal through coagulation and a non-sorbable fraction that can not be removed through practical methods (Edwards, 1997; Randtke, 1988; Croue et al., 1993), and 2) the dominant removal mechanism in the pH range of 5.5 – 8.0 is by adsorption to aluminum hydroxide surfaces (Hundt and O'Melia, 1988; Edwards, 1997). Therefore, over the pH range of interest to this study (6.0 – 7.5), it seems reasonable to assume that equivalent NOM removal can be attained if optimized alum doses are used. Although the conventional notion is that NOM removal is significantly improved at lower pH, it appears from the literature that a more accurate statement is that effective NOM removal requires lower alum doses at low pH than at high pH (Edzwald and Tobiason, 1999). Edzwald and Van Benschoten (1997) showed that equivalent removal is possible at pH = 7.0 (compared to pH = 5.5) if doses are increased proportionally to neutralize the increased negative charge density of NOM. The authors noted that the charge density of the particular aquatic fulvic acid used in their experiments increased from 7.5 to 10 μeq/mg C when pH increased from 5.5 to 6.5, while the alum dose required to provide the same amount of positive charge over that range increased by a factor of three.

Other studies have demonstrated that NOM can be removed effectively over a relatively wide pH range. Hundt and O'Melia (1988), for example, showed that, for a constant alum dose, removal of some types of fulvic acids was influenced by pH while for other types high removal rates were observed over a wide pH range. Overall, they concluded that a constant filtered removal percentage (80%) of fulvic acids could be achieved while pH was increased from 6.0 to 8.0, if alum doses were increased accordingly. Edwards (1997), in developing a semi-empirical predictive model for DOC removal, noted that inclusion of a pH-dependency factor in the sorption constant did not improve model fits. It was suggested that the affinity of DOC for oxide surfaces was not a function of pH. Exall and Vanloon (2000) did not directly examine the effect of pH on NOM removal, but used a relatively high pH (≅ 8.0) in their study of organic matter removal by different aluminum-based coagulants. High removal rates of humic acids (almost 75 percent) were observed at optimum alum doses. Bell-Ajy et al. (2000) compared conventional (baseline) and optimized coagulation for NOM removal. The authors examined 16 tests sites, four of which used alum, and concluded that the use of lower coagulation pH (5.5 – 6.5) optimizes NOM removal. However, at the four sites in which attempts were made to optimize alum coagulation, results were mixed. At two of the sites, reducing the coagulation pH from 7.0 to 6.2 and 6.9 to 5.8 had an insignificant effect on TOC removal. At the other two sites, TOC removal increased after the pH was depressed, but the alum was not changed, suggesting that the original baseline process was non-optimum in terms of ζ-potential.

Two-stage Coagulation Processes

Few studies were available that documented two-stage coagulation processes. In the treatment of high-TOC concentration (5 – 12 mg/L), spring runoff water it was shown that two-stage coagulant addition, compared to traditional single stage methods, consistently reduced settled water turbidity by 30 – 50 percent and increased filter run lengths in bench and pilot-scale experiments (Carlson et al, 2000; Billica et al, 2000; Gregory et al, 1998). The two-stage process used in these studies entailed simply splitting the total dose of metal salt coagulant between two distinct addition points, with adequate time (approximately 30 seconds) provided between the two points for coagulant-NOM reactions to occur.

Wahlroos (1991) reported the use of a two-stage coagulation process in which iron (III) sulfate-chloride was added at a pH of 4.8 – 5.1, followed by pH adjustment and then a second stage of iron coagulation at a pH of 8.0 – 8.5. The two-stage method was initially developed and tested in bench and pilot-scale experiments before being implemented at a full-scale facility. The process increased filter run times and increased removal of taste-and-odor compounds from 50 to 90 percent. Removal of chemical oxygen demand (COD) was also increased when the coagulation process was changed from one to two stages. The first coagulation process was intended for removal of humic substances and the second process was intended for particle removal and precipitation of metals.

Another study (Garrotte, 1995) describes effective treatment of a tannery waste stream, containing high concentrations of BOD, COD, and sulfides, by a two-step coagulation process. The authors, using COD reduction to evaluate the effectiveness of the process, found that two similar coagulation stages were far more effective than a single stage, but that three stages were only marginally more effective than two.

CHAPTER 3

MATERIALS AND METHODS

The experimental matrix for this project was conducted primarily in three phases, each of which consisted of bench and pilot-scale experiments. An overview of each of the three phases is provided in this chapter, followed by descriptions and photographs of the primary bench-scale apparatuses used as well as the pilot laboratory.

The three experimental phases correspond with the three stand-alone papers included in this dissertation (Chapters 4 – 6). Because each of these papers provides detailed information on experimental procedures and equipment and, as a whole, provide a complete *Materials and Methods* section for this project, this chapter will serve as an overall outline of the experimental plan and the most significant methods and analyses. The more detailed information provided in the papers is referenced as necessary.

EXPERIMENTAL PLAN

Phase 1: Optimizing Coagulation Processes for Spring Runoff Water. The goal of this initial phase was to identify and evaluate effective processes for filtration of spring runoff water from the Cache la Poudre River, characterized by a high TOC concentration and low-alkalinity (see Table 4-1 for water quality). These experiments were conducted in the pilot laboratory at the City of Fort Collins water treatment facility. Due to the low alkalinity of this source, initial bench-scale experiments (jar tests) focused primarily on optimizing pH, alkalinity dose, and alum dose, primarily in terms of TOC and, to a lesser extent, turbidity removal. The optimized alum doses were then applied in pilot-scale filtration experiments. The coagulation pH was based on historical operational data at the Fort Collins treatment facility and generally ranged from 6.2 to 6.7.

The concept of two-stage coagulation as a potential method to mitigate the negative impact of NOM on particle removal arose during this period. Single and two-stage coagulation was compared in jar tests as well as in head-to-head pilot-scale filtration experiments. Details of these experiments are provided in *Materials and Methods* of Chapter 4.

Phase 2: Impact of pH and ζ-potential on Floc Formation and Filtration. Although a general coagulation pH range was targeted in Phase 1 experiments, specific effects of pH on filtration were not fully explored. The three objectives in Phase 2 were to i) determine the impact of pH and ζ-potential on granular media filtration performance; ii) develop and apply a photometric dispersion analyzer (PDA), described in further detail below, to monitor particle aggregation during coagulation experiments; and iii) evaluate the PDA as an indicator of filtration performance. Because output from the PDA (flocculation index) is a sensitive indicator of the degree of aggregation of a particle suspension, it was thought that it could potentially be used as indicator of overall process performance, as floc particles become the primary particle collectors in filters after the initial ripening period (O'Melia, 1985).

The approach was to first examine the effect of different coagulation scenarios on particle/NOM removal and floc formation kinetics in a controlled laboratory environment. In these experiments, alum doses were optimized based on ζ-potential over the pH range of 5.5 – 7.5 (i.e. optimum doses were those that achieved a post-rapid mix ζ-potential ≅ 0 mV). Other than acid/base addition for pH control, no coagulation chemicals other than alum were used.

Pilot-scale experiments were then conducted to correlate bench-scale findings with granular media filtration results, i.e. determine the degree of correlation between output from the PDA with filter effluent particle counts. The filtration experiments were performed in the pilot laboratory of Fort Collins Water Treatment Facility. Runs were conducted at pH = 6.0, 6.7, and 7.5 using two different surface water sources: 1) the spring runoff source used in Phase 1 (see Table 4.1), and 2) a reservoir characterized by low-moderate NOM levels and generally stable water quality (see Table 4.2). During the reservoir water experiments, a two-stage alum addition process was applied in addition to the three single-stage processes, although a majority of the processes examined were traditional single-stage methods. Details of the experiments conducted in this phase of the project are provided in *Materials and Methods* of Chapter 5.

Phase 3: Minimizing NOM-induced Floc Restabilization with Two-stage Coagulation. Two-stage coagulation processes were more closely examined in this phase of the project. Using moderate-TOC water (5.0 mg/L), the approach was to first conduct bench-scale experiments that characterized the impact of two-stage coagulation on i) floc development and ii) the ζ-potential distribution of post-rapid mix and settled water particles at two coagulation pH levels (6.0 and 7.4). Although it was initially unclear whether two-stage coagulation would produce settled water particles with ζ-potential distributions significantly different than those obtained from single-stage processes, it was thought that the proposed mechanistic advantage of this process (i.e. mitigation of microfloc restabilization) might be illustrated by these analyses. Additional bench-scale experiments conducted during this phase of the project correlated the output from the PDA with physical floc size determined by microscopic analysis. The specific effect of TOC concentration (3.5 – 12 mg/L) on floc formation and size was also examined for single and two-stage coagulation processes, at pH = 6.0.

Pilot-scale experiments were conducted with high-TOC concentration raw water in an attempt to correlate the bench-scale findings with overall treatment performance and to further examine the impact of two-stage coagulant addition on the filtration process. Details of the Phase 3 experiments are provided in *Materials and Methods* of Chapter 6.

ANALYTICAL METHODS

This section describes the most important analytical instrumentation and experimental facilities used during the project, including the PDA, ζ-potential analyzer, TOC analyzer, and the Fort Collins pilot laboratory. Details of common laboratory instruments and procedures used—such as glassware, pH meters, turbidimeters, etc.—are provided in Chapters 4 – 6.

Photometric Dispersion Analyzer. Floc formation kinetics were monitored with a photometric dispersion analyzer (PDA). The output from the PDA, or flocculation index (FI), corresponds to particle size and has been shown to be a sensitive indicator of the state of aggregation of a particle suspension. The method was originally developed by Gregory (1985) and has been described in detail by several researchers who used it to monitor microfloc development during coagulation (Tambo et al., 1997; Ohto et al., 1993; Matsui and Tambo, 1991). It is based on the fact that turbidity measurements, i.e.

measurements of average transmitted light, of a flowing suspension fluctuate about the mean value. The intensity of transmitted light, which is converted to a voltage signal, will change continually because of fluctuations in the number and size of particles in the path of the beam. The FI is defined as the ratio of the root mean square of the fluctuations to the mean level. The voltage signal is split into its average (DC) and fluctuating (AC) components, which are used for calculating the FI. The most practical use of the FI is that it shows a significant increase as particles aggregate, thus allowing a dynamic assessment of coagulation mechanisms (Matsui et al, 1998).

Much of the early focus of this project was placed on developing a protocol for using the photometric dispersion analyzer (provided by Hach Co.) as well as understanding the flocculation index (FI) data obtained from it. The PDA experimental protocol was as follows: a 2.3 L sample of water was added to a standard jar test square container and the pH was adjusted according to the experimental conditions. A laboratory-scale mixer (IKA®-Works Eurostar model, rpm range = 50 – 2000) was lowered into the container and the sample was mixed at 300 rpm. At t = 0 the FI data logging using Labview software was started. Baseline FI data was collected for 150 seconds prior to coagulant addition. Coagulant was added at t = 150 seconds—injected with a micropipette--and the sample was mixed at 300 rpm for an additional 10 seconds, after which time the mixing intensity was decreased to 50 rpm. The sample was then mixed continuously at 50 rpm for an additional 12 minutes while the FI data was collected. At the conclusion of the experiment the data logger was turned off and the file was automatically saved to the computer hard drive.

Although the same flocculation process was used for the two-stage experiments, the rapid mix protocol differed slightly. The first half of the alum dose was provided with a 10-second rapid mix period followed by a 30-second slow mix period. The mixer speed was then increased again for a brief period (5 seconds) to provide rapid mix conditions for the second dose.

A photograph of the PDA system used in this study is provided in Figure 3.1 and a schematic diagram is shown in Figure 5.9. The peristaltic pump (flow rate = 46 mL/min.) was placed downstream of the flow-through cell to avoid disruption of the floc particles. The time lag between the 2-L beaker and the PDA was 3-4 seconds.

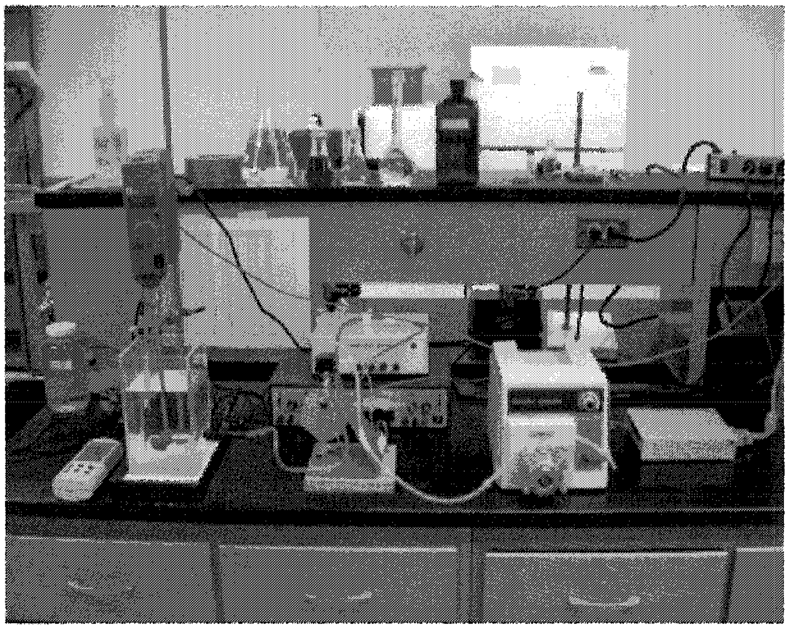

Figure 3.1 Experimental apparatus for photometric dispersion analyzer (PDA) and related equipment. The PDA, shown in the middle of the photo between the mixer and the pump (two stacked power supplies are directly behind it) was used to monitor particle aggregation during coagulation/flocculation.

ζ-Potential Analyses. ζ-potential analyses were performed using a state-of-the-art, automated analyzer (Malverne Instruments Zetasizer 2000). A detailed discussion of the analyzer and its operational parameters is provided in *Supporting Information* at the end of Chapter 5. For the coagulation conditions used (ionic strength ≅ $2.2*10^{-3}$ M at pH=6.0), the ζ-potential values calculated from electrophoretic mobility data (Henry equation) were considered valid for particles greater than approximately 1.3 μm. The fraction of sub-1.3 μm particles in the samples was assumed to be very small and not a significant factor in ζ-potential calculations.

One advantage of the automated ζ-potential analyzer used in this research was that it allowed five separate analyses of each injected sample to be performed (on different aliquots of water) in succession and provided the full distribution of values for each analysis. The individual ζ-potential distributions shown here represent the average of those five runs, each of which analyzed thousands of particles. Analyses that exhibited extremely high error, generally due to sample handling problems such as air bubble entrapment, were repeated.

Total Organic Carbon (TOC). TOC concentrations were measured using the UV/persulfate oxidation method (Sievers 800 TOC Analyzer).

Filtration Experiments

The Fort Collins pilot facility consists of three 8 gpm conventional treatment process trains that can be operated in parallel. The simultaneous use of multiple process trains allowed a direct comparison of the impact of different coagulation conditions on filtration performance. For the rapid mix process, both in-line static mixers and standard backmix-type units were available. For the single-stage coagulation processes, alum was added into the backmix basins (detention time = 15 sec., mixer speed = 1000 rpm, G value ≈ 1000 sec^{-1}). For the two-stage alum addition processes, the first alum dose was injected into a 2" PVC line containing an in-line static mixer, about 25 seconds upstream of the backmix basin and the second alum dose. Each pilot train included a three-stage, tapered mixing energy flocculation basin (total detention time = 45 minutes, G values ≈50, 30, and 18 sec^{-1}), Lamella plates settling basin (hydraulic loading rate = 0.34 gpm/ft^2), and dual media filters (30" anthracite, effective size = 0.95 mm; 10" sand, effective size = 0.50 mm). The filtration rate used for all experiments was 4 gpm/ft^2. Filtration performance was evaluated based on filter effluent particle counts (total > 2μm/mL; Met One particle counter) and TOC concentration. TOC samples were collected after the filters reached steady-state conditions. Each pilot train was equipped with on-line pH meters (Great Lakes Instruments) for raw and post-rapid mix water, as well as on-line turbidimeters for raw, settled, and filtered water (Hach 1700D). Alum doses at each pH level were optimized based on zeta potential (automated Malverne Instruments Zetasizer 2000).

A photograph of the pilot facility, showing the rapid mix, flocculation, and sedimentation basins, is provided in Figure 5.11. A photograph of the 6"-diameter pilot filtration colum is provided in Figure 3.2.

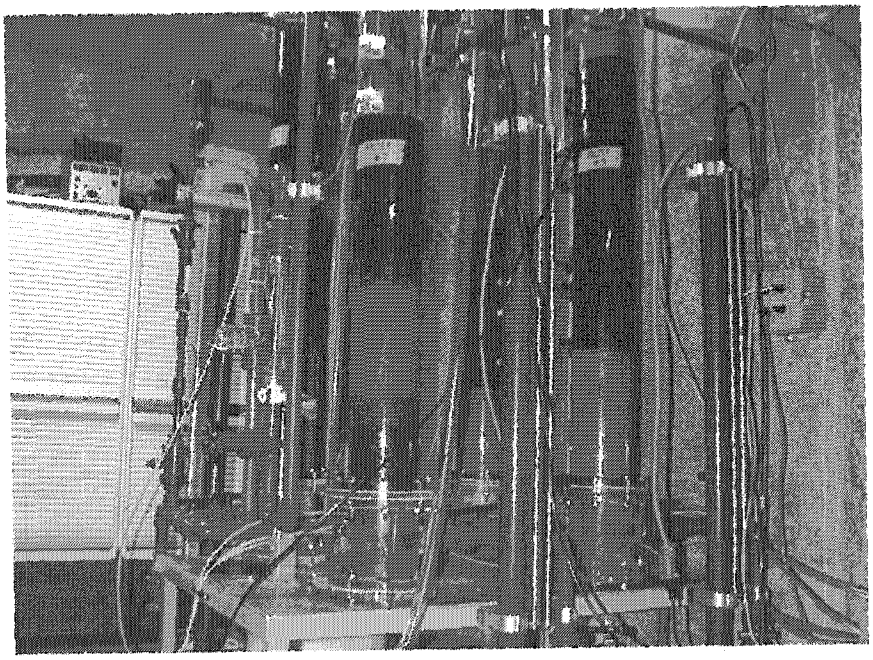

Figure 3.2 Pilot plant filter columns (6"-diameter). Dual media filter is shown on right (30" anthracite, 10" sand).

CHAPTER 4

RESULTS AND DISCUSSION

Optimizing Water Treatment with Two-stage Coagulation

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ABSTRACT

Drinking water utilities are facing increasing regulatory pressure to optimize treatment processes, particularly the filtration process that is relied on as a physical barrier to pathogen contamination. In the presence of high concentrations of natural organic matter, traditional coagulation processes can be inadequate to meet these future standards. In this study, a natural water with a high total organic carbon concentration (>6 mg/L) was used to compare one- and two-stage alum coagulation processes. The two-stage coagulation process involved the application of alum at two locations separated by approximately 60 seconds of detention time. Bench scale experiments were conducted with various water quality conditions and verified at the pilot scale. The settled water turbidity was 25% less using the two-stage process and the steady-state filter effluent particle counts for the two-stage process were approximately 50% lower than for the single-stage process. More importantly, the two-stage process did not exhibit particle breakthrough during a typical filter run whereas the one-stage process broke through 3 hours before the hydraulic completion of the run. Additional bench scale experiments allowed a mechanism for the improved process performance to be proposed.

Key Words: Drinking water, coagulation, treatment, natural organic matter, two-stage, filtration.

INTRODUCTION

Coagulation is an essential component in the conventional water treatment practice in which coagulation, sedimentation, and filtration are used in series to remove particles and natural organic matter (NOM) from raw water. The primary aim of coagulation in conventional treatment is to destabilize particles so that they may combine into larger aggregates that will settle efficiently in the sedimentation process or be removed in the subsequent filtration process.

In the United States, the two most commonly used primary coagulants are aluminum and iron (III) salts. When aluminum sulfate ($Al_2(SO_4)_3 \bullet 14.3H_2O$), or alum, is used, particle coagulation occurs primarily by two mechanisms: 1) adsorption of positively-charged hydrolysis species on colloid surfaces, which causes charge neutralization; and 2) enmeshment of particles in aluminum hydroxide precipitate (Gregory, 1978; Amirtharajah and O'Melia, 1990). Recent work by Licskó (1997) has shown that the most important aluminum species for particle destabilization are the positively charged, poorly soluble aluminum hydroxide sols formed during the first seconds after coagulant addition. These sols, which exist for only a few seconds, destabilize particles by adsorbing onto the surfaces of the oppositely-charged, larger natural colloids. Aluminum hydroxide flocs "aged" for a few minutes were less effective for removing colloidal particles or reducing their zeta potential. These results emphasize the importance of mixing and assuring rapid particle-sol interactions when destabilization is the primary goal of the coagulation process.

NOM makes up the bulk of the coagulant demand in most natural waters and its removal is accomplished by one of two mechanisms: adsorption to metal oxide solids or precipitation with metal salt coagulants (Edzwald and Van Benschoten, 1990). The fraction of NOM that is readily removed with coagulation is characterized as hydrophobic and is considered to be mostly humic in nature (Edzwald and Van Benschoten, 1990; Croue et al, 1993). Edwards (1997) used a Langmuir-based semi-empirical approach for modeling the DOC removal during metal salt coagulation. The model approach, recognizing a dominant sorbable fraction of DOC that forms strong complexes with metal hydroxide surfaces, was highly accurate without directly accounting for precipitation of NOM during coagulation.

Precipitation of NOM with metal salt coagulants involves charge neutralization reactions with the short-lived, highly charged, intermediate hydrolysis products (Dempsey et al., 1984; Licsko, 1997). The NOM removal mechanism depends on the pH of coagulation with the mechanism being metal hydroxide adsorption at pH values greater than 7.0. For NOM precipitation to occur at pH values lower than this, the coagulant mixing process must be efficient enough to contact the two reactants quickly before the metal hydrolyzes to the hydroxide solid. Under non-ideal mixing conditions, it is expected that most NOM will be removed through metal hydroxide adsorption, even at low coagulation pH values.

One approach for treating raw waters with elevated levels of NOM is to increase the coagulant dose which is typically applied at one location, either a rapid mix basin or an in-line mixer. The research described in this paper evaluates the use of a two-stage (two application points) metal salt coagulation process for treating a natural water with a high total organic carbon (TOC) concentration. It is hypothesized that the two-stage coagulation process can compensate for less than ideal mixing conditions for natural waters that have high concentrations of NOM.

LITERATURE REVIEW

Few studies can be found that investigate the use of a two-stage, or multi-stage, coagulant addition process for drinking water treatment. Recent chemical sequencing research by DiTommaso and van Benschoten looked at two modes of chemical addition. In one method the coagulant was added to the water, depressing the pH, and allowed to react before pH was increased to a desired level (variable pH pathway). In the second mode the coagulant was mixed with base prior to contact with the water (constant pH pathway). The effectiveness of each mode was measured by turbidity and UV 254 absorbance (UVA) removal after settling. In experiments that used a natural surface water, UVA removals were significantly greater for the variable pH pathway at lower alum doses. At higher doses UVA removals were marginally greater for the variable pathway. The pH range of 5.5-6.0 produced optimum UVA removal. Turbidity removal was greater for the variable pH pathway at all alum doses. These experiments suggest that the positively-charged hydrolysis species, which exist in higher concentration at lower pH levels, may be important in the NOM and particle removal process.

Wahlroos (1991) reported the use of a two-stage coagulation process in which iron (III) sulfate was added at a pH of 4.8 – 5.1, followed by pH adjustment and then a second stage of iron coagulation at a pH of 8.0 – 8.5. The two-stage method was initially developed and tested in bench and pilot-scale experiments before being implemented at a full-scale facility. The process increased filter run times and increased removal of taste-and-odor compounds from 50 to 90 percent. Removal of chemical oxygen demand

(COD) was also increased when the coagulation process was changed from one to two stages. The first coagulation process was intended for removal of humic substances and the second process was intended for particle removal and precipitation of metals.

Multi-stage coagulation processes have been documented for applications other than drinking water treatment. Garrote et al. (1995) describes effective treatment of a tannery waste stream, containing high concentrations of BOD, COD, and sulfides, by a two-step coagulation process. The authors, using COD reduction to gauge the effectiveness of the process, found that two similar coagulation stages were far more effective than a single stage, but that three stages were only marginally more effective than two. Although the use of two-stage coagulation processes are not well-documented, these studies indicate that the process may improve settling and filtration performance, particularly for high-NOM raw waters that can be encountered in drinking water treatment applications.

EXPERIMENTAL METHODS

Both bench and pilot scale experiments were conducted at the Fort Collins Water Treatment Facility (FCWTF) in Fort Collins, Colorado. The water used in the experiments was from the Cache la Poudre River (Poudre River) which originates in the Rocky Mountains and is subject to extreme water quality variations during the snow runoff period in late spring and early summer. The water quality during the two distinct annual periods are shown in Table 4.1. During most of the year, the river water is characterized by a low turbidity and low DOC with a moderate alkalinity. Effective treatment typically consists of alum addition with

Table 4.1 Poudre River raw water quality range: spring runoff and native flow conditions.

Constituent	Units	Typical Water Quality (August-April)	Runoff Water Quality (May-June)
Turbidity	NTU	0.4-1.0	4-50
DOC	mg/L	1.2-2.5	5-12
SUVA	$(\text{m-mg/L})^{-1}$	2.2-3.4	3-4.5
Alkalinity	mg/L as $CaCO_3$	24-32	10-16
pH		7.0-7.4	6.8-7.0
Temperature	°C	0.5-15	8-12

conventional sedimentation-filtration. During the snow run-off period, the DOC concentration and turbidity increase significantly and the alkalinity decreases by more than 50%. The increased DOC concentration results in an increased alum demand with alum doses increasing from an average of 18 mg/L to over 35 mg/L. The reduced source water alkalinity and increased alum dose results in an unacceptable pH depression and therefore base addition is required to stabilize the pH.

The FCWTF has traditionally treated Poudre river water by blending it with Horsetooth Reservoir water. The water quality of Horsetooth reservoir water used in bench scale blending experiments is shown in Table 4.2.

The bench scale testing was conducted using two temperature controlled jar testing units. The temperature during testing was generally controlled to 8±2°C using a continuous-flow, raw water bath. Two stirrers (Model 7790, Phipps and Bird, Richmond, VA) with a maximum mixing velocity of 300 rpm were used for both the coagulant rapid mixing and flocculation stages. Alum was used as the primary coagulant

Table 4.2 Raw water quality of Horsetooth Reservoir water during blending experiments.

Constituent	Units	Value
Turbidity	NTU	4.5
DOC	mg/L	3.2
SUVA	$(\text{m-mg/L})^{-1}$	2.3
Alkalinity	mg/L as $CaCO_3$	36
pH		7.3
Temperature	°C	6

and was introduced in an undiluted form (48.5% alum solution) by placing the required amount of liquid on to a Teflon septum and dropping the septum directly into the rapid mixed water. For the two-stage coagulation process, two additions of alum were made with separate rapid mix steps 60 seconds apart.

Bench scale experiments were conducted with and without the addition of a pH-stabilizing base. When pH stabilization was desired, hydrated lime ($Ca(OH)_2$) was added to achieve the pre-coagulation alkalinity target of 35 mg/L as $CaCO_3$. CO_2 gas was added to achieve a pre-coagulation pH of 7.0 without impacting the alkalinity.

