BIOFLOCCULATION: IMPLICATIONS FOR ACTIVATED SLUDGE PROPERTIES AND WASTEWATER TREATMENT

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ABSTRACT

Studies were conducted to determine the role of bioflocculation in the activated sludge unit processes. Laboratory and full-scale studies revealed that bioflocculation is important in determining settling, dewatering, effluent and digested sludge properties (activated sludge properties) and may be vital to the function of all processes related to the above properties. In these studies, it was shown that divalent cations such as calcium and magnesium improved activated sludge properties, whereas monovalent cations such as sodium, potassium and ammonium ions were detrimental to these properties. The divalent cations promoted bioflocculation through charge bridging mechanisms with negatively charged biopolymers (mainly protein and polysaccharide). It was found that oxidized iron plays a major role in bioflocculation and determination of activated sludge properties through surface interactions between iron and biopolymers. Oxidized iron was effective in removing colloidal biopolymers from solution in coagulation and conditioning studies. The research included experiments evaluating effects of potassium and ammonium ions on settling and dewatering properties; effects of magnesium on settling properties; effects of sodium, potassium, calcium and magnesium on effluent quality; effect of solids retention time on effluent quality; and evaluation of floc properties during aerobic and thermophilic digestion. A floc model is proposed in which calcium, magnesium and iron are important to bioflocculation and the functionality of aeration tanks, settling tanks, dewatering equipment and aerobic or anaerobic digesters. It is shown that activated sludge floc properties affect wastewater treatment efficiency.

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EXECUTIVE SUMMARY

The primary purpose of wastewater treatment is to remove the suspended and soluble organic constituents measured as chemical oxygen demand (COD) or biochemical oxygen demand (BOD). Biological treatment processes are used to degrade the organics in the wastewater before it is discharged. In the activated sludge process, the most common biological process for wastewater treatment, the microbes are suspended with the wastewater in a reactor. In order for this process to work effectively, the biomass must be separated from the water and this is accomplished by gravity settling in a 'final clarifier'. To effectively settle, the microbes must flocculate, then aggregate into units large enough and dense enough to settle out of solution. If the biomass does not flocculate well, some microbes will end up in the effluent (supernatant turbidity). Furthermore, the characteristics of the flocculated biomass will have important impacts on the biomass (sludge) disposal process.

Activated sludge flocs are thought to consist of microbial aggregates, filamentous organisms, organic and inorganic particles and exocellular polymers (Tezuka, 1969; Novak and Haugan, 1981; Eriksson and Alm, 1991; Bruus *et al.*, 1992; Higgins and Novak, 1997a, b). These flocs are held together by means of exocellular polymers (biopolymers) and divalent cations to form a 3-dimensional matrix. Although the flocculation process is important, it is not well understood. It is known that bioflocculation is responsible for many of the changes in biofloc characteristics.

Studies in this and other laboratories have shown that cations can affect bioflocculation and change the settling and dewatering properties of the activated sludge flocs (Eriksson and Alm, 1991; Bruus *et al.*, 1992; Higgins and Novak, 1997a, b). Divalent cations bridge across negatively charged biopolymers to form a dense, compact floc structure. Monovalent cations tend to prevent proper flocculation by forming a much weaker structure. As a result, divalent cations promote bioflocculation and produce subsequent improvements in settling and dewatering properties. Monovalent cations tend to cause a deterioration in settling and dewatering properties. It appears that the improvements in settling and dewatering properties are further enhanced when the

divalent cations are added to the feed rather than in the form of superficial addition to the settling tank (Higgins and Novak, 1997a). These cations need to be incorporated during the floc formation process.

The objective of this research was to evaluate the effects of bioflocculation on activated sludge floc properties and to determine its impact on settling properties, dewatering properties, effluent quality and digested biosolids properties.

Early studies during this research, which were essentially a continuation of studies conducted by several researchers in this laboratory, involved evaluation of cations on settling and dewatering properties for industrial processes. These studies (laboratory experiments and field verification) showed that sodium, potassium and ammonium ions caused a deterioration in settling and dewatering properties (Murthy and Novak, 1998a). Addition of magnesium ions to an industrial wastewater treatment process high in sodium ions resulted in considerable improvements in settling properties (Murthy *et al.*, 1998a).

These studies indicated that monovalent cations could affect effluent properties by interfering with bioflocculation. Industrial processes containing high concentrations of monovalent cations in the influent, with little or no feed protein or polysaccharide, were characterized by considerable concentrations of biopolymers in the effluent. Through the monitoring of changes in biofloc characteristics, it was shown that cations affected effluent quality through an exchange of biopolymers between flocs and solution (Murthy and Novak, 1998b). Laboratory and field experiments demonstrated that a decrease in divalent cations or an increase in monovalent cations resulted in an increase in release of biopolymers (mainly polysaccharides). The release of biopolymers resulted in both an increase in effluent COD and diminished treatment efficiency.

With regard to the waste biomass, the settled sludge may go through a series of steps where it is further thickened, stabilized and dewatered before it is disposed. The ability of the sludge to be separated, settled, thickened, stabilized and efficiently dewatered depends on its inherent properties, which in turn, appear to depend on bioflocculation properties and cations.

Stabilization is usually performed in aerobic or anaerobic digesters, in which a sufficient detention time is required to degrade organic matter and to destroy pathogens. This research has shown that aerobic digestion leads to a deterioration in dewatering

properties and increases the biopolymers (especially polysaccharides) in solution (Murthy and Novak, in press). Proteins appear to be degraded during digestion while polysaccharides accumulate. The accumulation of polysaccharides was hypothesized to be due to a lack of available enzymes for their hydrolysis. Variations in the cation content of aerobically digested biosolids affected the dewatering properties and conditioning chemical requirements. These effects coincided with a differential release of polysaccharides. A higher divalent cation content yielded good dewatering properties, low conditioning chemical requirements and low solution polysaccharides.

From the aerobic digestion study it was found that an increase in the endogenous biomass digestion time resulted in an increase in the release of polysaccharides and, therefore, a rise in supernatant COD. The activated sludge process is often operated endogenously as part of wastewater treatment. It was hypothesized that an increase in solids retention time (decay is more important relative to growth at higher SRTs) may result in an increase in the release of biopolymers, much like in the aerobic digestion study. A study was conducted using a laboratory system with a constant source of COD (acetate and Bactopeptone), where SRT was varied and the effluent properties were monitored (Murthy *et al.* 1998d). It was found that polysaccharides and COD increased with an increase in SRT. There was a small increase in proteins at higher SRTs. A corresponding increase in BOD with respect to COD was not found, indicating that the organics released may not be easily degraded. A substantial fraction of the protein was in the size range greater than 30,000 dalton and 0.45 μ (which is absent in Bactopeptone), and do not constitute residual substrate.

Anaerobic conditions or thermophilic digestion in autothemal thermophilic aerobic digesters (ATADs) was found to release substantial concentrations of biopolymers (Murthy *et al.* 1998b, c). The reduction of iron may have caused some of the release of proteins and polysaccharides, along with the presence of high concentrations of monovalent cations such as ammonium ions. Oxidized iron was capable of coagulating much of the released biopolymers. Mesophilic aeration improved conditioning and dewatering properties of digested biosolids considerably, perhaps through oxidation of iron and removal of ammonia. It is therefore suggested that iron may play an important role in bioflocculation through adsorption of organic biocolloids onto iron-hydroxy

mineral surfaces in the flocs. The use of iron as a chemical conditioner during autothermal thermophilic aerobic digestion coagulated much of the protein and polysaccharide, thereby diminishing additional cationic polymer conditioning requirements and subsequent operating costs.

It has been found that cations can significantly alter the inherent properties of the sludge. This study focused on how cations affect treatment, settling properties, digested biosolids properties and dewatering properties of activated sludge. Based in these results, a floc model is proposed where the attachment or release of biopolymers in activated sludge flocs is influenced by cations. Divalent cations enhance bioflocculation through improvements in floc structure and form dense flocs without substantial release of biopolymers. Divalent cations promote bioflocculation while monovalent cations hinder bioflocculation. Bioflocculation affects settling and dewatering properties, supernatant turbidity, effluent quality, and floc properties during digestion. Trivalent cations such as oxidized iron may play an important role in promoting bioflocculation, especially during digestion and for effluent properties during treatment. The deterioration of floc structure due to absence of trivalent cation (ferric ion) is evidenced during anaerobic digestion where reduction of iron and precipitation (FeS) leads to release of extracellular protein. This release of extracellular protein is not observed during aerobic digestion where the oxidized trivalent form is maintained. These observations are supported by coagulation and conditioning studies where oxidized iron associates strongly with proteins and to a lesser extent with polysaccharides. The role of iron in bioflocculation requires further investigation.

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LITERATURE REVIEW

Introduction

The primary purpose of wastewater treatment is to remove the suspended and soluble organic constituents measured as chemical oxygen demand (COD). The COD of the wastewater is the amount of oxygen required to completely degrade wastewater to carbon dioxide and water. The COD of the wastewater also provides an estimate of the energetics of the wastewater treatment process.

Biological treatment processes are used to degrade the organics (COD) in the wastewater before it is discharged. In activated sludge, the most common biological process for wastewater treatment, the microbes are suspended with the wastewater, in a reactor. In order for this process to work effectively, the biomass must be separated from the water and this is accomplished by gravity settling in a final clarifier. To effectively settle, the microbes must flocculate, then aggregate into units large enough and dense enough to settle out of solution. If the biomass does not flocculate well, there will be some microbes that end up in the effluent (supernatant turbidity). Furthermore, the characteristics of the flocculated biomass will have important impacts on the biomass (sludge) disposal process.

Although the flocculation process is important, it is not well understood. Activated sludge flocs are thought to consist of microbial aggregates, filamentous organisms, organic and inorganic particles and exocellular polymers. Bioflocculation is responsible for changes in supernatant turbidity and biofloc characteristics that result in variations in settling and dewatering properties. Activated sludge flocs are held together by means of exocellular polymers (biopolymers) and divalent cations (Bruus *et al.* (1992), Eriksson and Alm (1991), Novak and Haugan (1978), Tezuka (1969)) to form a 3-dimensional matrix. If the settling and dewatering properties of activated sludge is to be comprehended, a clear understanding of the role of biopolymers, biopolymer binding and the role of specific cations is required.

Recent studies in this laboratory have shown that changes in cation concentration change the effluent quality through an exchange of biopolymers between flocs and

solution. The impacts of this exchange may have important consequences on diminished treatment efficiency in terms of fractional residual carbon or oxygen demand.

With regard to the waste biomass, the settled sludge may go through a series of steps where it is further thickened, stabilized and dewatered before it is disposed. The ability of the sludge to be separated, settled, thickened, stabilized and efficiently dewatered depends on its inherent properties and this appears to depend on bioflocculation properties and cations.

Dewatering is typically performed using mechanically operated equipment, where pressure is used to force water from the flocs. Dewatering is performed usually by filtration or centrifugation. Cationic polymers are used to 'superflocculate' the sludge flocs for water removal. The inherent characteristics of the sludge will drive the amount of cationic polymer required and the ease of dewatering (time to filter and the final cake solids at a certain pressure).

In addition to dewatering, stabilization is usually performed in aerobic or anaerobic digesters, where a sufficient detention time is required to reduce the readily degradable organic content and to destroy pathogens. During digestion, solids reduction is achieved through lysis and regrowth of biomass, with release of carbon dioxide and water. Several studies have shown that aerobic digestion leads to poorer dewatering properties and an increase in biopolymers in solution (Novak *et al.*, 1977; Katsiris and Kouzeli-Katsiri, 1987). This suggests that the cation content in the sludge could influence the dewatering properties and conditioning chemical requirements of digested sludges.

Nature of Activated Sludge Biopolymers

An understanding of the composition of activated sludge flocs would offer means to change their properties and to enhance their settling and dewatering properties and to control the effluent characteristics of the activated sludge process. Where filamentous bacteria are not considered to be the main cause of deterioration in settling and dewatering properties, it is thought that biopolymers and cations are mainly responsible for many of the variations in settling and dewatering properties.

Biopolymers in activated sludge are either lysed cell products, metabolic products, or originate from the influent wastewater (Frolund *et al.* (1996), Urbain *et al.* (1993)). The metabolic products are largely identified as proteins and polysaccharides, the lysed products are mainly proteins, polysaccharides, lipids and nucleic acids, and the influent wastewater polymers are humic acids and other introduced synthetic or organic polymers.

Factors that Affect Floc Characteristics

Extracellular Proteins

Extracellular proteins in the floc (bound proteins) have been associated with improvements in settling and dewatering properties. Considerable shear exists in aeration tanks in the activated sludge process. The shear is a result of mixing due to aeration. Some flocs appear to be more sensitive to shear while other flocs are more resistant. Shearing of flocs is thought to result in a release of proteins and polysaccharides to the free liquid. The extracellular proteins free in the liquid (unbound proteins) have been associated with poor effluent quality (soluble microbial products) and poor dewatering characteristics.

Initial results of some experiments indicate that at least some of the proteins in activated sludge possess lectin-like activity (Higgins (1995)). Lectins are extracellular proteins that attach to polysaccharides to cause agglutination or bioflocculation. Lectins are considered to play a major role in the major mechanism for attachment and agglutination by bacteria in such diverse fields as food microbiology, pathogenic microbiology, industrial microbiology and plant-microbe interactions (Lodeiro *et al.* (1995), Siero *et al.* (1995), vanRhizn and Vanderleyden (1995), Mirelman (1986)).

Extracellular Polysaccharides

The effect of polysaccharides on settling and dewatering characteristics and effluent quality is less clear. Wahlberg *et al.* (1992) described a model in which sludge flocs aggregated and eroded with time, and the rate of floc breakup decreased with an increase in polysaccharides associated with the floc. The authors also observed a

decrease in supernatant turbidity with an increase in polysaccharides associated with the flocs.

In some literature, uronic acids present in polysaccharides have been indicated to benefit bioflocculation (Takeda *et al.* (1994), Bender *et al.* (1994), Steiner *et al.* (1976)). There are numerous suggestions that the negatively charged uronic acids in polysaccharides (specifically alginates) interact with divalent cation through charge bridging to promote bioflocculation.

Other research indicate that a release of polysaccharides is detrimental to settling and dewatering characteristics (Urbain et al (1993), Randall *et al.* (1971), Forster (1971)), through nutrient deficient (specifically nitrogen) conditions. It is suggested that bacteria incorporate the carbonaceous material into polysaccharide when sufficient nutrients are not present for metabolism.

There is considerable evidence that uronic acid containing polysaccharides benefit bioflocculation and nutrient deficient conditions promote deterioration in settling and dewatering properties. It is likely that both these conditions apply to activated sludge flocs.

Role of Cations that Affect Floc Characteristics

Cations significantly alter the settling and dewatering characteristics of activated sludge. It is suggested that cations interact with the negatively charged biopolymers in activated sludge to change the structure of the floc (Higgins (1995), Bruus *et al.* (1992), Eriksson and Alm (1991), Morgan *et al.* (1990), Novak and Haugan (1978), Tezuka (1969)). It has been observed that monovalent cations tend to cause deterioration in settling and dewatering characteristics whereas divalent cations tend to improve settling and dewatering characteristics (Higgins (1995)).

Models (Higgins (1995), Bruus *et al.* (1992), Novak and Haugan (1978), Tezuka (1969)) suggest that divalent cations participate in charge bridging of negatively charged sites on the biopolymers. The charge bridging between the biopolymers promote an increase in floc size and floc density and increase the floc resistance to shear. Monovalent cations reduce the strength of the bonds that leads to a loose structure, often

decreasing floc size and floc density and decreasing the floc resistance to shear (Higgins (1995)).

Evidence indicating improvements in settling and dewatering characteristics at equi-equivalent concentration or less of monovalent to divalent ions bolster the charge bridging model (Higgins (1995)). The theory is that charge competition between monovalent and divalent ions exists in activated sludge floc that requires an excess of divalent ions to achieve improvements in settling and dewatering characteristics.

The studies indicating the equi-equivalent monovalent to divalent ion ratio have mainly used sodium ion as the monovalent ion and calcium and magnesium ions as the divalent ions. The effect of potassium and ammonium ions on settling and dewatering characteristics has not been as thoroughly studied. Initial results obtained in this research indicate that the interactions of potassium and ammonium ions in the floc may be more complicated.

Addition of both potassium and ammonium ions appeared to increase the concentration of total extracellular proteins. High concentrations of these ions resulted in a release of extracellular proteins to the free solution and an increase in effluent total organic carbon (TOC). At lower concentrations of potassium ions, there appears to be a beneficial increase in the concentration of bound protein in the floc. The effects of potassium and ammonium ions appear to be both physiological and physico-chemical.

Studies conducted in this laboratory have shown that divalent cations tend to improve effluent quality through improvements in bioflocculation and increased association of biopolymers to the floc. Monovalent cations cause a release of these biopolymers resulting in deterioration of effluent quality.

Calcium and magnesium ions have been indicated to participate in lectin interactions where they enhance the activity of the proteins (Lodeiro *et al*. (1995), Siero *et al.* (1995), vanRhizn and Vanderleyden (1995), Mirelman (1986)). Other research conducted with activated sludge has indicated that equimolar concentrations of calcium and magnesium provide optimum settling and dewatering characteristics (Higgins (1995)). Some of the proteins in the extracellular matrix may participate in lectin-like interactions, and the addition of calcium and magnesium may cause more than just physico-chemical ion bridging interactions.

Floc Characteristics that Affect Settling and Dewatering Properties

The biopolymers in activated sludge flocs appear to affect the physico-chemical properties associated with the flocs such as floc density, floc particle size, specific surface area, charge density, bound water content and hydrophobicity. These physico-chemical floc characteristics express themselves among other things as activated sludge settling and dewatering properties.

Research indicates that an increase in floc density and floc particle size increases settling velocity. The theoretical basis for improved settling through an increase in floc density and floc particle size is presented in Stokes Law. Additionally Kolda (1995) has suggested that an increase in floc density results in improved dewatering properties through a decrease in bound water associated with the flocs.

Forster (1983) has indicated that the calcium may create denser sludge flocs through a decrease in bound water associated with the floc. The percent bound water associated with the floc is also an indicator of the maximum dryness that can be achieved in the sludge cake by mechanical means (Robinson (1989)).

Particle size distribution appears to affect dewatering properties, where smaller particles (colloidal and supracolloidal) cause blinding of filters and sludge cakes (Novak *et al.* (1988), Sorensen *et al.* (1997)) and deter the release of water in the sludge cake.

The hydrophobicity of activated sludge flocs has recently received much attention (Jorand *et al.* (1994)). These researchers have indicated that improvements in bioflocculation and settling are significantly as a result of an increase in floc hydrophobicity.

An increase in specific surface area of flocs caused a deterioration in settling and dewatering properties (Sorensen and Wakeman (1996), Andreadakis (1993), Alibhai and Forster (1986)).

Charge density increases have been observed with increases in anionic biocolloids in activated sludge. Although the effects of charge density on activated sludge properties have not been determined, it can increase the polymer demand for conditioning of activated sludge.

Significance of Cations and Biopolymers on Activated Sludge Characteristics

Altering the concentration of cations in activated sludge has been observed to be a simple and inexpensive means to change the inherent properties of activated sludge and enhance settling, dewatering and effluent properties. Some of the cations seen to impact activated sludge properties are sodium, potassium, calcium, magnesium and ammonium ions. Other ions that impact activated sludge properties are iron, copper and other heavy metals.

If changes in cation concentration can significantly benefit settling, dewatering and effluent characteristics, it can prove beneficial to both upstream and downstream processes.

The improvements in dewatering characteristics could result in a reduction in polymer demand and produce a drier cake (lower cost for ultimate disposal). The improvements in settling characteristics would result in smaller clarifier footprints and smaller sludge flow rates. A decrease in soluble microbial product would result in lower effluent chemical oxygen demand (COD) and facilitate tertiary treatment or reuse of treated wastewaters.

Concepts that Need to be Studied and Verified

In the biopolymer floc model, settling and dewatering characteristics depend on interactions between the bacteria, the biopolymers and the cations in the floc. Studies have shown that various biopolymers interact with different cations to enhance or deteriorate sludge characteristics. The addition of monovalent and divalent cations have been observed to cause changes in settling and dewatering properties as observed using lab-scale settling and dewatering tests.

In past studies, it has been observed that calcium and magnesium ions tend to enhance activated sludge settling and dewatering properties, whereas sodium, potassium and ammonium ions cause deterioration in activated sludge properties.

The role of some cations such as calcium, magnesium and sodium are better defined than other cations such as potassium and ammonium ions. However some of the mechanisms that cause bioflocculation still need exploration. The mechanisms that cause changes in settling and dewatering properties are important to understand the floc

properties. It would be useful to determine some of the interactions that are prominent in activated sludge in order to predict the effect of changes in concentration of these cations on settling and dewatering properties.

In more recent studies, the effects of ammonium and potassium ions on activated sludge properties were more closely studied. It was observed that addition of these ions enhanced the concentration of the extracellular proteins in activated sludge. An increase in small concentrations of potassium results in a sludge, which is less susceptible to shear and form larger flocs resulting in improvements in settling properties.

From initial results and experiments performed by Smith (1996), it appears that, at least for industrial processes having low concentrations of potassium in the feed wastewater, addition of small concentrations of potassium is beneficial, beyond which, further addition of potassium to the feed causes an increase in extracellular proteins not associated with the flocs (unbound proteins). The increase in unbound proteins tends to increase the effluent total organic carbon (soluble microbial product (SMP)) and supernatant turbidity and is associated with deterioration in dewatering properties. The results of the potassium experiments need to be further researched.

The aerobic and anaerobic digestion of activated sludge involves the degradation of easily metabolized organics, especially endogenous proteins and the destruction of pathogens. The end-products of digestion are inorganic substances and recalcitrant organics. The degradation of proteins and polysaccharides that occur during stabilization is not well understood. It is known however, that aerobically and anaerobically digested sludge produce flocs that dewater poorly. Divalent cations may play a role in preventing the deterioration of floc properties. The interactions that exist in the flocs during stabilization therefore need to be better understood. These interactions may influence dewatering properties.

The release of biopolymers into the free solution due to shear causes an increase in dissolved biopolymers (soluble microbial products). The increase in these products may be a function of the cations in the floc. The increase may affect effluent COD. There have been indications that some of these biologically generated organics may be toxic in nature (Boero *et al.* (1996)). Some results indicate that addition of divalent cation deter the release of some of these biopolymers by providing shear resistance to the sludge.

Monitoring the COD and the release of these biopolymers in activated sludge would provide a better understanding of this phenomenon.

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CHAPTER 1

MONITORING CATIONS TO PREDICT AND IMPROVE ACTIVATED SLUDGE SETTLING AND DEWATERING PROPERTIES

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Abstract

Laboratory and field tests were conducted on activated sludge from an industrial wastewater treatment plant in order to monitor the settling and dewatering properties and to assess the impact cations may have on these properties. The influent to the wastewater treatment plant contained a high concentration of sodium ions and a low concentration of divalent cations. The sludge exhibited poor settling and dewatering properties. Initial laboratory results indicated an improvement in settling and dewatering properties through the addition of calcium and magnesium. After addition of magnesium during field trials, floc density and settling properties improved considerably. In addition, residual ammonium ions in the mixed liquor appeared to interact with the activated sludge flocs to influence their dewatering properties. It was observed that an increase in ammonium ion in the soluble sludge fraction was related to deterioration in the dewatering properties.

During these trials, the ammonium ions demonstrated a greater influence on dewatering properties than did the magnesium ions. The tests conducted at the treatment plant revealed that complex interactions between cations and sludge influenced the settling and dewatering properties in a manner that depended on ratios and concentrations of monovalent and divalent cations in the activated sludge feed and solution.

Keywords

Cation, activated sludge, settling, dewatering, magnesium, ammonium.

Introduction

Activated sludge is comprised of microbial consortiums and organic and inorganic particles held together in a matrix formed by exocellular polymers and divalent cations (Tezuka, 1969; Novak and Haugan, 1981; Eriksson and Alm, 1991; Bruus *et al.*, 1992; Higgins and Novak, 1997a, b). Bruus *et al.* (1992) and Higgins and Novak (1997b) have shown that excess monovalent cations can cause a deterioration in floc structure and settling properties. Improvements in settling properties were observed with an increase in divalent cations.

Many industrial systems require influent water of high purity. Therefore, the addition of chemicals during the industrial process and wastewater pretreatment dictate the cationic composition of the wastewater entering the activated sludge basins. Often these wastewaters will be deficient in some cations and will contain an overabundance of others. An increase in monovalent ions has been observed to cause a deterioration in dewatering properties in activated sludge, whereas an increase in divalent ions has been shown to improve activated sludge dewatering properties (Higgins and Novak, 1997a, b). These observations were made for activated sludge flocs in laboratory and industrial systems. Higgins and Novak (1997b) evaluated the cations from seven industrial facilities and found that, when the monovalent to divalent cation ratio (M/D) on a charge

equivalent basis exceeded 2, deterioration in dewatering properties (specific resistance to filtration) occurred. The problems associated with a high M/D ratio were most often found in the industries that added caustic for pH control. Therefore, sodium ions were the prevalent monovalent ion input in these systems.

The purpose of this study was to evaluate the potential for identification of nonfilamentous settling and dewatering problems through screening of cations, to arrive at a strategy for laboratory or field trials, and to identify and address the associated problem(s).

The industrial system studied contained a high concentration of sodium ions (average of 2,000 mg/l) added as sodium hydroxide in the pretreatment step to prevent volatilization of acetic acid. The major component in the waste stream was acetic acid. The influent COD was in the order of 10,000 mg/l. The activated sludge had a pH of 8.8. The industrial wastewater treatment system was found to have extremely poor settling and dewatering properties due to a high concentration of sodium ions. Laboratory tests were initially conducted to evaluate a strategy for possible field application of divalent cations to achieve a lower M/D ratio, followed by field trials of weekly monitoring of activated sludge properties. Short and long term solutions were proposed.

Methods and Materials

Field Activated Sludge Samples

The industrial wastewater treatment plant consisted of an equalization basin, aeration basin and polishing ponds. The removal of most of the carbonaceous COD occurred in the aeration basin and nitrification occurred in the polishing ponds. Sludge samples were collected weekly from the industrial facility and analyzed for settling and dewatering properties in the laboratory using methods described below. The cations monitored were sodium, potassium, magnesium, calcium and ammonium ions. The field trial consisted of adding a dilute magnesium sulfate solution to the wastewater stream.

Laboratory Activated Sludge Samples

Four laboratory reactors were set up using activated sludge from the industrial facility. The wastewater was obtained from the facility in 55-gallon drums. The four reactors were fed wastewater augmented with calcium, magnesium, and a combination of calcium and magnesium. The fourth reactor was maintained as a control and fed unaltered wastewater.

Table 1-Influent cation concentration for laboratory reactors.

Industry	Sodium (meq/l)	Potassium (meq/l)	Magnesium (meq/l)	Calcium (meq/l)
Control	94	0.3	0.08	0.8
Ca & Mg	94	0.3	10	10
Ca	94	0.3	0.08	20
Mg	94	0.3	20	0.8

These reactors were completely mixed activated sludge reactors that were operated at a 20 day mean cell residence time and a 5 day hydraulic retention time. The laboratory system configuration is explained in Higgins and Novak (1997a). The influent COD was in the order of 10,000 mg/L containing mostly acetic acid as the organic substrate. Ammonia-N (500 mg/l) and phosphate-P (100 mg/l) were added as ammonium chloride and ammonium phosphate. The pH was not controlled. Temperature was maintained at 20° C. Since the influent did not contain any proteins, the solution proteins reflected products from metabolism or lysis. Calcium and magnesium were added as chloride salts. Non-steady state changes were monitored daily to observe variations in settling and dewatering properties and to obtain estimates of the time required to achieve these improvements.

Laboratory Steady State and Filamentous Organism Determination

Steady state for the laboratory reactors was determined as described by Higgins and Novak (1997a). Filamentous organisms in the laboratory reactors were quantified using the method of Jenkins *et al.* (1986), which rates the number of filamentous organisms on a scale of 0-6. A score of 0 corresponds to no filaments and a score of 6 corresponds to excessive filaments. The reactors were seeded with sludge with filament rated at 0. After one month of operation, there were no observable filaments in the reactor (rating 0). The feed lines and feed containers were bleached 3 times a week to prevent growth of *Sphaerotilus natans*.

Cation Analysis

Sodium, potassium, calcium, magnesium and ammonium ions were quantified using a Dionex Ion chromatograph with a CS12 column and conductivity detector (Dionex 2010I) with self regenerating suppression of the eluent. Methane sulfonic acid (20 mM) was used as the eluent at a flow rate of 1.0 ml/min. Table 2 presents the average soluble cations for the field activated sludge.

Table 2-Average soluble cation concentrations for industry.

Industry	Sodium (meq/l)	Potassium (meq/l)	Magnesium (meq/l)	Calcium (meq/l)	Ammonium-N (meq/l)
Field	94.22	0.16	0.99	0.27	6.12

Settling and Dewatering Properties

Mixed liquor suspended solids (MLSS) was analyzed using Method 2540D of APHA (1995). The settling property was measured using sludge volume index (SVI) as described in Method 2710D of APHA (1995). The dewatering property was measured using capillary suction time (CST) using Method 2710G of APHA (1995). Vacuum

filtered cake solids measurements were obtained using a Buchner funnel with a vacuum pressure of 38 cm mercury. Floc density measurements were determined using the isopycnic Percoll method described by Knocke *et al.* (1993).

Exocellular Protein Analysis

A 40 ml sample of biomass was centrifuged at 8,000 *g* for 15 minutes. The exocellular polymer in the centrate was removed and considered the soluble fraction.

Protein was measured using the Hartree (1972) modification of the Lowry *et al.* (1951) method. Protein standards were prepared using bovine serum albumin at respective pH of soluble and readily extractable bound fractions.

Results and Discussion

Laboratory Activated Sludge Characteristics

Reactor experiments were conducted in the laboratory for a period of 16 days. Measurements of settling and dewatering properties were initiated immediately after the reactors were setup. MLSS, pH, settling (SVI) and dewatering (CST) properties were monitored regularly to observe changes (Figure 1). A profile of settled volume versus time was also plotted to obtain settling trends beyond a half-hour for slowly settling sludges (Figure 2).

As can be seen in Figure 1, the pH remained fairly constant in the reactors (average pH of 8.3) although slightly lower than the pH of 8.8 at the wastewater treatment plant. The high pH in the reactors resulted in a precipitation of calcium. This phenomenon was characterized by the flocs appearing bleached and the formation of heavy white precipitates at the bottom of the reactor. The calcium precipitation also increased the MLSS of the calcium containing reactors in the final days of the data set. Otherwise, the MLSS remained fairly constant. Precipitates were not observed in the reactor altered with only magnesium ions.

The dewatering properties (CST) showed improvements almost immediately after the addition of divalent ions to the reactors (for the 3 augmented reactors). The improvements in dewatering properties occurred regardless of the divalent ions used.

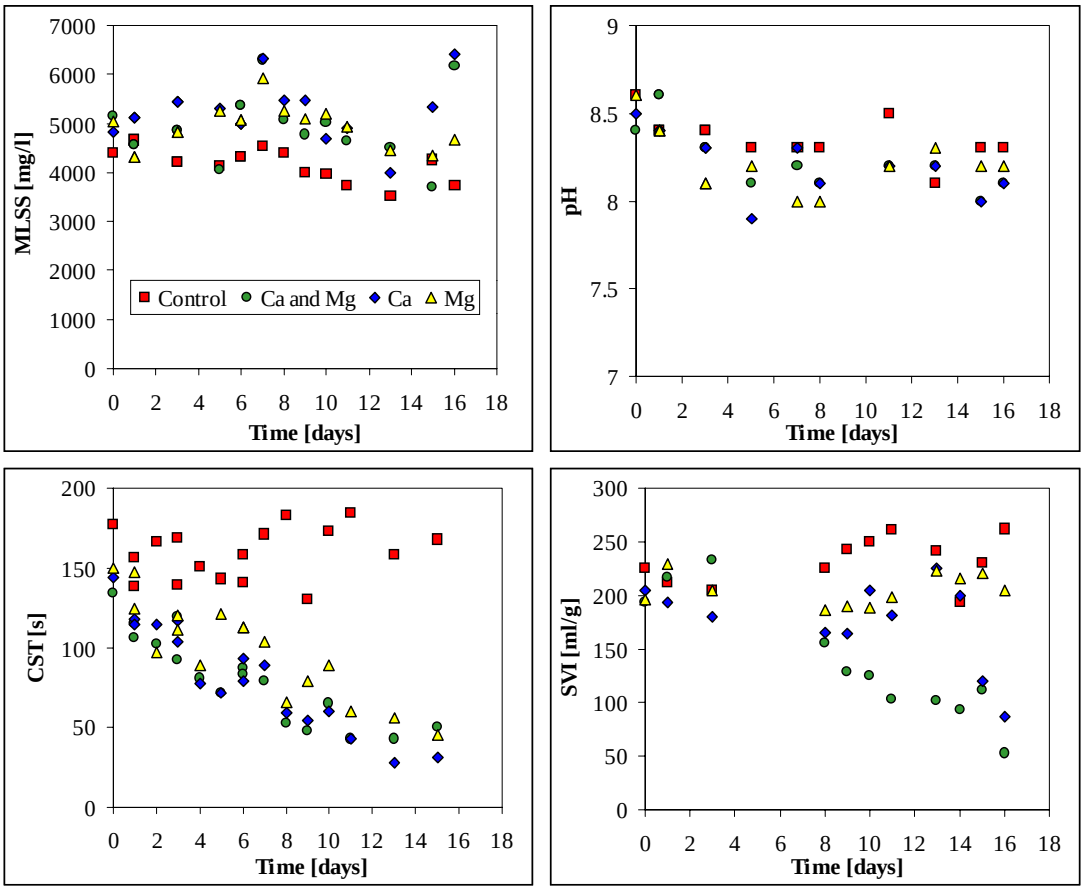

Figure 1-MLSS, pH, settling and dewatering properties for laboratory reactors.

On the other hand, settling properties did not improve until after a considerable time lag. The reactor containing both calcium and magnesium showed dramatic improvements in SVI after 9 days of operation and consistently maintained a SVI below 100 ml/g after 10 days of operation. The improvements in SVI for the 'calcium only' reactor occurred after 15 days of operation. The reactor experiment may have been curtailed too soon to show improvements in SVI (a larger time lag) for the 'magnesium only' reactor. The 'magnesium only' reactor showed improvements in settling properties (Figure 2) for two-hour settled volume (in 250 ml graduated cylinder) when compared

with the control. However, the calcium augmented reactors settled consistently better than the 'magnesium only' reactor.

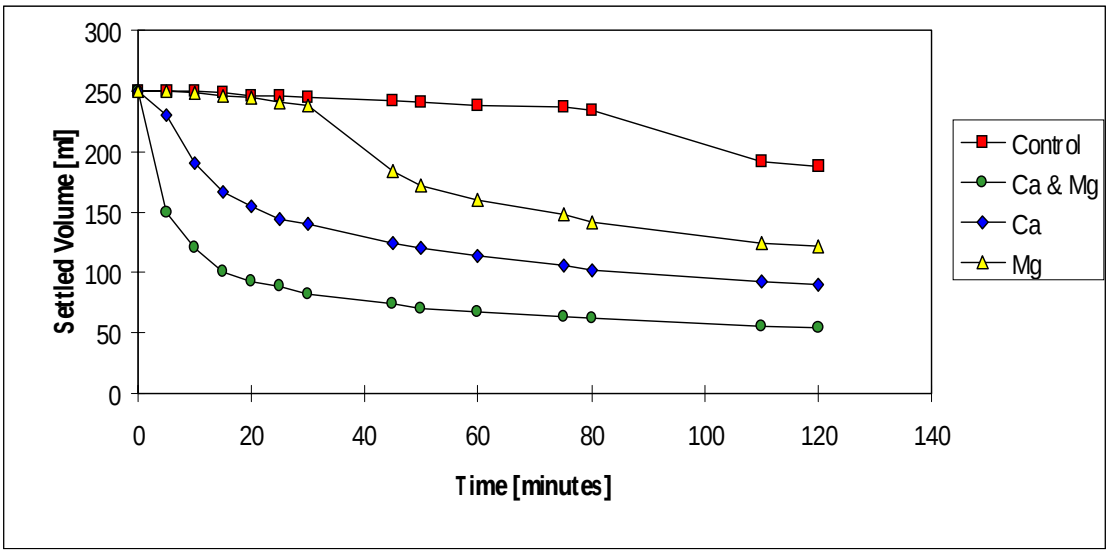

Figure 2-Profile of two-hour settled volumes for laboratory reactors (250 ml total volume).

The three divalent ion augmented reactors displayed considerable improvements in settling and dewatering properties compared to the control. The calcium fed reactor showed larger improvements in settling properties. However, it would be difficult to maintain the heavy calcium precipitates suspended in the aeration tank. Therefore, it was determined that addition of magnesium ions to the wastewater in the field trials would be appropriate. Field trials were initiated by adding magnesium sulfate solution to the feed of the industrial wastewater. The magnesium concentration in the feed was increased to 1 mM from an initial concentration of 0.04 mM.

Field Activated Sludge Characteristics

The soluble cation concentrations and activated sludge characteristics were monitored weekly after the application of magnesium sulfate (1 mM final feed concentration). The two-hour settled volume was collected daily by plant personnel. Figure 3 shows the improvements in the two-hour settled volume over the two months monitored. Large improvements were observed after 2 weeks of magnesium application.

