

Piloting DAF for Full-Scale Implementation to Mitigate Impacts of Changing Source Water
Quality

by

Ryan Douglas Swinamer

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Abstract

In the last few decades, water treatment facilities in Atlantic Canada have experienced changes in their source waters, specifically elevated natural organic matter (NOM) levels. This is widely referred to as brownification and has been reported in surface waters across the Northern Hemisphere. Lake recovery is noted as one factor behind brownification. Lake recovery is characterized by increasing acid neutralization capacity, alkalinity, and pH, which often correspond to increases in NOM concentrations. Climate change is also expected to promulgate the impacts posed by lake recovery with higher temperatures and increased frequency of runoff events. The conditions associated with lake recovery are also favourable for harmful algal blooms to occur which can produce toxins that are harmful to humans, and are difficult to remove through conventional water treatment processes.

Treatment plants with source waters experiencing brownification are noticing significant historical increases in chemical dosing for coagulation processes, leading to increased operational costs and waste residuals. Dissolved air floatation (DAF) has been noted as being an effective clarification process for removing low density contaminants such as NOM and algae. DAF poses great advantages as it can reduce chemical dosing as well as reduce flocculation time and tank volumes. This work evaluates the operations of a DAF pilot plant in Nova Scotia for the intended purpose of informing design decisions for full scale implementation. Parameters that were investigated included coagulant dose, coagulant type, and flocculation time. Results suggest that these factors may influence removal mechanisms and that consideration must be taken to effectively target contaminants of concern. The project was operated throughout various seasons which provided data depicting seasonal effects on the process. Data has shown DAF clarification to provide promising results in terms of turbidity and natural organic matter removal. Longer flocculation times may prove to be more robust with DAF but shorter flocculation times provide adequate results and are far more economically friendly.

List of Abbreviations and Symbols

Al – Aluminum

ANC – Acid neutralization capacity

CWRS – Centre for Water Resources Studies

Da – Daltons

DAF – Dissolved air flotation

DBPfp – Disinfection By-Product Formation Potential

DBPs – Disinfection by-products

DLVO – Derjaguin-Landau-Verwey-Overbeek theory

DOC – Dissolved organic carbon

G – Velocity Gradient

HAAs – Haloacetic acids

HRM – Halifax Regional Municipality

ICP-MS – Inductively Coupled Plasma Mass Spectrometry

LMWSP – Lake Major Water Supply Plant

MAC – Maximum acceptable concentration

mg – Milligram

µg – Microgram

min – Minute

MLD – Million litres per day

NOM – Natural organic Matter

NTU – Nephelometric turbidity units

PACl – Polyaluminum chloride

pH – Potential of hydrogen

Pt-Co – Platinum-cobalt units

SUVA – Specific ultraviolet absorbance

T – Hydraulic Retention Time

TCU – Total colour units

THMs – Trihalomethanes

TOC – Total organic carbon

UFRV – Unit filter run volume

UV254 – Ultraviolet absorbance at 254 nm

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Chapter 1 - Introduction

In the last few decades surface waters in the Northern Hemisphere have been experiencing changes in water quality, specifically increases in natural organic matter (NOM). This is a result of climate change impacts as well as a phenomenon referred to as lake recovery. Reduction in sulfate deposition has led to lake recovery which describes increasing acid neutralization, alkalinity, and pH in waters. These conditions have been linked to increases in NOM to levels found prior to acidification (Anderson et al., 2017). Additionally, climate change impacts such as more intense precipitation events and droughts have also been suggested to contribute to increasing NOM (de Wit et al., 2016; Kritzberg et al., 2020). Historical increases in NOM is typically referred as brownification and causes many difficulties for treatment plants. NOM causes taste, odour, and colour issues but most importantly is a precursor to the formation of carcinogenic disinfection by-products (DBPs) (Sillanpää et al., 2018). Brownification has led to increased chemical dosing, leading to higher operation costs and waste production. Lake recovery and climate change have also been suggested to increase the frequency of algal blooms (Anderson et al., 2017). Algae can lead to impacts during the treatment process such as filter clogging. Certain algae species can produce algal toxins which pose a human health concern. Treatment facilities are now upgrading their plants and considering alternative processes to mitigate challenges posed by lake recovery and climate change.

Dissolved air flotation (DAF) has been widely found to be effective in the removal of low density contaminants such as NOM and algae (Edzwald, 2010). DAF is a clarification process which typically follows conventional coagulation/flocculation processes. DAF uses flotation to separate particles and flocs from the water rather than relying on gravity. For this reason smaller flocs are more optimal with DAF compared to flocs formed in sedimentation. This poses great

advantages as it can reduce coagulant dosing. Various studies suggest that long floc times are not economically feasible and that short flocculation times are adequate with DAF which reduces tank volumes and space requirements (Edzwald et al., 1992; Plummer et al., 1995; Valade et al., 1996). For these reasons DAF is an attractive process to implement as a clarification step to improve efficiency. DAF provides another means of contaminant removal leading to higher removals and lower residuals in filter effluent. DAF can greatly improve filter performance by reducing influent particles and prolonging filter runs.

Before full scale implementation pilot testing is typically conducted to identify optimal set points and help inform design decisions. Important set points to be identified with DAF include processes prior to DAF which influence floc formation. Coagulant dose and type have been found to affect DAF performance as they relate to the size and charge of the flocs (Bunker et al., 1995; Miranda et al., 2020). Flocculation parameters such as mixing and retention time are also widely discussed in the literature. Many studies that suggest short floc times to be adequate primarily evaluated performance based on turbidity removal (Edzwald et al., 1992; Plummer et al., 1995; Valade et al., 1996). Brownification and focus on NOM removal may lead to closer consideration when it comes to DAF pre-treatment. More stringent drinking water regulations in recent years also put an emphasis on higher removals and high quality effluent.

1.1 Project Objectives

The goal of this project was to identify optimal DAF pre-treatment conditions for the Lake Major Water Supply Plant (LMWSP), located in Dartmouth, NS, which has been experiencing brownification. This was done using both bench-scale experiments and continuation operation of a DAF pilot plant. Specific objectives are outlined as follows:

- Identify an optimal coagulant dose using alum with DAF clarification and compare the efficacy of different coagulant types (conventional vs pre-hydrolyzed) in terms of turbidity and NOM removal while also investigating seasonal and temperature impacts on dosing.
- Compare the impact of flocculation time on optimal coagulant dose and DAF performance specifically with regards to NOM removal as well as how this changes seasonally and its impact on filter efficiency/performance.

1.2 Thesis Organization

Chapter 2 discusses important background relevant to results and discussion for this project including information about NOM, coagulation theory, and DAF. Chapter 3 outlines materials and methods used to perform the experiments and obtain the results for this project. Chapter 4 discusses results regarding coagulation including optimal dose, coagulant type comparison, and seasonal impacts. Chapter 5 discusses results focused on flocculation time and how it impacts coagulant dose, NOM removal, and filter performance. Chapter 6 encompasses the findings of this work and recommendations for future DAF use based on the results found.

Chapter 2 - Background and Literature Review

2.1 Lake Major Water Supply Plant

The Lake Major Water Supply Plant (LMWSP) was commissioned in 1999 and serves a population of approximately 103,000 including the communities of Dartmouth, Cole Harbour, Eastern Passage, North Preston, and Burnside in Nova Scotia, Canada. The LMWSP produces approximately an average of 40 million litres per day (MLD), making it the second largest treatment plant in HRM. The plant draws its water from Lake Major which is characterized as having low pH (< 6), low alkalinity (< 5 mg CaCO₃/L) and low turbidity (< 0.5 NTU) which is typical of surface waters in Atlantic Canada. The LMWSP is a conventional filtration plant, meaning there is a clarification stage prior to filtration. Upflow clarification is used in the LMWSP which is an adaptation of classic sedimentation clarifiers where the water flows upwards as the suspended solids settle. This improves solids contact and decreases settling time as the distance the particles need to travel is reduced. Lamella plates, which are used in the LMWSP, are typically used in conjunction with upflow clarification in drinking water treatment to increase the effective settling area to help improve solids separation.

The LMWSP has faced challenges over the last decade as a result of the water quality of Lake Major gradually changing. The average colour in Lake Major was found to have doubled from approximately 20 TCU to 40 TCU from 1999 to 2015 which is used to indicate the NOM levels in water. Additionally, over this same period average TOC concentrations were found to have increased by approximately 1 mg/L. These changes have impacted the treatment process, most prominently in terms of coagulant demand. The increases in NOM have led to coagulant dosing increasing by nearly 4 times from 2000 to 2015. The increase in coagulant dose has also resulted in an increase in lime consumption which is required to control pH levels and provide

alkalinity for coagulation chemical reactions. In addition to increased chemical consumption, the plant also has experienced a decrease in water production from 51.5 MLD in 2000 to 38 MLD in 2015 (Anderson et al., 2017). Decreased water production can typically be attributed to increased filter clogging and therefore increased frequency of filter backwashes. Evidently the efficiency of the plant has decreased as operating costs have increased, in way of increased chemical demand, while water production has decreased.

The increased occurrence of algae blooms, namely cyanobacteria, and their metabolites have also raised concerns for Halifax Water. Conditions that have led to the increases in NOM are also suggested to promote the growth of cyanobacteria including increasing temperatures and pH. The presence of cyanobacteria introduce many challenges for treatment. Algae does not settle favourably during clarification as it has low density, leading to low removals and filter clogging. Cyanobacteria is also noted to produce harmful and unwanted metabolites such as cyanotoxins. Cyanotoxins can have severe health implications including neurological effects (Health Canada, 2016; Ho et al., 2012). During the last decade, Halifax Water has especially experienced the presence of geosmin, a taste and odour compound produced by algae. Taste and odour compounds are not necessarily hazardous but do lead to customer dissatisfaction and decreased confidence for consumption. The removal of algae during treatment can help alleviate the presence of their metabolites in the treated water.

The challenges faced by the LMWSP has led Halifax Water to consider plant upgrades to improve treatment efficiency and to mitigate impacts faced with changing source water quality. This research focuses on evaluating DAF for full scale implementation to improve clarification performance prior to filtration which in theory would improve treatment efficiency by prolonging filter run times. The water quality of Lake Major suggests DAF as the appropriate

clarification process according to Valade et al. (2009). Their process selection guidelines based on total organic carbon (TOC) and turbidity levels are presented in Figure 2.1.

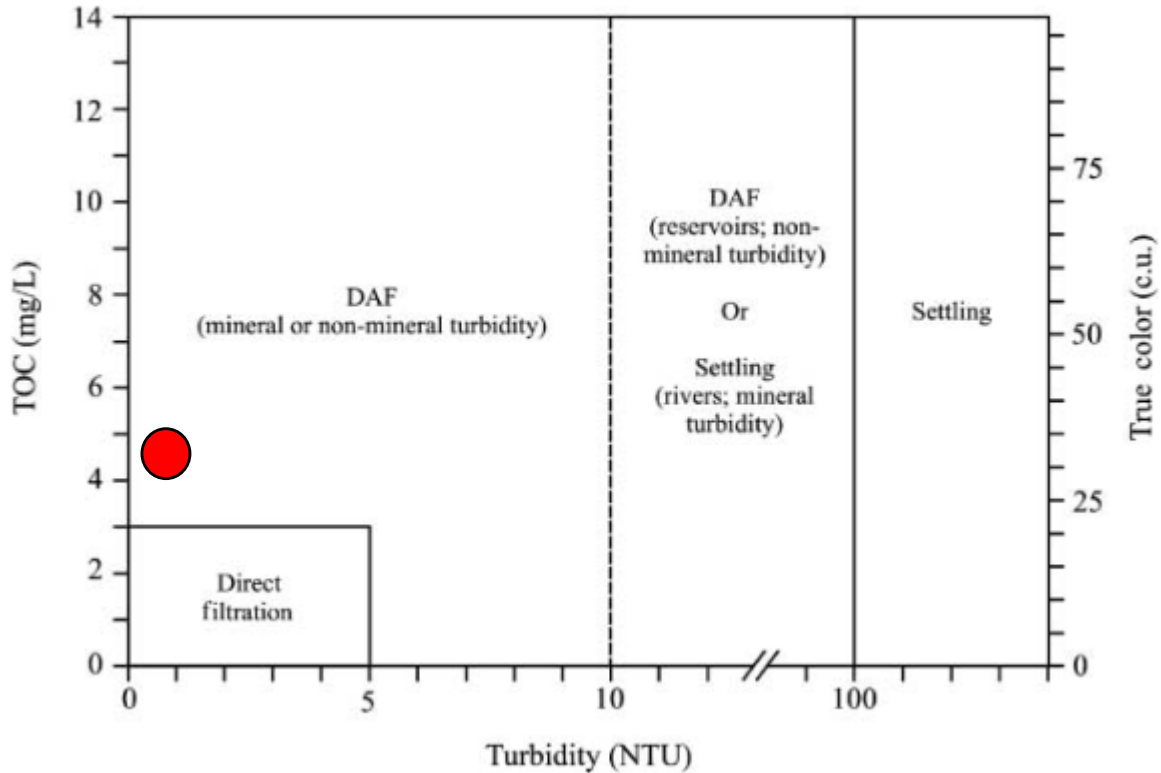


Figure 2.1. Process selection diagram based on source water TOC (mg/L) and Turbidity (NTU) (from Valade et al. 2009). Red circle denotes average Lake Major water quality in 2021.

Clearly the Lake Major water quality in 2021 is found within the DAF region. Even though the turbidity of Lake Major is very low, the DOC concentration in the lake is far too high to have direct filtration. It can be also noted that the turbidity is far too low for settling clarification. The advantages which DAF provides and its mechanisms will be discussed in detail in a later section.

2.2 Natural Organic Matter

NOM defines the complex matrix of organic material which is found in all surface waters in some quantity. NOM is introduced to the water matrix from sources found in the water through biological processes, such as algae growth and microbial activity. Additionally, NOM is produced through biogeochemical processes in surrounding areas which can be collected through rainfall and snowmelt runoff, transporting it to water bodies (Sillanpää et al., 2018). The diversity of processes which produce NOM lead to its complexity. The molecular weight of NOM can range anywhere from 100 to 100,000 daltons (Da). This is a result of their different hydrocarbon structures that typically have a variety of attached functional groups such as amide, carboxyl, and ketone groups, just to name a few (Leenheer & Croué, 2003). The variety of NOM production along with other factors influencing its makeup (i.e. pH, water chemistry, and temperature) lead to variations in the concentrations and composition between waters as well as seasonally in the same water. Microbial activity is higher in soils during warm and dry periods in the summer however an increase in NOM is not experienced until sufficient rainfall/snowmelt runoff occurs to transport it to the waters (Sharp, Parsons, et al., 2006). This leads to higher NOM concentrations typically being found in the fall and winter.

2.2.1 Impacts on Water Treatment

NOM is one of the key pollutants that is targeted for removal during treatment in low alkalinity and low turbidity source waters. NOM, on its own, simply causes aesthetic issues by affecting the colour, taste, and odour in drinking water as it is not inherently toxic (Sillanpää et al., 2018). However, NOM causes various challenges during the treatment process making its removal important. NOM has been found to be a carrier of toxic metals that can also impact treatment and distribution systems (Anderson et al., 2021; Health Canada, 1998). NOM can also

act as a carrier for other toxic organic and inorganic contaminants present in the water matrix (Sillanpää et al., 2018). The most notable reason highlighting the importance of its removal is the formation of disinfection by-products (DBPs). DBPs are formed during chlorination when residual NOM reacts with chlorine which is one of the most commonly used disinfectants in drinking water treatment. DBPs have been found to have adverse human health effects including being carcinogenic (Health Canada, 2006). Although there are different compounds that can be formed, Health Canada only has maximum acceptable concentrations (MACs) for trihalomethanes (THMs) and haloacetic acids (HAAs), 0.100 mg/L and 0.080 mg/L, respectively. These strict regulations put great emphasis on the removal of NOM during treatment.

Site specific NOM characteristics can dictate coagulant type and dose as well as process selection in a treatment facility. The concentration of NOM typically dictates the coagulant demand which could influence the selection of chemicals used in the treatment process (Edzwald, 1993). It can also influence the selection of clarification, as shown in Figure 2.1. The composition of the NOM can also influence design decisions for the treatment process due to its complexity and variety. It is important to understand its composition to achieve optimal removal during treatment.

2.2.2 Composition

There are two main fractions when referring to the composition of NOM, the hydrophobic portion and the hydrophilic portion. The hydrophobic fraction is mainly composed of humic and fulvic acids. These are considered humic substances and their molecular structures are aromatic, often containing attached hydroxyl groups and conjugated double bonds. The hydrophobic fraction typically accounts for over 50% of the total NOM (Sharp, Parsons, et al.,

2006). The hydrophilic fraction mainly consists of carboxylic acids, carbohydrates, and proteins, which are made up of aliphatic and nitrogenous compounds. This fraction is typically a small contribution to the overall NOM concentration, especially when NOM levels are high (Sharp, Parsons, et al., 2006). Hydrophobic NOM has been noted as being more susceptible for removal via coagulation than hydrophilic NOM due to mechanisms involved. This is related to the charge density associated with each fraction. Hydrophobic NOM contain more ionized groups leading to a higher charge density compared to hydrophilic NOM. This in turn leads to better reactivity during coagulation (Sillanpää et al., 2018).

Molecular mass is another important property when considering the composition of NOM. As previously mentioned, NOM compounds can vary in size from anywhere between 100 to 100,000 Da. It is widely noted that NOM with higher molecular masses have much higher removals via coagulation than compounds with low molecular mass. This is attributed back to hydrophobicity as higher molecular masses often contain more aromatic molecules (Matilainen et al., 2010; Nissinen et al., 2001). More advanced treatment processes, such as ozone and GAC filtration, have shown to achieve higher removals of NOM with low molecular mass (Nissinen et al., 2001). The hydrophilic fraction is typically responsible for DBP formation as it constitutes the majority of NOM residual following treatment.

2.2.3 Quantification

Typical water quality parameters used to represent NOM concentrations include total organic carbon (TOC), dissolved organic carbon (DOC), colour, UV_{254} , and specific UV absorbance (SUVA). Some of these parameters can also offer information towards the composition of the NOM. TOC provides a thorough measurement to help indicate the amount of NOM in the water by quantifying the amount of organic carbon present in all forms (i.e.

dissolved and suspended). DOC is similar but instead indicates only the portion of organic carbon which passes through a 0.45 μm filter membrane. This is intended to represent the dissolved portion of organic carbon which is typically found to be the largest portion at around 90% (Leenheer & Croué, 2003). TOC and DOC analyses typically take days or weeks as they are completed in commercial laboratories. These measurements are reported in concentrations in terms of mg/L.

Colour and UV_{254} are parameters that can be measured on a benchtop spectrophotometer and results are acquired instantly. Humic and fulvic acids, which are found in NOM compounds, produce yellow and brown colours which can be measured on a spectrophotometer. Measuring colour essentially determines how yellow-brown the sample is which can indicate the amount of humic/fulvic acid which alludes to the amount of NOM. Colour is typically reported in platinum-cobalt units (Pt-Co) or total colour units (TCU) which are equivalent. Colour is not always correlated with the NOM content as there can be other sources of colour present but it can give a quick estimation (Christman & Ghassemi, 1966). A more meaningful estimate can be obtained by measuring UV_{254} which measures the UV absorbance at a wavelength of 254 nm using a spectrophotometer. A large portion of NOM is comprised of aromatic structures which have been found to absorb light at a 254 nm wavelength. Because of only one wavelength being used, UV_{254} does not give a comprehensive representation of all NOM as non-aromatic compounds are missed (Matilainen et al., 2011).

SUVA is another parameter used to not only quantify but to also characterize the NOM. SUVA is calculated using DOC and UV_{254} which helps describe the composition of the NOM. Equation 2.1 is used to calculate SUVA.

$$SUVA = \frac{UV_{254} (cm^{-1})}{DOC (mg/L)} \times 100 \quad \text{Equation 2.1}$$

As shown in the equation, SUVA is the ratio of UV_{254} to DOC. TOC is sometimes substituted for DOC in cases where TOC and DOC are nearly equivalent (Matilainen et al., 2010). Since UV_{254} encapsulates the aromatic portion of the NOM, SUVA gives an indication the nature of the NOM in terms of the hydrophobicity and hydrophilicity by comparing UV_{254} to the entire NOM amount, represented by DOC. SUVA values less than 2 typically suggest poor NOM removal via coagulation. Fair NOM removals via coagulation can be expected with SUVA values between 2 and 4. SUVA values greater than 4 typically lead to good NOM removal via coagulation (Matilainen et al., 2011).

2.2.4 Increasing NOM Concentrations

Utilities have faced challenges in the last few decades as a result of experiencing historical NOM increases in their source waters. This phenomenon is typically referred to as brownification which describes increases in water colour, attributed to elevated DOC concentrations. The main drivers behind brownification have been suggested to be linked with climate change and the reduction of sulfate deposition (Kritzberg et al., 2020). The effect of climate change on hydrological cycles is noted as one of the main factors leading to increases in DOC concentration. Wetter climates caused by climate change lead to increased runoff which collect and transport organic carbon to surface water catchments. Additionally, wetter climates are suggested to lead to decreased organic carbon decomposition in water bodies as a result of reduced retention times (de Wit et al., 2016). Another key driver for brownification is the reduction in sulfate deposition in surface waters. Regulations on air emissions have led to this reduction which are widely reported in the Northern Hemisphere. Skjelkvåle et al. (2001) noted

sulfate deposition reductions in surface waters of about 60% in Nordic countries between 1990 and 1999. Garmo et al. (2014) reported sulfate deposition reductions between 15 and 59% in 11 of 12 study sites across North American and Europe. Anderson et al. (2017) reported decreased sulfate deposition by nearly 83% in a Nova Scotia lake from 1984 to 2015. Increasing trends in acid neutralization capacity (ANC), alkalinity, and pH have been reported in surface waters experiencing reductions in sulfate deposition (Evans & Monteith, 2001). This is evidence of chemical recovery occurring in surface waters to levels found prior to acidification, often referred to as lake recovery. Increases in DOC have also been reported in surface waters experiencing lake recovery, returning to levels found prior to acidification (Monteith et al., 2007). NOM mobility is suggested to increase with decreased acidity as the solubility of the NOM is impacted (Ekström et al., 2016).

Anderson et al. (2017) showed Pockwock Lake and Lake Major, the two main source waters used by Halifax Water, sulfate concentrations had decreased by 38% and 52%, respectively, between 1999 and 2015. During this same period, colour increased in Pockwock Lake and Lake Major by 0.55 TCU/year and 1.6 TCU/year, respectively. Most notably the water colour in Lake Major had doubled from 1999 to 2015. The TOC concentrations in both lakes were found to increase by approximately 1 mg/L since 1999 (Anderson et al., 2017). These increases in NOM have led to operational changes in each plant, namely increasing coagulant doses. Most significantly, the coagulant dose at Lake Major increased from 13 mg/L in 1999, the year the plant was commissioned, to 50 mg/L in 2015. Higher coagulant doses add to operational costs with increased chemical consumption. Higher coagulant doses can also lead to increased sludge production, increasing waste residuals needing to be disposed of. Clarification efficiency could also be affected through increased loading as the design of infrastructure likely did not

consider future changes in source water quality. Filter run times are also expected to be impacted with increased coagulant doses and potential clarification underperformance. This has led to treatment facilities looking towards implementing upgrades and new technologies to mitigate the current and potential future impacts of brownification.

2.3 Coagulation and Flocculation

Coagulation and flocculation are two main treatment processes that are widely used throughout the drinking water treatment industry, dating back to the turn of the 20th century. They are crucial steps in the treatment process for the removal of suspended and colloidal particles, which are otherwise difficult to extract from the water matrix (Bratby, 2016). Most notably, enhanced coagulation is very effective in the removal of NOM which aids in limiting the formation of DBPs following disinfection processes. Coagulation and flocculation are mainly used to target the reduction of turbidity and NOM concentrations but can also lead to the removal of a variety of contaminants including pathogens that may otherwise pass through filters (Sillanpää et al., 2018). The two components, coagulation and flocculation, work synergistically. Coagulation is the addition of a chemical, typically a metal salt, for the purpose of destabilizing colloidal particles. The colloids are destabilized by the cationic coagulant reducing the repulsive potential of their electrical double layers which are typically negatively charged. This occurs through various mechanisms with all achieving a similar outcome of creating suspended micro-particles (Matilainen et al., 2010). To enhance removal, the destabilized particles and other suspended particles are agglomerated during flocculation to create larger particles. The destabilized/neutralized micro-particles will agglomerate to create larger flocs through attractive van der Waals forces, providing higher removal efficiency (Hierrezuelo et al., 2010). These larger particles, commonly referred to as flocs, are more easily separated from the water during

the clarification stage which follows coagulation/flocculation (Bratby, 2016; Duan & Gregory, 2003). Coagulation/flocculation is a fairly complex process as there are many variables that need to be considered with its use. These variables include the type of coagulant, removal mechanisms, and source water characteristics (Davis & Edwards, 2014). It is important to understand the intricacies of coagulation/flocculation to achieve optimal removal.