A low molecular weight, high charge density, cationic flocculant aid (8110, Nalco, Inc, Naperville, IL) was added after mixing the coagulant for 30 seconds. Flocculation was conducted with three decreasing energy, 15 minute stages (45, 30 and 18 RPM). After flocculation, 9 minutes was allowed for settling, at which point TOC and turbidity samples were collected.

Pilot scale testing was the second phase of this research and was conducted using an 8 gpm pilot plant also located at the Fort Collins Water Treatment Facility. Two identical pilot treatment trains (Figure 4.1) were run simultaneously during this part of the testing. The control train was configured for single stage coagulation and the experimental train was configured for two-stage coagulation. The pilot plant was configured to apply the primary coagulant (alum) in any of three locations: (A) in-line mixer, (B) rapid mix basin 1 or (C) rapid mix basin 2. For the one-stage coagulation experiments, alum was applied directly to the first rapid mix basin. Alum was applied at the in-line mixer and in the first rapid mix basin with a detention time of 30 seconds between the two stages of coagulation. The rapid mix basins had a detention time of 30 seconds and were operated to achieve a mixing energy of approximately 1000 sec^{-1}. Hydrated lime and CO_2 were applied upstream of the coagulation process to achieve a target alkalinity of 35 mg/L as $CaCO_3$ and a pH of 7.0.

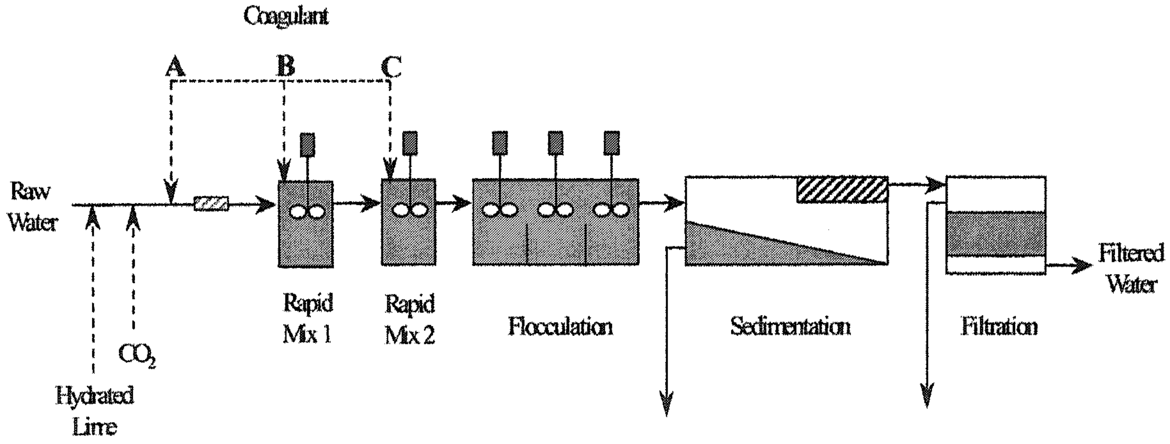


Figure 4.1 Schematic diagram of pilot plant used for pilot-scale verification experiments.

The pilot plant also had a three-stage tapered energy flocculation basin and an inclined plate settling basin that was operated at a loading rate of 0.83 m/hr (based on projected plate area). The same flocculation aid used in the bench scale experiments was applied immediately upstream of the flocculation basin at a dose of 0.3 mg/L. The settled water was applied to a 15 cm-diameter mixed media filter (42 cm depth of 1.1 mm anthracite, 20 cm depth of 0.4 mm sand and 10 cm depth of 0.25 mm fine garnet). The filters were operated in a constant head, declining flow rate mode with an initial loading rate of approximately 19 m/hr and a terminal loading rate of 7 m/hr.

TOC was measured using UV-persulfate oxidation followed by a CO_2 selective membrane which allows quantification by conductivity (Sievers 800, Sievers Inc., Boulder CO). Dissolved organic carbon (DOC) was determined using 0.45 µm silver filters (Poretics, Livermore, CA). Turbidity was measured using a Hach 2100AN turbidimeter (Hach Inc., Loveland CO).

RESULTS/DISCUSSION

Bench scale jar tests were initially used to compare coagulation effectiveness between one-stage and two-stage coagulation processes. Six alum doses were applied for each experiment ranging from 30 mg/L (as $Al_2(SO_3)_4$-14.3 H_20) to 80 mg/L in increments of 10 mg/L. The alum dose was split equally for the two-stage coagulation experiment. The pH was stabilized by adding lime and CO_2 to achieve a pre-coagulation alkalinity of approximately 35 mg/L as $CaCO_3$ and a pH of 7.0. These pre-coagulation conditions resulted in post-coagulation pH values ranging from 6.5 for a dose of 30 mg/L to 5.8 for an alum dose of 80 mg/L.

The results from these experiments, shown in Figure 4.2, indicated a significant improvement in settled water turbidity with the two-stage coagulation process.

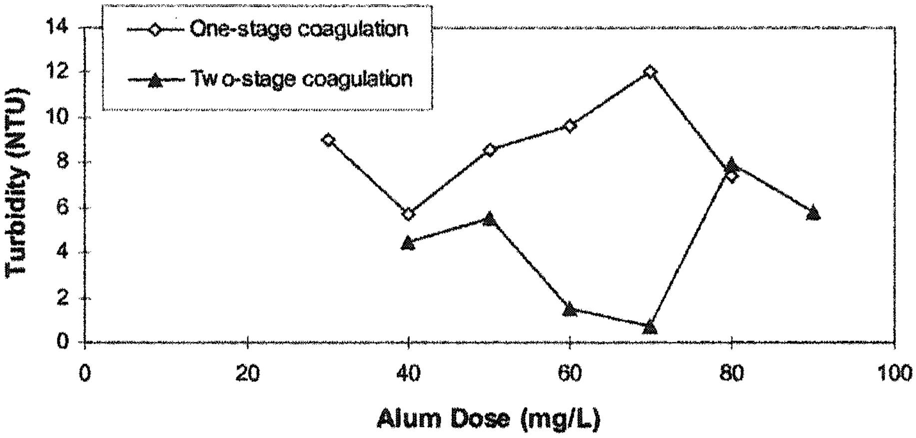


Figure 4.2 Jar test settled water turbidity results comparing single-stage and two-stage alum coagulation processes for Poudre water (turbidity = 5.3 NTU, TOC = 6.8 mg/L).

When alum was added in one stage, the optimum alum dose was 40 mg/L resulting in a settled water turbidity of 5.9 NTU, higher than the raw water turbidity of 4.3 NTU. As the alum dose was increased above 40 mg/L, the settled turbidity also increased, indicating that the additional aluminum hydroxide solids were not settling. The results from the two-stage coagulation process were considerably better, a settled water turbidity of 2.0 NTU at a total alum dose of 50 mg/L.

The next set of experiments were designed to understand which water quality constituents were causing the poor treatability of the water with the one-stage coagulation process. Plant operators have found that a 50%/50% blend of Horsetooth and Poudre waters produced acceptable treated water quality results. These experiments were designed to determine if the improvement in treatability was due to the dilution of the

NOM with a lower TOC source water or the addition of the inorganic solids from the reservoir source.

Three preparations of Poudre river water were tested at the bench scale using one-stage coagulation with alum: a control (100% Poudre), a Horsetooth/Poudre blend (50%/50%) and DI water/Poudre blend (50%/50%). The results of these experiments are shown in Figure 4.3. Coagulation of the two blended waters resulted in significantly lower settled water turbidities than the control (100% Poudre water). The blend of DI water (0.3 mg/L DOC) with Poudre resulted in a settled water turbidity of less than 0.5 NTU whereas the blend of Horsetooth water (3.2 mg/L DOC) resulted in a settled water turbidity of 2.7 NTU.

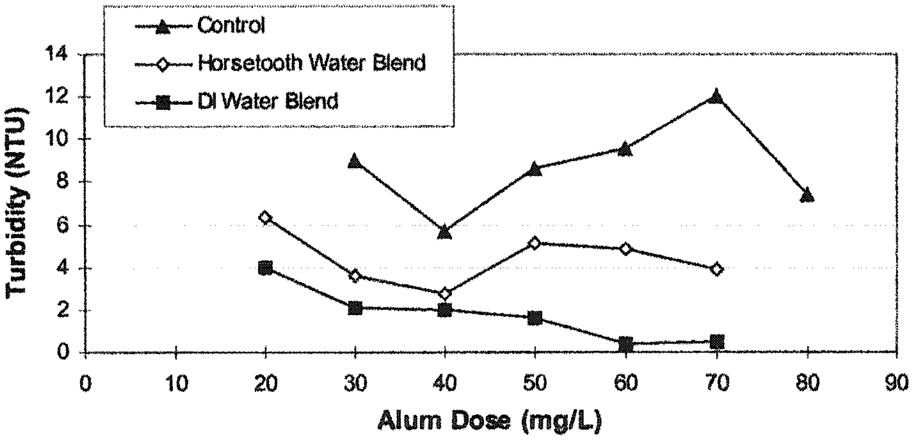


Figure 4.3 Jar test settled water turbidity results for one-stage coagulation conditions of Cache la Poudre River water (turbidity = 5.3 NTU, TOC = 6.8 mg/L): control, Horsetooth reservoir water blend and DI water blend.

Based on these results, a mechanism for the increased efficacy of the two-stage coagulation process is proposed in Figure 4.4. It is hypothesized that the Al^{+3} ion is being hydrolyzed to $Al(OH)_{3(s)}$ colloids and in the absence of ideal mixing, the positively

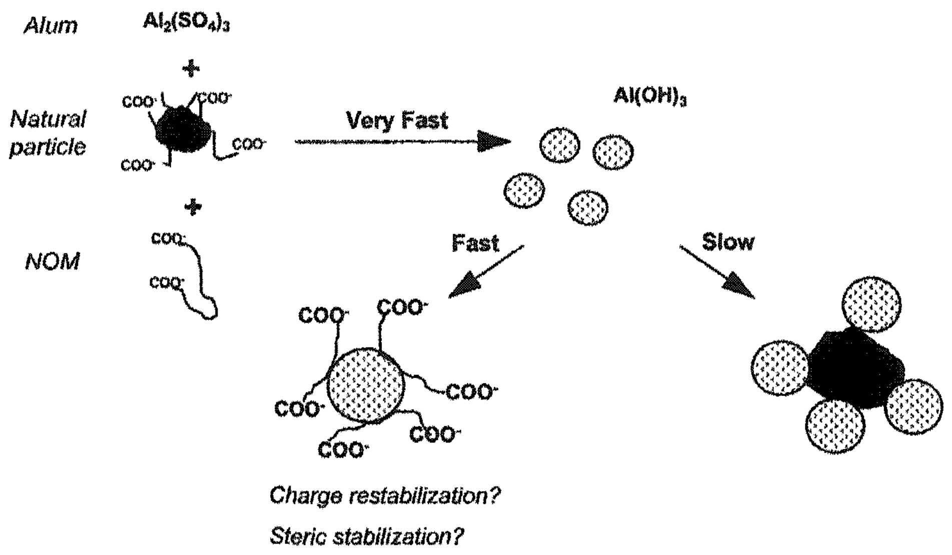
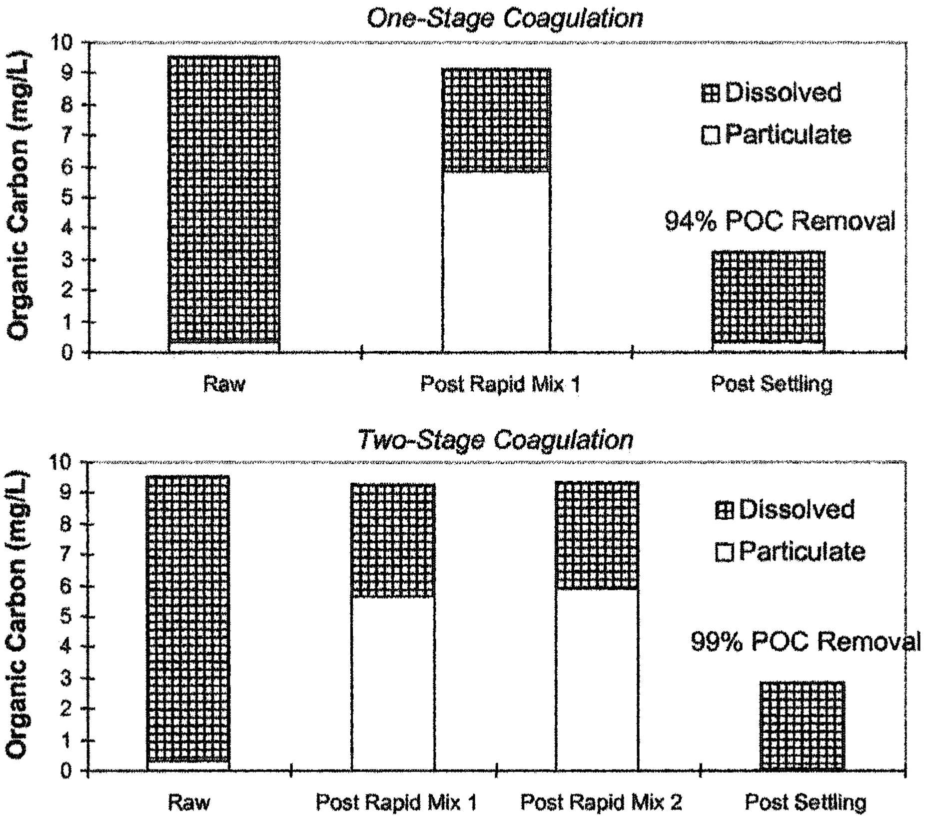


Figure 4.4 Proposed mechanism for restabilization of coagulated particles.

charged aluminum hydrolysis sols do not react with the hydrophobic NOM compounds immediately. Instead, hydrolysis produces aluminum hydroxide colloids. The hydrophobic NOM molecules adsorb to the surface of the freshly precipitated aluminum hydroxide resulting in either electrostatic or steric stabilization. The restabilization of the aluminum hydroxide colloids effectively prevents $Al(OH)_{3(s)}$ agglomeration resulting in stable, small, unsettleable, unfilterable floc that are less effective for sweep flocculation-type processes. The observed restabilization of colloidal particles with NOM has been documented in the literature by several researchers (Tipping and Cooke, 1982; Wilkinson and Negre, 1997).

If the proposed restabilization mechanism is accurate, a two-stage coagulation process should be effective since the hydrophobic NOM will be adsorbed to the $Al(OH)_{3(s)}$ colloids during the first stage of coagulation allowing the aluminum hydroxide solids formed during the second stage to agglomerate to a size that will result in sweep flocculation.

To explain the results further, the NOM was fractionated into dissolved (DOC) and particulate (POC) organic carbon fractions for each process step (Figure 4.5). POC in the raw water was negligible but immediately after the rapid mix step, this fraction becomes significant as the NOM sorbs to the freshly formed aluminum hydroxide solid surfaces. The presence of a second coagulation step does not increase the fraction of POC even though the solid surface area is increased. This result indicates that the sorption of NOM onto metal hydroxide surfaces is not limited by surface area through the first rapid mix step, but rather by the concentration of easily sorbable NOM. This result supports the hypothesis of Edwards (1997) that NOM can be characterized by sorbing and non-sorbing fractions. The effect of the second coagulation step can be seen by


One-Stage Coagulation

Two-Stage Coagulation

Figure 4.5 The fractionation of TOC with and without sequential coagulation steps.

comparing the relative fractions of POC after the settling step. It appears that with the two-stage coagulation process, more of the POC is settled. The proposed mechanism would require a first stage coagulant dose high enough to provide metal hydroxide surfaces for the sorbable fraction.

The bench scale results discussed above were collected using jar testers that potentially represent a worst case rapid mixing scenario since the equipment is limited to an energy of less than 300 sec^{-1}. The bench scale process was verified with more realistic mixing conditions using a pilot plant that was equipped with an in-line static mixer (G=1500 sec^{-1}) and a rapid mix energy of 1000 sec^{-1}.

A comparison of pilot scale one- and two-stage alum coagulation processes is presented in Figure 4.6. Operating two parallel treatment trains simultaneously for a period of over 12 hours, the settled water turbidity of the two-stage process was about

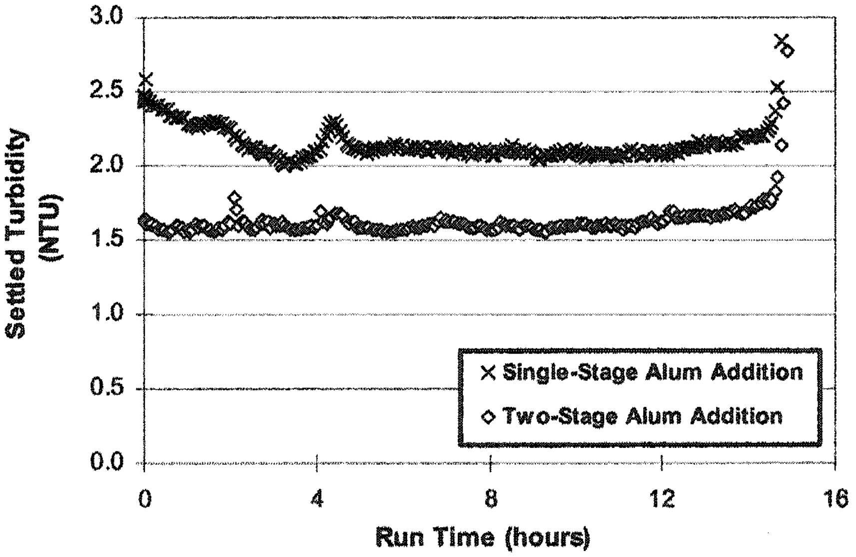


Figure 4.6 Pilot scale comparison of settled water turbidity for two-stage vs. single stage alum coagulation (turbidity=11.5 NTU, TOC=9.1 mg/L, $pH_{coagulation}$ = 6.5).

25% less than the one-stage process (1.6 NTU versus 2.1 NTU). The difference between the one- and two-stage coagulation processes was significantly less for the pilot scale experiments than the bench scale experiments. This could be due to the increased mixing effectiveness at the pilot scale which could reduce the impact of the hydrophobic NOM restabilization mechanism.

Settled water turbidity is important but the critical performance parameter for a drinking water treatment plant is filtered water turbidity or particle counts. The effect of the one- and two stage coagulation processes on filter performance was compared using particle counts for simultaneous filter runs (Figure 4.7). The results indicate that the steady-state baseline particle counts for the two-stage coagulation process are approximately 50% less than the one-stage process (10 particles>2µm/ml versus 20 particles>2µm /ml). Perhaps more importantly, the one-stage process began to show

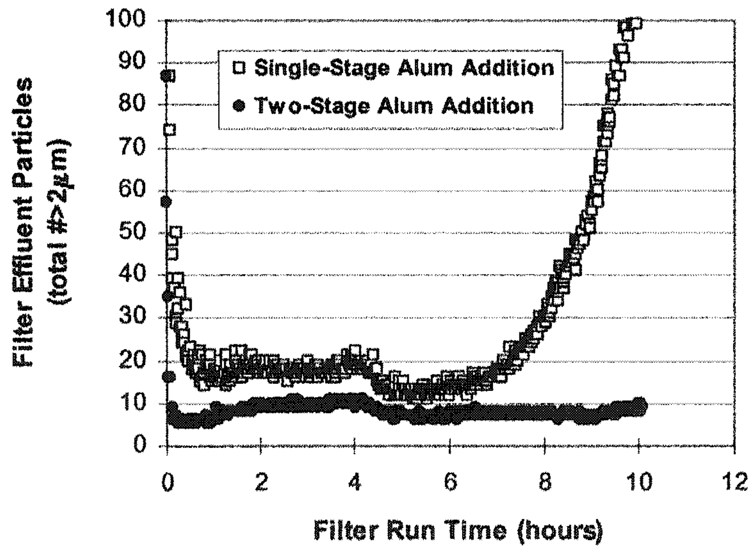


Figure 4.7 Pilot scale comparison of filtration performance between single and two-stage alum coagulation processes (turbidity=11.5 NTU, TOC=9.1 mg/L, $pH_{coagulation}$ = 6.5).

particle breakthrough 3 hrs before the filter run would have terminated based on headloss. The two-stage process did not exhibit particle breakthrough during the run.

Filter performance appears to be significantly more sensitive to the staging of the coagulant than the settling process performance when treating a water with a high concentration of NOM. The number of particles that are restabilized due to hydrophobic NOM adsorption appears to be important when considering filtered water particle counts but less so when measuring settled water turbidity. An important unresolved question is the impact of coagulant staging on the filtration process when treating waters with lower concentrations of NOM.

CONCLUSIONS

The treatment of storm or snow-runoff impacted water can be an issue for many drinking water utilities across the country. Treatability of these impacted source waters is often reduced due to the elevated concentrations of NOM, particularly the hydrophobic or humic fraction. A two-stage alum coagulation process has been compared with a single-stage process with positive results. When a two-stage coagulation process was used, the settled water turbidity was reduced by 25% and more importantly, the steady-state filtered water particle counts were decreased from 20 particles/ml to 10 particles/ml and the pre-mature particle breakthrough exhibited with the one-stage process was eliminated.

A mechanism for the improved performance of the two-stage process has been proposed based on the formation of NOM-restabilized aluminum hydroxide colloids.

Aluminum hydroxide colloids become restabilized by NOM when inadequate mixing allows the aluminum hydroxide colloids to begin flocculating without contacting the NOM molecules. With adequate mixing, efficient NOM-aluminum interactions would occur and adsorption to metal hydroxide surfaces would not result in the restabilization of the colloid.

The two-stage coagulation process has been shown to improve the treatability of a source water that has a high TOC concentration and a high fraction of hydrophobic NOM. When considering the effectiveness of a coagulation process, the impact on the entire filtration process must be considered. Two-stage coagulation processes need to be studied for a wider range of water qualities in this context.

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CHAPTER 5

RESULTS AND DISCUSSION

Relationship of pH and Floc Formation Kinetics to Granular Media Filtration Performance

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ABSTRACT

In drinking water treatment, destabilization of suspended particles through effective coagulation processes is critical for optimizing filtration performance. This study examined the impact of coagulation pH (6.0 - 7.4), ζ-potential, and floc formation kinetics on particle removal during settling and filtration. Increasing pH improved turbidity removal in the settling process and significantly increased the zeta potential range in which filtration performance was optimized. Although it was possible to optimize filtration (i.e. attain total particles < 10/mL) at each of the three pH levels examined, the ζ-potential range in which this was possible was approximately $^{+}2$ to $^{+}4$ at pH = 6.0 and $^{-}4$ to $^{+}4$ at pH = 7.4. Overall, these results indicate that the use of a higher coagulation pH—and thus higher alum doses—may be particularly advantageous during periods of rapidly changing water quality conditions, such as high-NOM runoff events. Results from PDA experiments indicated that the rate of floc formation (measured immediately following coagulant addition) was indicative of overall process performance.

INTRODUCTION

In raw water supplies lacking sufficient buffering capacity, particularly runoff from snowmelt or thunderstorms and those waters associated with reduced or low-pH environments, the use of alum during treatment requires alkalinity addition for pH control. Because runoff waters often contain relatively high concentrations of NOM, the alum demand in these waters is proportionally high, further emphasizing the need for pH control. The target coagulation pH (for non-softening plants) is usually between 6.0 and 7.5. Within this range it is possible to minimize the concentration of soluble aluminum in finished water and effectively remove organic and particulate matter, as demonstrated by previous authors (*1,2*). However, within this pH range the overall effectiveness of the treatment process, particularly filtration performance, can differ significantly.

Research Objectives The primary objective of this research was to understand the impact of coagulation pH and ζ-potential on floc formation kinetics and granular media filtration performance. The secondary goal was to determine effective coagulation processes for treating challenging (i.e. runoff-type) raw waters.

The intent of this paper is not to develop a theoretical model of filtration, but rather to understand some important chemical factors that influence coagulation and to extend these findings to filtration. It is hoped that the combination of laboratory and pilot-scale results to be presented will further the knowledge of the impact of coagulation chemical sequencing on filtration.

LITERATURE REVIEW

Role of aluminum species The subject of alum coagulation has been extensively researched and discussed in the literature. In the pH range of 6.0 – 7.5, the two Al species that appear to control coagulation processes are the short-lived highly positively-charged polymeric intermediates and the poorly water soluble aluminum hydroxide sols that are formed within a few seconds after alum addition (*2,3*). Although the existence of the former has been shown (*4*), their actual contribution to coagulation processes appears to be minor (*5*).

A majority of the evidence suggests that, under water treatment conditions, the positively-charged, insoluble aluminum hydroxide sols are the most realistic species responsible for particle destabilization during coagulation by adsorbing to the surface of the oppositely-charged, much larger natural colloids and entering into an electrical bond (*2, 6 – 8*). At higher pH levels (e.g. 7.5) and coagulant doses, this interaction between voluminous aluminum hydroxide precipitates and natural colloids is known as sweep coagulation (*3,9*). In this mode, particles are destabilized by adsorption of aluminum hydroxide sols and are enmeshed in sol aggregates, promoting the formation of relatively large, settleable floc. At pH=6.0, particles are also destabilized primarily by aluminum hydroxide sols, which are more positively-charged (compared to pH=7.5). However, at lower pH levels and thus lower alum doses, the physical enmeshment mechanism is less significant and smaller, lighter flocs develop. It should be noted that large aluminum hydroxide aggregates (formed after approximately 60 sec., for example) are by themselves ineffective for destabilizing natural colloids and removing turbidity (*6*). The adsorption of newly-formed, positively charged $Al(OH)_{3\,(s)}$ to colloid surfaces is critical at both pH levels.

Impact of coagulation pH In terms of the sedimentation process, upon which a majority of research has focused, results have shown that particle removal improves significantly as coagulation pH increases and is generally optimized in the range of 7.2 – 7.6 (*10-12*). Matsui et al. (*13*), using a photometric dispersion analyzer (PDA), also reported that the time required for particle destabilization and the onset of floc formation decreased as pH and alum dose increased. It is less clear whether the benefits of higher coagulation pH observed for the settling process extend to filtration.

Use of ζ-potential for process optimization Several excellent studies have demonstrated, under idealized laboratory conditions, the relative impact of various physical and chemical variables on particle attachment in packed beds (*14-17*). These studies emphasized the importance of optimizing particle zeta potential (or electrophoretic mobility)—not necessarily pH—to produce favorable conditions for particle removal. Elimelech and O'Melia (*15*), for example, clearly showed that the removal efficiency of 0.75 μm particles increased as ζ-potential decreased (i.e. approached zero). Because it is an indicator of the effective surface charge and therefore the degree of destabilization of a particle, which are perhaps the most dominant variables affecting attachment to filter media (*18-20*), a number of studies have used ζ-potential (or electrophoretic mobility) for coagulation process control (*2*). The ζ-potential range of properly destabilized particles is usually reported to be in the range of –4 - +3 mV (*9*). For these reasons, in the research presented here, optimum alum doses, at least initially, were considered to be those that achieved a ζ-potential of approximately 0.0 ± 2 mV.