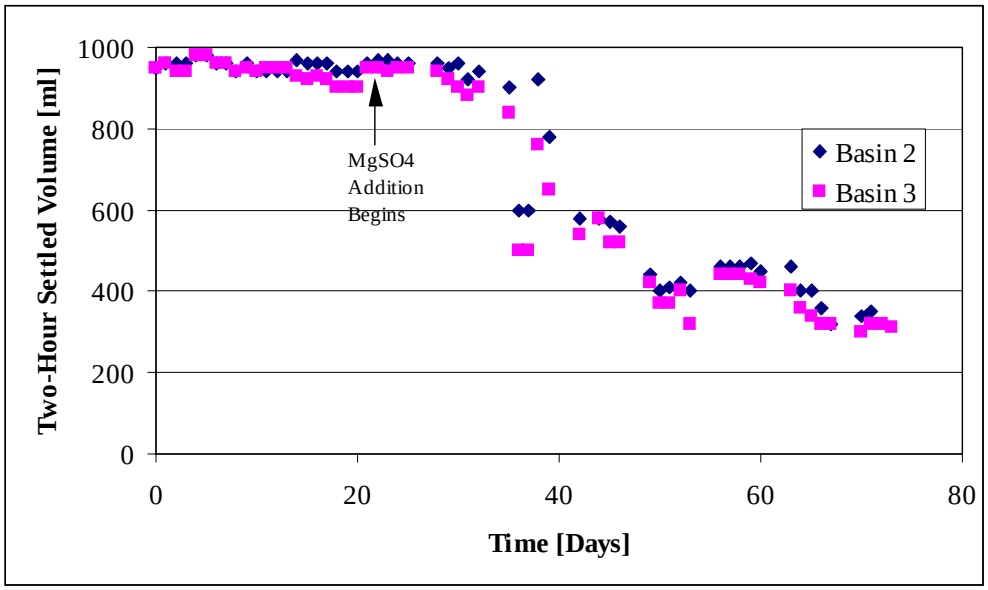

Figure 3-Effect of magnesium on two-hour settled volume during field trials.

Considerable improvements in floc density were observed with an increase in magnesium ions as shown in Figure 4. The increase in floc density suggests improved divalent bridging associated with an increase in magnesium ions.

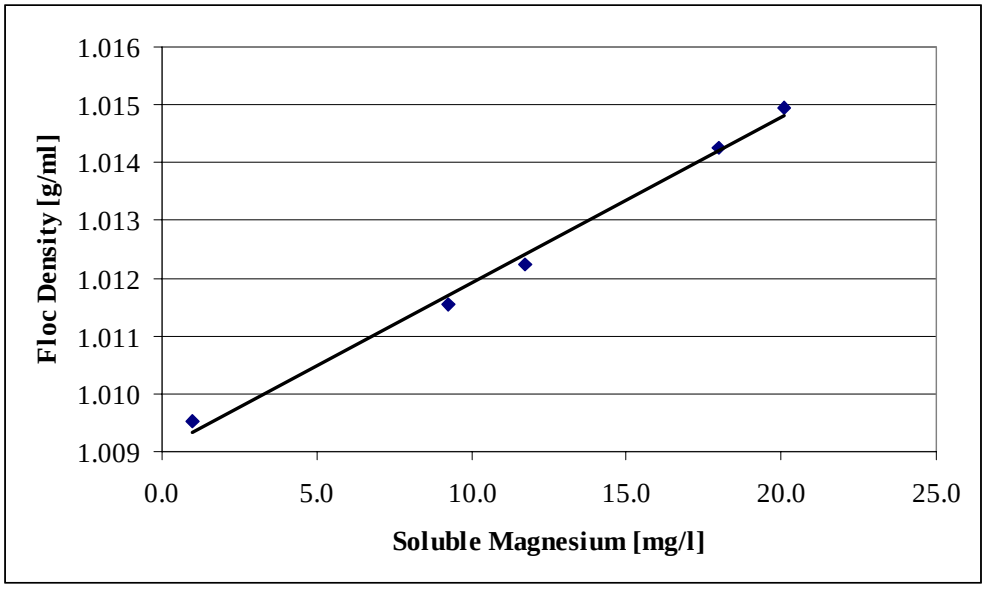

Figure 4-Effect of magnesium on floc density during field trials.

The improvements in floc density appeared to be the primary mode for improvements in settling properties for this plant. Plants reporting good settling properties have floc densities in the range of 1.025 – 1.035 g/ml range. An increase in floc density or floc particle size has been shown to be the primary means through which improvements in settling properties are achieved (Higgins and Novak 1997a and Murthy and Novak 1997). The increase in feed magnesium greatly improved the floc density, considerably ameliorating the poor settling property caused by the light and diffuse floc structure induced by sodium ions.

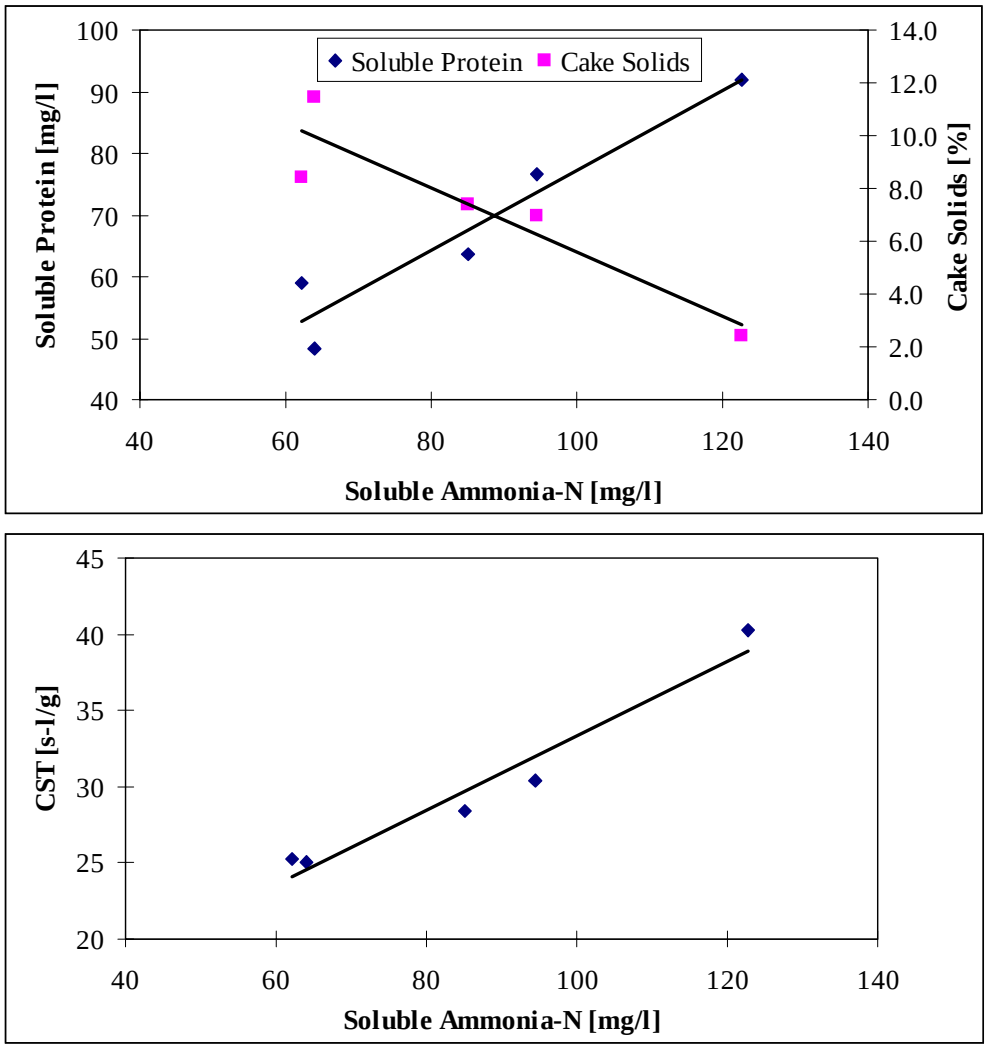

Figure 5-Effect of ammonium ions on dewatering properties.

Improvements in dewatering properties were not concurrent with the improvements in settling properties. Subsequent analysis of data revealed that the changes in the dewatering properties depended on the residual ammonium ions in the aeration basin (nitrification occurs in the subsequent polishing pond). Figure 5 shows the relationship between the soluble ammonium ions and the dewatering properties (vacuum filtered cake solids and CST). An increase in the soluble ammonium ions was related to a deterioration in vacuum filtered cake solids and CST. The deterioration in dewatering properties was associated with an increase in soluble proteins in the activated sludge.

Conclusions

Cations were directly related to changes in settling and dewatering properties. The laboratory study was an effective prelude to field trials. The laboratory treatability study indicated the unsuitability of calcium addition for the field trial. The laboratory research further showed that magnesium would be a suitable divalent cation alternative. Field trials demonstrated an improvement in floc density associated with an increase in magnesium ions. A time lag could be anticipated prior to achieving improvements in settling properties. Although cation exchange may take place, a complete replacement of sludge flocs may be required for the divalent ions to be completely incorporated into the sludge floc.

Magnesium ions improved dewatering properties in the laboratory study to a greater extent than demonstrated in the field trials, probably due to the higher concentration of the divalent ion used in the laboratory study. The field trials linked dewatering properties to an increase in the soluble ammonium ions. It appears that ammonium ions interact with activated sludge flocs in a manner similar to sodium ions, causing a release in soluble proteins and a deterioration in dewatering properties. Complex variations in several cations simultaneously may make it challenging to isolate the cause for changes in settling and dewatering properties. Interaction between different cations and the floc (cation incorporation into the floc) and amongst themselves (cation exchange) need to be taken into account when considering their influence on settling and

dewatering properties. The addition of magnesium sulfate proved to be extremely beneficial in improving settling properties. If further improvements are required, long term strategies are essential.

For the industrial facility, it may be useful to explore other alternatives for pH control. Achievement of nitrification in the aeration basin may further ameliorate activated sludge floc properties. The effect of nitrification on activated sludge properties require further exploration.

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CHAPTER 2

EFFECTS OF POTASSIUM ION ON SLUDGE SETTLING, DEWATERING AND EFFLUENT PROPERTIES

Sudhir N. Murthy and John T. Novak

Abstract

Potassium ions appear to play an important role in determining the nature of activated sludge flocs. Relative to sodium, the concentration of potassium ions in most industrial activated sludge is typically low. Laboratory and field studies were conducted to examine the influence of potassium on activated sludge properties. The concentration of potassium affected the concentration of readily extractable (slime) proteins in the floc and the proteins in the surrounding solution. In laboratory tests, an increase in this cation's concentration beyond nutrient requirements impeded sludge dewatering properties as measured by capillary suction time (CST) and specific resistance to filtration (SRF) and associated with an increase in soluble protein. An increase in effluent total organic carbon and effluent turbidity was observed at higher concentration of this ion. Conversely, an increase in concentration of potassium ion improved the settling properties of sludge with low equivalent monovalent to divalent cation ratio.

Keywords

Potassium, cation, activated sludge, settling, dewatering, exocellular polymer, protein, polysaccharide, bacteria, slime polymer.

Introduction

Activated sludge flocs usually consist of microbial aggregates, filamentous organisms, organic and inorganic particles and exocellular polymers. Solid-liquid separation of activated sludge in wastewater treatment systems is achieved primarily by the bioflocculation of microbes and other particulate matter. Bioflocculation is responsible for changes in supernatant turbidity and variations in settling and dewatering properties. The activated sludge flocs are held together to form a 3-dimensional matrix by means of exocellular polymers (biopolymers or extracellular polymers) and divalent cations (Tezuka, 1969; Novak and Haugan, 1981; Eriksson and Alm, 1991; Bruus *et al.*, 1992; Higgins and Novak, 1997a, b). Zita and Hermansson (1994) used potassium and calcium ions to show that flocculation depended on double layer theory rather than ion bridging mechanisms.

Bruus *et al.* (1992) and Higgins and Novak (1997b) have shown that excess monovalent cations can cause a deterioration in floc structure, an increase in polymer demand and a deterioration in settling properties. Higgins and Novak (1997b) evaluated the cations from seven industrial facilities and found that when the monovalent to divalent cation ratio (M/D) on a charge equivalent basis exceeded 2, deterioration in dewatering properties (specific resistance to filtration) occurred. The problems associated with high M/D were most often found in industries adding caustic for pH control. Therefore, sodium ions were the prevalent monovalent ion input in industrial systems. The M/D ratio established by Higgins and Novak (1997a, b) was essentially a comparison of sodium, calcium and magnesium ions. Many industrial processes operate at very low concentrations of potassium ion and often these ions are present in nutrient deficient concentrations. Five of the seven industrial and municipal processes evaluated by Higgins and Novak (1997b) were operated at potassium concentration of 0.25 meq/l (10 mg/l) or less. Novak *et al.* (1996) indicated that, for sludges containing a low concentration of potassium ion, addition of small concentration of this cation improved floc strength. Although under nutrient deficient conditions (usually less than 1% cellular biomass) a lack of potassium ions does not seem to impact treatment efficiency, it

appears that addition of small concentrations of potassium ions improves activated sludge settling and dewatering characteristics.

The purpose of this study was to evaluate the effect of potassium ion on activated sludge properties in industrial processes, and to evaluate any interrelationships found amongst potassium and other cations. Tests were conducted using 5 industrial activated sludges. None of these industries had a significant inflow of proteins into their activated sludge process. The effect of variation in potassium ions at one industry was explored in greater detail using laboratory reactors. Potassium ion concentrations were varied in the laboratory to obtain a wide concentration range.

Methods and Materials

Field Activated Sludge Samples

Sludge samples were collected from the industrial facilities and analyzed in the laboratory using methods described below.

Laboratory Activated Sludge Samples

Laboratory reactors were set up using activated sludge from an industrial facility (Industry A) to analyze the sludge at different potassium concentrations. These reactors were completely mixed activated sludge reactors that were operated at a 10 day mean cell residence time and a 2 day hydraulic retention time. The laboratory system configuration is explained in Higgins and Novak (1997a). The influent COD (simulated industrial) was maintained at 2000 mg/L using 84% acetic acid, 12% isopropyl alcohol and 3% acetone as COD. The influent was augmented with 1% Bactopeptone as COD to provide some additional nutrients. Proteins therefore made up only 1% as COD of the influent stream. The influent did not contain any sugars or polysaccharides. The solution and extracted proteins and polysaccharides therefore reflected products from metabolism or lysis. The dissolved oxygen was maintained between 3 and 5 mg/l. The influent pH was 4 for the laboratory feed system. Sodium was added as a sulfate salt, potassium and calcium were

added as chloride salts and magnesium was added as a mix of sulfate and chloride salts to mimic the conditions in the industrial facility.

Laboratory Steady State and Filamentous Organism Determination

Steady state for the laboratory reactors was determined as described by Higgins and Novak (1997a). Filamentous organisms in the laboratory reactors was quantified using the method of Jenkins *et al.* (1986), which rates the number of filamentous organisms on a scale of 0-6. A score of 0 corresponds to no filaments and a score of 6 corresponds to excessive filaments. The reactors were seeded with sludge with filament rated at 4. The filaments gradually disappeared with time. After one month of operation, there were no observable filaments in the reactor (rating 0). The feed lines and feed containers were bleached 3 times a week to prevent growth of *Sphaerotilus natans*.

Cation Analysis

Sodium, potassium, calcium, magnesium and ammonium ions were quantified using a Dionex Ion chromatograph with a CS12 column and conductivity detector (Dionex 2010I) with self regenerating suppression of the eluent. Methane sulfonic acid (20 mM) was used as the eluent at a flow rate of 1.0 ml/min. Table 1 presents the typical soluble cations for Industry A activated sludge and simulated cations for laboratory reactors.

Table 1-Typical soluble cation concentrations for Industry A laboratory and field study.

Industry A	Sodium (meq/l)	Potassium (meq/l)	Magnesium (meq/l)	Calcium (meq/l)
Field	5.2	0.28	71	7.0
Laboratory	4.4	0.06 – 26	41	5.0

Settling and Dewatering Properties

Total suspended solids (TSS) was analyzed using Method 2540D of APHA (1995). The settling property was measured using sludge volume index (SVI) as described in Method 2710D of APHA (1995). The dewatering property was measured using capillary suction time (CST) using Method 2710G of APHA (1995) and specific resistance to filtration (SRF) as described by Christensen and Dick (1985). Vacuum filtered cake solids measurements were obtained using a Buchner funnel with a vacuum pressure of 38 cm mercury. Floc density measurements were determined using the isopycnic Percoll method described by Knocke *et al.* (1993). A 12-channel HIAC PC-320 automatic particle size analyzer was used to measure floc particle size in the range of 5 – 300 μm. The size range is within the range indicated to represent most of the volume of activated sludge (Jorand *et al.*, 1995). The apparent mean particle diameter (d50 in μm) was calculated for sludge samples assuming spherical particles.

Exocellular Protein and Polysaccharide Extraction and Analysis

Exocellular polymer extractions were performed to yield a soluble and readily extractable bound fraction. A 40 ml. sample of biomass was centrifuged at 8,000 *g* for 15 minutes. The exocellular polymer in the centrate was removed and considered the soluble fraction. The solution was resuspended in 40 ml. of 10 mM NaCl and NaOH (pH 10.5) by mixing in a Waring blender for 3 s. The sample was mixed for 15 minutes and centrifuged at 8,000 g for 15 minutes. The resultant centrate was considered the readily extractable bound fraction. Frolund *et al.* (1996) have shown that base extraction of exocellular polymer yields less than half of that extracted using a strongly acidic cation exchange resin. Therefore, this method should be considered to extract the readily extractable bound exocellular (slime) polymer fraction. This readily extractable fraction is thought to reflect exocellular polymers that are subject to changes in binding strength which affects the wastewater cation content, the release of solution polymers, and the settling and dewatering properties of activated sludge.

Protein was measured using the Hartree (1972) modification of the Lowry *et al.* (1951) method. Polysaccharide was measured using the method of Dubois *et al.* (1956).

Protein standards were prepared using bovine serum albumin at respective pH of soluble and readily extractable bound fractions.

Results and Discussion

Industrial Activated Sludge Characteristics

It is difficult to compare the exocellular proteins, polysaccharides and other properties across several sludges and obtain useful correlations (Urbain *et al.*,1993). However, it is beneficial to perform this exercise to distinguish some factors that may be universal to activated sludges. Higgins and Novak (1997b), for example, discerned that a minimum M/D ratio existed for optimal dewatering.

Industrial activated sludge cations, exocellular polymer, CST and floc density are presented in Table 2. Coefficients of correlation were calculated for these samples and a minimum absolute value of 0.70 was selected to demonstrate trends. The industries were chosen such that together they comprised a wide concentration range of the selected cations. Multiple samples (n) were collected (weekly, over a period of several months for some sludges) to obtain averages for the industrial sludges. As can be seen, several processes contain potassium at concentrations less than 0.25 meq/l. On the other hand, Industry D contained a high concentration of potassium ions.

It can be seen from Table 2 that an increase in potassium was correlated with an increase in soluble protein in the activated sludge. It is also seen that an increase in soluble polymers is associated with deterioration in dewatering properties (increase in CST). Novak *et al.*(1977) demonstrated that a deterioration in dewatering properties occurred with an increase in natural polymers. Novak and Haugan (1980) determined a minimum cationic polymer conditioning demand in the supernatant liquor associated with free soluble exocellular polymers. An increase in polymer conditioning demand was seen at higher concentrations of potassium (data not shown). Higgins and Novak (1997a) have associated the increase in slime protein with improvements in settling properties. Potassium was the only ion that was positively correlated with slime protein and polysaccharide.

Table 2-Linear coefficients of correlation for activated sludge from 5 industries. (Coefficients of correlation > |±0.70|)

Industry	n	Na	K	Mg	Ca	Soluble Protein	Soluble Polysaccharide	Slime Protein	Slime Polysaccharide	CST	Floc Density
		meq/l	meq/l	meq/l	meq/l	mg/l	mg/l	mg/l	mg/l	s	g/ml
A	10	5.2	0.28	71	7.0	19	16	47	19	64	1.0315
B	5	94	0.16	0.99	0.27	68	62	47	9.1	123	1.0125
C	6	9.1	0.08	3.5	7.1	21	6.5	24	5.8	25	1.0303
D	3	15	66	42	2.2	190	59	66	32	107	1.0163
E	1	9.9	0.16	0.48	1.6	6.3	26	49	12	30	1.0210
Na		1.00									
K			1.00								
Mg				1.00							
Ca					1.00						
Sol. Protein			0.95			1.00					
Sol. Polysaccharide					-0.84	0.75	1.00				
Sl. Protein			0.73			0.73	0.73	1.00			
Sl. Polysaccharide			0.89			0.80		0.86	1.00		
CST		0.71				0.70	0.91			1.00	
Floc Density		-0.71			0.96		-0.94			-0.74	1.00

Correspondingly, for the data set shown in Table 2, sodium ions were not positively correlated with slime and soluble polymers, although this cation was associated with a deterioration in dewatering property (CST) and negatively correlated with floc density. Calcium ions was positively correlated with floc density as previously shown by Higgins and Novak (1997a, b), and negatively correlated with soluble polysaccharides. Interestingly slime protein and slime polysaccharides were positively correlated indicating that their binding and release mechanisms may be similar.

Activated sludge characteristics for Industry A (field and laboratory tests)

It is observed in data for Industry A that, at lower concentrations of potassium, an improvement in floc density was observed with increase in potassium ion (Figure 1). Simulated laboratory tests (Figure 3) for this industry indicated that the improvement in floc density was optimal at the higher potassium concentration range investigated for Industry A. Slime protein was observed to increase with potassium ions (Figure 2). A corresponding increase in slime protein was not observed for other ions.

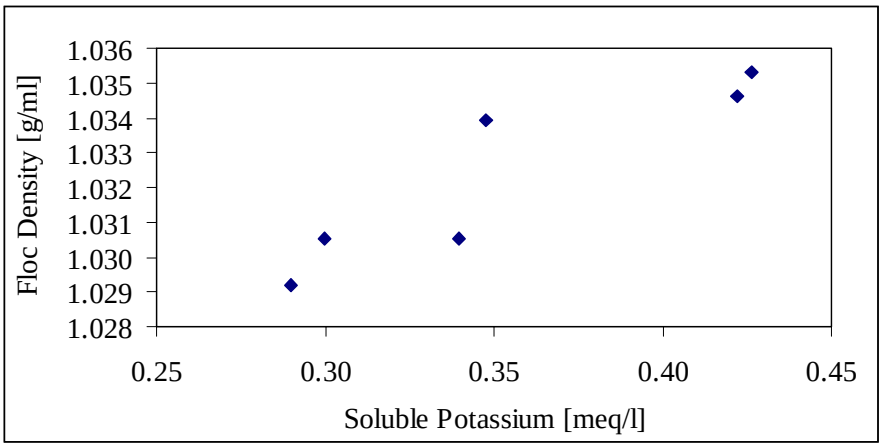

Figure 1-Effect of soluble potassium on floc density (Industry A).

The effect of potassium on activated sludge properties was further investigated in laboratory tests using simulated wastewater of Industry A. As can be seen in Figure 3, the dewatering properties and effluent turbidity were optimal for potassium ions in the range of 0.25-0.5 meq/l. The dewatering property (CST) deteriorated beyond this concentration range, associated with an increase in soluble protein. Other properties seen to deteriorate included specific resistance to filtration and vacuum filtered cake solids (data not shown). Novak *et al.*(1996) have indicated a deterioration in effluent total suspended solids with an increase in potassium. The increase in effluent turbidity is similar to the trend they observed.

Activated sludge settling property did not deteriorate with corresponding increase in potassium (Figure 3). The settling property (SVI) was seen to improve, associated with an increase in slime protein. The improvement in the settling property corresponded with an increase in the apparent mean particle diameter (d50 in μm) of activated sludge. The increase in potassium ions resulted in a concomitant increase in slime and soluble protein as predicted in Table 1.

Effluent total organic carbon (TOC) was seen to deteriorate with an increase in potassium, indicating deterioration in effluent characteristics as a result of increase in solution polymers. Further correlations between released solution polymers and effluent COD need to be performed to verify the effect of changes in solution polymers on effluent characteristics, especially during changes in monovalent and divalent cation concentration.

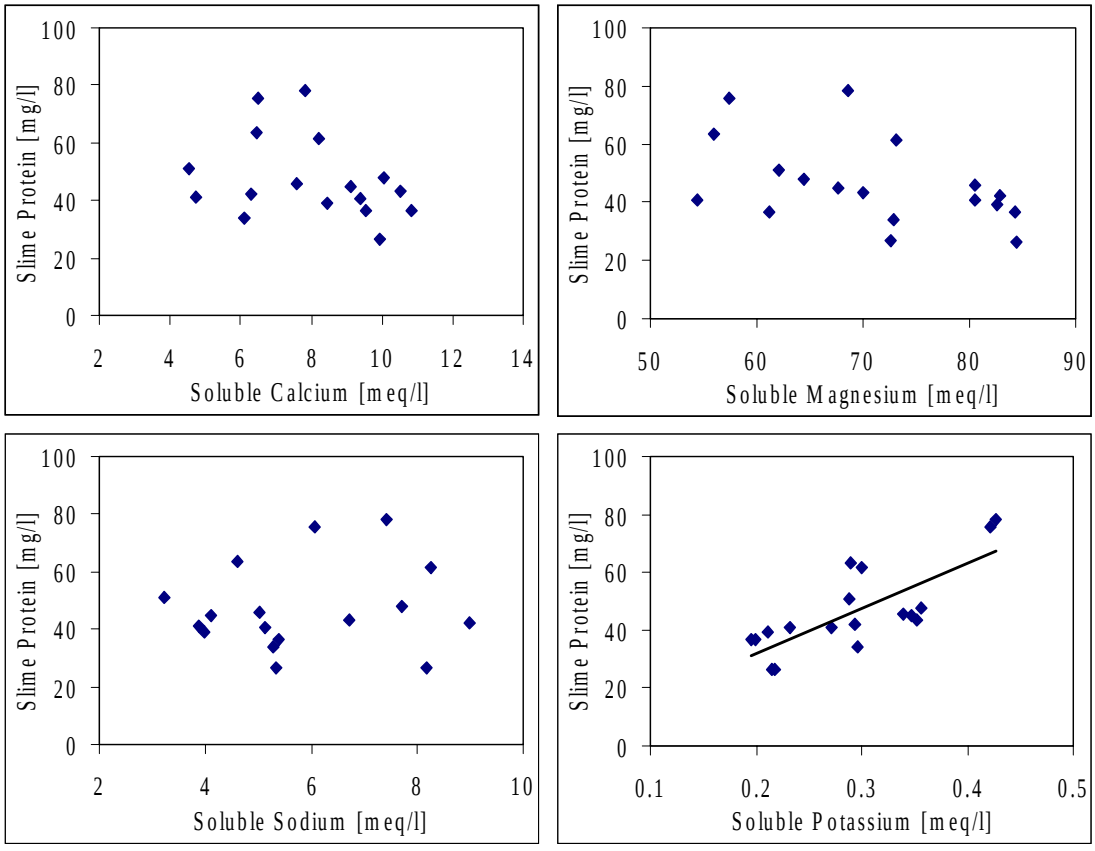

Figure 2-Effect of cations on slime protein in activated sludge from Industry A.

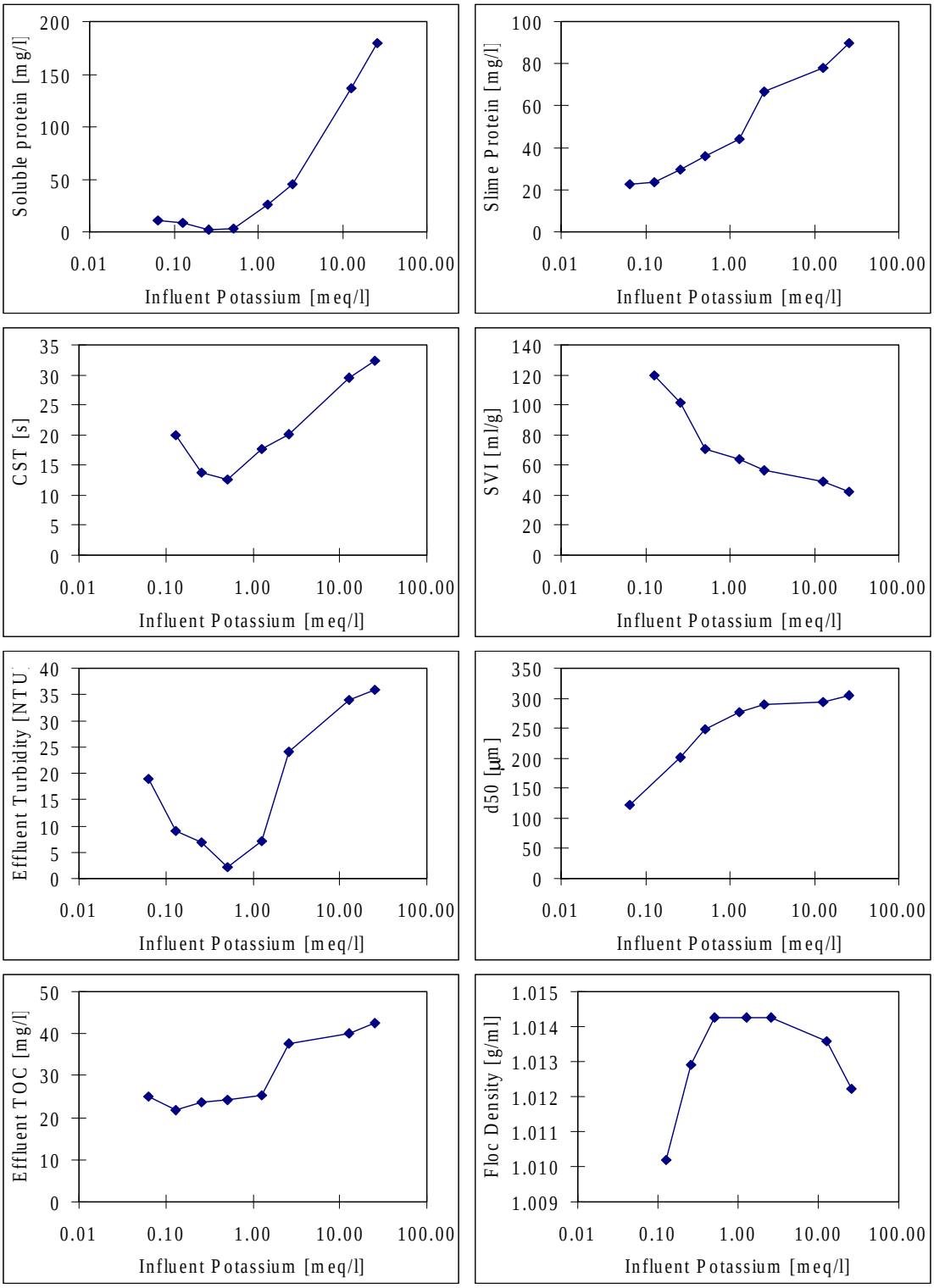

Figure 3-Effect of potassium on activated sludge properties for a laboratory simulated industrial wastewater treatment system (Industry A).

Following the study conducted by Novak *et al.*(1996) it was anticipated that potassium would not physico-chemically interact with activated sludge flocs in the same manner as sodium. High potassium sludges displayed higher floc strength characteristics while high sodium sludges did not. The interaction of potassium (unlike sodium) with activated sludge flocs is not completely explained by simple charge competition (M/D ratio) in the divalent charge bridging model. In general, excess sodium (as reported by Higgins and Novak (1997a)) always produced poorly settling sludges, poor dewatering and weak flocs. Excess potassium produced poor dewatering but flocs that were resistant to shear (Novak *et al.*, 1996) and settled well.

Conclusions

The effect of potassium on activated sludge properties of industrial systems was investigated. A detailed field and laboratory study of one such system was further researched. Potassium appears to strongly influence the settling and dewatering properties of activated sludge systems. An optimal potassium concentration exists (0.25–0.50 meq/l) to achieve optimal dewatering properties and to minimize supernatant turbidity. The concentration of potassium required is not excessive. It appears that concentrations approaching nutrient requirements (1% of cellular biomass) are sufficient. An excess of potassium (greater than 2 meq/l) is detrimental to the activated sludge process, as it is associated with poor dewatering properties and effluent quality. The effect the ion has on improvements in settling property and floc strength needs further investigation, as it is anomalous to the trend that would be explained by the divalent charge bridging theory and as expressed by sodium ion.

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CHAPTER 3

INFLUENCE OF CATIONS ON ACTIVATED SLUDGE EFFLUENT QUALITY

Sudhir N. Murthy and John T. Novak

Abstract

Laboratory and field studies were conducted to investigate the influence of cations on activated sludge effluent quality. Initial investigations of industrial wastewater activated sludges indicated that cations may be important in determining the effluent quality. Laboratory experiments were conducted with variations in calcium, magnesium and potassium ion concentration. From these experiments it was found that the concentration of biopolymers (protein and polysaccharide) that end up in solution depends on the concentration of monovalent and divalent ions in the influent wastewater. It appears that the divalent cation charge bridging mechanism said to be involved in bioflocculation affects effluent quality. Monovalent ions tend to increase the concentration of solution biopolymers, whereas divalent cations tend to retain the biopolymers in the floc. Polysaccharides are released to a greater extent than proteins. The biopolymers in solution affect effluent chemical oxygen demand (COD). The laboratory study was followed up by a field verification study for a municipal activated sludge. In the field study, it was found that sodium ions in the influent wastewater relative to the divalent ions may have been responsible for an increase in release of proteins and polysaccharides to the solution thereby increasing the effluent COD of the treated wastewater. It appears that a large fraction of the effluent COD may be microbial product rather than residual influent wastewater organic substrate at the sludge ages

commonly used for the activated sludge process. The fraction of what appears to be microbially derived organic compounds depends on the monovalent and divalent cation concentration in solution.

Keywords

Cation, activated sludge, effluent, COD, protein, polysaccharide, uronic acid, biopolymer, soluble microbial product.

Introduction

Activated sludge is comprised of flocs that contain microorganisms, debris, exocellular polymers and inorganic cations (Tezuka, 1969; Novak and Haugan, 1981; Eriksson and Alm, 1991; Bruus *et al.*, 1992; Higgins and Novak, 1997a, b). These researchers have suggested that cations interact with the negatively charged biopolymers (mostly proteins and polysaccharide) in activated sludge to change the structure of the floc. Through these studies, it has been observed that monovalent cations tend to cause deterioration in settling and dewatering characteristics whereas divalent cations tend to improve settling and dewatering characteristics.

Models (Tezuka, 1969; Novak and Haugan, 1978; Bruus *et al.*, 1992; Higgins and Novak 1997a) suggest that divalent cations participate in charge bridging of negatively charged sites on the biopolymers. The charge bridging between the biopolymers promote an increase in floc size and floc density and increase the floc resistance to shear. Monovalent cations reduce the strength of the bonds and this leads to a loose structure, often decreasing floc size and floc density and decreasing the floc resistance to shear (Higgins and Novak, 1997a).

Higgins and Novak (1997a) have shown that an increase in calcium and magnesium improves settling properties, while an increase in sodium results in deterioration of settling and dewatering properties. Improvements in settling properties

have since been demonstrated in field trials where calcium or magnesium ions were added to improve biosolids properties. The improvements in settling and dewatering properties were obtained more through the addition of divalent cations to the feed rather than superficial additions to the activated sludge. The incorporation of cations during the floc formation process was therefore important.

These studies have concentrated on improvements in bioflocculation brought about by divalent cations that lead to enhanced settling and dewatering properties. The impact that salts may have on activated sludge effluent quality has not been well characterized. When bioflocculation of activated sludge is negatively affected, the binding of exocellular polymer within flocs is poor. Under these conditions, it can be expected that effluent suspended solids and chemical oxygen demand (COD) may increase due to release of microorganisms and biopolymer into solution. This increase in COD can be expected even in activated sludge effluent samples that pass through a 0.45 μ filter commonly used to measure soluble effluent COD. Divalent cations foster improvements in bioflocculation. The addition of divalent cations to poorly flocculating sludge may therefore result in improvements to effluent turbidity and soluble effluent COD.

Background

Murthy and Novak (1998) have shown that an increase in potassium ions, while not necessarily causing a deterioration in biosolids settling properties, results in poorer dewatering properties and a deterioration in effluent quality. This deterioration in effluent properties was observed by measuring an increase in dissolved effluent total organic carbon and supernatant turbidity. The deterioration in effluent quality was also accompanied by an increase in soluble proteins. The authors also evaluated the solution protein and solution polysaccharide from 5 industries. The industries were selected because they contained a variety of influent cation concentrations. It was found that a high concentration of sodium or potassium led to greater concentration of solution protein and polysaccharide. On the other hand, a lower concentration of monovalent cations resulted in a smaller concentration of these biopolymers in solution (Table 1).

Table 1–Effect of cations on solution protein and polysaccharide.

