ENHANCING NATURAL ORGANIC MATTER REMOVAL IN AN ULTRAFILTRATION MEMBRANE PLANT THROUGH COAGULATION

by

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Water treatment requires decisions associated with process design that are specific to source water quality while remaining mindful of regulatory guidelines. Each source water is highly varied and unique, posing specific challenges to water treatment plants and municipalities. Small water treatment plants supplying rural communities are just as critical as large-scale plants in capital cities supplying hundreds of thousands of customers daily, though they face different challenges. One such challenge is the trade-off between effective treatment of water and financial considerations. Though a common coagulant such as aluminum sulfate may appear to be the most cost-effective due to its generally low initial investment, additional costs may arise further down the treatment train as chemical pH buffers are added to raw water and stringent pH monitoring becomes critical. As well, filters must be taken offline for frequent cleaning due to the production of solid waste residual (SWR) from insoluble aluminum hydroxide.

Coagulation and flocculation are chosen for removal of natural organic matter (NOM) in drinking water plants due to their high NOM removal rate capability and associated reduction in various characteristics, including disinfection by-products (DBPs). These are compounds formed by the reaction of humic NOM with chlorine disinfectants, which are known to be carcinogenic and can have adverse health effects if consumed over a long period of time.

Alternatives to coagulation with alum include pre-hydrolysed polyaluminum chlorides (PACls), which are more expensive to purchase but can be dosed at lower volumes due to their higher Al concentrations. Other benefits of these coagulants include high basicity, which decreases their effect on the pH of raw water, and their lower production from a lower required dosing volume. Four of these PACls were tested in bench-scale coagulation experiments to determine an optimal pH and dose for each, while also establishing an ideal treatment option for a small water treatment plant in North Sydney, Nova Scotia for removal of natural organic matter. PAC-A, PAC-B, PAC-C, and PAC-D were coagulated using raw water from Pottle Lake Water Treatment Plant at pH 5.5 and 6.5, and it was determined that the optimal pH for all coagulants was pH 6.5.

Coagulants were divided into two groups for comparison; Group 1 contained PAC-B and PAC-D, which were tested at doses of 5.0, 15.0, and 30.0 mg/L of aluminum. Through percent removal of UV_{254} as a deciding metric, 5.0 mg/L was determined to be the optimal dose for both. Group 2 contained PAC-A and PAC-C, which were dosed at 0.6 mg/L, 1.8 mg/L, 3.6 mg/L and 0.3 mg/L, 1.0 mg/L, 2.0 mg/L, respectively. The optimal dose of PAC-A was determined to be 1.8 mg/L, while the optimal dose for PAC-C was 1.0 mg/L.

There was no statistically significant difference in overall reduction of natural organic matter between any of the polyaluminum chlorides tested, indicating that each coagulant effectively removed natural organic matter equally. All four coagulants showed promising results in removing precursors of disinfection by-products for Pottle Lake Water Treatment Plant, but the optimal PACl coagulant was determined to be PAC-A-1.8 at pH 6.5 due to its reduction of UV_{254}, turbidity, and specific UV absorbance (SUVA).

LIST OF ABBREVIATIONS USED

ACH	Aluminum chlorohydrate
Al	Aluminum
$Al(OH)_3$	Aluminum hydroxide
Alum	Aluminum sulphate
ANOVA	Analysis of variance
AO	Aesthetic objective
DBP	Disinfection by-product
DOC	Dissolved organic carbon
HAA	Haloacetic acid
ICP-MS	Inductively coupled plasma mass spectrometry
km	Kilometres
L	Litres
m	Metres
mg	Milligrams
mg/L	Milligrams per litre
MAC	Maximum allowable concentration
MQ	Milli-Q
N	Normality
nm	Nanometres
NOM	Natural organic matter
NPOC	Non-purgeable organic carbon
NSE	Nova Scotia Environment
NTU	Nephelometric turbidity units
PACl	Polyaluminum chloride
PES	Polyethersulfone
PLWTP	Pottle Lake Water Treatment Plant
ppb	Parts per billions
PtCo	Platinum-Cobalt units
rpm	Revolutions per minute

s	Seconds
SD	Standard deviation
SG	Specific gravity
SUVA	Specific Ultraviolet Absorbance
SWR	Solid waste residual
TCU	True colour unit
TDS	Technical data sheet
THM	Trihalomethane
TOC	Total organic carbon
UV-Vis	Ultraviolet-visible spectrum
WTP	Water treatment plant
μg	Microgram
μL	Microlitre
μm	Micrometre

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CHAPTER 1 INTRODUCTION

1.1 Project Rationale

NOM is a mixture of compounds found in raw source waters, generally created by naturally-occurring environmental processes and anthropogenic activities (Health Canada, 2019a). Without proper filtration and removal of these compounds, water treatment plants (WTPs) can face problems in the treatment and distribution of drinking water. NOM can create treatment issues with disinfection by reacting with chlorine gas to produce carcinogenic compounds called DBPs while also reducing residual chlorine in pipes throughout the distribution system (Health Canada, 2019a), which could lead to inadequately sterilized water. Furthermore, interactions between NOM compounds and certain pipe materials like lead and copper can lead to corrosion of distribution pipes as well as potential negative health impacts of consumers (Schock & Lytle, 2011).

WTPs must appropriately treat raw water to remove NOM in order to avoid these issues, and most often do so through the processes of coagulation and flocculation. Coagulation removes NOM, microorganisms, and other impurities from source water. In drinking water, coagulation is followed by flocculation and filtration to clarify raw water prior to any optional further treatment, such as disinfection by chlorine or UV light. This paired treatment of coagulation and flocculation is critical in removing both organic and inorganic contaminants that would otherwise fail to settle out quickly or at all in a clarification tank.

Coagulant must be dosed at specific concentrations and under specific conditions in order to achieve proper treatment of water and reduce strain on the WTP. For aluminum-based coagulants, there is a pH range in which they will function effectively, and outside of this range aluminum may become soluble instead of the ideal insoluble form. This may lead to higher aluminum residual concentrations in finished drinking water and the potential for human health impacts. The concentration at which coagulant is dosed into raw water is also important; too little coagulant will not be able to flocculate sufficient amounts of NOM, potentially allowing harmful contaminants to remain in finished water. Conversely, an excess of coagulant will not only present a larger cost to the WTP, but also lead to more rapid fouling of subsequent filter membranes. More frequent cleaning of membranes results in unnecessary costs to the WTP and an increase in time spent treating raw water.

An optimal dose of coagulant will effectively clarify raw water and sufficiently remove contaminants without rapidly fouling the filtration membranes that follow the flocculation process.

Finished water from Pottle Lake Water Treatment Plant (PLWTP) in recent years has been found to contain above-acceptable concentrations of common DBPs such as trihalomethanes (THMs) and haloacetic acids (HAAs). Health Canada has laid out a maximum allowable concentration (MAC) of 0.1 mg/L THMs and 0.08 mg/L HAAs in finished water (Health Canada, 2019b). The treatment process at PLWTP consisted of filtration through an ultrafiltration (UF) membrane and disinfection by chlorine; however, NOM was not being sufficiently removed from water prior to the addition of chlorine. In April of 2019, PLWTP began coagulating with polyaluminum chloride (PACl) in order to sufficiently remove NOM from raw water but the implementation of this change required bench-scale testing in order to determine an optimal dose and pH.

Coagulation and flocculation are ideal methods for reducing DBP concentrations in finished water, due to coagulant's action of destabilizing particles and allowing negatively charged colloids to neutralize and form flocs composed of NOM and other contaminants. These flocs can be settled or filtered out of finished water. By clarifying water in this way, there is an associated reduction in turbidity and colour, two characteristics that can shield precursors to DBPs.

There are a variety of coagulants currently available to WTP operators. Among the most common are aluminum-based coagulants such as aluminum sulphate (alum) and PACl, including aluminum chlorohydrate (ACH). However, within the class of aluminum-based coagulants, there is a wide range of options that can appear similar but will provide specific advantages when chosen appropriately. As such, a comparison of these coagulants would be a valuable addition to current literature in order to provide essential information to WTP operators that may be considering a change in their treatment process.

1.2 Research Objectives

The main objective of this thesis was to determine an ideal coagulation practice for PLWTP in North Sydney, Nova Scotia in order to improve finished drinking water quality. In particular, a reduction in precursors for DBPs was the focus of characterization and analytical work.

To meet this objective, optimal removal of NOM from Pottle Lake source water was investigated through treatment with a range of aluminum-based coagulants in bench-scale coagulation experiments. These coagulants were tested at varying doses and pH to determine ideal conditions for optimal NOM removal.

The secondary objective of this research was to prepare a comparison of four PACl coagulants for use in future research. These coagulants vary in chemical properties and can be compared by their technical data sheets, but literature is lacking a practical evaluation of each coagulant in terms of NOM removal.

CHAPTER 2 LITERATURE REVIEW

2.1 Overview of Aluminum-Based Coagulants

Through the common clarification technique of consecutive coagulation and flocculation, WTPs employ an array of coagulating chemicals including those that are aluminum-based, iron-based, or even more experimental types such as *Moringa oleifera* seed (Shan, T.C., et al, 2017; Hendrawati et al 2016). Coagulation is a procedure which must be adjusted for specific conditions, and this process includes identifying characteristics of each class of coagulant and recognizing those which will function best with the particular category of water being tested.

Aluminum-based coagulants have been used extensively around the globe for decades. The most common of these is alum but others include ACH and PACl, which is a pre-hydrolysed chemical designed to enhance the coagulation process (Tolkou, 2014). These coagulants have different properties that make them ideal in various situations, and a determination of these will aid WTPs in producing high quality water while mitigating costs.

2.2 NOM Removal

NOM, the combined molecules of organic compounds created by natural processes and anthropogenic causes, is a main cause of concern for WTPs. Consumption of NOM in drinking water can lead to adverse health effects, as microorganisms are often sheltered by the compounds of NOM. Furthermore, interactions between NOM and chlorine disinfectant or lead pipes can increase the risk of DBPs and corrosion, respectively. It is the responsibility of WTPs to appropriately reduce NOM in treated water to minimize the risks associated with these interactions.

The action of removing NOM by aluminum-based coagulants is understood to be done in part by charge neutralization and beyond that, sweep flocculation (EPA, n.d.; Dentel & Gosset, 1988). Charge neutralization coagulation typically occurs at a relatively low pH and low coagulant dose, where positively charged coagulant neutralizes the negative charge of NOM to form a neutralized floc (Ghernaout, D, 2012; Li et al, 2006); while at a higher pH, sweep flocculation becomes the main action of coagulation, where NOM adsorbs onto the surface of solid aluminum hydroxide to form flocs.

Enhanced coagulation can be utilized to further improve NOM removal, which is important to reduce DBP precursors (Jiang & Graham, 1996). In this method, higher doses of coagulant are added at a lower pH in order to increase removal of NOM (Mao et all, 2013). A major downside of increasing coagulant dose above what may be minimally required is the amount of SWR that forms in the system, as well as membrane fouling after sedimentation. To combat this, pre-hydrolysed coagulants such as polyaluminum chloride can be used to reduce these operating costs (Jiang & Graham, 1996).

An estimate of the characterisation of NOM in raw water can be done by determining the SUVA value (Table 1). A low SUVA result of 2.0 or less implies non-humic, hydrophilic molecules; a medium value of between 2.0 and 4.0 means the presence of small hydrophobic molecules and hydrophilic molecules; and a high SUVA result of 4.0 or above shows the organic material in the raw water contains humic acid (Jiang & Graham, 1996; Edzwald & Tobiason, 1999). Humic acid is one main form of NOM that can be reduced through coagulation (Rucka, 2019; Weng, 2002), and a low SUVA value following coagulation indicates that all humic material has been removed, and further reduction of NOM through coagulation is unlikely. Reduction of NOM can also be quantified by a reduction in UV_{254}, colour, and turbidity.