Influence of coagulation pH on NOM removal A few general conclusions can be drawn from previous research that has examined NOM removal during alum coagulation: 1) there is a sorbable fraction of NOM, generally characterized by higher molecular weight and hydrophobic tendencies, that is amenable to removal through coagulation and a non-sorbable fraction that can not be removed through practical methods (*21-23*) and 2) the dominant removal mechanism in the pH range of 5.5 – 8.0 is by adsorption to aluminum hydroxide surfaces (*21,24*). Therefore, over the pH range of interest to this study (6.0 – 7.5), it seems reasonable to assume that NOM removal should be similar if optimized alum doses are used, as shown previously (*1,25*).

MATERIALS AND METHODS

The general experimental approach was to first characterize the relationship between coagulation pH and settling performance (turbidity/DOC removal) for optimized alum doses and to correlate these results with PDA experiments in which floc formation rates were measured vs. time. These experiments were performed at bench-scale using a synthetic water in order to precisely control water quality variables. In the second phase, the impact of pH (for both optimized and non-optimized alum doses, in terms of zeta potential) on granular media filtration performance was examined in pilot-scale experiments using two natural surface water sources. In the third and final phase, PDA experiments were conducted with the two surface waters in an attempt to correlate the filtration results with floc formation kinetics.

Water quality The synthetic water was made with DOC concentrations of 3.3 and 8.8 mg/L (Suwannee River NOM, from the International Humic Substance Society, was added to de-ionized water), alkalinity of 20 mg/L as $CaCO_3$, turbidity of 20 NTU (kaolin stock suspension) and a hardness of 25 mg/L as $CaCO_3$. The two natural surface waters were a mountain river during spring runoff, characterized by high-TOC/low alkalinity and a reservoir source characterized by low-moderate NOM levels and relatively stable water quality (see water quality data in Supporting Information, Figures 5.12 and 5.13). All bench and pilot-scale experiments were conducted at 8.0° ± 1.0° C.

Bench-scale protocol To characterize the relationship between pH and settling performance, jar tests were conducted with the synthetic water (Phipps & Bird programmable jar test apparatus). A four-stage mixing process, including rapid mix (15 sec. at 300 rpm [$G=300\ sec^{-1}$]), and flocculation (three 15-minute stages at 48, 32, and 18 rpm [$G=48$, 32, and 18 sec^{-1}]) was followed by a 15-min. settling period, after which samples were collected and analyzed for turbidity (Hach 2100), DOC (UV/persulfate oxidation method; Sievers TOC Analyzer, model 800). ζ-potential (Zeta-Meter, model 3.0^{+}) samples were collected approximately 15 seconds after the rapid mix stage. Prior to the addition of alum, an appropriate dose of acid (2.5 N HCl) or base (2.5 N NaOH), determined by titrations, was added to achieve the target coagulation pH of 5.5, 6.0, 6.7, or 7.5. The only coagulation chemicals added were alum and acid/base for pH control. Optimum doses in these experiments were defined as those that achieved a z.p. closest to zero *and* within the range of 0.0 ± 2.0 mV.

Photometric Dispersion Analyzer One parameter used to evaluate different coagulation scenarios was microfloc formation kinetics, monitored with a photometric dispersion analyzer (PDA). The output from the PDA, or flocculation index (FI), corresponds to particle size and has been shown to be a sensitive indicator of the state of aggregation of a particle suspension (schematic diagram of PDA apparatus provided in Supporting Information, Figure 5.9). A rapidly increasing FI following alum addition, for example, is indicative of optimum particle destabilization conditions. The method was originally developed by Gregory (*26*) and has been described in detail by several researchers who used it to monitor microfloc development during coagulation (*27,28*). The most practical use of the FI is that it shows a significant increase as particles aggregate, thus allowing a dynamic assessment of coagulation mechanisms (*13*).

Pilot-scale experiments A total of 17 and 27 filtration runs were conducted using the runoff and reservoir sources, respectively. The pilot facility consisted of three parallel, 8-gpm conventional treatment process trains (see facility photo in Supporting Information, Figure 5.11). Each train included a rapid mix basin (standard backmix-type reactor, detention time=15 sec.); three-stage, tapered mixing energy flocculation basins (total DT = 45 minutes, G values ~ 50, 30, and 18 sec^{-1}), Lamella plates settling basin (hydraulic loading rate = 0.34 gpm/ft^2), and dual media filters (30" anthracite, 10" sand). The initial filtration rate used for all experiments was 4.0 gpm/ft^2 and filters were operated in a constant head/declining rate mode. For both water sources, the decline in filtration rate vs. time was approximately equal at all three pH levels (see data in Supporting Information, Figure 5.10). Performance was evaluated based on filter effluent particle counts (Met One particle counter) and TOC concentration. Each pilot train was equipped with on-line pH meters (Great Lakes Instruments) for raw and post-rapid mix water.

The goal in a majority of the filtration experiments was to optimize alum dose at each pH level based on ζ-potential (automated Malverne Instruments Zetasizer 2000).

However, runs were also conducted at non-optimum z.p. in an attempt to characterize the optimum operating range for each process, particularly at pH=7.4, which exhibited a relatively wide optimum range. In the majority of experiments in which the alum doses were targeted to produce optimum ζ-potential conditions (doses were *not* set at a constant value for each pH condition), actual zeta potential values varied between 0 and +4.5 mV due to fluctuating raw water quality conditions, particularly during spring runoff ζ-potential sampling ports were located approximately 45 seconds downstream from the point of alum addition. For the ionic strength of these coagulated waters (approximately $2.2*10^{-3}$ M at pH=6.0), the ζ-potential values calculated from electrophoretic mobility data (Henry equation) were considered valid for particles greater than approximately 1.3 μm. The fraction of sub-1.3 μm particles present in the samples was assumed to be very small and not a significant factor in ζ-potential calculations (see Supporting Information for detailed discussions of ζ-potential calculations and related particle size issues).

In the runoff experiments, due to the limited duration of these conditions, only two target coagulation pH levels, 6.1 and 7.4 ± 0.1, were used. Alum doses ranged from 26 – 37 and 70 – 97 mg/L for the low and high pH levels, respectively. For the reservoir water the target coagulation pH levels were 6.0, 6.7, and 7.4 ±0.1 (see Supporting Information, Figure 5.11, for pH control methods used in pilot experiments).

RESULTS AND DISCUSSION

Bench-scale experiments In the first set of bench-scale experiments using the synthetic waters, alum doses were optimized based on ζ-potential for two TOC concentrations over a pH range of 5.5 – 7.5 (see Supporting Information, Figure 5.14). Settled water turbidity and DOC removal data corresponding to the optimized alum doses are shown in Figure 5.1. As noted by previous researchers (*10 – 12)*, turbidity removal increased directly with pH and alum dose, with a more dramatic impact observed for the high-TOC water. In both cases, particle removal was optimized at pH = 7.5. DOC removal was maximized at pH = 6.0 but, particularly for the high-TOC water, the impact of pH was relatively minor.

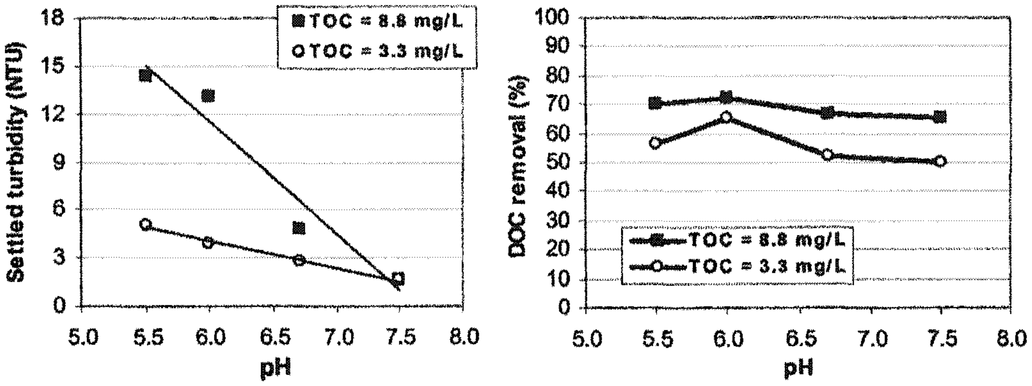

Figure 5.1 Bench scale turbidity and DOC removal for optimized alum doses (synthetic water, ζ-potential ≈0 mV). For TOC=8.8mg/L, alum doses were, from low to high pH: 33, 51, 80, and 100 mg/L. For TOC=3.3 mg/L, alum doses were 10, 22, 45, and 74 mg/L.

The rate of floc development vs. pH and alum dose for the high-TOC water is illustrated by PDA results in Figure 5.2. The rate of floc formation clearly increases with pH and optimized alum dose. It should be noted that the rate of FI increase is not solely a function of alum dose. As shown in Figure 5.3 (using a similar, high-TOC synthetic water), non-optimum alum doses are reflected by relatively small or slow changes in the FI. In this case the alum dose of 50 mg/L at pH = 7.2 was sub-optimum (ζ-potential = -7.2 mV).

Filtration results—spring runoff water The first set of pilot-scale filtration experiments were conducted using spring runoff water. In most cases, filter runs were terminated upon particle breakthrough. Although most runs using runoff water were short in terms of typical full-scale treatment, it should be noted that the goal was to isolate the relative effects of coagulation pH and ζ-potential on alum processes, without interference from other coagulation chemicals.

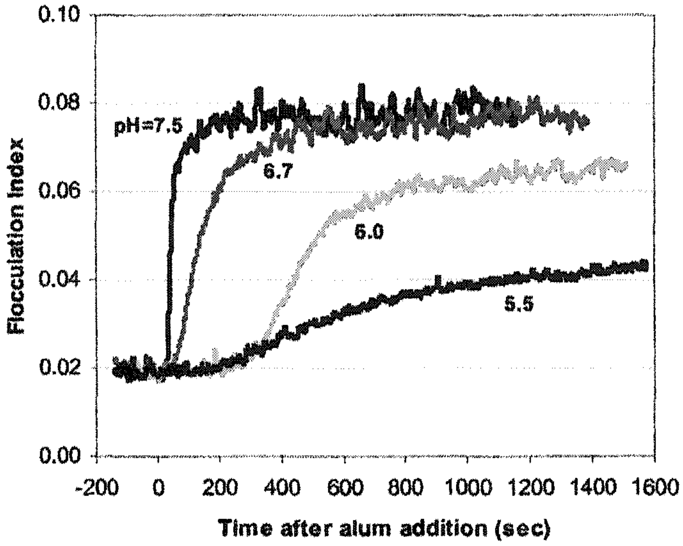

Figure 5.2 Flocculation index vs time for optimized alum doses at 4 pH levels. TOC=8.8 mg/L and T=9 deg C.

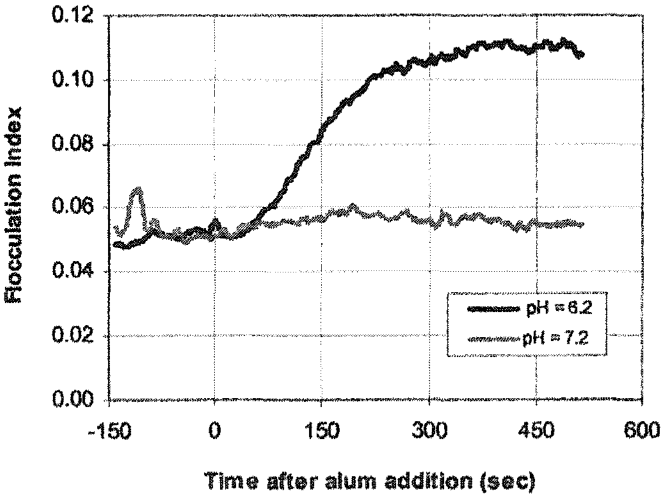

Figure 5.3 Flocculation index vs time after alum addition (50 mg/L). T= 10 deg, TOC=9.0 mg/L.

For experiments conducted at different pH values, a ζ-potential of zero, indicative of destabilized particles, was used as the initial target. However, after several preliminary filtration runs were conducted at different z.p. values, it was clear that a positive ζ-potential was optimum for the experimental conditions being used (see Supporting Information, Figures 5.15 and 5.16). The ζ-potential target was therefore adjusted to approximately +2.5 ± 1.5 mV, but runs were also performed at non-optimum ζ-potential (after all the runoff filtration data had been collected and reviewed, the trends indicated that the actual target coagulation ζ-potential should have been +4.0 – +5.0 mV).

Figure 5.4 presents typical results from filtration runs performed simultaneously on two parallel process trains. The primary goal in these runs was to operate at the same ζ-potential, as close as possible to the target of +2.5 mV. Depending on site-specific water quality goals, these results indicate that the use of a higher coagulation pH—and thus higher alum doses—may be particularly advantageous during periods of rapidly changing

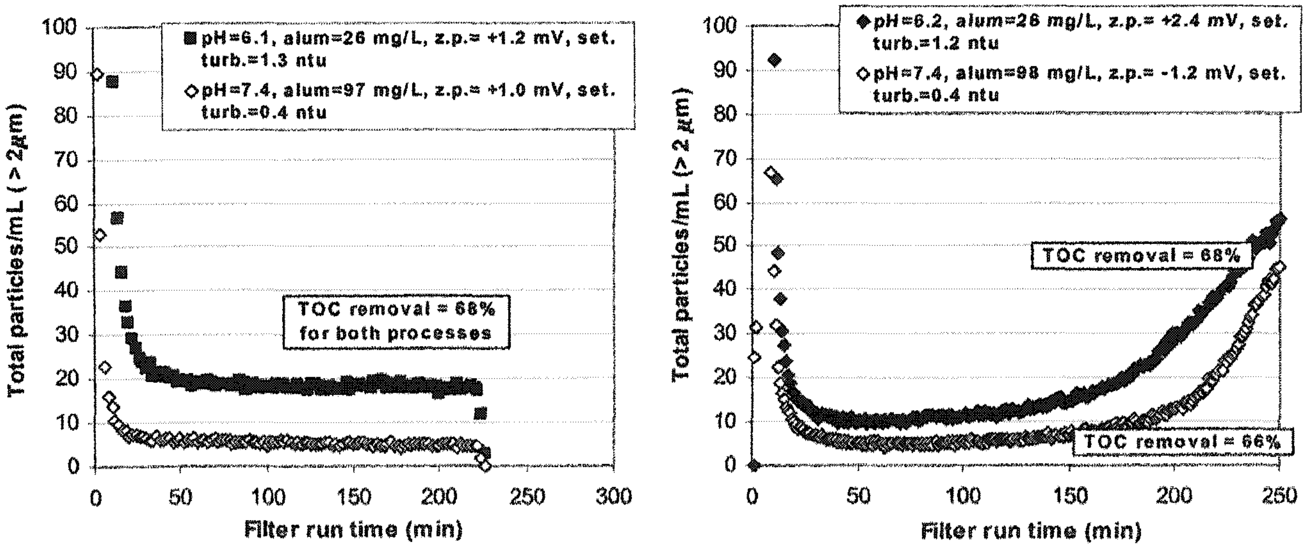

Figure 5.4 Filtration performance for constant ζ-potential using spring runoff water. Raw water TOC=7.5 mg/L.

water quality conditions, such as high-NOM runoff events. TOC removal for the two processes was approximately equal. Clearly, however, a high-pH process would not be practical, in terms of chemical feed costs and solids handling issues, for less challenging raw water that is effectively treated by conventional processes.

In Figure 5.5, steady-state (i.e. the relatively constant operating conditions following the filter ripening period) settled turbidity and filter effluent particle counts from all the runoff experiments are plotted against the corresponding coagulation ζ-potential from each run. As observed in the bench-scale experiments, turbidity removal in the sedimentation process was consistently greater at higher coagulation pH. Overall, the trends in filtration results showed that excellent filter effluent quality (total particles < 10/mL) was attainable at both pH levels, but that higher pH may provide more consistent performance over a wider range of coagulation conditions. At low pH, steady-state particle counts increased rapidly as ζ-potential moved from the optimum range (+2 – +4 mV) and towards zero. At high pH, optimum filtration performance was sustained over a wide range and was clearly less sensitive to ζ-potential. This effect was not due solely to the solids mass loading rate on the filters, as evidenced by the fact that particle counts at low pH (relatively high settled turbidity) *were* equivalent to those at high pH (low turbidity), but only when coagulation ζ-potential was in the optimum range of approximately 2 – 4 mV.

Filtration results—reservoir water The second set of pilot-scale filtration experiments was conducted using the lower-TOC concentration reservoir water at pH = 6.0, 6.7, and 7.4 ±0.1. As observed for the runoff water, alum dose and ζ-potential changes had a greater effect on filtration performance at lower pH levels (see Supporting Information, Fig. 5.17 – 5.19).

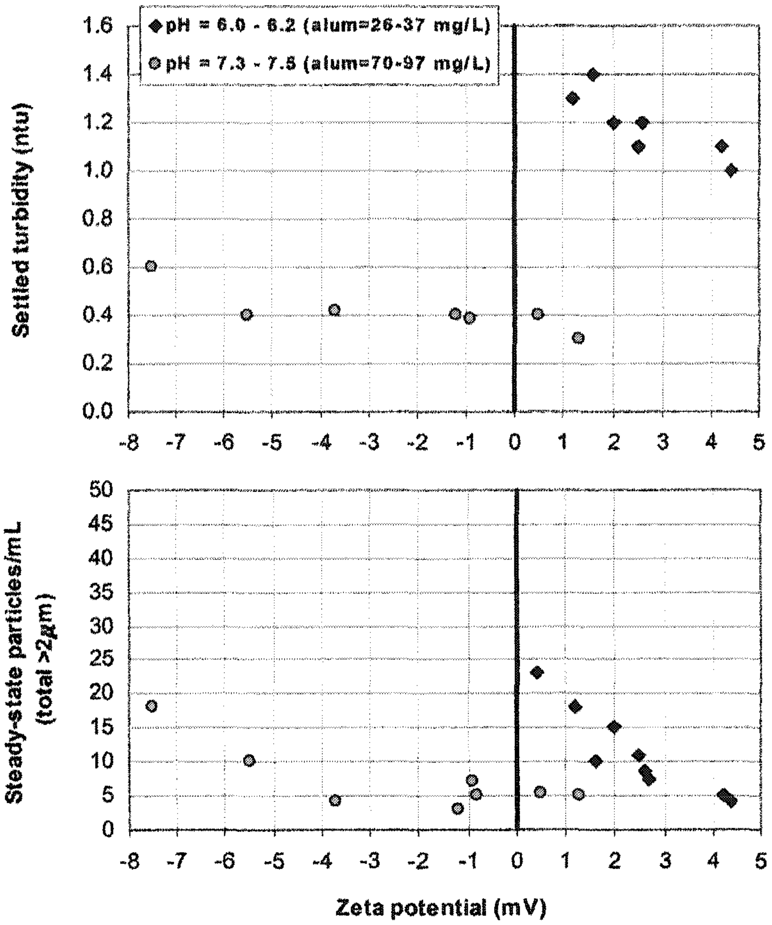

Figure 5.5 Steady-state filter effluent particle counts and settled turbidity vs. ζ-potential using spring runoff water. TOC=6-8 mg/L.

In Figure 5.6, steady-state settled water turbidity and filter effluent particle counts are plotted against the corresponding coagulation ζ-potential for the reservoir runs. The optimum ζ-potential range for filtration was similar at pH = 6.0 and 6.7 (+1 - +3 mV). Although identical ζ-potential values were not used for all coagulation conditions, it appears that the optimum range at pH=7.4 (approximately – 4 - +3 mV) was significantly wider than at the lower pH levels. The optimum z.p. range at pH = 6.0 and 7.4 was very similar for the reservoir and runoff sources, indicating that these ranges were not significantly impacted by the significantly different water quality conditions of the reservoir and runoff sources. Raw water turbidity, for example, which varied from 3 – 6 ntu for the runoff water and 15 – 19 ntu for a majority of the reservoir runs, appeared to exert an insignificant influence on filtration performance, compared to the alum dose and ζ-potential conditions.

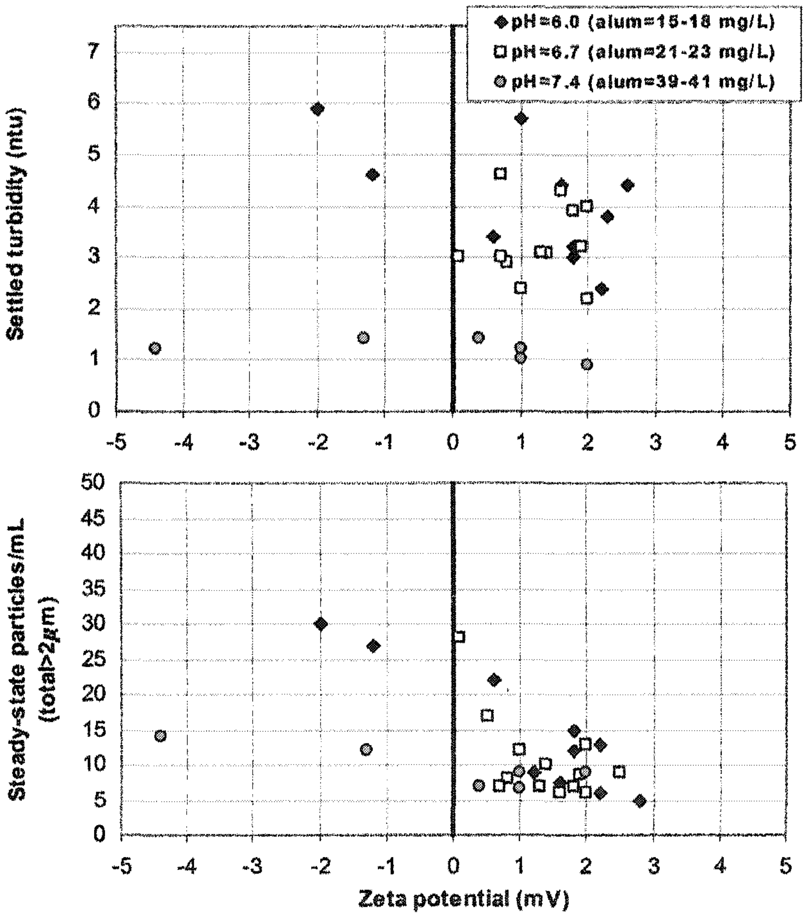

Figure 5.6 Steady-state filter effluent particle counts and settled turbidity ζ-potential for three coagulation pH levels using reservoir water. Raw TOC=3.5 mg/L.

As was observed in the runoff experiments, filtration performance was not solely a function of solids mass loading rate. As shown in Figure 5.6, steady-state particle counts equivalent to those attained at pH = 7.4 (settled turbidity ≈ 1 ntu) were possible to attain at pH = 6.0 and 6.7 (settled turbidity = 2 –5 ntu) when the ζ-potential was optimized. Settled water quality, although broadly predictive of filtration performance, was not always an accurate predictor of overall process performance.

Although steady-state particle counts at pH=7.5 were generally <10 total/mL, the importance of dose optimization, particularly for lower pH levels, should not be underestimated. To maintain an optimized process, changes in pH require dose changes because one can not be made without the other (as illustrated in Figure 5.3). As shown in Figures 5.5 and 5.6, the total range of ζ-potential examined in this study was relatively small, approximately -8 to +5 mV, probably within the realistic operational parameters of a full-scale water treatment system. This range indicates alum doses were either optimum or near-optimum. Even within this narrow range, however, significant differences in filtration performance were observed. At pH= 6.0 and 6.7 in Figure 5.6, for example, particle counts increase rapidly as ζ-potential decreases (becomes less positive) by only a few mV.

Filter attachment mechanisms One question that arises from these results is why the optimum zeta potential range, in terms of filtration performance, appears to increase with high coagulation pH and alum dose. As noted above, this result can not be explained by solids mass loading rate alone. A possible mechanism that may increase filter attachment efficiency is the relatively high concentration of adsorbed $Al(OH)_{3(S)}$ creating a more uniform distribution of positive charges on particle surfaces, therefore increasing the probability of successful particle-media grain collisions (for the post-ripening filtration data presented here, it can be assumed that the primary collectors in the filters were actually the previously retained particles [*20*], not the filter media itself). At low pH, particles are destabilized by fewer but more highly-charged sols, which may result in an uneven surface charge distribution and a reduced probability of successful particle-media collisions. The impacts of surface charge distribution on particle-particle and particle-media interactions have been discussed previously (*15, 29, 30*). Elimelech and O'Melia (*15*) discussed uneven distribution of surface charge as a possible explanation for discrepancies between theoretical and experimentally observed filter attachment coefficients. In discussing hematite particle aggregation, Liang and Morgan (*30*) noted that 1) the assumption of a uniform surface charge distribution was a potential problem because the sites are discrete, and 2) the potential at a given (very small) distance from a particle can differ for uniform and uneven surface charge distributions.

In terms of DLVO theory, a more uniform surface charge distribution on particle surfaces at high pH/alum dose conditions may be analogous to a uniformly compressed electric double layer. In this case the repulsive forces associated with this double layer are minimized, allowing the attractive van der Waals forces to dominate. However, although the electrostatic forces described by DLVO theory play a role in attachment efficiency, its applicability to suspended particle deposition during filtration—particularly under drinking water treatment conditions—has been shown to be quite limited (*15, 31, 32*).

Another effect of high alum doses may be on the *distribution* of ζ-potential in a suspension. Although ζ-potential is normally reported as a single, average value, in reality there is a relatively wide distribution of ζ-potential associated with a suspension of particles (*29,33*). An "optimized" coagulation process for filtration, therefore, may in fact be the one that minimizes the ζ-potential distribution and thus maximizes the fraction of favorably-conditioned particles. The use of high pH/dose processes—which presumably would promote a more uniform coating of positive charges on particle surface—may be an effective method of attaining this goal. Although this issue was beyond the scope of this work, it appears to warrant future investigation.

Correlation of filtration results with PDA output As shown in Figures 5.1 and 5.2, as well as by previous researchers (*34*), settled water turbidity appears to be directly related to the rate of FI increase (floc formation). One goal of this study was to determine the degree to which the PDA output correlates with overall process performance, i.e. filtration results. If rate of floc formation is indicative of the average suspended particle surface charge characteristics (i.e. the degree of destabilization achieved), then it seems reasonable to assume that FI would be related to filtration performance as well because, as noted above, floc particles become the primary particle receptors in filters after the initial ripening period (*20*).

Figure 5.7 presents representative FI curves for optimum and non-optimum alum doses at pH=6.6 ± 0.1 in reservoir water. It appears that a simple and effective method for using FI data to evaluate different coagulation scenarios is to compare FI values at a specific time. For the data presented in Figure 5.7, the FI value at the 180-sec. point (FI_{180}) appears to characterize the relative kinetics of floc formation for each process (these points are circled). At this pH level, the rate of FI increase was greatest for the alum dose (25 mg/L) that was optimum for filtration, in terms of ζ-potential. Higher doses did not significantly increase the rate of floc formation (see Supporting Information, Figure 20).