2.3.1 Types of Aluminum Based Coagulants

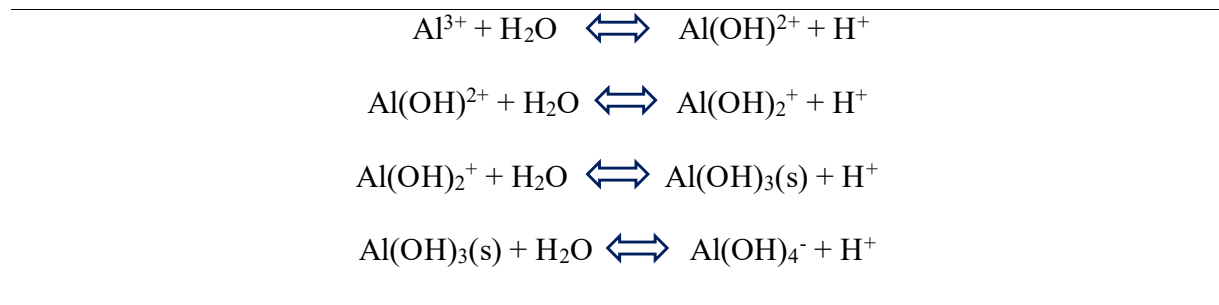
Various metal salts are used in the drinking water treatment industry for coagulation. Aluminum based coagulants are noted as being the most versatile which has led to their widespread use in the water treatment industry. This versatility stems from their stability and being easy to handle while at the same time having high reactivity with a variety of contaminants (Matilainen et al., 2010; Miranda et al., 2020). Aluminum sulfate $[Al_2(SO_4)_3 \cdot nH_2O]$ has historically been the most commonly used coagulant in the water treatment industry, referred to in the industry as alum. Its wide use in the industry stems from its performance in combination with its low cost and high availability (Sillanpää et al., 2018). However, there has been increasing use of prehydrolyzed aluminum coagulants as development and research have shown their advantages. The most commonly used coagulant of this type is polyaluminum chloride (PACl).

2.3.1.1 Alum

The chemistry involved with the dissociation of alum in water is fairly complex which leads to various reaction pathways. Different aluminum hydrolysis products can be created depending on the pH of the water (Van Benschoten & Edzwald, 1990). This leads to the performance of alum being highly reliant on the pH of the water. The hydrolysis of alum can also be affected by the temperature of the water as the reactions occur at slower rates at lower

temperatures (Yu et al., 2007). The aluminum species that are formed have been found to affect the means of floc formation and NOM removal (Qin et al., 2006). Temperature is also found to impact their distribution. These products include Al monomers such as Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_3$, and $\text{Al}(\text{OH})_4^-$ as well as Al polymers with the general formula of $\text{Al}_n(\text{OH})_y^{3n-y}$. However, polymeric species are not typically found in high concentrations during alum coagulation (Pernitsky & Edzwald, 2006). The dissociation and hydrolysis of various Al species with alum is shown in Table 2.1.

Table 2.1 Aluminum hydrolysis reactions for alum.



The positively charged monomers, which are typically found at pH lower than 6, are noted as being responsible for the destabilization and precipitation through charge neutralization of dissolved contaminants. Al precipitates, $\text{Al}(\text{OH})_3(\text{s})$, are found at pH closer to neutral and responsible for entrapment/enmeshment of colloidal particles but can also adsorb dissolved contaminants (Van Benschoten & Edzwald, 1990). It is important to understand the formation of each aluminum species as they influence the removal mechanism which impacts the removal efficiency of different contaminants. These different removal mechanisms will be discussed in more detail later in section 2.3.2.

2.3.1.2 Polyaluminum Chloride

Polymers containing aluminum have gained more popularity for their use for coagulation in drinking water treatment. These chemicals are considered to be pre-hydrolyzed meaning the reactive hydrolysis species are already formed before the addition to water. This is very advantageous when comparing to alum coagulation as the reactions can happen instantaneously with contaminants. This leads to faster reactions with contaminants and more efficient removal. These coagulants are more resilient in lower temperatures and can perform in a wide pH range (Matilainen et al., 2010; Pernitsky & Edzwald, 2006; Van Benschoten & Edzwald, 1990). The most common chemical of this form is polyaluminum chloride (PACl). PACl contains high amounts of the polymeric species Al_{13}^{7+} ($AlO_4Al_{12}(OH)_{24}^{7+}$) which is considered to be the most efficient species in terms of contaminant removal (Matilainen et al., 2010). The formation of this species with PACl does not depend on the pH of the water unlike alum. The pH can affect the stability of the species though (Krupińska, 2020). Al_{13}^{7+} is considered as the most efficient Al-species for coagulation due to its large size and high positive charge. Al_{13}^{7+} has relatively high stability which makes it readily available for charge neutralization and adsorption removal mechanisms (Duan & Gregory, 2003). Prehydrolyzed coagulants however are more expensive and are not as readily available compared to conventional coagulants like alum.

2.3.2 Removal Mechanisms

Attributed to the complexity of the chemistry involved with coagulation, there are a variety of removal mechanisms. The properties associated with each removal mechanism lead to different efficiencies when considering different contaminants. The main coagulation mechanisms that are discussed in the literature are charge neutralization, adsorption, and enmeshment/entrapment. Each mechanism is found to produce flocs with different sizes,

structures, and shear strength. The mechanisms can work simultaneously and even work in combination with each other.

2.3.2.1 Charge Neutralization

Almost all colloidal contaminants in the water matrix are negatively charged and are found to have electrical double layers in solution. This phenomenon is a result of the negative surface charge on the particles which attract positive counter-ions towards its surface which forms the first layer, called the Stern Layer. The second layer, called the Diffuse Layer, has a net negative charge as anions in the medium (water) are attracted to the layer of positive cations. Zeta potential is used to characterize the electrical potential at the outer plane of the second layer (Park & Seo, 2011). A diagram of the electric double layer phenomenon is shown in Figure 2.2.

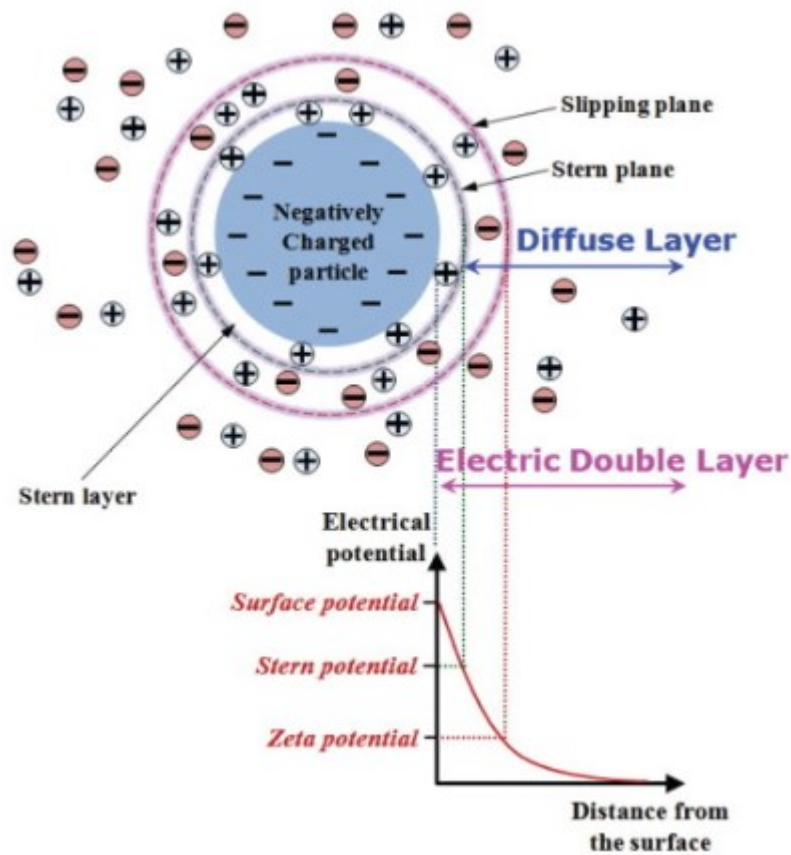


Figure 2.2. Electric double layer of colloid in water (from Park & Seo, 2011).

The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory describes the effect of van der Waals forces and electrostatic double layer forces acting on two particles. The forces are said to act independently and can be added to determine the total force acting on the two particles. The van der Waals attractive forces are impeded by the electrostatic repulsion between colloids in water (Adair et al., 2001). The negative zeta potentials shared amongst the colloids do not allow them to come close to each other. The addition of a coagulant leads to the formation of cationic Al-species which are attracted to the colloids. This leads to the neutralization of their surface charge and a reduction of the thickness of their electric double layer. Eliminating the electrostatic repulsion allows for colloids to agglomerate, precipitate, and form flocs through van der Waals attractive forces (Hierrezuelo et al., 2010). Charge neutralization has been noted as being able to

form strong microflocs as it is a stoichiometric process and does not use excessive coagulant doses (Alansari & Amburgey, 2020; Cruz et al., 2020).

2.3.2.2 Adsorption

Adsorption is another mechanism for the destabilization of soluble colloids, namely humic NOM. Humic substances are noted as having a high affinity for aluminum hydroxide (Davis & Edwards, 2014). Unlike charge neutralization which relies on cationic Al species, adsorption of soluble contaminants typically takes place on precipitated solid aluminum hydroxide ($\text{Al}(\text{OH})_3(\text{s})$) (Dempsey et al., 1984). Adsorption can also take place with Al polymers. The polymers have reactive hydroxyl groups that can react with the colloidal particles by binding to their surfaces. Larger flocs are then formed when the polymers bridge together with the adsorbed contaminants (Ghernaout & Ghernaout, 2012). It can be difficult in practice to differentiate when charge neutralization or adsorption mechanisms are occurring. However, charge neutralization is dominant at pH lower than 6 while adsorption is considered dominant at higher pHs. This is because the precipitation of aluminum hydroxide is said to occur rapidly at higher pH (Davis & Edwards, 2014).

2.3.2.3 Sweep Flocculation

Sweep flocculation is considered a secondary removal mechanism as it typically occurs once the coagulant demand for charge neutralization and adsorption mechanisms are satisfied (Pernitsky & Edzwald, 2006). Sweep flocculation is defined as the enmeshment or entrapment of colloidal sized particles. Sweep flocs are formed with excess amounts of aluminum hydroxide entrapping the particles (Ghernaout & Ghernaout, 2012). This leads to higher coagulant demands which increases chemical consumption and costs. Increased sludge production are also experienced with high coagulant doses when sweep flocculation is targeted. However, an

advantage that sweep flocculation poses is that it is less reliant on an optimum coagulant dose as overdosing does not impact removal. Sweep flocculation is not reliant on stoichiometry regarding particle concentration because it is non-selective. This can be advantageous but does not make it particularly effective in removing soluble NOM. DOC is found to have strong stoichiometric relationships with alum doses, particularly at high concentrations (Shin et al., 2008). Flocs formed through sweep flocculation are found to have different properties than those found with other mechanisms. Sweep flocculation tends to form larger flocs with high positive charges, attributed to the larger coagulant doses (Bache, Rasool, et al., 1999; Han et al., 2001). Different floc properties can impact the selection and operation of clarification processes.

2.3.2.4 Effect on Floc Formation

The type of coagulation mechanism can affect the formation of flocs. Sweep flocculation typically results in larger flocs compared to those created through charge neutralization. This is attributed to sweep flocculation using larger coagulant doses (Cruz et al., 2020). The time of floc formation is also found to be impacted by coagulation mechanisms. Alansari & Amburgey (2020) found that sweep flocculation took just under 10 minutes for the flocculation index to reach a plateau while charge neutralization took upwards of 20 minutes, shown in Figure 2.3.

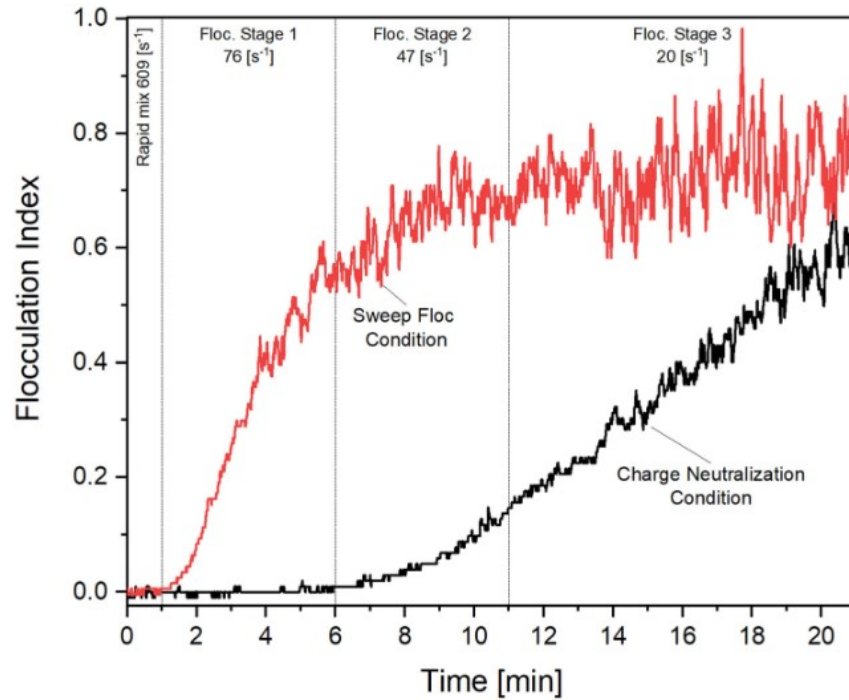


Figure 2.3. Flocculation index based on flocculation time for charge neutralization and sweep flocculation (from Alansari & Amburgey, 2020).

Flocculation index essentially indicates the degree of aggregation of particles in suspension. It is measured using a photometric dispersion analyzer which compares fluctuations in light beam intensity passing through a sample to the average of the beam intensity. An increase in flocculation index indicates aggregation (Alansari & Amburgey, 2020).

Figure 2.4 shows results from the same study on the performance of each coagulation mechanism based on settled and filtered turbidity removal.

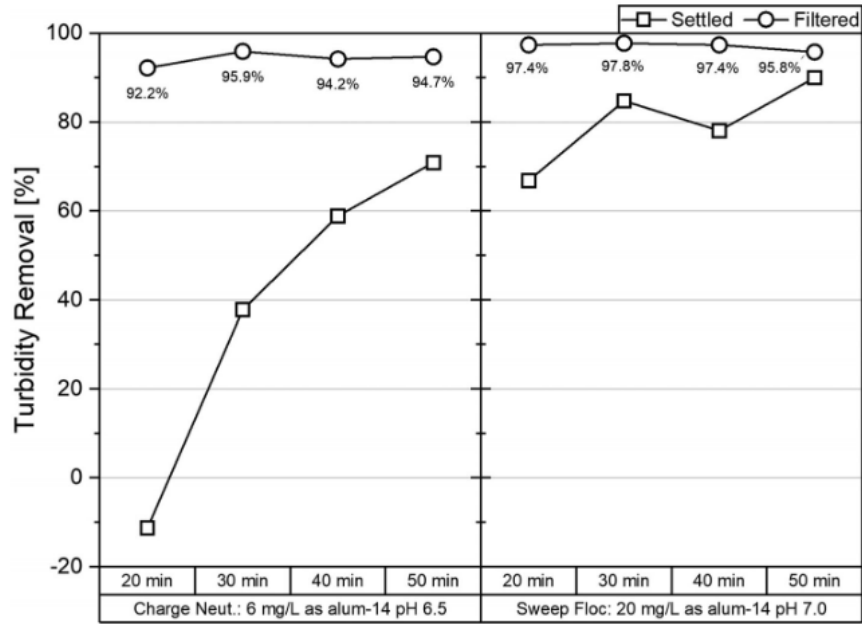


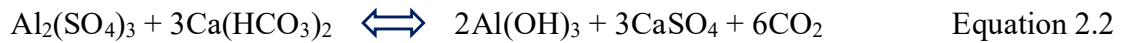
Figure 2.4. Flocculation index based on flocculation time for charge neutralization and sweep flocculation (from Alansari & Amburgey, 2020).

Turbidity removal following sedimentation with charge neutralization conditions was found to increase from -11% to 71% as flocculation time increased from 20 to 50 minutes. A similar trend was found with sweep flocculation but to a less extent with settled turbidity removal increasing from 67% to 90% over the same time period. Filtered turbidity removal was found to be independent of flocculation time or mechanism as filtered removals for both charge neutralization and sweep flocculation were within 4% of each other. This suggests that even with 20 minute flocculation for charge neutralization flocs were large enough to be filtered but not for settling (Alansari & Amburgey, 2020). Alternative clarification methods such as flotation may be able to improve removal of flocs this size.

2.3.3 Water Characteristic Effects

2.3.3.1 pH

The dissociation and hydrolysis of alum relies on the consumption of alkalinity as the pH would be reduced significantly without it. Waters typically contain natural alkalinity in the form of HCO_3^- which leads to the hydrolysis of alum outlined in Equation 2.2 (Krupińska, 2020).



If natural alkalinity is not present then a buffer is added to increase the pH. Sodium hydroxide (NaOH) is one of the most commonly used buffers. Without alkalinity, hydrolysis cannot happen which prohibits the formation of reactive Al species necessary for coagulation. The concentration of each Al species is pH dependent which is shown in Figure 2.4.

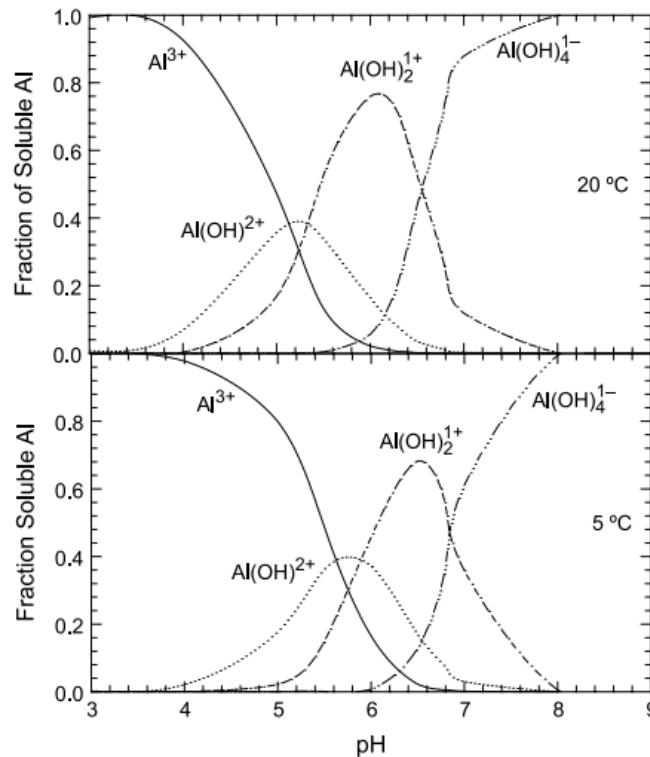


Figure 2.5. Fraction of soluble Al-species based on pH. Shown for water temperature of 5 and 20 °C (from Pernitsky & Edzwald, 2006).

At pH values less than 5, Al^{3+} is the most dominant dissolved Al species which is highly charged. As the pH increases, so does the fraction of cationic aluminum hydroxides which are key for charge neutralization. Anionic Al species, $\text{Al}(\text{OH})_4^-$, are found to be dominant at pH greater than 6.5. The minimum solubility of alum is approximately 6, meaning solid aluminum hydroxide, $\text{Al}(\text{OH})_3(\text{s})$, is found to precipitate the greatest at this pH. Consequently, the optimum pH range for alum coagulation is suggested to be around 6 to promote the amount of cationic Al species as well as aluminum hydroxide precipitate which are responsible for coagulation mechanisms (Pernitsky & Edzwald, 2003, 2006; Qin et al., 2006).

Pre-hydrolyzed coagulants, such as PACl, provide many advantages in terms of pH impacts. Pre-hydrolyzing leads to PACl being partially neutralized during manufacturing. As a result it has less effect on the pH once added to the water compared to alum. This reduces chemical dosing for pH adjustment, decreasing plant chemical consumption (Duan & Gregory, 2003). The degree of neutralization can be varied which leads to PACl typically being categorized into three categories; low, medium, and high basicity. The level of basicity is typically selected depending on the natural pH of the source water. To promote optimal performance, the pH at which minimum solubility occurs that should be targeted is 6.4 for PACl. However, there is more tolerance for deviating from this pH as PACl already contains reactive Al species prior to dosing and leads to a wider acceptable operating range for pH (Krupińska, 2020; Pernitsky & Edzwald, 2006).

2.3.3.2 Temperature

As shown in Figure 2.4, temperature is also found to impact coagulation and the hydrolysis of alum. Lower temperatures are found to increase the pH of minimum solubility thus increasing the optimum pH for coagulation (Pernitsky & Edzwald, 2006). Lower water

temperatures also change the viscosity and density of the water which impacts the kinetics and precipitation of aluminum hydroxide. Slower reaction times and poorer coagulation is typically experienced with colder water. This leads to decreased removal efficiency as smaller and weaker flocs are formed which are not removed well (Knocke et al., 1986; Morris & Knocke, 1984). This may warrant the need for longer flocculation times and increased alum doses during colder periods. The performance of PACl has been found to be fairly insensitive to water temperature (Matilainen et al., 2010). Being pre-hydrolyzed, PACl does not experience delayed kinetics for hydrolysis reactions in colder water. Higher PACl doses may need to be used in colder water to overcome changes in water density and viscosity to accelerate settling of flocs (Zhang et al., 2018).

2.3.3.3 NOM

NOM typically requires a greater coagulant demand compared to particulate matter. The cationic exchange capacity per milligram of DOC is over 10 times greater than particulate matter. This leads to NOM controlling coagulation rather than turbidity, especially for source waters with relatively low turbidity (Edzwald & Van Benschoten, 1990). NOM molecules are typically negatively charged due to their anionic functional groups. As a result, charge neutralization is typically the most effective coagulation mechanism for the removal of NOM. Charge neutralization is noted as being a stoichiometric process which puts more of emphasis on finding the optimal coagulant dose (Alansari & Amburgey, 2020). Optimal NOM removal is found at pH levels between 4.5 and 6 where a mixture of aluminum hydroxide species are found, as discussed in section 2.3.3.1, including those with high charges responsible for charge neutralization. Sweep flocculation conditions are typically found at a pH closer to neutral where

precipitated aluminum hydroxide species are found (Cruz et al., 2020; Ghernaout & Ghernaout, 2012).

The composition of NOM can significantly influence coagulant demand. Humic NOM, with high hydrophobicity and high molecular weight has been found to be the most susceptible to removal via coagulation. These characteristics and certain functional groups give higher charge densities which results in high reactivity through charge neutralization and adsorption with coagulants (Randtke, 1988; Sharp, Parsons, et al., 2006). The concentration of the hydrophilic fraction is generally a good indication for expected NOM residual post coagulation. Hydrophilic NOM is highly soluble with little to no charge density leading to low reactivity with coagulants (Sharp, Parsons, et al., 2006). Characterizing the composition of the NOM is therefore essential in regards to treatment, especially for coagulation. SUVA can provide indications for expectations in terms of NOM removal. SUVA values greater than 4 are correlated with NOM that is mostly humic with high hydrophobicity and high molar masses which lead to good removals. SUVA values between 2 and 4 indicate a mixture of hydrophobic and hydrophilic NOM. SUVA values less than 2 indicate NOM that is mostly hydrophilic with low molar mass which lead to poor removals (Matilainen et al., 2010).

2.3.3.4 Zeta Potential

Zeta potential is the charge at the slipping plane of an electrical double layer and essentially describes the surface charge. Zeta potential is typically negative in raw water due to colloids carrying negative charges for the most part. The zeta potential of raw waters differ as it is affected by the water quality. The addition of a coagulant increases the zeta potential as coagulant produce cationic species (Han et al., 2001). Figure 2.5 shows a general trend of how zeta potential is changed with the addition of alum.