Table 1 Characterization of NOM by associated SUVA values.

SUVA (L/mg•m)	Natural Organic Matter Characterization
< 2.0	Generally non-humic
3.0 – 4.0	Humic and non-humic mix
> 4.0	Generally humic

2.3 Classes of Aluminum-Based Coagulants

2.3.1 Aluminum sulfate

Aluminum sulfate is an extremely common coagulant on the market for water treatment. It is a relatively low-cost, widely effective chemical used on a variety of source waters around the world. However, it contains no basicity, which necessitates the addition of chemicals to adjust the pH of the raw water to between pH 5.5 and 7.5 (Brandt, 2017). This creates an additional cost for WTPs and requires regular monitoring of pH.

Though alum is highly useful and adaptable, one of main considerations of coagulating with alum is the production of SWR formed from solid aluminum hydroxide during the coagulation reaction (Fouad et al, 2017). Due to the aluminum ions being less charged, alum may need to be dosed at high volumes in order to sufficiently remove NOM and other contaminants, and this can lead to a higher production of waste SWR in WTPs (Brandt, 2017).

2.3.2 Polyaluminum chloride

Hydrolysed aluminum coagulants such as PACl are less commonly used than alum but have specific advantages. The primary of these is the high basicity of PACl, which requires little buffering of raw water prior to coagulant addition (Brandt, 2017). Furthermore, PACl can be dosed at a wider range of pH, from 6-9, as well as a lower dose (Ratnayaka et al, 2009; Brandt, 2017). There is the potential of high residual aluminum in the water after coagulation, with Lin & Ika (2019), implying PACl can leave excess aluminum in treated water while older research states that the lower dosing requirements of PACl would in fact reduce aluminum residuals (Wei et al, 2015; Yang et al 2011). Unlike alum, there are a variety of PACl types on the market, each with varying aluminum concentrations and basicity. While this allows more options for operators of a WTP, there is no literature evaluating different varieties of PACl to provide a comparison of their efficacy in removing NOM.

Generally, it is thought that PACl can be dosed at a lower volume than alum (Zouboulis et al, 2007), likely due to its more highly charged aluminum ions. Furthermore, due to the lower dose, there is an associated reduction in SWR production during the coagulation reaction.

2.3.3 Aluminum chlorohydrate

Under the umbrella term of polymerised PACl is another coagulant, ACH. Along with the benefits of conventional PACls, ACH can be dosed at approximately one-third the dose of alum (Gebbie, 2006) and one-half that of PACl (Verma et al, 2012). This reduction in dosing volume would be useful in reducing costs and SWR production as discussed above with PACl. The lower volume required for dosing can be attributed to the high percentage of aluminum by weight (% w/w) in general ACH solutions, with specific % w/w being found in literature produced by manufacturers. ACH, being a subset of PACl, shares similar characteristics with that class of coagulant; namely, more highly-charged ions and higher basicity than alum. Furthermore, due to its ability to be dosed at higher pH, WTPs may be able to remove the typical step of chemically buffering raw water prior to dosing with coagulant in order to achieve a certain operating pH (Gebbie, 2006).

Despite the apparent usefulness of ACH, it is not as commonly selected as alum in WTPs around the world. This may be due to the higher upfront cost of purchasing this coagulant, but the savings from a lower required dose and reduction in buffering chemical may in fact be enough to negate any increased purchasing cost (Doyle, 2009).

2.4 Factors Affecting Aluminum Coagulation

2.4.1 Basicity of coagulant

Basicity is a measure of available hydroxyl ions in polymerised coagulants, typically given in a range by % w/w. In terms of coagulation theory, basicity is the capacity of a coagulant to buffer acids. The amount of basicity in coagulant is inversely related to that coagulant's effect on the pH of raw water; low-basicity coagulant will have a high impact on pH, driving it down significantly and requiring the addition of a buffering chemical; whereas a high-basicity coagulant will have little effect on pH of raw water (Gebbie, 2006). Commercially, alum has zero basicity, PACl can have up to 70% basicity, and ACH can have up to 85% basicity. As such, alum would require more buffering chemical addition than PACl would, and ACH would require the least amount of buffering chemical, if any at all.

2.4.2 Dosing

WTPs using coagulation must first optimize the procedure to ensure sufficient clarification of water. This process can involve bench-scale testing, as there are a variety of factors which must be studied to determine the optimal dose. A dose too low may not adequately remove natural organic matter, which may in turn be hiding compounds that could form carcinogenic DBPs further down the treatment stream (Edzwald, 1993). This can be seen by a minimal reduction in turbidity at low doses (Malik, 2018). Viruses, bacteria, and other pathogens must also be inactivated in the water to prevent unnecessary health impacts. Conversely, an excess of coagulation will foul filter membranes too quickly, requiring more frequent cleanings (Lee, 2009). Both an excessive coagulant dose and recurrent membrane cleanings can increase costs in the WTP, leading to the potential for financial strain.

2.4.3 pH

pH is another critical factor to study when determining optimal dose of aluminum-based coagulant. If the pH of the raw water is below that of the ideal range for the coagulant, the addition of coagulant can further drop the pH (Government of Oregon, n.d.). The overall goal of coagulation is to produce metal hydroxide (Wills, 2016), and hydrolysis species are dependent upon the pH of raw water. In the case of aluminum-based coagulants, the ideal metal hydroxide is aluminum hydroxide ($Al(OH)_3$) (Gebbie, 2006), which precipitates between the pH range of 5.5 and 7.5 (Brandt, 2017) and outside of this range, may no longer form (Jaouadi, 2013). It is important to properly adjust the pH of raw water using buffering chemicals, such as sodium hydroxide or sodium bicarbonate to increase pH, and sulfuric acid to lower pH.

Coagulants that are pre-hydrolysed, such as PACl and ACH, require less buffering of raw water due their ability to coagulate properly over a wide pH range. Furthermore, the high basicity of these coagulants adds to their ability to withstand higher or lower pH than a coagulant with no basicity.

Coagulation at pH lower than that of the ideal operating range can lead to high residual aluminum concentrations. In Canada, the operational guideline (OG) value of aluminum residual in treated water is < 0.2 mg/L in conventional filtration plants, and < 0.1 mg/L for all other plants (Health Canada, 2019b). Residual aluminum is most often caused by $Al(OH)_3$ in its soluble form, which does not precipitate out of solution like its insoluble form, as well as soluble polymeric Al hydrolysis species that pass through filters (Zhao et Al, 2009). Though Health Canada does not list any adverse health effects of consumption of residual aluminum in drinking water, there is literature to suggest there may be links to Alzheimer's disease (Kawahara, 2011).

2.5 Disinfection By-Products

When NOM in source water comes into contact with chlorine gas for disinfection, harmful compounds called DBPs can be formed. These compounds can be detrimental to human health (Teixeira, 2010) and are most commonly monitored by concentrations of two categories, THMs and HAAs (McCormick, 2010). Humic acid is typically a precursor to DBP formation (Teixeira, 2010) and thus stresses the importance of NOM characterization in source waters prior to chemical treatment. The functional groups present on humic acid molecules can bind with free chlorine from chlorine disinfection in order to create these carcinogenic compounds (Lu et Al, 2016; Pomes et al, 1999)

In Canada, there is a maximum allowable concentration of 0.1 mg/L for THMs and 0.08 mg/L for HAAs (Health Canada, 2019b) which must be considered when designing appropriate water treatment techniques. Proper removal of NOM during treatment is critical to mitigating the risks of DBP formation during disinfection, and thus stresses the importance of selecting suitable treatment options in WTPs.

2.6 Conclusion

There is significant literature published regarding the efficacy of aluminum sulfate as a coagulant for a range of source waters, with fewer studies evaluating polyaluminum chlorides, and even less regarding aluminum chloride. As such, there is the potential for future research to compare not only these three main chemicals, but to go further and study the classes of hydrolysed aluminum coagulant available on the market. This assessment of coagulants could prove highly valuable to municipalities designing new water treatment plants or modifying existing infrastructure to keep pace with a changing environment. The options of alum, PACl, and ACH must be given appropriate consideration to ensure optimal clarification of raw water in order to produce, at minimum, adequately clean treated water; however, beyond meeting or exceeding drinking water guidelines, many WTPs must take costs and operator effort into account when selecting a treatment plan. In this way, a detailed analysis of the variances and financial considerations of these coagulants could provide useful not only in fulfilling gaps in the literature, but to real-world, practical applications.

CHAPTER 3 WATER QUALITY METHODS

3.1 Sample Site

3.1.1 Pottle Lake, North Sydney, Nova Scotia

The focus site of this research is Pottle Lake, source water for a drinking water plant in North Sydney, Nova Scotia as well as Sydney Mines and surrounding rural communities. Pottle Lake has an area of 2.85 km$_2$, while the entire protected watershed is comprised of 11.26 km$_2$ (CBRM Water Utility, 2013). There is a single large basin in the centre of the lake with a depth of 9.79 m, and a smaller basin with a depth of 3 m in each of the northern and southern arms (Spooner, 2010). Pottle Lake is spring fed and has a single outlet, Smelt Brook, at which there are stoplogs that are responsible for maintaining positive hydraulic pressure from the lake to the outlet. Despite being a protected watershed, Pottle Lake faces anthropologic contamination mainly from 8 km of Highway 125 that directly run off into the watershed, but also from illegal dumping of waste in the area (CBRM Water Utility, 2013). To mitigate highway runoff, measures such as finger dykes, rip-rap drains, and a settling pond are installed.

3.1.2 Pottle Lake Water Treatment Plant

PLWTP used UF membrane technology for ten years and supplies approximately 6700 metered customers with an average 2.5 million gallons of water used per day (CBRM). The plant is located directly across the highway from its source water and fed from the intake by gravity pipe. Commissioned in 2010, PLWTP was designed to employ UF membrane technology to treat raw water prior to disinfection but was built with additional infrastructure in place to allow for coagulation in the future. Since April 2019 this coagulation infrastructure is now in use, and PLWTP now most closely resembles a standard direct filtration plant; PAX-54 coagulant at the dose of 5.0 mg/L Al is added to raw water in a small rapid mix tank before the water continues to a larger tank, where mixing is slower to encourage flocculation. There is no subsequent sedimentation tank as in conventional treatment, but instead the flocculated water continues through UF membranes prior to disinfection.