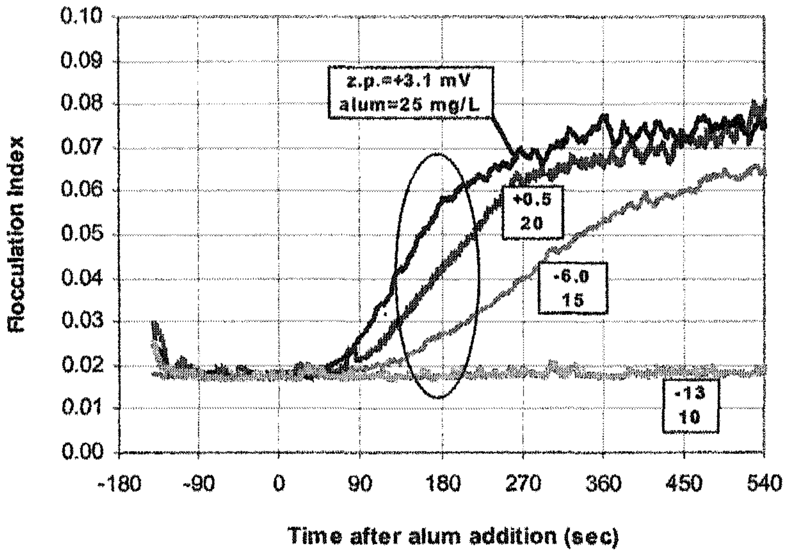

Figure 5.7 FI vs. time in reservoir water for optimum and non-optimum alum doses. T=8 deg C, pH=6.6 +/-0.1, TOC=3.5 mg/L. Applied doses and ζ-potential are given.

These results may indicate that, when using the PDA to optimize overall process performance, the optimum alum dose is the lowest dose beyond which FI does not increase more rapidly. In other words, if FI_{180} were plotted vs. alum dose, the dose at which the slope of the trendline begins to approach zero would be the optimum (this approach is illustrated in Supporting Information, Figure 21). Although use of FI_{180} for comparison of the Figure 5.7 experiments seems reasonable, it appears that selection of the appropriate FI time should be system-specific.

In Figure 5.8, PDA results are shown for each of the three pH levels used in the reservoir filtration experiments. Floc formation kinetics clearly increased as pH/dose increased. In this case, use of FI_{90}, for example, would better characterize relative floc formation kinetics. These data appear to correlate with the results presented in Figures 5.5 and 5.6, which indicate that the ζ-potential range for optimum filtration performance increased as pH and alum dose increased (limited data using runoff water, which show further correlation between PDA and filtration results, are provided in Supporting

Information, Figure 5.22). As a result, the PDA may be a useful alternative to jar tests for determining optimum coagulant doses and quickly evaluating different coagulation scenarios.

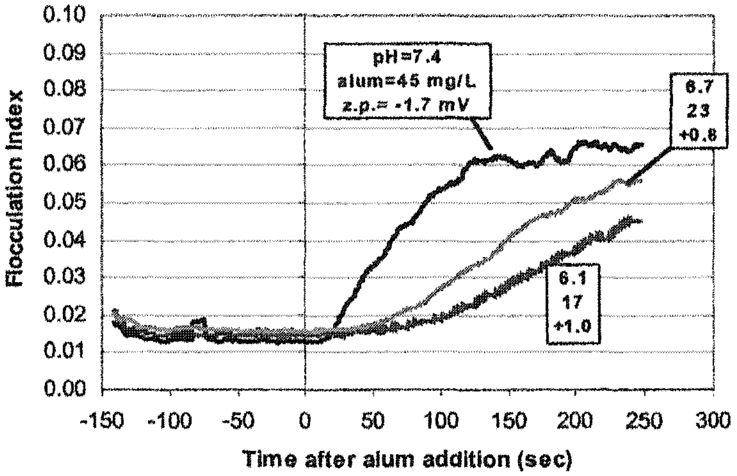

Figure 5.8 FI vs time for for three pH levels in reservoir water. Coagulation pH, alum dose, and z.p. are given. Although these experiments were conducted using reservoir water collected directly from the pilot plant, it appears the alum may have been slightly underdosed, as evidenced by the fact that ζ-potential values are on the low end of the optimum range for each pH level (see Fig. 6).

Acknowledgments

The authors would like to express sincere gratitude to Kevin Gertig and Judy Billica of Fort Collins Utilities for their generous support and the use of the Fort Collins pilot facility.

Supporting Information Available

The Supporting Information that accompanies this manuscript contains water quality data, a photo of the pilot facility, detailed information concerning the zeta potential measurements, additional PDA results, and filtration data (particle counts vs. time for the reservoir and runoff water).

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Relationship of pH and Floc Formation Kinetics to Granular Media Filtration Performance

Supporting Information

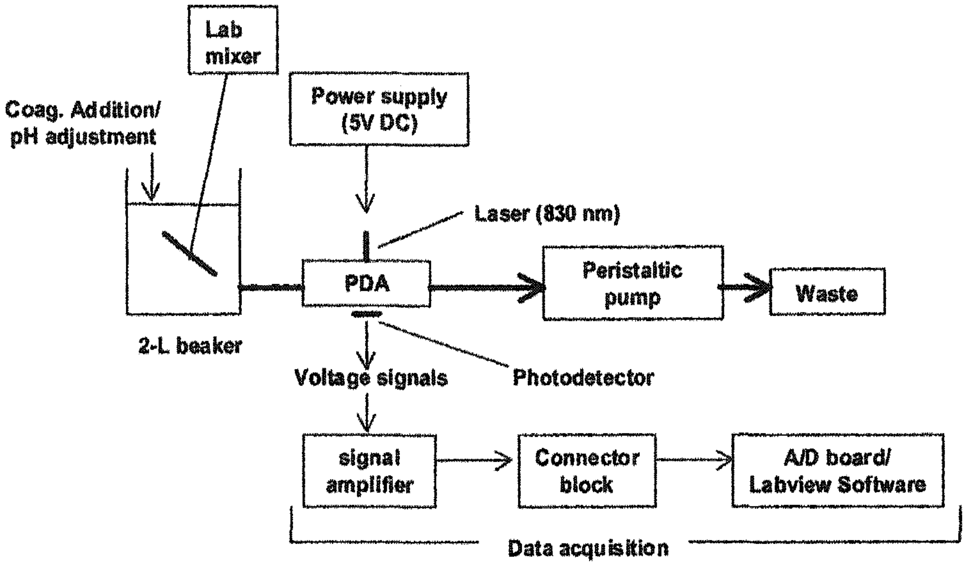
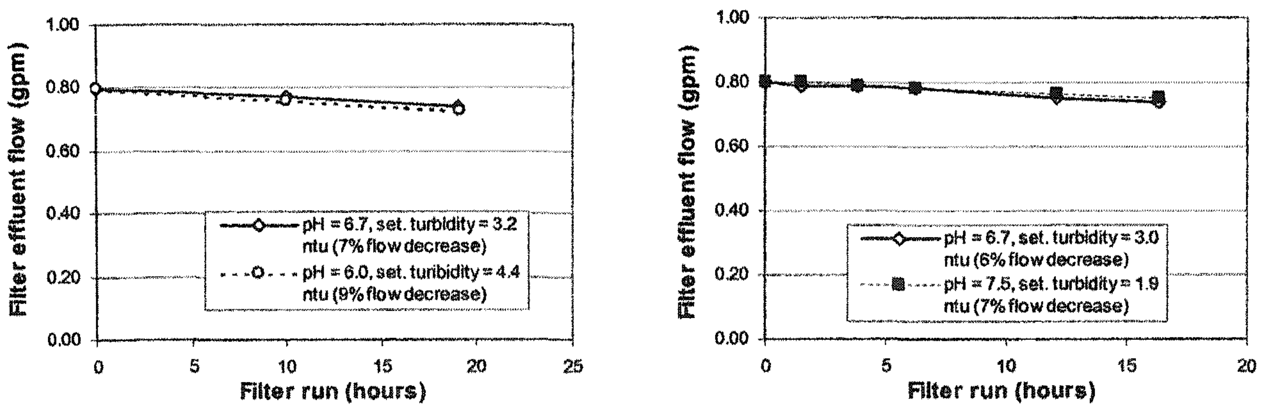


Figure 5.9 Schematic diagram of PDA apparatus and data acquisition system. A 15-sec. rapid mix period was provided after alum addition (RPM = 350), followed by a 10-min. slow-mix stage.



a) pH = 6.0 vs. 6.7 **b) pH = 6.7 vs. 7.5**

Figure 5.10 Typical filter effluent flow vs. time data for reservoir water filtration runs at a) pH = 6.0 vs. 6.7 and b) pH = 6.7 vs. 7.5. Rate of flow decrease, due to headloss accumulation, was consistently similar at pH = 6.7 and 7.5 (generally within 1% after 20 hours) and slightly higher (by approximately 2% over 20 hours) at pH = 6.0, apparently due to higher settled water turbidity residual at low pH. For the generally shorter runoff experiments (usually 4 – 8 hours), the difference in filter flows was insignificant. The steady-state particle count data shown in Figures 5 and 6 (main paper) were collected at approximately t = 3 hours.

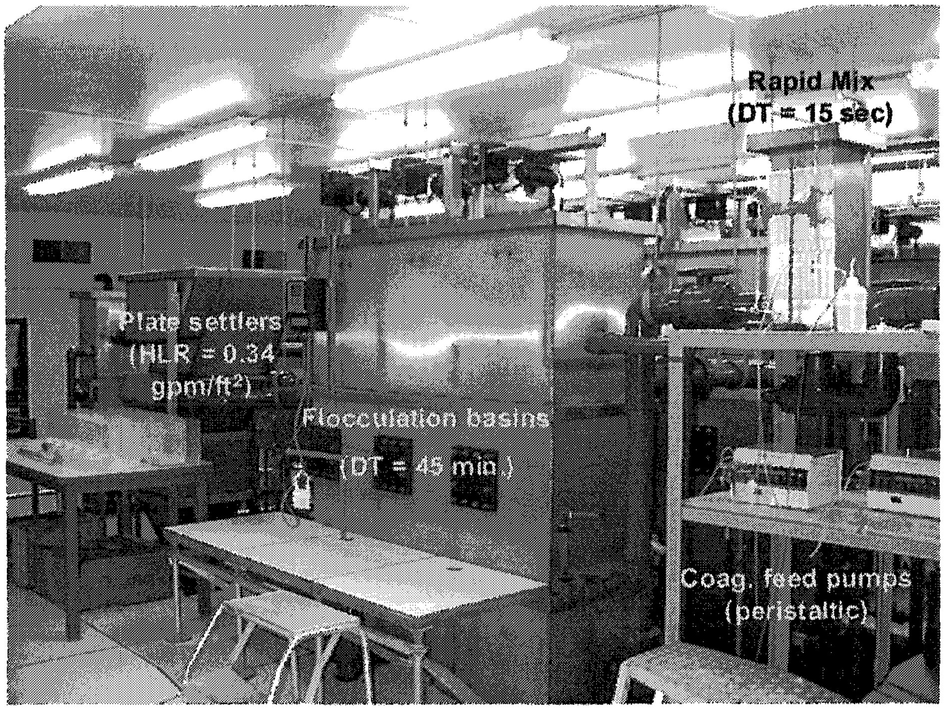


Figure 5.11 Fort Collins pilot laboratory. Rapid mix, flocculation, and Lamella plates settling basin are shown with corresponding hydraulic detention times. the high NOM content required the use of relatively high alum doses, which in turn necessitated base addition for pH control (200 g/L NaOH solution). The pH = 6.0 conditions were achieved by diffusing carbon dioxide gas ($CO_{2\,(g)}$) into a PVC contactor, thirty minutes upstream of the alum addition point. The pH = 6.7 process required no acid or base addition (ambient conditions) prior to alum addition. For the pH = 7.4 process, NaOH solution was added approximately 3 minutes upstream of alum.

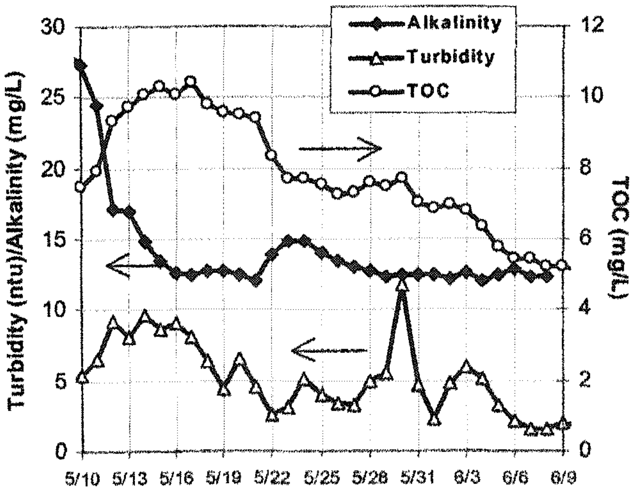


Figure 5.12 Poudre River water quality during spring runoff, 2001. pH = 6.8 - 7.0, T = 7 - 8 deg C.

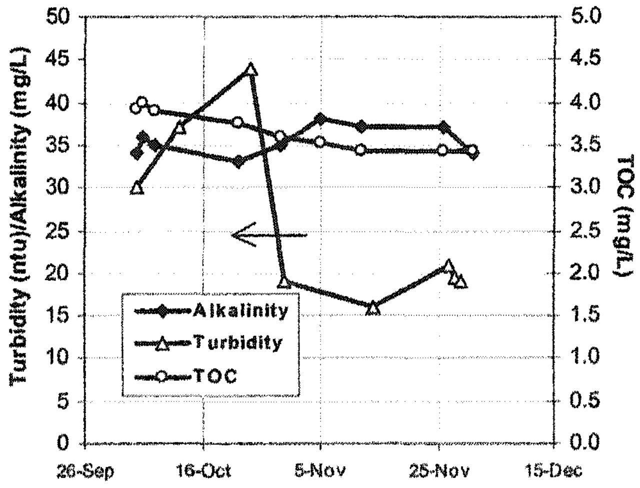


Figure 5.13 Horsetooth reservoir water quality, fall 2001. pH = 7.4-7.5, T = 7 - 9 deg C.

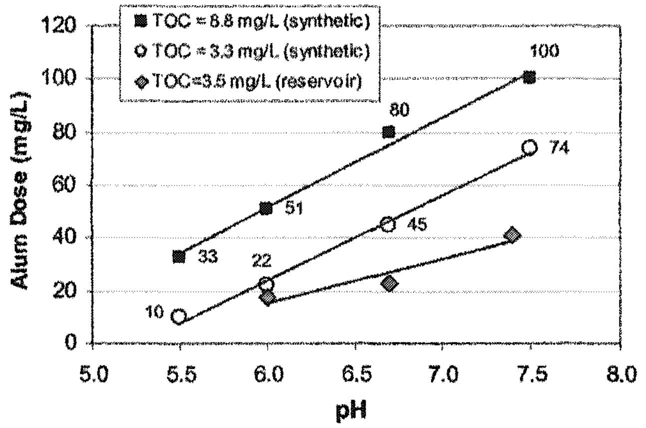


Figure 5.14 Optimized alum dose (values shown) vs. pH for two TOC concentrations (synthetic water) and reservoir water.

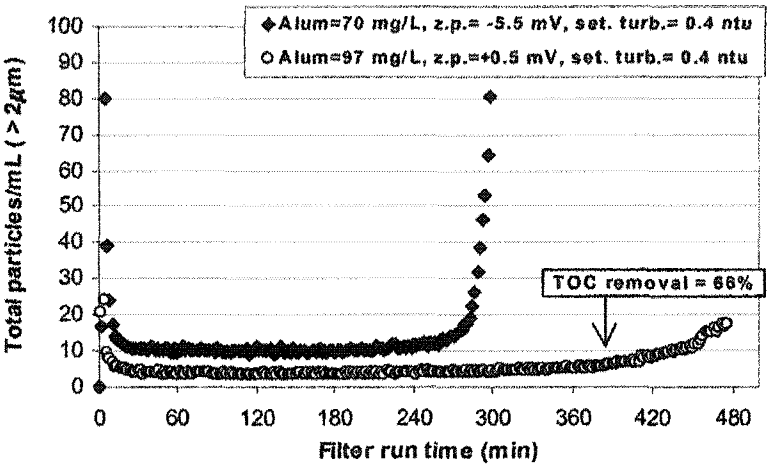


Figure 5.15 Impact of alum dose optimization on filtration performance at pH = 7.4 using runoff water. TOC = 7.5 mg/L.

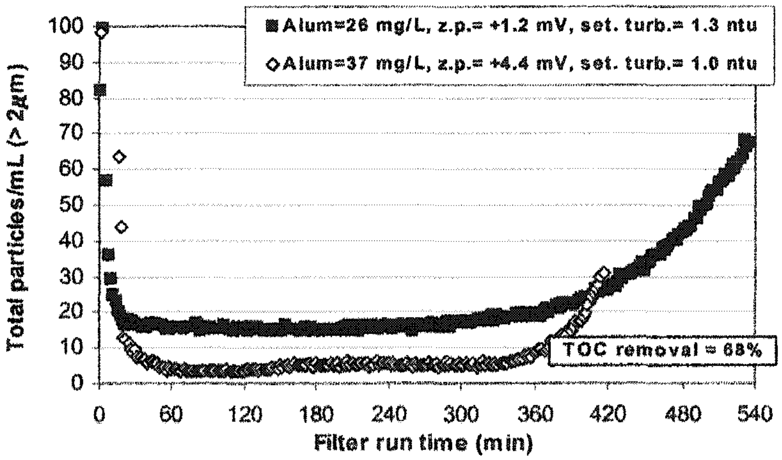


Figure 5.16 Impact of alum dose optimization on filtration performance at pH = 6.0 using runoff water. TOC = 7.5 mg/L.

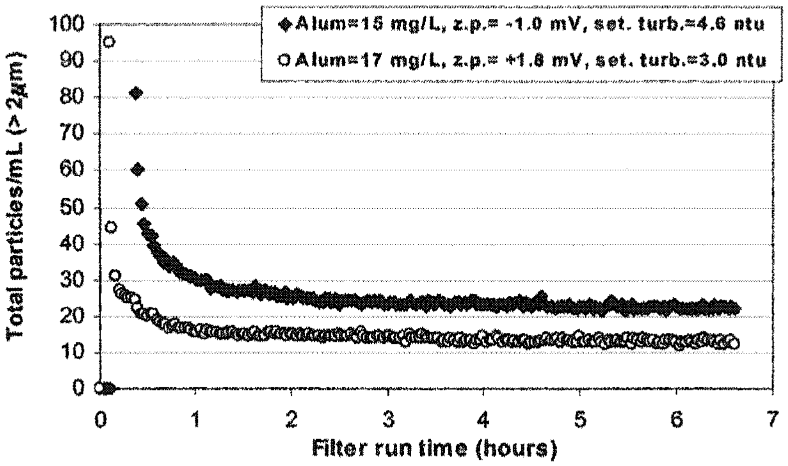


Figure 5.17 Impact of alum dose optimization on filtration performance at pH = 6.0 using reservoir water. TOC = 3.5 mg/L.

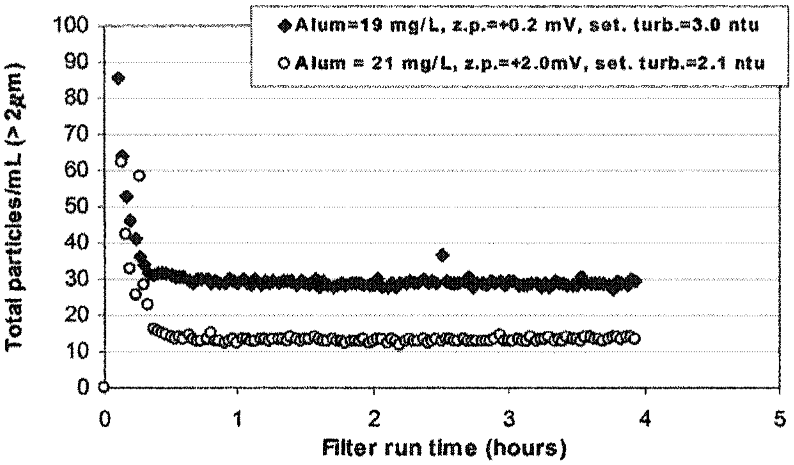


Figure 5.18 Impact of alum dose optimization on filtration performance at pH = 6.7 using reservoir water. TOC = 3.5 mg/L.

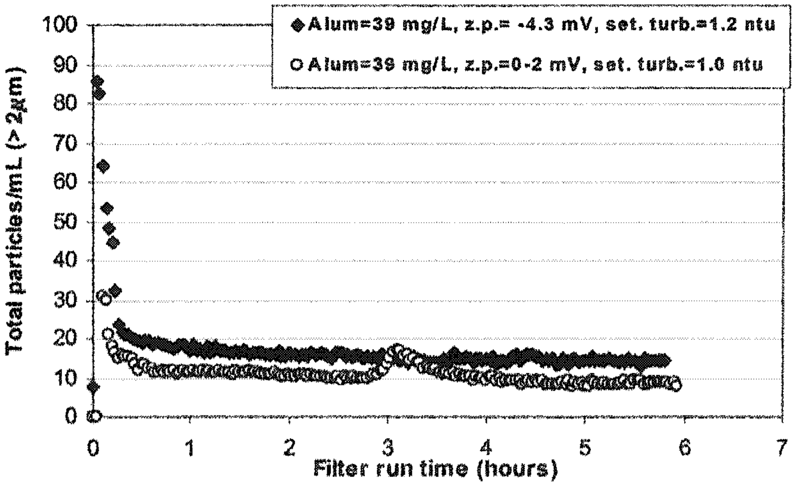


Figure 5.19 Impact of alum dose optimization on filtration performance at pH=7.4 using reservoir water. TOC = 3.5 mg/L.

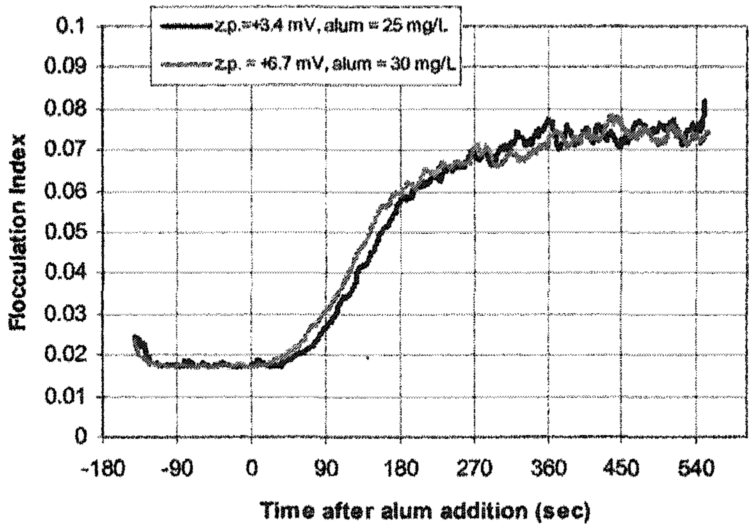


Figure 5.20 FI vs time for optimum alum dose (25 mg/L) and overdose (30 mg/L) in reservoir water, pH = 6.6, TOC=3.5 mg/L.

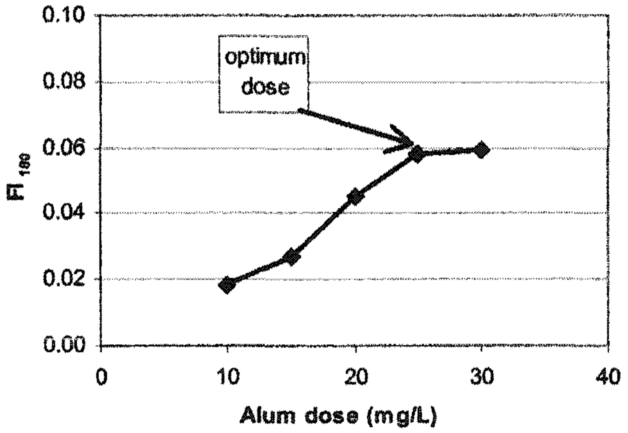


Figure 5.21 FI_{180} vs. alum dose for data shown in Figure 5.7 and Figure 5.20..

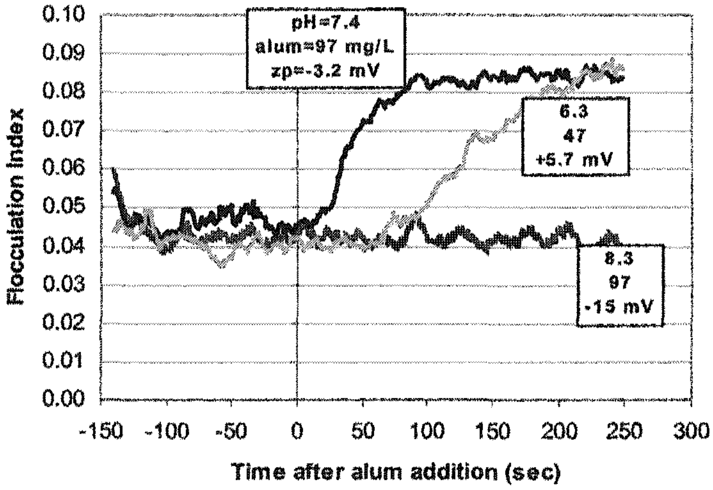


Figure 5.22 FI vs. time for three pH levels using spring runoff water. Although the coagulation conditions were not exactly matched to the filtration runs, these results do support the correlation between the PDA and filtration results. In addition, the pH=8.3 trendline demonstrates that FI increase is not solely a function of alum dose, as does Figure 3 in the manuscript.

Supplemental Information on zeta potential measurements

The zeta potential analyzer used for all of the pilot-scale filtration experiments and the bench-scale PDA experiments was the ZetaSizer 2000 from Malvern Instruments (US contact info.: Southborough, MA; phone: 1-508-480-0200). Only in the initial jar test experiments (results shown in Figure 1 of manuscript and Supporting Information Figure 6) was a different analyzer used (Zeta-Meter, model 3.0^{+}). In using the Zeta-Meter unit, the velocity of individual particles in a suspension (which is proportional to the applied electric field and thus determines the electrophoretic mobility of the particle) is obtained by the traditional method of viewing the particles through a microscope fitted with a reticule and manually timing the movement. Although there are obvious limitations to the accuracy and repeatability of this method—due to operator error in the timing process, heating of particles, and the fact that only particles large enough to be visible are measured, for example—it was used only in the initial bench-scale experiments. The aim in this phase was to confirm the general relationship between coagulation pH and settling performance for optimized alum doses, which were considered to be those that resulted in z.p between -2.0 and +2.0 mV (or closest to zero, if more than one dose was within this range). All experiments were performed in duplicate and the Zeta-Meter instrument provided consistent measurements with resolution that was considered adequate for this phase of the project.

For the filtration experiments, however, small differences in z.p. (approximately 1.0 mV, for example) sometimes produced significantly different results and therefore the more state-of-the-art, automated Malvern analyzer was used to increase repeatability and resolution. In this instrument, laser Doppler velocimetry (LDV) is used to determine the velocity of particles in an electric field. This method is based on the well-known fact that light scattered from a moving particle experiences a frequency shift proportional to the velocity of the particle. The scattered light is detected by a photon-counting photomultiplier. Particles are illuminated by intersecting laser beams that are configured to reduce the impact of Brownian motion on the instrument's resolution (Brownian motion makes it difficult to resolve mixtures of particles with different sizes and mobilities). Advantages of this method include 1) a far greater number of particles can be measured (thousands per second), and 2) smaller particles (as low as 5 – 10 nm) can be measured. Although the analyzers from Zeta-Meter and Malvern use significantly different methods for determining particle velocity, comparisons between the two using raw and treated water generally showed close agreement (within 2.0 mV). The automated Malvern analyzer allowed six separate analyses of each injected sample to be performed (on different aliquots of water) in succession. The z.p. values reported in the manuscript represent the average of those six runs, each of which analyzed thousands of particles. Although an extensive analysis of the standard deviations associated with these measurements was not included in this paper, a review of the data showed that these values were typically 0.2 – 0.4 mV. Therefore, the difference in the z.p. values of +1.0 and +1.2 mV shown in Figure 4 of the manuscript, for example, was considered to be insignificant. Zeta potential analyses which exhibited extremely high standard deviations (>2.0 mV, for example) were repeated. Standard deviations of this magnitude were generally caused by errors due to sample handling, air bubble entrapment, etc.