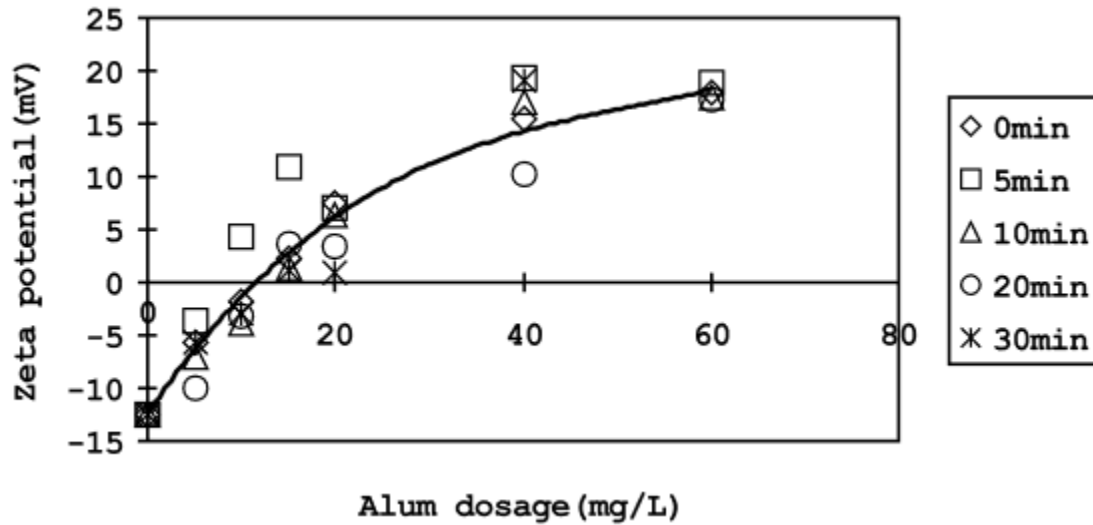


Figure 2.6. Zeta potential based on alum dose (from Han et al., 2001).

Zeta potential is found to impact coagulation especially when considering charge neutralization. Sharp et al. (2006) found that DOC removal was the most optimal and stable in a zeta potential range of -10 to +3 mV. Other studies have shown results that agree with this optimal range (Gregory & Carlson, 2003; Sharp et al., 2005). Han et al. (2001) investigated the impact of zeta potential on turbidity removal using DAF. They found that optimal removal was found a zeta potentials near or just slightly above zero.

2.4 Dissolved Air Flotation

Dissolved air flotation (DAF) is a clarification process that has been used in place of sedimentation. Sedimentation is ineffective in most cases for clarification in drinking water treatment as low solids concentrations mean flocs do not become large or heavy enough to settle in a practical sense. Instead of relying on gravity, DAF uses flotation to separate flocs which is more efficient for removing smaller and less dense solids.

DAF has been used extensively in Europe since the 1970s as the primary clarification method in drinking water treatment. The use of DAF in North America became increasingly

popular in the 1990s and has been incorporated in the design of treatment plants for large cities. Most notably, the Croton Water Treatment Plant supplies New York City and has a capacity of producing in excess of 1100 million litres per day (MLD) (Edzwald, 2010; Edzwald et al., 1992). The widespread use of DAF is attributed to the many advantages that it provides, which will be further discussed in this section along with its general process and characteristics.

2.4.1 Process

DAF clarification generally follows conventional coagulation and flocculation to preform flocs that are readily separated from the water. Instead of waiting for flocs to settle to the bottom of the tank, flocs are floated to the surface with air in DAF. The DAF tank consists of two different zones, the contact zone and the separation zone which are separated by a baffle. After coagulation/flocculation the water enters the contact zone where air bubbles are injected. Turbulence is high in the contact zone which promotes collisions and attachment between air bubbles and flocs. The attachment of bubbles to the flocs increases buoyancy leading to efficient flotation. After the contact zone the water contains a mix of floc-bubble aggregates, free bubbles, and unattached floc particles and flows over a baffle into the separation zone. Floc-bubble aggregates and free bubbles float to the surface forming a concentrated sludge that is skimmed off and disposed of. The clarified water leaves the bottom of the DAF tank to increase separation from the floated sludge. A portion of clarified water is taken from the effluent for recycle flow. Recycle flow is saturated with air bubbles in a vessel called a saturator that is pressurized with an air compressor. After saturation, the recycle flow is injected into the contact zone of the DAF tank where microbubbles are produced. Recycle rates are typically 10% for DAF (Edzwald, 2010; Gorczyca & Klassen, 2008). Figure 2.6 outlines the general DAF process.

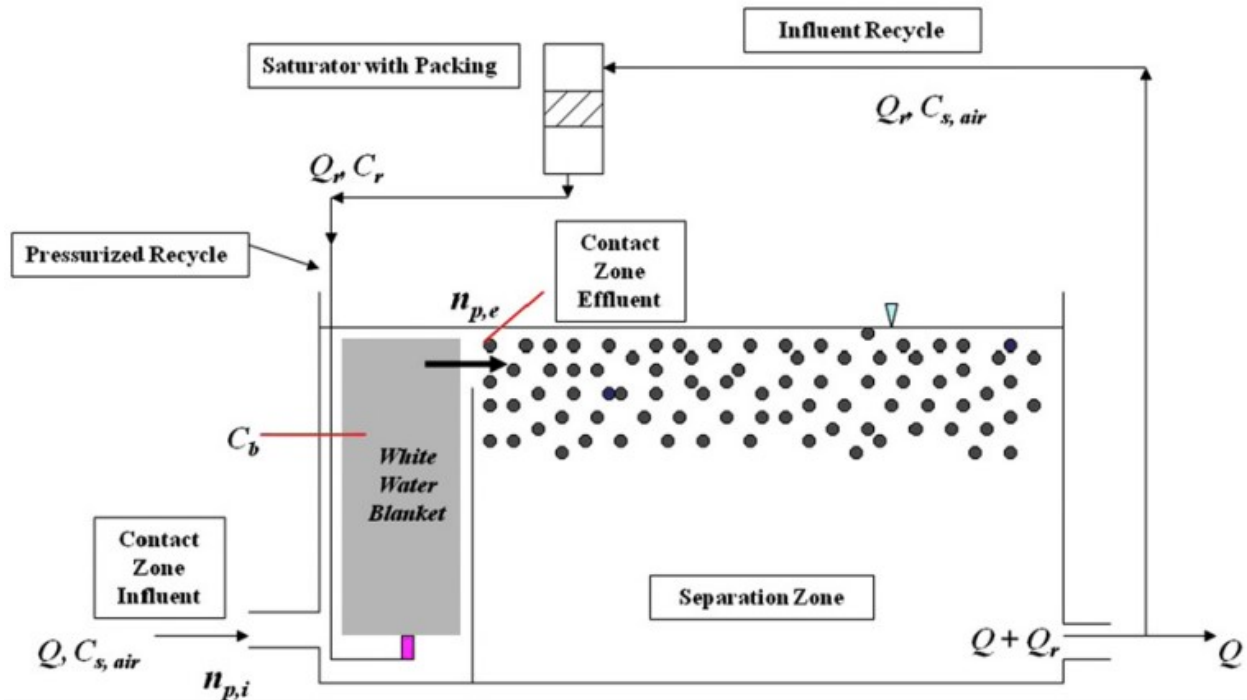


Figure 2.7. General DAF Clarification Process (from Edzwald 2010).

2.4.2 Pre-Treatment

2.4.2.1 Floc-Bubble Attachment

Coagulation and flocculation are crucial processes for effective DAF performance. Certain floc properties involving size and surface charge have been found to be desirable for DAF. Flocs must be made large enough to promote collision opportunities with air bubbles in the contact zone. Research has shown particles of $100\mu\text{m}$ and greater in size to have a contact zone efficiency of 100%. However, particles with sizes of between $25\text{-}50\mu\text{m}$ have been noted to be optimal as they were shown to have collision efficiencies near 99% (Edzwald, 2010). The larger the floc the more energy and chemical are needed. Other studies have agreed with these floc sizes being optimal as they suggest floc sizes should be similar to bubble sizes to obtain good opportunities for collisions. Bubble sizes are typically around $50\mu\text{m}$ but depend on the pressure used in the saturator (Mun et al., 2006). More bubbles are required to float larger flocs and

bubble detachment is more likely (Edzwald, 2010). Shear conditions are also considered to be quite significant in the contact zone of DAF tanks at G values of upwards of 1000 s^{-1} . Larger flocs could be more susceptible to breakage under shear stress due to their size but they have also been noted as being more fragile due their open structure (Bache & Rasool, 2001; Jarvis et al., 2005).

Another important property of flocs when using DAF clarification is their surface charge. In water air bubbles adsorb HCO_3^- and OH^- ions onto their surface which creates an electrical double layer on their surface. Consequently contaminant particles and air bubbles would share negative charges which would lead to electrostatic repulsion and poor attachment efficiency. This highlights the importance of coagulation to produce flocs with near neutral charges to lower electrostatic forces or opposing (positive) charges to produce electrostatic attraction (Edzwald, 2010). Charge neutralization coagulation mechanisms may need be targeted as they are based around reducing/reversing particle surface charge. This is supported by Han et al. (2001) who showed that optimal removal efficiencies are achieved with zeta potentials slightly above 0 mV at flocculation times greater than 10 minutes. However, at flocculation times less than 10 minutes optimal removal efficiency is found with higher zeta potentials around 10 mV.

2.4.2.2 Flocculation Time

During the early years of the use of DAF long flocculation times around 20-30 minutes were used, similar to those used with sedimentation. Many studies in the last few decades have suggested long flocculation times are counterintuitive with DAF clarification. Longer flocculation times allow for the formation of larger flocs which as previously discussed are not necessarily desirable with DAF. Longer flocculation times also reduce efficiency and are suggested to not be economically feasible. These studies have reported flocculation times as low

as 5 minutes to achieve adequate removals due to the formation of ‘pin-point’ flocs that are efficiently removed with DAF. The same studies have noted that longer floc times lead to slightly better performance but the differences are not entirely significant (Edzwald et al., 1992; Edzwald, 2010; Plummer et al., 1995; Valade et al., 1996). Therefore it is widely considered that short floc times are more economically feasible. These studies do not directly discuss the coagulation mechanism occurring during the experiments. The duration of flocculation in addition to the coagulant dose may facilitate different coagulation mechanisms which can impact removal efficiency especially when considering different contaminants, as discussed in section 2.3.2. Targeting charge neutralization mechanisms may require longer flocculation times which also demand lower coagulant doses and limit the size of the flocs.

2.4.3 Key Contaminant Removal

The ability of DAF to remove low density particles provides considerable benefits especially in treating water sources with natural colour, low turbidity, or that experience algae blooms. Many source waters in Atlantic Canada are found to have these water quality characteristics. Metal hydroxide-NOM complexes have relatively low density which do not settle readily making flotation a more attractive approach. The NOM concentration is not found to impact removal efficiency with DAF as it is effective in both low and high DOC waters (Valade et al., 2009). Turbidity is noted as affecting the density of flocs, especially mineral turbidity. High mineral turbidity may require additional air for flotation. DAF is suggested to be used in waters with non-mineral turbidity less than 100 NTU or mineral turbidity less than 50 NTU (Valade et al., 2009). DAF is also noted to be much more effective in removing algae compared to sedimentation as the density of algae is very low. Insufficient removal of algae can lead to filter clogging. The presence of diatoms, a type of algae, are widely known to lead to filter

clogging that cause major disruptions in water production. Other types of algae like cyanobacteria, also known as blue-green algae, produce algal toxins which can cause serious health problems for humans and animals (Brophy et al., 2019). Algae can also produce taste and odour compounds including geosmin. These compounds are not inherently toxic but do lead to customer dissatisfaction and a lack of confidence in consumption if not removed (Anderson et al., 2017). DAF has been shown to be able to remove 90-99% of algae whereas removal via sedimentation can be as low as 60% (Edzwald, 2010).

2.4.4 Pilot Scale Studies

Full scale plants have been turning towards the implementation of DAF to overcome impacts of brownification and to meet more stringent drinking water regulations. These plants include those that use direct filtration, which do not use clarification, as well as those using sedimentation or a variation. Many studies have been conducted to evaluate the performance of DAF compared to the current treatment process used. The Massachusetts Water Resources Authority piloted DAF to compare its performance to direct filtration. Their source water was characterized as low turbidity and moderate organics with ranges of 0.2-0.6 NTU and 2.3-4.6 mg/L for raw water turbidity and TOC, respectively. DAF and direct filtration provided similar UV₂₅₄ removal at around 50%. But DAF was found to improve unit filter run volume (UFRV) by approximately 50% when algae blooms were experienced. DAF was also shown to have considerable flexibility in terms of the optimal coagulant dosing range while producing similar water quality compared to other processes (Johnson et al., 1995). A pilot study conducted at the Lackareback Water Treatment Plant in Sweden investigated the impact of coagulation/flocculation conditions on DAF performance. The source water had low turbidity (0.5-1.5 NTU) and moderate TOC (4.0-4.9 mg/L). Most notably, the performance of DAF with

flocculation times of 5 and 20 minutes was evaluated. A 20 minute flocculation time produced better DAF performance but a 5 minute flocculation time was considered to be good with an effluent turbidity of 1 NTU. A 20 minute flocculation time was also found to have higher UFRVs compared to 5 minute flocculation which had higher head loss and lower UFRVs due to increases particles being deposited (Valade et al., 1996). Edzwald et al. (1992) also looked at the performance of DAF based on flocculation time. The raw water that was used had an average turbidity of 5.2 NTU and DOC of 4.6 mg/L. A flocculation time of 16 minutes led to clarified turbidities of approximately 0.4 NTU while an 8 minute flocculation time led to clarified turbidities between 0.4-0.5 NTU. DOC removals were found to be identical for both flocculation times. UV removal was found to be slightly higher with a 16 minute floc time by 5%.

Chapter 3 - Materials and Methods

3.1 Lake Major (source water)

The raw water used for the pilot plant and jar testing was drawn from Lake Major for the entirety of this work. It is located in Halifax Regional Municipality (HRM) and is the source water for the LMWSP, one of Halifax Water's primary drinking water supply plants. The water was supplied to the pilot plant via a connection to the raw water intake of the LMWSP. The lake is characterized as having low pH (<6), low alkalinity (<5 mg CaCO₃/L), and low turbidity (<0.5 NTU). Seasonal variations were experienced in the raw water quality as the project spanned all four seasons. Table 3.1 outlines the average as well as the range of various water quality analytes measured in the raw water during the project. The number of samples for each parameter were well over 100 except for THM and HAA which were sampled 5 times each during the study period. The methods used for measuring these analytes are outlined in section 3.5.

Table 3.1 Lake Major water quality between September 2020 and October 2021.

Analyte	Average	Max	Min
pH	5.4	5.7	5.1
Turbidity (NTU)	0.3	1.0	0.2
TOC (mg/L)	4.6	5.3	3.8
UV ₂₅₄ (cm ⁻¹)	0.216	0.277	0.167
SUVA	4.6	5.2	4.0
Colour (Pt/Co)	42	78	26
Mn (mg/L)	0.03	0.06	0.01
Fe (mg/L)	0.06	0.11	0.02
Al (mg/L)	0.077	0.153	0.002
THM (µg/L)	279	303	240
HAA (µg/L)	320	351	285

3.2 DAF Pilot Plant

The pilot plant for this project was a pre-existing system rented from Xylem Water Solutions. The pilot system is a standalone system that is contained within a semi-trailer and is

setup for a piping connection to receive an influent water source. Table 3.2 outlines general process characteristics of the pilot.

Table 3.2 Process characteristics of DAF pilot plant.

Process Flow	40 to 200 gpm
DAF Loading Rate	4 to 20 gpm/ft ²
Flocculation Time	3 to 30 minutes
Flocculation Stages	1 to 3
Filtration	2-1 ft ² independent media filters

The pilot plant was supplied by water that was directed from the raw water header in the LMWSP. The water entered the pilot plant system where it first encountered the addition of chemicals which included a coagulant, pH control chemicals, and an oxidant. The chemicals were fed into the influent pipe where static inline mixers helped to ensure adequate dispersal throughout the entire influent water volume.

Once chemicals were added the water entered a 2,600L rapid mix tank, which acted as the first stage for coagulation and flocculation to occur. The water then flowed into two multi-stage flocculation trains which provided tapered flocculation. Each flocculation tank had a volume of 2,000L. An adaptable piping configuration along with various valves allowed for pre-treatment tanks to be bypassed, meaning different flocculation times could be used. All pre-treatment tanks contained hydrofoil style mixers that were connected to variable frequency drives allowing for different velocity gradients to be achieved in each tank.

Following the flocculation stages the water was clarified in a 2,400L Leopold Clari-DAF system. Two headers with multiple nozzles injected air saturated recycled clarified water into the contact zone of the tank. A baffle separated the contact zone with the flotation zone which forced the water to the top of the tank, expediting flotation. The sludge was skimmed off the surface of

the tank and disposed of. The clarified water exited the DAF tank through collector pipes at the bottom of the tank and was directed to the filter columns.

The pilot was equipped with two one-square foot filter columns that operated in parallel, allowing for different filter media to be operated. The filters were dual media of anthracite and sand for the majority of the project. The filters were fed with progressive cavity pumps which had valves downstream allowing for targeted flow rates and certain filter loading rates to be attained. The filters were backwashed using an automated backwash sequence which used air scouring as well as low and high rate backwash flows. Figure 3.1 is a general process diagram of the DAF pilot plant.

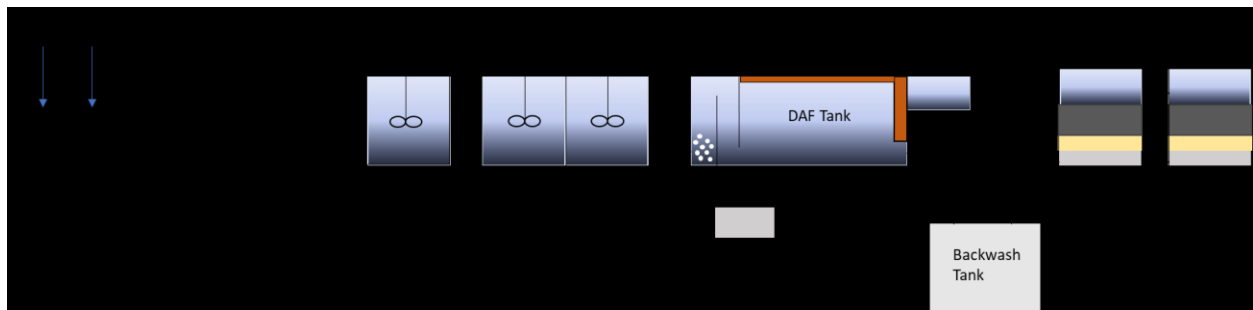


Figure 3.1. DAF pilot plant process flow diagram.

3.3 DAF Jar Tester

A DAF Platypus Jar Tester unit was used for bench-scale experiments for this study. It is equipped with four mixing stations that can be programmed to have up to three different flocculation stages with different mixing speeds and durations. Each jar has a volume of 2L with sample ports and special adapters for air saturated water injection. A fixed volume of water from a Milli-Q purification system is poured into a 2L saturator which uses an air compressor to create the air saturated water. Once the saturator vessel reaches the desired pressure, the water is released into the jars with a distribution manifold. Flotation time was manually timed with

samples being collected at the end of this time. Samples were filtered through 0.45 µm filter paper and then analyzed for a variety of water quality parameters.

3.4 Chemicals

The chemicals used for coagulation and pH control were supplied by Univar Solutions. Aluminum Sulphate ($\text{Al}_2(\text{SO}_4)_3$) was the main chemical used for coagulation. The alum was technical grade, 48% w/w aluminum sulphate liquid. This composition leads to an aluminum content of approximately 4.3% w/w. The PACl used for the bench-scale experiments was a proprietary product by Chemtrade. A range is provided for the pH and specific gravity of the chemical which are 2.5-4.4 and 1.30-1.36, respectively. These ranges align with typical PACl products which contain approximately 5.4% w/w of aluminum. The PACl used for the pilot scale experiments was supplied by Univar Solutions. The solution was approximately 20% w/w of PACl and had an aluminum content of 5.4% w/w. A 50% w/w caustic soda (NaOH) solution was used to control the pH of the water. All of the aforementioned chemicals were of technical grade and delivered in 55 gallon barrels. Each chemical consisted of a balance of water. Potassium permanganate (KMnO_4) was used for oxidation, primarily for manganese removal. Potassium permanganate powder was weighed out and added to filtered water in a 20L tote to attain a certain concentration depending on the intended dosing level.

3.5 Analytical Methods

Data collected for this work was done using benchtop spectrometers, inline probes at the pilot plant, and analytical equipment at the Centre for Water Resources Studies (CWRS) at Dalhousie University. The methods that were followed will be outlined in this section. The *Standard Method for the Examination of Water and Wastewater* (APHA et al., 2012) was primarily followed along with standard methods prescribed by Hach. All glassware used to

analyze samples was thoroughly rinsed before each use with Milli-Q water followed by a rinse with the sample.

3.5.1 General Water Quality Parameters

General water quality parameters that were regularly measured throughout this project include pH, Turbidity, UV_{254} , and colour. pH was measured using an Fisher Scientific Accumet XL50 pH meter. Turbidity was measured using a Hach 2100N turbidimeter. UV_{254} absorbance was measured using the internal program on a DR 5000 UV-Vis Spectrophotometer manufactured by Hach. Apparent colour was also measured using the same DR 5000 UV-Vis Spectrophotometer, recorded with Pt/Co units.

3.5.2 Metals

The metals measured in samples during this work included iron, aluminum, and manganese. Metal concentrations measured in jar test samples were done using an inductively coupled plasma mass spectrometry (ICP-MS) instrument at the CWRS. 5mL of sample was diluted with 5mL of Milli-Q water in plastic test tubes. This was done to ensure the concentrations were within the detection range of the instrument. Nitric acid was added to acidify the samples to pH <2 for preservation before analysis. The test tubes were capped with acid washed caps to avoid contamination.

Metal concentrations measured for samples collected at the pilot plant were done using a DR 5000 UV-Vis Spectrophotometer on site. Methods prescribed by Hach were followed for each element. Table 3.3 outlines the methods set forth by Hach that were used for analysis. Note, all benchtop analysis for manganese was completed by operators at the LMWSP as a fume hood is required to carry out this method.

Table 3.3 Hach analytical methods for measuring metals.

Element	Method
Iron	FerroVer
Aluminum	Eriochrome Cyanine R
Manganese	1-(2-Pyridylazo)-2-Naphthol PAN

3.5.3 Organic Carbon

To measure TOC 40mL glass vials were completely filled, headspace free. 4 drops of 85% phosphoric acid were added to each vial to preserve the sample. Samples were capped and then stored at 4 °C until analysis on a Shimadzu TOC analyzer. The procedure for DOC was identical except the sample was passed through a 0.45µm filter before preparing the sample.

3.5.4 Disinfection by-product formation potential

Standard Method 5710 from the Standard Methods For the Examination of Water and Wastewater was used to analyze samples for disinfection by-product formation potential (DBP_{fp}). 130mL amber bottles were soaked with concentrated sodium hypochlorite for 24 hours. After 24 hours they were emptied, rinsed 3 times with Milli-Q water, and baked in an oven at 105°C for 24 hours. 20mL glass vials were baked in an oven for 24 hours.

Water samples were first buffered to pH 8 using a pH 8 borate buffer and adding sodium hydroxide or hydrochloric acid as necessary. The samples were then transferred to 130mL amber bottles and dosed with pH 8 buffered sodium hypochlorite. The dose for each sample was selected in order to achieve a free chlorine residual of 1±0.4mg/L after a 24 hour incubation period at room temperature in a dark room. Samples that fell within this range for residual chlorine were then be prepared for DBP extraction. These samples were transferred to 20mL glass vials and preservative chemicals added before refrigerating. Extraction took place within

14 days of preparation. Samples were analyzed using gas chromatography for four different forms of trihalomethanes (THMs) and nine different forms of haloacetic acids (HAAs).