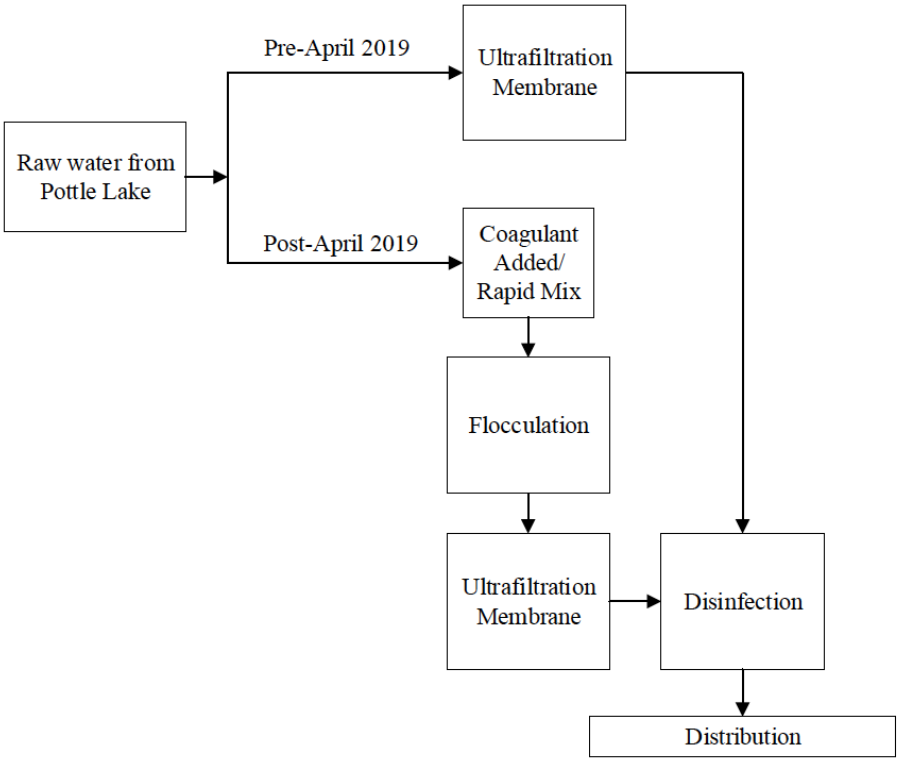

Figure 1 **Schematic of Pottle Lake Water Treatment Plant design indicating treatment train before and after April 2019.**

Figure 2 Ultrafiltration membrane cassettes at Pottle Lake Water Treatment Plant. Taken October 2018 by Mikaela Zwicker.

3.1.3 Sample collection

Raw water from Pottle Lake was collected by Cape Breton Regional Municipality (CBRM) staff and shipped to the Centre for Water Resource Studies at Dalhousie University for the purpose of this research. Water was stored in laboratory refrigerators, then brought to room temperature prior to analysis. For bench-sale coagulation experiments with alum, water was shipped in October. PACl bench-scale coagulation tests were conducted with water shipped in February.

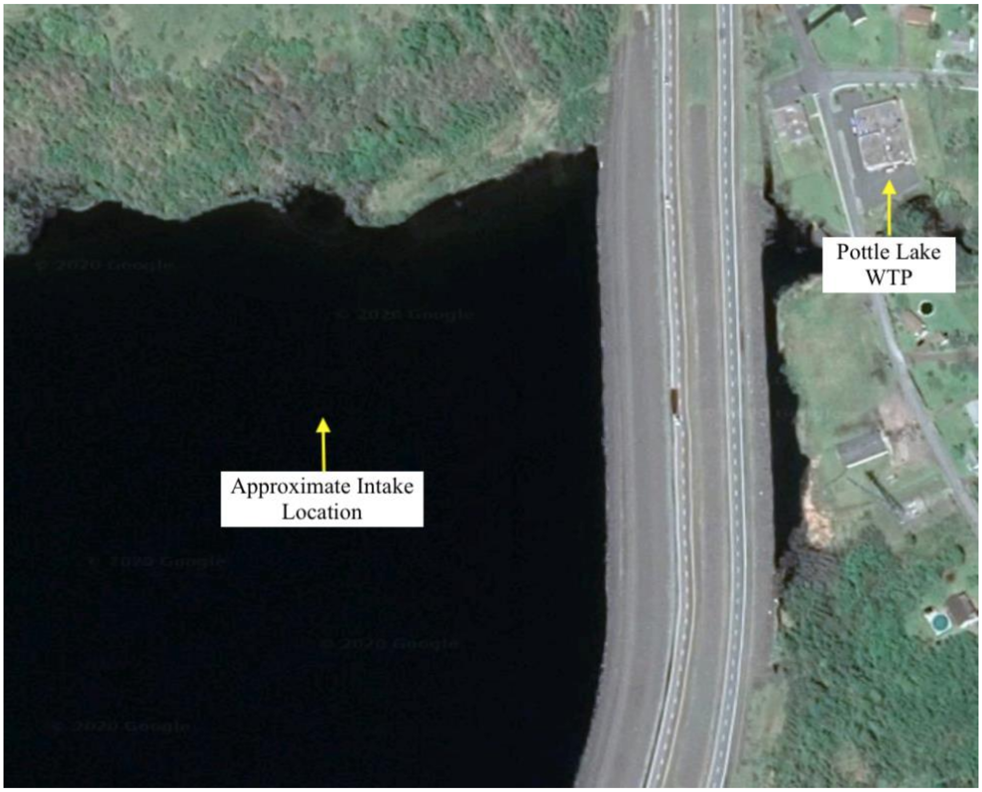

Figure 3 **Location of Pottle Lake Water Treatment Plant and approximate location of Pottle Lake water intake.**

3.2 Water Quality Analysis

3.2.1 General water quality characterization

Prior to testing for NOM, raw water was analysed for two general water quality analytes. pH was measured using a standard laboratory pH probe that was properly calibrated to pH 4.0, pH 7.0, and pH 10.0 immediately before use.

For testing of turbidity, raw water sample was placed into a 43 mL laboratory turbidimeter cell and entered into the Hach TL2350 turbidimeter. The measurement was performed three times and data produced from the turbidimeter was given in Nephelometric Turbidity Units (NTU).

3.2.2 Natural organic matter

In order to develop an overview of NOM in this study, several analytes were tested for in Pottle Lake source water. True colour, UV_{254}, total organic carbon (TOC), dissolved organic carbon (DOC), and SUVA were used to provide a summary of NOM before and after bench-scale treatment.

Colour and UV_{254} were both analysed using a HACH DR5000™ UV-Vis spectrophotometer. True colour samples were prepared by priming a fresh 0.45 µm polyethersulfone (PES) filter with 500 mL ultrapure MQ water before filtering each water sample. A square cell was prepared by rinsing thoroughly with MQ water and then sample. Subsequently, filtered sample was placed into the prepared cell for testing. The cell was placed into the spectrophotometer and the colour program was selected, testing in triplicate at the 455 nm wavelength. Apparent colour was tested for by using raw water sample instead of filter water and following the same procedure for preparation of the sample cell. Data for colour was given in units PtCo.

Similarly, UV_{254} was tested for by rinsing a sample cell with MQ, then sample, before the cell was filled with filtered sample and placed into the spectrophotometer. The UV_{254} program was selected, and the sample was tested in triplicate. UV_{254} data was given in cm^{-1}.

The sample for TOC analysis was prepared by placing raw Pottle Lake water headspace-free into a glass laboratory vial with a volume of 43 mL. Subsequently, four drops of 85% H_3PO_4 were added to the sample as acidification before the vial was closed tightly with aluminum foil and a cap. DOC was prepared using the identical procedure, however the sample used was water that had been jar-tested under specific conditions before being filtered through a 0.45 µm PES filter. Following collection of samples, TOC and DOC were measured in duplicate using a Shimadzu TOC-VCPH Total Organic Carbon Analyser, and data produced was given in non-purgeable organic carbon (NPOC) mg/L.

Table 2 Average raw water characteristics of Pottle Lake.

Analyte	Average Value (n = 3)	Standard Deviation (±)
Apparent colour (units PtCo)	33	0.58
pH	6.65	0.16
TOC (mg/L)	2.452	0.001
Turbidity (NTU)	0.378	0.019
UV$_{254}$ (cm^{-1})	0.090	< 0.001
SUVA	3.67	0.00

SUVA was calculated using UV$_{254}$ and DOC values from treated water to characterise NOM remaining after coagulation and filtration. For raw water, TOC was used in the calculation as the TOC and DOC values for Nova Scotia source waters are very similar. SUVA can be determined through the following calculation:

$$SUVA = \frac{UV_{254}\ (cm^{-1})}{DOC\ (\frac{mg}{L})} * 100$$

Figure 4 Formula for determination of SUVA.

CHAPTER 4 BENCH-SCALE COAGULATION TREATMENT

4.1 Introduction

Five coagulants were tested in raw Pottle Lake water to establish optimal parameters for removal of NOM. These were alum, PAC-A, PAC-B, PAC-C, and PAC-D. Each coagulant was jar tested at a series of doses at one pH, and the optimal dose from this set of experimentation was chosen to be tested at a second pH. The optimal dose was that which effectively reduced UV_{254} at the point of diminishing returns, where an increase in coagulation dose would not significantly improve the quality of finished water.

4.2 Materials and Methods

4.2.1 Jar test procedure

Prior to bench-scale coagulation experiments, raw water pH was adjusted through standard laboratory procedure. 1 L of raw water was placed in a large beaker on a stir plate, and a magnetic stir stick added to the beaker. The stir plate was turned on low and a pH probe placed into the stirring water, away from the side of the beaker. The pH of the raw water was recorded once the measurement stabilized on the pH probe screen and recorded again after the appropriate dose of coagulant had been added. 0.1 N NaOH or 0.1 N H_2SO_4 was added in 10 – 100 μL increments from a pipette in order to increase or decrease the pH to the required value, respectively. The pH probe was permitted to stabilize after each addition of buffering chemical in order to produce an accurate measurement. The volume of chemical added to raw water was recorded for future use.

To simulate mixing of coagulants in a direct filtration WTP, a Phipps and Bird bench-scale jar test apparatus with 2 L jars and rotating paddles was used. The apparatus has variable speed control for the paddles, and thus mixing speed was able to be regulated. As a bench-scale representation of coagulation addition and rapid mix, samples were mixed in jars at 300 rpm for 60 s. Water samples were jar tested at room temperature with appropriate pH adjustment, and coagulant was added by being measured onto silicone septas placed onto the corner of each jar. Once appropriate pH adjustment had been added and paddles were rotating at 300 rpm, septas were simultaneously tipped into the jars and the 60 s rapid mix period began.

In order to filter treated samples for laboratory use after jar testing, a filter apparatus was placed above an Erlenmeyer filtration flask and attached to a vacuum pump. A 0.45 μm PES filter was primed in the apparatus by filtering 500 mL ultrapure MQ water. Jar tested water samples were filtered immediately following the 60 s rapid mix, and filtrate was collected in 250 mL plastic laboratory bottles to be refrigerated until further testing.

4.2.2 Alum dose determination

Alum doses were selected from literature and previous research on the basis of choosing a dose that was sufficiently high to remove NOM, determined using UV_{254} as a metric. Previous research had tested alum in Pottle Lake raw water at a standard range of doses of 5 mg/L, 10 mg/L, 30 mg/L, and 50 mg/L, and it was determined that at 10 mg/L, the point of diminishing returns was reached, and higher alum doses had no further effect on reduction of UV_{254}.

4.2.3 Alum dose optimization

Using this data, alum doses 5 mg/L and 10 mg/L were chosen; where 10 mg/L was the optimal dose and 5 mg/L was a comparative to determine if a lesser dose could adequately treat raw water. Both alum doses were jar tested at pH 5.5 and 5.8; pH 5.5 being the lowest pH at which alum can optimally coagulate, and pH 5.8 being slightly higher to imitate a pH that would still form pin flocs but would require less addition of buffering chemical. In this case, 0.1 N H_2SO_4 was used to adjust pH.

4.2.4 PACl dose determination

The four PACl coagulants used in this research varied in basicity, specific gravity (SG), and aluminum by % w/w. Using the following equation from Gebbie (2006), an estimated volume of aluminum in each coagulant was found in order to establish appropriate doses.

$$Aluminum\,\frac{mg}{L} = 10000 * \%\frac{w}{w}\,Al * SG$$

Figure 5 Equation determining aluminum concentration in mg/L using percent by weight aluminum and specific gravity (Gebbie, 2006).

In technical data sheets produced by the manufacturer, a range of both specific gravity and aluminum by percent weight was given. For the purpose of this equation, the average of the values given in each range was used. Basicity, also provided in a range by the manufacturer, is shown along with other chemical properties in Table 3.