In the calculation of zeta potential from electrophoretic mobility (Henry equation), the Malvern analyzer software assumed $f(\kappa a) = 1.5$, where a = particle radius and kappa, κ, is the Debye parameter related to the ionic strength of the water and defined as the inverse of the double layer thickness. For small values of κa, $f(\kappa a)$ approaches 1.0 (very small particles in media with low permittivity). For large values of κa (≥ 100), $f(\kappa a)$ approaches 1.5 (particle radius is much larger than compressed double layer). Error due to the use of $f(\kappa a) = 1.5$ in calculation of zeta potential, which is known as the Smoluchowski approximation, is considered negligible for values of $\kappa*a \geq 100$ (Kosmulski, M. *Chemical Properties of Material Surfaces*, Marcel Dekker, New York, **2001**, pp. 239-240). In this research, therefore, to satisfy the requirement of $\kappa*a \geq 100$, given the minimum calculated ionic strength of approximately $2.1*10^{-3}$ M for the low pH conditions, the particle size was assumed to be ≥ 1.3μm (a = 650 nm).

The assumption of a minimum particle size of approximately 1.3 μm in the zeta potential calculations was considered valid because the study focused on particles coagulated at optimum or near-optimum conditions, with a minimum detention time of 45 seconds between alum addition and the sampling ports (there was an additional time lag of approximately 1 – 2 minutes before the samples were physically injected into the z.p. analyzer). Under these circumstances, larger aggregates are rapidly formed upon collisions between small, destabilized particles. The positively-charged aluminum hydroxide sols that are primarily responsible for particle destabilization form within 1-2 seconds, adsorb immediately to natural particle surfaces, and commence the aggregation process. Licsko *(6)*, for example, using similar pH conditions as those used in the present study, showed that within 10 seconds of coagulant addition, 75 percent of the suspended particles were in the form of microfloc of "several dozen" microns in size. Chakraborti et al. (Chakraborti, R.K., Atkinson, J.F. & Van Benschoten, J.E. *Envir. Sci. Technol.*, **2000**, 34:18:3969) showed that natural particles in a lake water fell into the size range of 7 – 100 μm, with the peak occurring at 10 μm. The addition of sufficient alum to cause charge neutralization (i.e. zero z.p.) moved the peak to 30 – 50 μm, with at least 95 percent of particles > 10 μm. Matsui et al. *(13)* showed that destabilization and aggregation of small particles can occur within 50 seconds for even very low alum doses (2.0 mg/L). In addition, Tambo et al. *(12)* showed that the average microfloc size immediately following rapid mixing was 20 - 30 μm for optimum coagulant doses.

Although it is likely that some particles < 1.3 μm were present in the coagulated water at the point of sample collection, it appears that they were a very small fraction of the total. Use of the Smoluchowski approximation for this fraction of particles much smaller than 1.3 μm (i.e. κa value much lower than 100) would result in a maximum negative bias of 50 percent. For this research, a typical example would be that a z.p. of +1.7 mV would be given for a particle with a true z.p. of +2.5 mV. The magnitude of this potential error (-0.8 mV) is still less than differences attributed to coagulation pH/dose conditions. The contribution of this small fraction of particles, therefore, to the overall zeta potential measurements did not appear to be significant.

CHAPTER 6

RESULTS AND DISCUSSION

Minimizing NOM-induced Floc Restabilization with Two-stage Coagulation

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Submitted to *Journal AWWA*, May 2003.

ABSTRACT

The purpose of this research was to further the understanding of two-stage coagulation processes and the mechanisms that, compared to traditional single-stage coagulant addition, increase particle removal during the treatment of high-TOC concentration waters. Bench-scale experiments characterized the impact of two-stage alum addition on floc size, floc formation kinetics, and the ζ-potential of post-rapid mix and settled water particles. In pilot-scale experiments the effect of two-stage processes on filtration performance was examined. In the presence of moderate to high levels of natural organic matter (NOM), two-stage coagulation appeared to increase the collision efficiency of particles, as evidenced by significant increases in floc formation rates, turbidity removal during sedimentation (30 – 50 percent), and the length of filtration runs prior to particle breakthrough. Two-stage coagulation may be a method to more directly control hydrophobic NOM-aluminum hydroxide reactions and optimize particle removal during treatment of NOM-laden waters.

INTRODUCTION

During treatment of raw waters containing elevated concentrations of natural organic matter, the development of floc suitable to solid-liquid separation is complicated by the adsorption of these hydrophobic, high molecular weight organic molecules to metal hydroxide surfaces during coagulation. When aluminum sulfate (alum) is used as the primary coagulant, these surfaces are provided by i) poorly-soluble, positively-charged aluminum hydroxide sols formed within a few seconds after alum addition (Licsko, 1997; Letterman et al, 1999), and ii) charge-neutralized $Al(OH)_{3\,(S)}$-colloid complexes (microfloc). In the latter case, the microfloc aggregate can be effectively restabilized by the NOM, potentially hindering the formation of larger aggregates (Carlson et al, 2000). Although the adsorption/precipitation of NOM on aluminum hydroxide surfaces is desirable as a primary removal mechanism (Edwards, 1997; Croue et al, 1993; Randtke, 1988), it has been demonstrated that turbidity removal is adversely affected by this process, even for relatively low-TOC (2 mg/L C) water (Exall et al, 2000; Tseng et al, 2000; Van Benschoten et al, 1990).

One method that appears to mitigate the restabilization of microfloc and optimizes particle removal, particularly during the treatment of high-TOC waters, is two-stage coagulation. In the treatment of high-TOC concentration waters (5 – 12 mg/L), for example, it has been shown that two-stage coagulant addition, compared to traditional single stage methods, consistently reduced settled water turbidity by 30 – 50 percent and increased filter run lengths in bench and pilot-scale experiments (Carlson et al, 2000; Billica et al, 2000; Gregory et al, 1998). The two-stage process used in these studies entailed simply splitting the total dose of metal salt coagulant between two distinct addition points, with adequate time (approximately 30 seconds) provided between the two points for coagulant-NOM reactions to occur.

Effective two-stage coagulation processes have been developed for other high-TOC concentration applications. In a water treatment application (TOC = 7 – 16 mg/L), for example, it was reported that finished water quality was significantly enhanced, in terms of TOC removal and disinfection by-products, by implementation of a two-stage coagulation (Wahlroos, 1991). The process involved a low-pH coagulation step, which targeted removal of organic compounds, followed by a high-pH step aimed at particle removal. The authors recognized that the dual objectives of coagulation—removal of particulate and organic contaminants—were most effectively achieved when approached as separate processes. Another study (Garrote et al, 1995) described the effective treatment of an extremely high-TOC tannery waste stream by a two-step coagulation process. In terms of removal of organic compounds it was found that, for the same total coagulant dose ($FeCl_3$), two similar coagulation stages were significantly more effective than a single stage, but that three stages were only marginally more effective than two.

Two-stage coagulation hypothesis. Although the two-stage coagulation process discussed in the present study has not been shown to increase overall TOC removal (Billica et al, 2000; Gregory et al, 1998), it may be a more effective use of coagulant and a method to control and minimize the adverse impact of NOM on floc development and subsequent particle removal. It is hypothesized that in the first coagulant addition stage, a significant fraction of the sorbable NOM adsorbs to aluminum hydroxide surfaces, effectively stabilizing these freshly formed colloids. In the second stage, the newly-formed, positively-charged sols are then subjected to fewer reactions with NOM molecules, as well as other sols, and more effectively charge neutralize both the natural colloids and the restabilized metal hydroxide particles. Mechanistically, an explanation for the advantage of this process may be that, between the first and second alum addition points, more NOM is adsorbed per mole of $Al(OH)_3$ $_{(S)}$ than during single stage processes, increasing the probability of successful sol-colloid interactions in the second stage. For example, it has been shown that the adsorption of fulvic acid onto positively-charged surfaces (initial ζ-potential = +50 mV) did not reach equilibrium until the particle ζ-potential was approximately –40 mV (Amal et al, 1992). The authors concluded that electrostatic interactions were but one of several forces driving adsorption.

This discussion of the mechanistic advantages of two-stage coagulation assumes non-ideal rapid mixing conditions. Under ideal mixing conditions, the short-lived, positively-charged aluminum hydroxide sols would be instantaneously (<0.1 seconds) dispersed *homogeneously* throughout the raw water stream. A certain percentage of the sols would rapidly form insoluble complexes with the hydrophobic NOM fraction while the remaining sols would be free to adsorb to and destabilize colloidal particles. Sol-sol interactions (an ineffective use of these species) and the restabilization of microfloc by NOM would thus be minimized, effects that are also hypothesized for two-stage processes. Because a majority of rapid mix processes, particularly backmix reactors, produce non-ideal mixing conditions (Klute, 1990), the practical effect of splitting the coagulant dose between two application points may be to more closely simulate ideal mixing. Indeed, it has been demonstrated (Billica et al, 2000) that, while a two-stage process was clearly most effective relative to a single-stage backmix process, the use of a more efficient in-line static mixer for single-stage coagulant addition also enhanced particle removal, a conclusion reached by previous researchers (Clark, 1994; Vrale et al, 1971).

Research objectives The primary objectives of this research were to demonstrate the effectiveness of two-stage coagulation processes for treating waters containing moderate to high NOM levels and to further the understanding of the mechanisms that, compared to the traditional single-stage approach, appear to promote increased particle removal. To facilitate this understanding, experiments were designed to characterize the impact of two-stage processes on 1) the ζ-potential distribution of post-rapid mix and settled water particles, and 2) floc size and floc formation rates in the period immediately following coagulant addition. The secondary objective was to extend these findings to overall treatment performance and to characterize the impact of single and two-stage coagulant addition on the filtration process.

MATERIALS AND METHODS

General approach. Using moderate-TOC water (5.0 mg/L), the approach was to first conduct bench-scale experiments that characterized the impact of two-stage coagulation on i) floc development and ii) the ζ-potential distribution of post-rapid mix and settled water particles at two coagulation pH levels (6.0 and 7.4). Although it was initially unclear whether two-stage coagulation would produce settled water particles with ζ-potential distributions significantly different than those obtained from single-stage processes, it was thought that the proposed mechanistic advantage of this process (i.e. mitigation of microfloc restabilization) might be illustrated by these analyses. Additional bench-scale experiments conducted during this phase of the project correlated the output from the optical instrument used to monitor floc growth (photometric dispersion analyzer) with physical floc size determined by microscopic analysis. In the second bench-scale phase, the specific effect of TOC concentration (3.5 – 12 mg/L) on floc formation and size was examined for single and two-stage coagulation processes at pH = 6.0. Pilot-scale experiments were conducted with high-TOC concentration raw water in an attempt to correlate the bench-scale findings with overall treatment performance and to specifically examine the impact of two-stage coagulant addition on the filtration process.

Water quality. The raw water used in all bench-scale experiments was collected from Horsetooth Reservoir, one of two supplies for the City of Fort Collins (CO). The reservoir water quality, except for occasional turbidity spikes, is relatively constant year-round (ambient pH = 7.4, TOC = 3.50 mg/L, turbidity = 5 – 20 NTU, alkalinity = 35 – 40 mg/L as $CaCO_3$). For the first bench-scale phase, a 60-L sample of reservoir water was collected and the TOC concentration was increased from 3.5 to 5.0 mg/L (Suwannee River NOM, International Humic Substance Society). This NOM-spiked water was allowed to equilibrate for 72 hours before it was used in experiments. The turbidity of these samples was approximately 6 NTU.

For the second bench-scale phase, three 40-L samples were collected from the reservoir. The TOC was left unchanged in one sample (3.5 mg/L) and was increased to 8.0 and 12 mg/L, respectively, in the remaining two samples. The turbidity of the reservoir water had increased to 14 NTU at the time these samples were collected.

For the pilot-scale filtration experiments a high-NOM river source during the spring runoff period was used. The TOC concentration of this water was 9 – 10 mg/L.

ζ-Potential distribution. For the ζ-potential distribution analyses, single and two-stage bench-scale experiments were conducted at coagulation pH of 6.0 and 7.4, values chosen to represent relatively low- and high-pH coagulation conditions. Five repetitions were performed for each of the four coagulation scenarios (total of 20 experiments). The temperature for all experiments was 20°C. Prior to alum addition, appropriate volumes of acid (2.5 M HCl) or base (5 M NaOH), determined by titration, were added to 2-L samples of the reservoir water to achieve the target final coagulation pH. For the two-stage processes, the pH after the first alum dose was approximately 6.4 and 9.5 for the low and high-pH experiments, respectively. The reaction vessel was a square, 2-L beaker into which a laboratory mixer (IKA®-Works Eurostar model, rpm range = 50 to 2,000) was lowered. For the single-stage experiments a 10-sec. rapid mix (350 RPM, G=350 sec^{-1}) was followed by a two-stage flocculation process (15-min. stages at G=48 and 18 sec^{-1}) and then a 15-min. settling period.

Although the same flocculation process was used for the two-stage experiments, the rapid mix protocol differed slightly. The first half of the alum dose was provided with a 10-second rapid mix period followed by a 30-second slow mix period. The mixer speed was then increased again for a brief period (5 seconds) to provide rapid mix conditions for the second dose. Settled water turbidity was measured following the settling period (Hach 2100 N).

The ζ-potential distributions of suspended particles were measured for post-rapid mix and settled water samples (Malverne Instruments Zetasizer 2000). A detailed discussion of the analyzer and its operational parameters has been provided elsewhere (Gregory et al, 2003a). For the coagulation conditions used (ionic strength ≅ $2.2*10^{-3}$ M at pH=6.0), the ζ-potential values calculated from electrophoretic mobility data (Henry equation) were considered valid for particles greater than approximately 1.3 μm. The fraction of sub-1.3 μm particles in the samples was assumed to be very small and not a significant factor in ζ-potential calculations.

One advantage of the automated ζ-potential analyzer used in this research was that it allowed five separate analyses of each injected sample to be performed (on different aliquots of water) in succession and provided the full distribution of values for each analysis. The individual ζ-potential distributions shown here (in Figure 1, for example) represent the average of those five runs, each of which analyzed thousands of particles. Analyses that exhibited extremely high error, generally due to sample handling problems such as air bubble entrapment, were repeated.

The only coagulation chemicals added were alum and acid/base for pH control. The optimum alum doses for this water (TOC = 5.0 mg/L), which were defined as those that achieved a ζ-potential of 0.0 ± 2.0 mV, were 26 and 117 mg/L at pH = 6.0 and 7.4, respectively.

Photometric dispersion analyzer. Floc development and floc size were monitored using a photometric dispersion analyzer (PDA). Details of the PDA apparatus used in this research are provided elsewhere (Gregory et al, 2003a). In this instrument, the intensity of light transmitted across a 1 cm^2 quartz flowthrough cell (660 nm laser source) is converted to a voltage signal, which is separated into its fluctuating (AC) and average (DC) components. The flocculation index (FI), which was calculated by the data acquisition software (LabVIEW) and is equal to the root mean square of the AC signal divided by the DC signal, corresponds to average particle size and has been shown to be a sensitive indicator of the state of aggregation of a particle suspension (Wang et al, 2002; Matsui et al, 1998; Matsui et al, 1993; Matsui et al, 1991; Gregory, 1985). A rapidly increasing FI following alum addition, for example, is indicative of floc formation and optimum destabilization conditions. The method was originally developed by Gregory (Gregory, 1985) and has generally been used to provide a dynamic assessment of coagulation processes.

These experiments were conducted at a coagulation pH of 6.0 using TOC concentrations of 3.5 (ambient), 8.0, and 12 mg/L. The two higher concentrations were achieved by adding appropriate amounts of Suwannee R. NOM to the reservoir water. The optimized alum doses, from lowest to highest TOC concentration, were 18, 45, and 76 mg/L. Floc formation was monitored during the first twelve minutes of the slow mix period. The data presented here represent the average of at least five experiments conducted at each coagulation condition. Experiments that produced excessive error, which in most cases was due to air bubbles interfering with the PDA instrument, were repeated.

Floc size measurements. Although FI has been previously correlated to average particle size during coagulation/flocculation processes (Matsui et al, 1991; Ohto et al, 1993), FI values are PDA system-specific and it was therefore necessary to repeat this analysis for the present study. In addition, the degree to which FI and particle size correlated in natural systems was unclear, as previous research has focused primarily on monodisperse suspensions (e.g. latex beads or kaolin particles). Using reservoir water (TOC = 5.0 mg/L) at coagulation pH = 6.0, a total of five 20-mL samples were collected from the PDA apparatus from 0.5 to 6 minutes after the start of the slow mix stage.

A photographic technique coupled with digital image processing was used to determine floc size (Chakraborti et al, 2000; Chakraborti et al, 2003). Samples were examined with a phase contrast microscope (Olympus CH-30) at a magnification of 100×. A pipette with a 0.5-cm opening was used to place suspended floc particles on a well slide. This sampling method minimized disturbance of the delicate floc particles. A high-resolution digital camera (Nikon Coolpix 995) was used to capture images of floc particles through a microscope attachment. These images were analyzed using digital image analysis software (ImageJ; National Institutes of Health: Bethesda, MD). Images were adjusted to enhance contrast and thresholded in order to clearly define particle boundaries. A stage micrometer slide was used to calibrate the images to known dimensions (980 pixels = 1 mm for this study). The software measured the area of each aggregate and determined a best-fit ellipse, resulting in a major and minor axis length calculation. For each sample time, a minimum of 60 aggregates was analyzed and the average major axis length was calculated and plotted against the corresponding FI at the time of sampling.

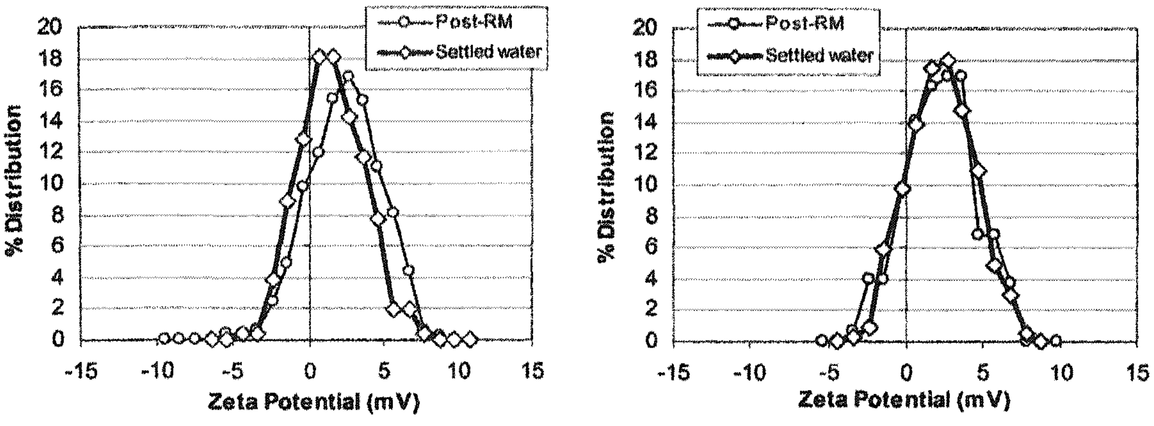
Filtration experiments. Single and two-stage coagulation processes were compared directly in pilot-scale filtration runs that were conducted on parallel, 8-gpm conventional treatment trains. A detailed description of the pilot plant unit processes has been provided elsewhere (Gregory et al, 2003b). Coagulant addition in the rapid mix was followed by three-stage flocculation (detention time = 45 minutes), inclined plate sedimentation (HLR = 0.34 gpm/ft^2), and dual media filtration (30" anthracite, 10" sand). The filters were operated in declining rate mode with an initial HLR = 6.0 gpm/ft^2, which was considered relatively high for the challenging water quality conditions. The applied alum doses for the two runs presented, which were optimized to achieve a post-rapid mix ζ-potential of 0.0 ± 2.0 mV, were 41 and 44 mg/L and the coagulation pH ranged from

6.1 – 6.2. Filter effluent particle counts, turbidity, and run lengths (based on particle breakthrough) were used to evaluate filtration performance.

RESULTS AND DISCUSSION

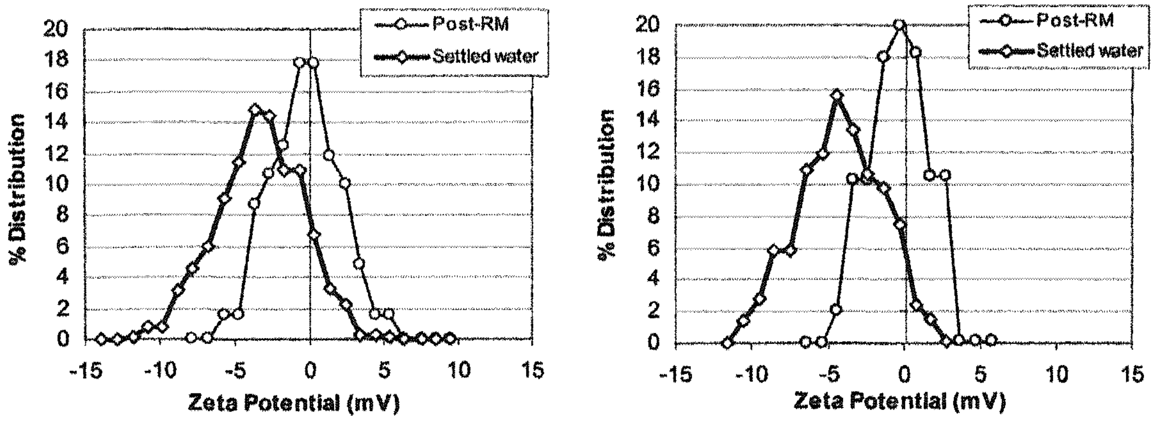
ζ-Potential distributions The purpose of comparing the ζ-potential distributions of post-rapid mix and non-settleable particles (jar test supernatant) was to provide potential information on the homogeneity of particle destabilization achieved by each coagulation process. A significant difference in these distributions, for example, may indicate that a fraction of the particles were restabilized by NOM or poorly destabilized during coagulation. The primary statistical characteristics examined for each distribution were mean, standard deviation, and range.

Figure 6.1 shows typical ζ-potential distributions for single and two-stage alum addition experiments at pH = 6.0 and 7.4, as well as for the raw water. For single-stage addition at pH = 6.0 (1a) there was a small but clearly distinguishable shift towards more negative values that was consistently observed in the settled water. For the two-stage process at pH = 6.0 (1b) there was essentially no difference in the ζ-potential distributions. At pH = 7.4 (1c and 1d) the magnitude of the shift increased significantly. Figure 6.2 shows the average negative shift in mean ζ-potential for all the experiments (n = 6) conducted for each coagulation process. The error bars in Figure 6.2 represent the standard deviation of the six values (each of which was itself the average of the six separate analyses conducted for each run). The fact that essentially no shift in distribution was observed for the two-stage process at pH = 6.0 suggests i) this process produced uniformly destabilized particles that were not subsequently restabilized—at least not



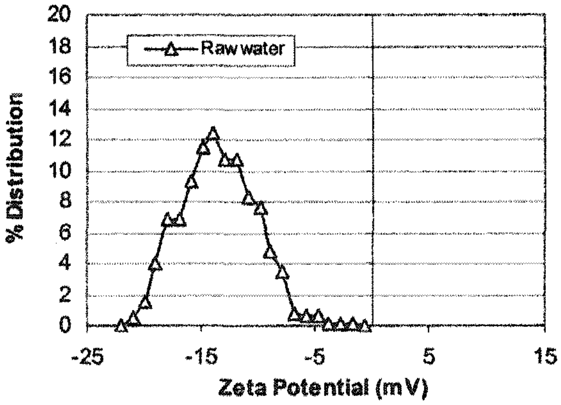
a) pH = 6.0, single-stage coagulation

b) pH = 6.0, two-stage coagulation



c) pH = 7.4, single-stage coagulation

d) pH = 7.4, two-stage coagulation



e) Raw water

Figure 6.1. ζ-potential distribution of post-rapid mix and settled water particles for single and two-stage coagulation processes (a – d). Raw water distribution also provided (e). Alum doses for the pH = 6.0 and 7.4 processes were 26 and 117 mg/L, respectively. Raw water TOC = 5.0 mg/L, temp. = 20°C, turbidity = 6 NTU.

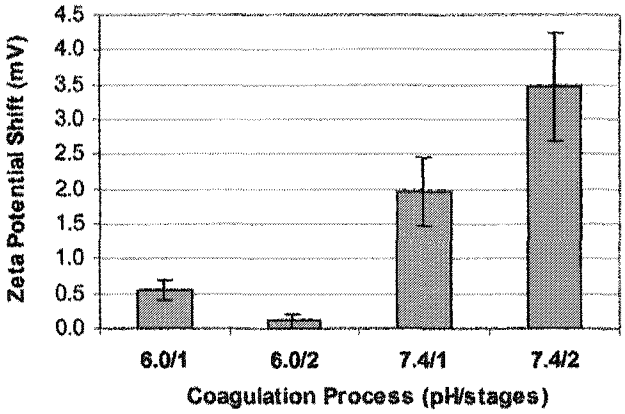


Figure 6.2. Average shift in mean ζ-potential between post-rapid mix and settled water particles (n = 5). Error bars represent standard deviation of data.

significantly—by NOM, and ii) there was little difference in the surface charge characteristics of the larger (settleable) and smaller (non-settleable) particles. At pH = 7.4, conversely, the relatively large shift in distribution for both processes suggests restabilization of a significant fraction of particles.

The ineffectiveness of the high-pH two-stage process, which showed the largest shift in distribution (Figure 6.2), can be explained by the fact that the pH after the first alum dose was approximately 9.5 before being reduced to 7.4 with the second dose (pre-coagulation pH was ≅ 10.6). In these conditions, aluminum hydroxide solids are negatively charged (pH_{zpc} ≅ 8.2) and the proposed mechanistic advantage of the two-stage process—rapid adsorption of a majority of the sorbable NOM—may be reduced or lost altogether. The two-stage high-pH process may be, therefore, essentially a worst-case scenario for minimizing the restabilization of floc by NOM, as suggested by the results in Figure 6.2. If it is assumed that the largest shift in Figure 6.2 was a result of the least effective process for minimizing NOM-induced particle restabilization, then the only process that produced no shift—two-stage, low-pH—could represent the most effective process. These results, therefore, may actually serve as indirect evidence of the two-stage NOM-adsorption mechanism at lower pH levels.