Chapter 4 - Investigating Coagulant Dosage and Type for Use with DAF

4.1 Introduction

Coagulation is an especially important pre-treatment process when dissolved air flotation (DAF) is used for clarification. Air bubbles have electrical double layers, similar to NOM, that are formed through the adsorption of bicarbonate (HCO_3^-) and hydroxide (OH^-) ions onto their surfaces (Karakashev & Grozev, 2020), resulting in a negative surface charge (Han & Dockko, 1998). Thus, coagulation is effectively used to destabilize the negatively charged NOM by neutralizing/reversing its charge. Like surface charges between particles and bubbles would lead to electrostatic repulsion with insufficient bubble-particle attachment and consequently poor removals. Coagulation is able to increase zeta potentials of floc particles with positive metal ions attaching to the NOM, raising the surface charge to give slight positive or net zero zeta potentials (Han et al., 2001). Flocs having positive zeta potentials can be electrostatically attracted to the negatively charged bubbles to promote attachment. For flocs having low or near neutral zeta potentials, attractive van der Waals forces are the main driver for particle-bubble attachment. (Edzwald, 2010). Some studies have even looked at the addition of polymers in the saturator of DAF processes to instead change the surface charge of the bubbles to become positive (R. K. Henderson et al., 2009).

Poor particle removal efficiency can also be observed if zeta potentials of the particles become too high. This is due to sweep coagulation becoming the main mechanism behind destabilizing particles instead of charge neutralization (Han et al., 2001). Sweep flocculation is a secondary mechanism of coagulation and is noted as being less efficient in NOM removal compared to charge neutralization. This is a result of sweep flocculation relying on enmeshment of particles while charge neutralization relies on stoichiometry to destabilize the NOM (Cruz et

al., 2020; Van Benschoten & Edzwald, 1990). It has been shown that organic matter is better removed through charge neutralization while inorganic contaminant removal is dominated by sweep flocculation (R. Henderson et al., 2006). Therefore, when using DAF with regards to NOM removal, an optimal coagulant dose (e.g. enhanced coagulation) needs be found to target charge neutralization to be the dominant mechanism. This can be found experimentally using jar tests but can also be predicted using a predictive model developed by Edwards (1997).

Even with an optimal coagulant dose NOM removal may be incomplete, as hydrophobic substances are readily removed through coagulation while hydrophilic substances are not easily removed through coagulation (Edwards, 1997). Further surface charge and molecular weight properties of NOM also contribute to removal during coagulation (Volk et al., 2000). White et al. (1997) showed DOC removal percentages via coagulation that were slightly higher than the percentage of hydrophobic DOC. It was suggested that the hydrophobic content was nearly entirely removed with a small portion of hydrophilic DOC removal accounting for the difference. They also showed that the hydrophilic portion requires a much greater coagulant dose. Lower doses would primarily target the hydrophobic fraction as it is readily removable. The composition of the NOM can be estimated by calculating specific ultraviolet absorbance (SUVA). A higher SUVA is related to a larger portion of hydrophobic and high molar mass which is more susceptible to coagulation. A SUVA value greater than 4 typically indicates the potential for very good NOM removal via coagulation (Matilainen et al., 2010).

During the course of this research, experiments were carried out to optimize coagulation with a particular emphasis on DAF clarification. This chapter discussed coagulant doses that were found to be optimal for NOM and turbidity removal via DAF. Data was first collected using a bench-scale jar testing unit. These tests primarily looked at various coagulant doses to achieve

optimal removal of turbidity and NOM. This data set a basis for a range of doses to be used at the pilot scale. The trials at the pilot scale further looked at the performance of coagulant doses but emphasized its effect on DAF removal efficiency. Data was also collected to identify the NOM composition and determine the removal of different fractions of NOM with certain coagulant doses. The performance of conventional and prehydrolyzed coagulant types were also investigated to compare removal efficiencies. The economic implications of operating with different doses and coagulant types was also considered in this analysis.

4.2 Materials and Methods

4.2.1 Study Site Lake Major

The water used for the experiments was taken from Lake Major in Dartmouth, Nova Scotia between September 2020 and October 2021. For the bench-scale experiments, the water was collected in 20 litre containers and stored at 4°C before use. For pilot scale experiments, the water was pumped directly from the lake into the pilot plant that was onsite. The water quality characteristics for the Lake Major water during the entire duration of the project was previously outlined in Table 3.1. The lake is characterized as having low pH (<6), low alkalinity (<5 mg CaCO₃/L), and low turbidity (<0.5 NTU) which is typical of surface waters in Atlantic Canada.

4.2.2 Bench-scale Experiments

The raw water used for the bench-scale experiments was collected in December 2020 directly from the pilot plant influent flow. The water was collected in bulk which kept the water quality fairly consistent for each batch of experiments. Table 4.2 outlines the water quality of the collected water. A measurement for each parameter on the raw water was taken before conducting the jar tests.

Table 4.1 Lake Major water quality characteristics for water collected in December 2020 for bench-scale experiments.

Analyte	Measurement
pH	5.45
Turbidity (NTU)	0.31
TOC (mg/L)	4.48
UV ₂₅₄ (cm ⁻¹)	0.22
Colour (Pt/Co)	44
Mn (mg/L)	0.05
Al (mg/L)	0.16

The bench-scale experiments were carried out as outlined in section 3.3. These experiments were conducted to evaluate a range of coagulant doses and identify an optimal dose for the removal of NOM. The procedure used at the bench-scale was designed to model the process in the pilot plant including mixing durations and speeds. For jar testing experiments, sodium hydroxide (NaOH) was used for pH adjustment where the required amount was added to achieve the desired pH for coagulation. A pH of 6 was targeted for each jar. The NaOH volume was found by completing a titration with the raw water and each coagulant dose. The NaOH was added to each jar and mixed briefly to ensure proper distribution. Both alum and PACl were trialed as coagulants for these experiments which were added after the pH adjustment. Three different stages were used for flocculation whose mixing intensities and durations matched the stages in the pilot plant. The automated mixing program was started immediately following the addition of the coagulant. The program operated automatically which provided seamless transitions between mixing stages. The first stage had a velocity gradient of 70 s⁻¹ for 7.5 minutes. The next stage had a velocity gradient of 37 s⁻¹ for 5.5 minutes. The last stage had a velocity gradient of 17 s⁻¹ and also lasted for 5.5 minutes. At the end of the flocculation stages air saturated water was injected which simulated a recycle ratio of 10%, identical to the pilot plant. Seven minutes were given for flotation to occur and samples were collected at the end of this

period. Approximately 1L of sample was collected from each jar using sample ports located approximately $\frac{1}{4}$ of the way up the jar. Samples were filtered through 0.45 μ m polysulfone filter paper to remove any remaining suspended matter. Before filtering samples, 500mL of deionized water was passed through the filter paper to rinse and avoid leaching from paper. Filtered samples were analyzed for pH, turbidity, UV₂₅₄, Colour, and DOC.

4.2.3 Pilot Scale Experiments

Pilot scale trials were carried out using the DAF pilot plant rented from Xylem Water Solutions, outlined in section 3.2. The objective for these experiments was to identify an optimal coagulant dose or doses to produce the best removal efficiency with DAF clarification, specifically focusing on a dose that provides optimal floc-bubble attachment. These experiments also looked at two kinds of coagulants that were trialed during this project to compare removal efficiencies and doses. Since the pilot was operated during all four seasons the effect of water temperature on coagulation was investigated. Data was collected for the same coagulant dose range during both cold and warm water temperatures. These experiments were all conducted at an influent flow rate of 340 L/min. This flow rate provided a retention time of 7.5 minutes in the rapid mix tank with the mixer providing a velocity gradient of 70 s⁻¹. This was followed by retention times of 5.5 minutes in each of the first and second floc tanks which had velocity gradients of 37 s⁻¹ and 17 s⁻¹, respectively.

NaOH, used for pH adjustment, was added to the water through an inline static mixer which provided thorough mixing and dispersion in the water. Alum was the primary coagulant used during the course of the pilot project while PACl was trialed briefly. The coagulant was added in the same manner as the caustic only in at a later point in the piping. The chemicals were fed using peristaltic pumps with rubber tubing. The coagulant dose was simply varied by

adjusting the pumping rate to attain the desired concentration. The dose of caustic soda was adjusted accordingly to achieve a pH in the range of 6-6.4, as suggested for enhanced coagulation where NOM removal is the primary goal with coagulation.

After the flocculation stages the water entered the DAF clarifier. The DAF system was set to use a recycle ratio of 10%. The recycle ratio describes the ratio of the volume of air saturated water injected into the DAF tank to the volume of the influent water. The retention time in the DAF tank was approximately 7.5 minutes.

Samples were collected twice daily for both the influent raw water and the effluent water from the DAF clarifier. Samples were analyzed onsite at the pilot plant for pH, turbidity, UV_{254} , colour, total iron, and total aluminum. Periodically samples were prepared and taken to the CWRS for TOC and DBP_{fp} analysis.

4.2.4 Coagulant Chemicals

The chemicals used for bench and pilot scale experiments are outlined in section 3.4.

4.2.5 Analytical Methods

All of the analytical methods used to collect data in this chapter are outlined in Chapter 3.

4.2.6 Statistical Analysis

Paired t-tests were conducted using RStudio software to evaluate statistical significance of differences in results between operational parameters. Error bars represent one standard deviation from the mean, also calculated using RStudio software.

4.3 Results and Discussion

4.3.1 Bench-scale Jar Tests

4.3.1.1 Optimal Alum Dosing for Coagulation

A range of alum doses were trialed in order to determine an optimal dose for coagulation using DAF, specifically for the removal of NOM. The bench-scale experiments were conducted in December 2020, when the pilot was shut down for upgrades. The coagulant dosing range that was tested was selected based on previous studies involving Lake Major as well as existing operations at the full scale plant at the LMWSP. The tested alum doses ranged from 41 mg/L to 58 mg/L. DOC and UV₂₅₄ were used to measure and represent the removal of NOM from the raw water. Figure 4.1 outlines the results for residual DOC based on coagulation while Figure 4.2 shows the results for UV₂₅₄.

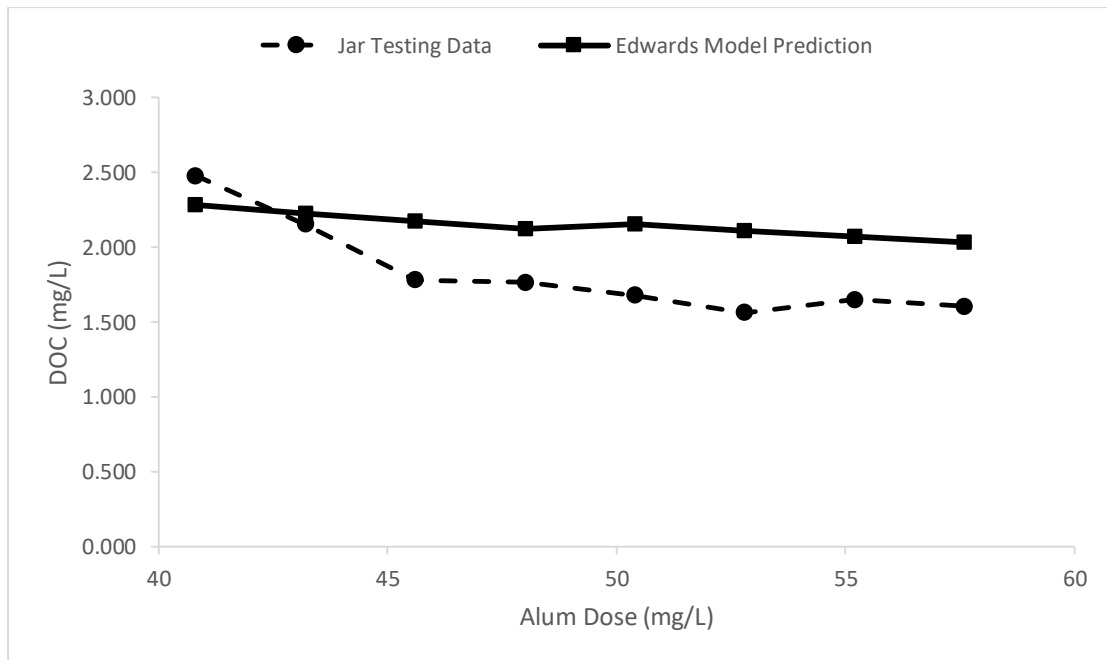


Figure 4.1. Residual DOC based on coagulant dose during bench-scale experiments. Residual DOC as predicted from the Edwards Model is also shown (Edwards, 1997).

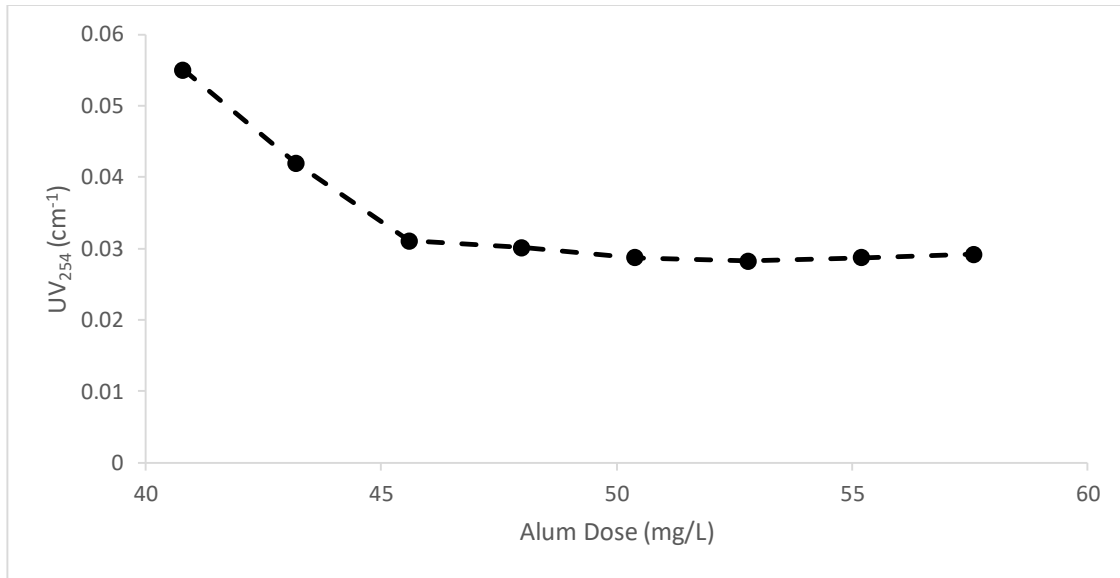


Figure 4.2. UV254 results based on coagulant dose during bench-scale experiments.

The results for residual DOC and UV₂₅₄ display a distinct optimal coagulant dose. The optimal alum dose with regards to organic matter removal was found to be 46 mg/L. A dose of 46 mg/L resulted in a residual DOC of 1.78 mg/L (60% removal) and a UV₂₅₄ of 0.031 cm⁻¹ (86% removal). The residual SUVA was 1.7 meaning the remaining NOM was mainly non-humic, hydrophilic compounds with low molecular mass. The SUVA of the raw water was 5 which allowed for high NOM removal as SUVA values greater than 4 are correlated with DOC removals greater than 50% (Matilainen et al., 2010). A dose of 46 mg/L had greater removals compared to 43 mg/L by 8% and 5% for DOC and UV₂₅₄, respectively. Doses higher than 46 mg/L did not improve DOC removal by more than 5% and did not improve UV₂₅₄ by more than 1%. This is considered the point of diminishing returns as there is insignificant improvements in residual NOM with any higher doses. It could be argued that an alum dose of 53 mg/L provides optimal DOC removal. However, the additional 7 mg/L results in a 16% increase in chemical usage and only provides 5% more DOC removal and 1% UV₂₅₄ removal.

The experimental data from the jar tests was found to result in lower residual DOC concentrations compared to those calculated using the Edwards Model which predicts DOC removal with coagulation (Edwards, 1997). The predicted residual DOC was greater than 2 mg/L for every alum dose. The experimental data showed residual DOC less than 2 mg/L for alum doses greater than 46 mg/L. The discrepancy between experimental data and predicted values likely stems from assumptions made to create the model. SUVA is used to estimate the amount of sorbable-DOC molecules and assumes that they all have the same affinity for metal-hydroxide species (Edwards, 1997). However, this is a general assumption as the makeup of the compounds contributing to DOC concentrations are fairly complex and differ between sources. As a result this model lacks accuracy to a certain extent.

The optimal dose of 46 mg/L for NOM removal is suggested to be slightly higher compared to what is expected for optimal turbidity removal. This is based on other studies that have reported lower coagulant doses being required for particle removal compared to that needed for optimal NOM removal. Turbidity removal has been noted as being dominated by particle bridging. Particles primarily responsible for turbidity typically carry negligible charges meaning lower coagulant doses are needed to agglomerate the particles. Conversely, NOM removal relies on charge neutralization as aqueous NOM particles are negatively charged. Consequently a higher coagulant demand is required to neutralize the negatively charged NOM particles to destabilize them and remove them from solution (Yan et al., 2008). Pilot scale experiments further investigated this hypothesis.

4.3.1.2 Comparison between Alum and PACl

A small range of PACl doses were trialed to compare its performance against alum in terms of NOM removal. For simplicity and ease of comparison, only the data from the point of

diminishing return and onward were used for alum in this section. Since alum and PACl have different chemical compositions, their doses were normalized on an aluminum content basis for comparison. As shown in the figures presented later in this section, the four doses that were trialed for PACl were fairly similar to the alum doses when normalized. Figure 4.3 shows the results for residual DOC for both alum and PACl while Figure 4.4 shows UV₂₅₄.

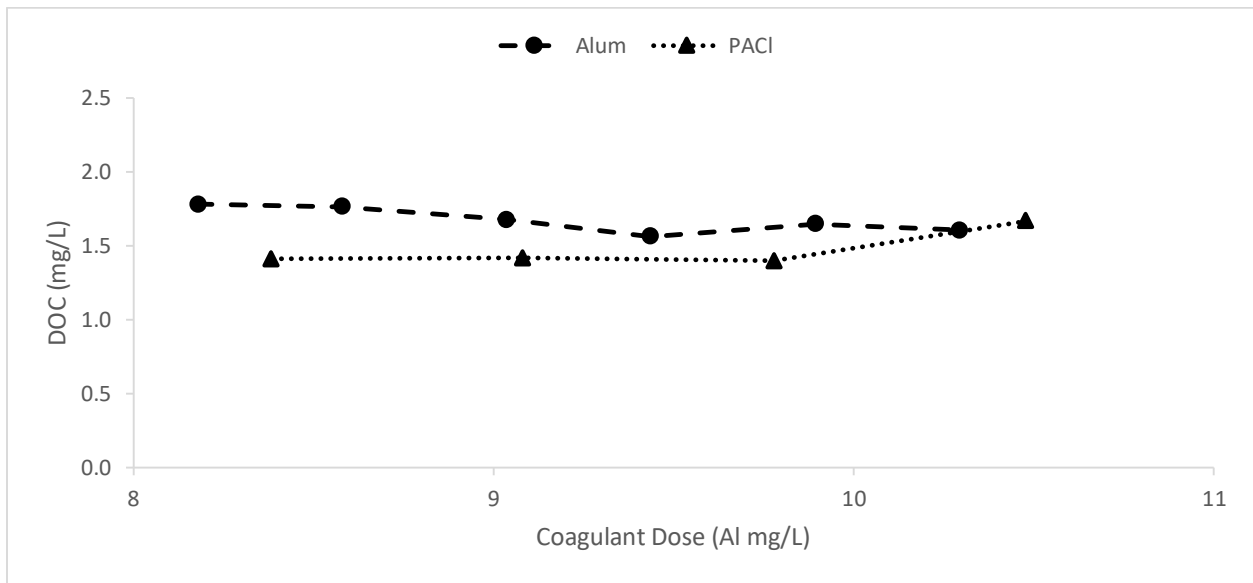


Figure 4.3. Bench-scale DOC results based on coagulant dose for alum and PACl coagulants. Coagulant dose is reported in aluminum concentration.

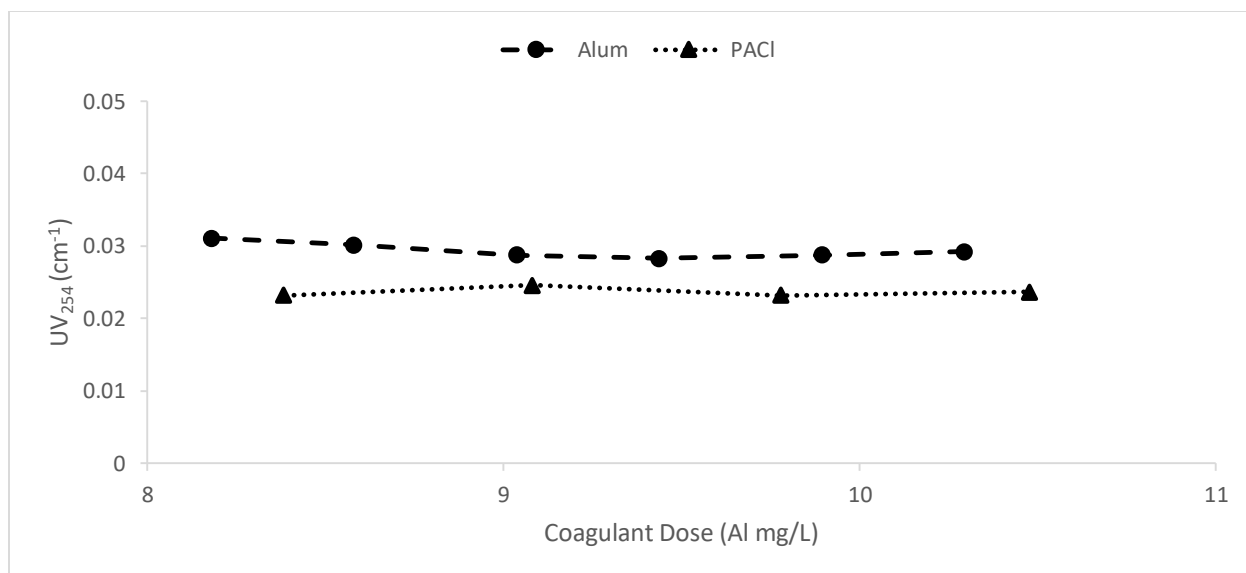


Figure 4.4. Bench-scale UV₂₅₄ results based on coagulant dose for alum and PACl coagulants. Coagulant dose is reported in aluminum concentration.

The DOC stayed relatively consistent across all doses except for the largest dose of 10.5 mg/L of aluminum. The DOC is approximately 1.4 mg/L for the other three doses while the DOC at this dose is 1.7 mg/L. The slight difference could be a result of the degree of error or variance in the measuring instrument. However, it has been noted that larger doses of PACl can result in particles restabilising which could lead to lower removals (Yan et al., 2007). This may suggest that at this higher PACl dose NOM could be restabilising, leading to decreased removal. This trend is not observed with the UV₂₅₄ data as the UV₂₅₄ with the higher dose remains consistent with the other doses of PACl. This could be a result of substances contributing to the DOC concentration but they did not have UV absorption at 254 nm. Interferences in the water matrix can also lead to UV₂₅₄ and DOC not correlating.

Comparing the results between alum and PACl we can see that PACl provided slightly higher removals overall in terms of NOM, especially at lower doses. PACl led to residual DOC concentrations of 1.4 mg/L, with the exception of the highest PACl dose, while the lowest residual DOC for alum was 1.6 mg/L. The differences in DOC were found to be significant as

the p-value was found to be 0.04 when completing a t-test. PACl also had lower UV_{254} results which were between 0.023 and 0.025 cm^{-1} across all doses while alum had results between 0.028 and 0.031 cm^{-1} . The PACl UV_{254} results were found to be significantly different as the p-value was found to be approximately 0. Though statistically significant, the difference in performance between the two coagulants was marginal from a practical standpoint. Increasing the DOC removal by 0.2 mg/L and the UV_{254} by 0.005 cm^{-1} is not monumental when considering the increased cost of PACl.

The results suggest that PACl may provide higher NOM removal than alum. The higher NOM removal is likely attributed to PACl being prehydrolyzed which provides many advantages compared to alum, which hydrolyzes once in solution. Prehydrolyzed coagulants mobilize Al-species more efficiently that are more reactive with contaminants, namely NOM. These Al-species are larger in size and have higher positive charges which are properties that enhance the removal of NOM (Matilainen et al., 2010). These properties are why PACl has been noted at being able to perform better than alum in colder water temperatures. This could prove to be very beneficial, especially in Atlantic Canada's climate, and could better support the use of PACl.

4.3.2 Pilot-Scale DAF Coagulant Dose Optimization

4.3.2.1 *Optimal Alum Dose*

A range of alum doses were also tested at the pilot scale in order to determine the optimal dose for NOM and turbidity removal with DAF clarification between the months of March and May. Pilot scale experiments more accurately represent DAF clarification results that could be expected at the full scale. This is because the pilot plant operated with continuous flow while bench-scale jar tests are batch experiments. Again, with DAF adding a coagulant not only destabilizes contaminants in the water matrix but it also helps enhance particle-bubble

attachment. The optimal coagulant dose will create the ideal floc size for flotation as well as creating the proper charge difference between particles and bubbles that will lead to improved clarification. Turbidity was used as the primary parameter to evaluate the optimal coagulant dose for proper particle-bubble attachment. Figure 4.5 shows the results of residual turbidity in the DAF clarified effluent across different alum doses.