Table 3 Basicity, specific gravity, aluminum by percent weight, and calculated aluminum concentration for PACl coagulants.

Sample	Basicity by percent weight: range	Specific gravity: range	Specific gravity: used	Aluminum by percent weight: range	Aluminum by percent weight: used	Aluminum concentration: calculated (mg/L)
PAC-B	65.0—75.0	1.20—1.28 at 20°C	1.24	5.20—5.80	5.50	68 200
PAC-D	82.0—83.7	1.32—1.35 at 25°C	1.33	12.10—12.70	12.40	164 900
PAC-A	48.0—58.0	1.18—1.26 at 20°C	1.22	5.10—5.70	5.40	65 880
PAC-C	70.0—80.0	1.28—1.32 at 25°C	1.30	10.22—11.02	10.62	138 060

Once the aluminum concentration in each PACl was calculated in mg/L, this concentration was used to determine the volume of coagulant added to raw water in order to achieve desired doses. The four coagulants were divided into two groups, each containing one PACl with a high Al % w/w and one with a low Al % w/w. The first group, PAC-B and PAC-D, were dosed at volumes comparable to alum; 5 mg/L, 15 mg/L, and 30 mg/L. The second group, PAC-A and PAC-C, were dosed at ultra low volumes. PAC-A was tested at 0.6 mg/L, 1.8 mg/L, and 3.6 mg/L, while PAC-C was dosed at 0.3 mg/L, 1 mg/L, and 2 mg/L. All preliminary jar tests were conducted at pH 5.5, slightly below the optimal range for PACl in order to determine if coagulation would still effectively occur at this pH.

Table 4 Grouping of PACl coagulants, their aluminum percent by weight, and doses.

Group	Coagulant	Al (% w/w)	Doses (mg/L)
1	PAC-B	5.50	5.0, 15.0, 30.0
	PAC-D	12.40	5.0, 15.0, 30.0
2	PAC-A	5.40	0.6, 1.8, 3.6
	PAC-C	10.62	0.3, 1.0, 2.0

4.2.5 PACl dose optimization

Following jar tests of all four PACl, the optimal dose was selected by using reduction of UV_{254} as a metric. The optimal doses were then jar tested at pH 6.5, within the ideal range for PACl, to determine how effective coagulation would be at a higher pH and with less addition of buffering chemical. For pH adjustment, 0.1 N H_2SO_4 was used to lower pH and 0.1 N NaOH was used to raise pH.

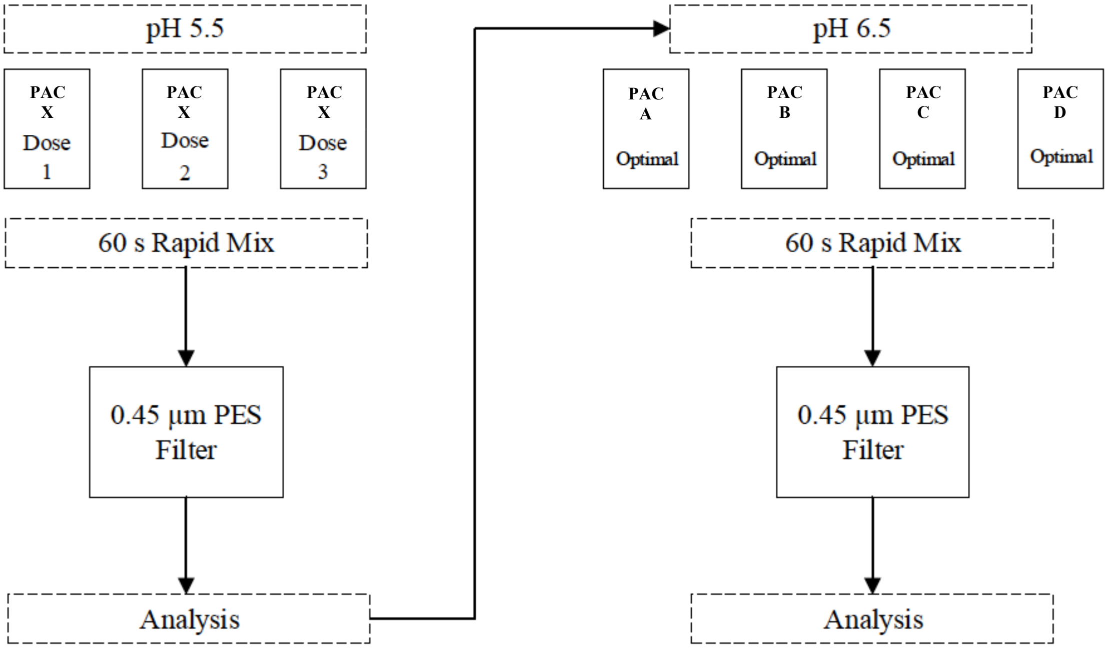

Figure 6 **Process of bench-scale jar test procedures for PACl, from testing each PACl at pH 5.5 to optimization jar tests at pH 6.5. Each test was completed in triplicate.**

4.2.5 Statistical analysis

4.2.5.1 Percent removal

Each of the four PACl coagulants were tested at three doses at pH 5.5. The optimal dose for each coagulant was determined by calculating percent removal of UV_{254}. Each PACl dose had been jar tested three times, and filtrate from each jar was tested in triplicate for UV_{254}. As such, a single average UV_{254} value was generated from each triplicate to calculate percent removal for each individual jar test. Standard deviation (SD) was calculated for triplicate jar tests at each of the three doses for every PACl.

Optimal alum doses were selected from research performed earlier in the year and were also based on reduction of UV_{254}. Percent removal can be found using the following formula in Figure 7:

$$Percent\ removal\ of\ X = \frac{Raw\ X - Treated\ X}{Raw\ X} * 100$$

Figure 7 Formula for determining percent removal of an analyte.

Percent removal were also used to determine effectiveness of each optimal dose for reducing colour, turbidity, and SUVA.

4.2.5.2 One-Way ANOVA

Statistical analysis was completed using Microsoft Excel and Minitab 19. One-way ANOVA was performed on percent removals by the optimal alum dose and optimal PACl dose in order to determine if there was a significant difference in NOM removal between these coagulants.

4.2.5.3 Paired t-test

Paired t-tests were used to establish where differences lay. Using PACl data, these tests were conducted between optimal doses at each pH, and then between pHs to determine which pH was overall better at reducing NOM.

Following PACl t-tests, optimal alum doses of 5.0 mg/L and 10.0 mg/L were assessed through paired t-tests to establish if the change in dose had a significant impact. Tests on the difference between pH 5.5 and pH 5.8 at these doses were also conducted.

Finally, the optimal alum dose and optimal pH was compared to the optimal PACl dose at the optimal pH to determine the most effective coagulant for reduction in NOM characteristics.

4.3 Results and Discussion

4.3.1 NOM Removal Efficacy by Group 1 PACl

4.3.1.1 PAC-B

PAC-B and PAC-D were placed into Group 1 for comparison based on their Al % w/w values; PAC-B contains an average of 5.5 % Al, while PAC-D contains an average of 12.4 % Al. These coagulants were selected to compare NOM removal at the doses of 5.0, 15.0, and 30.0 mg/L Al.

The optimal dose of PAC-B was determined by calculating percent removal of UV_{254} after jar testing at pH 5.5 in triplicate at doses of 5.0, 15.0, and 30.0 mg/L Al. It was determined that at the lowest dose, 5.0 mg/L, PAC-B achieved the highest percent removal of UV_{254} (81.11 ± 2.94 %) and was the optimal dose (Figure 8). There was no significant difference between reduction of UV_{254} by PAC-B-15.0 and PAC-B-30.0, indicating that increasing the dose of PAC-B did not result in an improved reduction of UV_{254}.

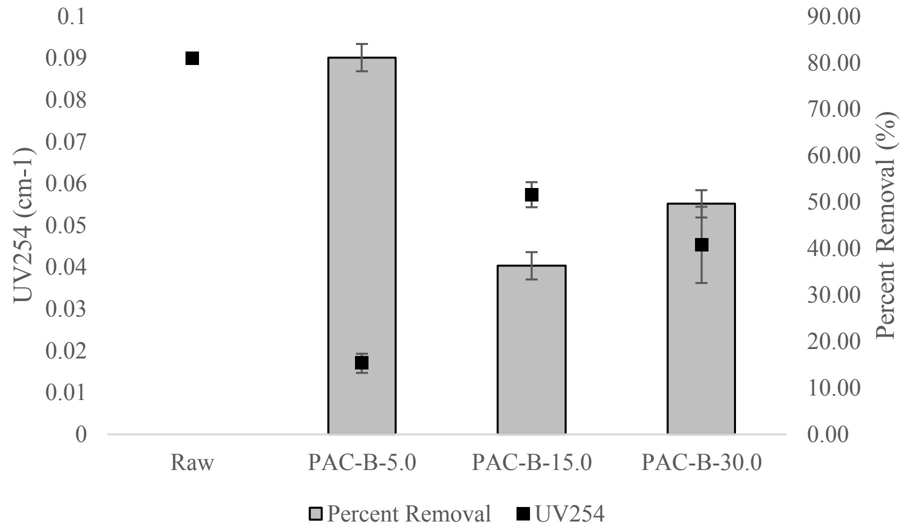

Figure 8 **Percent removal of UV_{254} by PAC-B doses at pH 5.5.**

After determining that 5.0 mg/L was the optimal dose of PAC-B, triplicate UV_{254} values were tested from filtrate of PAC-B-5.0 at pH 6.5 to establish at which pH this PACl dose performed most effectively. Mean UV_{254} values for PAC-B-5.0 at pH 5.5 and pH 6.5 were 0.017 ± 0.003 cm_{-1} and 0.016 ± 0.005 cm_{-1}, respectively (Figure 9).

A paired t-test was performed to determine if there was a significant difference between performance of PAC-B-5.0 at pH 5.5 and pH 6.5. At the 0.05 level of significance, there was an insignificant difference in UV_{254} values between the two pH of 0.001 (95% CI, -0.015 to 0.016) cm_{-1}, $t(2) = 0.19$, $p = 0.868$. This indicates that there is no advantage to reducing pH beyond 6.5 for coagulation with the optimal dose of PAC-B, as performance at both pH 5.5 and 6.5 is equally effective for this source water.

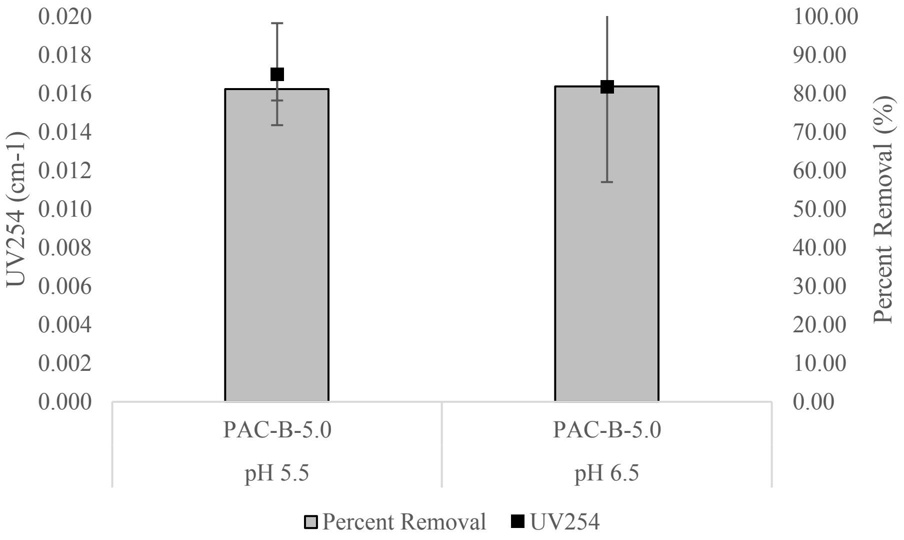

Figure 9 **Average percent removal and UV_{254} values of PAC-B-5.0 at pH 5.5 and pH 6.5.**

Triplicate colour values for water treated with PAC-B-5.0 at pH 5.5 and pH 6.5 were then compared. Mean colour values for PAC-B-5.0 at pH 5.5 and pH 6.5 were 10.1 ± 2.2 units PtCo and 0.0 (SD < 0.001) units PtCo, respectively (Figure 10).