Industry	Sodium (meq/L)	Potassium (meq/L)	Magnesium (meq/L)	Calcium (meq/L)	Solution Protein (mg/L)	Solution Polysaccharide (mg/L)
A	5.2	0.3	71	7.0	19	16
B	94	0.2	1.0	0.3	68	62
C	9.9	0.2	0.5	1.6	6.3	26
D	9.1	0.1	3.5	7.1	21	6.5
E	15	66	42	2.2	187	59

It is hypothesized that low concentrations of divalent ions or high concentrations of monovalent ions, in activated sludge plants, will result in poorer attachment of negatively charged biopolymers. This poor attachment will result in a release of biopolymers. Since these biopolymers are composed of proteins and polysaccharide molecules, an increase in solution proteins and polysaccharides will be observed in activated sludge effluents.

The objective of this study was to investigate the attachment or release of biopolymers resulting from changes in the calcium, magnesium and potassium ions in activated sludge. The overall goal was to determine if effluent quality could be significantly impacted by changes in cations, and, if these changes were observed, to show that they were related to variations in biopolymer binding. The laboratory study was followed up with field analysis of effluent from a municipal wastewater treatment facility with an activated sludge system.

Methods and Materials

Experiments were conducted with 10-L laboratory reactors that were seeded with activated sludge from a municipal wastewater treatment facility. Twelve reactor sets were operated with varying calcium and magnesium or potassium ions. The reactors were completely mixed activated sludge systems with 10-day mean cell residence time and 2-day hydraulic retention time. These reactors were operated for greater than two sludge ages prior to sample analysis. Each reactor set was started using fresh municipal activated sludge. The laboratory system configuration is described by Higgins and Novak (1997a).

The influent COD was maintained at 800 mg/l using 400 mg/L acetate and 400 mg/L Bactopeptone (protein source), expressed as COD. The influent did not contain any sugars or polysaccharides. The dissolved oxygen was maintained at approximately 7 mg/L using compressed air fed through diffuser stones. Magnesium and sodium were added as sulfate salts and calcium and potassium were added as chloride salts. Ammonium phosphate was added to provide additional nitrogen and phosphorous.

Floc properties measured included floc density, polymer conditioning requirements, soluble cations, soluble COD, soluble proteins, polysaccharides and uronic acid. Acetate was measured to monitor for residual substrate.

Analysis of protein, polysaccharide, COD and cations were performed for a municipal wastewater treatment plant (Radford, Virginia). The cations at Radford were variable due to an industrial input into the plant. The industrial wastewater was high in sodium ions resulting in a variable monovalent cation concentration.

Sample Preparation

Samples were taken from the effluent of laboratory reactors and filtered through a 0.45 μ filter. The samples were analyzed for cations, anions, protein, polysaccharide, uronic acid, COD and acetate.

Cation Analysis

Sodium, potassium, calcium, magnesium and ammonium ions were quantified using a Dionex Ion chromatograph with a CS12 column and conductivity detector (Dionex 2010I) with self-regenerating suppression of the eluent (Table 2).

Table 2–Influent cations for the laboratory reactors.

Reactor	Sodium (mM)	Potassium (mM)	Magnesium (mM)	Calcium (mM)
1	3.0	0.1	2.3	2.6
2	3.0	0.3	2.3	2.6
3	3.0	0.6	2.3	2.6
4	3.0	2.5	2.3	2.6
5	3.0	0.1	1.2	1.3
6	3.0	0.3	1.2	1.3
7	3.0	0.6	1.2	1.3
8	3.0	2.5	1.2	1.3
9	3.0	0.1	0.4	0.4
10	3.0	0.3	0.4	0.4
11	3.0	0.6	0.4	0.4
12	3.0	2.5	0.4	0.4

COD and Solids Analysis

Soluble COD was analyzed using Method 5220C of *Standard Methods* (1995). Mixed liquor suspended solids (MLSS) was analyzed using Method 2540D of *Standard Methods* (1995). Supernatant turbidity was measured using Method 2130B of *Standard Methods* (1995).

Acetate Analysis

Residual acetate was measured on a Hewlett-Packard 5880 gas chromatograph fitted with a flame ionization detector.

Solution Protein, Polysaccharide and Uronic Acid Analysis

Solution proteins and polysaccharides samples were measured using the Hartree (1972) modification of the Lowry *et al.* (1951) method. Polysaccharides were measured using the method of Dubois *et al.* (1956). Protein standards were prepared with bovine serum albumin, and polysaccharide standards were prepared with glucose. Uronic acid was measured using the Kintner and Van Buren (1982) modification of the Blumenkrantz and Asboe-Hansen (1973) method.

Coagulation Study

Coagulation tests were performed using 0.45 μ filtered effluent from the laboratory reactor. The jar test was performed using six square-shaped jars individually stirred by a common motor. The test was conducted using ferric chloride at 0, 10, 20, 100, 200 and 400 mg/L simultaneously added to 500 mL filtered effluent. Alkalinity was provided using sodium bicarbonate (500 mg/L) to maintain pH greater than 6. The effluent was rapid-mixed for 1 minute at 100 rpm, followed by 30 minutes flocculation at 30 rpm. The solution was allowed to settle for one hour, after which turbidity, protein, polysaccharide and COD were measured for the supernatant.

Polymer Conditioning

Polymer conditioning tests were performed using low molecular weight cationic polymer at 0.05% stock concentration. Optimum polymer dose was measured using the CST device. The optimum polymer dose reflects conditioning at minimal shear conditions. The optimum conditioning dose will be higher and can be appropriately calibrated based on the shear in the dewatering device.

Results and Discussion

Improvements in bioflocculation were observed through an increase in calcium and magnesium ion. Microscopic observations of the flocs showed tightly packed flocs for higher calcium and magnesium ions in the feed. Polymer conditioning demand increased with an increase in potassium and a decrease in calcium and magnesium (data not shown). An increase in polymer conditioning demand implies a higher number of negative charged sites available in the floc and an increase in negative biocolloids in solution. These two sets of observations indicate that the floc structure under higher divalent cation and lower potassium ion was dense with lower number of sites for biopolymer release. For lower divalent cation and higher potassium ion, the flocs appear to be loosely bound with some biocolloids in solution. The effects of cations on floc structure were primarily observed through changes in floc density and cationic polymer conditioning demand. Higher soluble effluent COD should result from the higher anionic biocolloids and poorer floc structure.

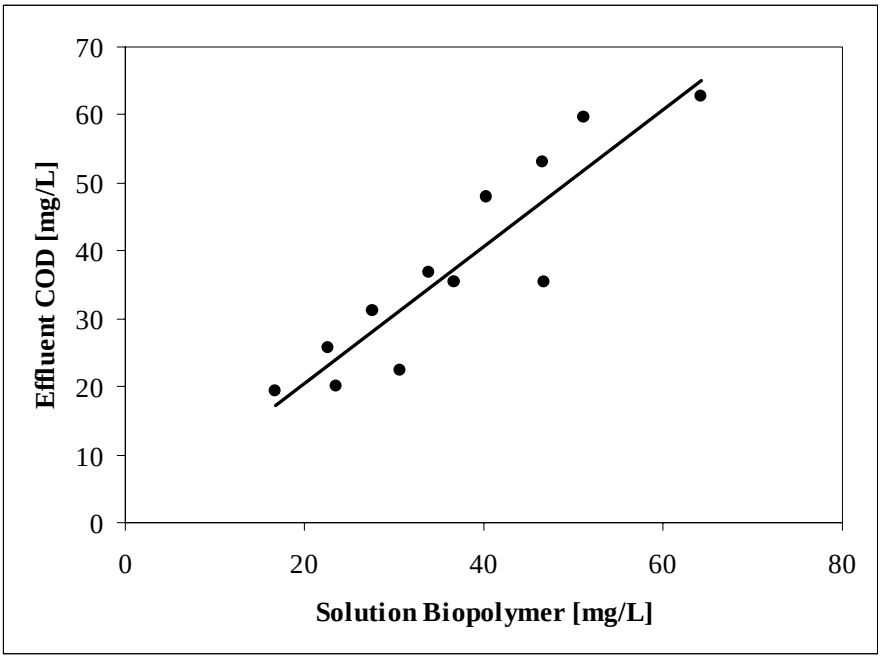

Figure 1-Effect of solution protein and solution polysaccharide on effluent COD.

Protein and polysaccharide were measured to evaluate soluble effluent quality. Uronic acid was analyzed to estimate the negative-charge fraction in the polysaccharide. The effluent was tested for COD to determine effects of cations on this parameter. An increase in COD was directly related to an increase in the sum of solution protein and polysaccharide (Figure 1). The y-intercept for this figure was nearly zero, indicating that the effluent COD mostly represented these compounds in the laboratory study.

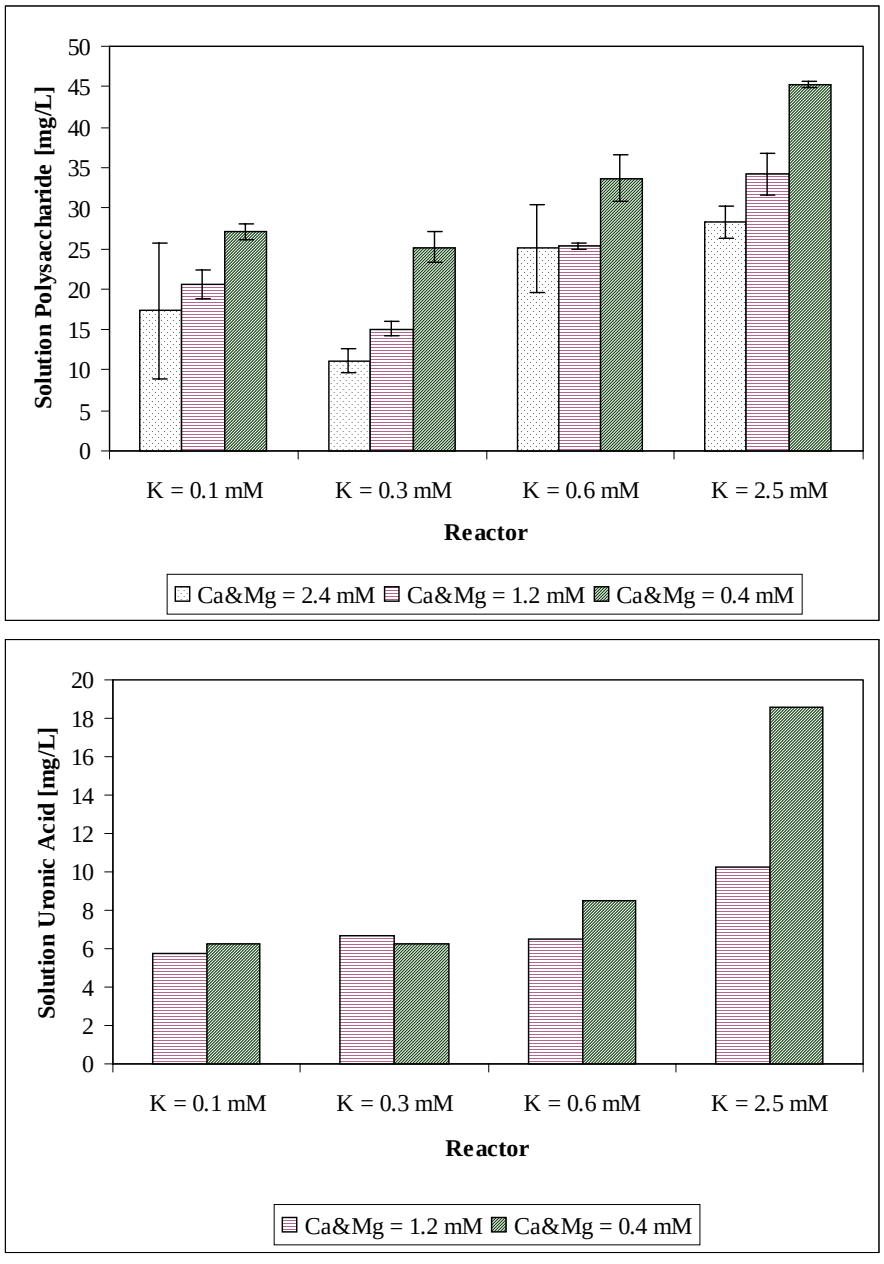

Figure 2-Effect of cations on solution polysaccharide and uronic acid.

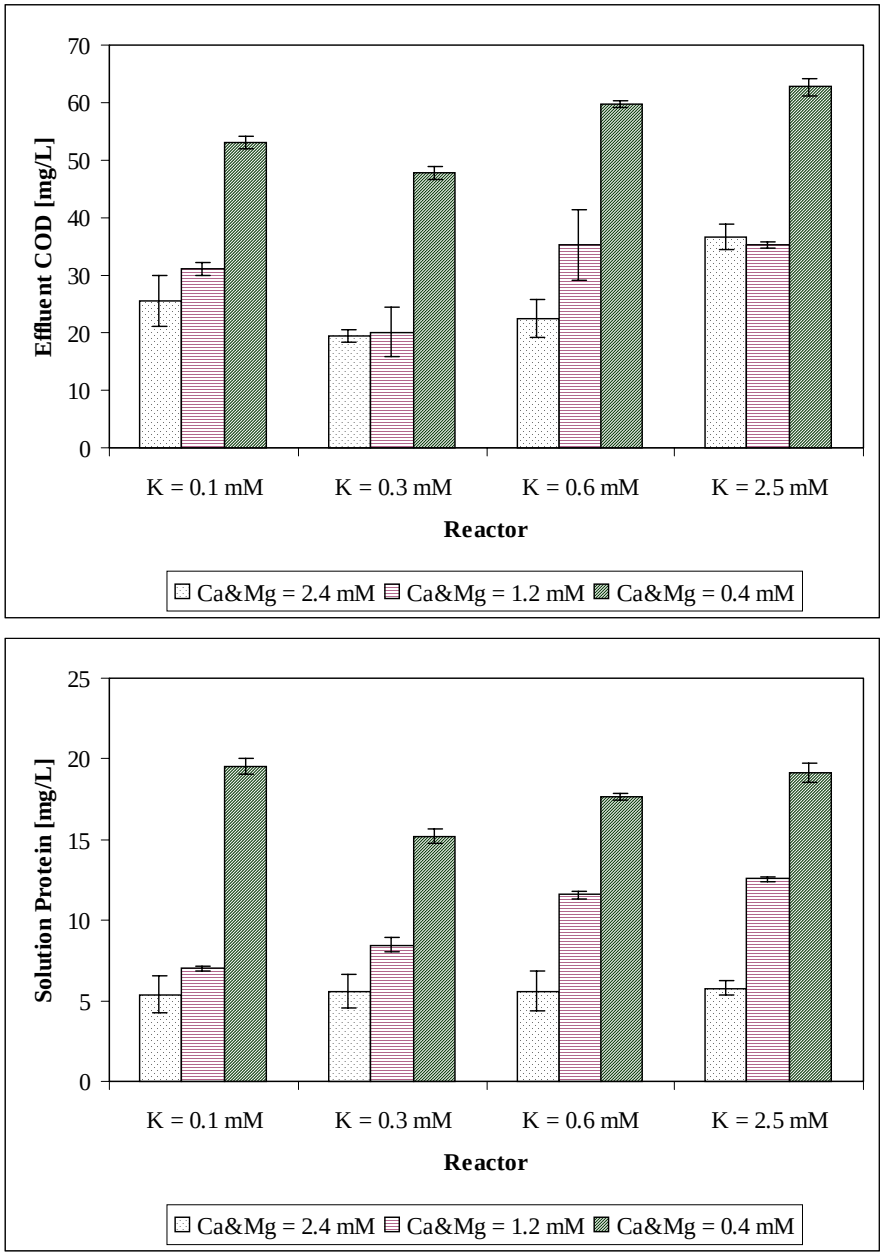

Figure 3-Effect of cations on solution protein and effluent COD.

At an average calcium and magnesium concentration of 2.4 mM the polysaccharide concentration was the lowest (Figure 2). An increase in solution polysaccharide was observed beyond a potassium concentration of 0.3 mM. The release of solution polysaccharide increased with a decrease in calcium and magnesium or an increase in potassium. At the highest potassium ion concentration, the polysaccharide

released was between 3 – 4 higher than the lower potassium ion concentrations. The addition of divalent cations reduced the amount of polysaccharide released to the solution. The effects of cation on the uronic acid component of polysaccharide is shown in the same figure. The greatest release of uronic acid occurred at the highest potassium ion concentration. The amount of uronic acid released decreased at higher calcium and magnesium ion concentrations.

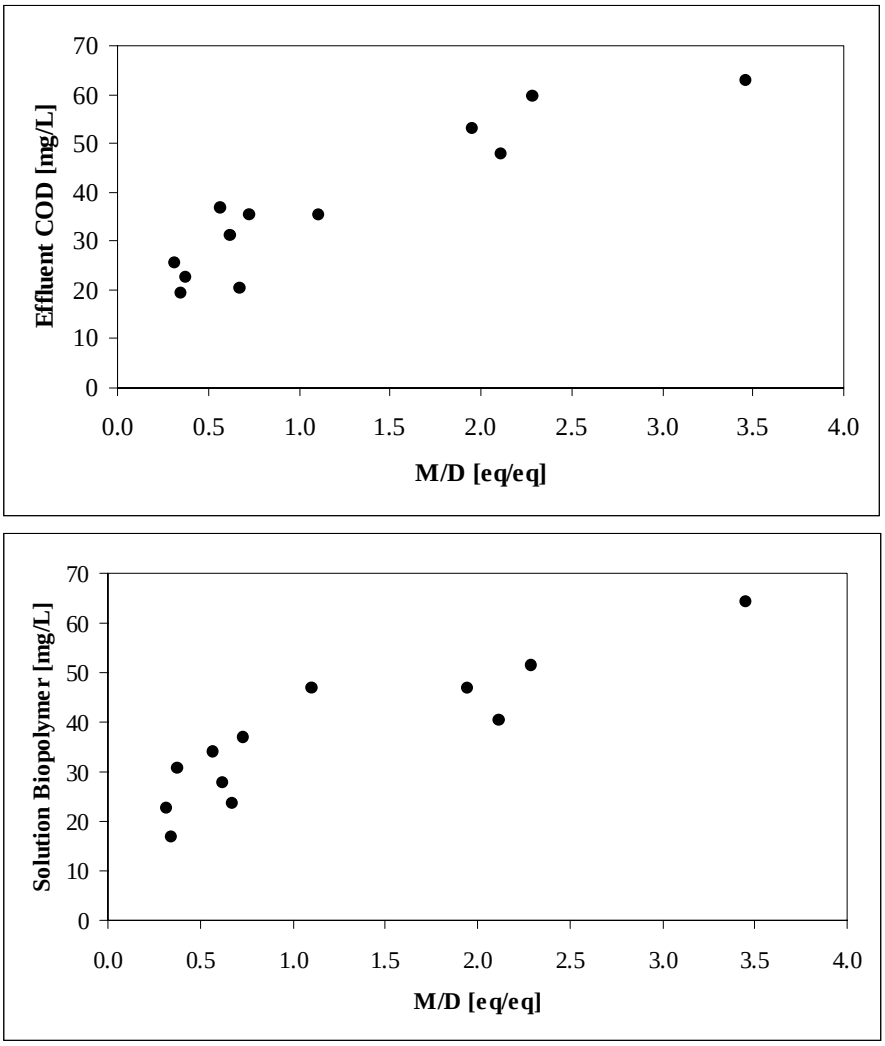

Figure 4-Effect of M/D on solution biopolymer and effluent COD.

The proteins in solution were particularly affected by the amount of calcium and magnesium ions in the influent, with higher solution protein at lower concentrations of the divalent cations (Figure 3). Potassium ions had very little effect at the highest

divalent cation concentration used. The effect of the cations on effluent COD is shown in the same figure. Higher effluent COD was observed at higher potassium ion concentration and lower calcium and magnesium ion concentration.

Effluent COD and solution biopolymer (sum of protein and polysaccharide) were plotted against M/D (Figure 4). As can be seen in this figure, the solution biopolymer and effluent COD were greater at higher M/D, especially for M/D greater than 2. From the laboratory study it appears that cations may indeed affect effluent characteristics. No detectable acetate was found in the effluent (greater than 1 mg/L as COD) suggesting that the effluent COD is mostly representative of organic products from the activated sludge biomass themselves.

Coagulation studies were performed for the solution protein and polysaccharide obtained from the effluent of laboratory reactors to evaluate the interactions between oxidized iron and the biopolymers (Figure 5). Other studies conducted in this laboratory have indicated that iron may play an important role in retaining the protein and polysaccharide within the activated sludge floc during digestion. As can be seen in the figure, ferric chloride was capable of removing most of the solution protein and some of the solution polysaccharide. The removal of the biopolymers was associated with a removal of soluble COD and supernatant turbidity. It appears that iron minerals may play an important role in maintaining floc structure and retaining proteins within the floc and reducing effluent COD. Oxidized iron was less capable of removing polysaccharides as compared to proteins. These observations are consistent with other coagulation studies conducted in this laboratory. Municipal plants can have considerable concentration of iron in the floc as compared with industrial processes. Industrial processes that are often deficient in iron have been observed to release more protein and polysaccharide than municipal facilities with similar M/D. The use of iron in conjunction with divalent cations may be important in maintaining good effluent quality at industrial plants.

Full-scale analysis of effluent from a municipal wastewater treatment plant (Radford, Virginia) was conducted to evaluate the effect of cations on activated sludge effluent quality. Radford wastewater contained a highly variable sodium ion concentration due to a high sodium ion intermittent industrial wastewater input to the plant. The samples were collected from a sampling tap after dechlorination of the treated

effluent, just prior to discharge. It was observed that an increase in M/D at Radford led to an increase in protein, polysaccharide and COD biopolymers (Figure 6). The increase in protein, polysaccharide and COD occurred especially for unfiltered samples of the effluent.

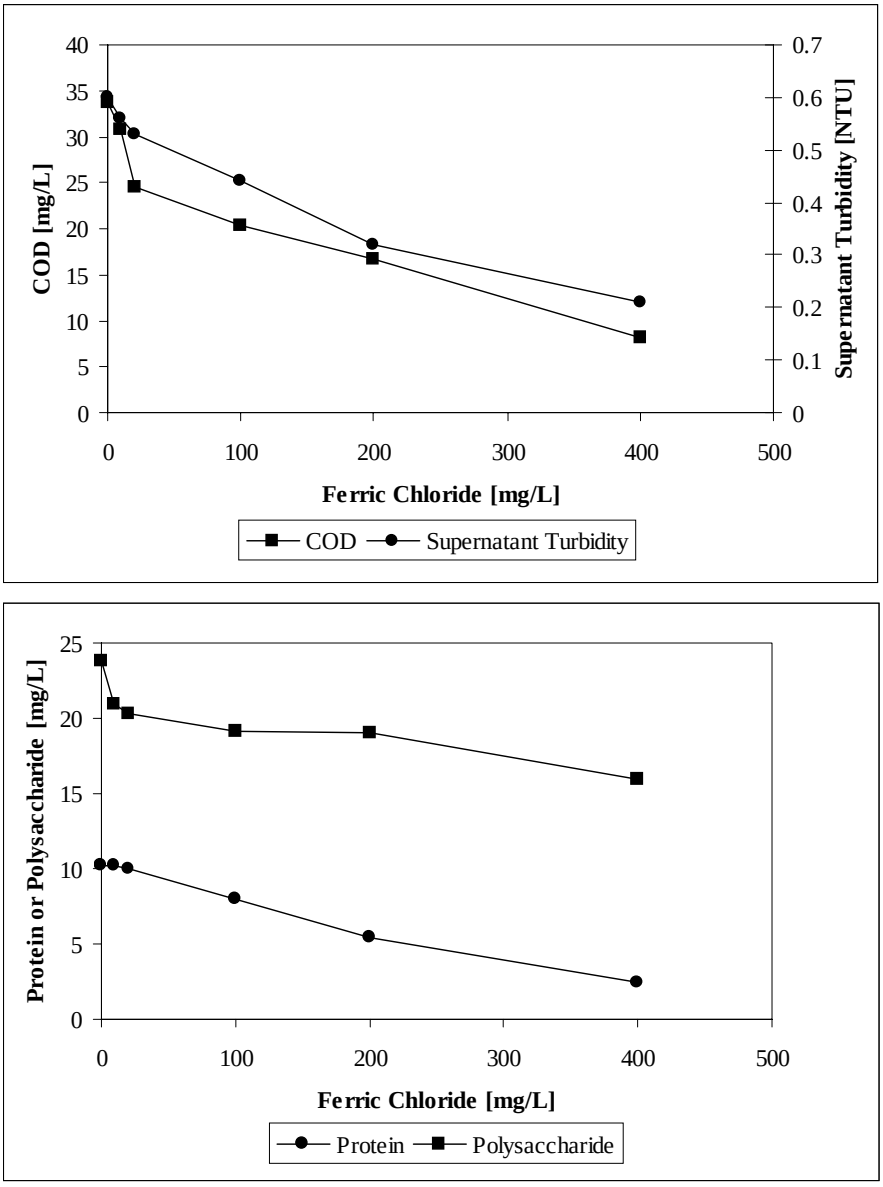

Figure 5-Coagulation of protein and polysaccharide by oxidized iron.

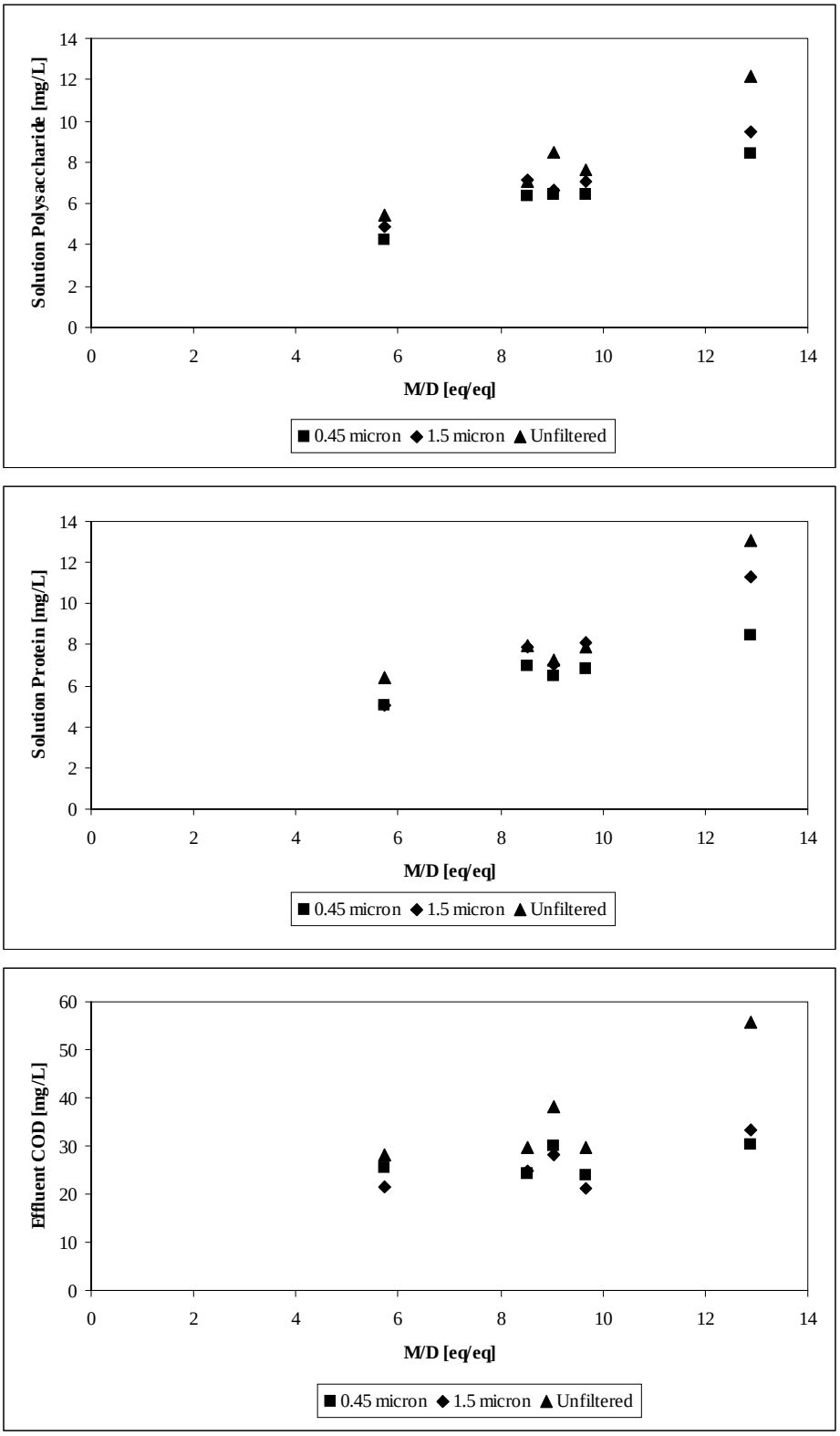

Figure 6-Effect of M/D on solution biopolymer and effluent COD at Radford.

Biopolymer-Cation Floc Model

Activated sludge flocs are composed of active cells and endogenous product. A number of approaches have been used to estimate the active biomass fraction. There are variations in the approaches and the predictions. The range varies from 10 – 30 % and depends mainly on the sludge age of the biomass. It is difficult to accurately enumerate the fraction, because of the difficulty in effectively identifying active cells in such a tightly packed heterogeneous biomass. Typical of endogenous metabolism is the presence of intracellular products in the extracellular medium (Urbain *et al.,* 1993; Jorand *et al.*, 1994; Frolund *et al.*, 1996; Palmgren and Nielsen, 1996). Therefore, intracellular enzymes and nucleic acids commonly found within the bacterial cell may also be found in the extracellular matrix. For this reason, the presence or activity of intracellular compounds is not always a good measure of active biomass. As the sludge age increases, the fraction of active biomass decreases. As a result, the steady state concentration of organic intracellular product increases in the extracellular matrix of activated sludge flocs.

In the extracellular matrix, most of these lysis constituents as well as the exported extracellular compounds are negatively charged, contributing to the negative charge of the activated sludge floc. Divalent cations bridge these negatively charged molecules thus providing a tight and dense structure to the flocs. Other interactions in the floc may include adsorptive interactions between the biopolymers and oxidized iron-hydroxy minerals present in the floc. The absence or removal of divalent or trivalent ions will result in a release of the major biopolymer constituents (proteins and polysaccharides) and other constituents (DNA, RNA and lipids) into the solution as evidenced by the use of multi-valent cation chelators such as EDTA (Fang and Jia, 1996) or cation exchange resins (Frolund *et al.,* 1996) for extraction of floc-bound biopolymers. Further, Eriksson and Alm (1991) demonstrated that deflocculation of activated sludge flocs occurred on addition of EDTA.

Cation exchange can occur in the absence of these compounds (EDTA or cation exchange resins) and depends on the concentration of monovalent and divalent cations present in the activated sludge process. The relative proportion of these cations can be

enumerated in the form of a monovalent to divalent cation equivalent ratio (M/D) (Higgins and Novak, 1997b). These researchers observed a deterioration in dewatering properties at M/D greater than 2. The M/D in the activated sludge therefore may be important for bioflocculation or floc structure determination in general, and may more specifically influence the effluent properties.

The effluent quality at municipal plants is usually better than that at industrial plants for similar concentrations of monovalent and divalent cations. Municipal plants may have higher trivalent cations such as iron. The presence of trivalent cations may promote additional retention of biopolymers within the activated sludge flocs.

It has been found that, for industrial wastewater treatment facilities operating the activated sludge process with no proteins and polysaccharides in the influent stream, there is a substantial concentration of these biopolymers in the effluent (Murthy and Novak, 1998). These biopolymers contribute to the effluent COD. For municipal facilities, it is more difficult to separate the microbial component from the influent stream. Frequently, the influent streams of municipal processes contain microbial product because of biological activity at the source and in the sewers. Therefore it is difficult to distinguish between the influent and effluent compounds. From this study, it can be concluded that a large fraction of the effluent COD from activated sludge plants may be from the biomass itself, and this effluent COD can be controlled by addition of divalent and trivalent cations to the influent of the activated sludge. Residual substrate in the effluent is found at lower solids retention time. What is unexpected is the variation in effluent COD with changes in cations.

Conclusions

The influent to the laboratory activated sludge system consisted of readily degradable soluble organics. For this influent and at sufficiently long hydraulic and solids retention times, the effluent COD is almost entirely composed of extracellular microbial product (mainly protein and polysaccharide). The concentration of these solution biopolymers is strongly dependent on the cations in the process. Divalent

cations deter the release of these biopolymers, while monovalent cations promote this release. The effect of cations on effluent quality was studied for municipalities, with similar results. It is therefore concluded that, for sludge ages typically used in municipal and industrial plants, the effluent COD in the activated sludge process may depend more on the influent monovalent, divalent and trivalent cation concentration than on other operational considerations.

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CHAPTER 4

FACTORS AFFECTING FLOC PROPERTIES DURING AEROBIC DIGESTION: IMPLICATIONS FOR DEWATERING

Sudhir N. Murthy and John T. Novak

Abstract

Laboratory aerobic digestion studies were conducted to determine the effect of divalent cations on the characteristics of aerobically digested sludge. Separate reactors were operated at two divalent cation concentrations. Sludge characteristics examined included dewatering properties (cake solids, SRF and CST), polymer conditioning requirement, floc strength, supernatant COD, supernatant turbidity, soluble cations (sodium, potassium, calcium, magnesium and ammonium ions), soluble anions (nitrate and nitrite) and soluble exocellular polymers (proteins and polysaccharides). The reactor containing higher amounts of calcium and magnesium (1.0 mM each) exhibited much better dewatering properties, higher floc strength, lower polymer conditioning requirement, lower soluble COD, lower supernatant turbidity and lower soluble exocellular polymers than the reactor containing lower calcium and magnesium (0.25 mM each) concentrations. Floc deterioration was associated with a release of soluble proteins and polysaccharides, and monovalent cations (sodium and potassium) into the bulk solution. Divalent cations were not released into the bulk solution, indicating they participated in floc binding. Mineralization of nitrogen (as evidenced by an increase in inorganic nitrogen) was not impacted, suggesting that aerobic digestion of sludge solids was not affected. These results imply that the addition of divalent cations improve aerobic digestor performance.

Keywords

Aerobic digestion, activated sludge, dewatering, exocellular polymer, cation, conditioning.

Introduction

Waste activated sludge is often digested prior to disposal to make it acceptable for land application. Because many of these sludges will be dewatered following digestion, the impact of digestion on dewatering properties may be an important consideration in the design of biosolids handling and disposal facilities. Although the literature is not clear on the impact of digestion on biosolids dewatering properties (EPA, 1987), several studies have reported that both aerobic (Novak, *et al.*, 1977; Katsiris and Kouzeli-Katsiri, 1987) and anaerobic storage (Bruus *et al.*, 1992; Novak, *et al.*, 1987) can lead to poorer dewatering properties.

Activated sludge is comprised of a microbial consortium and organic and inorganic particles held together in a matrix formed by exocellular polymers and divalent cations (Tezuka, 1969; Novak and Haugan, 1981; Eriksson and Alm, 1991; Bruus *et al.*, 1992; Higgins and Novak, 1997a, b). Although most of the biopolymer is incorporated into the sludge floc matrix, a portion of the biopolymer remains unattached in solution as biocolloids. Novak *et al.* (1977) and Novak and Haugan (1980) have shown that polymer conditioning requirements for waste activated sludge are dependent on satisfying both the polymer demand associated with anionic biocolloids and the polymer demand associated with conditioning floc particles through polymer bridging.

One important factor in determining the distribution of the biopolymer (attached to the floc or existing as biocolloids) is the inorganic cation content of the wastewater. Studies have shown that an increase in monovalent cations or, a decrease in divalent cations causes an increase in the polymer conditioning requirement (Higgins and Novak,

1997a; Novak *et al.*, 1996). It is thought that the monovalent ions decrease the binding strength of the biopolymer to the floc matrix, thereby releasing biocolloids into solution.

Aerobic digestion has been shown to cause poorer dewatering properties and at the same time, increase the biopolymer content in solution (Novak *et al.*, 1977). The mechanisms that result in the binding and release of biocolloids from the floc surface are not well understood and this is especially true for changes that occur during aerobic digestion. However, because cations play an important role in polymer binding in flocs, it seems that the relationship between cations and the changes in biosolids that occur during digestion may be important.

The purpose of this study was to evaluate the effects of divalent cations on the dewatering properties of aerobically digested sludge. The hypothesis is that divalent cations will affect the properties of aerobically digested sludge by influencing the quantity and/or characteristics of the polymer demanding biocolloids in solution and the floc properties.

Methods and Materials

Approach

Laboratory activated sludge samples

Two laboratory reactors, seeded with activated sludge from a municipal wastewater treatment facility were used to conduct the experiments. These reactors were operated as completely mixed activated sludge systems at a 10-day mean cell residence time and a 2-day hydraulic retention time. The laboratory system configuration is described by Higgins and Novak (1997a). The influent COD was maintained at 800 mg/l using 400 mg/l acetate and 400 mg/L Bactopeptone as COD. The influent did not contain any sugars or polysaccharides. The dissolved oxygen was maintained at approximately 7 mg/l using compressed air fed through diffuser stones. The reactor influent cation concentrations are presented in Table 1. Reactor 1 (0.25 mM reactor) received 0.25 mM

each of calcium and magnesium in the influent and Reactor 2 (1 mM reactor) received 1 mM each of calcium and magnesium in the feed.

Table 1-Influent cation concentration for laboratory reactors.