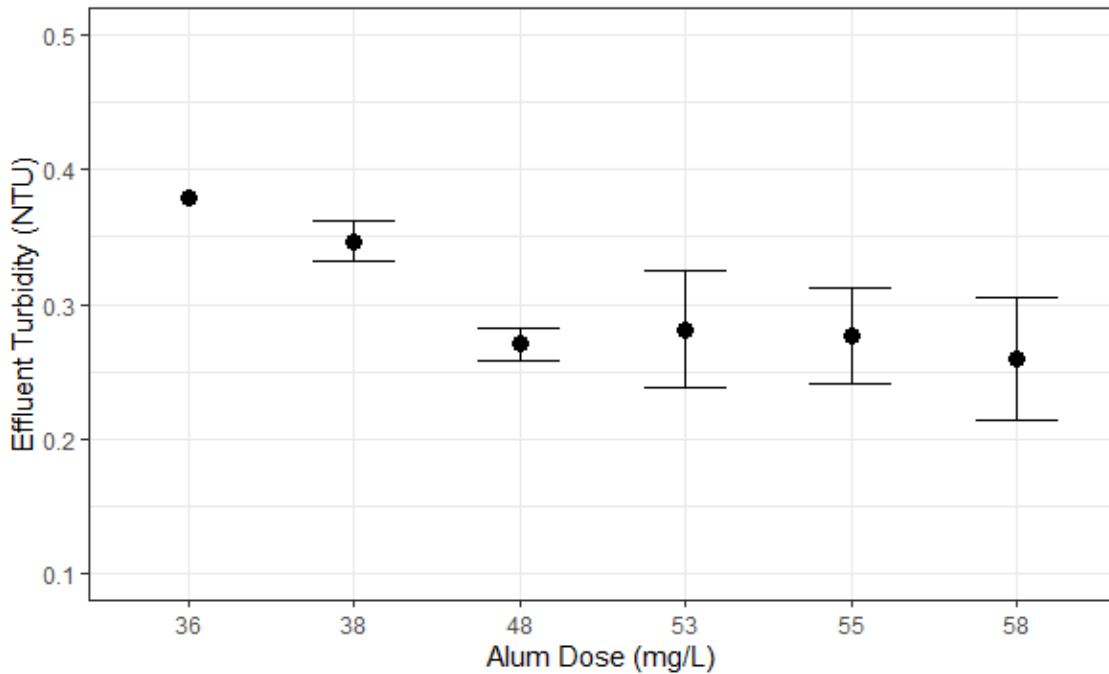


Figure 4.5. Average DAF effluent turbidity at pilot plant. Data from the March to May 2021. Error bars represent one standard deviation from the mean.

The average effluent turbidity is shown for each alum dose as well as the standard deviation. The figure represents a fairly distinct pattern for residual turbidity based on alum dose. An alum dose of 48 mg/L is shown to result in the lowest residual turbidity in the DAF effluent with an average of 0.271 NTU. Doses lower than 48 mg/L lead to higher residual turbidity, above the goal for clarified effluent of 0.3 NTU. This is likely due to the lower doses not being able to increase the zeta potential enough to reduce repulsive forces between the flocs and bubbles, leading to insufficient bubble-particle attachment and flotation. It can also be observed

that doses higher than 48 mg/L result in similar effluent turbidity, between 0.26 NTU and 0.29 NTU. Further increases in alum dose may lead to overdosing and decreased removals.

Overdosing could lead to the formation of larger aggregates which have higher densities and are more difficult to float, leading to reduced removal efficiency. Higher alum doses could also lead to sweep flocculation rather than charge neutralization mechanisms which, as mentioned before, can be less effective for DAF clarification. Sweep flocculation leads to the formation of highly positive charged flocs whereas flocs with near neutral or slightly positive charges are desired for DAF as is created with charge neutralization (Edzwald, 2010; Ghernaout & Ghernaout, 2012). A dose of 48 mg/L likely produces particles with optimal sizes and sufficient surface charges for efficient attachment to the negatively charged bubbles.

Turbidity may suggest an optimal coagulant dose for particle removal via DAF, however NOM must be considered as it typically influences coagulant dose more so than turbidity (AWWA, 2011). Similarly to the bench-scale experiments, UV_{254} and organic carbon concentration were used to evaluate the performance of DAF with regards to NOM removal. Figure 4.6 shows the UV_{254} results based on alum dose.

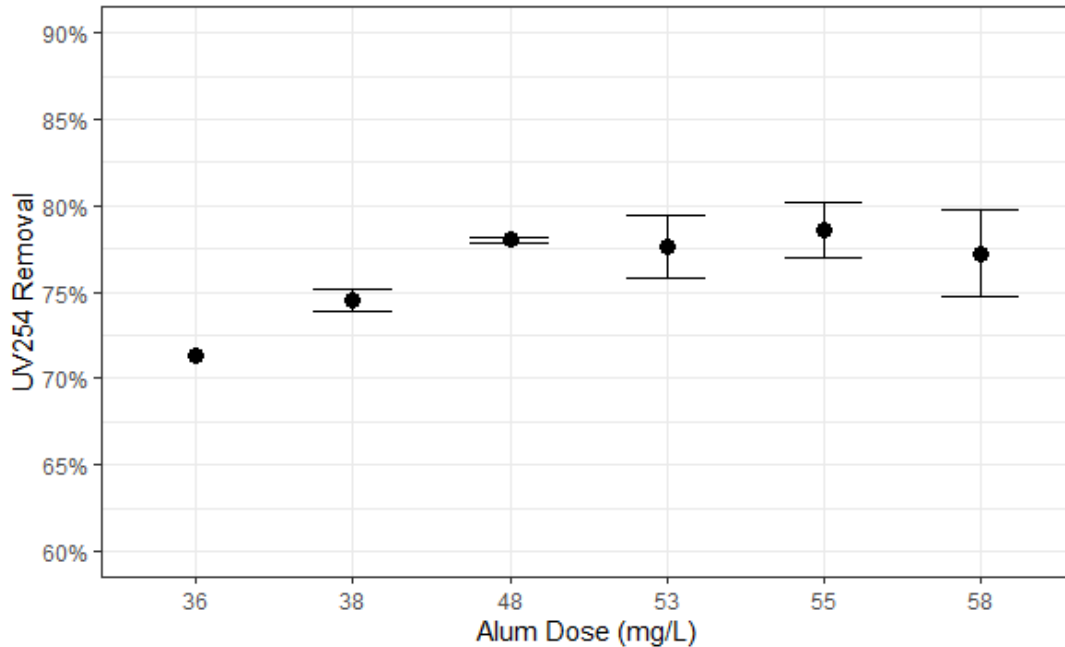


Figure 4.6. Average UV₂₅₄ removal following DAF clarification at pilot plant. Data from the March to June 2021. Error bars represent one standard deviation from the mean.

Similarly to turbidity, the optimal alum dose was also found to be 48 mg/L for NOM removal based on UV₂₅₄. This dose was found to have a UV₂₅₄ removal of 78% after clarification from the influent water. As found with the turbidity results, doses greater than 48 mg/L have very similar UV₂₅₄ removals as they are all between 77 and 78%. A dose of 58 mg/L started to show a decline in UV₂₅₄ removal. The reduced UV₂₅₄ removal at the higher dose is most likely related to the decreased floc removal shown with the turbidity results, attributed to overdosing. A dose of 38 mg/L was found to have lower UV₂₅₄ removal at 74% which was found to be statistically significant ($p < 0.05$). This dose is likely not quite high enough to meet the coagulant demands for NOM removal.

The optimal dose was found to be 48 mg/L in pilot scale DAF experiments which is very similar compared to what was found with the bench-scale jar tests which was 46 mg/L. The slight difference could simply be a result of bench-scale experiments not directly translating to

the pilot-scale. Additionally, the exact same dose of 46 mg/L could not be trialled at the pilot scale due to the inability of the alum feed pump to be adjusted exactly to achieve 46 mg/L.

4.3.2.2 Optimal Alum Dose with Favourable Influent Water Quality Conditions

Like any surface water, Lake Major experienced variable water quality throughout the year. Lower NOM levels were experienced in the pilot influent during the summer. The combination of decreased NOM and warmer water temperatures could provide benefits towards coagulation, potentially leading to a decrease in coagulant demand. Turbidity was used to evaluate clarification performance and whether a decreased coagulant dose could be used during these periods with DAF. Figure 4.7 displays results for DAF effluent turbidity for different alum doses during the months of July and August 2021.

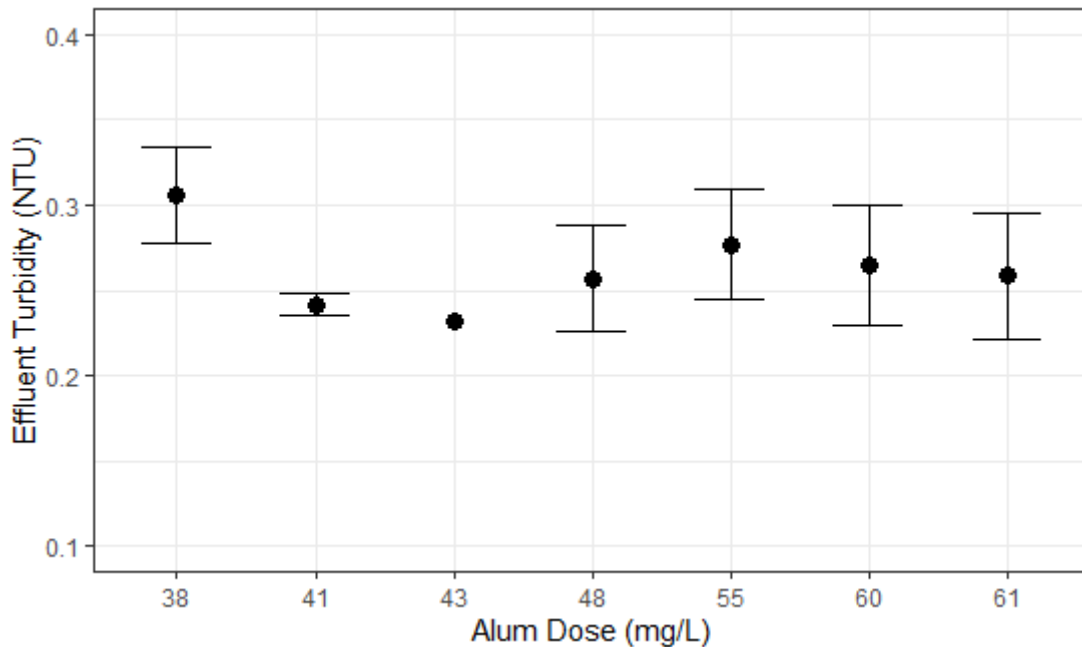


Figure 4.7. Average DAF effluent turbidity at pilot plant. Data from July and August 2021. Error bars represent one standard deviation from the mean.

The changes in influent water conditions appear to change coagulant demand as an alum dose of 41 mg/L was suggested to be optimal for turbidity removal during the summer months.

The average effluent turbidity was 0.242 NTU at this dose. Higher doses still lead to effluent turbidity less than 0.3 NTU, between 0.25 and 0.28 NTU, but overdosing is likely experienced leading to reduced turbidity removal compared to 41 mg/L. The average effluent turbidity at the optimal dose in the summer was 0.028 NTU lower than in the winter and spring months (shown in Figure 4.5). The colder water temperatures in the winter and spring, impeding reactions involved in the coagulation process, is likely the factor behind this discrepancy.

Like the turbidity results, NOM results showed that a lower alum dose can be used in the summer. UV₂₅₄ results during the months of July and August 2021 are shown in Figure 4.8.

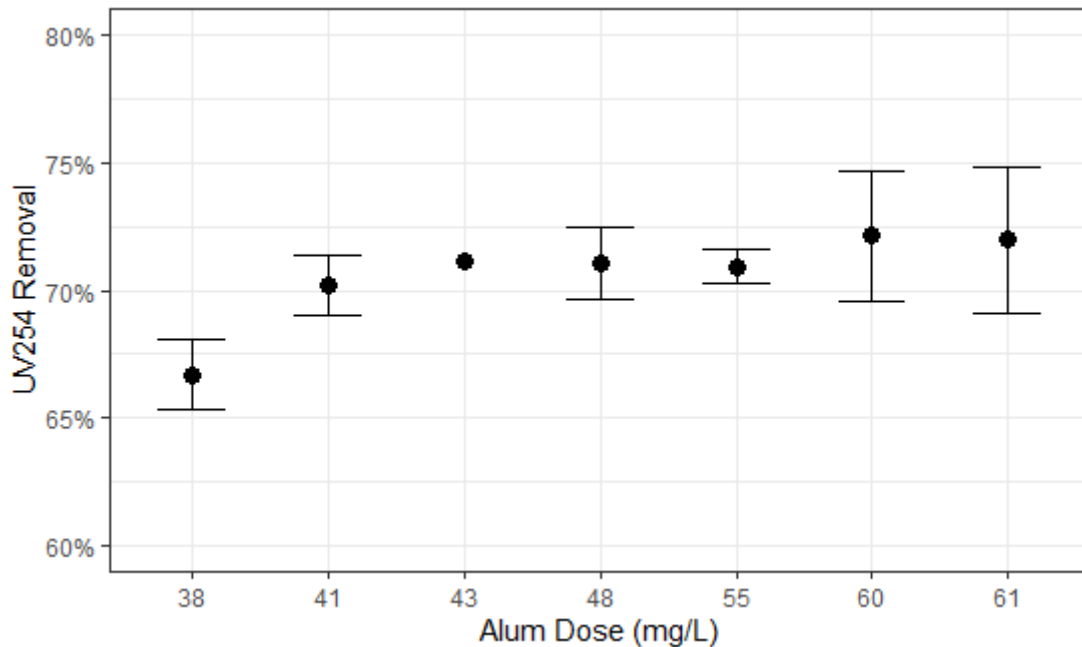


Figure 4.8. DAF pilot UV₂₅₄ results based on alum dose. Data from July and August 2021. Error bars represent one standard deviation from the mean.

The optimal dose for NOM removal based on UV₂₅₄ was found to be 41 mg/L with an average removal of 70%. As found with the turbidity results, higher doses had similar UV₂₅₄ removals which were between 70% and 72%. Unlike the turbidity results, better UV₂₅₄ removal was actually experienced with the optimal dose in the winter and spring compared to that in the

summer. The removal at the optimal dose in the winter and spring months (shown in Figure 4.6) was found to be 8% higher than in the summer. Higher SUVA values were experienced in the winter and spring than the summer which suggest increased portions of humic NOM with high hydrophobicity (Matilainen et al., 2010). NOM of this nature is highly susceptible to coagulation which can explain the increased removals experienced even with colder water.

4.3.2 Coagulant Type Performance Comparison

PACl was trialed briefly in pilot experiments to compare its performance to alum when used in conjunction with DAF. Only one PACl dose was used during these experiments due to the limited supply that was available. This dose was 4.4 mg/L as Al and the alum doses used for comparison were between 4.7 and 4.9 mg/L as Al. The data used in the section was all collected in April and May of 2021 so the raw water quality throughout the trials was relatively similar. This is also a period of relatively colder water temperatures which could highlight its impact on each coagulant's performance. The comparison of residual turbidity produced by PACl and alum is shown in Figure 4.9.

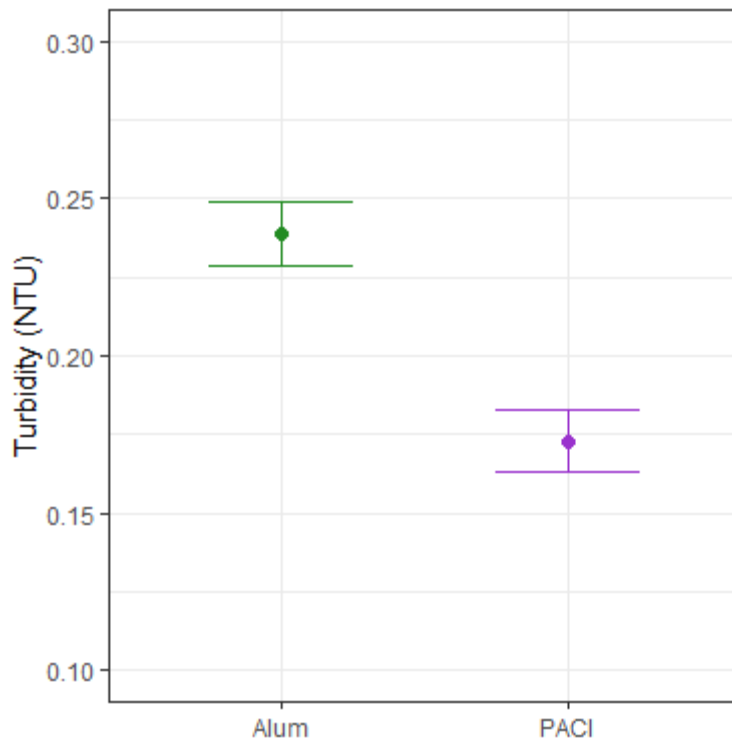


Figure 4.9. DAF pilot turbidity results comparing alum and PACl. Samples collected from effluent of DAF clarifier. (Alum dose: 4.7-4.9 mg/L as Al, PACl dose: 4.4 mg/L as Al). Error bars represent one standard deviation from the mean.

As expected based on the properties of PACl, the residual turbidity in the DAF effluent was found to be much lower when PACl was used. The mean effluent turbidity was found to be 0.173 NTU with PACl and it was 0.239 NTU for alum. The turbidity removal with PACl was found to be significantly higher than alum when performing a t-test ($p < 0.05$). Higher turbidity removal using PACl could be attributed to its pre-hydrolysis characteristic. As previously mentioned, being pre-hydrolyzed allows PACl to react more quickly and more efficiently with contaminants. Pre-hydrolysis results in the production of Al-species that are larger and have higher positive charges (Matilainen et al., 2010). This could lead to optimal charge differences being created between the flocs and negatively charged bubbles more efficiently. The electrostatic repulsion would be reduced more efficiently leading to better bubble-particle collision efficiency being experienced with PACl than alum.

The results for NOM removal are similar to those found for turbidity removal. UV₂₅₄ removal results for the two coagulants are shown in Figure 4.10 while Figure 4.11 shows the TOC results.

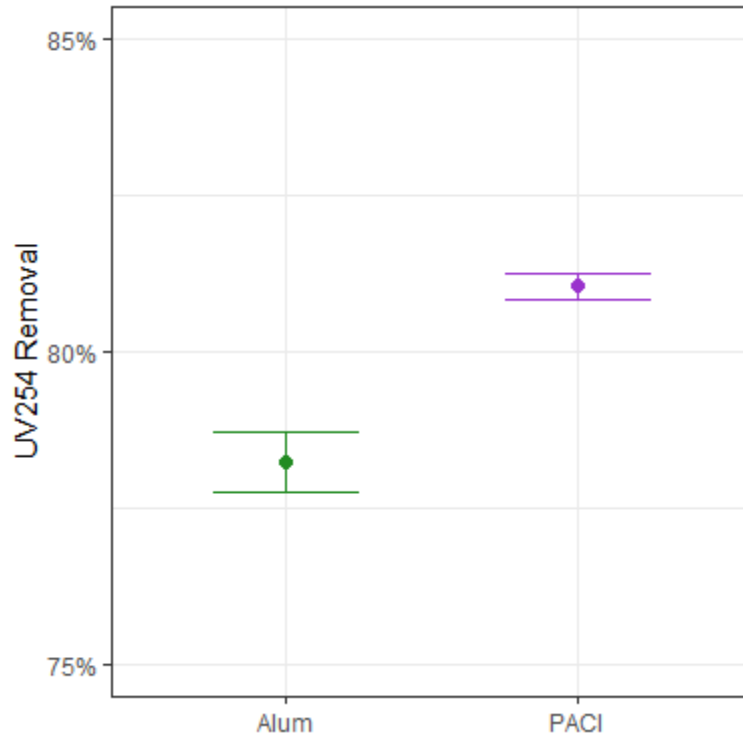


Figure 4.10. DAF pilot UV₂₅₄ percent removal results comparing alum and PACl. Samples collected from effluent of DAF clarifier. (Alum dose: 4.7-4.9 mg/L as Al, PACl dose: 4.4 mg/L as Al). Error bars represent one standard deviation from the mean.

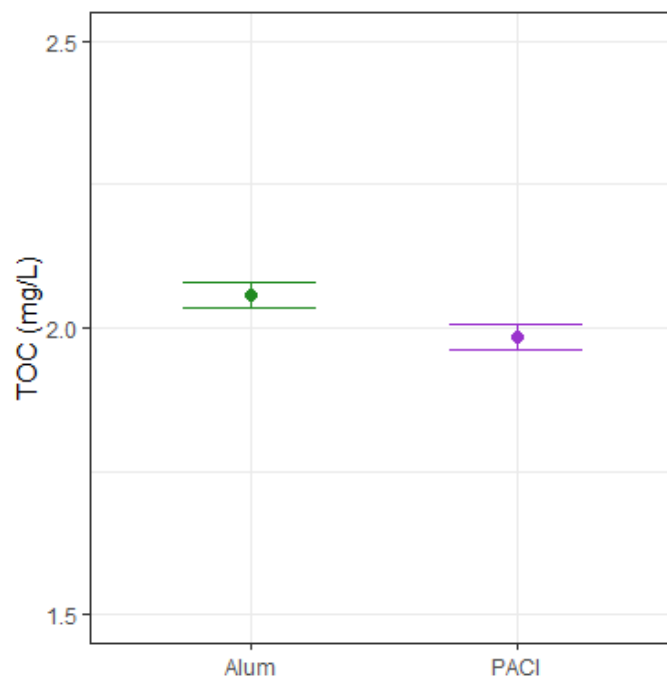


Figure 4.11. DAF pilot TOC results comparing alum and PACl. Samples collected from effluent of DAF clarifier. (Alum dose: 4.7-4.9 mg/L as Al, PACl dose: 4.4 mg/L as Al). Error bars represent one standard deviation from the mean.

PACl had significantly higher UV_{254} removal compared to alum ($p < 0.05$). Water treated with PACl had a mean UV_{254} removal of 81% while the effluent when alum was used had a mean of 78%. Marginal differences were found between the mean TOC residuals of each coagulant, just below 2.0 mg/L for PACl and 2.1 mg/L for alum. This difference is marginal and was found to be statistically insignificant ($p > 0.05$). These results of slightly improved NOM removal were expected and agree with the bench-scale results. Being pre-hydrolyzed, PACl generally promotes higher NOM removal with the formation of highly reactive Al-species. As found with turbidity, higher NOM removal experienced with PACl may be a result of improved particle-bubble attachment than with alum. However it could be that the better hydrolysis efficiency of PACl simply improves NOM destabilization leading to increased removal regardless of the clarification process. Additionally, these results allude that PACl performs

better in colder water which typically impedes the hydrolysis process with alum, hindering its efficiency.

The improvements in clarified water quality that are found with PACl could also benefit processes downstream of clarification. Lower residual turbidity with PACl could reduce filter clogging and result in prolonged filter runs. Longer filter run times improve efficiency by increasing water production and reducing the frequency of backwashes. Increased NOM removal experienced with PACl could reduce the formation of DBPs after disinfection. DBP concentrations have been of great concern for utilities in recent years due to brownification and NOM concentration increases in source waters. Figure 4.12 shows DBP_{fp} for THMs and HAAs.