The average standard deviation and range of the ζ-potential distributions (n = 5), shown in Figure 6.3 along with raw water data, generally correlate with the distribution shift data. An effective coagulation process would be expected to decrease the range and standard deviation of a raw water particle suspension, as was observed for all four scenarios represented in Figure 6.3. Overall, however, for settled water the low-pH processes resulted in the largest decrease in these characteristics. The range and standard deviation of ζ-potential distributions for the post-rapid mix and settled water particles were approximately equal at pH = 6.0. For both the single and two-stage processes, in fact, a slight decrease in both characteristics was observed in the settled water. At pH = 7.4, conversely, an increase in both characteristics was observed, significantly in the case of the two-stage process. These high-pH results correlate with Figure 6.1, in terms of the significant differences between post-rapid mix and settled water particles. They also

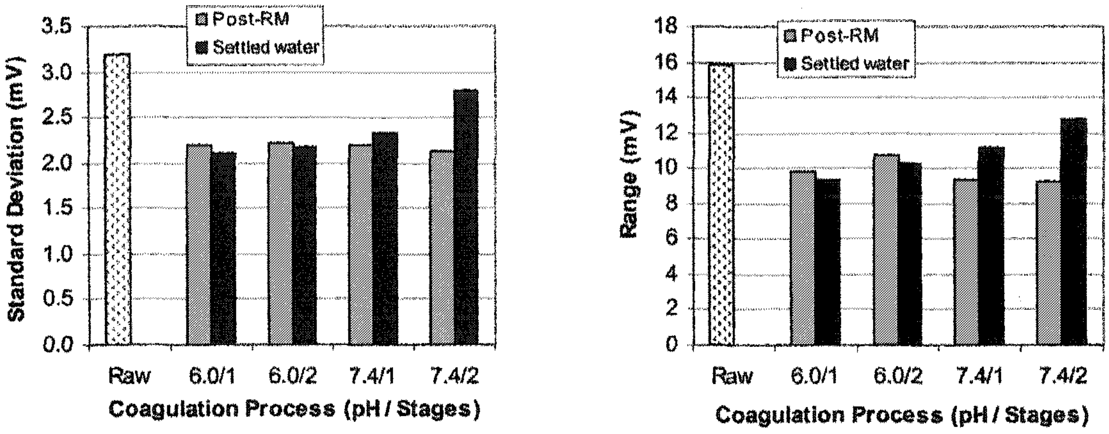


Figure 6.3. Average standard deviation (left) and range of ζ-potential distributions for single and two-stage alum addition processes at pH = 6.0 and 7.4. Raw water data is also provided.

illustrate the restabilizing effect of NOM on floc particles, particularly in the worst-case conditions of high-pH, two-stage coagulation.

Because the mechanistic advantage in mitigating NOM interference appears to be greatly reduced under high-pH conditions, two-stage processes would be expected to produce coagulation effects similar to those of the single-stage process. Indeed, the corresponding turbidity removal data for these four coagulation scenarios, presented in Figure 6.4, suggest equivalent particle removal performance, at least during settling, for the two high-pH processes. Although the significant difference in particle removal performance between the two low-pH processes is clear, perhaps more compelling are comparisons to the high-pH single-stage process. Using approximately one-fifth the alum dose (26 vs. 117 mg/L), the low-pH two-stage process decreased settled water turbidity by approximately 35 percent. These results appear to support the hypothesis that the low-pH two-stage process produces particles more effectively destabilized and therefore amenable to the development of floc suitable to solid-liquid separation.

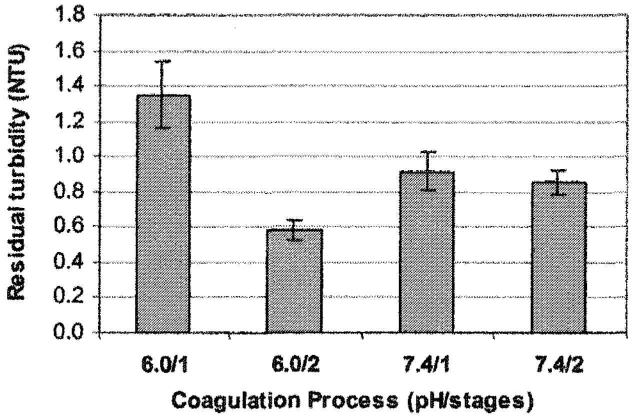


Figure 6.4. Settled water turbidity for single- and two-stage alum addition processes at pH = 6.0 and 7.4. Raw water TOC = 5.0 mg/L, temperature = 20°C, turbidity = 6 NTU. Error bars represent standard deviation of data (n=5).

FI vs. measured floc size. As demonstrated previously (Ohto et al, 1993; Matsui et al, 1991; Gregory, 1985), FI was found to correlate well with the average measured floc size (major axis), as illustrated in Figure 6.5. Although FI-particle size relationships are water quality specific, the highly linear relationship ($R^2 = 0.99$) shown in Figure 6.5 provided confidence that FI was a direct surrogate for particle size and would be an effective tool for dynamic comparisons of floc development under different coagulation scenarios.

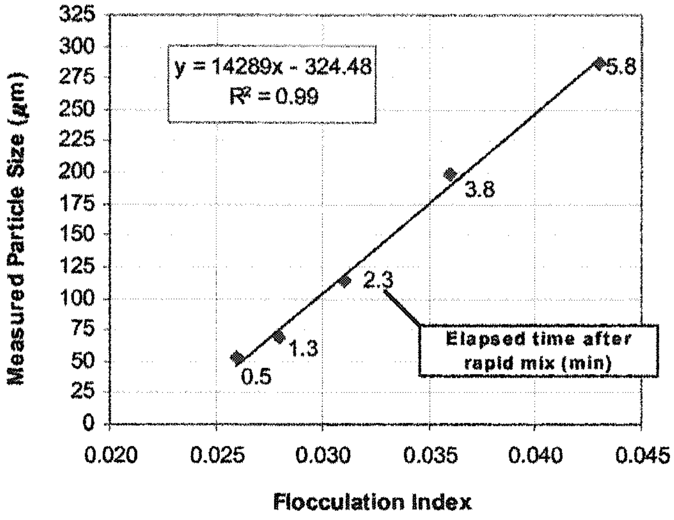


Figure 6.5. Correlation between FI and measured floc size. Alum dose = 26 mg/L (single-stage coagulation), pH = 6.0, TOC = 5.0 mg/L.

Impact of coagulant addition mode. Floc development for single- and two-stage alum addition processes is shown in Figure 6.6 for the raw water (TOC = 5.0 mg/L) used for Figures 6.1 – 6.5. The FI data show that particle aggregation occurred at the same rate for both processes until approximately t = 200 seconds, at which point the trendlines begin to diverge. After pseudo-equilibrium conditions—indicated by a plateau in the FI trendlines—were attained at approximately t = 500 seconds, average floc size was 175 and 250 μm for the single and two-stage processes, respectively. The difference

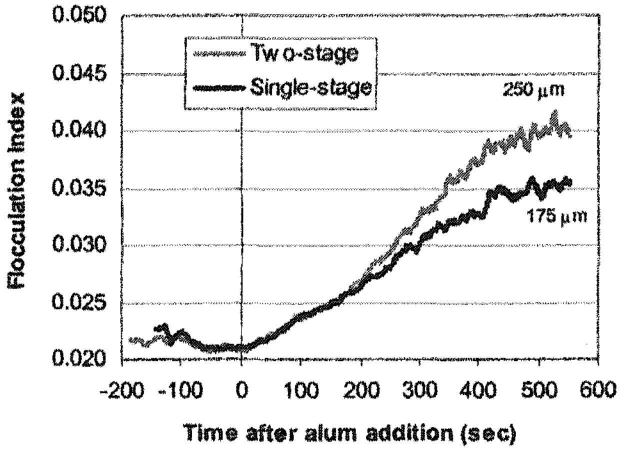


Figure 6.6. Impact of alum addition stages on floc development at pH = 6.0. Alum dose = 26 mg/L, TOC = 5.0 mg/L, turbidity = 6 NTU, temperature = 20°C.

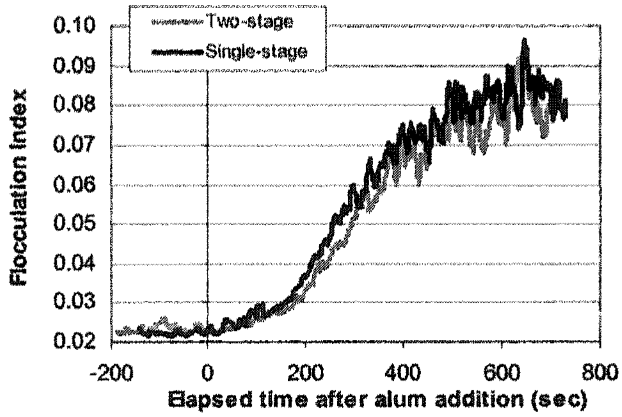
in rate of floc development after t = 200 seconds, as well as final size, indicated that the two-stage particles were more effectively destablized in the initial stages of coagulation and therefore more amenable to the formation of larger aggregates. Specifically, it appears the primary impact is on the collision efficiency, α, of the particles. The significance of α in floc growth is illustrated by equation [1], which describes the change in particle concentration for a monodisperse system as a first-order reaction given by

[1] $$\frac{dN_p}{dt} = -\alpha k_{th} N_p$$

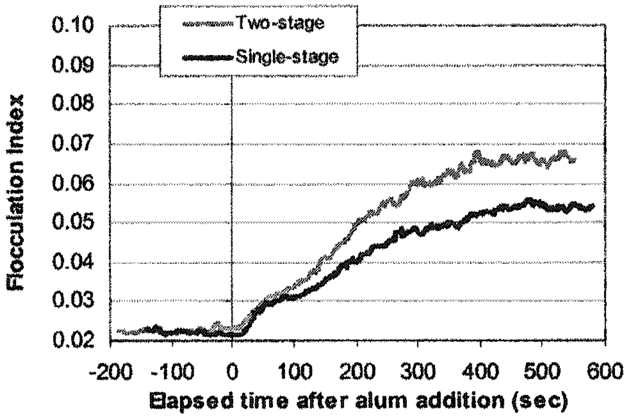
where N_p = number concentration of particles, k_{th} = predicted collision rate constant (dependent on particle volume fraction, ϕ, and velocity gradient, G), and the collision efficiency, α = the ratio of particle attachment to particle collisions (Jiang et al, 1996). Although the suspended particles used in the present study, a majority of which were aluminum hydroxide precipitates, were not monodisperse, mixing conditions and initial N_p were approximately equal for the single and two-stage processes with equivalent pH values. Under these circumstances α is the primary variable affecting the kinetics of particle aggregation, dN_p/dt, which is analogous to floc growth in a system with a constant volume fraction (Wang et al, 2002). The FI trends in Figure 6.6, which are proportional to average floc size, are therefore an effective means of comparing α between systems with approximately equal N_p, and k_{th}.

Impact of TOC concentration. It has been hypothesized that two-stage processes may be a more effective use of coagulant and a method to control and minimize the adverse impact of NOM on α (i.e. floc development) and subsequent particle removal. It was expected, therefore, that raw water TOC concentration would significantly influence the degree to which two-stage coagulant addition enhances floc development. This issue was examined by comparing floc development for single and two-stage processes at TOC concentrations of 3.4, 8.0, and 12 mg/L (Figure 6.7).

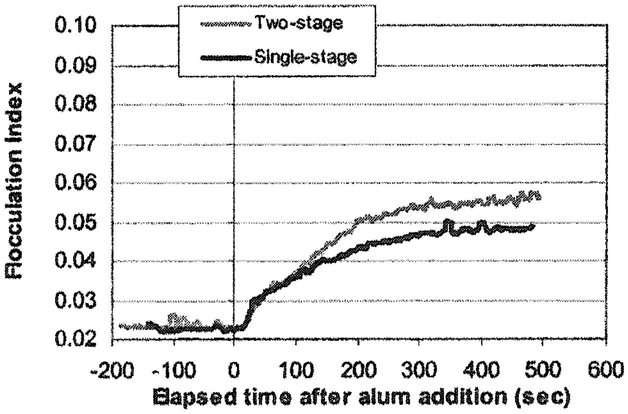
At the lowest TOC concentration of 3.4 mg/L, the benefits of two-stage coagulation—in terms of floc development—were negligible, as evidenced by the fact that the two FI curves in Figure 6.7a are nearly identical. At TOC = 8.0 and 12 mg/L (Figure 6.7b and 6.7c), however, the difference in final floc size and formation rate between the two processes was significant. Of particular interest in Figure 6.7b and 6.7c is the shape of the FI curves in the initial period following coagulant addition. For both processes the rapid formation of $Al(OH)_{3\,(S)}$ is indicated by the steep slope of the curve in approximately the first 20 – 50 seconds immediately following alum addition. Following this period, the aggregation process slows down considerably for single-stage alum



a) TOC = 3.4 mg/L



b) TOC = 8.0 mg/L



c) TOC = 12 mg/L

Figure 6.7. Floc development for single and two-stage alum coagulation at three TOC concentrations. Temperature = 20°C, pH = 6.0.

addition as NOM begins restabilizing floc particles, thus shifting the α downward and producing a lower FI response. For the two-stage process, the change in aggregation kinetics appeared to be far less impacted by NOM-induced particle restabilization. These results indicate that α is not constant as NOM restabilization occurs during single-stage coagulation and appear to support the hypothesis that two-stage coagulant addition mitigates the interference of NOM in floc development.

Although the FI data in Figures 6.6 and 6.7 can not be used for direct comparisons of particle size (because the raw water turbidity of the two samples differed significantly), it was clear that two-stage coagulant addition also significantly affected floc formation for the raw water TOC concentration of 5.0 mg/L. Overall, these results suggest that the benefit of two-stage coagulation may be negligible in low-TOC concentration waters but becomes more significant as TOC concentration increases.

One question that arises from this discussion concerns the precise mechanistic impact of two-stage alum addition on α, the magnitude of which is dependent primarily upon particle surface charge characteristics. An advantage of two-stage processes may be that in the second stage the positively-charged sols, which exist for only a few seconds (Licsko, 1997), are subjected to fewer reactions with NOM molecules—a large fraction of which were adsorbed to aluminum hydroxide in the first stage—as well as other sols. Natural colloids are thus destabilized by a greater concentration of $Al(OH)_{3\ (S)}$ (compared to single-stage processes) and restabilization of charge neutral $Al(OH)_3$-colloid complexes (microfloc) is minimized. Increasing the concentration of destabilizing $Al(OH)_{3\ (S)}$ would likely promote a more uniform positive charge distribution on particle surfaces, which in terms of DLVO theory would be analogous to a more uniformly compressed electrical double layer. Under these circumstances, the probability of successful particle-particle collisions is increased and floc growth is enhanced, conditions that appear to exist under two-stage coagulation scenarios. Although direct examination of surface charge distribution was not performed, its potential impact on particle aggregation and attachment has been noted (Elimelech et al, 1990; Liang et al, 1990).

Filtration implications. In addition to increasing the probability of successful particle-particle collisions during coagulation, two-stage coagulant addition may also produce particles more effectively removed by filtration, as floc particles become the primary particle collectors in filters after the initial ripening period (O'Melia, 1985). The pilot-scale filtration results presented in Figures 6.8 and 6.9, which directly compare single and two-stage coagulant addition for high-TOC concentration water, support this hypothesis. Each figure presents settled and filtered water data from filtration runs conducted on two different days during a single runoff event. In Figure 6.8 particle counts were used to compare filtration performance while in Figure 6.9 turbidity data were used. These results were typical of the pilot experiments in that the filter run length for the two-stage process was significantly greater than for single-stage alum addition. Although steady-state particle counts in Figure 6.8 were significantly lower for the two-stage process for a majority of the run, these data suggest that the most important effect of two-stage coagulant addition may be to increase filter run length, as noted by previous researchers (Billica et al, 2000).

Of the two mechanisms generally proposed to explain particle breakthrough—either lack of capture or detachment of previously retained particles—increasing evidence

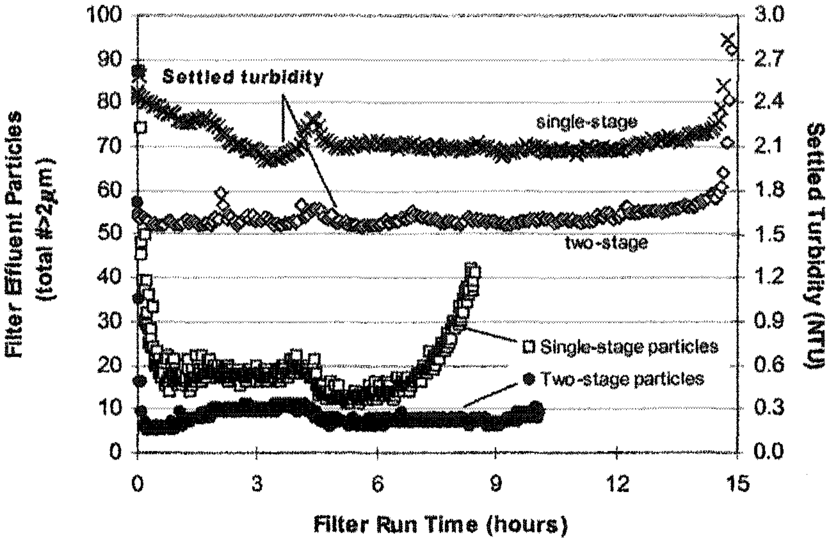


Figure 6.8. Impact of two-stage coagulation on settled turbidity and filter effluent particle counts. Raw water TOC = 9.1 mg/L, turbidity = 11 NTU. Coagulation pH = 6.1, alum dose = 41 mg/L. Initial filtration rate = 6 gpm/ft^2.

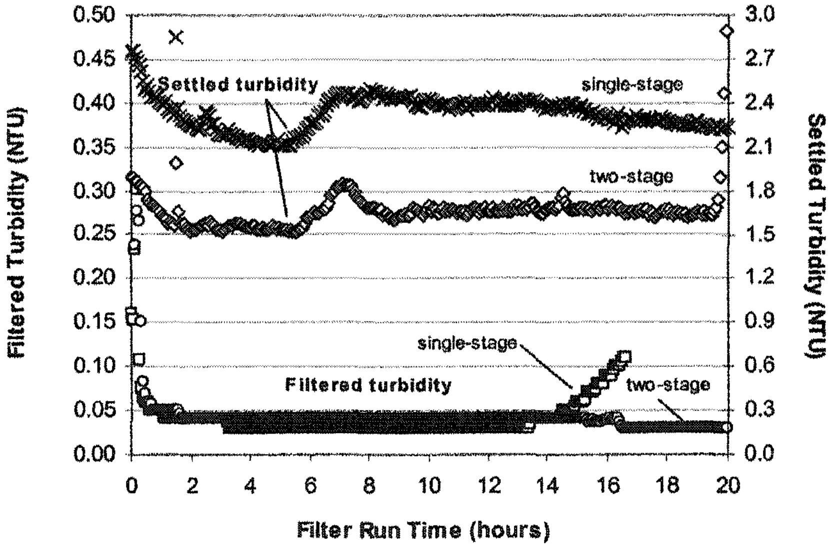


Figure 6.9. Impact of two-stage coagulation on settled turbidity and filter effluent turbidity. Raw water TOC = 9.4 mg/L, turbidity = 10 NTU. Coagulation pH = 6.2, alum dose = 44 mg/L. Initial filtration rate = 6 gpm/ft^2.

has shown the latter to be the primary cause (Benjamin et al, 2003). If detachment is the primary cause of particle breakthrough, then the consistently increased filter run lengths observed for two-stage coagulant addition suggest that this process produces particles that are more likely to re-attach to previously deposited floc particles. If lack of capture also contributes to breakthrough, then two-stage processes appear to produce particles that are more likely to be captured. In either case, two-stage coagulation appears to increases α, thus increasing the probability of successful particle-particle collisions both during coagulation, which promotes floc development, and filtration, which increases particle removal.

CONCLUSIONS

The overall objectives of this research were to demonstrate and understand the effectiveness of two-stage coagulation processes for increasing particle removal during the treatment of high-TOC concentration waters. Compared to traditional single-stage coagulant addition, experimental results indicated that two-stage processes appeared to increase the collision efficiency, α, of coagulated particles. The increase in α was evidenced by an increase in the rate of floc development and floc size for two-stage processes, which was significant for moderate to high-TOC concentration waters but almost negligible for low-TOC sources. Two-stage coagulation significantly increased particle removal during sedimentation—a result which correlated with the observed increase in floc size—and appeared to increase filter run length (in terms of particle breakthrough) as well. The increase in filter run length also appeared to be due to an increase in α, as breakthrough is due either to particles failing to attach (i.e. low α) or to re-attach after detachment.

The lack of a shift in ζ-potential distributions between post-rapid mix and settled water particles (for the lower-pH conditions) indicated that two-stage processes may produce more uniformly destabilized particles that are not subsequently restabilized—at least not significantly—by NOM. Overall, the results of this research suggest that two-stage coagulation processes may be an effective alternative for optimizing particle removal during the treatment of NOM-laden water.

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CHAPTER 7

SUMMARY OF FINDINGS

AND

IMPLICATIONS FOR WATER TREATMENT INDUSTRY

The overall objective of this project was to develop and understand effective coagulation processes for optimizing filtration performance during the treatment of moderate to high-TOC concentration raw waters. Specific objectives were to determine the impact of coagulation pH, ζ-potential, and alum addition mode (single vs. two-stage) on floc formation and filtration performance. Another goal of the project was to develop and evaluate the PDA as an indicator of overall process performance.

In terms of alum coagulation mechanisms, a review of the literature indicated that the positively-charged, insoluble aluminum hydroxide sols are the most realistic species responsible for particle destabilization during coagulation by adsorbing to the surface of the oppositely-charged, much larger natural colloids and entering into an electrical bond. In high-TOC concentration water, the development of floc suitable to solid-liquid separation is complicated by the adsorption of hydrophobic, high molecular weight organic molecules to i) sol surfaces, rendering them incapable of destabilizing natural colloids, and ii) destabilized sol-colloid complexes. In the latter case, the microfloc aggregate can be effectively restabilized by the NOM, potentially hindering the formation of larger aggregates.

Two-stage coagulation was proposed as a potentially more effective use of coagulant and a method to control and minimize the adverse impact of NOM on floc development and subsequent particle removal. It was hypothesized that in the first coagulant addition stage, a significant fraction of the sorbable NOM adsorbs to aluminum hydroxide surfaces, effectively stabilizing these freshly formed colloids. In the second stage, the newly-formed, positively-charged sols are then subjected to fewer reactions with NOM molecules, as well as other sols, and more effectively charge neutralize both the natural colloids and the restabilized metal hydroxide particles.

The major findings of this research and implications for full-scale water treatment facilities are discussed below.

High-pH Coagulation Processes. Overall, in terms of filtration performance during the treatment of high-TOC concentration waters, single-stage high-pH and two-stage coagulation processes were most effective. The high alum doses required at pH = 7.4 (to achieve a post-rapid mix ζ-potential of approximately 0 mV) created essentially "super sweep" conditions that promoted floc development and significantly increased turbidity removal in the sedimentation process, compared to lower pH conditions. Improved filtration at high pH, however, could not be explained solely by a reduction in solids mass loading rate on the filters. It was hypothesized that a mechanism that may increase filter attachment efficiency in these conditions is the relatively high concentration of adsorbed $Al(OH)_{3(S)}$ creating a more uniform distribution of positive charges on particle surfaces, therefore increasing the probability of successful particle-media grain collisions. This hypothesis appeared to be supported by the fact that filtration performance for the high-pH process was far less sensitive to changes in post-rapid mix ζ-potential. For example, although it was possible to optimize filtration (i.e. attain total particles < 10/mL) at each of the three pH levels examined, the ζ-potential range in which this was possible was relatively small at pH = 6.0 (approximately +2 to +4 mV) but increased significantly at pH = 7.4 (–4 to +4 mV). At pH= 6.0 and 6.7 particle counts increased rapidly as ζ-potential decreased (became less positive) by only a few mV.

Impact of pH on Filtration. The filtration results indicate that pH alone, when the ζ-potential is constant, does not significantly impact performance, i.e. filtration is not inherently worse at pH 6.0 vs. 7.0 as long as alum doses are optimized at each level. Increasing the pH from 6.0 to 7.0 without an appropriate adjustment to the alum dose, however, would create a significant underdose situation and negatively impact filtration performance.

The primary effect of pH is on the alum dose required to achieve effective particle destabilization. The use of a high coagulation pH provides additional process benefits—optimized particle removal in sedimentation, perhaps a more uniform charge distribution on particle surfaces—that contribute to a more robust filtration process and, overall, increased particle removal. It was also noteworthy that, contrary to the commonly held notion, TOC removal was not compromised by high-pH coagulation processes when alum doses were optimized. The dual objectives of enhanced coagulation—optimization of NOM removal in addition to particles—can therefore be achieved at high pH as well as low pH.

Full-scale Implications of High-pH Processes. Although filtration performance in general was improved at higher pH levels for both water sources, the effect was greater for the more challenging runoff water. Because higher pH significantly increases the optimum ζ-potential range for filtration, a practical implication of this result is that use of a high coagulation pH process may be the most effective short-term treatment strategy for rapidly changing, runoff-type waters containing low alkalinity and high NOM levels. Clearly, a high-pH process would not be practical, in terms of chemical feed costs and solids handling issues, for raw water that is effectively treated by conventional processes. If a high-pH process is unfeasible for treating runoff water, the ζ-potential of coagulated water should be continuously monitored and the coagulant dose adjusted accordingly.

Two-stage Coagulation. Two-stage coagulation processes also improved filtration performance, evidenced primarily by extended runs prior to particle breakthrough, and may be a more realistic full-scale alternative than high-pH processes for treating challenging water quality. Two-stage coagulant addition consistently increased turbidity removal, oftentimes dramatically, during the sedimentation process in bench as well as pilot-scale experiments. This result was explained by the increase in floc formation rates and floc size, compared to single-stage coagulant addition, consistently observed for the two-stage processes, particularly in high-TOC concentration waters. The fact that two-stage processes did not impact floc formation in low-TOC conditions supported the proposed mechanistic advantage of this process, i.e. mitigation of NOM-induced floc restabilization.

It was suggested that the practical effect of splitting the coagulant dose between two application points is to more closely simulate ideal mixing conditions. Under ideal mixing conditions, the short-lived, positively-charged aluminum hydroxide sols would be instantaneously (<0.1 seconds) dispersed *homogeneously* throughout the raw water stream. A certain percentage of the sols would rapidly form insoluble complexes with the hydrophobic NOM fraction while the remaining sols would be free to adsorb to and destabilize colloidal particles. Sol-sol interactions (an ineffective use of these species) and the restabilization of microfloc by NOM would thus be minimized, effects that are also hypothesized for two-stage processes.

Settled water results. Although broadly predictive of filtration performance, settled water quality was not always an accurate measure of overall process performance. In many cases, similar filter effluent steady-state particle counts but significantly different settled turbidities were observed for high and low-pH processes. In other cases, filter effluent particle counts increased while settled turbidity decreased after changes to the coagulation conditions. These results reinforce the importance of proper particle conditioning, through effective coagulation processes, for overall process optimization.

Photometric Dispersion Analyzyer. Results from PDA experiments indicated that the rate of floc formation (measured immediately following coagulant addition) was indicative of overall process performance. The PDA appears to be a useful alternative to jar tests for determining optimum coagulant doses and quickly evaluating different coagulation scenarios. Overall, processes that the PDA indicated were optimum, in terms of the kinetics of floc development, were shown to be optimum in terms of filtration performance as well.