A paired t-test was conducted, and it was determined that there was a significant difference between colour values at pH 5.5 and pH 6.5, with PAC-B-5.0 at pH 6.5 showing a difference of 10.1 (95% CI, 4.75 to 15.45) units PtCo, $t(2) = 8.13$, $p = 0.015$ from pH 5.5.

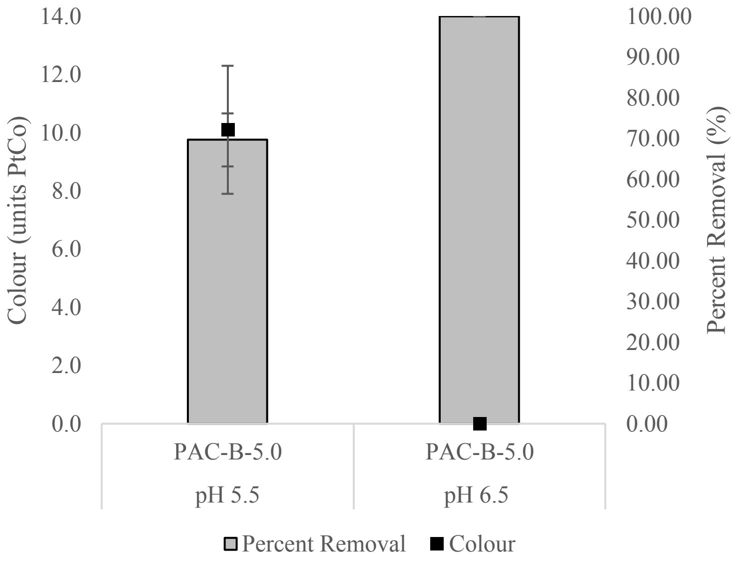

Figure 10 **Average percent removal and colour values by PAC-B-5.0 at pH 5.5 and pH 6.5.**

PAC-B reduced colour by 100 % at pH 6.5, indicating that the higher pH significantly improved performance in terms of reducing colour. As outlined in the Canadian Drinking Water Guidelines, colour has an aesthetic objective (AO) of ≤ 15 true colour units (TCU), which are equivalent to units PtCo (Health Canada, 2019b). PAC-B at both pH levels met and exceeded this guideline, reducing colour to below the AO. However, it is clear that PAC-B is more effective at the higher pH of 6.5 for reduction of colour.

Turbidity values were also compared in triplicate between PAC-B pH 5.5 and pH 6.5 filtrate. Mean turbidity for PAC-B-5.0 at pH 5.5 and pH 6.5 were 0.238 ± 0.005 NTU and 0.131 ± 0.012 NTU, respectively (Figure 11).

A paired t-test was used to determine that there was a significant difference between turbidity values at the two pH values, with pH 6.5 showing an improvement of 0.107 (95% CI, 0.087 to 0.127) NTU, $t(2) = 23.35$, $p = 0.002$ over pH 5.5.

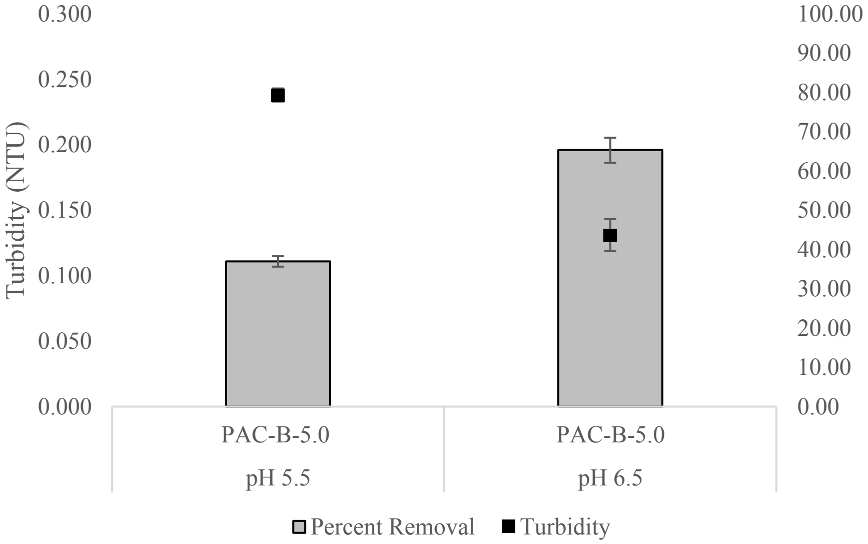

Figure 11 Average percent removal and turbidity values by PAC-B-5.0 at pH 5.5 and pH 6.5.

PAC-B-5.0 performed significantly better at pH 6.5 for reduction of colour and turbidity, and removed UV_{254} equally well at pH 6.5 as at pH 5.5, demonstrating that reducing the pH beyond 6.5 for coagulation with PAC-B is unnecessary. This provides incentive for WTP operators, as it is possible raw water may not require any buffering prior to addition of coagulant, depending on the characteristics of the source water.

SUVA was also calculated for PAC-B at pH 5.5 and pH 6.5 to analyse NOM remaining in treated water (Table 5). PAC-B-5.0 at both pH reduced SUVA below 2.0, at which threshold NOM in water is generally hydrophilic, and would not be able to be reduced further by coagulation. As PAC-B-5.0 at both pH successfully reduced SUVA beyond 2.0, they can be considered equally successful in reduction of this analyte.

Table 5 **SUVA values for raw water and PAC-B-5.0 at pH 5.5 and pH 6.5.**

Dose	SUVA (L/mg•m)
Raw water	3.7
pH 5.5; PAC-B-5.0	0.7
pH 6.5; PAC-B-5.0	1.0

From paired t-tests and comparing percent removal for these water quality tests, it was determined that at pH 6.5, PAC-B-5.0 performed most effectively in reduction of NOM characteristics. For colour and turbidity, values of pH 6.5 were significantly lower than those of pH 5.5, and for UV_{254} and SUVA, pH 6.5 performed equally well as pH 5.5. These results demonstrate that it is not necessary to reduce pH of coagulated water beyond 6.5 when coagulating with PAC-B, as there is no significant advantage to coagulating at the lower pH for this source water.

4.3.1.2 PAC-D

Percent removal of UV_{254} was used as a metric to determine the optimal dose of PAC-D after jar testing in triplicate at pH 5.5. It was determined from calculating percent removal that PAC-D-5.0 was the optimally performing dose at pH 5.5, with an average percent removal of 70.74 ± 2.94 % (Figure 12). Neither dose of 15.0 nor 30.0 mg/L resulted in percent removal of UV_{254} above 25 %.

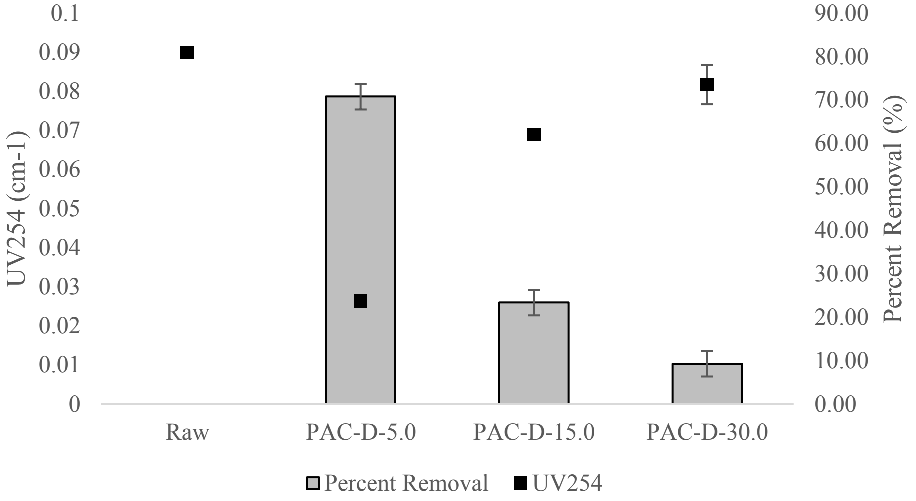

Figure 12 Percent removal of UV254 by PAC-D at pH 5.5.

UV_{254} values were also tested in triplicate from PAC-D-5.0 at pH 6.5 in order to compare performance of this dose at each pH (Figure 13). Mean UV_{254} values at pH 5.5 and pH 6.5 were 0.026 ± 0.001 cm_{-1} and 0.028 ± 0.008 cm_{-1}, respectively (Figure 13).

A paired t-test determined that there was an insignificant difference of -0.001 (95% CI, -0.019 to 0.016) cm_{-1}, $t(2) = -0.33$, $p = 0.776$ between the two pH. This result indicates that there is no significant improvement in reduction of UV_{254} beyond pH 6.5, and further pH reduction is redundant.

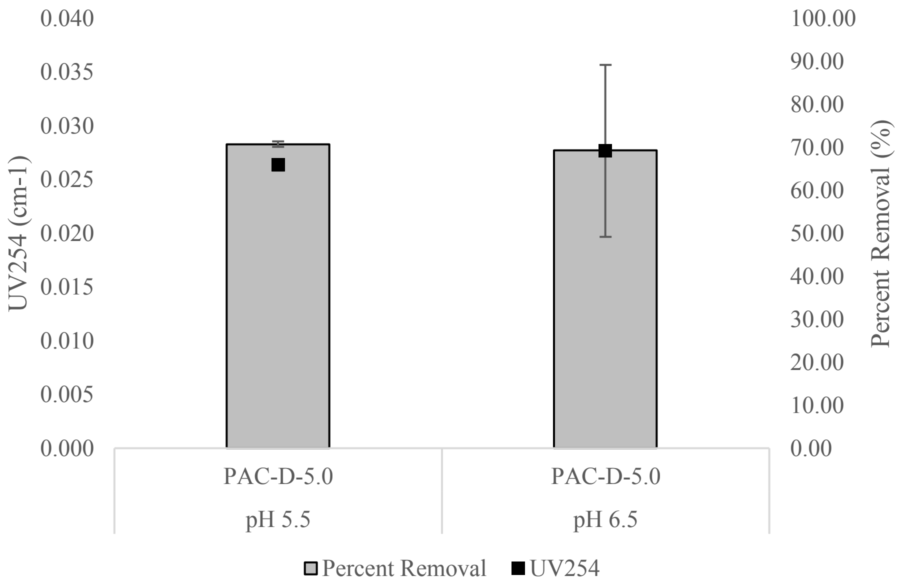

Figure 13 Average percent removal and UV254 value of PAC-D-5.0 at pH 5.5 and pH 6.5.