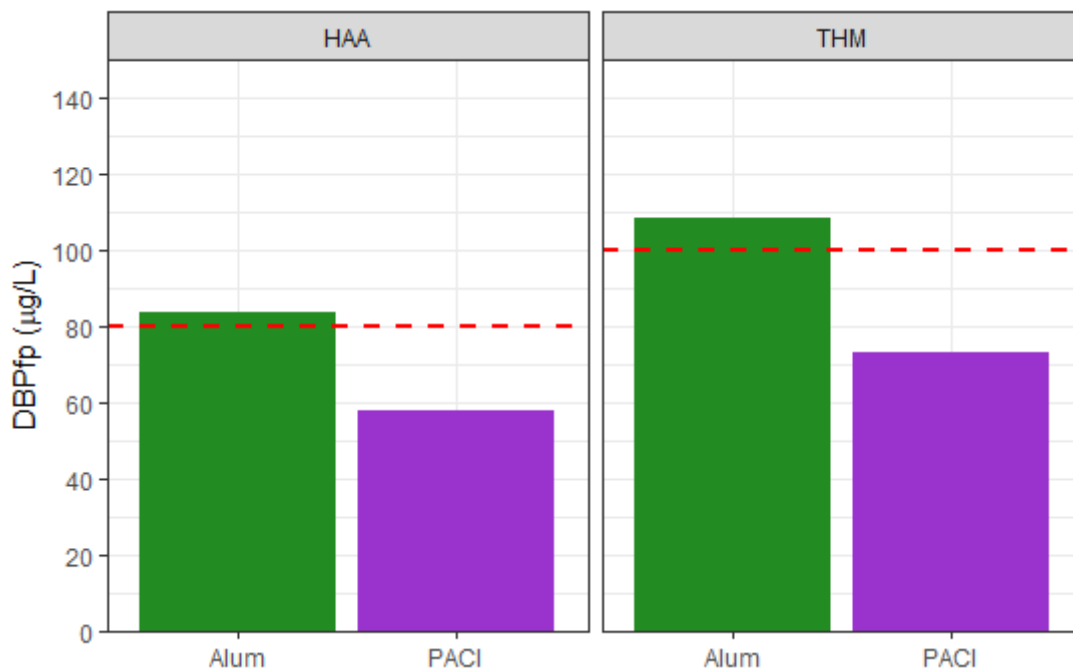


Figure 4.12. DBP_{fp} results comparing alum and PACl. Samples collected from effluent of DAF clarifier. (Alum dose: 4.9 mg/L as Al, PACl dose: 4.4 mg/L as Al). Dotted line represents Health Canada maximum acceptable concentration for each compound.

The DBP_{fp} results are quite interesting considering the marginal differences in residual TOC produced by each coagulant. The TOC for each sample collected for DBP_{fp} analysis were

2.0 mg/L and 2.2 mg/L for PACl and alum, respectively. Both HAA and THM concentrations for alum were above the Health Canada MACs of 80 µg/L for HAAs and 100 µg/L for THMs. PACl led to HAA and THM concentrations of 58 µg/L and 73 µg/L, respectively, well below the MACs. This may be significant for the treatment process as having DBP concentrations below the MACs prior to filtration may eliminate the risk of ever exceeding them. Future work to investigate the impact of coagulant type on filter performance, including filter run time, may be interesting.

4.4 Conclusions

The goal of this chapter was to identify the optimal coagulant dose for NOM removal using bench-scale jar tests. Pilot scale experiments were conducted in order to identify the optimal coagulant dose to be used with DAF. Additionally the performance of alum was compared with PACl to observe advantages of prehydrolyzed coagulants. Key findings from this work are discussed below.

- Optimal alum dosing was identified through bench-scale jar tests for the removal of NOM from the Lake Major source water. A dose of 46 mg/L was identified as the point of diminishing returns for NOM removal (60% DOC removal, 86% UV₂₅₄ removal). Any doses higher than this showed marginal improvements and their use was determined impractical. Therefore 46 mg/L is suggested to be the optimal alum dose for the destabilization of particles and a starting point for pilot-scale adaptation.
- PACl outperformed alum in terms of NOM removal in bench-scale jar tests. Alum led to a residual DOC of 1.6 mg/L and UV₂₅₄ of 0.028 cm⁻¹ while PACl led to a residual DOC of 1.4 mg/L and UV₂₅₄ of 0.023 cm⁻¹. The differences were marginal but could still suggest PACl leading to improved NOM removal, especially in colder water.

- An alum dose of 48 mg/L was found to be optimal with the use of DAF clarification. This dose resulted in optimal residual turbidity (0.271 NTU) and highest UV₂₅₄ removal (78%). Removal was found to be worse with lower doses and higher doses started showing slight declines in removal. Doses lower than 48 mg/L likely led to flocs with negative surface charges creating repulsive forces between flocs and air bubbles which would impact particle-bubble attachment. Doses higher than 48 mg/L likely caused sweep flocculation and created flocs that were too large and more difficult to float.
- A marginally higher dose was found to be optimal with DAF clarification (48 mg/L) compared to the optimal dose for the destabilization of particles (46 mg/L). This may be a result of working at a larger scale with the pilot compared to bench-scale as well as limitations at the pilot scale to achieve exact same doses.
- A lower coagulant dose was found to provide optimal removals during the summer compared to the winter and spring (41 mg/L vs 48 mg/L). Influent water conditions experienced in the summer including warmer water and decreased NOM concentrations are likely the reason for the decreased coagulant demand.
- Pilot scale experiments showed that PACl outperforms alum with DAF clarification. PACl had far lower mean residual turbidity (0.173 NTU) compared to alum (0.239 NTU). The improvement in residual turbidity for PACl compared to alum was likely a result of being prehydrolyzed leading to increased coagulation efficiency. Like the bench-scale experiments, PACl showed slightly better NOM removal with a UV₂₅₄ removal of 81% compared to 78% for alum, however no significant difference was found in TOC removal.

- PACl was found to meet Health Canada DBP regulations prior to filtration while alum was found to exceed the limits for HAAs and THMs. Having DBP concentrations below the limits prior to filtration would alleviate concerns of exceedances in the finished water.
- Only one PACl dose was trialed with DAF at the pilot scale so future experiments could be conducted to identify an optimal dose. However, the dose used had a lower Al content compared to that of alum and produced better water quality. Based on the composition of PACl this also results in a lower volume of product being used reducing the overall chemical usage. However, PACl manufacturing is specialized leading to lower availability and higher costs.

Chapter 5 - Impact of Flocculation Time on DAF Performance

5.1 Introduction

Flocculation is a key process that follows coagulation in drinking water treatment. The two processes go hand in hand and are sometimes used interchangeably. In this work coagulation is used to refer to the addition of the coagulant itself (chemical and dosage), while flocculation is used to refer to the conditions that are used following coagulant addition and preceding clarification. Flocculation facilitates the formation of larger aggregates (flocs) through mixing and retention times that are experienced in the tanks. Flocs can be created through coagulation mechanisms, such as entrapment and complexation, which is increased with the collision of destabilized particles (Matilainen et al., 2010). Destabilized particles that are neutralized via coagulation can also agglomerate through attractive van der Waals forces between particles (Hierrezuelo et al., 2010). Flocs can also be formed through sweep flocculation which, as discussed in the previous chapter, typically occurs with excess coagulant dosing (Gheraout & Gheraout, 2012).

Flocculation is vital prior to clarification processes. Sedimentation requires the formation of particles/flocs whose density are greater than water to promote settling and increase efficiency. Conversely, DAF requires flocs whose density are near or less than that of water. This ensures adequate buoyancy which allows for faster flotation and efficient removal. There has been disagreement regarding the appropriate floc size for DAF. Edzwald (1995) recommended that strong flocs with small size distributions should be created for DAF clarification, stating short pre-treatment times are feasible. Pin-point flocs with sizes of less than 50 μm have been suggested to be used with DAF. Although collision efficiencies have been shown to approach 100% with floc sizes of 100 μm or greater (Edzwald, 2010). Others have suggested that flocs

should be slightly larger as collision efficiency between flocs and bubbles increases as the floc size increases. These studies suggest flocs should be similar to the size of the bubbles, which are typically found to be anywhere from 10 μm to 100 μm with DAF (Fukushi et al., 1998; Mun et al., 2006). The size of the bubbles are dependent upon the pressure of the saturator where higher pressures produce smaller bubbles (Han et al., 2007). A point will be reached where removal is impaired with flocs becoming too large as flotation becomes less efficient and bubble detachment can occur (Edzwald, 2010).

The mechanism of floc formation can influence the size of the flocs as well as bubble attachment efficiency. Charge neutralization typically results in the formation of smaller flocs as it requires a lower coagulant dose and bridging is not widely experienced (Cruz et al., 2020). On the other hand, sweep flocculation leads to the formation of larger flocs with its larger coagulant demand and enmeshment of colloids (Bache, Johnson, et al., 1999). The nature of the two mechanisms, which is dictated by their respective coagulant demands and pH, lead to different zeta potential ranges. Zeta potential and alum dose are known to be correlated as the addition of alum leads to the formation of soluble complexes with high positive charges (Han et al., 2001; Matilainen et al., 2010). During charge neutralization coagulation processes near neutral zeta potential is targeted for flocs while sweep flocculation is associated with a higher zeta potential owing to its large coagulant demand. Charge neutralization has been suggested to be targeted for DAF so electrostatic forces between particles and bubbles do not become repulsive (Edzwald, 2010). Han et al. (2001) showed that optimal removal efficiencies are achieved with zeta potentials slightly above 0 mV at flocculation times greater than 10 minutes. At flocculation times less than 10 minutes optimal removal efficiency is found with higher zeta potentials around 10 mV. The dependence on flocculation time is attributed to the floc formation efficiencies of the

two mechanisms. Charge neutralization has been shown to take upwards of 20 minutes to achieve stable floc aggregation while sweep flocculation took only 6 minutes (Alansari & Amburgey, 2020). This may suggest longer flocculation times are needed to achieve charge neutralization mechanisms which are noted as being more efficient in NOM removal.

Temperature may also impact DAF removal efficiency when comparing different floc times. As discussed in the previous chapter lower temperatures exert adverse effects on the hydrolysis of metals (e.g. Al) and impede coagulation processes. For this reason, the aggregation of particles as well as structure of the formed flocs can be affected by temperature. Additionally, collision frequency, adsorption, and overall aggregation of colloids have been found to be reduced in colder temperatures (Dayarathne et al., 2022). Flocs formed in colder temperatures are typically smaller and weaker than those in warmer water which can impact treatment performance. Longer floc times may be able to mitigate the impacts temperature has on floc formation and subsequent removal (Fitzpatrick et al., 2004).

Many papers suggest that short floc times should be used with DAF, highlighting that longer floc times are not necessary given the space that is needed and extra costs (Edzwald et al., 1992; Plummer et al., 1995; Valade et al., 1996). Edzwald et al. (1992) reported residual turbidity of approximately 0.4 NTU and 0.4-0.5 NTU for flocculation times of 16 minutes and 8 minutes, respectively. Since the difference was slight, shorter flocculation times were suggested to be adequate. They used Ferric chloride for coagulation at a dose between 23-27 mg/L. This high dose range would suggest sweep flocculation occurring however it was not stated what mechanism was being targeted. Plummer et al. (1995) conducted trials with various flocculation times and found the lowest residual turbidity to be with a flocculation time of 10 minutes (0.33 NTU). A flocculation time of 20 minutes resulted in a residual turbidity of approximately 0.41

NTU. This study used ferric chloride instead of alum as a coagulant but commented that sweep flocculation conditions were targeted during experiments. Valade et al. (1996) reported what was considered to be good performance with only 5 minutes of flocculation, resulting in a residual turbidity of approximately 1 NTU. They stated that 20 minute flocculation produced better DAF performance (< 1 NTU) but a longer flocculation time is not considered to be economically feasible. This study used an alum dose of 30 mg/L which may have led to sweep flocculation occurring, however the authors did not comment on the coagulation mechanism. The 5 minute floc time resulted in lower filtered turbidity than the 20 minute floc time. However, higher UFRV was found with the 20 minute floc time as higher head loss and lower UFRV was experienced with a 5 minute floc time.

While these studies mainly judge DAF performance on residual turbidity, some discuss NOM removal. Edzwald (1992) reported no significant difference in DOC removals between 16 minute and 8 minute flocculation times, both having 62% removal following flotation and 64% removal following flotation and filtration. Plummer et al. (1995) showed that UV_{254} removal was independent of flocculation time, with 60% removal across all times. DOC and UV_{254} may not be representative of clarifier performance as these parameters are measured after filtering the sample. Filtering the sample would not be representative of the NOM being removed in clarification and the residual being passed onto the filters in the treatment process. There appears to be a lack of papers which focus on the removal of NOM with DAF, particularly as a function of floc time. This aspect may be of interest for future work, given that brownification is a predominant issue, specifically in Atlantic Canada and throughout the Northern Hemisphere. DAF technology is being considered as an adaptation strategy for NOM removal in regions undergoing brownification and therefore this work is of critical importance for the future design

of treatment facilities, particularly considering climate change and extreme variations in water quality. A shift in thinking towards DAF may be required when considering its use for treating source waters experiencing changes in their water quality (e.g. increasing NOM).

It is important to identify operational parameters associated with optimal DAF performance to promote higher removal during clarification as this will benefit downstream processes, namely filtration. Lower residual turbidity in the clarified effluent will reduce filter loading and clogging, leading to prolonged filter run times. Longer filter run times lead to increased treatment efficiency as less backwashes are required which waste treated water and obstruct production. Lower NOM concentrations in clarified effluent will reduce the risk of filter breakthrough and ensure DBP regulations are met following disinfection. The experiments and results discussed in this section are intended to outline the impact that flocculation time has on DAF clarification.

5.2 Materials and Methods

5.2.1 Study Site: Lake Major

The Lake Major study site and methods used to obtain results for this section were previously outlined in section 4.2.1.

5.2.2 Alternate Study Site: Pockwock Lake

The pilot plant was relocated to the J.D Kline Water Supply Plant in April 2022 where Pockwock Lake was used for source water. Like Lake Major, Pockwock Lake is characterized as having low pH (<6), low alkalinity (<5 mg CaCO₃/L), and low turbidity (<0.5 NTU). However, NOM concentrations are typically much lower in Pockwock Lake than Lake Major as shown in Table 5.2.

Table 5.1 Pockwock Lake water quality between April 2022 and August 2022.

Analyte	Average	Max	Min
pH	5.49	6.01	4.49
Turbidity (NTU)	0.524	1.250	0.416
UV ₂₅₄ (cm ⁻¹)	0.137	0.154	0.105
Colour (Pt/Co)	28	42	22
Mn (mg/L)	0.028	0.035	0.022
Fe (mg/L)	0.08	0.11	0.02
Al (mg/L)	0.049	0.109	0.019

5.2.3 Pilot Experiments

Pilot experiments were carried out in the same manner as outlined in the previous chapter in section 4.2.3. To achieve different flocculation times for the results in this chapter some flocculation tanks were bypassed and the influent flow was varied. Shorter flocculation times utilized only 1 flocculation tank while longer flocculation times used 2 or 3 flocculation tanks, providing multiple stages. Only pilot scale experiments were conducted to observe the affect of flocculation time.

5.3 Results and Discussion

5.3.1 Variance in Raw Water Quality

The raw water quality of Lake Major was variable during the course of this research. High levels of organics were experienced during the spring and gradually declined during the summer. The nature of the pilot project was dynamic with operations being changed based on treatment performance and raw water quality. Before comparing the performance between different configurations, the raw water quality should be considered to provide context on results. Figure 5.1 shows the apparent colour for the raw water quality throughout the course of the project.

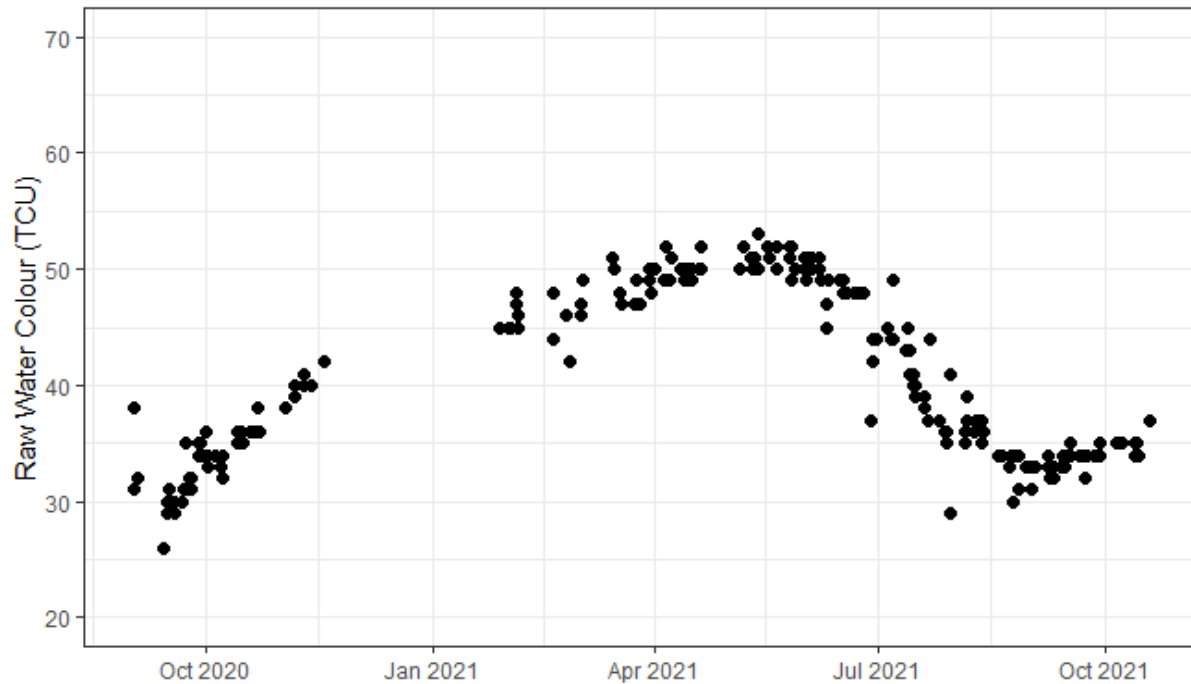


Figure 5.1. Lake Major raw water apparent colour experienced during the project.

The colour of Lake Major consistently rose during the winter reaching above 50 TCU in the spring and falling back below 35 TCU during the summer and early fall. Higher coagulant doses were used during the winter and spring to satisfy the coagulant demands for the increased organic levels. A 19 minute floc time was used throughout the winter and spring, when the raw water colour was variable. The colour in the raw water stayed relatively consistent during the trials for a 7 minute floc time which was mainly trialed in the early fall of 2021. As previously mentioned, a short floc time of 6 minutes was briefly trialed when organic levels were elevated in March 2021 to evaluate its efficacy with colder water and increased NOM. SUVA values, which can suggest the composition of the NOM, also varied during the year. Higher SUVA values were found in the winter and spring, around 5.2, while SUVA declined in the summer down to around 4.1. This would suggest that higher NOM removal may be experienced in the winter and spring due to a higher portion of hydrophobic compounds in its composition.

5.3.1 Impact of Flocculation Time on DAF Performance

Various flocculation times were trialed during the project to investigate its impact on DAF performance. The flocculation times were varied by manipulating the influent flow as well as the number of flocculation tanks used prior to clarification. Two flocculation times were selected to be focused on based on their performance and intentions for full scale adaption. A flocculation time of 7 minutes was selected for a short floc time while 19 minutes was selected to represent a longer floc time. A short floc time of 6 minutes was also trialed briefly in March 2021 to investigate the impact of cold temperature. UV₂₅₄ and apparent colour were used to evaluate performance in terms of organic removal while turbidity was used to evaluate overall particle removal during clarification.

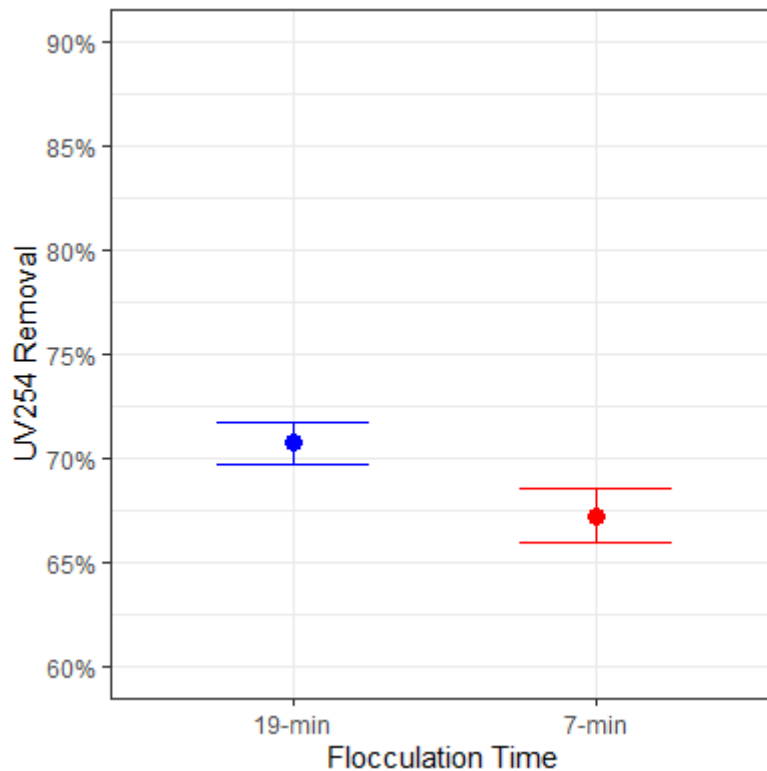


Figure 5.2. Average percent removal of UV₂₅₄ during DAF clarification for 19 minute and 7 minute floc times. Data from August and September 2021. Alum doses between 41 and 55 mg/L for each floc time.

Figure 5.2 compares the performance of each floc time on UV₂₅₄ removal. The data used in this figure was from the months of August and September, when NOM concentrations in the raw water were relatively low. Influent UV₂₅₄ was between 0.18 and 0.2 cm⁻¹ during this time and SUVA values were found to be between 4 and 4.4. These SUVA values suggest organic matter that is ideal for charge neutralization and removal via coagulation (Edzwald, 1993; Matilainen et al., 2010; Sharp, Jarvis, et al., 2006). The difference in removal between the floc times of 19 minute and 7 minute was found to be significant ($p < 0.05$). However, the longer floc time only provided 4% higher removal, 71% for 19 minutes compared to 67% for 7 minutes. The discrepancy may be a result of different removal mechanisms occurring. Studies have shown that charge neutralization mechanisms require a longer time to form strong flocs (Alansari & Amburgey, 2020). Charge neutralization has been suggested to be more efficient in removing NOM compared to other coagulation mechanisms (Cruz et al., 2020). A 7 minute floc time may not provide enough time for charge neutralization to occur completely, resulting in a lower removal in organics. However, the slight improvement in removal that is gained with a longer floc time may not be economically feasible. A 12 minute increase in flocculation time would require larger tanks and therefor a larger footprint in a full scale water treatment facility. An extended flocculation time would also prolong and reduce water production efficiency. Higher energy consumption would also be associated with longer floc times. Similar results to Figure 5.2 are found with colour removal, which can be found in the appendix.

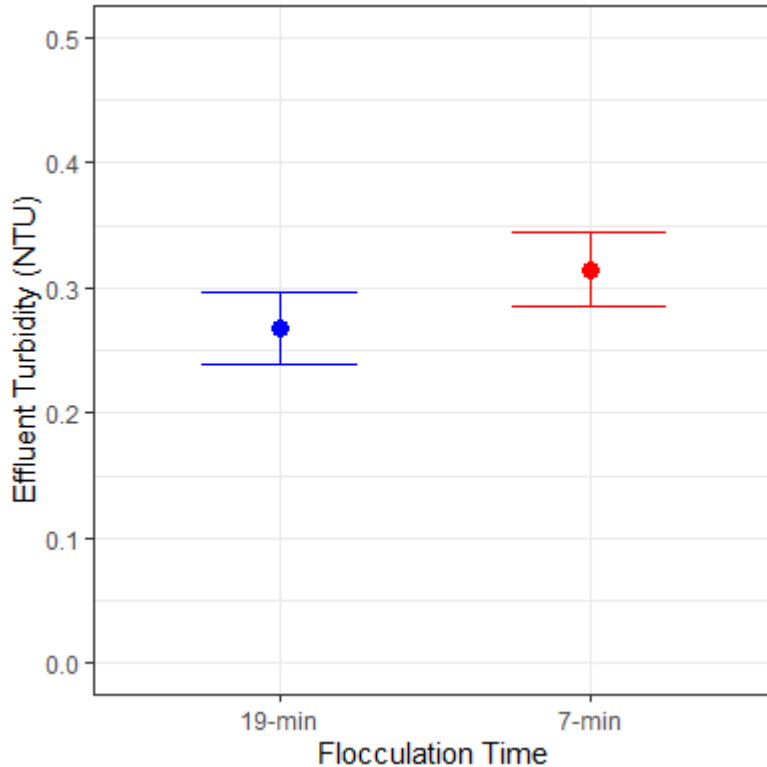


Figure 5.3. Average effluent turbidity following DAF clarification for 7 minute and 19 minute floc times. Data from August and September 2021. Alum doses between 41 and 55 mg/L.