Reactor	Sodium (meq/L)	Potassium (meq/L)	Magnesium (meq/L)	Calcium (meq/L)
1	3.6	0.4	0.5	0.5
2	3.6	0.4	2	2

Ammonium phosphate was added to the feed to provide supplemental nitrogen and phosphorus. No other nutrients were added and the pH was not controlled. The temperature was maintained at 20° C. Calcium, magnesium and sodium were added as acetate salts. Additional sodium was provided using sodium sulfate. Potassium was added using potassium chloride. Higgins and Novak (1997b) suggested that at a monovalent to divalent cation ratio (M/D) greater than 2, sludge physical properties were likely to deteriorate. Therefore, the reactors were operated so that Reactor 1 (M/D = 4) would be expected to have poorer properties than for Reactor 2 (M/D = 1).

The reactors were operated as continuous flow activated sludge units for 25 days after which the input of feed stopped and the units were operated as batch aerobic digesters. The contents were aerobically batch digested for 20 days. Digestion times of between 10-20 days are often recommended to achieve stabilization. Soluble proteins and polysaccharides, total polysaccharides and volatile solids removal were measured after 10 and 20 days of digestion. Dewatering properties, polymer conditioning requirements, soluble COD, supernatant turbidity and soluble cations and anions in the reactors were measured after 10 days of digestion.

Laboratory steady state and filamentous organism determination

Steady state for the laboratory reactors was determined as described by Higgins and Novak (1997a). Filamentous organisms in the laboratory reactors were quantified using the method of Jenkins *et al.* (1986), which rates the number of filamentous organisms on a scale of 0-6. A score of 0 corresponds to no filaments and a score of 6 corresponds to excessive filaments. The reactors were seeded with sludge with filament rated at 2. After 25 days of operation, the filament rating was between 2 and 3. The feed lines and feed containers were bleached 3 times a week to prevent growth of *Sphaerotilus natans*.

Analytical Methods

Cation and Anion Analysis

Sodium, potassium, calcium, magnesium and ammonium ions were quantified using a Dionex Ion chromatograph with a CS12 column and conductivity detector (Dionex 2010I) with self-regenerating suppression of the eluent. Methane sulfonic acid (20 mM) was used as the eluent at a flow rate of 1.0 ml/min.

Nitrite and nitrate were monitored using a Dionex ion chromatograph with AS4A-SC column and conductivity detector with self-regenerating suppression of eluent. A mix of sodium bicarbonate (1.7 mM) and sodium carbonate (1.8 mM) was used as the eluent at a flow rate of 2 ml/min.

Dewatering Properties and Polymer Conditioning

Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) was analyzed using Method 2540D and 2540E of *Standard Methods* (1995) respectively. The dewatering properties were measured using capillary suction time (CST) using Method 2710G of *Standard Methods* (1995), and specific resistance to filtration (SRF) as described by Christensen and Dick (1985). Supernatant turbidity was measured using Method 2130B of *Standard Methods* (1995).

Vacuum filtered cake solids measurements were obtained using a Buchner funnel with a vacuum pressure of 38 cm mercury and 4 minutes filtration time. Centrifuge cake solids were measured using a laboratory centrifuge at 5,000 *g* for 15 minutes.

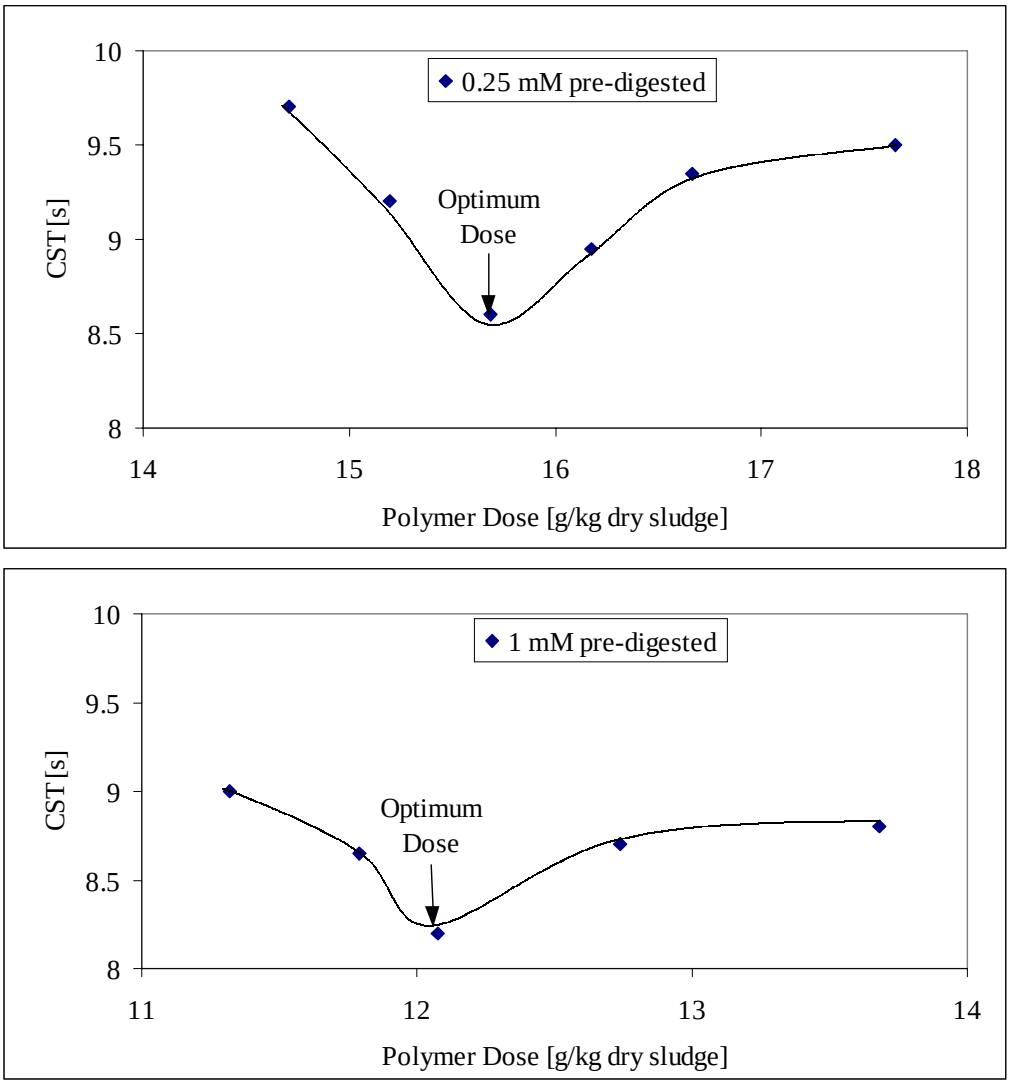

Figure 1-Optimum polymer dose profiles for reactors before digestion.

Polymer conditioning tests were performed using low molecular weight cationic polymer at 0.5% and 0.05% stock concentrations. Optimum polymer dose was measured using the CST device and reported as g/kg dry sludge (Figure 1). The optimum polymer

dose reflects conditioning at minimal shear conditions. The optimum conditioning dose will be higher and can be appropriately calibrated based on the shear in the dewatering device (Murthy and Novak, 1997; Novak *et al.*, 1993; Novak and Lynch, 1990).

COD Analysis

Soluble COD was analyzed using Method 5220C of *Standard Methods* (1995).

Soluble Protein and Soluble and Total Polysaccharide Analysis

Soluble proteins and polysaccharides samples were obtained by centrifuging a 40 ml sludge sample and analyzing the centrate. Total polysaccharides were analyzed by digesting the total sludge sample (solids and supernatant). Protein was measured using the Hartree (1972) modification of the Lowry *et al.* (1951) method. Total and soluble polysaccharides were measured using the method of Dubois *et al.* (1956). Protein standards were prepared with bovine serum albumin, and polysaccharide standards were prepared with glucose. The concentrated sulfuric acid used in the polysaccharide test was able to digest the mixed liquor solids used for the total polysaccharide analysis.

Aminopeptidase Analysis

An assay for leucine-aminopeptidase was performed using L-leucine-p-nitroanilide (substrate for the colorimetric determination of leucine-aminopeptidase). The sludge sample (40-ml) was centrifuged at 8,000 x *g* for 15 minutes. The pellet was resuspended in buffer (50 mM Tris, pH 7.5, 10 mM sodium chloride and 5% glycerol by volume) to 4-ml and sonicated for 5 minutes at 1 minute intervals to disperse the flocs. The sample was centrifuged at 8,000 x *g* for 8 minutes, and 100-µl of cell-free extract was assayed for leucine-aminopeptidase using the method of Prescott and Wilkes (1976).

Results And Discussion

Laboratory Activated Sludge Characteristics

The concentration of divalent cations (0.25 mM and 1 mM calcium and magnesium) used in this study is not uncommon in municipal activated sludges. The relative hardness of waters at particular locations and sources can affect the divalent cation concentrations in municipal wastewaters. The concentration of sodium ions is variable, and is often higher than that used in this study, because caustic soda and other supplements are often used in water treatment, wastewater treatment and other processes that increase the sodium ion input.

Table 2-Dewatering properties for reactors before and after digestion.

Reactor	CST (s)	SRF (Tm/kg)	Cake Solids (vacuum filtered) (%)	Cake Solids (centrifuge) (%)
1 (pre-digested)	12	0.99	11	3.8
2 (pre-digested)	11	0.23	17	5.4
1 (digested)	50	46	*	3.5
2 (digested)	14	3.1	18	3.9

*The cake solids were measured after 4 minutes filtration time. In this case, the filters were clogged and no cake was formed.

Reactor 1 (M/D = 4), as expected, displayed poorer settling and dewatering properties during the normal activated sludge treatment mode than Reactor 2 (M/D = 1). This difference in performance is evidenced by the SRF, centrifuge solids and filter cake solids data presented in Table 2. The most important effect of the divalent ions for the

predigested sludges was on cake solids. Higher levels of calcium and magnesium led to drier cakes (17% versus 11% for the vacuum filtered sludges and 5.4% versus 3.8% for the centrifuged sludges). The drier cakes suggest a more tightly bound floc matrix where less water is incorporated into the floc structure.

After 25 days of operation as an activated sludge system, the feed was stopped and the units were operated as batch aerobic digesters. After 10 days of aerobic digestion, the dewatering properties had deteriorated considerably. As can be seen from the data in Table 2, the CST, SRF, and centrifuge cake solids deteriorated to a greater extent for the reactor which had the lowest divalent ion feed compared to the high divalent feed. The centrifuge cake solids test has been used as a general indicator of the dewatered cake solids content for a number of different dewatering processes (Novak and Calkins, 1972). Recently, Bullard and Barber (1996) described the use of laboratory centrifuge solids content in predicting polymer conditioning dose requirements, solids production rates and dewatered cake solids for a belt filter press. The cake solids determined by the laboratory centrifuge test appear to be a useful indicator of the moisture retention characteristics of the biosolids.

Table 3-Conditioning requirements for reactors before and after digestion.

Reactor	Cationic Polymer Conditioning Dose (g/kg dry sludge)
1 (pre-digested)	16
2 (pre-digested)	12
1 (digested)	279
2 (digested)	39

The conditioning requirements, before and after digestion were measured for the two reactors and the results of these tests are shown in Table 3. The polymer conditioning dose for the 1 mM reactor was lower than the 0.25 mM reactor both before and after digestion. The polymer conditioning requirement increased by a factor of about 17 for the 0.25 mM reactor compared to an equivalent increase by only a factor of about 3 for the 1 mM reactor. The polymer conditioning requirement is a significant operating expense for wastewater treatment plants. These data indicate that small changes in divalent cations could result in considerable variation in polymer costs. Although divalent salts are not normally added to biosolids prior to aerobic digestion, these data suggest that this approach should be investigated to determine if it can reduce polymer costs.

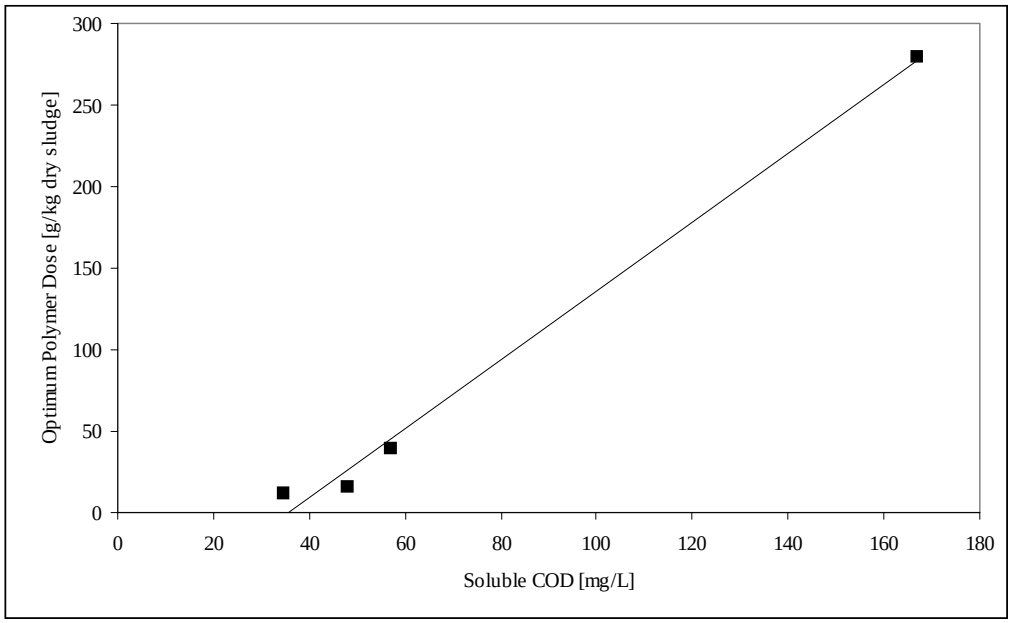

Figure 2-Effect of soluble COD on optimum polymer dose.

The soluble COD and supernatant turbidity were measured to evaluate release of biopolymers from the floc surface during digestion and the resulting impact on effluent quality (Table 4). The increase in soluble COD for the 1 mM reactor was much lower than the increase in soluble COD for the 0.25 mM reactor. Similar observations were

made for the increase in supernatant turbidity. The increase in turbidity and in soluble COD may be due a destruction of floc structure during stabilization promoting the release of colloidal and soluble organics into solution. Part of the increase in supernatant turbidity may also be due to release of unicellular organisms from the floc matrix. A comparison of the data in Tables 3 and 4, presented in Figure 2, suggests that the increase in soluble COD is associated with increased polymer demand.

Table 4-Soluble COD and supernatant turbidity of reactors before and after digestion.

Reactor	Soluble COD (mg/L)	Supernatant Turbidity (NTU)
1 (pre-digested)	48	4.6
2 (pre-digested)	35	4.8
1 (digested)	170	52
2 (digested)	57	12

Table 5 presents the soluble protein and polysaccharide concentrations from pre-digested and digested mixed liquors. The soluble protein and polysaccharide concentration of the 0.25 mM reactor was consistently higher than the 1 mM reactor before and after digestion. The lower divalent cation concentration of the 0.25 mM reactor promoted the release of soluble proteins and polysaccharides from the floc. The data suggest that the increase in soluble COD and the increase in polymer conditioning demand result from the release of protein and carbohydrates by the floc matrix. The data for total polysaccharides also suggests that the difference in the soluble components for the high and low Ca and Mg reactors is due to release, not a differential biopolymer content or production in the two systems.

Table 5-Soluble protein and polysaccharide, and total polysaccharide in reactors before and after digestion.

Reactor	Soluble Protein (mg/L)	Soluble Polysaccharide (mg/L)	Total Polysaccharide (mg/L)
1 (pre-digested)	15	25	127
2 (pre-digested)	15	17	135
1 (10-day digested)	36	76	174
2 (10-day digested)	6	58	173
1 (20-day digested)	34	124	196
2 (20-day digested)	15	85	197

Higgins and Novak (1997a) have found that extracellular proteins play an important role in the maintenance of floc structure. Their conclusion was partly based on the observation that the addition of a proteolytic enzyme resulted in the deterioration of floc structure. On the other hand, the addition of polysaccharide degrading enzymes did not cause sludge deflocculation perhaps due to the specific nature of the polysaccharides. Aerobic digestion appears to be responsible for the destruction of floc structure through the degradation of easily metabolized organic substrates, possibly proteins, during the stabilization process.

Aminopeptidases are enzymes found in the extracellular matrix of bacteria (Prescott and Wilkes, 1976; Gonzales and Robert-Baudouy, (1996)) and reportedly are common in activated sludges (Teuber and Brodisch, 1977; Nybroe *et al.*, 1992; Frolund *et al.*,1995). These enzymes participate in the degradation of exogenous and endogenous proteins (Hermes *et al.*, 1993; Gonzales and Robert-Baudouy, (1996)). Leucine-aminopeptidase was one of the aminopeptidases found in activated sludge (Teuber and Brodisch, 1977).

Table 6-Leucine aminopeptidase activity before and after digestion (10-day).

Reactor	Leucine aminopeptidase activity (mUnits/mL)
1 (pre-digested)	13.2
2 (pre-digested)	12.2
1 (digested)	13.7
2 (digested)	13.2

In this study, leucine-aminopeptidase activity remained relatively constant with the destruction of volatile solids (Table 6). Throughout the digestion process, the concentration of soluble proteins remained low. These data suggest that the sludge retained a strong ability to degrade proteins during digestion. The increase in soluble organics in both reactors appeared to be due to primarily the release of soluble polysaccharides. As digestion time increased, the concentration of soluble polysaccharides increased. These polysaccharides seemed to be somewhat resistant to degradation over the 20-day hydraulic retention time. Relative to polysaccharides, proteins continued to be degraded within the floc throughout digestion leading to a destruction of floc structure (as evidenced by an increase in inorganic nitrogen). Enzymes for polysaccharide breakdown tend to be specific to the sugar molecule and

glycosidic bonds (Moran *et al.*, 1994). The absence of some of these enzymes during 20-day aerobic digestion can result in the persistence of polysaccharides. The lower protein content in flocs and higher polysaccharide content in solution that evolves during digestion may cause a deterioration in dewatering properties and an increase in polymer conditioning demand.

An increase in total polysaccharides was observed with an increase in digestion time. It appears that some of the energy and carbon released during digestion may be incorporated into creating more polysaccharides. During digestion, cell growth can only occur by lysis and subsequent regrowth fed by lysed cells. The new cells therefore, produce more polysaccharides as part of cell synthesis. Since the existing polysaccharides appear to be somewhat resistant to degradation, there is an increase in total polysaccharides with time.

Table 7-Cations and anions before and after digestion (10-day).

Reactor	Sodium (mg/L)	Potassium (mg/L)	Magnesium (mg/L)	Calcium (mg/l)	Inorganic N (NH_4^+ & NO_3^-) (mg/L)
1 (pre-digested)	76	10	16	23	96
2 (pre-digested)	75	9	45	61	96
1 (digested)	102	22	13	26	128
2 (digested)	104	20	36	66	122

Cations and anions were measured for these reactors as shown in Table 7. Nitrite was not observed in the reactors before or after digestion. The sum of ammonia-N and nitrate-N is reported as inorganic nitrogen. The increase in inorganic nitrogen is used as an indicator of degradation of nitrogen containing organics (primarily proteins) and may also be used to measure the extent of digestion of organics in the sludge. As can be seen

from Table 7, similar increases in inorganic nitrogen occurred before and after digestion for the two different reactors. WPCF (1985) predicted about 25% volatile solids destruction over 10 days hydraulic retention time and temperature of 20° C. The initial volatile solids in the reactors were between 850 to 900 mg/l. Endogenous respiration of bacteria ($C_5H_7NO_2$) results in 1 mole of ammonia released per mole of cell consumed. As seen in Table 7, about 28 mg/l (2 mM) inorganic N was released in these reactors representing 225 mg/l cells destroyed. From the inorganic N released, it can be calculated that about 25% cellular destruction was achieved.

After 10 days of digestion, the 0.25 mM reactor indicated a 31% volatile solids reduction whereas the 1 mM reactor indicated an 18% volatile solids removal (Table 8). The difference in the volatile solids reduction between the two reactors may be attributed more to the differential attachment and release of polysaccharides caused by divalent cations rather than differences in the actual extent of digestion process. The lower apparent volatile solids destruction in the high divalent ion reactor can be explained by the retention of polymerized organics in the floc matrix whereas, in the low divalent cation reactor, the biopolymer was released into solution.

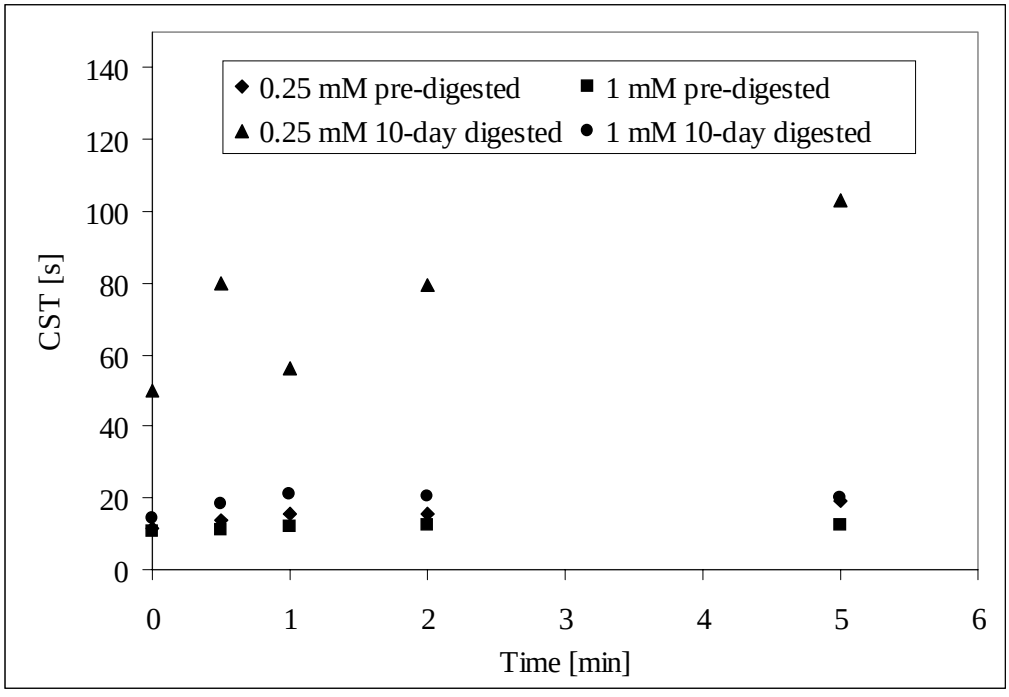

Figure 3-Effect of mixing time (800 rpm) on dewatering property.

Large changes in soluble calcium and magnesium were not observed in the two reactors after 10 days of digestion, indicating that these cations are retained in the floc structure and play an important role in maintaining the floc structure (Table 7). The high divalent biosolids also maintained its floc strength as indicated in Figure 3. However, monovalent ions were released during the digestion process. The release of monovalent ions appears to be associated with the progression of the digestion process.

Table 8-Volatile solids removal.

Reactor	Volatile Solids Removed (%)
1 (10-day digested)	31
2 (10-day digested)	18
1 (20-day digested)	50
2 (20-day digested)	32

Engineering Significance

It has been shown that a high monovalent cation content in the feed to activated sludge systems can cause poor biosolids settling and dewatering properties (Higgins and Novak, 1997a). A survey of the literature indicates that dewatering properties and polymer conditioning demand vary widely following both aerobic and anaerobic digestion. At times the biosolids dewatering properties are extremely poor. Based on this research, it appears that the partial degradation and release of biopolymers that participate in the binding of cells within the floc matrix account for some of these changes in dewatering properties associated with aerobic stabilization, and this release is controlled by the cation content in the system.

The role of divalent cations in promoting the binding of biopolymers to the floc matrix appears to be especially important during digestion. The inorganic nitrogen data,

along with the total polysaccharide content indicates that biodegradation of the biosolids is not affected by the divalent cation content. However, when divalent cations are low, polysaccharides are released from the floc into solution. The retention of polysaccharides in flocs by high divalent cations yields digested sludge that dewaters better and requires less polymer for conditioning.

These data suggest that the properties of digested sludges can be expected to vary considerably depending on the cation content of the sludge. For anaerobic systems, the production of the ammonium ion as part of the digestion process should contribute to poorer dewatering properties by exchanging for calcium and magnesium ions in the floc matrix. The influence of cations in digestion may also be important in determining the appropriate handling of dewatering side streams. The higher organic content in the liquid phase of low divalent cation slurries may cause problems with recycling or disposal of these streams.

These results will have considerable impact on the design of biosolids handling systems. Through monitoring monovalent and divalent cation concentrations, it may be possible to qualitatively predict which sludges are likely to be more difficult to dewater when digested or which will be most expensive to condition and this may lead to selection of alternative stabilization processes. There may also be benefit in addition of divalent cations to wastewaters, either directly or as part of the biosolids treatment process. For example, the use of lime or magnesium hydroxide instead of caustic soda for pH control or the direct addition of divalent cation salts to the process prior to digestion may be considered.

Conclusions

Higher concentrations of divalent cations in the wastewater improved aerobic digestion of the waste activated sludge. The effects of divalent cations on aerobic digestion are summarized below:

- Improvement in dewatering properties and reduction of cationic polymer conditioning requirement was observed at higher divalent cation concentration when compared to lower divalent cation concentration.
- Deterioration of dewatering properties and an increase in polymer conditioning demand was associated with increases in soluble COD, supernatant turbidity and soluble polysaccharides.
- The generation of inorganic nitrogen during digestion suggests that the biological degradation process was not affected by the addition of divalent cations.
- Volatile solids removal is not analogous to volatile solids destruction. Release of biopolymers from the floc into solution more readily occurs in the solution containing low divalent cations.
- The proteins in the activated sludge matrix appear to be readily degraded. Digestion does not appear to affect the activity of aminopeptidases.
- The release of inorganic nitrogen may be a more suitable indicator of the extent of the aerobic digestion process than volatile solids reduction.

This study indicated that changes in monovalent and divalent cation affect activated sludge properties and to a greater extent influence aerobically digested sludge properties. Achieving a proper balance between monovalent and divalent cations would assist in maintaining desirable floc properties after digestion. The same implication may hold for anaerobic digestion.

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CHAPTER 5

EFFECT OF SOLIDS RETENTION TIME ON EFFLUENT QUALITY DUE TO PRESENCE OF POLYMERIC SUBSTANCES

Sudhir N. Murthy, Gary P. Phillips and John T. Novak

Abstract

Laboratory studies were conducted to evaluate the effect of solids retention time in the activated sludge process on effluent quality. It was found that an increase in solids retention time (SRT) resulted in an increase in polysaccharide in the solution and in the effluent. At higher SRTs, there was also a small increase in solution protein. The protein and polysaccharide appear to constitute extracellular microbial product. The increase in solution protein and polysaccharide resulted in an increase in effluent COD. The increase in effluent COD was not accompanied by a similar increase in effluent BOD, indicating that the organic matter released was not easily degradable. Evaluation of size distribution of the protein and polysaccharide indicated that a substantial fraction was colloidal (greater than 30,000 daltons). It was also found that a substantial portion of the effluent COD of microbial origin passed through a 0.45 μ membrane used as a benchmark to quantify soluble organic fraction.

Keywords

Solids retention time, activated sludge, effluent, COD, BOD, protein, polysaccharide, biopolymer, soluble microbial product, extracellular microbial product.

Introduction

Activated sludge is comprised of flocs that contain mainly microorganisms and extracellular polymers (Novak and Haugan, 1981; Eriksson and Alm, 1991; Bruus *et al.*, 1992; Higgins and Novak, 1997a, b).

In industrial wastewaters treated by the activated sludge process and characterized by limited amounts of proteins or polysaccharides in the influent, considerable concentrations of these biopolymers appear in the effluent stream (Murthy and Novak, 1998a). Due to the strictly industrial origin of these wastewaters, it is easy to identify the effluent polymer generated by the treatment process. The situation for municipal wastewaters is not as straightforward. The influent streams of municipal processes contain microbial products as a result of biological activity at the source and in the sewers. It is difficult to distinguish between the biopolymers already present in the influent and those compounds produced during treatment.

Murthy and Novak (1998b) have shown that the concentration of biopolymers in solution is influenced by the cationic composition in the influent. The researchers suggested that the divalent charge bridging mechanism that improves bioflocculation simultaneously prevents the release of biopolymers from the floc to the surrounding medium. Monovalent cations disrupt floc structure by preventing charge bridging and releasing biopolymers to the solution. A higher concentration of monovalent cations or lower concentration of divalent cations in the influent will result in higher solution biopolymers and higher effluent COD.

The organic fraction of activated sludge originates from active cells and is mostly endogenous products. Endogenous metabolism results in the presence of intracellular products in the extracellular medium (Urbain *et al.*, 1993; Jorand *et al.*, 1994; Frolund *et al.*, 1996; Palmgren and Nielsen, 1996). Frolund *et al.*, 1996 have indicated that the active biomass fraction in activated sludge may be small and may range between 10-15%. Even with more conservative estimates, the active biomass fraction is not very high. As the solids retention time increases, the fraction of active biomass decreases. As a result, the steady state concentration of organic intracellular product in the extracellular matrix of activated sludge flocs increases.

Other researchers, most notably Grady and Williams (1975) and Grau *et al.* (1975), have shown that the quantity of extracellular microbial product (EMP) is dependant on the influent substrate concentration to the process. The implication of this is that a constant fraction of the metabolized COD is converted to soluble, non-degradable organic matter. Although attempts have been made to incorporate this non-degradable COD fraction into kinetic models, predictions of the EMP concentration have been unsuccessful. Namkung and Rittman (1986) have shown that, for biofilms, only a small fraction of effluent soluble organic carbon was residual organic substrate, whereas the majority was soluble microbial product.

Aerobic digestion of activated sludge (Murthy and Novak, in press) showed that under endogenous conditions existing during digestion, proteins are easily degraded but polysaccharides tend to accumulate. These polysaccharides are released to the solution and increase the supernatant COD in the digesters. An increase in digestion time resulted in a greater release of polysaccharides to the solution. In an early paper on activated sludge characteristics, Bisogni and Lawrence (1971) concluded that an increase in SRT resulted in an accumulation of polysaccharides in the effluent (although no data was shown). These studies indicated that an increase in SRT may result in an increase in biopolymers released into the solution.

The objective of this study was to evaluate the effect of SRT on effluent quality. Effluent quality was monitored by measurement of influent substrate, solution protein, solution polysaccharide, effluent COD and effluent BOD. The study was conducted in a laboratory using a constant COD source. It was hypothesized that under SRTs normally used in the activated sludge process, the residual substrate would play a minor role in determining effluent quality.

Methods and Materials

Experiments were conducted with 10-L laboratory reactors that were freshly seeded with activated sludge from a municipal wastewater treatment facility. Seven reactor sets were operated to examine 5, 7, 10, 20, 30, 40 and 50 days SRT. The SRT

was controlled by compensating for effluent solids in the wastage rate. Steady state operation with respect to solids concentration was usually achieved in 7-10 days. The reactors were operated for 2 SRTs prior to sampling and analysis. The reactors were completely mixed activated sludge systems with a 2-day hydraulic retention time. The laboratory system configuration is described by Higgins and Novak (1997a).

The influent COD was maintained at 600 mg/l using 200 mg/L acetate and 400 mg/L Bactopeptone (protein source), expressed as COD. The influent did not contain any sugars or polysaccharides. The dissolved oxygen was maintained at approximately 7 mg/L using compressed air fed through diffuser stones. Magnesium and sodium were added as sulfate salts and calcium and potassium were added as chloride salts. Ammonium phosphate was added to provide additional nitrogen and phosphorous.

Effluent properties measured included effluent COD, effluent BOD, solution proteins, solution polysaccharides and solution cations. Effluent acetate was measured to monitor for residual substrate.

Sample Preparation

To quantify the smaller size fractions, samples were ultrafiltered at 55 psi through Amicon® YM30 and YM3 partly hydrophilic membranes (approximate molecular size 30,000 dalton and 3,000 dalton respectively).

Samples were taken from the effluent of laboratory reactors and filtered through a 1.5 μ glass microfiber membrane, 0.45 μ hydrophilic polypropylene membrane, 30,000 dalton (30K) and 3,000 dalton (3K) ultrafilters. The fractionated samples were analyzed for protein, polysaccharide, COD and BOD. Acetate and cations were measured for samples filtered through a 0.45 μ filter.

Cation Analysis

Sodium, potassium, calcium and magnesium ions were quantified using a Dionex Ion chromatograph with a CS12 column and conductivity detector (Dionex 2010I) with self-regenerating suppression of the eluent (Table 1).

Table 1–Influent cations for the laboratory reactors.

Sodium (mM)	Potassium (mM)	Magnesium (mM)	Calcium (mM)
4.1	0.1	1.1	0.6

COD and BOD Analysis

Solution COD was analyzed using Method 5220C of *Standard Methods* (1995) and solution BOD (5-day BOD test) was measured using Method 5210B of *Standard Methods* (1995).

Solids Analysis

Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were analyzed using Method 2540D and 2540E of *Standard Methods* (1995) respectively.

Acetate Analysis

Residual acetate was measured on a Hewlett-Packard 5880 gas chromatograph fitted with a flame ionization detector.

Solution Protein and Solution Polysaccharide Analysis

Solution proteins and polysaccharides samples were measured using the Hartree (1972) modification of the Lowry *et al.* (1951) method. Polysaccharides were measured using the method of Dubois *et al.* (1956). Protein standards were prepared with bovine serum albumin, and polysaccharide standards were prepared with glucose.

Results And Discussion

Solution Protein and Solution Polysaccharide

The laboratory reactors were operated at SRTs ranging from 5 days to 50 days. The reactor feed was completely soluble (< 30K molecular size) and consisted of 400

mg/L Bactopeptone as COD and 200 mg/L acetate as COD. In Bactopeptone, a protein feed, 55% of the protein was found in the 30K-3K range and 45% of the protein was found to be less than 3K molecular size. At all SRTs, the concentration of acetate in the effluent was less than 1 mg/L as COD.

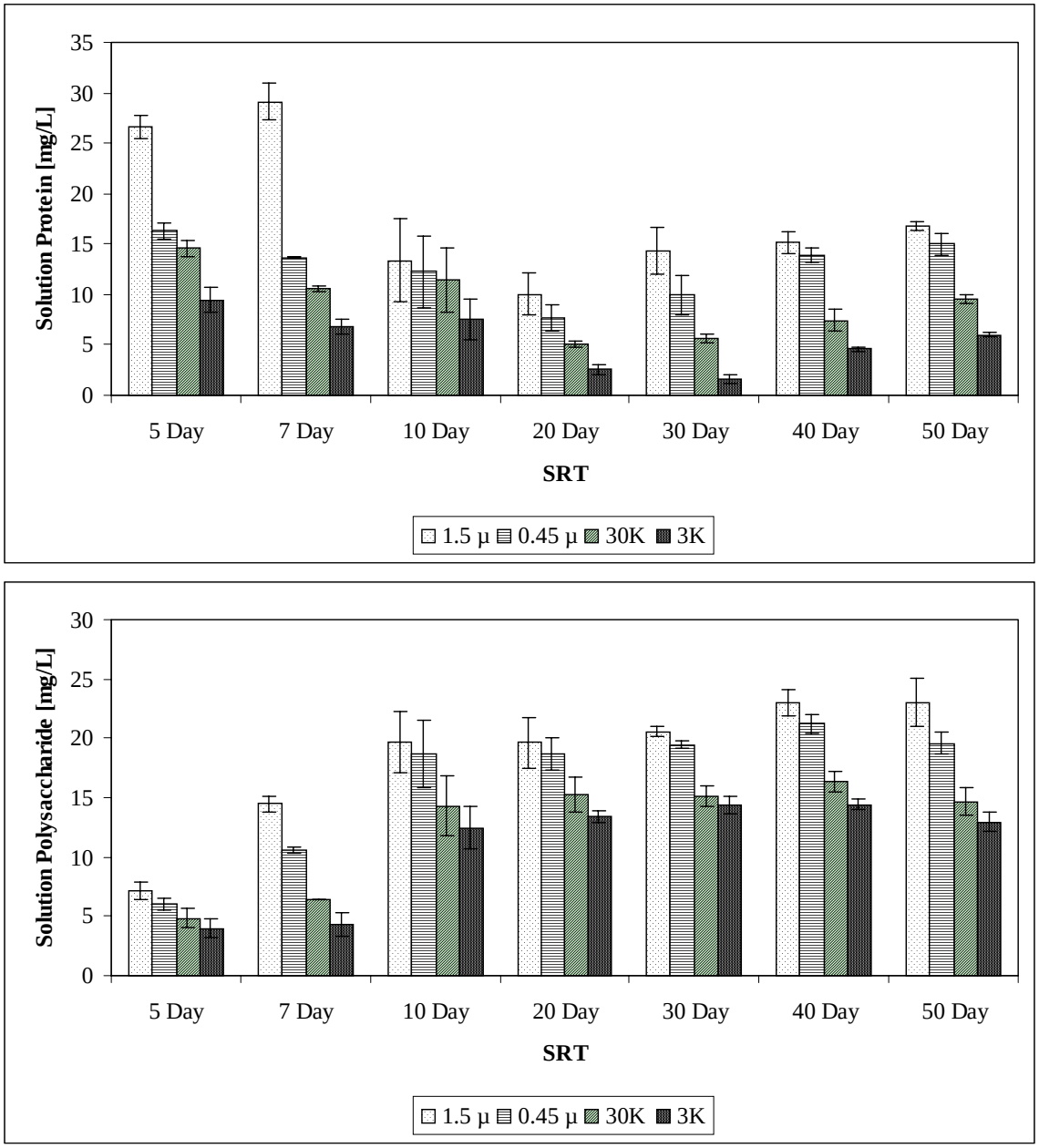


Figure 1-Effect of SRT on solution protein and solution polysaccharide.