Colour values were analysed in triplicate for water treated with PAC-D-5.0 at pH 5.5 and pH 6.5. Mean colour values for PAC-D-5.0 at pH 5.5 and pH 6.5 were 30.0 (SD < 0.001) units PtCo and 2.9 ± 2.0 units PtCo, respectively. Mean colour values were compared between the two pH values using a paired t-test. It was determined that there was a significant difference in colour between pH 5.5 and pH 6.5, with a mean difference of 27.10 (95% CI, 22.11 to 32.09) units PtCo, $t(2) = 23.38$, $p = 0.002$. PAC-D-5.0 performed significantly better at pH 6.5 for reduction of colour and indicates that effective reduction of colour takes place at higher pH. Only at pH 6.5 did PAC-D-5.0 meet the federal AO of < 15 TCU, and colour values at pH 5.5 were twice as high as this guideline.

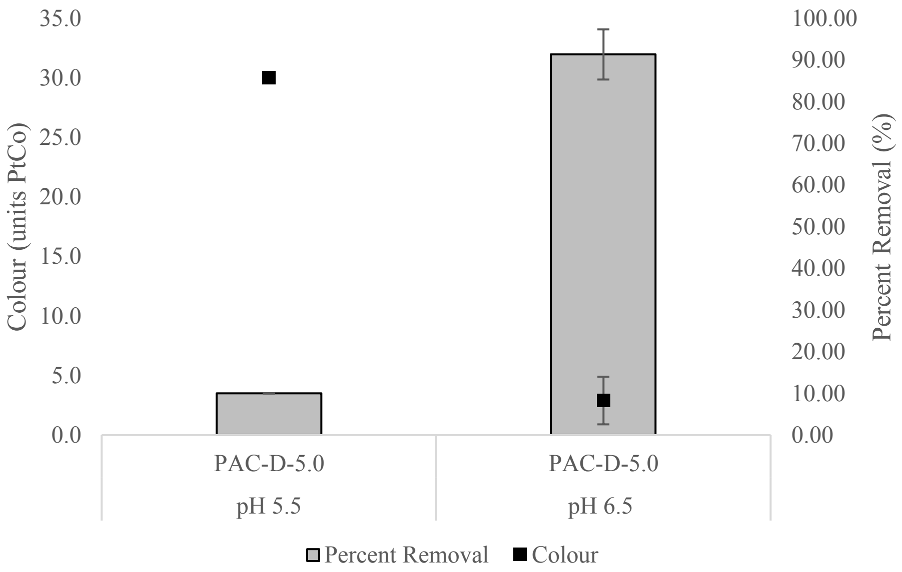

Figure 14 **Average percent removal and colour values of PAC-D-5.0 at pH 5.5 and pH 6.5.**

Turbidity values were analysed between pH 5.5 and 6.5. Mean turbidity for PAC-D-5.0 at pH 5.5 and pH 6.5 were 0.327 ± 0.044 NTU and 0.189 ± 0.086 NTU, respectively (Figure 15).

From a paired t-test, it was determined that there was no significant difference in turbidity between PAC-D-5.0 values at pH 5.5 and pH 6.5, $t(2) = 2.22$, $p = 0.156$. This result indicates that PAC-D-5.0 performed most effectively at pH 6.5 for reduction of turbidity.

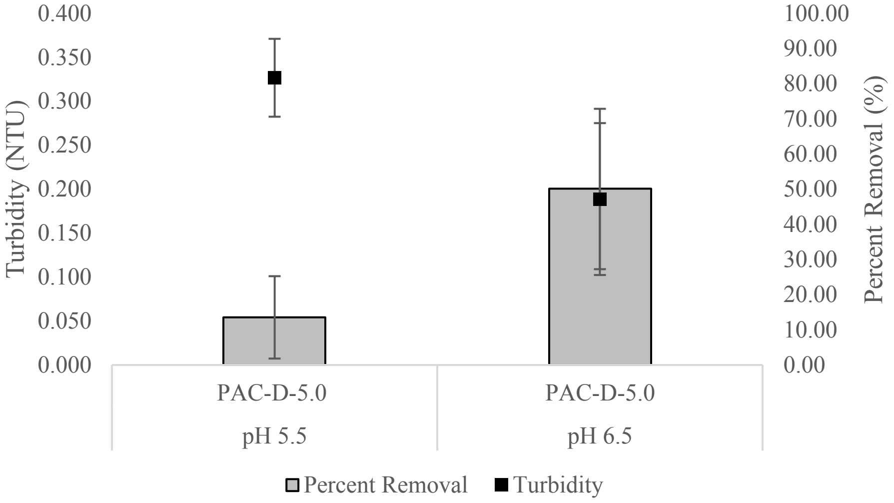

Figure 15 **Average percent removal and turbidity values of PAC-D-5.0 at pH 5.5 and pH 6.5.**

Health Canada requires a maximum turbidity value of ≤ 0.3 NTU for direct and conventional filtration WTPs (Health Canada, 2019b), while Nova Scotia recommends a limit of ≤ 0.2 NTU (Nova Scotia Environment, 2012). At pH 5.5, PAC-D-5.0 is above both federal and provincial limits.

At pH 6.5, PAC-D-5.0 narrowly meets the provincial limit and successfully meets the federal limit for turbidity value. This result indicates that PAC-D should be dosed at pH 6.5 in order to comply with Canadian drinking water standards.

There was no significant difference between performance of PAC-D-5.0 at pH 5.5 or pH 6.5 for removal of UV_{254}, colour, or turbidity, indicating that for this source water with high pH, coagulating at pH 6.5 is ideal. Reduction of pH beyond 6.5 is unnecessary for improvement of water quality for PAC-D-5.0.

PAC-D-5.0 was also analysed for SUVA values after treatment at pH 5.5 and pH 6.5 to analyse NOM remaining in treated water (Table 6). At both pH, PAC-D-5.0 was able to reduce SUVA to below 2.0, indicating that remaining NOM is hydrophilic and generally cannot be removed further by coagulation treatment.

Table 6 SUVA values for PAC-D-5.0 at pH 5.5 and 6.5.

Dose	SUVA (L/mg•m)
Raw water	3.7
pH 5.5; PAC-D-5.0	1.6
pH 6.5; PAC-D-5.0	1.7

Through analysis of percent removal and paired t-test results, it was established that PAC-D-5.0 performed most effectively at pH 6.5 in all NOM characteristics, pH 6.5 showed either significantly improved results or equal improvement as pH 5.5. This corresponds with literature stating that PACl performs extremely well at higher pH (Ratnayaka et al, 2009; Brandt, 2017) and reiterates that chemical adjustment of pH may not be required prior to coagulation with PACl.

4.3.2 NOM Removal Efficacy by Group 2 PACl

4.3.2.1 PAC-A

PAC-A and PAC-C were grouped together because of their Al % w/w values; PAC-A contains low Al at 5.4 %, while PAC-C contains high aluminum of 10.62 %. They were coagulated at low doses of Al; 0.6, 1.8, and 3.6 mg/L and 0.3, 1.0, and 2.0 mg/L, respectively.

The optimal dose of PAC-A was determined through percent removal of UV$_{254}$, calculated from triplicate values after treatment of 0.6 mg/L, 1.6 mg/L, and 3.6 mg/L at pH 5.5. It was determined that PAC-A-1.8 and PAC-A-3.6 had similarly high percent removal of UV$_{254}$, 81.11 ± 2.94 % and 81.85 ± 3.57 % respectively (Figure 16). However, PAC-A-1.8 was selected as the optimal dose, as the improvement of less than 1 % removal of UV$_{254}$ by PAC-A-3.6 was not enough to warrant a doubling of the dose.

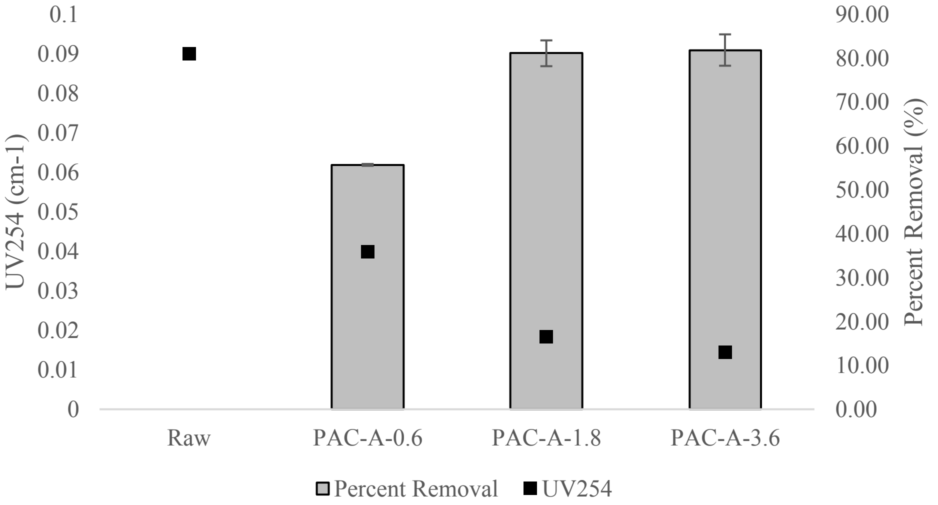

Figure 16 **Average percent removal and UV$_{254}$ values from PAC-A doses at pH 5.5.**

UV$_{254}$ values from PAC-A-1.8 at pH 6.5 were then analysed with pH 5.5 values in order to determine at which pH this PACl was more effective at reducing UV$_{254}$. Mean UV$_{254}$ values for PAC-A-1.8 at pH 5.5 and pH 6.5 were 0.018 ± 0.001 cm$_{-1}$ for both pH conditions (Figure 17).

A paired t-test confirmed there was no significant difference between these two conditions, *t*(2) = -0.00, *p* = 1.000. These results indicate that performance of PAC-A-1.8 does not improve beyond pH 6.5, and further reduction of pH is not necessary to achieve effective reduction of UV_{254} in this source water.

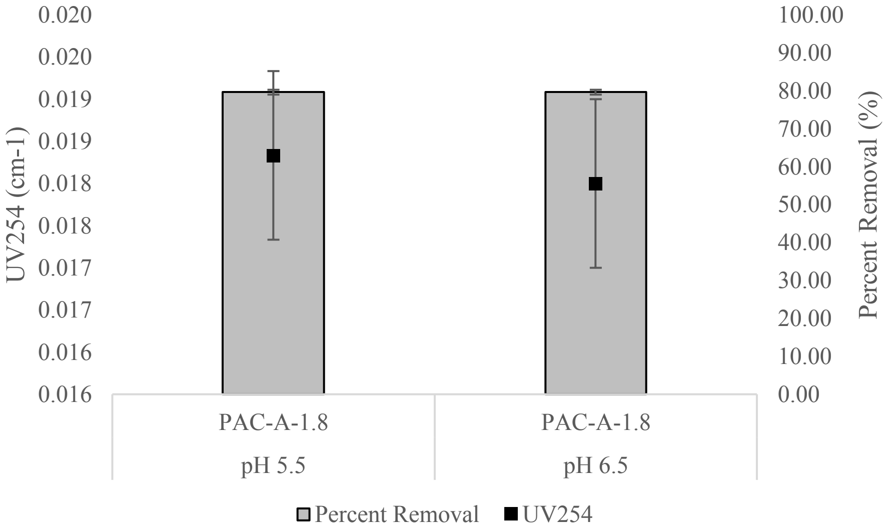

Figure 17 Percent removal and UV_{254} values of PAC-A-1.8 at pH 5.5 and pH 6.5.

Mean colour values for PAC-A-1.8 were taken from triplicate jar tests at pH 5.5 and pH 6.5. Mean colour values for PAC-A-1.8 at pH 5.5 and pH 6.5 were 0.1 ± 0.2 units PtCo and 1.7 ± 2.9 units PtCo, respectively (Figure 18).