Figure 5.3 displays the results for effluent turbidity following DAF clarification for each floc time tested. The results are presented in effluent turbidity instead of removal, as this was a key parameter used to gauge the DAF clarification performance on a day to day basis. The results show that a 19 minute floc time led to better residual turbidity than a 7 minute floc time. Average effluent turbidity with a 7 minute floc time was found to be 0.315 NTU. Effluent turbidity from the clarifier was typically greater than the turbidity in the influent water with a 7 minute floc time, as the influent average turbidity was 0.285 NTU during these trials. Turbidity is created during coagulation and flocculation with flocs being formed. Evidently removal was inadequate during clarification with a 7 minute floc time. This is likely a result of floc formation needing more time than 7 minutes to reach an optimum point, especially for charge

neutralization mechanisms, as previously discussed in this chapter (Alansari & Amburgey, 2020). Achieving charge neutralization can lead to improved turbidity removal with DAF as flocs with near neutral or slightly positive charges are suggested to be targeted when using DAF (Edzwald, 2010). Larger coagulant doses may be required to improve turbidity removals with a 7 minute floc time to further target sweep flocculation. This will be discussed further later on in this chapter. Trials with a 19 minute floc time had an average clarified effluent turbidity of 0.267 NTU. This was significantly lower than effluent turbidity following clarification with a 7 minute floc time ($p < 0.05$). The effluent turbidity was typically lower than the influent turbidity, which was an average of 0.336 NTU, during the trials with a 19 minute floc time. The trials with a 19 minute floc time also had higher average influent turbidity (0.336 NTU) than what was experienced during the 7 minute floc time trials (0.285 NTU). Providing a longer period of 19 minutes for floc formation possibly resulted in proper charge neutralization which led to better particle-bubble attachment and improved turbidity removal compared to a shorter floc time. Efficient turbidity removal is important to achieve during clarification as it can greatly impact performance of downstream treatment processes, namely filtration, which will be outlined in a section later in this chapter.

The results in this section mainly highlighted the improved DAF performance found with a floc time of 19 minutes versus 7 minutes. Testing a wider range of coagulant doses for each floc time could illustrate the coagulant demands required to optimize coagulation mechanisms for each floc time. These results will be presented later in section 5.3.3.

5.3.2 Seasonal Impact on Flocculation Time

As shown in Figure 5.1, organic levels were found to fluctuate throughout the year while the pilot plant was being operated. Higher organic levels were found in the winter months while

organic levels were the lowest towards the end of summer and early fall. Lower water temperatures in the winter months make it more challenging to remove organic matter, let alone the increased concentrations. Colder water temperatures slow down the mobilization and reaction rates of hydroxide species created by the coagulant which destabilize contaminants. A short floc time (6 minutes) was trialed briefly during the winter to identify seasonal impacts on floc time. These results could be compared with data collected when a longer floc time (19 minutes) was used during the same month. This data was collected in March 2021 which represents a period of cold water temperatures and high organic matter. Results from September 2021 were also used for comparison to represent trials when organic levels were low and water temperatures were higher. The data for the September trials use the same floc times as the previous section, a short floc time of 7 minutes and a long floc time of 19 minutes. The difference between the short floc times for March and September are a result of a change in the influent flow to the pilot plant for full scale design consideration.

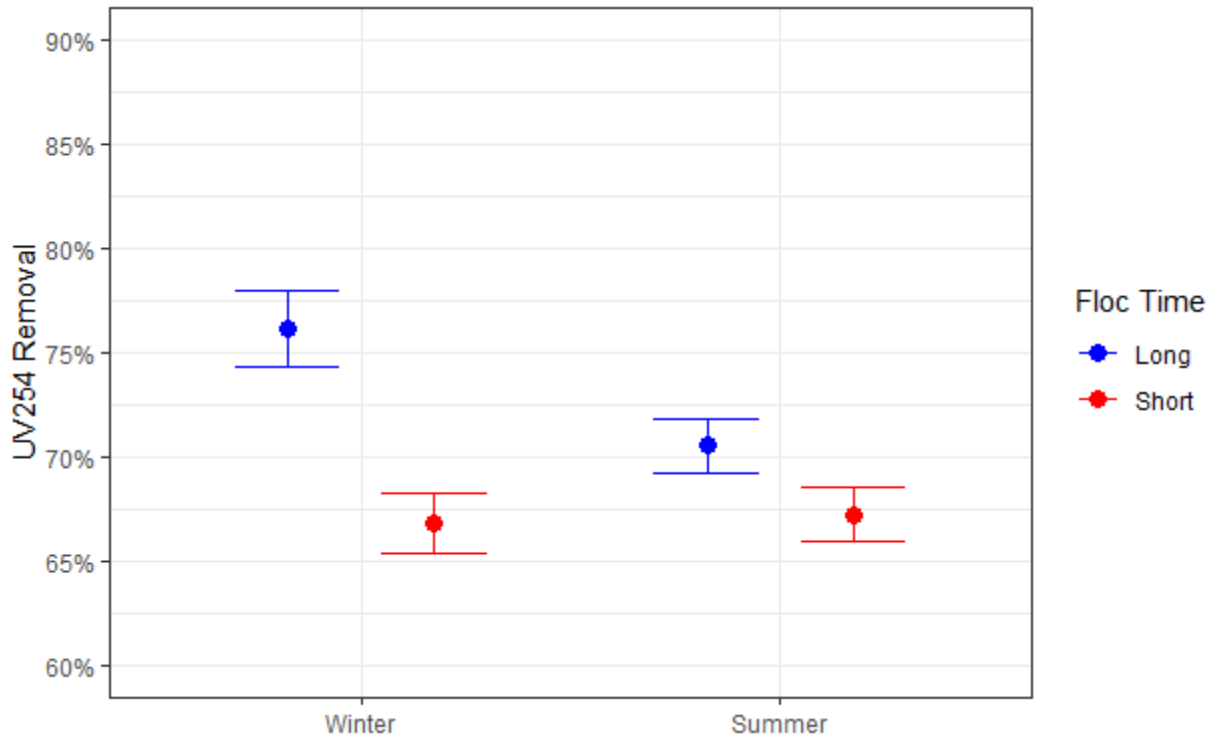


Figure 5.4. Average UV₂₅₄ percent removal during DAF clarification for short and long floc times during different times of the year (Note: March short floc time = 6 minutes; September short floc time = 7 minutes; Both long floc time = 19 minutes).

Figure 5.4 shows the results of UV₂₅₄ removal for winter and summer trials for long and short floc time scenarios. Higher UV₂₅₄ removal was experienced during the winter (76%) compared to the summer (71%) with a long floc time. The difference was found to be statistically significant ($p < 0.05$). Higher SUVA values were found in the winter, approximately 5.2, compared to the summer, approximately 4.3, which could explain better removal in the winter. Higher SUVA values are correlated with better NOM removal (Matilainen et al., 2010). No significant difference was found between the removals during the winter and summer with a short floc time, both having average removals of 67%. Comparing the performance between the two floc times during each season shows interesting results. A longer floc time showed significantly greater average UV₂₅₄ removal ($p < 0.05$), nearly 10% more compared to a short floc time during winter trials. Improved removals with a longer floc time in the winter are likely

related to the cold water temperatures. Colder temperatures slow down reaction rates and impede the efficiency of the coagulant (Morris & Knocke, 1984). Longer floc times could promote better removals during winter conditions. Average UV₂₅₄ removal was only 4% greater comparing the long floc time scenario to when a short floc time was used during the summer. This may further support the impact temperature has on the performance of each floc time. Similar results are found with colour removal, another indicator of organic matter, which can be found in the appendix.

Similar to the previous figures, Figure 5.5 is intended to illustrate the performance of each floc time scenario during different times of the year, however in regards to effluent turbidity.

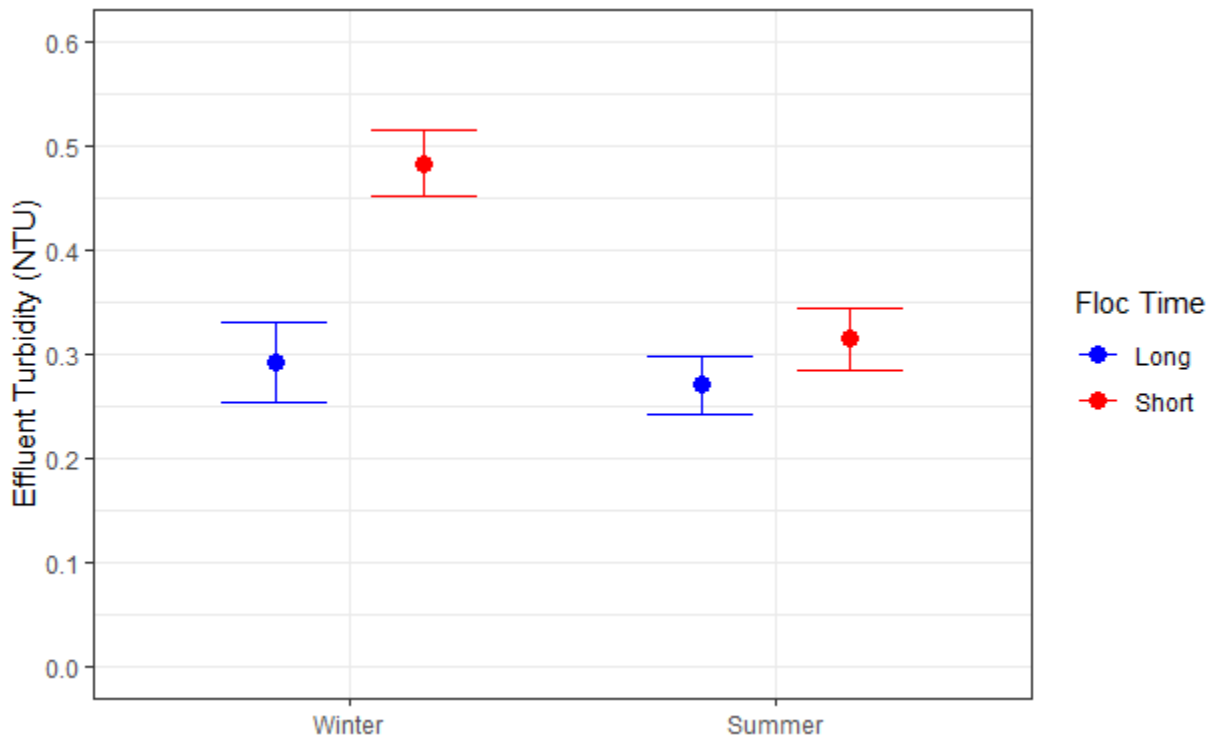


Figure 5.5. Average effluent turbidity following DAF clarification for short and long floc times during different times of the year (Note: Winter short floc time = 6 minutes; Summer short floc time = 7 minutes; both long floc time = 19 minutes).

No significant difference ($p > 0.05$) was found in the effluent turbidity between the winter and summer for the long floc time scenario. Both sets of trials had average effluent turbidity just below 0.3 NTU. However, better turbidity removal was found in the summer than the winter when considering the raw water turbidity. During the winter, turbidity was higher in the DAF effluent than the raw water as the average turbidity removal was -4%. This meant that more turbidity was created during flocculation than was removed in clarification. Summer trials led to an average turbidity removal of 14%. Better turbidity results were found in summer trials than the winter for a short floc time, in terms of both effluent turbidity (0.31 NTU and 0.48 NTU, respectively) and overall turbidity removal (-10% and -81%, respectively). A short floc time produced DAF effluent turbidity that was greater than the raw water as both removal values were negative. The average effluent turbidity in the summer with a short floc time was similar to that with a long floc time, 0.28 NTU and 0.31 NTU, respectively. In the winter a long floc time produced much lower effluent turbidity of 0.29 NTU compared to 0.48 NTU with a short floc time. With the cold water temperatures in the winter impeding coagulation efficiency, the floc size or charge neutralization may not be optimized for collision and attachment with DAF bubbles for removal.

DAF performance was found to be similar with both short and long floc times in the summer. However, in the winter much better performance was experienced with a long floc time and results were more consistent with those found in the summer. A longer floc time is likely able to mitigate adverse effects that are presented with cold water temperatures, providing the coagulant increased time to hydrolyze and react with contaminants.

5.3.3 Impact of Flocculation Time on Coagulant Demand

A wider range of coagulant doses were trialed when the pilot plant was operated at Pockwock Lake for source water. This provided sufficient data to observe how the flocculation time influenced optimal coagulant doses. It should be noted that Pockwock Lake has lower NOM concentrations compared to Lake Major which leads to lower overall coagulant demands during treatment. Figure 5.6 presents UV₂₅₄ removal results for 7 minute and 23 minute floc times with various alum doses.

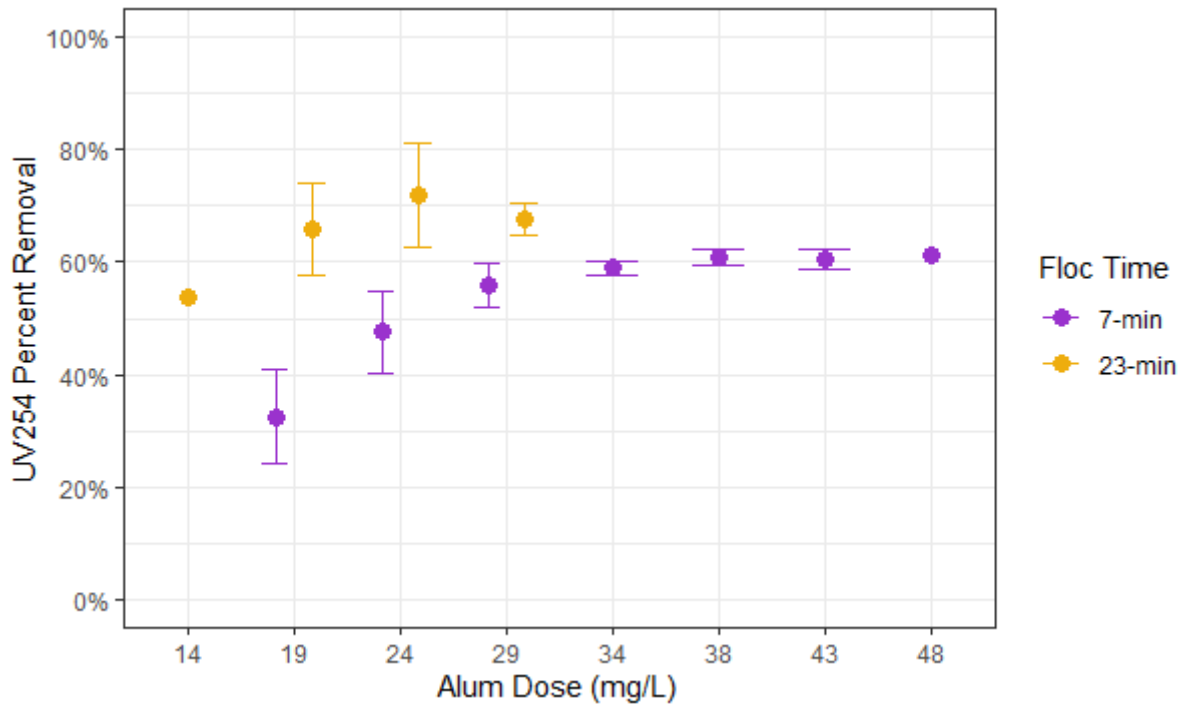


Figure 5.6. Average UV₂₅₄ removal during DAF clarification for 7 minute and 23 minute floc times across various alum doses.

Both floc time scenarios show the same trend with increasing removals as the alum dose is increased until a plateau is reached. A plateau for removal appears to be reached at an alum dose of 19 mg/L when a long floc time is used. A short floc time forms a plateau after a dose of 34 mg/L, a 75% increase in dose compared to the long floc time. Furthermore, as shown in previous sections, the long floc time provided higher removals overall compared to the short floc

time. Alum doses of 14 and 19 mg/L with a long floc time were able to achieve similar removals to doses of 34 mg/L and greater with a short floc time. A dose of 19 mg/L with a long floc time had an average UV_{254} removal of 66% while a dose of 34 mg/L with a short floc time had an average UV_{254} of 59%. These results agree with findings from Han et al. (2001). They showed that optimal removal required higher coagulant doses with short floc times than what is needed for longer (> 10 minutes) floc times. Different removal mechanisms are likely behind the discrepancy between the coagulant demands for each floc time scenario. Charge neutralization requires lower coagulant doses since it is stoichiometrically related to the amount of NOM in the water (Cruz et al., 2020; Shin et al., 2008). Sweep flocculation mechanisms occur at higher coagulant doses as it does not rely on stoichiometry and rather depends on the amount of hydroxide species produced which enmesh/entrap particles (Bache, Johnson, et al., 1999; Shin et al., 2008). As mentioned in the introduction, charge neutralization has been shown to take longer for stable floc formation to occur compared to sweep flocculation (Alansari & Amburgey, 2020). A floc time of 7 minutes may be reliant on sweep flocculation mechanisms while a floc time of 23 minutes allows enough time for charge neutralization to occur leading to a lower coagulant demand. Colour removal showed a similar trend as the UV_{254} results which can be found in the appendix.

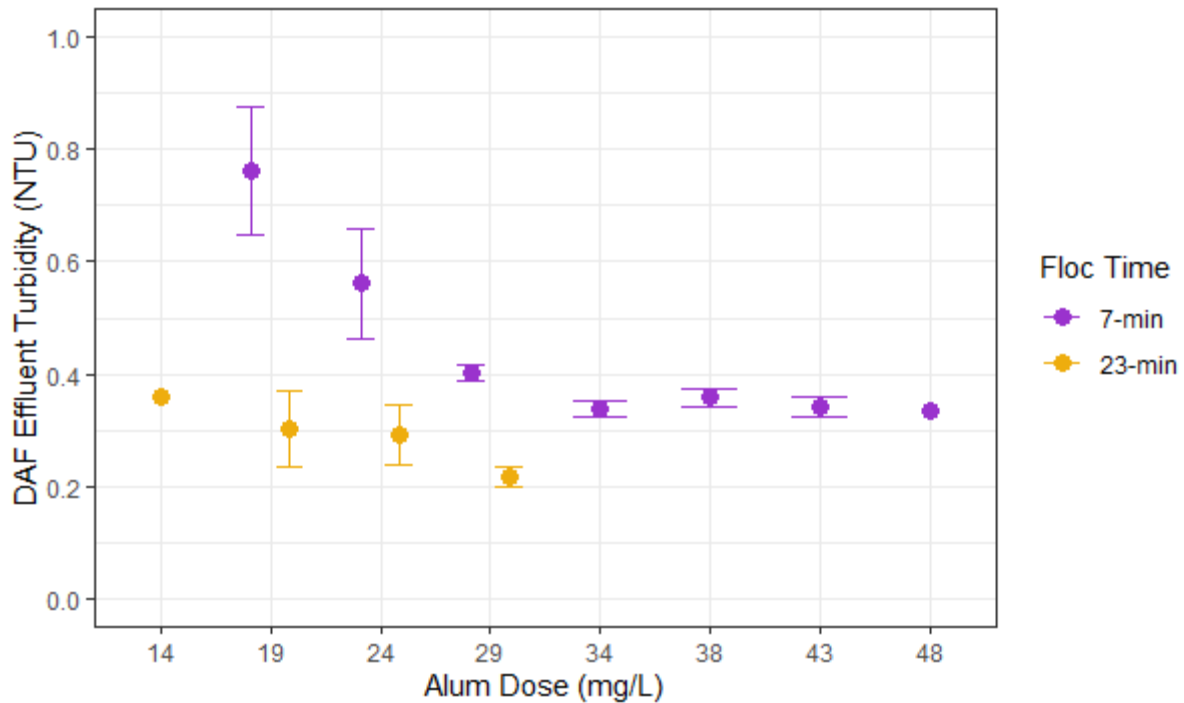


Figure 5.7. Average effluent turbidity following DAF clarification for short and long floc times across various coagulant doses (Note: Short floc time = 7 minutes; Long floc time = 23 minutes).

Effluent turbidity results from the DAF clarifier follow a similar trend to organics removal, shown in Figure 5.7. Average DAF effluent turbidity was 0.3 NTU with an alum dose of 19 mg/L at a floc time of 23 minutes. Comparatively, a plateau for average DAF effluent turbidity was reached at an alum dose of 34 mg/L for a floc time of 7 minutes, resulting in 0.34 NTU turbidity. Similar to organic removals, a lower coagulant demand with a 23 minutes floc time likely produced better turbidity results due to charge neutralization being achieved. Creating flocs whose charge is neutralized or slightly positive have been suggested to promote high bubble attachment efficiency (Edzwald, 2010). As previously mentioned, a shorter floc time likely leads to sweep flocculation, which is indicated by the higher coagulant demand. Flocs produced via sweep flocculation are noted as having positive charges and larger sizes (Cruz et al., 2020; Ghernaout & Ghernaout, 2012). These properties can diminish removal efficiency via

flotation. Larger flocs can lead to bubble detachment requiring more bubbles to increase their buoyancy to be lifted to the surface (Edzwald, 2010).

5.3.4 Impact of Mixing Intensity on DAF

Various mixing intensities were trialed to view its impact on flocculation alongside of floc time. Figure 5.8 displays SUVA removal results based on the GT value which is the velocity gradient (G) multiplied by the hydraulic retention time (T).

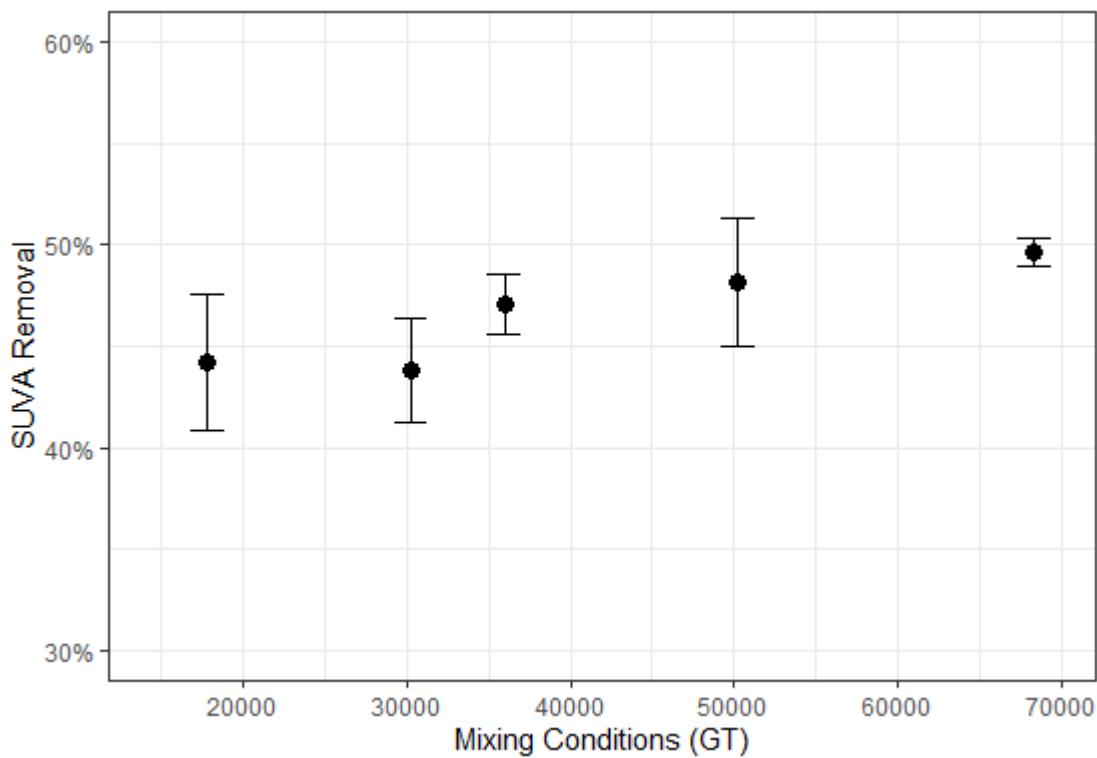


Figure 5.8. Average SUVA percent removal following DAF clarification based on mixing conditions. Mixing conditions are represented by multiplying the mixing velocity gradient (G) by the hydraulic retention time (T). Error bars represent the standard deviation.