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Appendix A

Horsetooth Reservoir Filtration Runs

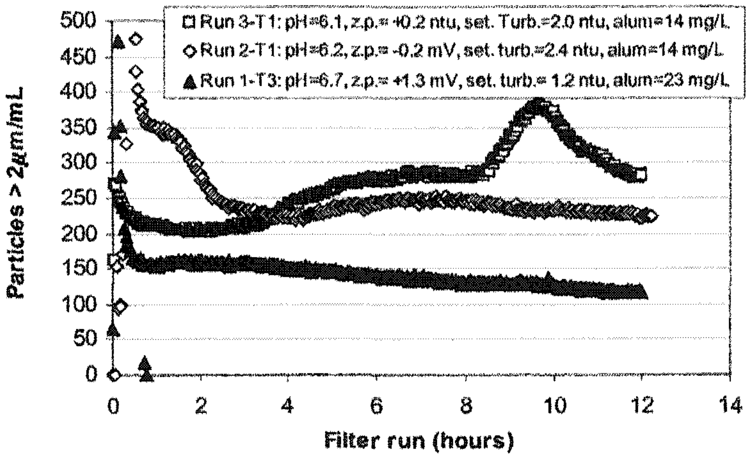

Figure A-1 Runs 1-3 (preliminary), conducted in series. Single-stage alum (added in static mixer). Coagulation process was not optimized.

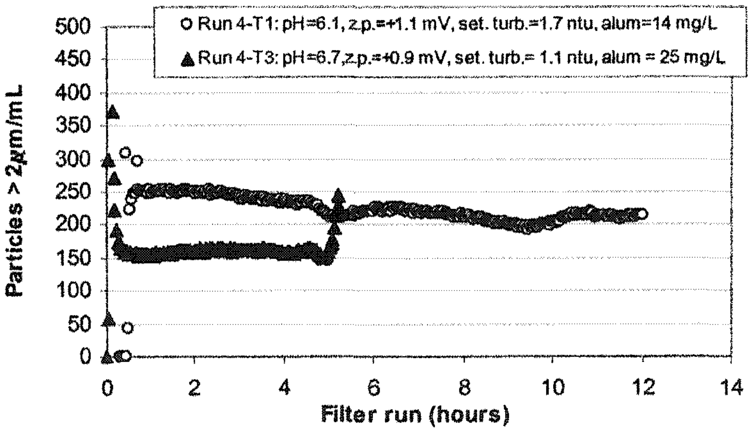

Figure A-2 Run 4 (preliminary), simultaneous filter runs at pH=6.1 and 6.7. T1 alum added in static mixer. T3 alum added in backmixer. All T3 runs were at ambient conditions, i.e. no acid/base addition, with alum added in backmixer.

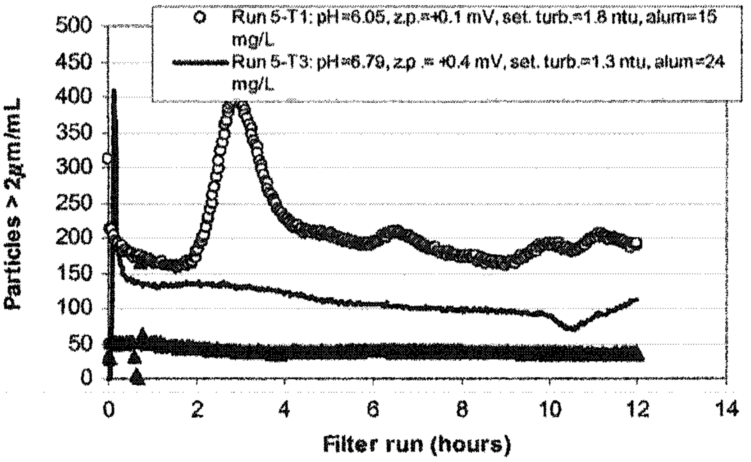

Figure A-3 Runs 5-6 (preliminary, Run 6 was T3 only). Alum doses were sub-optimum. These runs were conducted before zeta potential target became +2-3 mV.

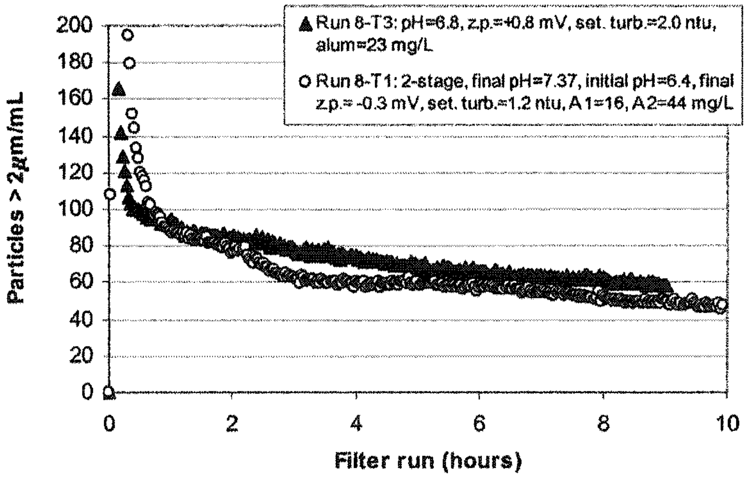

Figure A-4 Run 8, simultaneous filter run, two-stage vs. single-stage alum addition. Zeta potential was not optimized.

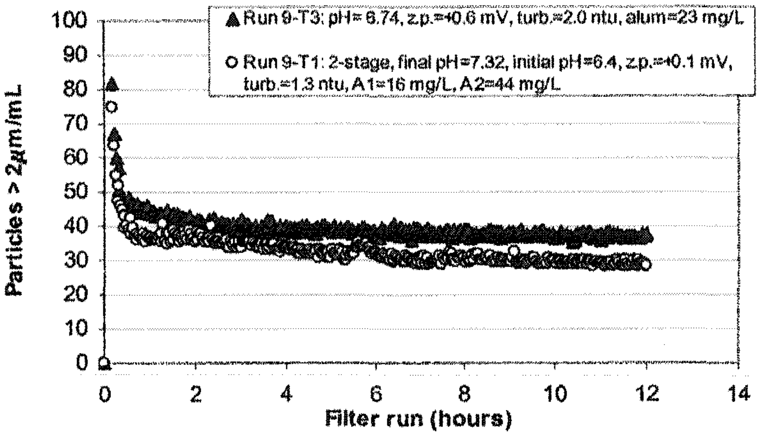

Figure A-5 Run 9, simultaneous tw o-stage vs. single-stage coagulation. Zeta potential w as not optimized, but tw o-stage coagulation process improved filtrationk performance.

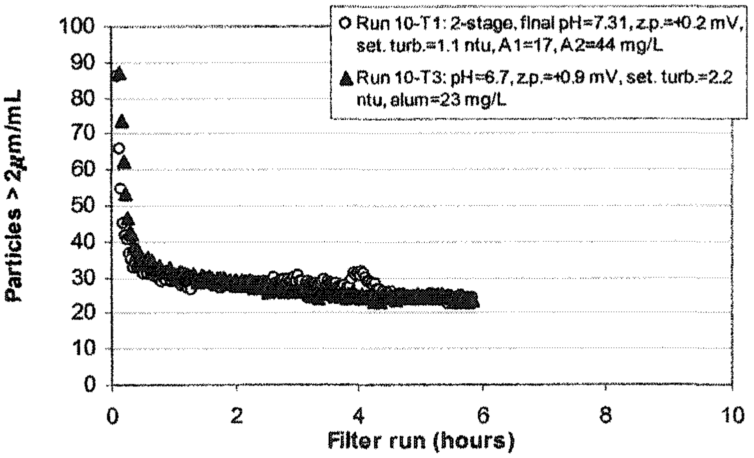

Figure A-6 Run 10, abbreviated simultaneous run, tw o-stage vs. single-stage coagulation. Zeta potential w as sub-optimum (approx. 0 mV w as the target at this point).

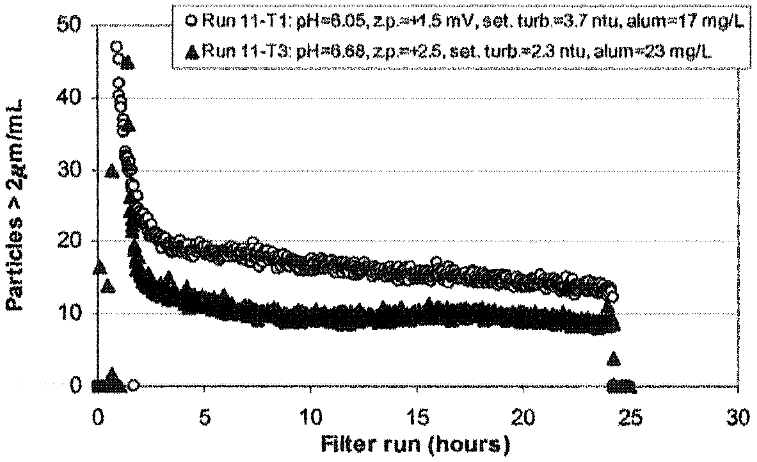

Figure A-7 Run 11, simultaneous filter runs for single-stage alum addition at pH 6.1 and 6.7. T1 alum added in static mixer. Zeta potential is optimized. Note difference in settled turbidity.

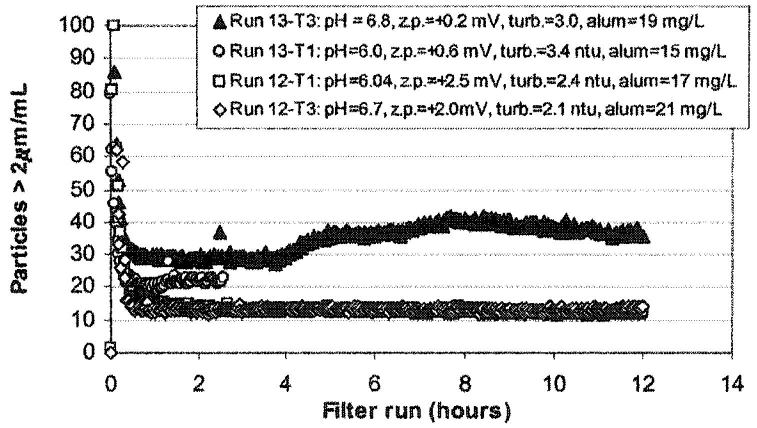

Figure A-8 Runs 12-13, simultaneous filter runs at pH=6.0 vs. 6.7. In Run 12, z.p. was optimized (particle counts were almost identical for the two processes). Run 13 was non-optimized. The T1 particle counter failed during run 13.

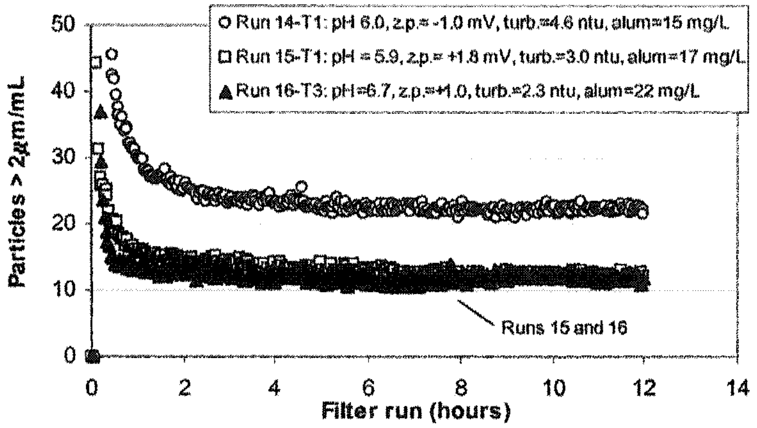

Figure A-9 Runs 14-16, conducted in series because only one particle counter was available at this time. Note difference between Run 14 and 15 for a relatively small difference in alum dose and z.p.

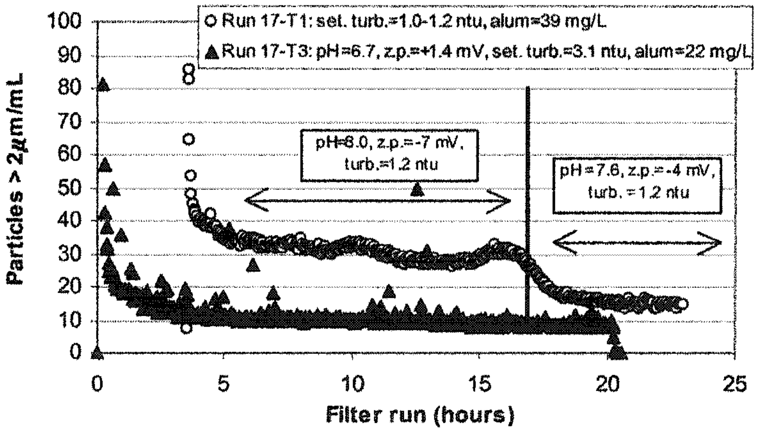

Figure A-10 Run 17, simultaneous filter runs at high pH (T1) vs. pH=6.7 (ambient). T1 was operated at two non-optimized z.p. conditions to demonstrate impact on filtration. Note difference in settled turb. Between T1 and T3.

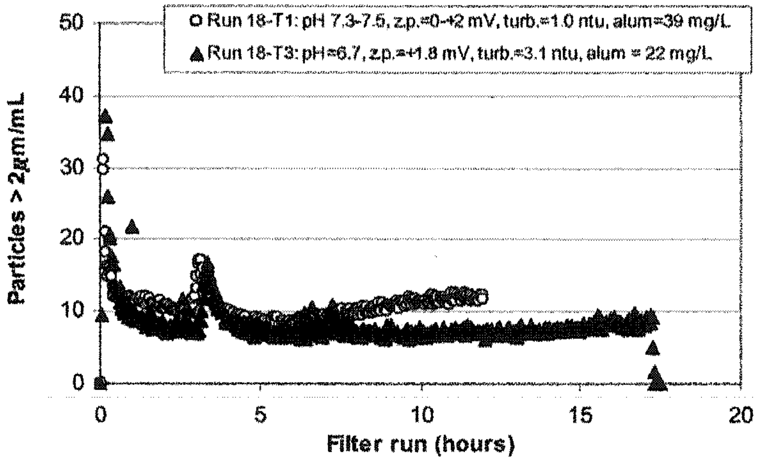

Figure A-11 Run 18 , simultaneous filter runs at pH=7.5 vs. 6.7, single-stage alum. T1 alum was added in static mixer. Note difference in settled turb, alum dose.

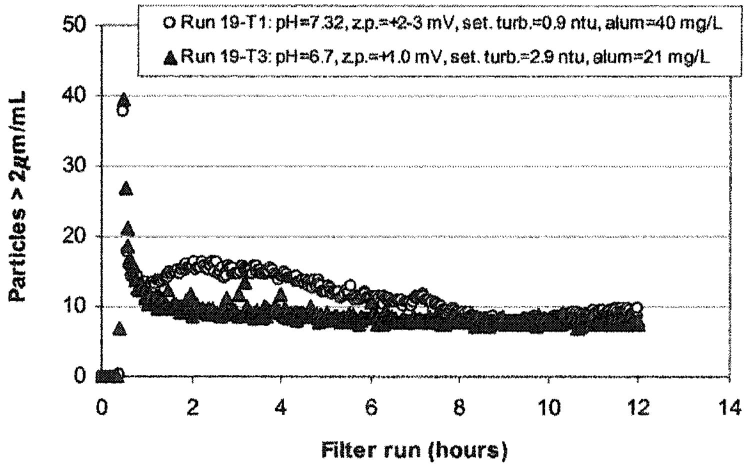

Figure A-12 Run 19, simultaneous filter runs at pH = 7.3 vs. 6.7. Zeta potential was optimized for both processes. T1 alum added in static mixer.

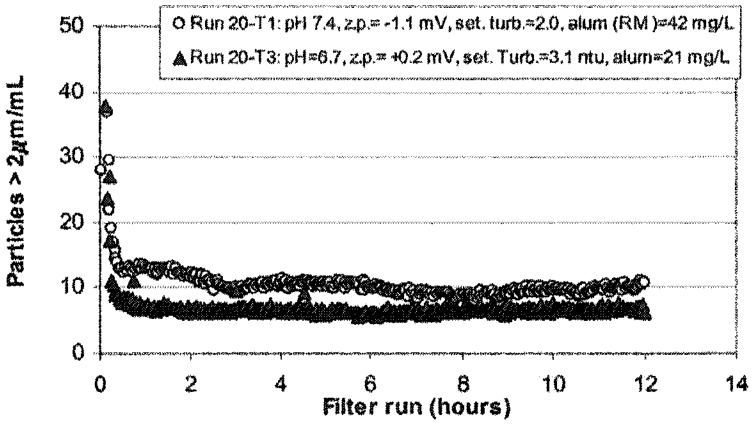

Figure A-13 Run 20, simultaneous filter runs at pH = 6.7 vs. 7.4 for single-stage coagulation. Switching alum from static mixer (Runs 18 and 19) to backmixer increased set. turb. from 1 to 2 ntu, but did not appear to impact filtration.

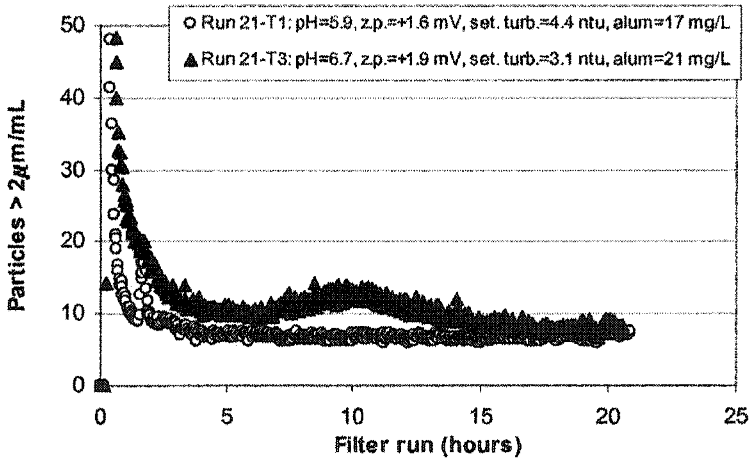

Figure A-14 Run 21, simultaneous filter runs at pH= 5.9 vs. 6.7, single-stage coagulation. Zeta potential is optimized for both processes. T1 alum was added at static mixer.

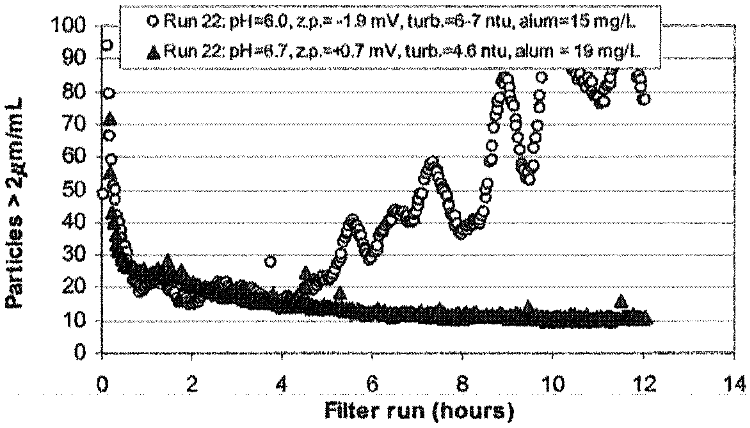

Figure A-15 Run 22, simultaneous filter runs at pH=6.0 vs. 6.7, single-stage coagulation. T1 alum was added in backmixer (first low-pH run using backmixer). Both processes were non-optimized in terms of z.p.

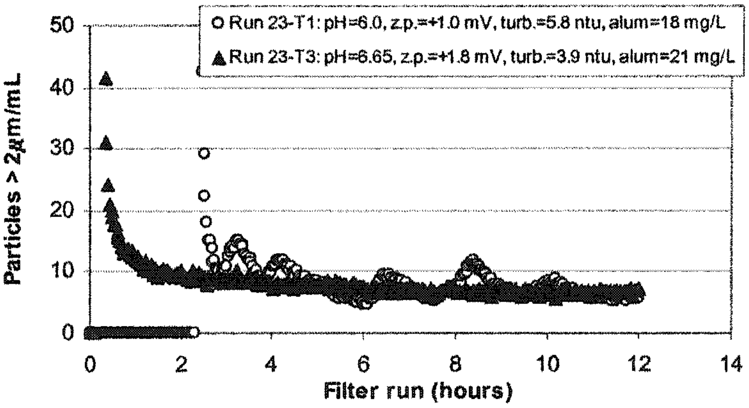

Figure A-16 Run 23, simultaneous filtrations runs at pH=6.0 vs. 6.7. T1 alum was added in backmixer. Zeta potential was optimized for both processes. Unstable T1 particles were due to erratic settled turbidity. Note set. turb. on T1 (compare to Run 21).

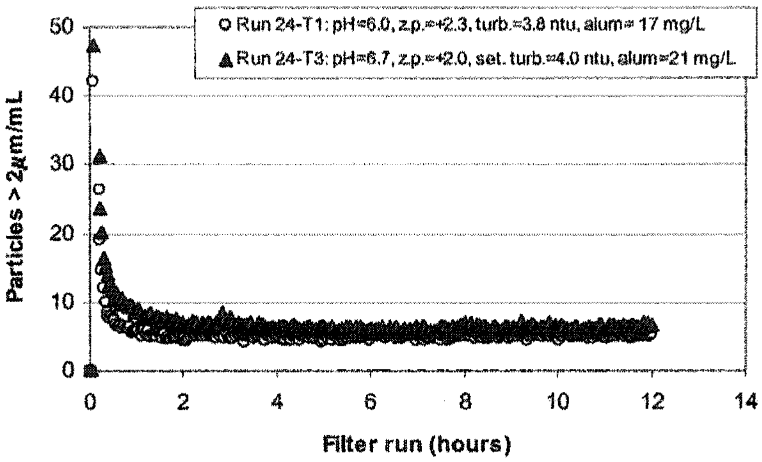

Figure A-17 Run 24, simultaneous filtration runs at pH=6.0 vs. 6.7. T1 alum added in static mixer, zeta potential was optimized for both processes.

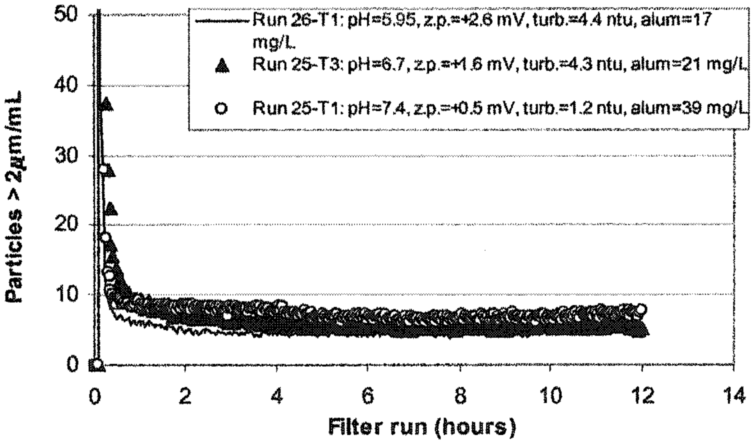

Figure A-18 Runs 25-26, comparison of three single-stage processes at pH = 6.0, 6.7, 7.4. Zeta potential was optimized except for pH=7.4 (slightly underdosed).

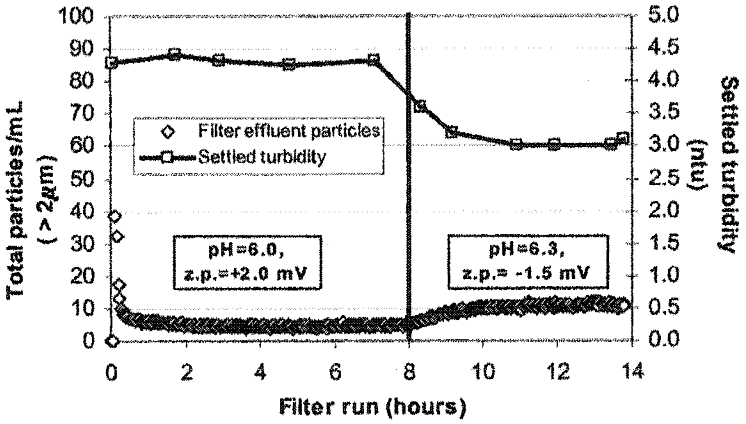

Figure A-19 Run 27, effect of z.p. on filtration for lower pH conditions using reservoir water. Settled turb. decreased while filter effluent particles increased when pH was increased by reducing CO_2 dose.

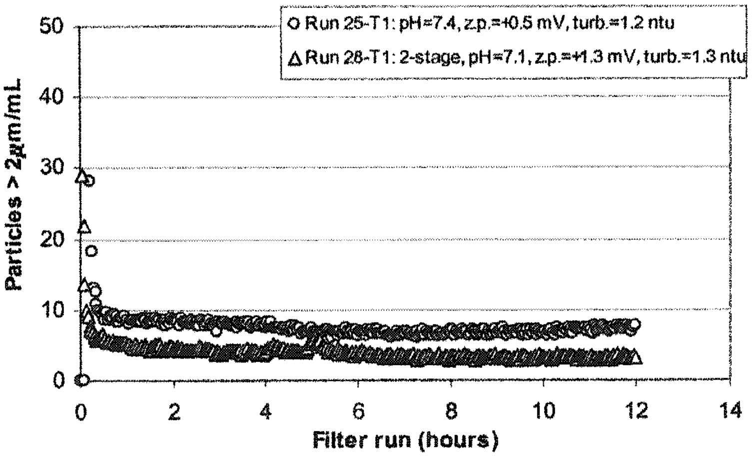

Figure A-20 Runs 25, 28. Comparison of most effective single-stage (pH = 7.4) and a two-stage alum addition process. Two-stage process was slightly more effective.

Appendix B

Poudre River Filtration Runs

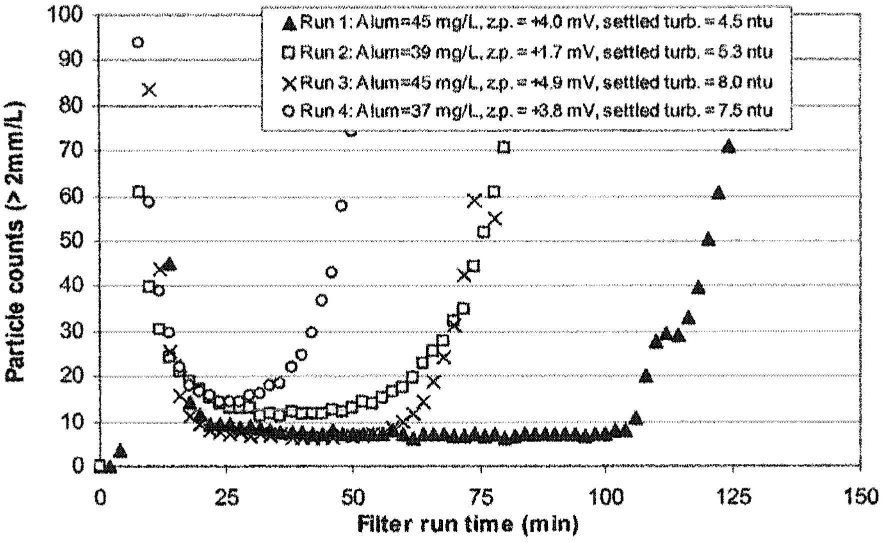

Figure B-1 Runs 1-4, preliminary runoff filtration runs at pH = 6.0. Sed. basin HLR was 0.34 gpm/ft^2 (this rate was used for runs 1-5 only).