A paired t-test on these values indicated that there was no significant difference between colour reduction at pH 5.5 and pH 6.5, *t*(2) = -0.91, *p* = 0.458. PAC-A-1.8 at both pH reduced colour values well below the federal AO of ≤ 15 TCU. Due to this result, it was established that performance of PAC-A-1.8 is comparable at both pH conditions, and there is no advantage to reducing pH beyond 6.5 for reduction of colour.

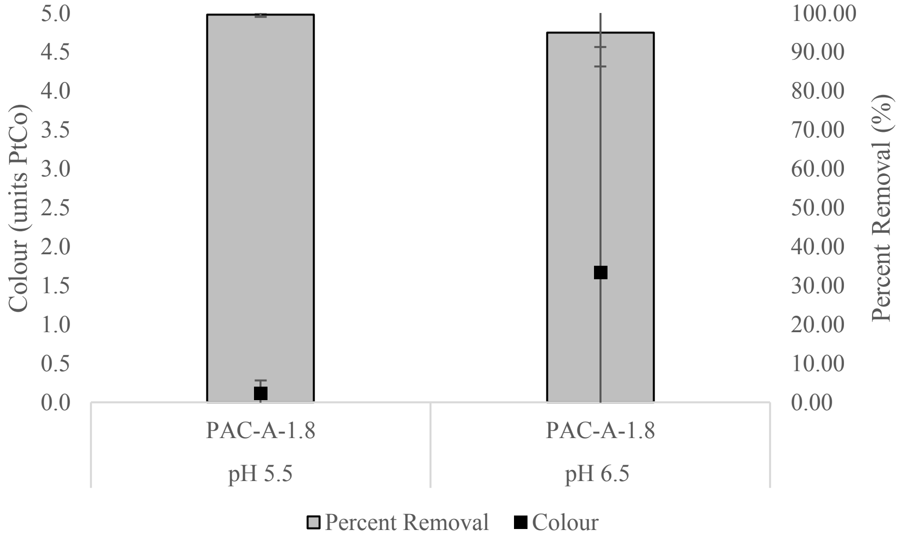

Figure 18 Percent removal and colour values of PAC-A-1.8 at pH 5.5 and pH 6.5.

PAC-A-1.8 turbidity values were then compared in triplicate between pH 5.5 and 6.5. Mean turbidity values for PAC-A-1.8 at pH 5.5 and pH 6.5 were 0.055 ± 0.001 NTU and 0.055 ± 0.021 NTU, respectively (Figure 19).

Using a paired t-test, it was concluded that there was no significant difference in turbidity values between the two pH, $t(2) = 0.03$, $p = 0.981$. PAC-A-1.8 performed comparably well at removing turbidity at both pH 5.5 and pH 6.5, but since there was no significant improvement in reduction of turbidity at the lower pH, it was determined that the optimal pH was 6.5 for this source water. Turbidity values of PAC-A-1.8 met both the federal limit of 0.3 NTU and the provincial limit of 0.2 NTU at both pH.

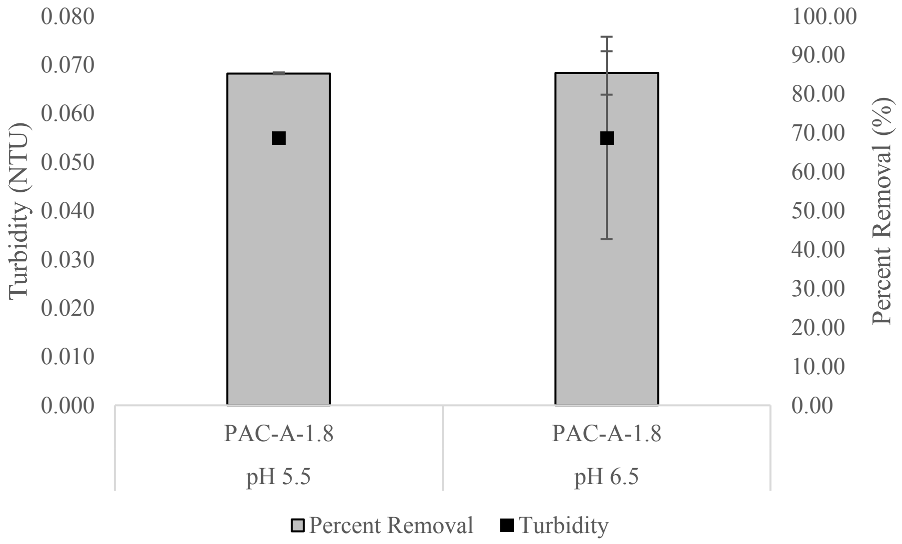

Figure 19 Percent removal and turbidity values of PAC-A-1.8 at pH 5.5 and pH 6.5.

There was no significant difference in reduction of UV_{254}, colour, or turbidity by PAC-A-1.8 between pH 5.5 and 6.5, indicating that reducing pH beyond 6.5 for this source water was unnecessary for effective removal of NOM under the conditions studied.

SUVA values were calculated for PAC-A-1.8 at pH 5.5 and 6.5 to analyse NOM remaining in water after coagulation treatment (Table 7). SUVA values at both pH 5.5 and 6.5 are below the hydrophilic average of 2.0, so PAC-A-1.8 reduced NOM as far as possible at both pH. However, since there was no significant reduction in NOM characteristics beyond pH 6.5, it is determined to be the optimal pH. All characteristics tested for PAC-A-1.8 were equally reduced at pH 5.5 and 6.5, indicating no need to reduce pH to 5.5 in order to effectively remove NOM.

Table 7 SUVA values of PAC-A-1.8 at pH 5.5 and pH 6.5.

Dose	SUVA (L/mg•m)
Raw water	3.7
pH 5.5; PAC-A-1.8	1.3
pH 6.5; PAC-A-1.8	1.0

4.3.2.2 PAC-C

In order to establish the optimal dose of PAC-C, percent removals of UV_{254} of PAC-C at 0.3 mg/L, 1.0 mg/L, and 2.0 mg/L at pH 5.5 were calculated (Figure 20). From percent removal calculations, it was determined that PAC-C-1.0 and PAC-C-2.0 had similar percent removals of UV_{254}, 57.00 ± 2.94 % and 62.59 ± 2.94 % respectively. However, the improvement of approximately 5% further reduction from 2.0 mg/L to 1.0 mg/L was not enough to justify a dose of twice as much coagulant. Therefore, PAC-C-1.0 was determined to be the optimal dose.

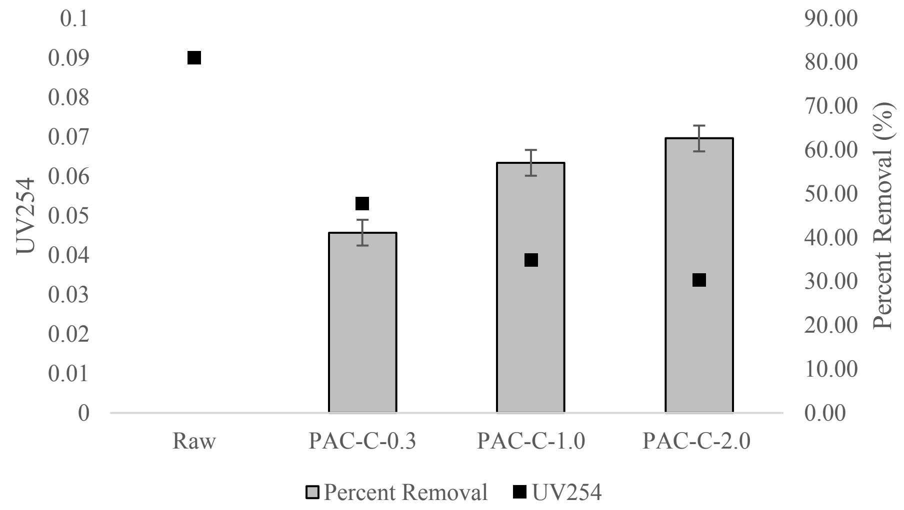

Figure 20 Average percent removal and UV_{254} values of PAC-C at pH 5.5.

UV_{254} values of PAC-C-1.0 at pH 6.5 were compared to the values at pH 5.5 in order to determine at which pH this PACl performed best. Mean UV_{254} values for PAC-C-1.0 at pH 5.5 and pH 6.5 were 0.039 ± 0.001 cm^{-1} and 0.037 ± 0.003 cm^{-1}, respectively (Figure 21). A paired t-test determined that there was no significant difference between UV_{254} values of PAC-C-1.0 at pH 5.5 and pH 6.5, $t(2) = 1.15$, $p = 0.370$. Therefore, there proved to be no advantage to coagulating PAC-C at a pH below 6.5 in order to reduce UV_{254}, and the optimal pH was confirmed to be 6.5 for this source water.

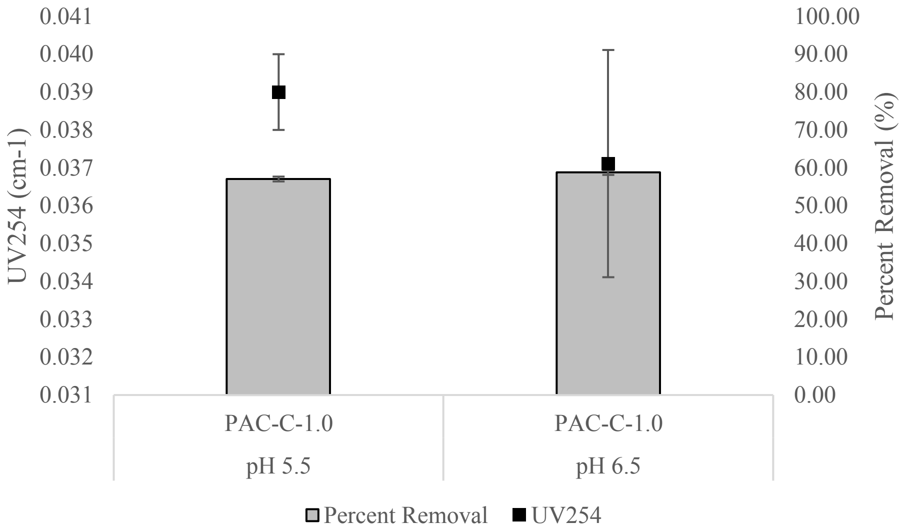

Figure 21 **Percent removal and UV_{254} values of PAC-C-1.0 at pH 5.5 and pH 6.5.**

Colour values for PAC-C-1.0 at pH 5.5 and pH 6.5 were then compared. Mean colour values for PAC-C-1.0 at pH 5.5 and pH 6.5 were 3.3 ± 1.5 units PtCo and 1.2 ± 0.4 units PtCo, respectively (Figure 22).

A paired t-test indicated that no significant difference existed between values of both pH, *t*(2) = 3.15, p = 0.088. The insignificant difference result demonstrates that PAC-C reduces colour effectively at both pH, but that there is no reason to further reduce pH beyond 6.5.

Both pH meet the AO of colour, but using the t-test result, pH 6.5 was determined to be the optimal pH for coagulation with PAC-C.