Higher GT values are shown to lead to higher SUVA removal with a GT of nearly 70,000 providing approximately 50% SUVA removal. Conversely, a GT value of 18,000 has a SUVA removal of 44%. The difference was found to be significant ($p < 0.05$). SUVA removal gradually increases between these GT values, except for a GT value of 30,000. GT values of 18,000 and

30,000 are found to have the same SUVA removal at 44%. A GT of 30,000 was achieved with a floc time, or hydraulic retention time, of 7 minutes. Adjusting the floc time involved manipulating the flow path of the water to bypass tanks. As a result a 7 minute floc time was limited to having only 1 flocculation stage. If a 7 minute floc time was selected to be used at the full scale then the design would provide infrastructure for tapered flocculation. Tapered flocculation may result in a GT of 30,000 having higher SUVA removal than a GT of 18,000 which only had one flocculation stage. All other GT values were achieved with longer floc times which used multiple flocculation tanks, providing tapered flocculation.

GT values of 18,000 and 35,000 were both attained with a flocculation time of 11 minutes, resulting in average SUVA removals of 44% and 47%, respectively. The difference between the removals of these two GT values was found to be insignificant ($p > 0.05$). GT values of 50,000 and 68,000 both had a flocculation time of 19 minutes, resulting in average SUVA removals of 48% and 50%, respectively. The difference between the removals of these two GT values was also found to be insignificant ($p > 0.05$). These findings may suggest that the flocculation time has a greater impact on DAF performance since the differences were found to be insignificant between GT values that share the same flocculation time.

5.3.5 Impact of Floc Time on Filter Performance

The impact of floc time on filter performance was evaluated with data when the pilot was operated at Lake Major. Data was collected from one of the filter columns used in the pilot plant which contained 2ft of anthracite and 1 ft of sand. The impact of floc time on its performance was investigated using filter effluent UV_{254} results to represent organic removal and effluent turbidity from the filter for overall particle removal. These results are shown in the following figure.

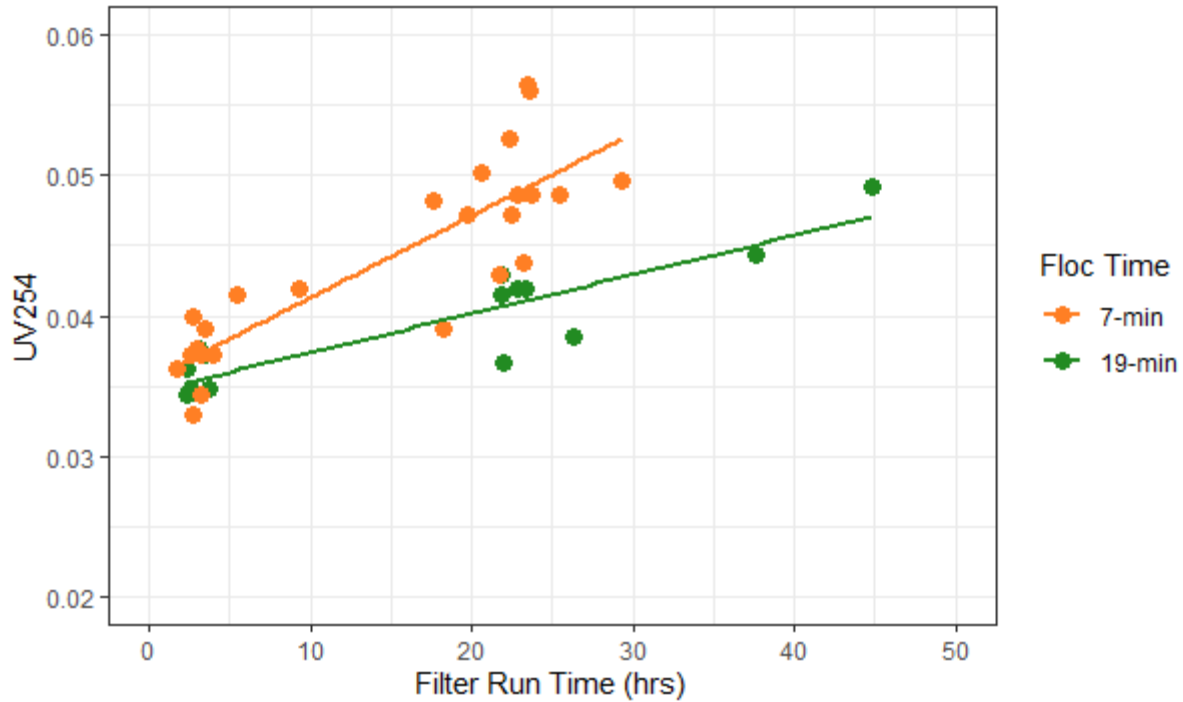


Figure 5.9. Filter effluent UV₂₅₄ results based on floc time.

Lines of best fit for the data were created using a linear regression model. UV₂₅₄ results were found to be fairly similar for both floc times following a backwash. However, a floc time of 19 minutes led to better UV₂₅₄ in the filter effluent as the filter run progressed, displayed in Figure 5.9. Only one data point is found above 0.045 cm⁻¹ during trials with a 19 minute floc time and this occurs towards the end of a filter run (44.9 hours). During 7 minute floc time trials the majority of data is found above 0.045 cm⁻¹ as the filter run time approaches 20 hours. No data was available for filter run times beyond 30 hours for a 7 minute floc time as breakthroughs were experienced beyond this point and backwashes were required. Differences in filter performance when each floc time was used is likely attributed to the water quality of the clarified water being fed into the filters. A 19 minute floc time may lead to the formation of flocs containing more organic matter and that are better removed during filtration. Flocs created after 7 minutes of flocculation may not encapsulate as much organic matter resulting in more NOM residual in the water matrix, leading to lower removals in filtration. These results suggest that a 19 minute floc

time could promote improved organic removal efficiency during filtration. The discrepancy in the range of filter run times for each floc time can be explained with effluent turbidity results shown in Figure 5.10.

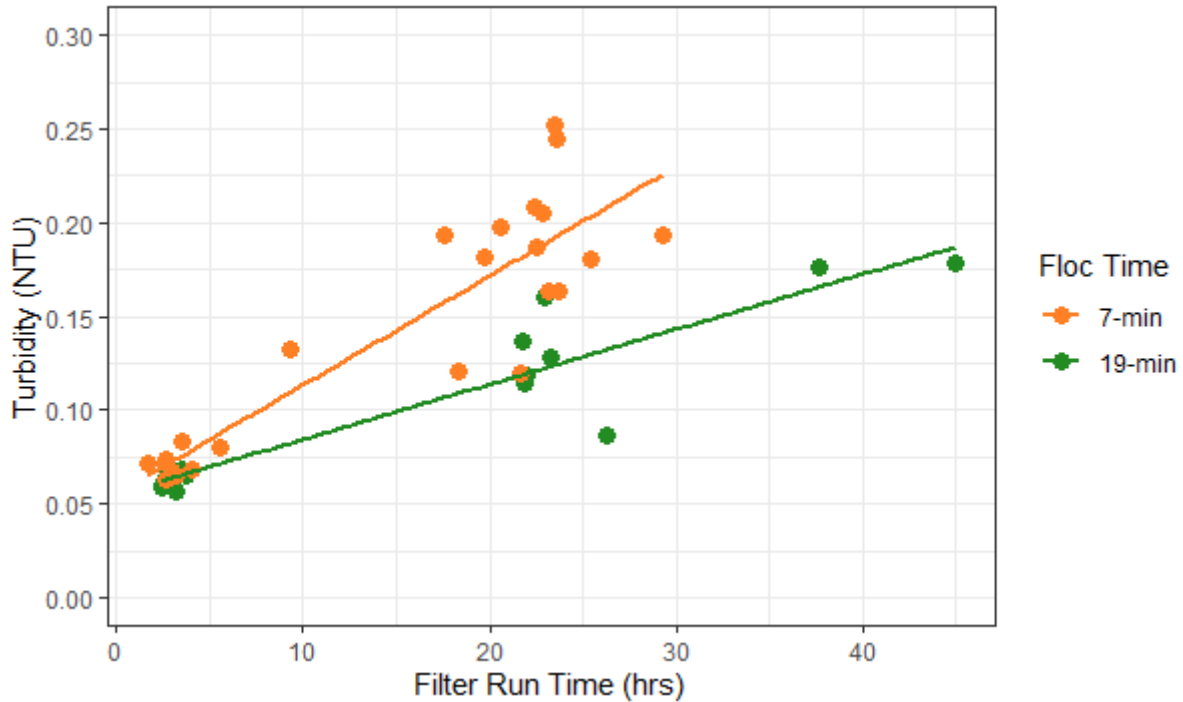


Figure 5.10. Filter effluent turbidity results based on floc time.

Effluent turbidity was found to be similar for both floc times at the beginning of filter runs, between 0.06 and 0.08 NTU. As filter runs progressed a 19 minute floc time led to lower filtered turbidity with a maximum of 0.178 NTU after 45 hours of filtration. Filtered turbidity surpassed this value and approached 0.2 NTU with a 7 minute floc time typically between 20 and 25 hours of filtration. This again highlights that when a floc time of 19 minutes was used, longer filter run times were achieved. As shown earlier in this chapter a 7 minute floc time produced worse clarified water quality compared to a 19 minute floc time, especially in terms of clarified turbidity. Increased influent turbidity and poorer water quality being fed into the filters would diminish filter efficiency due to more rapid filter clogging and consequently a reduction in filter

run time. It is important to prolong filter run times to reduce the frequency of backwashes as backwashes obstruct water production and wastes treated water.

5.4 Conclusions

The results presented in this chapter express the dynamic nature of water treatment. Specifically highlighted in this chapter, variance in water temperature as well as influent NOM composition and concentration can impact removal efficiencies. This is a difficult operational challenge as typically changes are needed to be made in coagulant dose throughout the year to maintain targeted removals. The results in this chapter suggest that 19 minute floc time could potentially mitigate impacts of variance in raw water quality, especially during colder periods.

- A 19 minute floc time provided 4% higher UV_{254} removal and 7% higher colour removal compared to a 7 minute floc time during periods of warm water temperatures and relatively low NOM. Even though the differences were found to be significant ($p < 0.05$), the improvements are marginal. A long floc time may not be economically feasible as longer floc times increase energy costs and require more tank volumes.
- Lower effluent turbidity was found following clarification with a 19 minute floc time (0.267 NTU) than a 7 minute floc time (0.315 NTU). The discrepancy is likely attributed to the time required to allow proper charge neutralization flocs to form. Additionally, for the most part a 7 minute floc time led to a higher turbidity following clarification than the influent turbidity into the pilot. Targeting sweep flocculation by using higher alum doses may lead to better removals when considering 7 minutes of floc time.
- In the winter, with colder water temperatures and higher SUVA, a 19 minute floc time provided nearly 10% higher UV_{254} removal, 14% higher colour removal, and an effluent turbidity nearly 0.2 NTU lower than a 6 minute floc time. These results suggest that a

longer floc time could mitigate challenges experienced with coagulation when water temperatures are colder.

- Lower alum doses were found to achieve similar or even better NOM and turbidity removals with a 23 minute floc time compared to when higher alum doses were used with a 7 minute floc time. An alum dose of 19 mg/L with a 23 minute floc time led to 66% UV₂₅₄ removal, 71% colour removal, and effluent turbidity of 0.3 NTU. Comparatively, an alum dose of 34 mg/L with a 7 minute floc time led to 59% UV₂₅₄ removal, 71% colour removal, and effluent turbidity of 0.34 NTU. This might suggest different coagulation mechanisms being optimal for each floc time scenario, charge neutralization for a longer floc time and sweep flocculation for a shorter floc time.
- Higher NOM removals generally found with longer floc times throughout the experiments in this chapter are likely a result of the longer floc times providing enough time for efficient charge neutralization. Charge neutralization is widely noted as being more efficient for NOM removal. Adaptive designs that allow for different floc times may help mitigate challenges when implementing DAF into treatment facilities that are experiencing brownification in their source waters.
- It should be noted that limitations in terms of the design and infrastructure in the pilot, tapered flocculation could not be achieved for a flocculation time of 7 minutes whereas it was with longer flocculation times. Full scale designs would incorporate tapered flocculation which may improve DAF performance with a shorter flocculation time.
- A 19 minute floc time was shown to achieve prolonged filter runtimes compared to a 7 minute floc time, approximately 45 hours compared to 29 hours. This likely stems from the water quality produced during clarification with each floc time scenario. A 7 minute

floc time leads to higher turbidity being fed into the filters which leads to more rapid filter clogging and reduced run times.

Chapter 6 - Conclusions and Recommendations

6.1 Conclusions

Optimal alum doses were identified using both bench-scale and pilot-scale experiments. Bench-scale jar tests were used to determine the appropriate alum dose for the destabilization and removal of NOM. This dose was found to be 46 mg/L which resulted in 60% DOC removal and 86% UV₂₅₄. This provided a starting point for pilot-scale experiments. Pilot scale experiments identified the optimal alum dose for DAF clarification which was found to be 48 mg/L. Seasonal impacts were observed on the optimal alum dose for pilot-scale DAF performance. 48 mg/L was optimal for trials in the winter and spring months (colder temperatures) while a lower dose of 41 mg/L was optimal during summer trials (warmer temperatures). The lower coagulant demand was attributed to improved coagulation efficiency in warmer water and reduced NOM concentrations.

PACl was found to outperform alum with regards to clarified effluent water quality. The use of PACl with DAF led to a lower residual turbidity of 0.173 NTU compared to 0.239 NTU for alum. PACl also showed better NOM removal with a lower UV₂₅₄ of 0.048 cm⁻¹ compared to 0.056 cm⁻¹ for alum. The comparison also took place during April, suggesting the advantage of using PACl in colder temperatures. Prehydrolyzed coagulants like PACl contain highly reactive cationic Al-species which lead to improved efficiency. PACl was also found to lower HAAs below 80 µg/L and THMs below 100 µg/L in the clarified effluent, meeting the Health Canada DBP regulations.

The impact of flocculation time on DAF was also investigated where a 19 minute floc time had higher NOM removal and lower residual turbidity compared to a 7 minute floc time. The UV₂₅₄ removal was 71% with a 19 minute floc time and 67% with a 7 minute floc time.

Effluent turbidity was 0.267 NTU with a 19 minute floc time and 0.315 NTU with a 7 minute floc time. The better performance for a longer floc time is likely attributed to it facilitating the formation of flocs better suited for the removal via DAF. Although a longer floc time produced better water quality the differences are marginal and a short floc time still provides good performance when considering typical goals in the industry ($> 0.05 \text{ cm}^{-1} \text{ UV}_{254}$ and effluent turbidity $< 0.5 \text{ NTU}$). A longer floc time would increase operating costs and energy consumption therefore a shorter floc time would be more economically feasible. These results were from trials during summer months. To evaluate seasonal impacts on the performance of each floc time scenario, trials in the winter were also looked at.

The difference in performance was magnified during colder water temperatures (winter) compared to warmer water temperatures (summer). In the winter a 19 minute floc time had nearly 10% higher UV_{254} removal and effluent turbidity 0.2 NTU lower compared to 7 minutes of flocculation. This could be attributed to the colder water exaggerating the decreased efficiency the shorter floc time has on floc formation. Adequate performance was still found with the short floc time during winter as the effluent turbidity was $< 0.5 \text{ NTU}$. NOM removal was found to be the same percentage with a short floc time in both the winter and summer (approximately 67% UV_{254} removal). However, higher NOM residual was found in the winter with a short floc time as a result of the increased influent NOM levels in the winter.

A range of coagulant doses were used for different floc time scenarios to investigate the influence of floc time on optimal dose when the pilot was operated at Pockwock Lake. An alum dose of 19 mg/L provided optimal UV_{254} removal and effluent turbidity with a longer floc time (23 minutes) while the optimal dose was 34 mg/L with a shorter floc time (7 minutes). A higher optimal dose with a shorter floc time could suggest that sweep flocculation mechanisms are

responsible for removal. Charge neutralization may be properly achieved with a longer floc time suggested by the lower alum dose.

The flocculation time was also found to impact downstream filter performance. Filter runtime was found to approach 48 hours before UV_{254} reached 0.05 cm^{-1} and 0.2 NTU for turbidity with 19 minutes of flocculation. A 7 minute flocculation time did not allow for filter run times to pass 30 hours due to filter breakthrough. The shorter filter run times with a shorter flocculation time stems from decreased removals during clarification which increases contaminant loading on the filters and leads to more rapid clogging.

6.2 Recommendations

More research is needed to support the selection of coagulant type. The supply of PACl was limited during this work which led to limited trials being performed with it. More PACl doses should be tested to properly evaluate the optimal dose for PACl. Trials should also be conducted during both cold and warm water conditions as results for PACl were only collected over a 2 week period. PACl was shown to be able to mitigate the impacts of cold water on coagulation but it would be interesting to see how its performance changes over the course of different seasons. The limited supply also did not allow for trials to be performed for short flocculation times with PACl. More rapid and efficient coagulation found with prehydrolyzed coagulant may be able to improve DAF performance with a short floc time. Further research should be conducted to investigate this.

Results pertaining to the comparison of long and short floc times could possibly be skewed as a result of pilot-scale limitations. Equivalent mixing conditions, such as amount of mixing stages, could not be achieved for each floc time scenario investigated. Therefore further

research should be conducted to determine how performance can be impacted by mixing conditions.

Further consideration should be taken into account for the design and economic implications for the use of longer floc times. Shorter floc times result in smaller footprints in the plants, reduced energy consumption and treatment times making them more economically feasible. The results of this work suggest that longer floc times lead to improved DAF performance and the potential to use reduced alum doses. Adaptive designs could incorporate flocculation tanks that could be used to increase flocculation times when challenging influent conditions are encountered, such as those found in the winter. This could improve removal with DAF, reduce coagulant demand changes, and prolong filter run times during these periods. Utilities experiencing brownification may benefit from this concept as it would make them more resilient to changes in their source waters.

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Appendix A

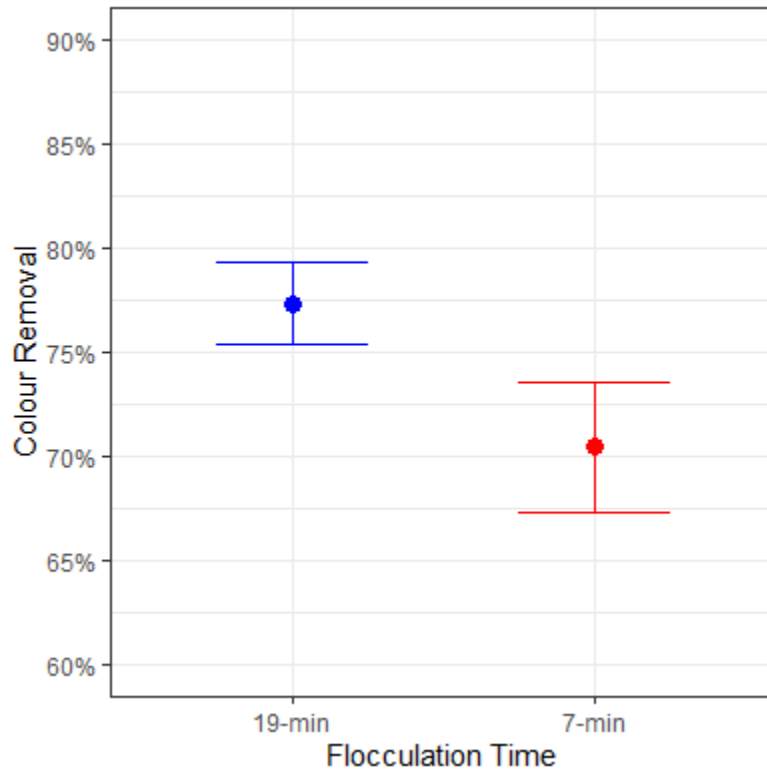


Figure A.1. Average colour removal during DAF clarification for 7 minute and 19 minute floc times based on coagulant dose. Data from August and September 2021. Alum doses between 41 and 55 mg/L for each floc time.

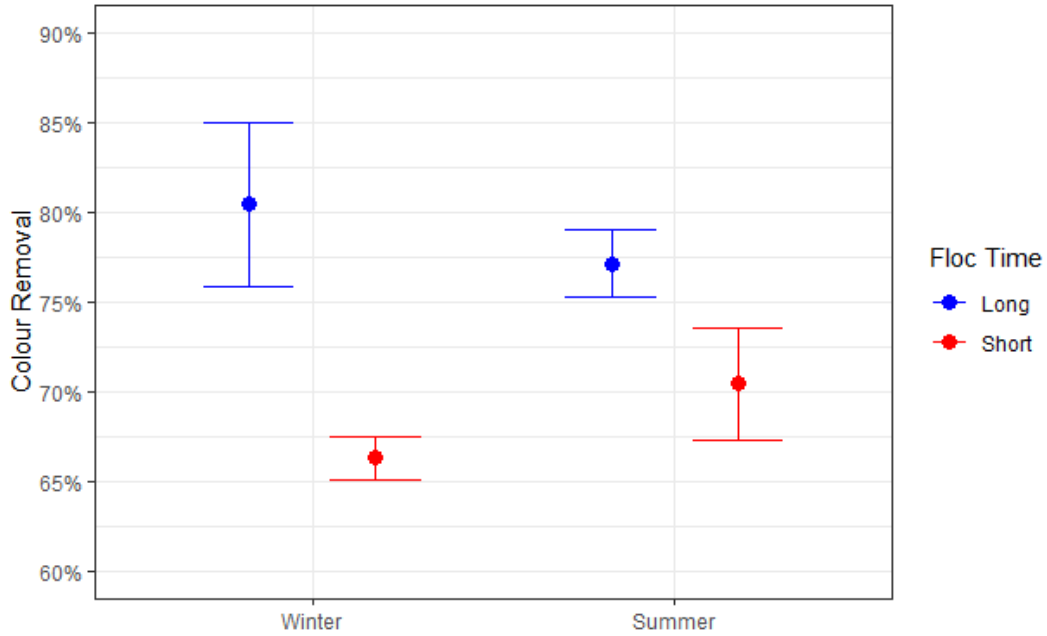


Figure A.2. Average apparent colour percent removal during DAF clarification for short and long floc times during different times of the year (Note: March short floc time = 6 minutes; September short floc time = 7 minutes; Both long floc time = 19 minutes).

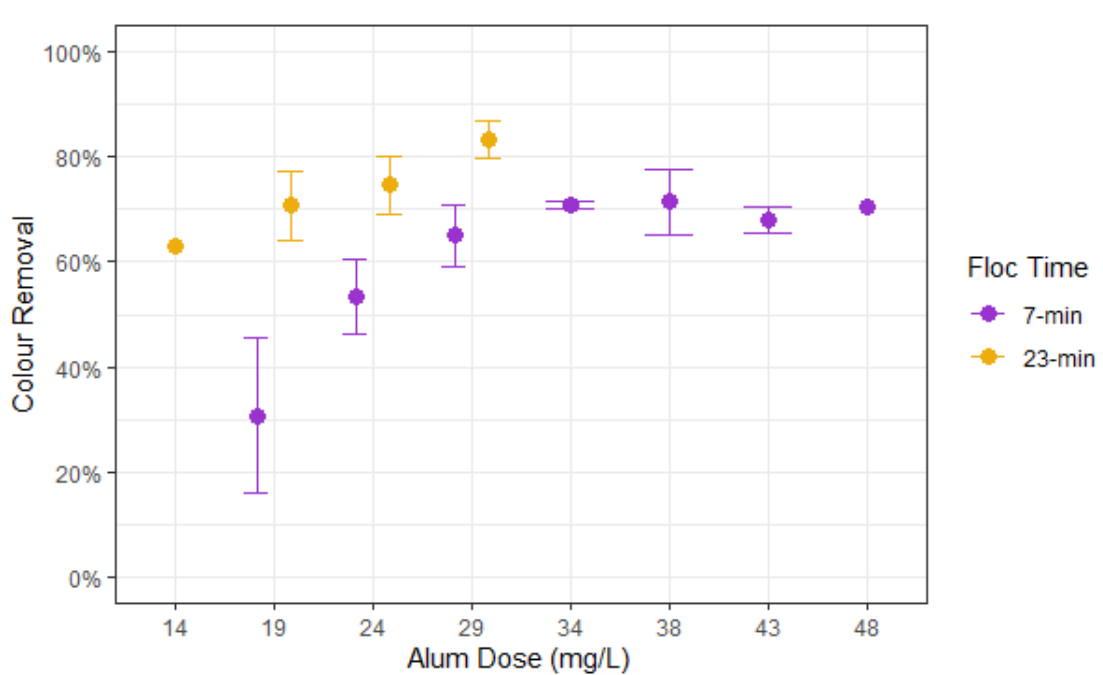


Figure A.3. Average colour removal during DAF clarification for short and long floc times across various coagulant doses (Note: Short floc time = 7 minutes; Long floc time = 23 minutes).