Figure 1 shows the effect of SRT on solution protein and polysaccharide. The solution polysaccharide concentration clearly increased with an increase in SRT. This result was observed for all of the size ranges monitored. The increase in solution polysaccharide concentration is consistent with observations in other studies (Bisogni and Lawrence, 1971; Murthy and Novak, in press).

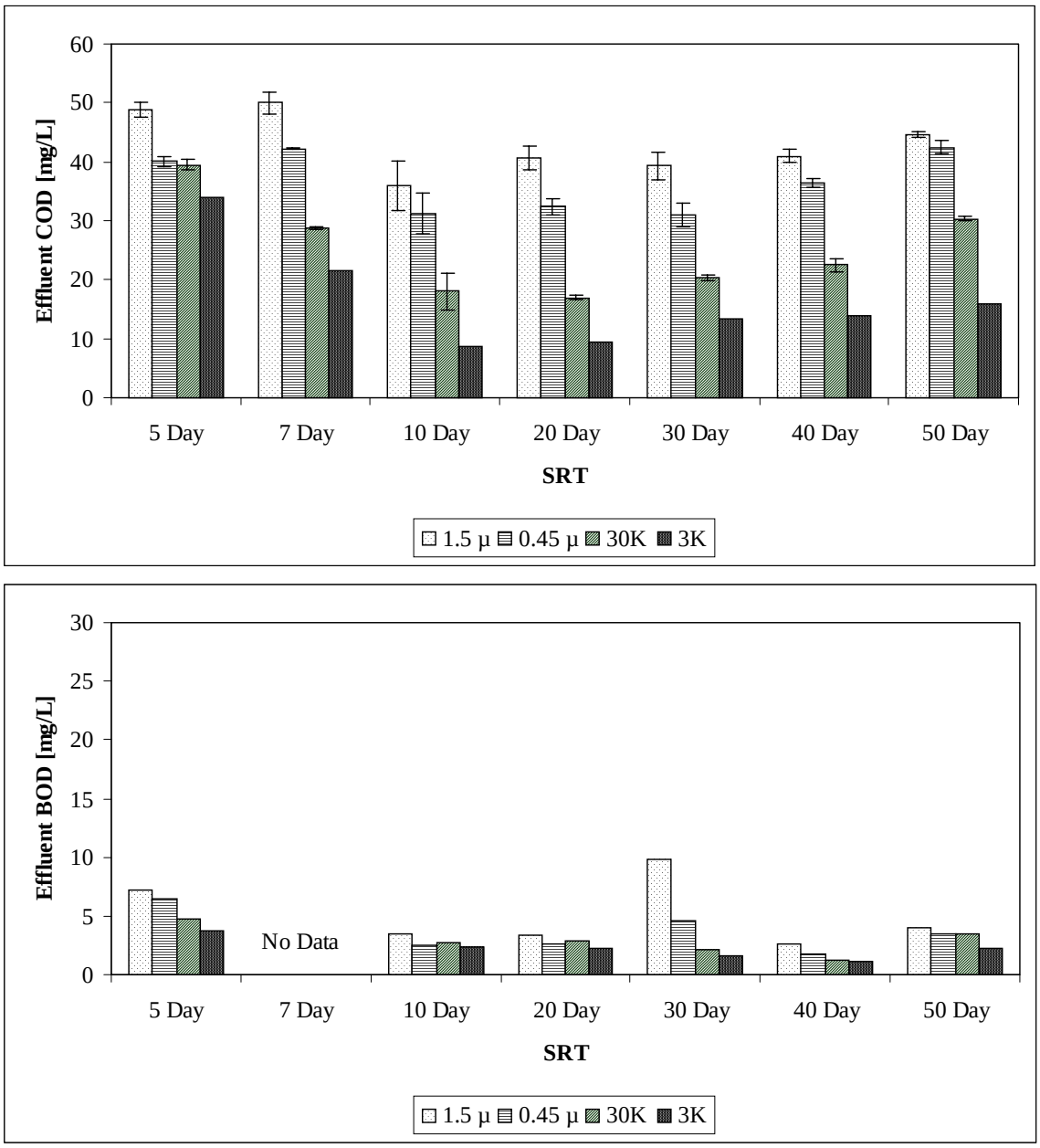


Figure 2-Effect of SRT on effluent COD and effluent BOD.

The lowest protein concentration was in the 20 – 30 days SRT range. The higher protein concentration at the lower SRTs may have been due to protein release from dispersed flocs. Dispersed flocs are usually observed at lower SRT (Bisogni and Lawrence, 1971). The higher concentration of protein, in the ultrafiltered samples (< 30K and < 3K) at the lower SRTs, may have been due to the slower hydrolysis and metabolism of protein (Bactopeptone feed) relative to acetate. The increase in solution protein beyond 20-day SRT was probably due to release of organic matter from the activated sludge flocs.

Effluent COD and Effluent BOD

Corresponding to the increase in solution protein and solution polysaccharide, from SRT of 10 days to 50 days, an increase in effluent COD was observed (Figure 2). A decrease in effluent COD was observed in the 5 - 10 days SRT range. This decrease in effluent COD is consistent with the decrease in proteins in the same range.

Optimum (lowest) effluent COD was observed in the 10 - 20 days SRT range for all the size fractions. This optimum reflects a combination of lower polysaccharides observed at SRTs less than 10 days and the optimum proteins observed in the 20 - 30 days SRT range. The optimum effluent COD with respect to SRT may vary for reactor systems and may depend on the complexities of substrate, cations and reactor configuration.

Effluent BOD (Figure 2) remained very low for all the SRTs monitored, indicating that much of the COD was due to the slowly degrading organic matter released from the activated sludge flocs into the surrounding medium. The low effluent BOD and the high effluent COD/BOD ratio are consistent with concentrations and ratios found at many wastewater treatment plants.

Figure 3 summarizes the solution protein, solution polysaccharide, effluent COD and effluent BOD data for the 'soluble' ultrafiltered fractions (< 30K and < 3K). The changes in effluent COD with SRT reflect the combination of changes in solution protein and solution polysaccharides. Again, BOD concentration remained very low (less than 5 mg/L) and appeared to be unaffected by SRT.

The data indicate that for SRTs commonly employed at most activated sludge facilities, effluent COD depends to a much greater extent on biopolymer released from the flocs than residual wastewater substrate. At lower SRTs, protein release from the floc due to dispersed growth (in the larger size fraction) or substrate protein hydrolysis (in the smaller size fraction) may govern the effluent COD.

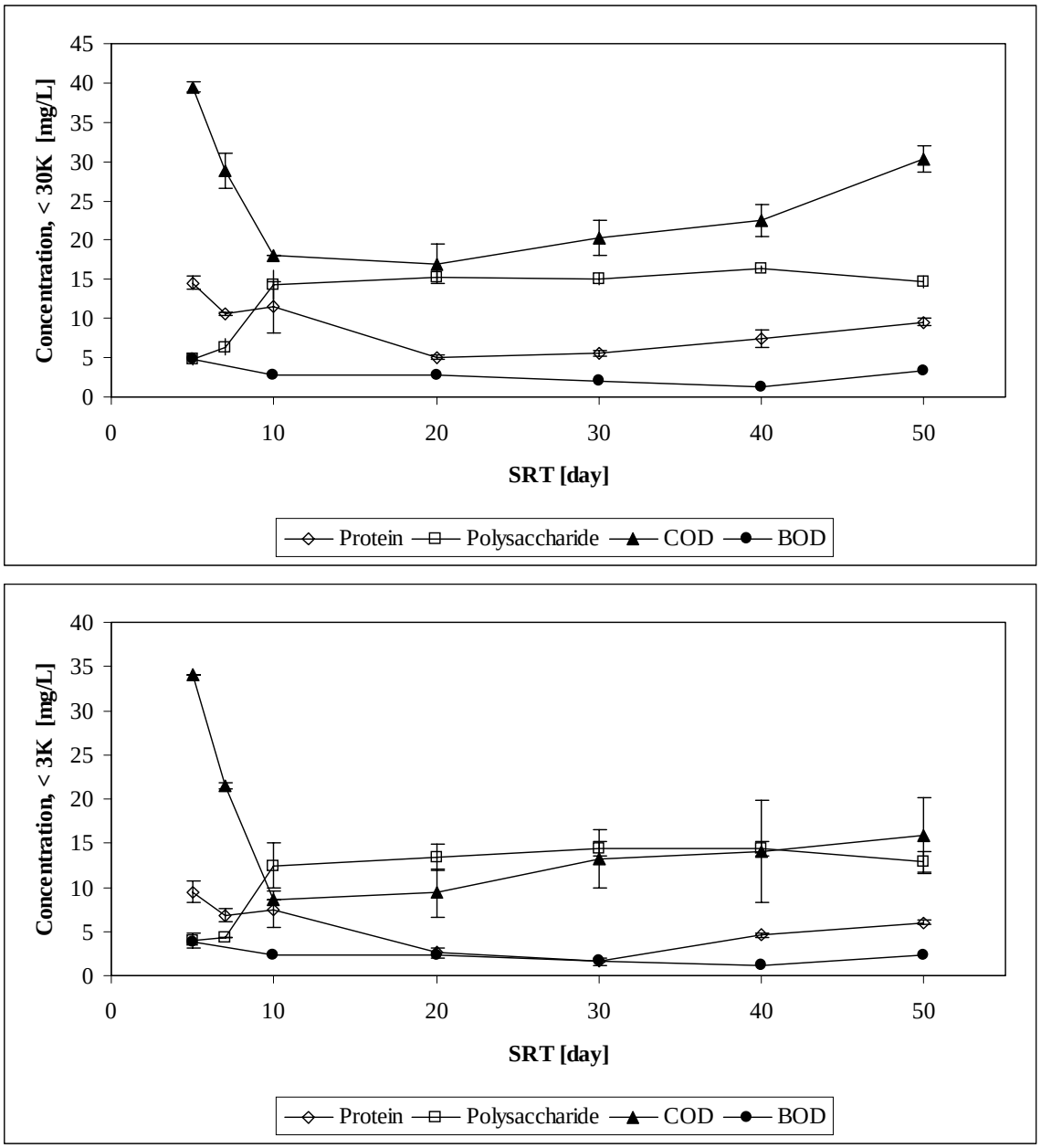


Figure 3-Effect of SRT on solution protein, solution polysaccharide, solution COD and solution BOD in ultrafiltered samples (< 30K and < 3K).

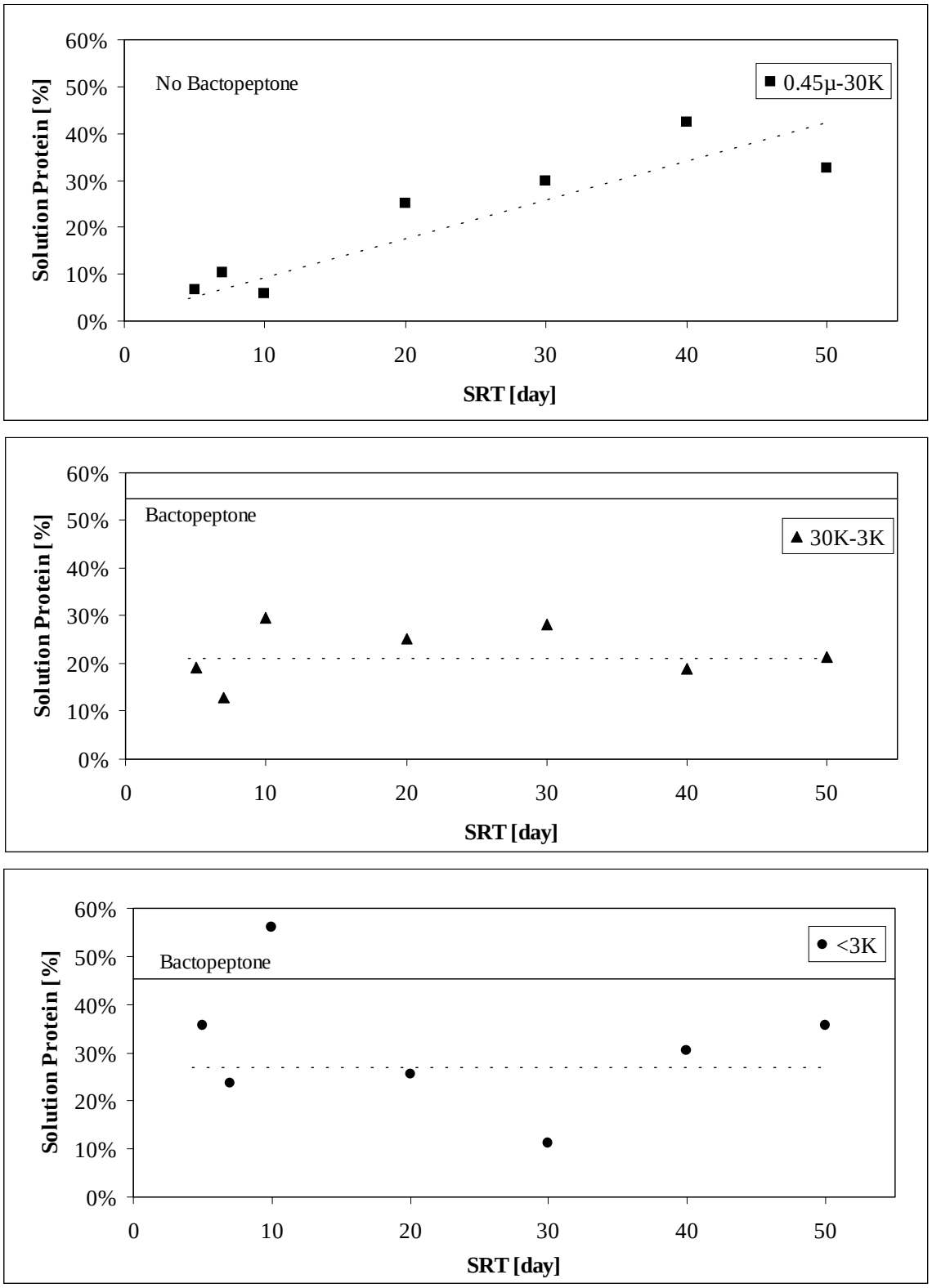


Figure 4- Effect of SRT on solution protein size fractions expressed as percentage of total (1.5 micron).

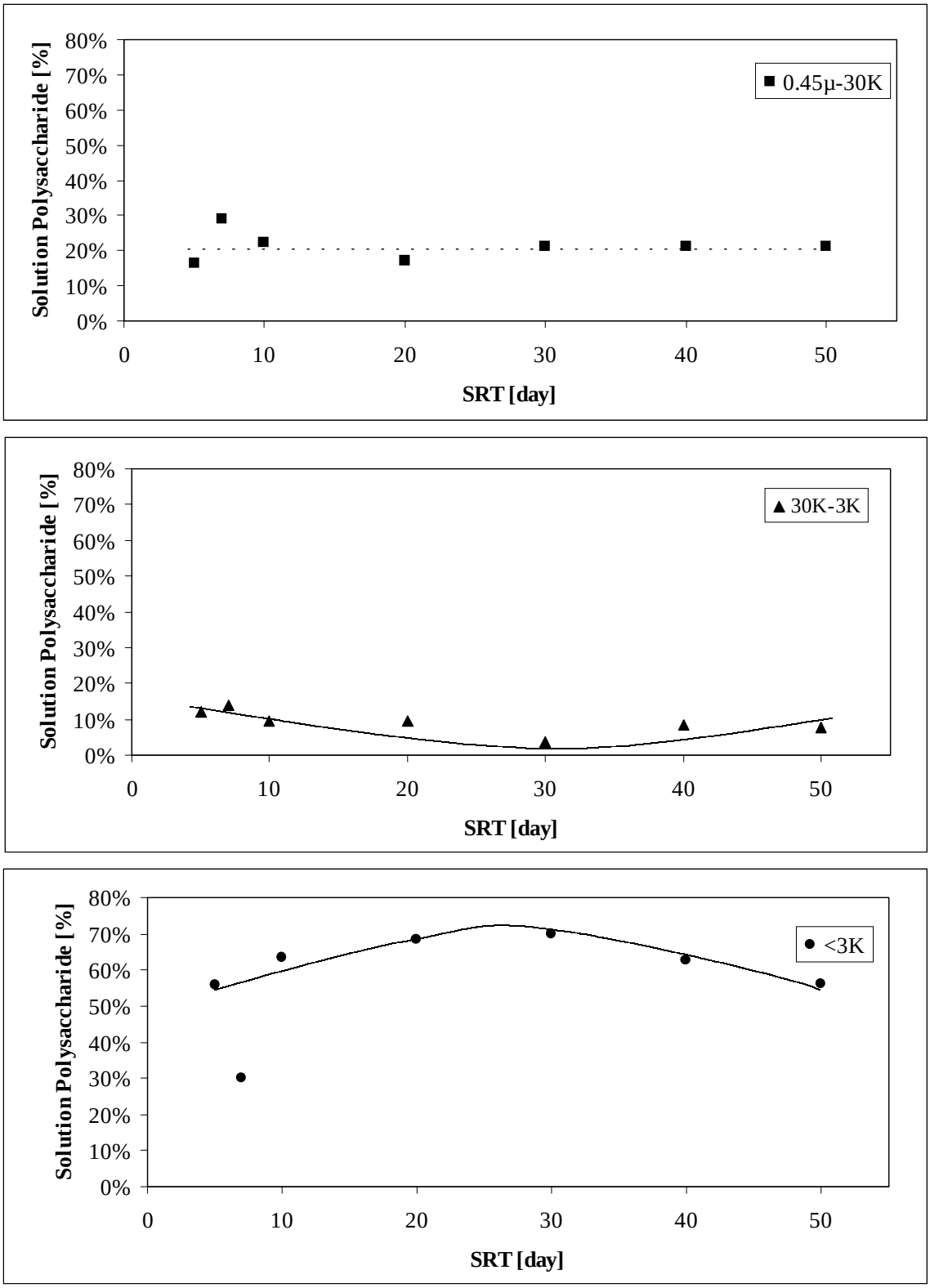
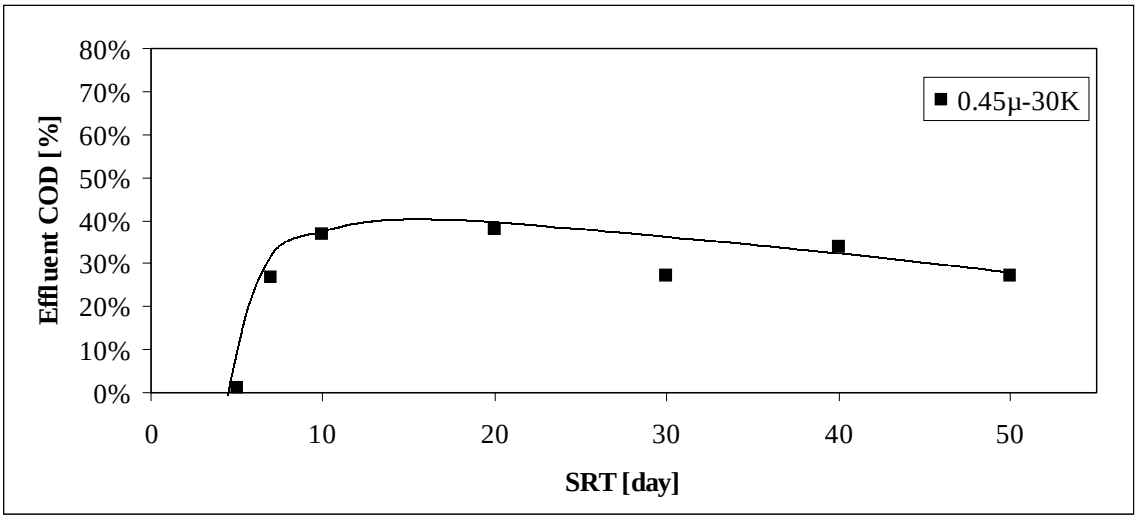
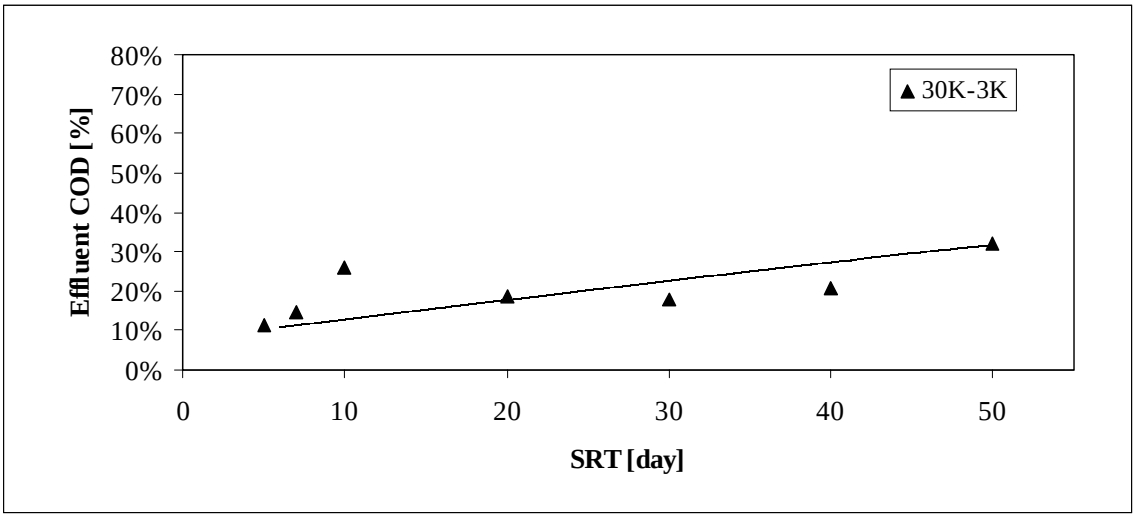


Figure 5- Effect of SRT on solution polysaccharide size fractions expressed as percentage of total (1.5 micron).





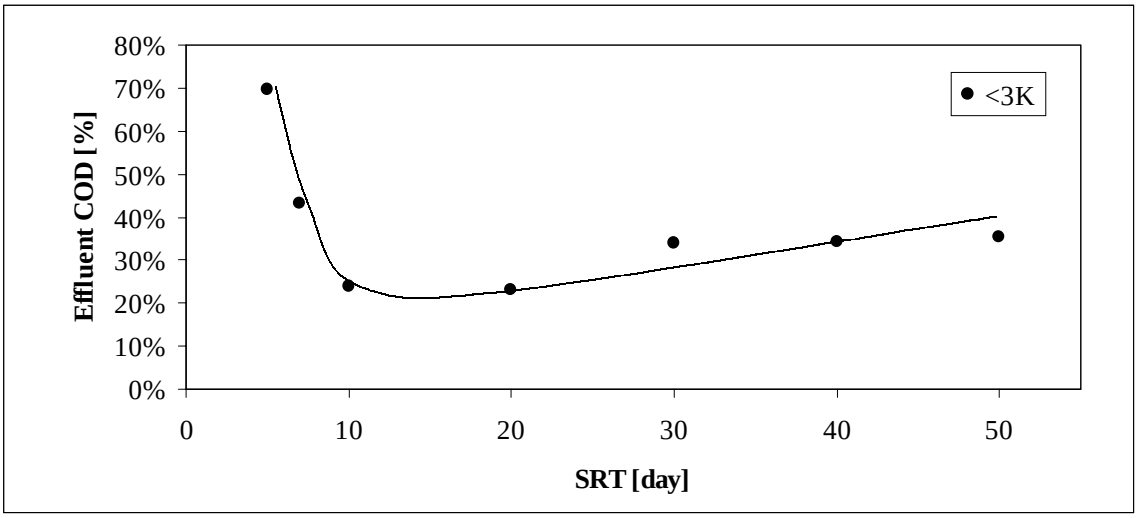


Figure 6- Effect of SRT on effluent COD size fractions expressed as percentage of total (1.5 micron).

Solution Protein, Solution Polysaccharide and Effluent COD Size Fractions

The organic matter fraction retained by a 1.5 μ glass microfiber filter is usually considered volatile suspended solids. In this study, therefore, the fraction passing through a 1.5 μ glass microfiber was considered part of the solution phase. The total solution fraction passing through the liquid portion of this membrane was used to measure solution protein, solution polysaccharide, effluent COD and effluent BOD. In wastewater treatment, often only the organic matter passing through a 0.45 μ filter is considered soluble. The percentage solution protein, solution polysaccharide and effluent COD in the soluble size fractions 0.45 μ - 30K, 30K – 3K and less than 3K were compared with SRT.

As can be seen in Figure 4, the fraction protein found in size range 0.45 μ - 30K increased with an increase in SRT. The influent feed, Bactopeptone, did not contain any protein in this size range. Therefore, the proteins in this size range were most likely released from the activated sludge floc into solution. More of this protein (about 40%) was released at higher SRTs. At the higher SRTs, the amount of protein found in the less than 3K fraction was probably a product of hydrolysis of the larger molecular weight fraction. This is consistent with the hydrolysis of proteins seen by Murthy and Novak (in press) for aerobic digestion of waste activated sludge. The protein fraction in the 30K – 3K range is fairly constant at about 20% for all SRTs monitored.

The feed to the laboratory activated sludge system did not contain any polysaccharides. Only small concentrations of polysaccharide were found in the higher size fractions (Figure 5). Most of the polysaccharides appeared to constitute small polymer chains or oligosaccharides in the less than 3K molecular size fractions. The small decrease in polysaccharides in the less than 3K fraction at higher SRT was offset by an increase in the 30K – 3K fraction. The presence of polysaccharides in the larger size fractions may be due more to association with proteins in the higher molecular weight fractions rather than the presence of larger size polysaccharide molecules.

The COD initially dropped between SRT of 5 to 10 days (Figure 6). Corresponding with the increase in polysaccharide in the less than 3K fraction, there was an increase in effluent COD. An increase in effluent COD was observed in the 30K – 3K

fraction, while the COD appeared fairly constant at higher SRTs in the 0.45 μ - 30K fraction.

Conclusions

For the study conducted, a large fraction of effluent COD was found to be extracellular or soluble microbial product. Proteins released from the floc tended to be larger molecules (0.45 μ - 30K), the hydrolysis of which produced smaller molecular fractions (< 3K). Polysaccharides tended to be smaller polymer molecules or oligosaccharides (< 3K). The release of polysaccharide increased with an increase in SRT. In this study, the lowest solution proteins were found in the 20-30 days SRT range, and the lowest effluent COD occurred in the 10-20 days SRT range. The effluent COD in these activated sludge systems, especially at higher SRTs, was more a result of extracellular microbial product released from the floc rather than residual influent substrate. Residual readily biodegradable soluble substrates such as acetate and most proteins are unlikely to be found in properly functioning activated sludge systems.

The implications of this study is important to activated sludge systems (including membrane systems) operating at very high SRTs, where accumulation of extracellular microbial products (EMP) may take place. In membrane systems, this accumulation of EMP may result in biofouling problems.

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CHAPTER 6

MESOPHILIC AERATION OF AUTOTHERMAL THERMOPHILIC AEROBIC DIGESTER (ATAD) BIOSOLIDS TO IMPROVE PLANT OPERATIONS

Sudhir N. Murthy, John T. Novak, R. David Holbrook, Fred Sukovitz

Abstract

The autothermal thermophilic aerobic digester (ATAD) has been observed to exhibit a higher polymer demand for acceptable dewatering when compared to conventional mesophilic aerobic digestion. Foaming episodes have occurred in the activated sludge process reactors and recycling of the dewatered centrate. Field studies indicated that an increase in thermophilic detention time promoted the release of proteins and polysaccharides from the biosolids into the bulk solution with corresponding increases in cationic polymer demand and dewatered sludge filtrate COD. These biopolymers appeared to be the primary cause of in-plant foaming. Tests indicated that mesophilic aeration reduced the polymer demand necessary for acceptable dewatering through removal of protein and polysaccharide from solution. Reduction in polymer demand after aeration appears to depend on both thermophilic and mesophilic aerobic detention times, while the dewatered cake solids appeared not to be affected.

Keywords

ATAD, digestion, activated sludge, dewatering, biopolymer, protein, polysaccharide, cation, conditioning, mesophilic aeration.

Introduction

Autothermal thermophilic aerobic digestion has been utilized for biosolids stabilization in Europe for over two decades and has seen a renewed interest in the United States in the past few years. The process has been competitive in small (0.3 MGD) to medium sized (15 MGD) plants requiring pathogen destruction of their biosolids. The trademark of the ATAD process is that digestion is carried out at thermophilic temperatures (50 - 65°C) with relatively short hydraulic retention times of 6-8 days. These elevated temperatures are obtained through heat released by the destruction of volatile solids during the digestion process. A minimum influent solids concentration (typically 4 - 5%) is required as well as efficient aeration, mixing, foam control and heat retention. Design fundamentals and operational experience of the ATAD process have been discussed elsewhere (USEPA, 1990; Schwinning *et al.*, 1993; Schwinning *et al.*, 1997).

In an effort to reduce transportation, handling and disposal costs of treated biosolids, a large number of wastewater treatment facilities utilize some type of dewatering process. For the dewatering process to be effective, chemical conditioning of the biosolids is necessary. Since one of the goals in dewatering biosolids is to reduce overall operational costs, selecting the correct polymer for conditioning is critical. Past experience has shown that the conditioning requirements for biosolids treated with conventional, mesophilic aerobic digestion are approximately $20–30/dry ton of solids, and with mesophilic anaerobic digestion are approximately $30–40/dry ton of solids.

Prior experience with the dewatering of thermophilic aerobically digested biosolids is limited. Few European ATAD facilities utilized dewatering since the majority practiced liquid land application (Schwinning *et al.*, 1997). One of the first ATAD plants to employ dewatering is located in Banff, Canada. Although there was some early difficulty, the plant personnel tested and adjusted different conditioning agents until acceptable dewatering performance was obtained. Vik and Kirk (1993) report a substantial improvement in the cake solids after switching from mesophilic

aerobic digestion to the ATAD process at the Grand Chute, Wisconsin facility. This plant was able to increase the dewatered solids content from 16 to 27% after the ATAD achieved steady-state operation.

The College Station, Texas ATAD system began operation in November, 1995. The ATAD system replaced a conventional mesophilic aerobic digestion process and used an existing centrifuge for dewatering the treated biosolids. Prior to the start-up of the ATAD system, polymer conditioning costs for dewatering had averaged approximately $25/dry ton of solids. Almost six months after start-up, the polymer conditioning cost had increased to over $200/dry ton of solids (Burnett *et al.*, 1997). Plant operators had also noticed a relation between foaming episodes on the activated sludge basins and recycling of the centrate during periods of dewatering.

The continuing operational problems of the College Station, Texas, plant associated with handling of the treated biosolids prompted a rigorous examination of the ATAD process. The objective of this study was to isolate the cause of the high polymer demand and in-plant foaming, and to improve plant operations by addressing these factors.

Methods and Materials

Approach

Conditioning and dewatering tests on biosolids from College Station, Texas, and Princeton, Indiana were either conducted in the field or collected in the field and shipped to Virginia Tech for study in the laboratory.

Reactor Profile

The biosolids were analyzed across the reactor process train at both College Station, Texas and Princeton, Indiana. The College Station, Texas, digestion process consisted of a thickener with three ATADs in series. The detention time in each ATAD was 2.3 days. The temperature in the ATADs averaged 34 $^{\circ}$C, 49 $^{\circ}$C and 59 $^{\circ}$C in progression down the treatment train. Therefore, the cumulative product of temperature

and detention time (°C-day product) after ATAD 1, ATAD 2 and ATAD 3 were 78 °C-day, 191 °C-day and 327 °C-day, respectively. The biosolids from College Station, Texas was mesophilically aerated for 25 days in two holding tanks. The detention time in Holding Tank 1 was 20 days, and the detention time in Holding Tank 2 was 5 days.

The Princeton, Indiana, digestion process consisted of a thickener with two ATADs in series. The detention time in ATAD 1 and ATAD 2 was 7.4 days each. The temperature in the ATADs averaged 52 °C and 50 °C, respectively. Therefore, the cumulative °C-day product after ATAD 1 and ATAD 2 were 385 °C-day and 755 °C-day, respectively. The sludge from ATAD 1 and ATAD 2 were mesophilically aerated (20 °C) in the laboratory for 15 days.

Analytical Approach

Protein, polysaccharide, COD, cations, anions, conditioning and dewatering analyses were performed at each stage of the ATADs for the two plants. Analyses were performed after mesophilic aeration for College Station, Texas and for the laboratory experiments for Princeton, Indiana.

Conditioning tests were performed on Princeton, Indiana, and College Station, Texas, biosolids for each reactor in series across the process train. The conditioning agent was a high molecular weight cationic polymer flocculant (Nalco 9909).

Dewaterability was measured using a capillary suction time device and a belt filter press wedge zone simulator. Cake solids were obtained from the wedge zone simulator at optimum conditioning dose.

Cations and anions were measured to determine their effect on floc properties and dewaterability. Total iron was measured in the centrate from the ATADs of College Station, Texas.

The biosolids were microscopically examined to determine if foam-causing *Nocardia* was present. The microorganism was not found in substantial numbers in the biosolids analyzed. The conditioned filtrates were therefore aerated to visually monitor for foaming.

Analytical Methods

ATAD Biosolids Analyses

Gravity solid-liquid separation of the ATAD biosolids could not be achieved. The biosolids were therefore centrifuged at 8,000 x g to separate the solids from the solution. The centrate was then filtered using a 1.5 µ glass microfiber filter commonly used for suspended solids measurement. The filtered centrate was analyzed for solution protein, solution polysaccharide, solution COD, solution iron, cations and anions.

ATAD Filtrate Analyses

The conditioned sludge filtrate was filtered through a 1.5 µ glass microfiber filter to exclude solid particles. The sample was analyzed for filtrate proteins, filtrate polysaccharides and filtrate COD.

Solution Protein and Polysaccharide Analysis

Protein was measured using the Hartree (1972) modification of the Lowry *et al.* (1951) method. Polysaccharides were measured using the method of Dubois *et al.* (1956). Protein standards were prepared with bovine serum albumin, and polysaccharide standards were prepared with glucose.

COD Analysis

Soluble COD was analyzed using Method 5220C of *Standard Methods* (1995).

Cation and Anion Analysis

Sodium, potassium, calcium, magnesium and ammonium ions were quantified using a Dionex Ion chromatograph with a CS12 column and conductivity detector (Dionex 2010I) with self-regenerating suppression of the eluent. Methane sulfonic acid (20 mM) was used as the eluent at a flow rate of 1.0 ml/min.

Sulfate and phosphate were monitored using a Dionex ion chromatograph with AS4A-SC column and conductivity detector with self-regenerating suppression of eluent.

A mix of sodium bicarbonate (1.7 mM) and sodium carbonate (1.8 mM) was used as the eluent at a flow rate of 2 ml/min.

Solution iron was measured using spectrophotometric analysis. The centrate was filtered through a 1.5 μ filter before analyzing for total iron as described in Method 3500-Fe D of *Standard Methods* (1995).

Dewatering Properties and Polymer Conditioning

Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) was analyzed using Method 2540D and 2540E of *Standard Methods* (1995) respectively. The dewatering properties were measured using capillary suction time (CST) using Method 2710G of *Standard Methods* (1995).

Laboratory tests were also conducted using a belt filter press wedge zone simulator (WZS) developed by Arus-Andritz company to simulate gravity drainage and dewatering using low pressures. The WZS was calibrated to apply a pressure of 30 psi for the tests. The apparatus consisted of a pneumatic cylinder attached to a wooden frame, mounted over a box type dewatering chamber. A 200 mL conditioned sludge sample was poured into the dewatering chamber, a square Plexiglas box, 3" x 3" and 3 1/8" deep. The bottom of the box was drilled with 1/8" holes to allow for filtrate drainage. The bottom was covered with a piece of belt filter cloth. The device was operated as described by Novak *et al.* (1993). The authors have demonstrated that the dewatering properties from this device is similar to a full-scale belt filter press. Samples were analyzed for cake solids.

Polymer conditioning tests were performed using a high molecular weight cationic polymer (Nalco 9909) at 1% stock concentrations. Optimum polymer dose was determined using the CST device and reported as g/kg dry sludge (DS). The optimum polymer dose reflects conditioning at minimal shear conditions. The actual optimum conditioning dose may be higher and can be appropriately calibrated based on the shear in the dewatering device (Murthy and Novak, 1997; Novak *et al.*, 1993; Novak and Lynch, 1990).

Results And Discussion

Operational Results

To satisfy the volatile reduction criteria of 38% (USEPA, 1990) in ATADs, Kelly *et al.* (1993) suggested a 400 °C-day product. Figure 1 shows the volatile solids reduction in the process units at College Station, Texas. As seen in the figure, an excess of 37 % volatile solids reduction was achieved in the three reactor system. The ATAD reactors from College Station, Texas, had a 327 °C-day product and nearly achieved the volatile solids reduction criteria. Additional removal occurred in the mesophilic aerobic holding tanks. Total volatile solids reduction was greater than 50% for the combined thermophilic-mesophilic process. This reduction of volatile solids was obtained with a 7 and 25 day hydraulic retention time in the ATAD reactors and the mesophilically aerated holding tanks, respectively. Figure 1 demonstrates the ability of ATAD reactors to rapidly destroy volatile solids. A small decrease in the total solids content occurred with a reduction of volatile solids.