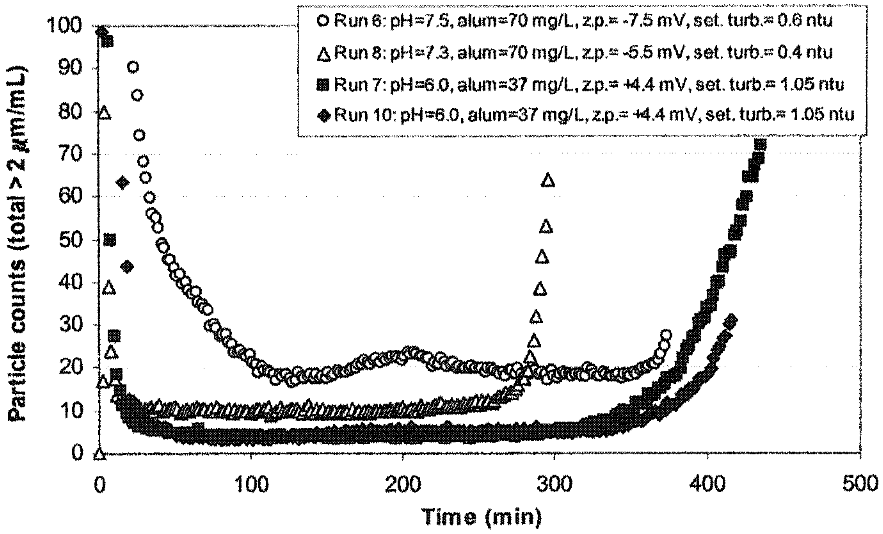

Figure B-2 Runs 6 - 10 (Run 9 omitted). Filter runs at pH = 6.0 and 7.3 - 7.5. High-pH processes were not optimized in terms of zeta potential. Raw TOC = 7.5 mg/L. Sed. basin HLR was 0.17 gpm/ft^2.

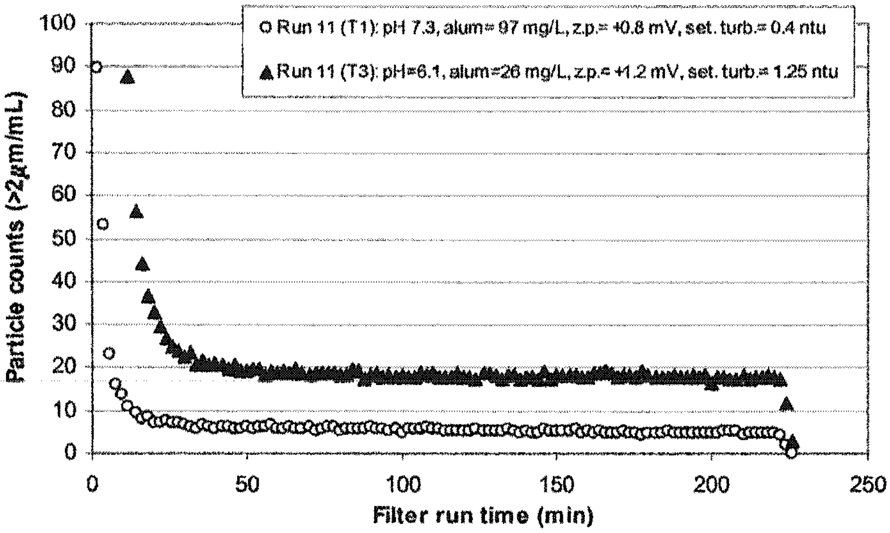

Figure B-3 Run 11, simultaneous filtration runs at pH = 6.0 vs. 7.3. Note impact of optimizing alum dose/z.p. on high-pH particle counts (compare to Runs 6 and 8 in Figure B-2).

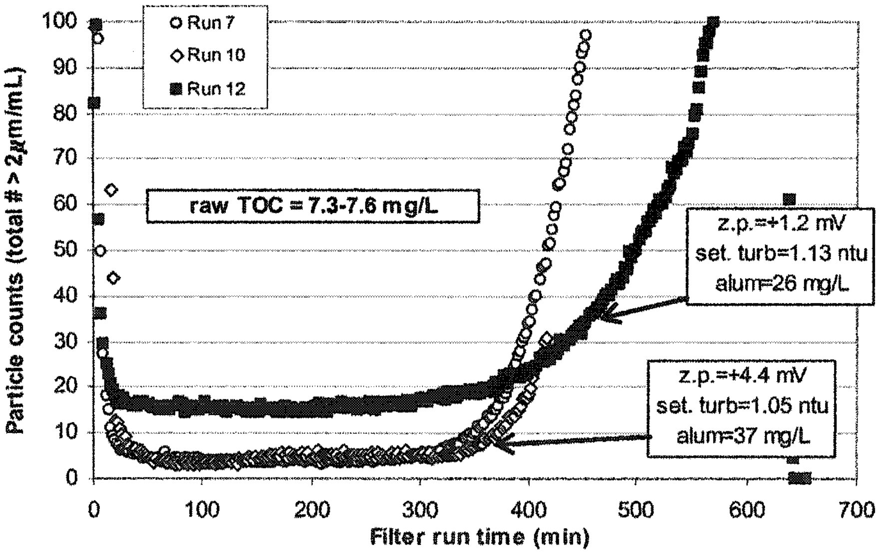

Figure B-4 Effect of alum dose optimization on filtration for low-pH conditions. Run 12 was low-pH process only.

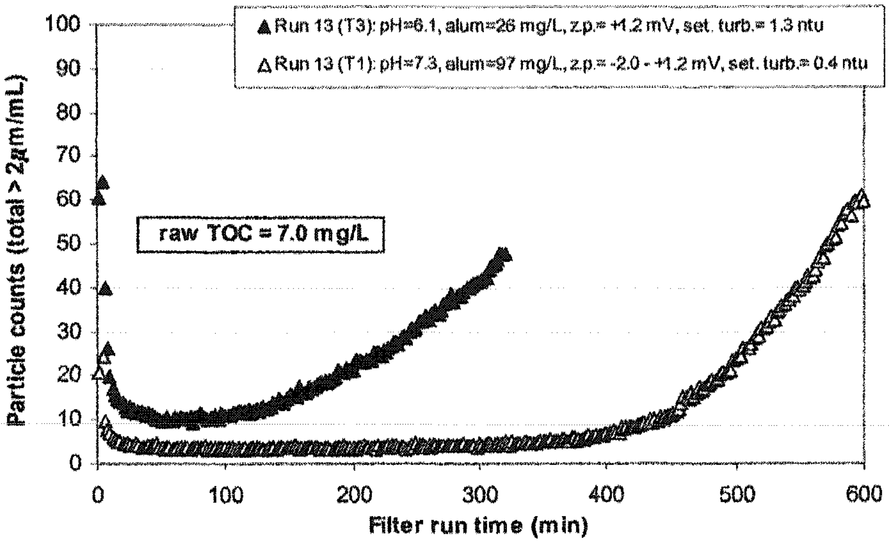

Figure B-5 Run 13, simultaneous filtration runs at pH 6.1 and 7.3. Low-pH process was not optimized in terms of zeta potential.

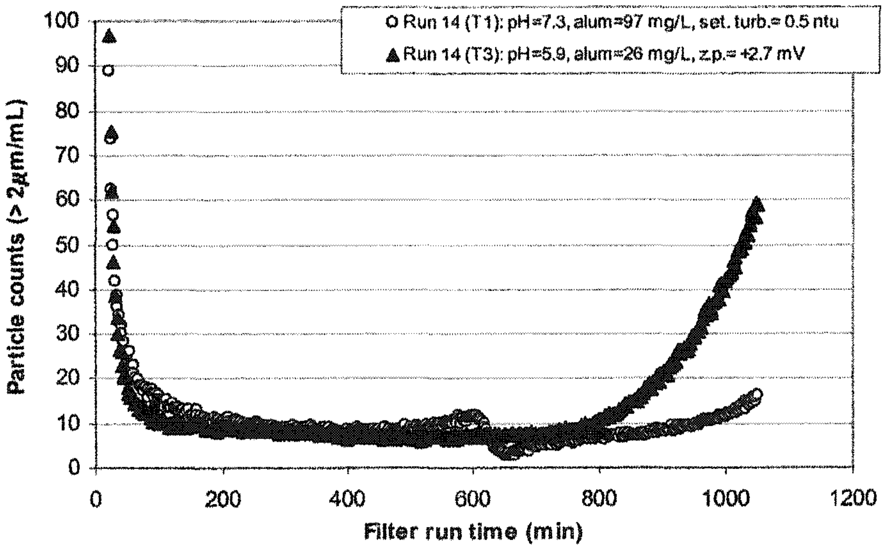

Figure B-6 Run 14, simultaneous filtration runs at pH 5.9 and 7.3. Zeta potential data was not available for high-pH process.

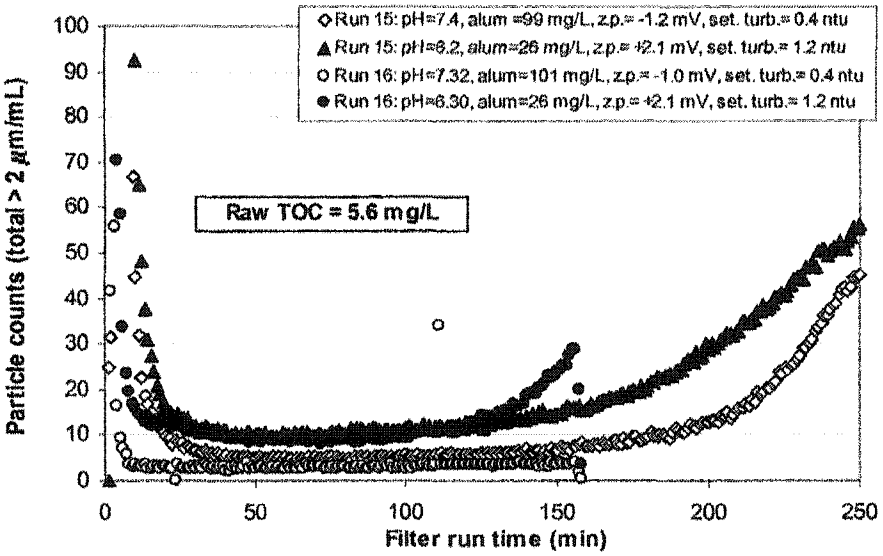

Figure B-7 Runs 15 - 16, comparison of filtration performance for optimized coagulant doses at pH 6.2 and 7.4.

Appendix C

Preliminary PDA Experiments (C-1 – C-7)

and

PDA data illustrating impact of NOM on particle aggregation (Figure C-8)

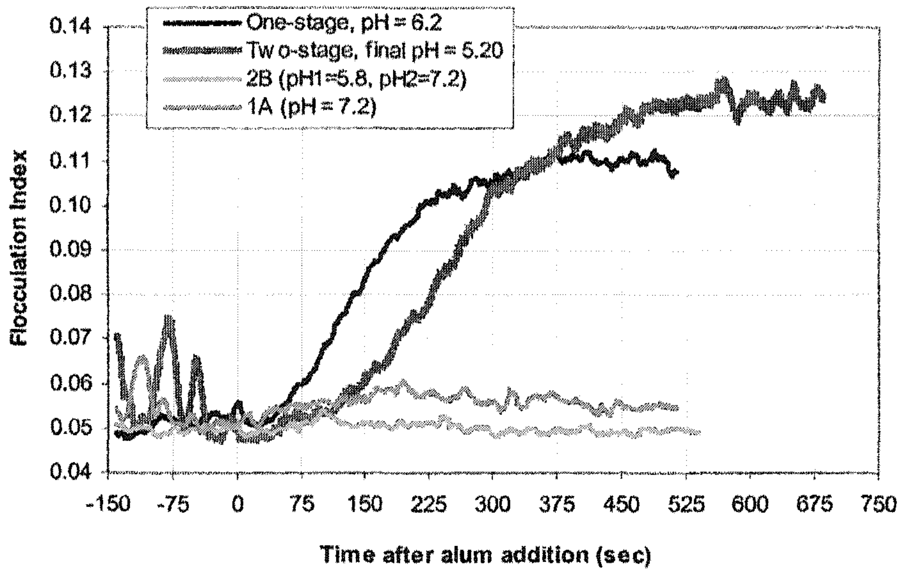

Figure C-1 Flocculation index (FI) vs. time after alum addition (50 mg/L) for 4 coagulation scenarios in high-TOC water. TOC = 9.2 mg/L, turbidity = 60 NTU (kaolin added), T = 20°C. Polymer added at t = 20 sec (polymer use was discontinued after initial experiments). At final pH = 7.2 alum was clearly underdosed, as indicated by flat trendlines for these conditions. Overall, two-stage coagulant addition produced the largest steady-state floc, although the use of polymer in these experiments generally produced larger floc than those observed in later phases of the project. A focus in these preliminary experiments was characterizing the response of the PDA to different coagulant processes.

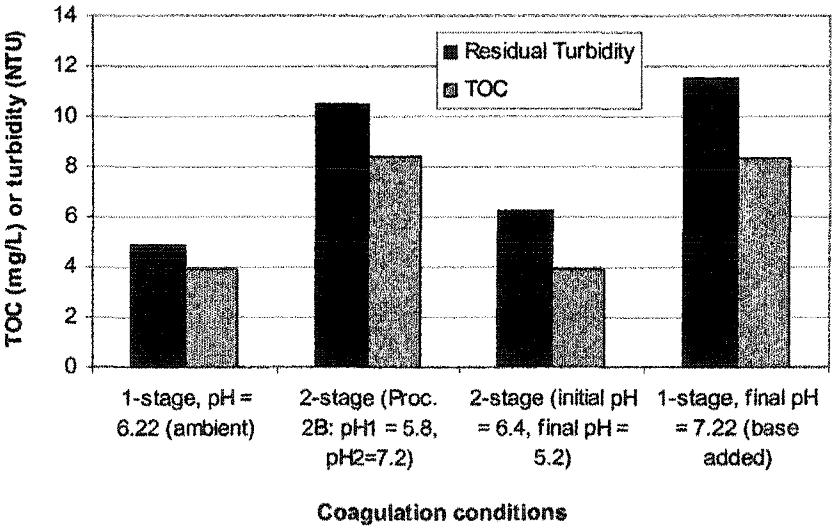

Figure C-2 Residual turbidity and TOC concentration for the four coagulation processes illustrated in Figure D-1. Alum = 50 mg/L, TOC = 9.2 mg/L. High-pH processes, as suggested by Figure D-1, appeared to be underdosed. Single-stage ambient process (far left) was most effective for turbidity removal. Although ς-potential analyses were not conducted during these experiments, it appeared that the final pH of 5.2 for the two-stage low-pH process (second from right) promoted the restabilization of a fraction of floc particles.

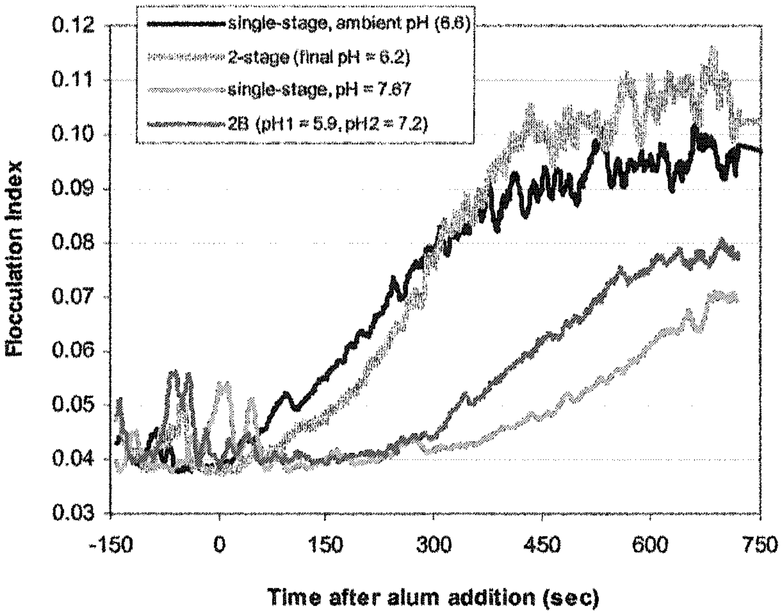

Figure C-3 FI vs. time after alum addition (22 mg/L) for 4 coagulation scenarios using Horsetooth Reservoir water. TOC = 3.6 mg/L, turbidity = 4 NTU, temperature = 20°C. Process "2B" was a two-stage process in which the first alum dose is applied under low-pH conditions and the second dose reacts under high-pH conditions, in this case pH = 7.2. The alum dose of 22 mg/L was sub-optimum for both processes that used a relatively high final pH. As observed in Figure C-1, two-stage process produced largest steady-state floc. Polymer was used in these experiments, applied at t = 20 sec (immediately following rapid mix).

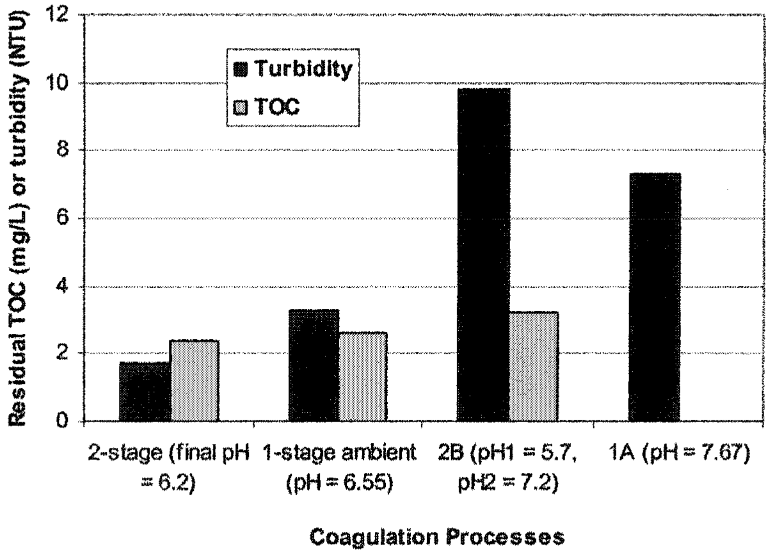

Figure C-4 Turbidity and TOC residuals for the 4 coagulation processes illustrated in Figure C-3. Alum = 22 mg/L, TOC = 3.6 mg/L. The low-pH two-stage process (far left) was significantly more effective for turbidity removal than the low-pH single-stage process. Both high-pH process (right side of figure) were ineffective for turbidity removal, as suggested by Figure C-3.

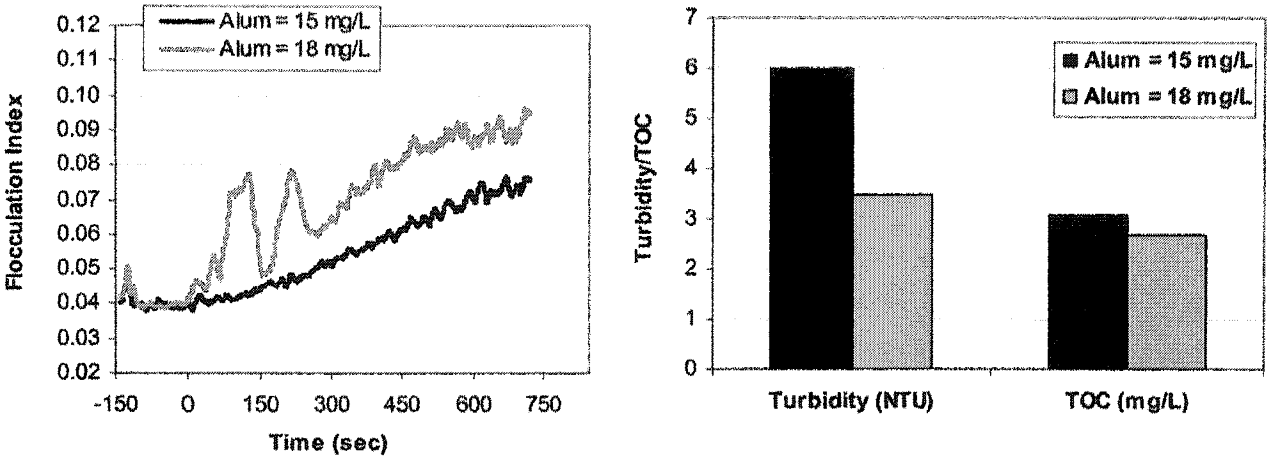

Figure C-5 Correlation of PDA output (flocculation index) with turbidity and TOC removal for two alum doses in Horsetooth Reservoir water. TOC = 3.75 mg/L, turbidity = 5 NTU, temperature = 20°C. Figures C-5 – C-7 represent preliminary experiments correlating FI with particle removal in low-TOC conditions.

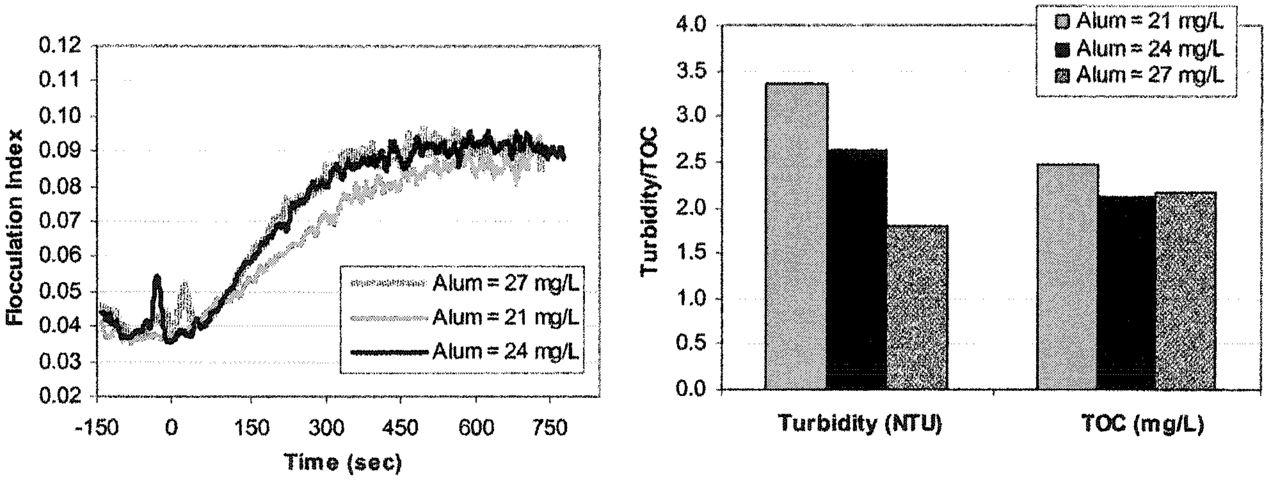

Figure C-6 FI vs. time and turbidity/TOC residuals after sedimentation for three alum doses in Horsetooth Reservoir water. TOC = 3.62 mg/L.

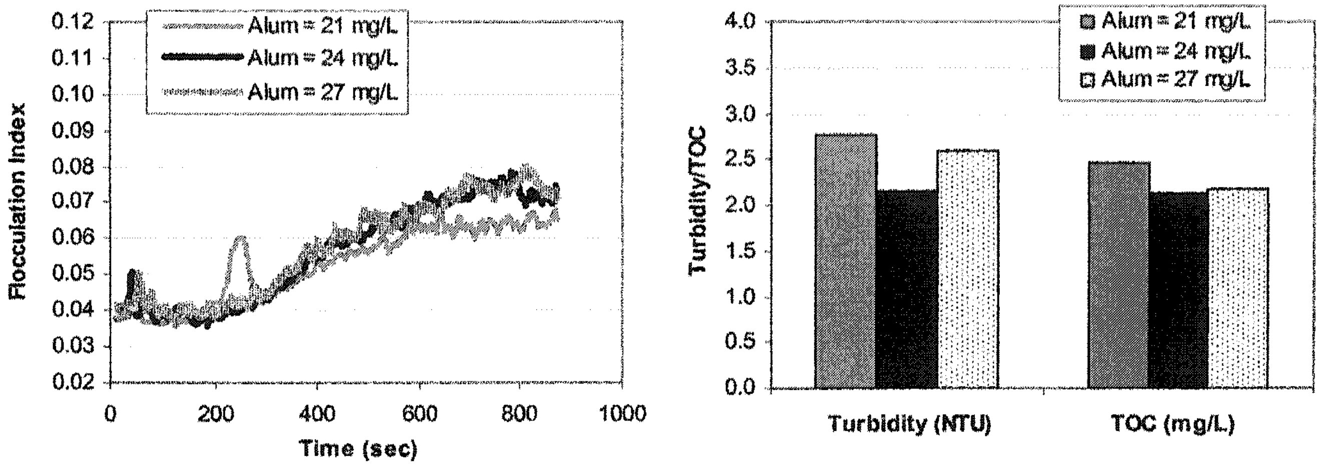

Figure C-7 FI vs. time and turbidity/TOC residuals after sedimentation for three alum doses in Horsetooth Reservoir water. TOC = 3.52 mg/L. These data indicate that an alum dose of 24 mg/L was optimum. The PDA output indicates no further advantage, in terms of floc formation kinetics, of increasing alum dose from 24 to 27 mg/L.

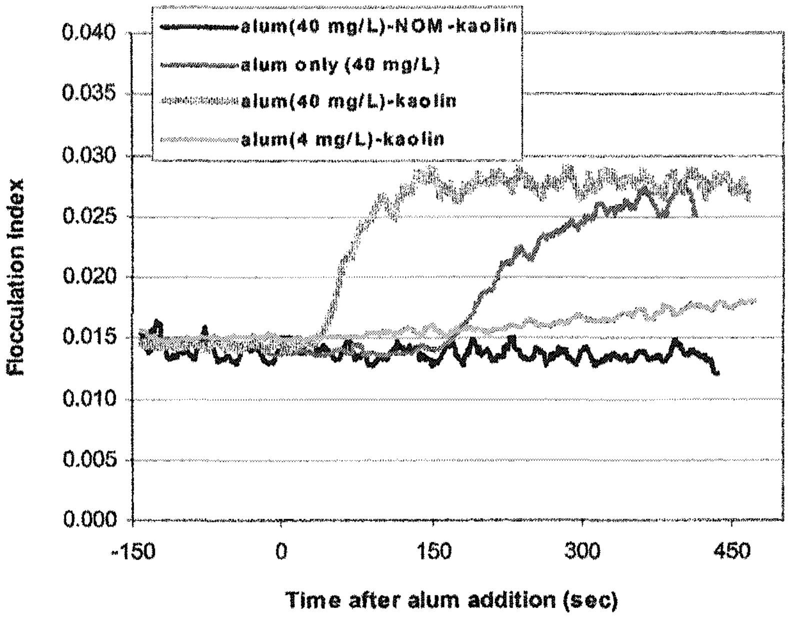

Figure C-8 PDA results illustrating the impact of NOM on floc development. When NOM was added to the system (black trendline), floc formation was not observed. For an alum dose of 40 mg/L without the presence of NOM, significant particle aggregation was observed. Floc formation kinetics were more rapid for the alum-kaolin system (compared to alum only) due to increased collision frequency of particles.