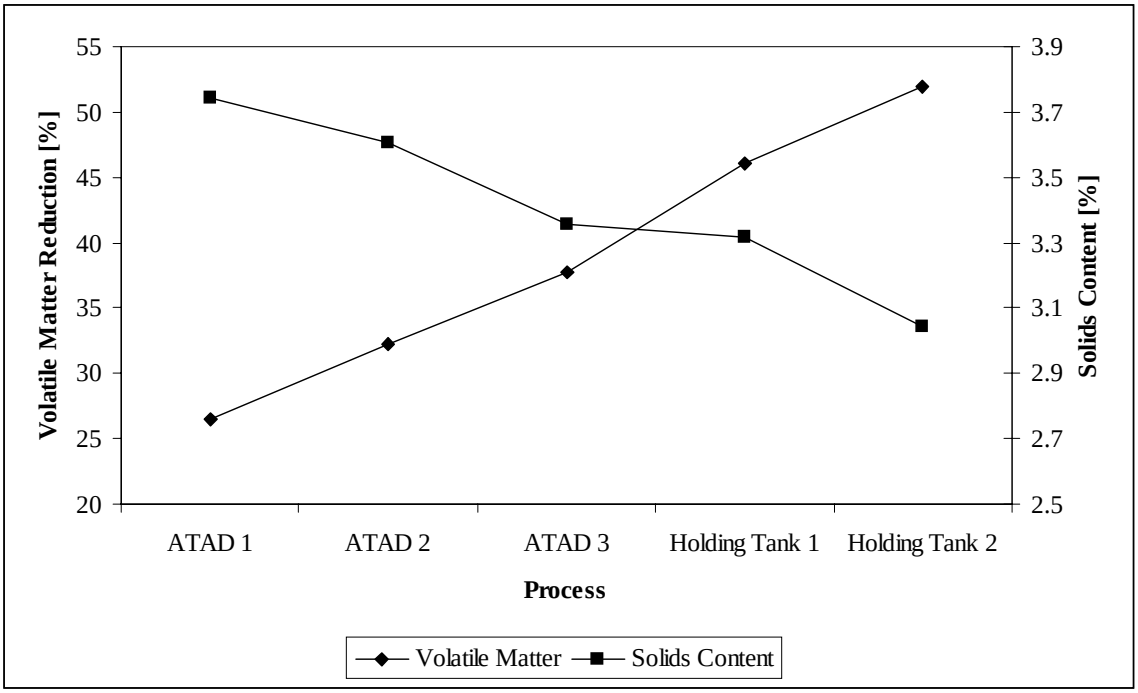

Figure 1-Volatile matter reduction at College Station, Texas.

Anions and Iron Analyses

Figure 2 presents the changes in phosphate, sulfate and total iron in the ATAD process train at College Station, Texas. As more volatile solids are destroyed, cellular matter will be released into the bulk solution, increasing the phosphate concentration throughout the ATAD reactor series.

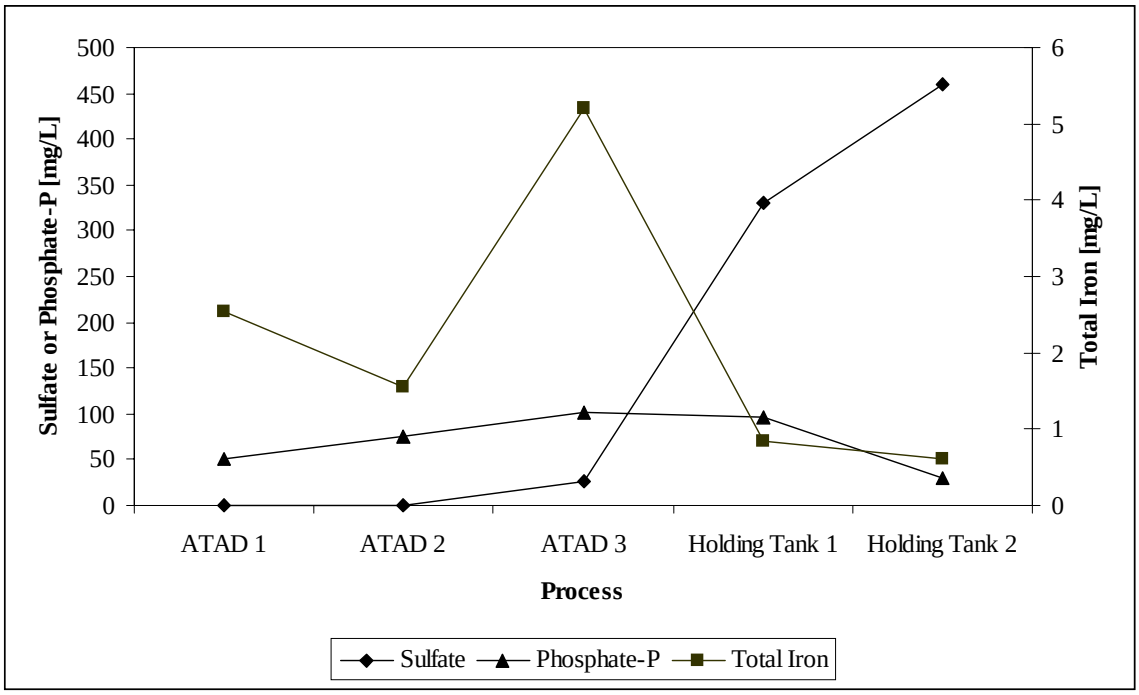

Figure 2-Sulfate, phosphate and total iron in solution at College Station, Texas.

The sulfate profile indicates that reducing conditions existed in ATAD 1 and ATAD 2 at College Station, Texas. However, as the biosolids become more stabilized and the oxygen uptake decreased through the system, the oxidizing potential of the reactor increased resulting in oxidation of sulfide to sulfate. The sulfate concentration increased substantially within the mesophilic holding tanks. Kelly *et al.* (1993) have indicated that, for the ATAD systems they studied, the redox potential was usually in the range of 0 to –300 mV. The sulfate reducing and sulfide oxidizing conditions found in the College Station, Texas, ATAD are within this redox potential range.

The fate of the iron in solution may also reflect the oxidizing potential of the environment. Initially, iron is removed from solution. This removal may be due to reduction to the ferrous state and subsequent precipitation as ferrous sulfide (Nielsen *et al.*, 1998). The sulfate production in ATAD 3 may release some of the iron into solution. Oxidizing conditions in the two holding tanks may result in formation of insoluble oxidized iron species and therefore disappearance from solution. The removal of total iron from the solution of the holding tanks coincides with protein removal (Table 5). The concentration of iron in the floc may actually be much larger than that observed in solution, and the iron may participate in protein removal from solution through coagulation reactions occurring in the floc and in the solution. The coagulation processes that may involve iron are explained in greater detail in Murthy *et al.* (submitted).

Cation Analysis

Higgins and Novak (1997a, b) have shown that cations have a major impact on the dewatering properties of biosolids. Divalent cations such as calcium and magnesium participate in charge bridging mechanisms with predominantly anionic biopolymer molecules. Monovalent ions such as sodium, potassium and ammonium ions can interfere with charge bridging mechanisms occurring in the floc. The presence of divalent cations in solution is indicative that biosolids will dewater well. On the other hand, the presence of monovalent ions in the solution is indicative of poorly dewatering biosolids. Higgins and Novak (1997b) arrived at a monovalent to divalent equivalent ratio (M/D) to evaluate the effect that cations may have on dewatering properties. They found that when M/D was greater than 2 the biosolids dewatered poorly. In general, a higher M/D is indicative of poorly dewatering biosolids, whereas the reverse holds for a low M/D.

Table 1 and Table 2 summarize the changes in cations during digestion for College Station, Texas, and Princeton, Indiana. Figure 3 shows the cation data for College Station, Texas. While the release of sodium and potassium ions increased with an increase in digestion time, and is indicative of the progress of the digestion process, the calcium and magnesium ions were removed from solution. These observations are consistent with results from an earlier study (Murthy and Novak, in press).

Table 1-Typical cation concentration at College Station, Texas.

Location	Sodium (mM)	Potassium (mM)	Magnesium (mM)	Calcium (mM)	Ammonium-N (mM)
Pre-ATAD	12.7	1.4	0.5	1.3	5.4
ATAD 1	13.0	2.4	0.9	2.4	32.0
ATAD 2	13.9	2.5	0.7	2.0	42.1
ATAD 3	13.3	2.5	0.3	1.2	45.1
Holding Tank 1	13.4	2.3	0.2	1.4	21.7
Holding Tank 2	14.9	2.5	1.1	4.3	7.5

Table 2-Typical cation concentration at Princeton, Indiana.

Location	Sodium (mM)	Potassium (mM)	Magnesium (mM)	Calcium (mM)	Ammonium-N (mM)
Pre-ATAD	2.3	4.4	4.1	3.0	7.2
ATAD 1	2.6	6.3	0.2	1.8	47.2
ATAD 2	4.4	6.8	0.1	1.5	48.4

The removal of magnesium from solution is thought to be partly due to struvite precipitation in the digesters as observed by plant operators. The removal of calcium from solution is perhaps due to strong interactions between the divalent ion and the extracellular biopolymers in the floc. A smaller concentration of the divalent ions in solution may be indicative of not only lower initial divalent ion concentration but also greater extracellular matter.

Due to the high operating temperature, nitrification does not take place in the ATAD process. The release of ammonium ions is due to the absence of nitrification in the thermophilic process. However, as the biosolids are cooled in the aerated holding tanks, there is a substantial decrease in the ammonium ion concentration. Subsequent sampling has shown that the reduction in ammonium ion can be attributed primarily to nitrification (data not shown).

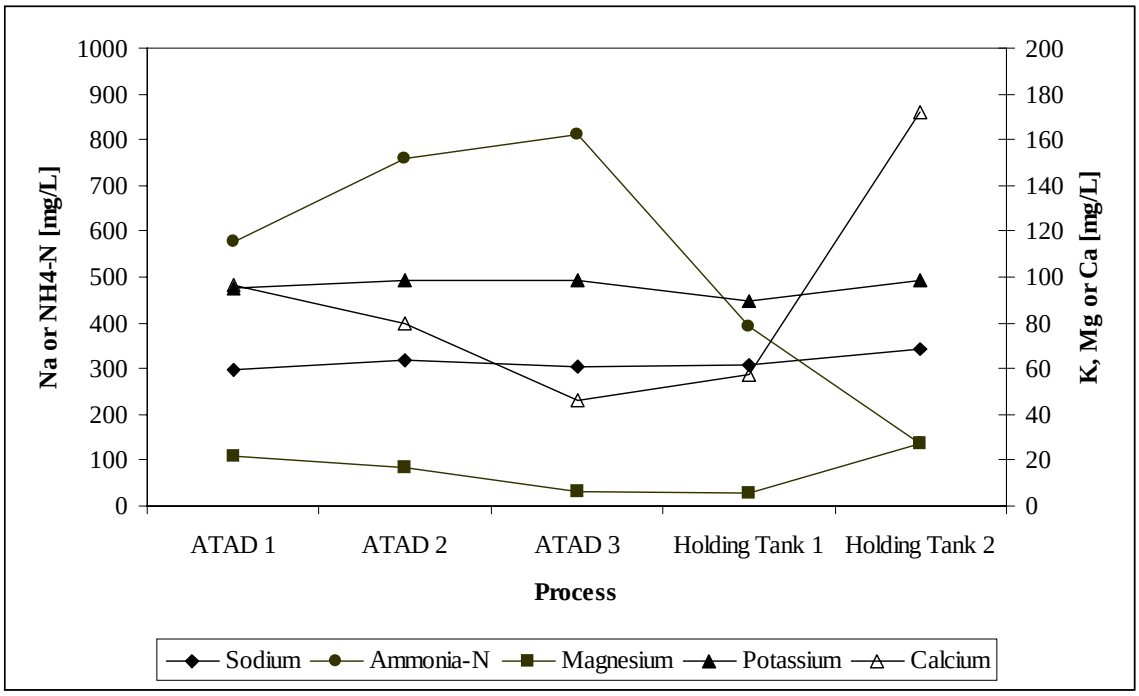

Figure 3-Cations at College Station, Texas.

Figure 4 shows the trends in protein release with ammonia-N release. Although there may be multiple reasons for the increase in concentration of protein in solution, the ammonium ion concentration may contribute to protein release from flocs and a subsequent increase in polymer conditioning demand.

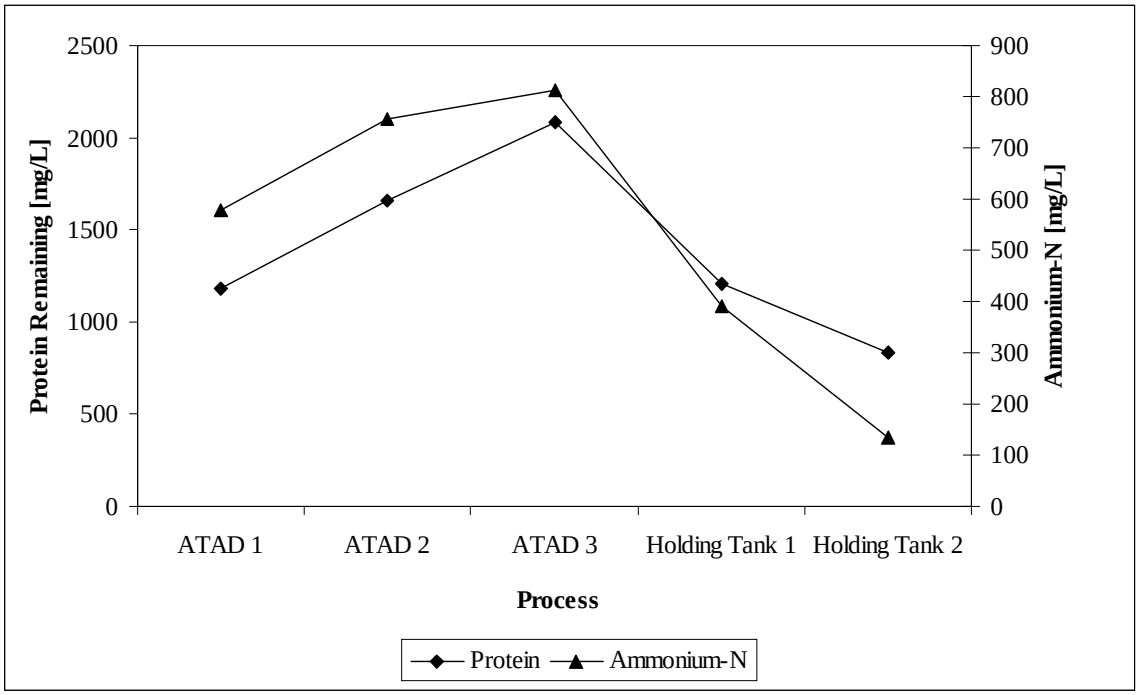

Figure 4-Relationship between solution protein and ammonia-N at College Station, Texas.

Monovalent to Divalent Equivalent Ratio (M/D)

The M/D across the process train for College Station, Texas, and Princeton, Indiana, is provided in Table 3 and Table 4. As shown in the tables, the M/D in solution depended on the unit process, with the ammonium ion concentration having a major impact on the ratio.

An improvement in M/D was observed with mesophilic aeration (Table 3). Mesophilic aeration results in a decrease in ammonium ions (nitrification) and an increase in divalent ions in the solution, decreasing the M/D. The reason for the increase in divalent ions is not clear, but could be due to the degradation of the proteins that were in solution or in the biosolids.

Table 3- Monovalent/Divalent equivalent ratio for process units at College Station, Texas.

Location	M/D with NH_4-N (eq/eq)	M/D without NH_4-N (eq/eq)
Pre-ATAD	5.6	4.1
ATAD 1	7.2	2.3
ATAD 2	10.9	3.1
ATAD 3	21.4	5.6
Holding Tank 1	11.2	4.7
Holding Tank 2	2.3	1.6

Table 4- Monovalent/Divalent equivalent ratio for process units at Princeton, Indiana.

Location	M/D with NH_4-N (eq/eq)	M/D without NH_4-N (eq/eq)
Pre-ATAD	1.0	0.5
ATAD 1	14.2	2.3
ATAD 2	18.2	3.4

Biopolymer and COD Analysis

Digestion results in consumption of cellular material. The primary components of cellular matter are proteins and polysaccharides. Proteins are molecules that tend to be neutral or negatively charged at physiological pH (Moran *et al.*, 1994).

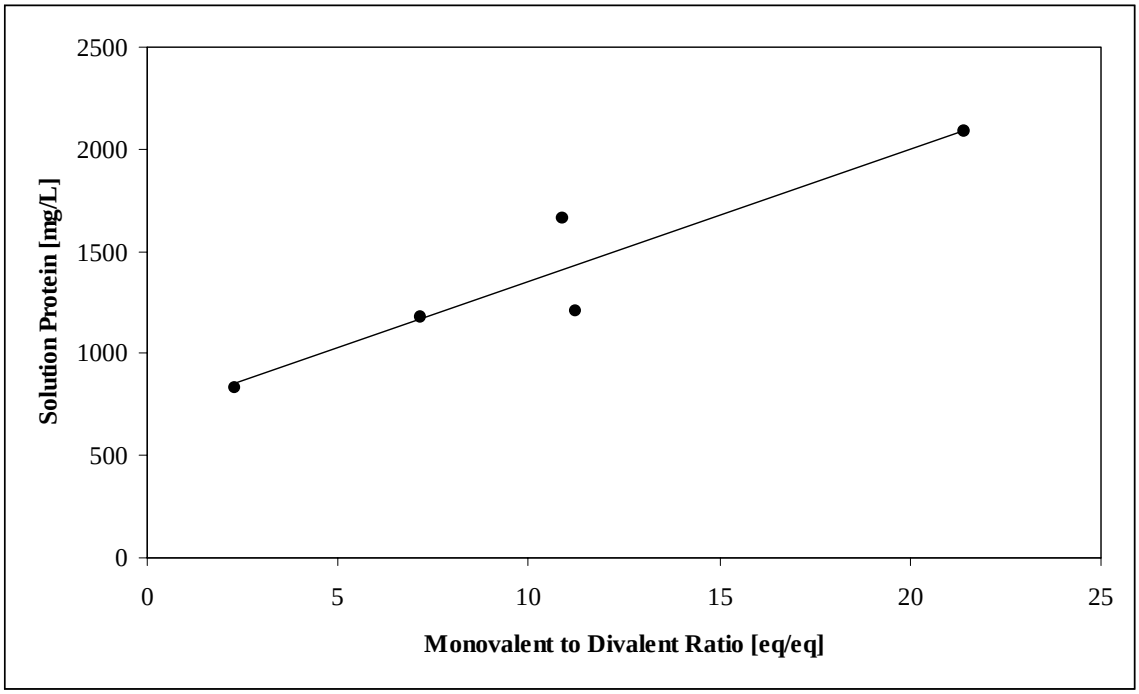

Figure 5-Effect of M/D on protein release.

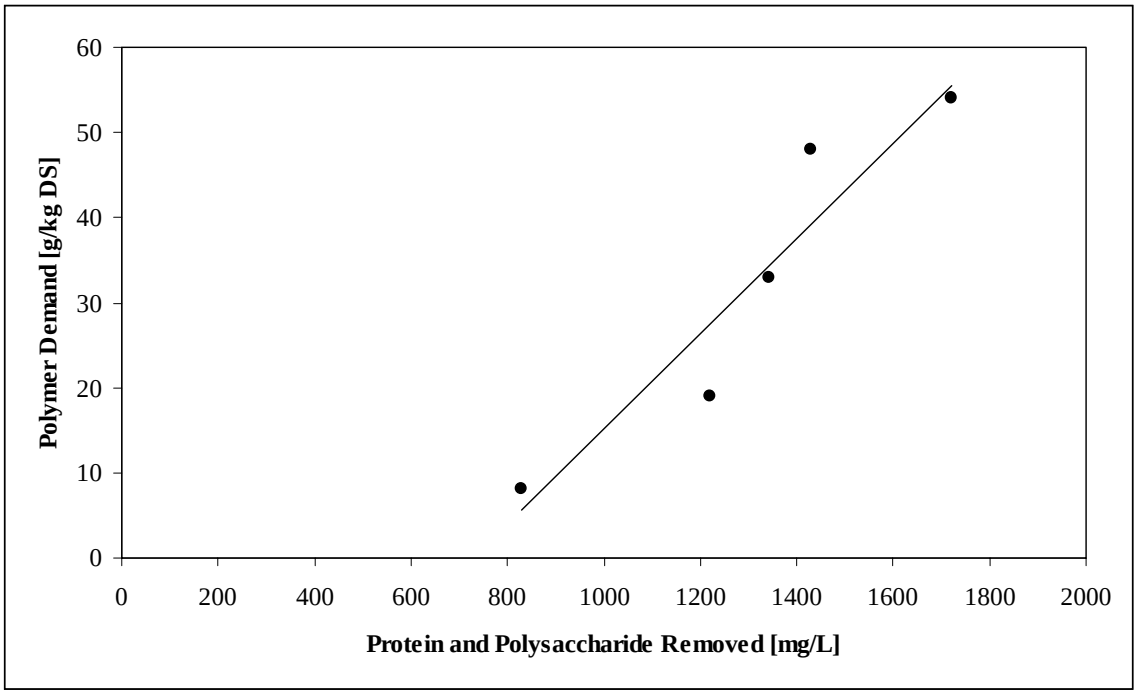

Figure 6-Effect of solution protein and polysaccharide on polymer demand.

The effect of M/D (including NH_4-N) on protein release is indicated in Figure 5. An increase in M/D resulted in an increase in protein release. The release of proteins is one of the primary cause of increase in cationic polymer conditioning demand (Figure 6). Therefore, an analysis of M/D in the thermophilic and mesophilic digestion process provides an indicator of biosolids conditioning properties in the digestion train.

Table 5- Temperature, detention time, protein, polysaccharide and COD for College Station, Texas ATAD reactors.

Location	Temperature (°C)	Detention Time (Days)	Protein (mg/L)	Polysaccharide (mg/L)	COD (mg/L)
Pre-ATAD	-	-	410	110	-
ATAD 1	34	2.3	1180	330	7060
ATAD 2	49	2.3	1660	570	8420
ATAD 3	59	2.3	2080	900	8620
Holding Tank 1	35	20	1210	740	3700
Holding Tank 2	30	5	830	1970	3460

Table 6- Temperature, detention time, protein, polysaccharide and COD for Princeton, Indiana ATAD reactors.

Location	Temperature (°C)	Detention Time (Days)	Protein (mg/L)	Polysaccharide (mg/L)	COD (mg/L)
Pre-ATAD	-	-	240	94	-
ATAD 1	52	7.4	2790	1690	9250
ATAD 2	50	7.4	3420	2020	10090

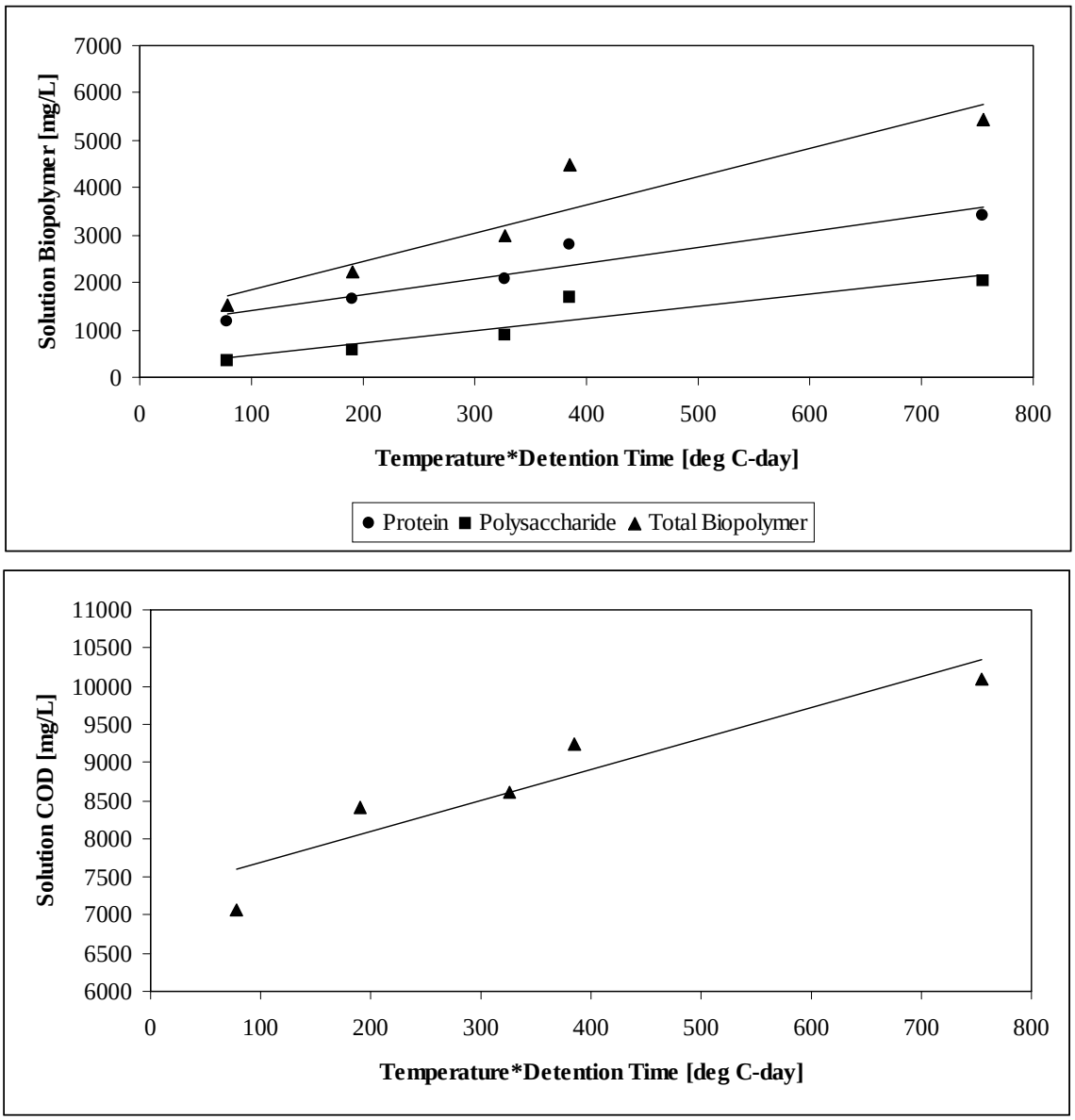

Figure 7-Effect of temperature-detention time product on protein, polysaccharide and COD release.

Table 5 and Table 6 show the release of solution protein and solution polysaccharide during thermophilic digestion at College Station, Texas and Princeton, Indiana. As can be seen in the tables, an increase in protein and polysaccharide was observed with an increase in digestion time. Associated with an increase in the solution biopolymers was an increase in solution COD. When combining the ATAD process data

from College Station, Texas, and Princeton, Indiana, it was observed that the biopolymer release was concomitant with an increase in detention time and temperature (Figure 7). Some of the variability in Figure 7 may be related to the initial M/D and the operations of the process (shear, oxygen etc.) at the two plants.

From Figure 7, the increase in solution COD and biopolymer can be limited by decreasing the $^{\circ}$C-day product. College Station, Texas, limits its detention time to 7 days (2.3 days per ATAD) with strict control of temperature. Cooling water is used to prevent overheating. Although College Station, Texas, possesses a high initial M/D, process controls have limited COD, protein and polysaccharide release. The ATAD process itself has consistently obtained close to 38% volatile destruction. Since holding tanks achieve USEPA regulatory requirements, higher degradation rates in the ATADs are not necessary and may be detrimental to process operations due to increased protein and polysaccharide release. The higher detention time for the Princeton, Indiana, ATADs (7.4 days per ATAD) results in a much higher release of biopolymers and COD than at College Station, Texas.

Figure 8 shows the relationship between COD and biopolymer release (sum of protein and polysaccharides) for College Station, Texas, and Princeton, Indiana. The y-intercept for Figure 8 is 6,500 mg/L. Although the relationship between COD and biopolymer release is fairly linear in the ATADs, the y-intercept indicates that there may be a substantial fractional oxygen demand (not due to protein and polysaccharide) that is still not determined. Part of this fractional oxygen demand may be due to sulfides oxidized by the COD test. However, there may be an organic fraction that is different and unique to the thermophilic processes. This fractional COD (organic or inorganic), shown in Figure 5, is considerably diminished during mesophilic aeration (Holding Tank 1 and Holding Tank 2) which is consistent with sulfide oxidation in the holding tanks. The mesophilic removal of the biopolymers and the COD not associated with biopolymers may largely eliminate odor causing compounds (sulfides, mercaptans, ammonia etc.) associated with anaerobic and thermophilic processes.

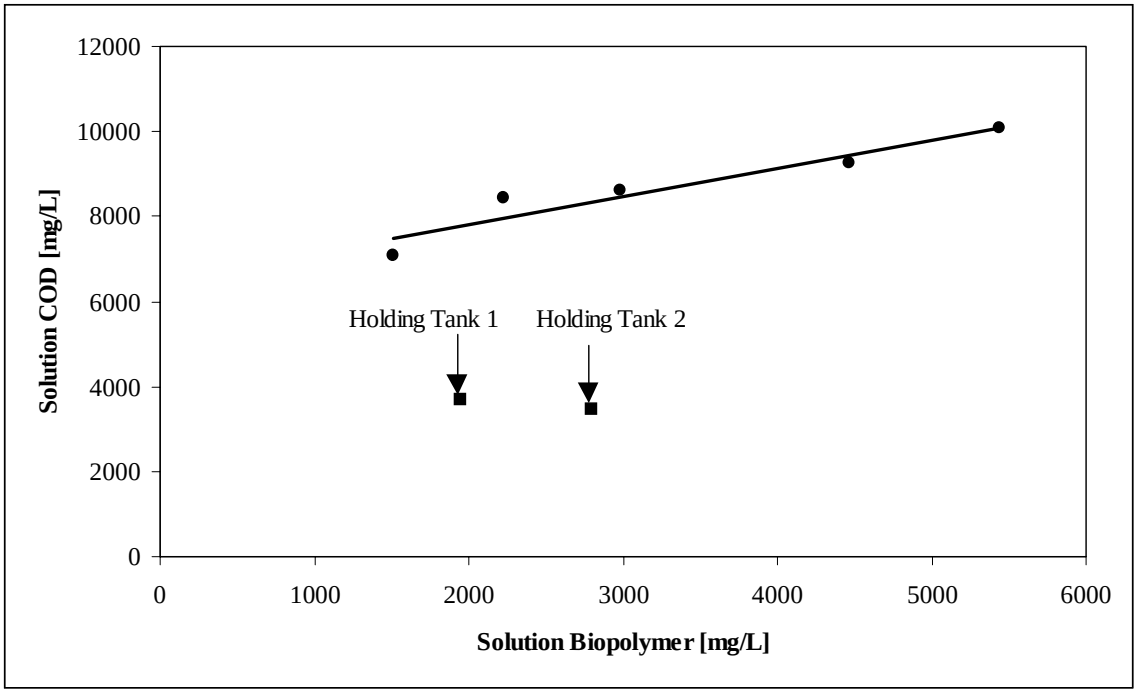

Figure 8-Relationship between COD and total biopolymer (protein and polysaccharide) for College Station, Texas and Princeton, Indiana.

Polymer Conditioning Tests

Biopolymer release has direct implications for cationic polymer conditioning demand. The polymer conditioning requirement using Nalco 9909 polymer for College Station, Texas ATADs and Princeton, Indiana ATADs are shown in Table 7 and Table 8. This cationic polymer was found in preliminary studies to be best suited for dewatering biosolids from ATAD processes. The polymer demand for Princeton, Indiana, ATADs is higher than that for College Station, Texas, due to the higher $^{\circ}$C-day product at Princeton, Indiana.

Table 7- Polymer demand and protein and polysaccharide for College Station, Texas ATAD reactors after conditioning with high molecular weight polymer flocculant (Nalco 9909).

Location	Polymer Demand (g/kg DS)	Protein After Conditioning (mg/L)	Polysaccharide After Conditioning (mg/L)	COD After Conditioning (mg/L)
ATAD 1	8	590	100	4110
ATAD 2	19	810	200	5760
ATAD 3	54	860	400	4340
Holding Tank 1	48	310	210	1500
Holding Tank 2	33	230	1230	1690

Table 8- Polymer demand and protein and polysaccharide for Princeton, Indiana ATAD reactors after conditioning with high molecular weight polymer flocculant (Nalco 9909).

Location	Polymer Demand (g/kg DS)	Cake Solids (%)	Protein After Conditioning (mg/L)	Polysaccharide After Conditioning (mg/L)	COD After Conditioning (mg/L)
ATAD 1	61	21.6	730	690	2960
ATAD 2	96	22.0	580	660	2800

The filtrate protein, polysaccharide and COD after conditioning is shown in Table 7 and Table 8. Considerable protein and polysaccharide removal was achieved by the cationic polymer flocculant. However, a large fraction was not removed. The protein, polysaccharide and COD remaining in solution comprise the in-plant filtrate recycle. A substantial reduction of the oxygen demand through mesophilic aeration (Table 7) reduces some of the air requirements in the aeration tanks during treatment. The reduction of the organic fraction also decreased surfactant associated foaming.

Table 8 shows cake solids obtained by a belt filter press wedge zone simulator. The cake solids obtained from the ATAD are usually higher than those obtained from other processes (Burnett *et al.*, 1997). However, the improvement of ATAD 2 over ATAD 1 for Princeton, Indiana, is small. A very high $^{\circ}$C-day product may therefore not produce substantially higher cake solids.

Analysis of the Foaming Problem

Filtrate from ATAD 3 and Holding Tank 2 of College Station, Texas were aerated to qualitatively investigate the effect of aeration/mixing on foaming. The filtrate from ATAD 3 generated considerably more foam than the filtrate from Holding Tank 2, indicating that mesophilic aeration reduced foam. The reduction in foam may be mainly due to the removal of proteins and other hydrophobic organics in the filtrate. The proteins have regions of hydrophobicity that along with hydrophilic polysaccharides may cause surface-active reactions in the flocs that result in foaming.

Field Study Summary

Mesophilic aeration improved polymer conditioning properties through the removal of biopolymers in solution. The improvement in conditioning properties may be due to several reasons. The oxidation of iron may cause surface associated precipitation of the biopolymer. The decrease in M/D through the oxidation of ammonium ions may allow for improved divalent charge bridging. The proteins in solution may undergo degradation under mesophilic conditions.

Table 9- Capillary suction time, protein, polysaccharide and COD for Princeton, Indiana ATAD reactors under mesophilic conditions.

Location	Time (Day)	Diluted CST (s)	Protein (mg/L)	Polysaccharide (mg/L)	COD (mg/L)
ATAD 1	0	2600	2780	1690	9250
ATAD 1	2	2700	2810	1600	8570
ATAD 1	5	2400	2650	1530	8450
ATAD 1	10	2000	2270	1270	7400
ATAD 1	15	1400	2020	1290	6160
ATAD 2	0	2600	3420	2020	10090
ATAD 2	2	2900	2850	1850	9990
ATAD 2	5	3200	2840	1850	9870
ATAD 2	10	2400	2810	1860	9520
ATAD 2	15	2300	2880	1540	8530

Princeton Laboratory Study

Laboratory experiments were conducted on biosolids obtained from the two ATADs from Princeton, Indiana. The biosolids were batch aerated at 20°C for 15 days. Upon aeration, ATAD 1 biosolids produced considerably less foam than the ATAD 2 biosolids. The amount of foam produced decreased over time, especially in ATAD 1. A corresponding decrease in protein, polysaccharide and COD was observed over the same period (Table 9).

Dewatering properties were measured as diluted CST (1:4 dilution). Improvements in dewatering properties were observed with an increase in detention. There was a considerably larger improvement in CST for ATAD 1 than ATAD 2. Reductions in protein, polysaccharide and COD were accomplished after 5 days of laboratory mesophilic detention time for ATAD 1.

It appears that recovery with respect to conditioning properties under aerobic conditions occurred more rapidly when thermophilic detention time was lower. Thermophilic conditions may result in a destruction of viable bacteria, both pathogenic and otherwise. An increase in thermophilic detention time may result in greater levels of cellular destruction, thus impeding recovery. An increase in thermophilic detention time will increase the time and decrease the extent of subsequent mesophilic aerobic recovery.

Conclusions

Studies were conducted to improve the performance of ATADs in the laboratory and in the field. Some of the concerns associated with ATADs are similar to those experienced by other digestion (thermophilic and anaerobic) processes and are outlined below:

- High polymer conditioning costs.
- In-plant and digester foaming.
- High filtrate recycle COD.
- Odors released during digestion.
- Recycle of nutrients (phosphate and ammonia) released during digestion.

The objective of this study was to identify the cause of some of these concerns and to identify means to minimize or eliminate them.

It was found that biopolymers released from the floc into solution during digestion were primarily responsible for the high polymer conditioning costs and in-plant foaming. The hydrophobic groups found in proteins and other hydrophobic organics along with relatively hydrophilic polysaccharides could produce surface-active conditions that generate foam. Additionally, the anionic biocolloids result in high cationic polymer conditioning demand. Removal of these biopolymers was instrumental in reducing in-plant foaming and cationic polymer demand.

These biopolymers, other volatile organic compounds and reduced inorganics result in high recycle COD and may cause some of the odors produced during the

digestion and processing of biosolids. The removal of these compounds would diminish these concerns.

The effect of mesophilic aeration on reducing polymer conditioning costs was investigated. Mesophilic aeration may be capable of reducing polymer costs through oxidation of iron and ammonia. Coagulation reactions may occur with oxidized iron. A favorable M/D is obtained through the removal of ammonium ions, thereby improving divalent charge bridging interactions. Greater interactions of biopolymer with the floc lead to smaller concentrations of biopolymer remaining in solution. Degradation of these biopolymers may occur in aerobic conditions.

Mesophilic aeration in a completely mixed mode is effective in removing biopolymers and COD and therefore reducing polymer conditioning demand and odor causing chemicals. Some of the nutrients are removed as struvite in the ATAD process. More phosphate removal occurs during mesophilic aeration. Ammonia-N is nitrified during aeration. Although still not confirmed for post-ATAD mesophilic aeration, pulsed aeration may result in some denitrification and alkalinity recovery. Pulsed aeration has been used in other mesophilic aerobic digestion processes (Daigger *et al.*, 1997) and could be used to increase alkalinity and reduce nitrogen recycle to the treatment process. This removal may be important for processes employing biological nitrogen removal in their process stream to reduce methanol or other substrate requirements.

Post-ATAD processing of biosolids may be crucial to the elimination of some of the concerns associated with anaerobic and thermophilic digestion. Mesophilic aeration of biosolids after thermophilic digestion may substantially reduce or eliminate all these concerns. Further study is required to investigate the effect of mesophilic aeration on purely anaerobic processes.

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CHAPTER 7

OPTIMIZING DEWATERING OF BIOSOLIDS FROM AUTOTHERMAL THERMOPHILIC AEROBIC DIGESTERS (ATAD) USING INORGANIC CONDITIONERS

Sudhir N. Murthy, John T. Novak, R. David Holbrook

Abstract

The biosolids obtained through the ATAD process require much higher polymer requirements then the conventional mesophilic process. The process is also associated with in-plant foaming due to the recycle of dewatered sludge filtrate containing high levels of COD and foam causing material. It was found that an increase in ATAD detention time and operating temperature resulted in an increase in the release of proteins and polysaccharides that caused a corresponding increase in cationic polymer demand, increase in dewatered biosolids filtrate COD and increase in in-plant foaming. Alternative chemical conditioners were used to reduce polymer demand and foaming. Coagulation of the biopolymers using ferric chloride or alum was extremely effective in reducing cationic polymer conditioning demand, dewatered cake filtrate COD and in-plant foaming. Ferric chloride and alum in laboratory experiments were also able to precipitate and remove phosphate, thus preventing its recycle to the influent of the plant.

Keywords

ATAD, digestion, activated sludge, dewatering, biopolymer, protein, polysaccharide, cation, conditioning, ferric chloride, alum.

Introduction

Autothermal thermophilic aerobic digesters (ATADs) stabilize biosolids at elevated temperatures of between 50-70 degrees Celsius. The process uses oxygen to accelerate volatile solids destruction under thermophilic conditions and pathogen destruction is achieved at the high temperatures used in this process. ATADs are mainly autothermal; the heat being produced by the endogenous microbial metabolism of biosolids during the digestion process.

A combination of temperature and detention time (degrees C x days or °C-day product) has been used to estimate volatile solids reduction and pathogen destruction. A 400 °C-day product is considered the minimum product (Kelly *et al.*, 1993) to achieve 38% volatile solids destruction as required by USEPA (1990). Pathogen destruction can be achieved at lower °C-day products. An increase in thermophilic detention time also lowers the specific oxygen uptake rates (SOUR) of the biosolids. Therefore, higher °C-day products will result in improved plant performance with respect to pathogen destruction, volatile solids reduction, and a lower SOUR.

ATADs have consistently produced higher dewatered cake solids than mesophilically digested biosolids (Vik and Kirk, (1993); Burnett *et al.*, 1997). However, it has been observed that dewatering properties as measured by capillary suction time (CST) deteriorates and cationic polymer demand increases with an increase in the ATAD °C-day product (Murthy *et al.*, submitted). Post-Mesophilic aeration following thermophilic digestion has proved successful in reducing polymer conditioning demand (Murthy *et al.*, submitted). Filtrate COD was considerably lower after mesophilic aeration and reductions in in-plant foaming were observed.

The objective of this study was to investigate if the addition of inorganic conditioning agents could enhance the benefits obtained from mesophilic aeration in an economic manner. The inorganic conditioning chemicals were tested to investigate their efficacy in improving biosolids dewatering and in reducing filtrate protein, polysaccharide and COD and associated in-plant foaming.

Methods and Materials

Approach

Conditioning and dewatering tests were conducted in the laboratory and in the field using biosolids from several publicly owned treatment works (POTW) which use ATADs. The tests were conducted for College Station, Texas; Princeton, Indiana; Surprise, Arizona and Titusville, Florida.

The College Station digestion process consisted of a thickener with three ATADs in series, followed by two mesophilic aerobic holding tanks. The Princeton digestion process consisted of a thickener with two ATADs in series. Analysis for protein, polysaccharide, COD, cations, anions, conditioning and dewatering were conducted at each stage of the ATADs for the two plants. The Surprise and Titusville biosolids were obtained at the end of the thermophilic digestion process for the two plants.

The conditioning tests were conducted to ascertain optimum polymer demand and cake solids that could be obtained from the different ATAD systems. Conditioning tests were performed on biosolids from College Station and Princeton for each reactor in series across the process train. Conditioning tests were performed using cationic polymer, alum and ferric chloride.

Dewaterability was measured using a capillary suction time (CST) device and a belt filter press wedge zone simulator. Shear tests were performed to determine the shear resistance of the biosolids after conditioning, before and after digestion.

Cations and anions were measured to determine their impact on floc properties and dewaterability. The cations measured included sodium, potassium, magnesium, calcium and ammonium ions.

Coagulation tests were performed for diluted Surprise centrate using ferric chloride at several concentrations to examine the coagulation mechanisms that may exist for the removal of soluble and colloidal protein and polysaccharide molecules.

The conditioned filtrates were analyzed for COD and were aerated to visually monitor for foaming. Analysis of biosolids for foam causing *Nocardia* was

microscopically examined. The microorganism was not found in substantial numbers in the biosolids analyzed.

Analytical Methods

ATAD Biosolids Analyses

Gravity solid-liquid separation of the ATAD biosolids could not be achieved. The biosolids were therefore centrifuged at 8,000 x g to separate the solids from the solution. The centrate was then filtered using a 1.5 μ glass microfiber filter commonly used for suspended solids measurement. The filtered centrate was analyzed for solution protein, solution polysaccharide, solution COD, cations and anions.

ATAD Filtrate Analyses

The conditioned sludge filtrate was filtered through a 1.5 μ glass microfiber filter. The sample was analyzed for filtrate proteins, filtrate polysaccharides and filtrate COD.

Solution Protein and Polysaccharide Analysis

Solution proteins and polysaccharides samples were measured using the Hartree (1972) modification of the Lowry *et al.* (1951) method. Polysaccharides were measured using the method of Dubois *et al.* (1956). Protein standards were prepared with bovine serum albumin, and polysaccharide standards were prepared with glucose.

COD Analysis

Solution COD was analyzed using Method 5220C of *Standard Methods* (1995).

Cation and Anion Analysis

Sodium, potassium, calcium, magnesium and ammonium ions were quantified using a Dionex Ion chromatograph with a CS12 column and conductivity detector (Dionex 2010I) with self-regenerating suppression of the eluent. Methane sulfonic acid (20 mM) was used as the eluent at a flow rate of 1.0 ml/min.

Phosphate-P was monitored using a Dionex ion chromatograph with AS4A-SC column and conductivity detector with self-regenerating suppression of eluent. A mix of sodium bicarbonate (1.7 mM) and sodium carbonate (1.8 mM) was used as the eluent at a flow rate of 2 ml/min.

Dewatering Properties and Polymer Conditioning

Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) was analyzed using Method 2540D and 2540E of *Standard Methods* (1995) respectively. The dewatering properties were measured using capillary suction time (CST) by Method 2710G of *Standard Methods* (1995).

Polymer conditioning tests were performed with high molecular weight cationic polymer at 1% stock concentrations (Nalco 9909 or Nalco PL250). Optimum polymer dose was measured using the CST device and reported as g/kg dry sludge (DS). The optimum polymer dose reflects conditioning at minimal shear conditions. The actual optimum conditioning dose will be higher and can be appropriately calibrated based on the shear in the dewatering device (Murthy and Novak, 1997; Novak *et al.*, 1993; Novak and Lynch, 1990).

The mixing intensity tests were conducted using a baffled chamber and a paddle attached to a motor capable of a high mixing intensity as described by Werle *et al.* (1984). The mixing device was calibrated so that the mean velocity gradient, G, could be related to the torque and the mixing speed using the viscosity of unconditioned biosolids. The conditioned biosolids deterioration under 600 s^{-1} and a range of mixing time was measured using the CST device.

Coagulation Study

Coagulation tests were performed using 1:40 diluted (1.5 μ filtered) Surprise centrate and iron chloride. The jar test was performed using six square-shaped jars individually stirred by a common motor. The test was conducted using ferric chloride at 0, 10, 20, 100, 200 and 400 mg/L simultaneously added to 500 mL diluted centrate. The solution was rapid-mixed for 1 minute at 100 rpm, followed by 30 minutes flocculation at 30 rpm. The solution was allowed to settle for one hour, after which turbidity, protein,

polysaccharide and COD were measured for the supernatant. Ultrafiltration using a 30,000 dalton (30K) and 3,000 dalton (3K) membrane (Amicon® YM30 and YM3 partly hydrophilic ultrafiltration membranes) was performed for jars coagulated with 0, 20 and 400 mg/L ferric chloride. The samples were analyzed for phosphate to evaluate the ability of iron chloride to remove the anion from the centrate.

Results And Discussion

Cation Concentration

A preliminary investigation was conducted to evaluate the cation concentration of the thickened (pre-ATAD) and final digested biosolids from three of the plants as indicated in Table 1 and Table 2. The three biosolids were characterized by different cation compositions. This variation may explain some of the difference in the digestion properties as predicted by Murthy and Novak (in press).

Higher concentrations of divalent cations are considered favorable since they reduce cationic polymer conditioning demand through charge bridging interactions that might occur in the flocs. On the other hand, sludges characterized by higher monovalent cations concentrations will tend to produce poorer dewatering biosolids (Higgins and Novak, 1997a, b).

Table 1-Thickened biosolids solution cation concentration.

Location	Sodium (mM)	Potassium (mM)	Magnesium (mM)	Calcium (mM)	Ammonium-N (mM)
College Station	12.7	1.4	0.5	1.3	5.4
Titusville	5.1	7.7	6.5	3.2	7.4
Surprise	5.8	3.7	3.0	2.1	3.5

Table 2-Digested biosolids solution cation concentration.

Location	Sodium (mM)	Potassium (mM)	Magnesium (mM)	Calcium (mM)	Ammonium-N (mM)
College Station	13.3	2.5	0.3	1.2	45.1
Titusville	4.9	7.2	0.4	0.8	33.4
Surprise	5.8	5.4	0.6	0.9	30.3

The influent cation concentration may have exerted some influence on the cation concentration during digestion, especially for College Station and Surprise. As can be seen in Table 1 and Table 2, the College Station thickened and digested biosolids contained a high concentration of sodium ions. Surprise thickened and digested biosolids contained a lower concentration of monovalent ions. On the other hand, Titusville thickened biosolids appeared to have a high divalent ion concentration but the digested biosolids contained a low divalent ion concentration.

Monovalent to Divalent Ratio

A monovalent to divalent equivalent ratio (M/D) can be calculated for these biosolids (Table 3) and a lower M/D (less than 2) is considered favorable with respect to dewatering properties (Higgins and Novak, 1997b). College Station for example, possessed an unfavorable M/D (M/D = 5.6), whereas Surprise and Titusville possessed favorable M/D's (less than 2) for the thickened biosolids. Because of the increase in ammonium ions during digestion, all possessed high concentrations of monovalent ions following digestion.

Titusville possessed higher calcium and magnesium ions relative to sodium ions for the thickened biosolids, however, the digested biosolids monovalent cation concentration was very high. Operators of ATAD facilities have observed struvite

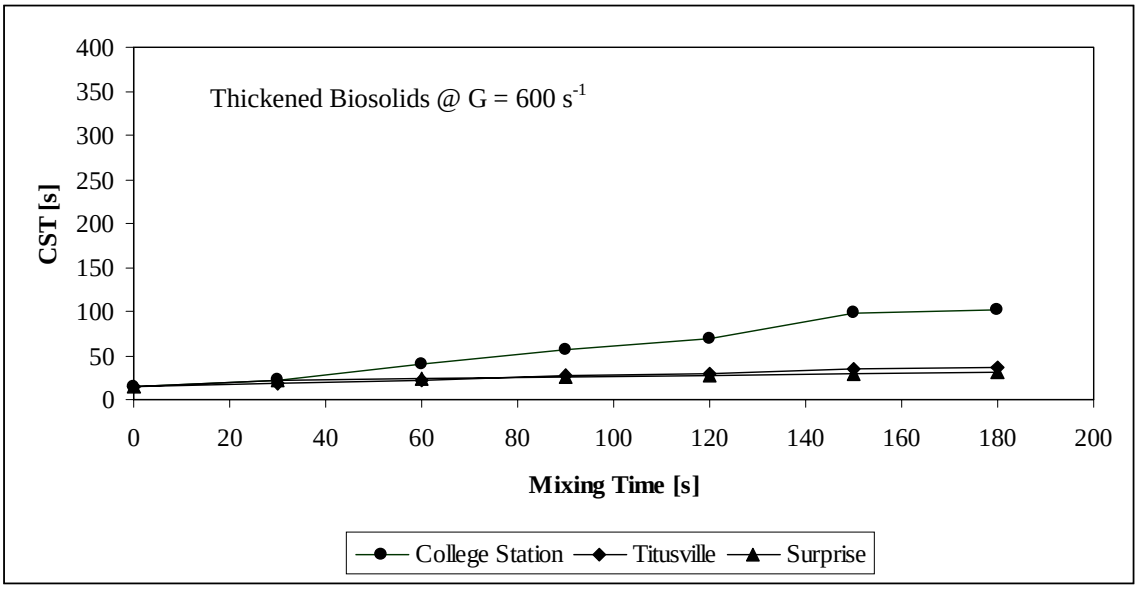
(magnesium ammonium phosphate) precipitation during digestion. The magnesium concentration decreased from 6.5 mM to 0.4 mM following digestion. This decrease coupled with the increase in ammonium ion caused the M/D to go from 1.0 to 19.9. The presence of calcium may be crucial in determining the dewatering properties and cationic polymer demand for redox conditions where magnesium may precipitate during digestion. Hence, corresponding to the M/D for digested biosolids, the cationic polymer conditioning demand for College Station and Titusville (Table 3) was much higher than that for Surprise.

Table 3- Monovalent/Divalent equivalent ratio for thickened and digested biosolids and high molecular weight cationic polymer demand for digested biosolids (Nalco PL250).

Location	M/D Before Digestion (eq/eq)	M/D After Digestion (eq/eq)	Polymer Demand After Digestion (g/kg DS)
College Station	5.6	21.4	175
Titusville	1.0	19.9	285
Surprise	1.3	13.2	85

Sensitivity to Shear

Thickened and digested biosolids from College Station, Titusville and Surprise were subjected to mixing intensity tests at optimum conditioning dose for the biosolids (Figure 1) to determine the sensitivity of the flocs to shear (Werle *et al.*, 1984). Shearing of biosolids will result in a deterioration of dewatering properties, a release of biopolymers from the floc, and an associated increase in cationic polymer demand. The mixing intensity (G) used in these tests was 600 s^{-1}, is similar to the shear imparted to the biosolids in full-scale ATADs (Kelly *et al.*, 1993).



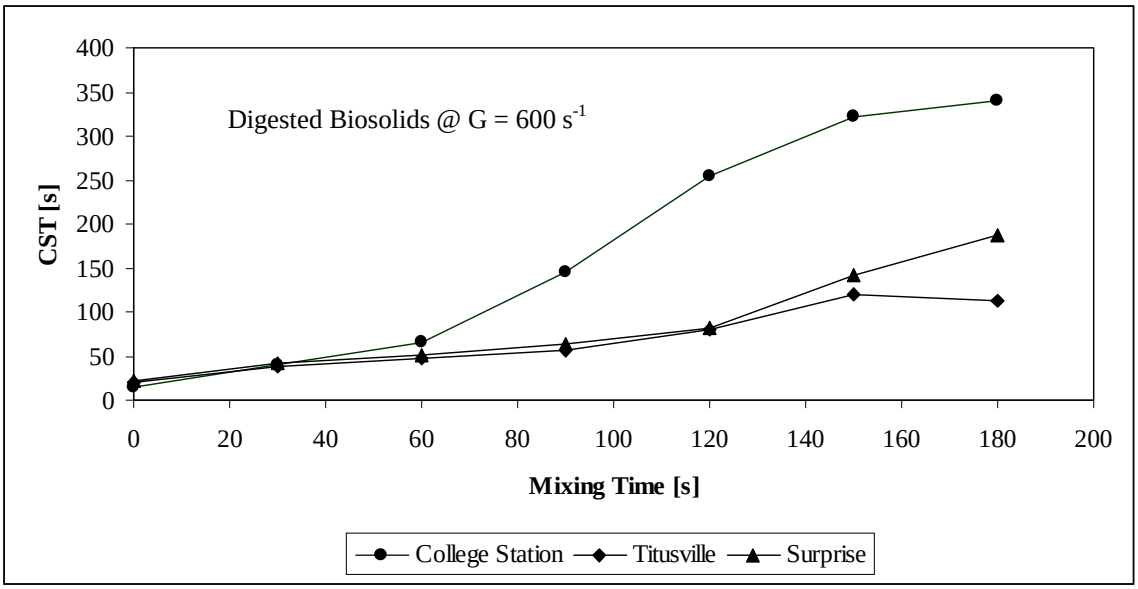


Figure 1-Effect of shear (G = 600 s^{-1}) and mixing time on thickened and ATAD digested biosolids dewatering property (CST) for cationic polymer conditioned biosolids.

The thickened biosolids were much more resistant to mixing intensity than the digested biosolids (Figure 1). When subjected to shear, the College Station thickened and digested biosolids exhibited higher CST's than biosolids from either Titusville or

Surprise. The poor performance of College Station biosolids is probably due to the higher concentration of sodium in the biosolids (Higgins and Novak, 1997a, b; Novak *et al.*, 1996), and the unfavorable M/D prior to digestion (Murthy and Novak, in press). A higher sodium ion concentration has been associated with poor shear resistance. The sodium concentration and shear conditions in the ATADs may be important in determining polymer conditioning demand (Novak *et al.*, 1996; Novak *et al.*, 1993).

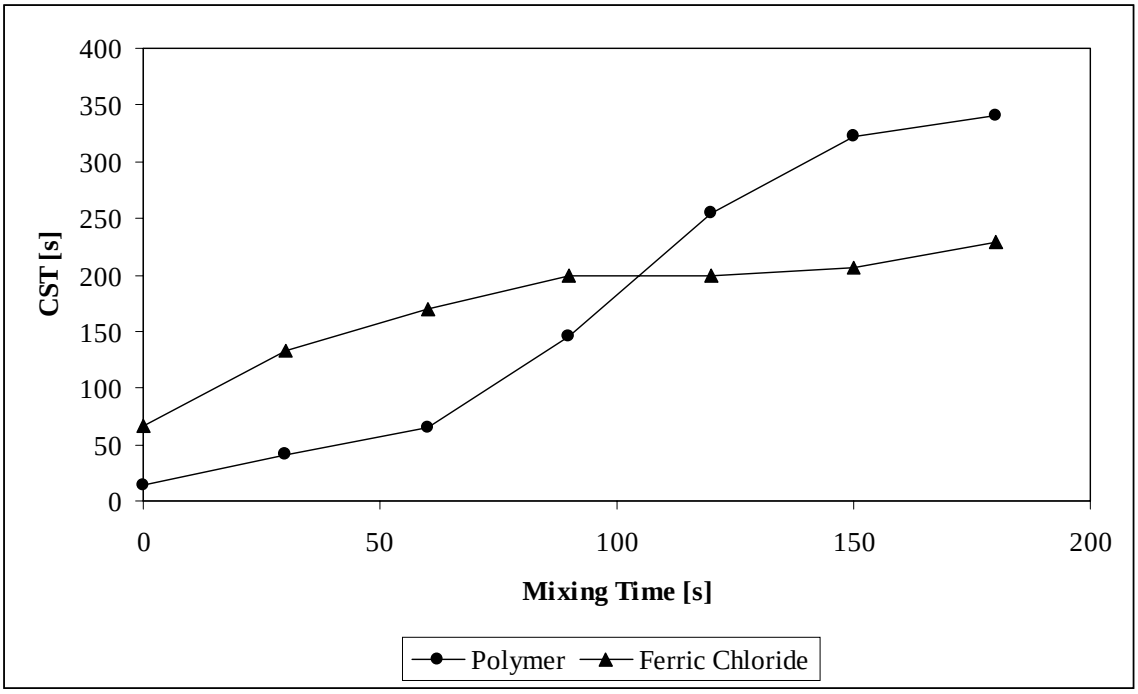


Figure 2-Effect of shear (G = 600 s^{-1}) and mixing time on College Station ATAD digested biosolids dewatering property (CST) for cationic polymer and ferric chloride conditioned biosolids.

Mixing intensity tests were performed on the digested biosolids from College Station using cationic polymer flocculant and ferric chloride to examine their relative performance under shear (Figure 2). Ferric chloride appears to promote shear resistance after an initial deterioration in floc properties. The cationic polymer flocculant was more susceptible to shear at longer mixing times. During dewatering tests, it was found that

conditioning with ferric chloride alone resulted in poor filtrate quality, but conditioning with ferric chloride followed by cationic polymer flocculant provided considerable stability to the biosolids.

Table 4- Protein, polysaccharide and COD for College Station ATAD and Mesophilic Holding Tanks.

Location	Cumulative Product (°C-day)	Protein (mg/L)	Polysaccharide (mg/L)	COD (mg/L)
ATAD 3	327	2080	900	8620
Holding Tank 1	-	1210	740	3700
Holding Tank 2	-	830	1970	3460

Table 5- Temperature, detention time, protein, polysaccharide and COD for Princeton ATAD reactors.

Location	Cumulative Product (°C-day)	Protein (mg/L)	Polysaccharide (mg/L)	COD (mg/L)
ATAD 1	385	2790	1690	9250
ATAD 2	755	3420	2020	10090

Centrate Characteristics

Table 4 and Table 5 show the solution protein, polysaccharide and COD concentrations for College Station and Princeton. The increase in °C-day product resulted in an increase in release of proteins, polysaccharide and COD. The protein, polysaccharide and COD release at Princeton was therefore greater than the release at

College Station. Mesophilic aeration (Holding Tank 1 and Holding Tank 2) resulted in a decrease in proteins and COD, but an increase in polysaccharide. These changes are explained in detail elsewhere (Murthy *et al.*, submitted).

Cationic Polymer Conditioning

The polymer conditioning requirement using Nalco 9909 polymer for College Station ATADs and Princeton ATADs is shown in Table 6 and Table 7. The filtrate protein, polysaccharide and COD after conditioning are also shown. Removal of protein, polysaccharide and COD was achieved after conditioning when compared to the biosolids centrate. An increase in $^{\circ}$C-day product led to an increase in the amount of protein and polysaccharide (solution biopolymers) released. The mechanisms for cationic polymer associated flocculation is primarily through charge bridging of solution biopolymers (Novak *et al.*, 1977, Novak and Haugan, 1980). The increase in cationic polymer conditioning demand was directly related to an increase in solution biopolymers (negative biocolloids).

Table 6- Polymer demand, protein and polysaccharide for College Station ATAD and Mesophilic Holding Tanks after conditioning with high molecular weight polymer flocculant (Nalco 9909).

Location	Polymer Demand (g/kg DS)	Protein Remaining (mg/L)	Polysaccharide Remaining (mg/L)	COD (mg/L)
ATAD 3	54	860	400	4340
Holding Tank 1	48	310	210	1500
Holding Tank 2	33	230	1230	1690

Table 7- Polymer demand, protein and polysaccharide for Princeton ATAD reactors after conditioning with high molecular weight polymer flocculant (Nalco 9909).

Location	Polymer Demand (g/kg DS)	Protein Remaining (mg/L)	Polysaccharide Remaining (mg/L)	COD (mg/L)
ATAD 1	62	730	690	2960
ATAD 2	96	580	660	2800

The Use of Metal Ion Conditioners

To investigate the effect of ferric chloride on coagulation of protein, polysaccharide and COD, the digested biosolids centrate from Surprise was diluted (1:40) and subjected to laboratory tests. Jar tests were conducted using ferric chloride at 0, 10, 20, 100, 200 and 400 mg/L to evaluate coagulation of proteins, polysaccharides and the associated removal of COD. Phosphate-P, turbidity and pH were also monitored.

Ferric chloride was very effective in removing biopolymers and COD. As indicated in Figure 3, greater than 90% removal of proteins was achieved. Polysaccharide (76%) and COD (80%) were also removed. The relative removals at increasing ferric chloride concentration indicate that the coagulant removes proteins preferentially over polysaccharide. The removal of protein, polysaccharide and COD was achieved subsequent to removal of phosphates from solution. Associated with the removal of protein, polysaccharide and COD was a removal of turbidity. Considerable alkalinity was present in the centrate. Even with this pH buffer present, the pH dropped from approximately 7.6 to 7.2 during phosphate removal. Subsequent protein and polysaccharide removal coincided with a further pH decrease to 6.6.

To explain the removal process, the inorganic chemistry of the system must be considered. In both its ferrous and ferric forms and under a variety of redox conditions, iron forms insoluble hydroxy-phosphate precipitates (Nriagu, 1972). The soluble iron content will be determined by precipitation reactions with phosphate and hydroxides.

Formation of hydroxy-minerals serves to reduce the hydroxyl ion concentration in solution, decreasing the pH. Contact between the negatively charged biopolymers with iron-hydroxy-phosphate amorphous minerals will result in adsorption of the organic molecule onto the mineral phase.

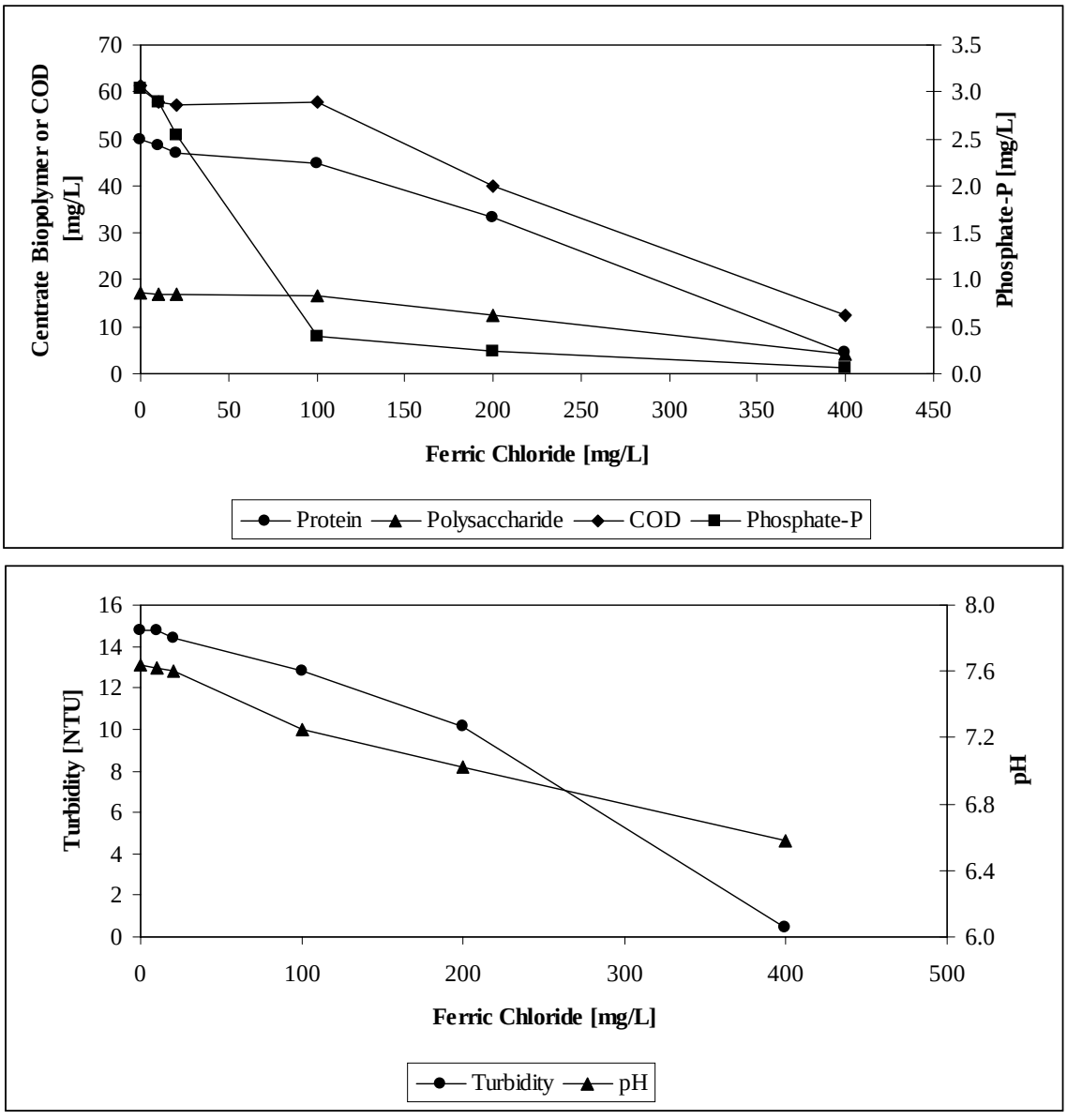


Figure 3-Coagulation of ATAD (Surprise, Arizona) solution biopolymers using ferric chloride.

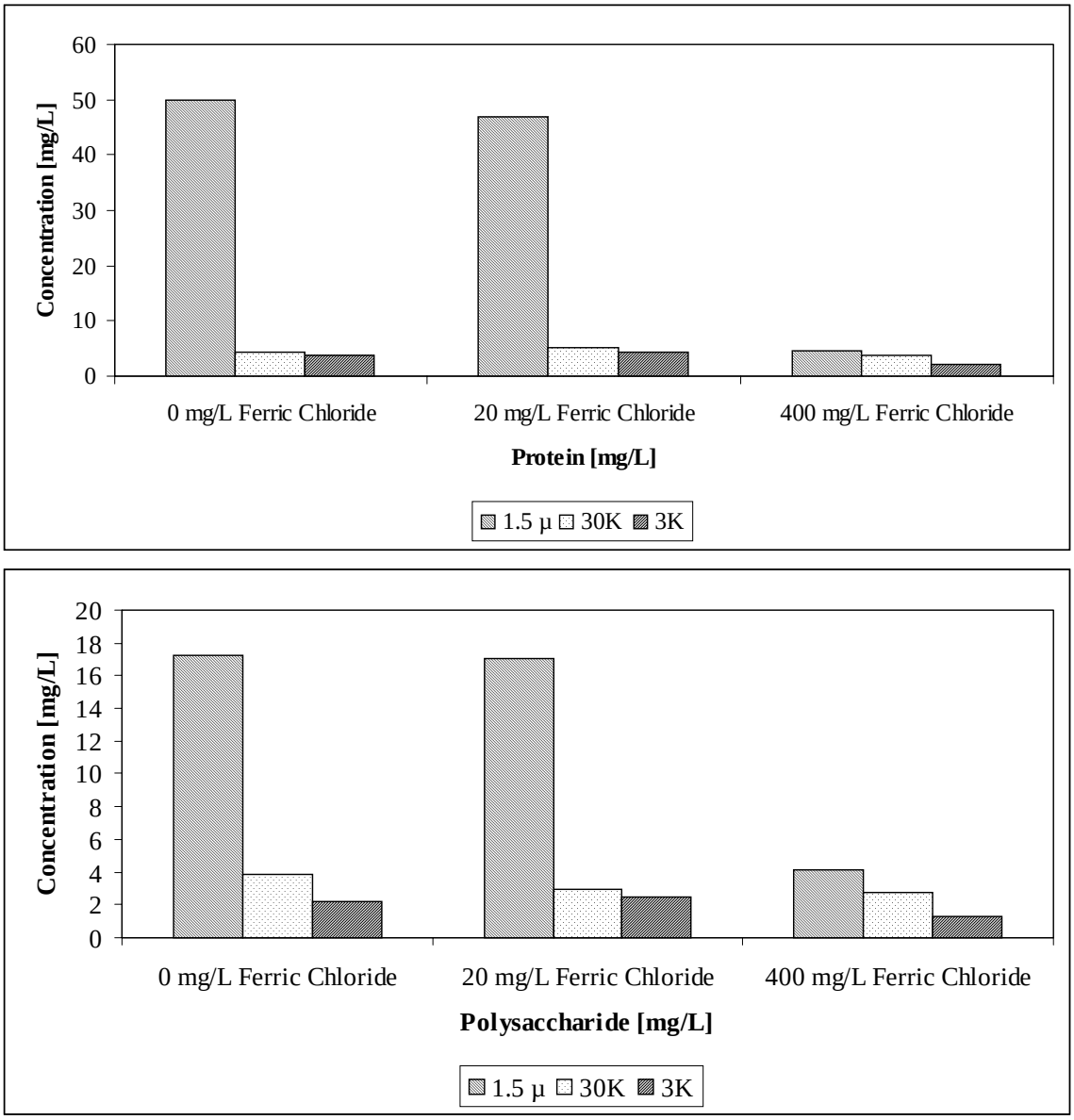


Figure 4-Concentration of protein and polysaccharide passing through filters for ATAD (Surprise, Arizona) coagulation study.

The addition of inorganic chemical conditioners can be very effective in removing biopolymers. The removal of colloidal protein and polysaccharide can occur prior to achieving charge neutralization (Gosset and Dentel, 1987). The mechanism for destabilization of anionic biocolloids has been suggested to be double layer compression (Gosset and Dentel, 1987) or adsorption of biopolymer molecules onto ferric hydroxide

flocs (Novak and Haugan, 1979). Thus, the removal of protein and polysaccharide at the onset of ferric hydroxide precipitation may occur through association with freshly precipitated minerals.

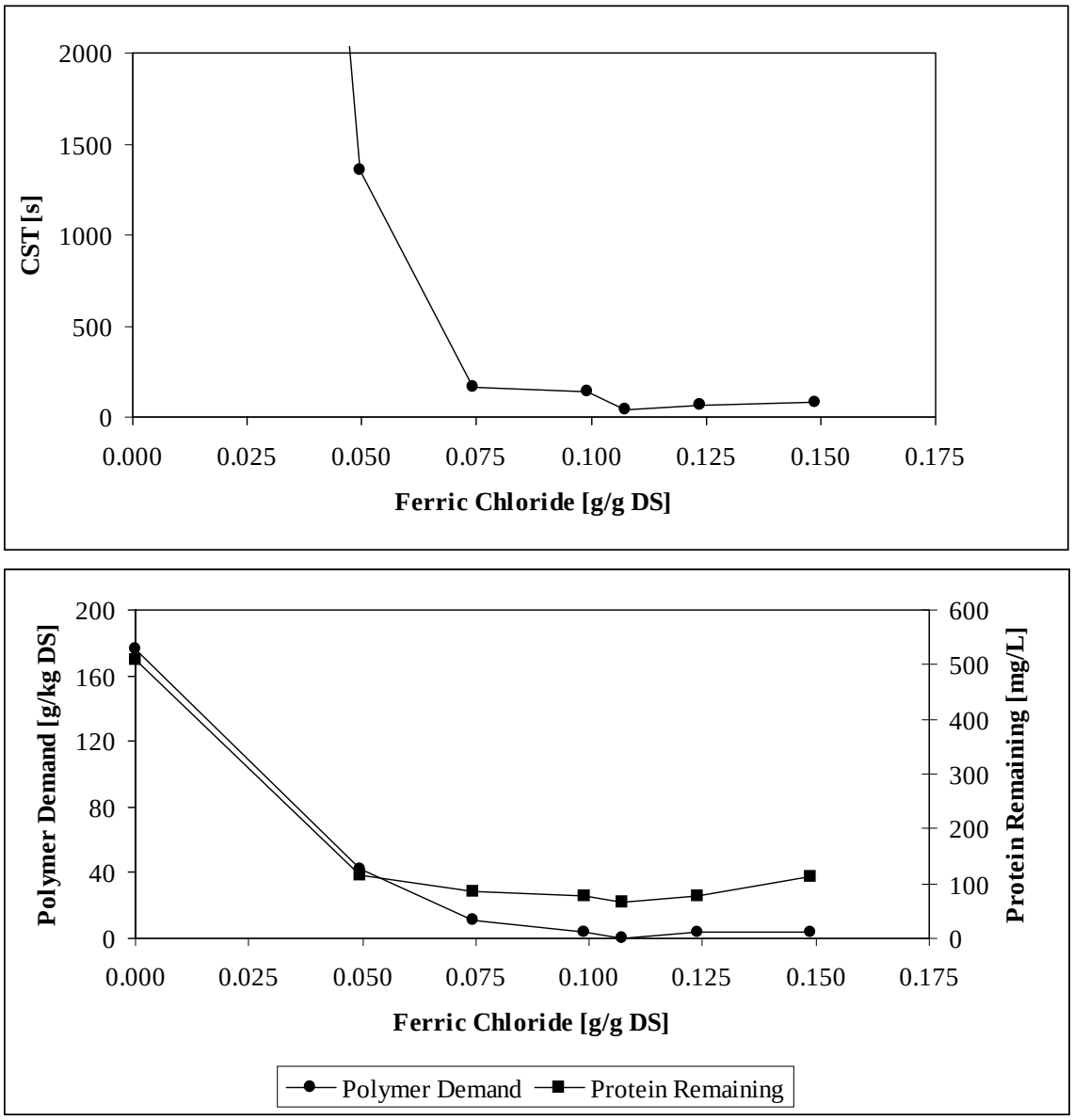


Figure 5-Effect of ferric chloride conditioning on additional polymer demand (Nalco PL250) and filtrate protein remaining for College Station Holding Tank 2 biosolids.

The supernatant from the 0, 20 and 400 mg/L ferric chloride coagulated diluted centrate was ultrafiltered through a 30,000 dalton (30K) and a 3,000 dalton (3K) membrane. The results of this test indicated that the fraction not removed by ferric chloride appeared to be smaller protein and polysaccharide molecules that were filterable through the 30K membrane (Figure 4). The removal of protein and polysaccharide molecules occurred mainly for the colloidal size range defined by molecular size greater than 30,000 daltons.

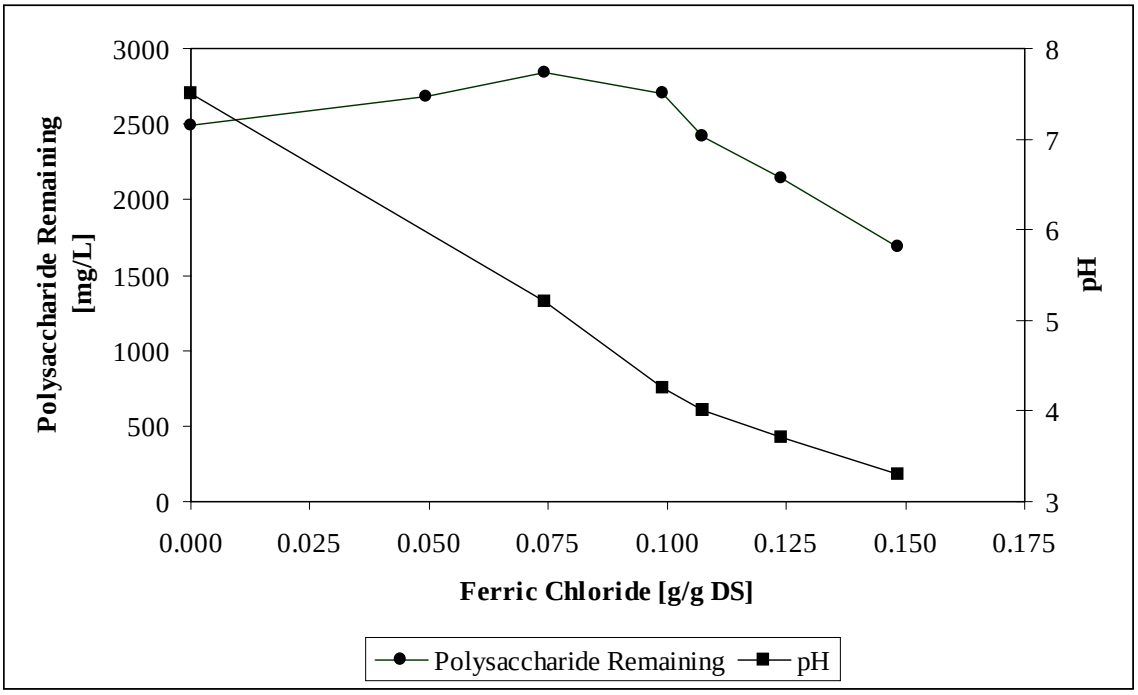


Figure 6- Effect of ferric chloride conditioning on filtrate polysaccharide remaining and pH for College Station Holding Tank 2 biosolids.

Protein and Polysaccharide Removal by Ferric Chloride

The removal of solution protein and solution polysaccharide by ferric chloride was studied using biosolids from Holding Tank 2 from College Station. The biosolids were thermophilically digested and mesophilically aerated prior to conditioning. The reduction in CST and optimum cationic polymer demand (Nalco PL250) with the use of

ferric chloride as a conditioner is shown in Figure 5. The reduction in CST and additional cationic polymer demand was concomitant with the removal of proteins from solution by ferric chloride.

The removal of polysaccharides occurred at higher conditioning doses of ferric chloride (Figure 6). This removal of polysaccharide may be related to its reduced solubility at lower pH or through its precipitation on additional iron-hydroxy minerals surfaces formed from hydroxyl ion consumption. Conditioning with ferric chloride dropped the pH much more so for Holding Tank 2 than for the ATADs. The greater drop in pH may be due to the consumption of alkalinity by nitrification reactions in Holding Tank 2.

Conditioning with Ferric Chloride and Cationic Polymer

The mechanisms for conditioning of biosolids with iron or aluminum salts and cationic polymer appear to be different. The optimum cationic polymer conditioning dose can be determined electrokinetically based on electrophoretic mobility or the use of streaming current detectors (WERF, 1995). Optimum dose is achieved at charge neutralization between the cationic polymers and the anionic biosolids at approximately zero electrophoretic mobility (Novak and Haugan, 1979). In this study, ferric chloride removed biocolloids prior to charge neutralization (since additional cationic polymer conditioning dose is required to optimally condition the biosolids). The initial use of ferric chloride coagulant with subsequent addition of cationic polymers is feasible, and, the removal of anionic biocolloids by ferric chloride during biosolids conditioning results in a greatly reduced cationic polymer requirement. Without ferric chloride, the chemical costs (cationic polymer) associated with satisfying the large number of negative charge sites in ATAD biosolids through purely charge neutralization may be huge, and may constitute substantial operations cost (54 g/kg DS versus 13 g/kg DS). The addition of iron or aluminum salts in fairly small quantities can greatly reduce the number of these negative charged sites, thereby reducing additional cationic polymer flocculant requirements and conditioning chemical costs.

Table 8- Additional polymer demand, protein and polysaccharide for College Station ATAD and Mesophilic Holding Tanks after conditioning with 0.10 g/g ferric chloride and high molecular weight polymer (Nalco 9909).

Location	Polymer Demand (g/kg DS)	Protein (mg/L)	Polysaccharide (mg/L)	COD (mg/L)
ATAD 3	13	620	340	4030
Holding Tank 1	3	120	120	1080
Holding Tank 2	1	95	780	850

Table 9- Polymer demand, protein and polysaccharide for Princeton ATAD reactors after conditioning with 0.10 g/g iron chloride and high molecular weight polymer (Nalco 9909).

Location	Polymer Demand (g/kg DS)	Protein (mg/L)	Polysaccharide (mg/L)	COD (mg/L)
ATAD 1	17	550	620	2560
ATAD 2	33	440	600	2520

The coagulation study indicated that ferric chloride was effective in precipitating proteins and polysaccharides from the centrate of ATAD biosolids from Surprise. Conditioning using ferric chloride was tested at College Station and Princeton to evaluate its feasibility for dewatering ATAD biosolids. Some of these results are summarized in Table 8 and Table 9. The biosolids were conditioned using 0.10 g/g DS ferric chloride. This concentration of ferric chloride is commonly applied for dewatering anaerobically digested biosolids and is not considered unusual in cost or quantity. Additional cationic polymer flocculant was added until optimum conditioning was achieved. As can be seen

in the tables, the optimum polymer demand was substantially reduced for the ATADs from College Station and Princeton. Also, there was a reduction in protein, polysaccharide and COD in the filtrate when compared to the use of cationic polymers.

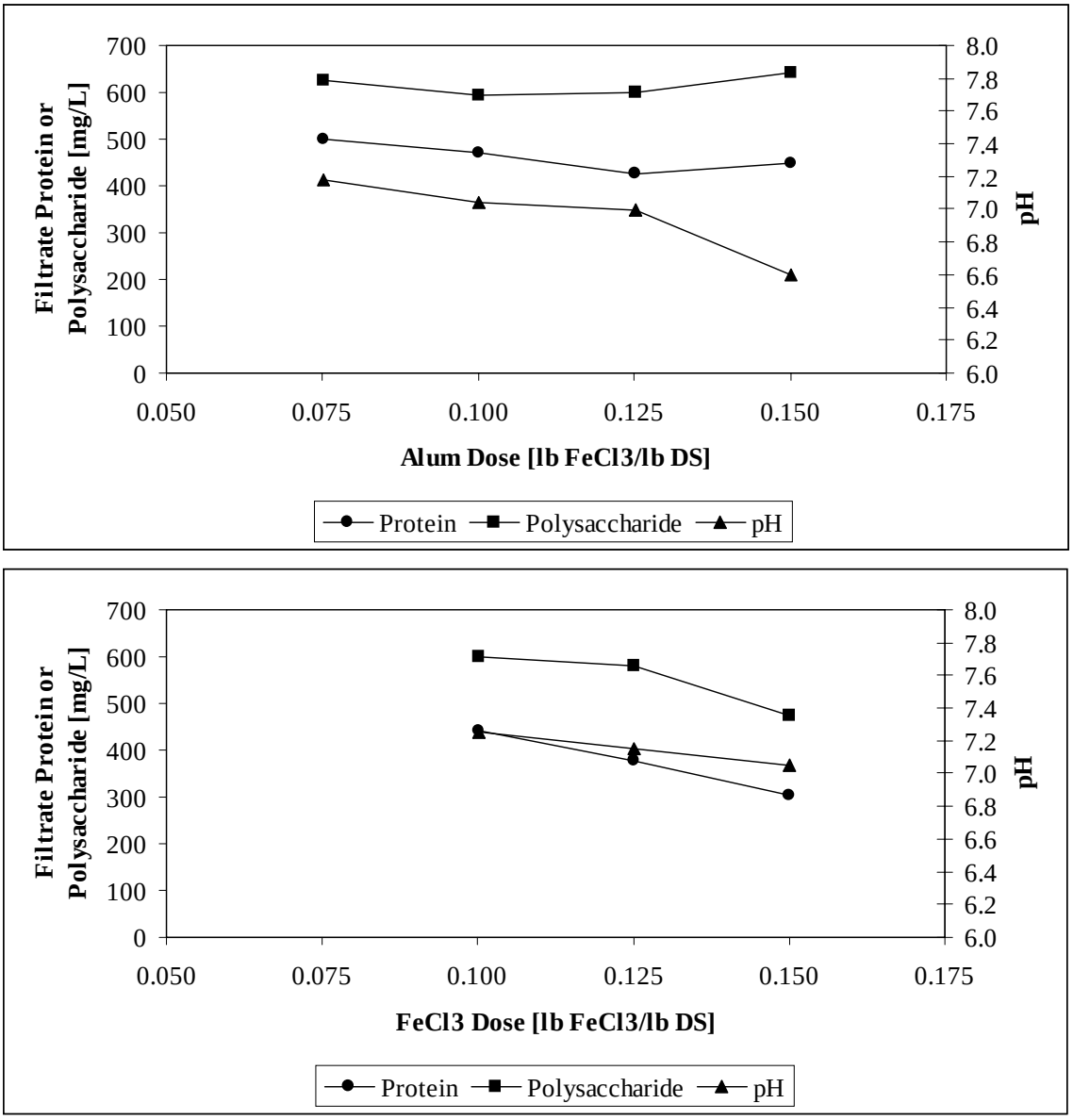


Figure 7-Comparison between alum and ferric chloride conditioning of ATAD biosolids from Princeton, Indiana.

The reduction in the polymer conditioning demand was also seen following additional mesophilic aeration as shown in Table 8. Mesophilic aeration (Holding Tank 1 and Holding Tank 2) when combined with ferric chloride conditioning resulted in a low polymer conditioning requirement and low protein and COD in the filtrate. The concentration of the protein in the filtrate was lower than the concentrations found in the pre-ATAD biosolids for College Station.

The removal of proteins resulted in a corresponding reduction in foaming in the activated sludge basin. Aeration of filtrates after mesophilic aeration and ferric chloride conditioning did not produce any foam in laboratory trials.

Ferric Chloride and Alum

Alum was added to determine its effect on reducing the polymer demand at Princeton. Alum may be the preferred conditioner at some plants due to the corrosive nature of ferric salts.

Figure 7 shows the change in protein, polysaccharide and pH with an increase in ferric chloride and alum (concentrations expressed as ferric chloride). The pH was very stable due to the high alkalinity in the ATAD biosolids. Removal of protein and polysaccharide was achieved when the biosolids from ATAD 2 at Princeton were conditioned with ferric chloride. Alum did not cause a removal of polysaccharides, but protein removal was achieved. Overall, ferric chloride appears to be more effective than alum in removing proteins from the filtrate (Figure 7).

The additional polymer flocculant dose required when using alum or ferric chloride were very similar (Figure 8). Both ferric chloride and alum produced a substantial reduction in cationic polymer flocculant dose required. Figure 8 shows the reduction in polymer demand after using ferric chloride and alum for ATAD 2 at Princeton. The equivalent reduction in polymer demand (slope) was higher at lower doses of the inorganic conditioners. The requirement of additional cationic polymer dose (Figure 8) implied that both ferric chloride and alum were interacting with the biosolids prior to charge neutralization being achieved. The reduction of this additional polymer dose appears to be due to removal of negatively charged solution biocolloids.

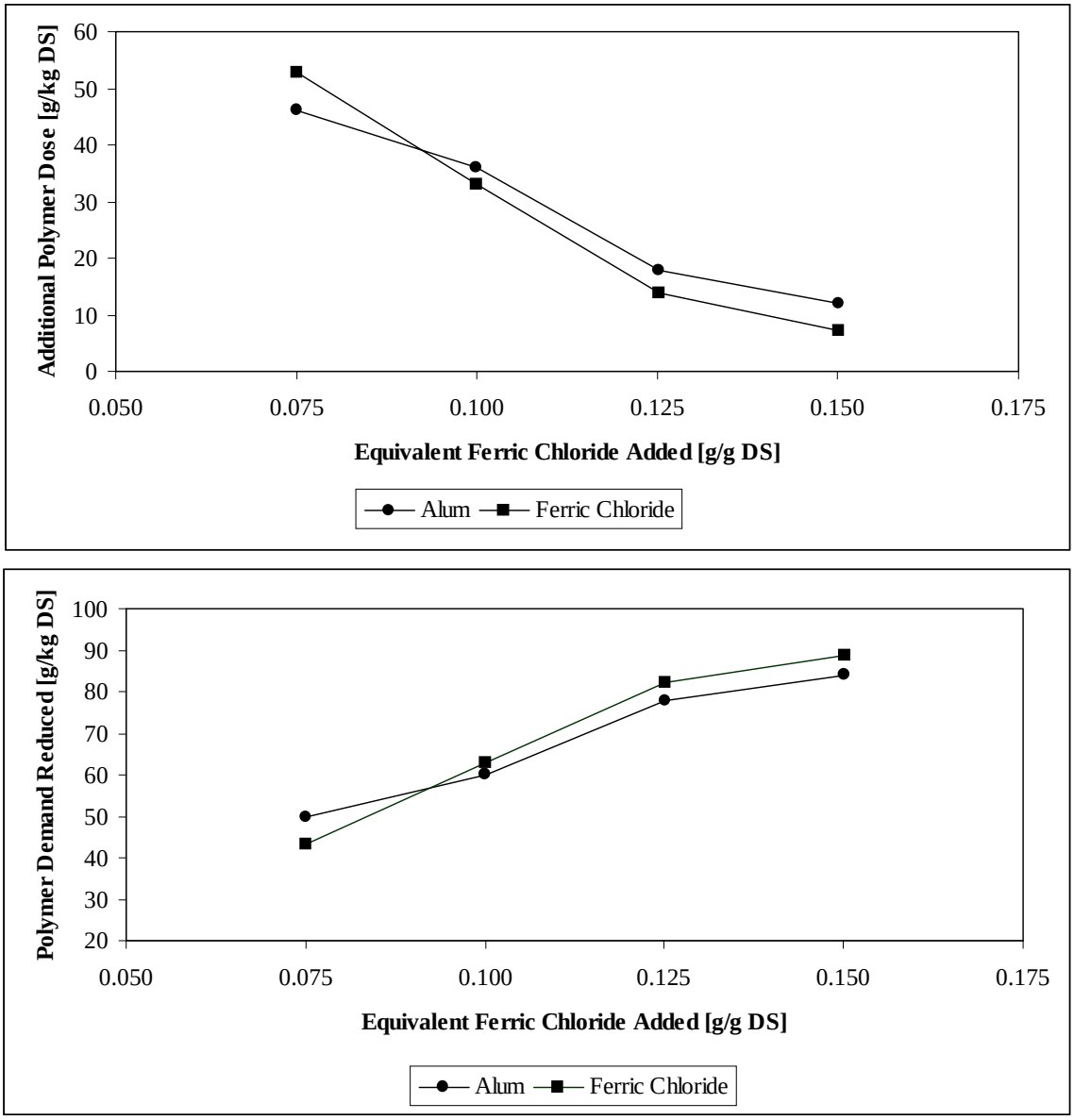


Figure 8-Polymer dose required and polymer demand reduced on addition of inorganic conditioners for Princeton, Indiana ATAD biosolids.

The amount of equivalent polymer demand reduced by ferric chloride or alum may not be stoichiometric and may depend on the protein, polysaccharide or COD concentration in solution as explained earlier. This is demonstrated in Figure 9. Princeton ATAD 1 and College Station ATAD 3 biosolids contained lower concentrations of biopolymer and COD in solution. The equivalent reduction in polymer

demand when using ferric chloride was not as much for these biosolids when compared to biosolids from ATAD 2 at Princeton.

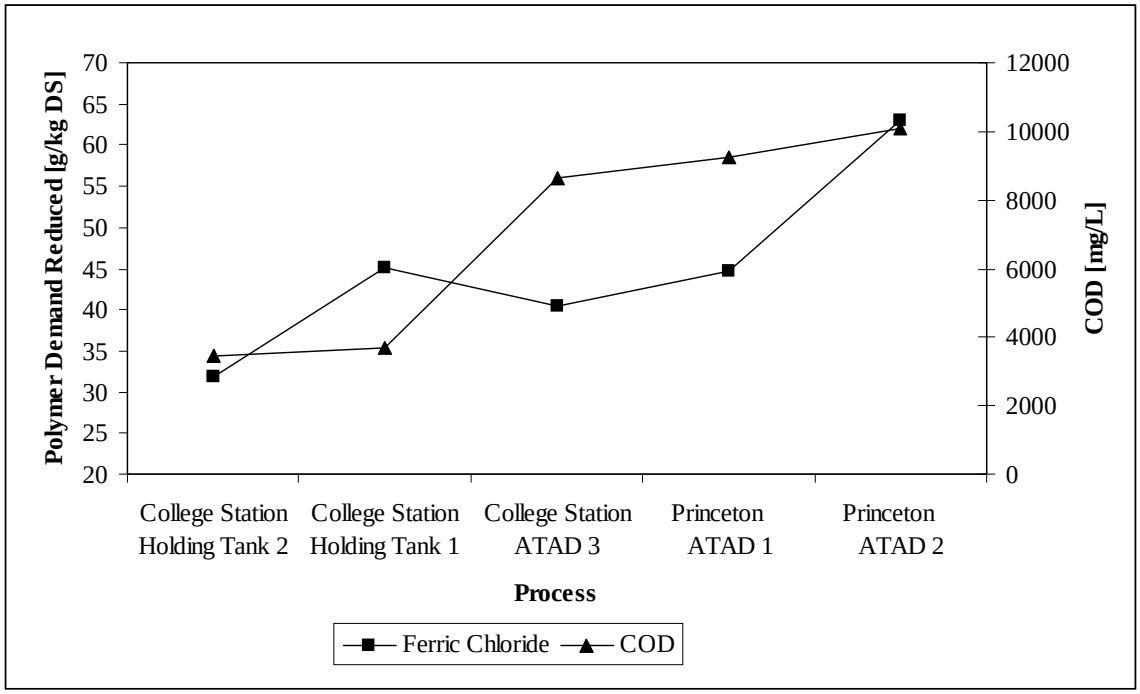


Figure 9-Non-Stoichiometric process related polymer demand reduction on addition of 0.1 g/g DS ferric chloride at College Station, Texas and Princeton, Indiana. Solution chemical oxygen demand for these processes.

It appears that the longer the detention time in the ATADs, inorganic conditioners appear to remove greater equivalent cationic polymer demand. For Princeton ATAD 2, the reduction in polymer demand was as much as 60 g/kg DS for 0.1 g/g DS ferric chloride or alum used.

A greater reduction in polymer demand after using ferric chloride (as compared with polymer demand shown in Table 6) was observed for mesophilically aerated Holding Tank 1 when compared with ATAD 3 for College Station biosolids (Figure 9). The improvement in conditioning properties of ferric chloride occurred despite a decrease in solution biopolymers. These observations were confirmed for full-scale tests at Princeton (data not shown). Oxidizing conditions appear to improve the conditioning

properties of ferric chloride. The reasons for the improvement in conditioning properties of ferric chloride is likely due to higher concentrations of mineralized ferric species being formed rather than the ferrous species (ferrous sulfide). The redox conditions may be important for both the added ferric conditioner and for the iron naturally found in the biosolids.

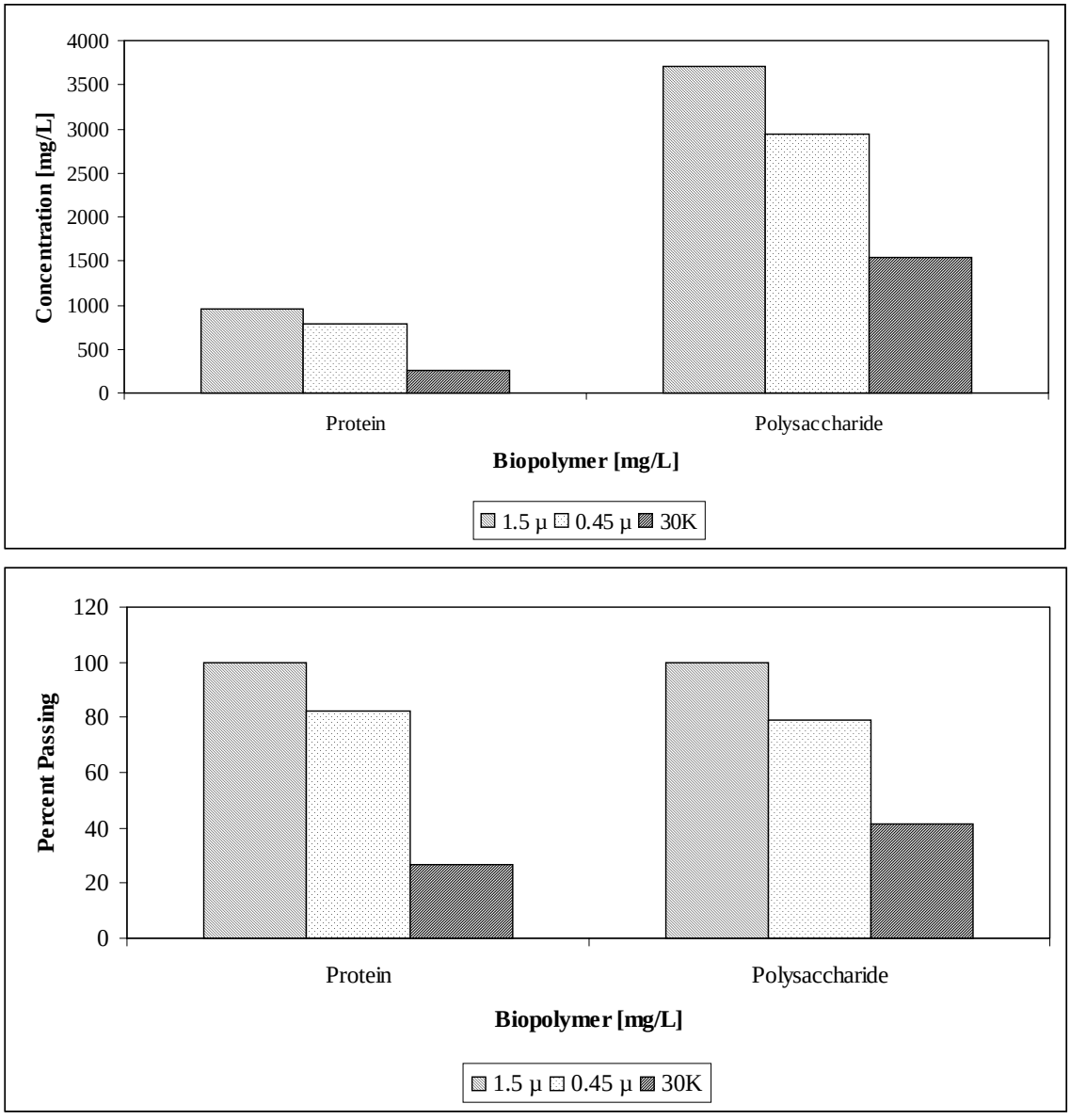


Figure 10-Concentration of protein and polysaccharide passing through filters for College Station Holding Tank 2 biosolids.

The solution proteins and COD was quite low after mesophilic aeration in Holding Tank 2. The additional cationic polymer required after conditioning with ferric chloride in Holding Tank 2 was only 1 g/kg DS.

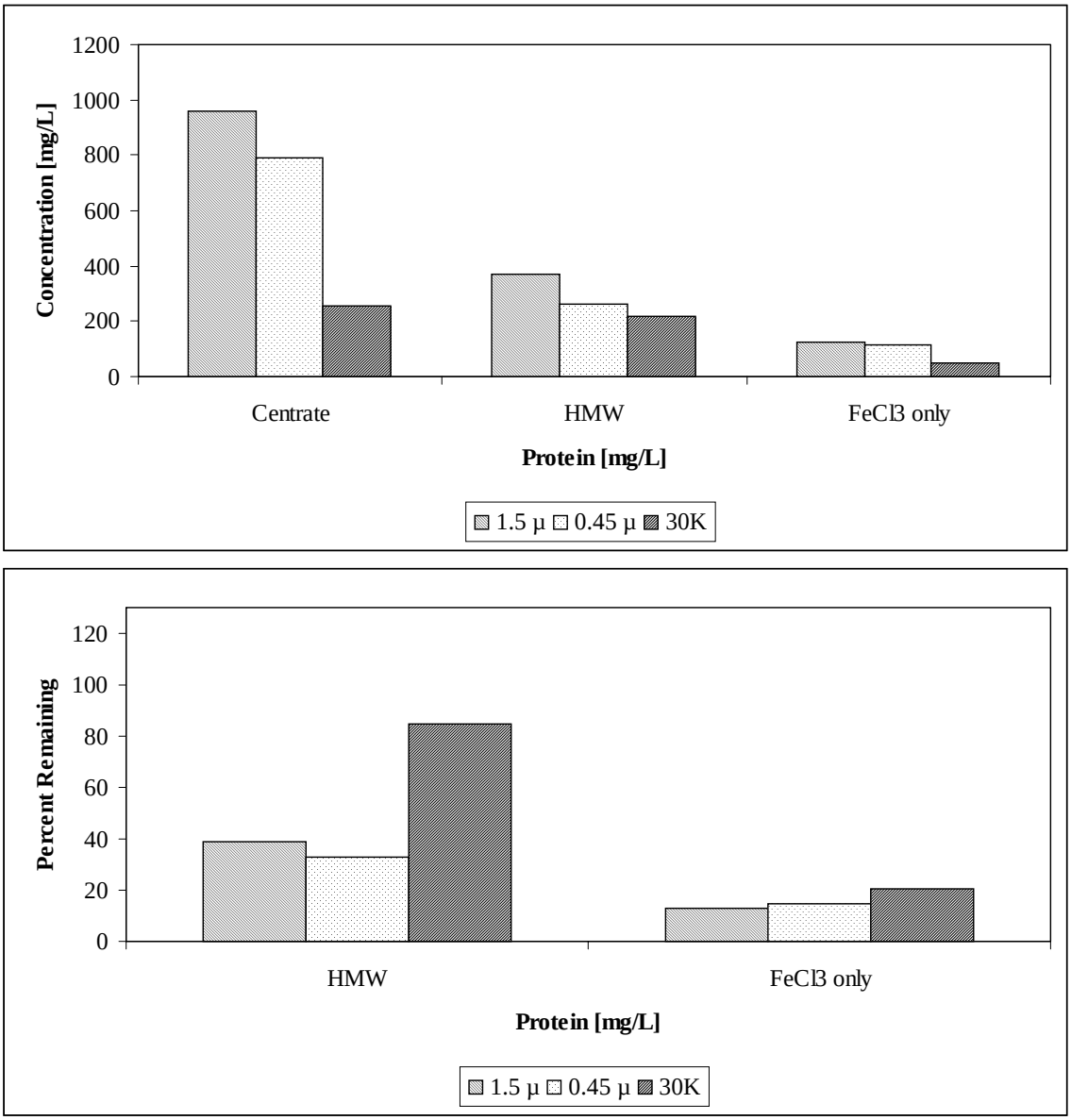


Figure 11-Comparison of solution protein (centrate), and filtrate protein after conditioning with cationic polymer or ferric chloride for College Station Holding Tank 2 biosolids.

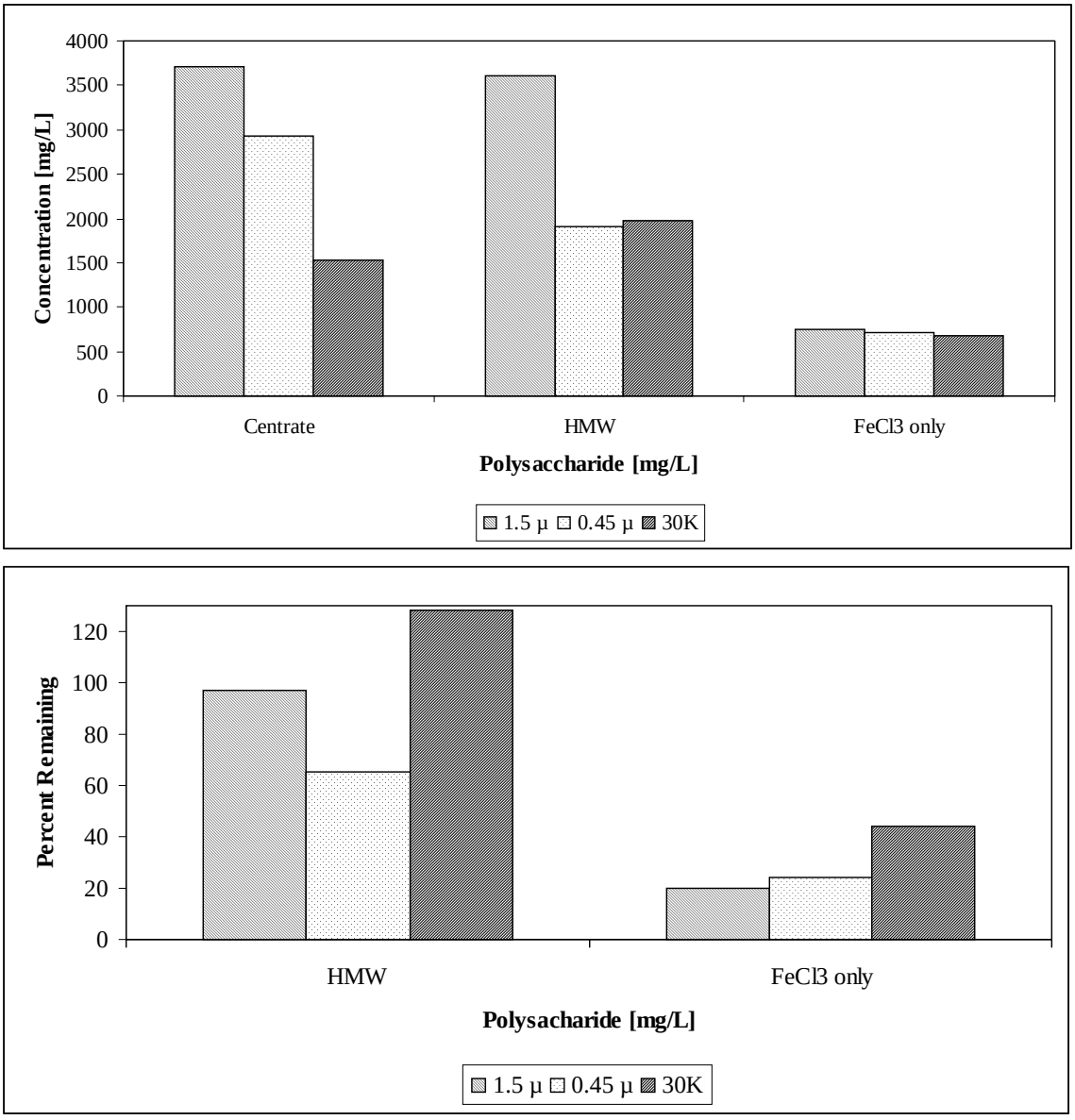


Figure 12- Comparison of solution polysaccharide (centrate), and filtrate protein after conditioning with cationic polymer or ferric chloride for College Station Holding Tank 2 biosolids.

College Station Ultrafiltration Study

The centrate from Holding Tank 2 at College Station was filtered through 1.5 µ, 0.45 µ and a 30,000 dalton (30K) filters to identify the size fraction of the protein and polysaccharide (Figure 10). As can be seen in the figure, both protein and polysaccharide

were well distributed in the size fractions examined. A protein fraction of 27% and a polysaccharide fraction of 41% passed though the 30K ultrafiltration membrane. As seen in Figure 11 and Figure 12, a greater fraction of protein and polysaccharide that passed through the 30K ultrafiltration membrane were not removed after conditioning. The bulk of protein and polysaccharide in the filtrates after conditioning passed through the 30K membrane. Ferric chloride removed more of these smaller sized biopolymers than the cationic polymer. The polysaccharide remaining in the filtrate after conditioning with iron chloride was almost completely the fraction passing though the 30K ultrafiltration membrane. Therefore, ferric chloride appears to be effective in removing organic biocolloids defined by a molecular size greater than 30,000 daltons.

Conditioning Study Summary

At College Station, the combined use of mesophilic aeration and inorganic chemical conditioner (alum) resulted in a much reduced conditioning chemical cost. The reduction in cationic polymer demand after using inorganic conditioners appears to depend on the amount of solution biopolymers present and on the redox potential of the biosolids. The effectiveness of ferric chloride was improved after mesophilic aeration in Holding Tank 1, and in full-scale testing at Princeton. Mesophilic aeration at Princeton (data not shown) did not produce any ammonia-N removal, but resulted in substantial reduction of polymer demand after using ferric chloride.

Inorganic conditioners are very effective in reducing polymer demand for short mesophilic aeration detention times. On the other hand, if the mesophilic aeration detention time is sufficiently long, inorganic conditioners may not be required (Murthy *et al.*, submitted), and inorganic conditioners may be less efficient at reducing polymer demand.

At College Station, the addition of ferric chloride resulted in a reduction of protein and polysaccharide in the filtrate. The reduction of filtrate biopolymers resulted in a reduction in cationic polymer demand.

The ultrafiltration study indicated that the amount of biopolymer not captured by cationic polymer flocculant or ferric chloride depends on the size of the biopolymer. Conditioning with ferric chloride resulted in a greater reduction of the biopolymer

fraction passing through the 30K ultrafiltration membrane as compared to conditioning with cationic polymer.

Conclusions

Laboratory and field studies were conducted to evaluate the conditioning options for the dewatering of ATAD biosolids. The objective of this study was to investigate opportunities to reduce chemical conditioning costs. Studies were conducted using cationic polymer and a combination of inorganic conditioners (ferric chloride or alum) and cationic polymer.

This study indicated that inorganic conditioners such as ferric chloride and alum were very effective in reducing conditioning chemical requirements, thereby reducing operation costs, for ATADs. The inorganic conditioners were effective in removing anionic biocolloids. Removal of the anionic biocolloids occurred prior to achieving charge neutralization. The removal of these anionic biocolloids may be through ferric-hydroxy mineral associated precipitation as observed in the coagulation study. The conditioning mechanisms associated with cationic polymer is through charge neutralization. Pre-coagulation of biosolids with inorganic conditioners will reduce the negative charges in solution, thereby eliminating some of the cationic polymer demand.

The different mechanisms lead to different conditioning requirements. Ferric chloride and alum were more effective in removing larger sized protein and polysaccharide molecules (greater than 30K). The inorganic coagulants were also more effective then the biopolymer and COD release was greater. The use of inorganic chemical coagulants should be considered when large release of protein, polysaccharide and COD occur during the digestion process.

A combination of mesophilic aeration followed by conditioning with alum and cationic polymer flocculant greatly reduced conditioning chemical costs at College Station. The costs were similar to or lower than that required for mesophilic anaerobic digestion.

Filtrate recycle COD was much reduced and in-plant foaming at College Station was largely eliminated by employing a combination of mesophilic aeration and using alum.

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