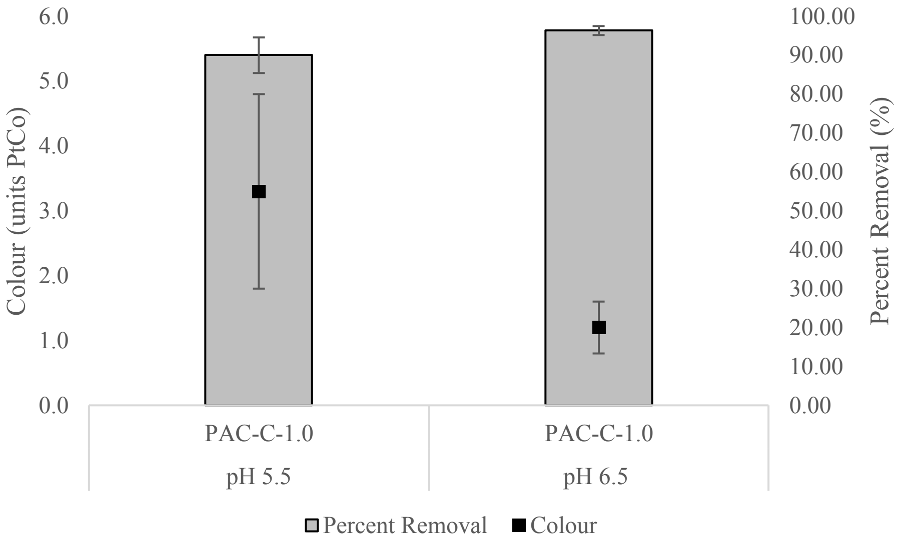

Figure 22 Percent removal and colour values of PAC-C-1.0 at pH 5.5 and pH 6.5.

Turbidity values from jar tests of PAC-C-1.0 at pH 5.5 and pH 6.5 were analysed using a paired t-test. The mean turbidity values of PAC-C-1.0 at pH 5.5 and pH 6.5 were 0.254 ± 0.046 NTU and 0.064 ± 0.014 NTU, respectively (Figure 23).

A paired t-test was used to determine that at pH 6.5, PAC-C-1.0 was significantly more effective at reducing turbidity than at pH 5.5, demonstrating a statistically significant difference of 0.189 (95% CI, 0.109 to 0.269) NTU, $t(2) = 10.17$, $p = 0.010$.

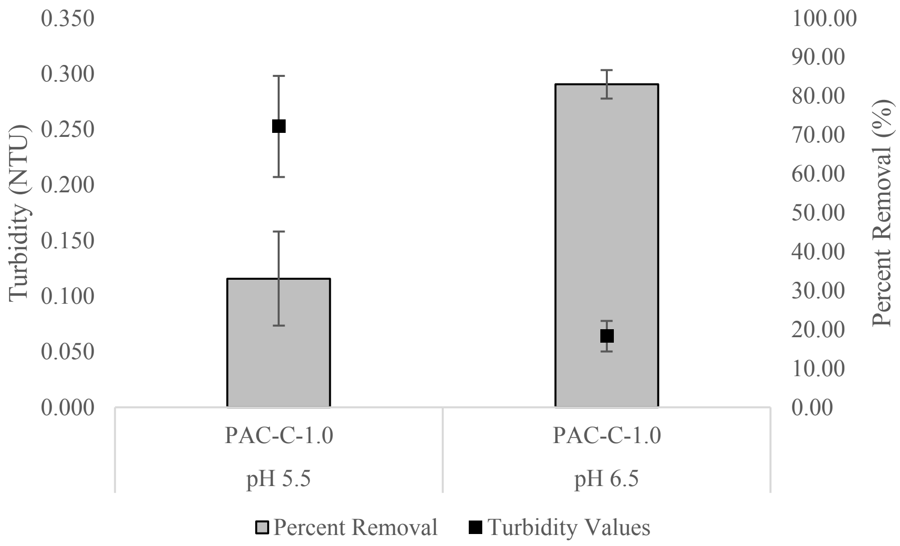

Figure 23 **Percent removal and turbidity values of PAC-C-1.0 at pH 5.5 and pH 6.5.**

This significant result indicates that turbidity was reduced significantly more at pH 6.5 than at pH 5.5. Following federal and provincial guidelines of 0.3 NTU and 0.2 NTU, respectively, PAC-C-1.0 met both limits at pH 6.5 but met only the federal limit at pH 5.5. It was established that PAC-C-1.0 performed best in terms of turbidity reduction at pH 6.5, and thus the optimal pH was confirmed to be 6.5.

PAC-C-1.0 demonstrated no significant difference in reduction of UV_{254} or colour between pH 5.5 and 6.5, and exhibited significantly better colour values at pH 6.5. For this high pH source water, it was determined that pH 6.5 was the overall most effective pH for PAC-C-1.0. This confirms that PACl coagulants operate well at a wide range of pH, and do not necessarily require buffering of raw water prior to coagulation, depending on the pH of raw source water.

SUVA values of PAC-C-1.0 treatment at both pH 5.5 and pH 6.5 were then analysed for their NOM composition (Table 8). At both pH 5.5 and pH 6.5, PAC-C-1.0

reduced SUVA to approximately 2.0. As a SUVA value of between 2.0 and 3.0 indicates a mix of hydrophilic and hydrophobic NOM material, there is a possibility that PAC-C was not able to remove NOM sufficiently at the optimal dose.

Table 8 SUVA values for PAC-C-1.0 at pH 5.5 and pH 6.5.

Dose	SUVA (L/mg•m)
Raw water	3.7
pH 5.5; PAC-C-1.0	2.1
pH 6.5; PAC-C-1.0	2.4

4.3.3 Optimal PACl Conditions

4.3.3.1 Optimal pH

Since each optimal PACl dose was either significantly improved at pH 6.5 or not statistically different between pH 5.5 and 6.5 for all NOM characteristics, it was established that the optimal pH for coagulation with PACl in this source water was pH 6.5. This is a beneficial finding for PLWTP, as a reduction in costs associated with chemical buffering could aid in the decision to use PACl, despite its higher initial cost. Furthermore, for colour and turbidity, all PACl met or exceeded both federal and provincial drinking water standards at pH 6.5, while the same did not occur at pH 5.5. The determination of this optimal pH concludes that PACl operate best in practice, not only in theory, at a higher pH. WTPs with high pH source waters such as Pottle Lake may find it beneficial to select a PACl from available aluminum-based coagulants, due to the fact that they may not need to buffer the raw water as much, if at all, prior to adding coagulant as they would with low-basicity coagulation options.

4.3.3.2 Optimal PACl

To establish the optimal PACl coagulant for NOM removal, data from paired t-tests were analysed along with percent removal of each UV_{254}, turbidity, and colour at pH 6.5. These percent removals were then averaged to provide an overall average NOM removal for each optimal PACl dose (Figure 24).

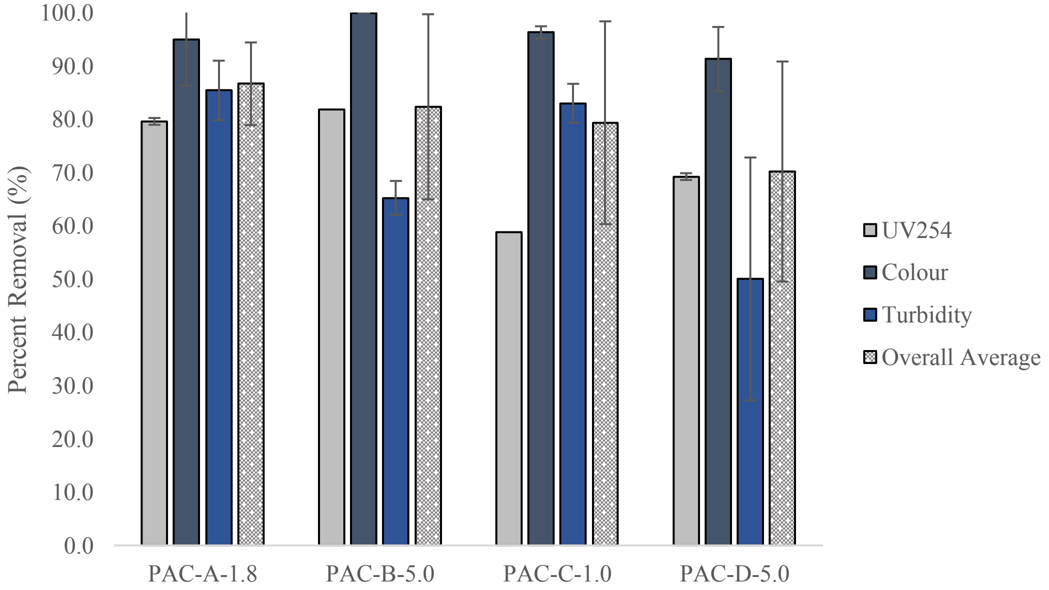

Figure 24 **Percent removal of each NOM characteristic, including overall average percent removal, for each PACl at optimal pH 6.5.**

A one-way ANOVA was used to determine that there were significant differences between each PACl for reduction of UV_{254}, $F(3, 8) = 11.76$, $p = 0.003$. Paired t-tests demonstrated that PAC-A (0.018 ± 0.002 cm^{-1}) and PAC-C (0.037 ± 0.003 cm^{-1}) showed a significant decrease of 0.019 (95% CI, -0.029 to -0.009) cm^{-1}, *t*(2) = -8, *p* = 0.015. PAC-B (0.016 ± 0.005 cm^{-1}) and PAC-C also showed a significant difference of -0.021 (95% CI, -0.038 to -0.004) cm^{-1}, *t*(2) = -5.26, *p* = 0.034. There were no statistically significant differences between any of the other coagulants, generating a ranking of PAC-B, PAC-A, PAC-D, and PAC-C from lowest value of UV_{254} to highest.

Using one-way ANOVA, it was determined that there was no significant difference between the performance of each optimal PACl dose for reduction of colour, *F*(3, 8) = 1.37, *p* = 0.319. This result indicates that each optimal PACl dose was comparably effective at removing colour from treated water.

Results of turbidity values from optimal PACl doses were analysed using one-way ANOVA and paired t-tests, and it was established that there was a statistically significant difference between PACl coagulants, *F*(3, 8) = 5.72, *p* = 0.022. PAC-A (0.055 ± 0.021 NTU) was significantly more effective than PAC-B (0.131 ± 0.012 NTU), with a mean difference of -0.076 (95% CI, -0.122 to -0.030) NTU, *t*(2) = -7.11, *p* = 0.019. PAC-C (0.064 ± 0.014 NTU) was significantly different from PAC-B, showing a mean difference of 0.067 (95% CI, 0.047 to 0.087) NTU, *t*(2) = 14.18, *p* = 0.005. There were no further statistically significant differences between PACl data, so PAC-A and PAC-C demonstrated statistically comparably low values of turbidity, followed by PAC-B and PAC-D.

One-way ANOVA indicated that there was no significant difference between the overall NOM removal performance of any PACl, *F*(3, 8) = 0.51, *p* = 0.688.

Though there were individual PACl that performed better than others in some NOM characteristic testing, the final ANOVA determines that each of the optimal doses of PACl are comparably effective at removing NOM from this source water when used as coagulation pre-treatment.

SUVA values were also considered in order to assess efficacy of PACl. PAC-A and PAC-B were able to reduce SUVA further than PAC-D, and PAC-C was the only PACl that was unable to remove all hydrophobic NOM material from water through coagulation.

Table 9 SUVA values of optimal PACl doses at pH 6.5.

Optimal Dose at pH 6.5	SUVA (L/mg•m)
PAC-A-1.8	1.0
PAC-B-5.0	1.0
PAC-C-1.0	2.4
PAC-D-5.0	1.7

From these results, WTP operators are able to select the PACl with chemical properties most beneficial for each plant, knowing that effective reduction of NOM will occur with each one.

PAC-A has a low Al % w/w of 5.4 % and mid-range basicity of 53 %, and was able to successfully reduce NOM in water at a very low dose of 1.8 mg/L Al. PAC-A-1.8 had excellent UV_{254} and colour removal at pH 6.5 (79.63 ± 0.64 % and 95.00 ± 8.70 %, respectively), and reduced SUVA to 1.0 L/mg•m through coagulation at pH 6.5.

PAC-B also has low Al % w/w of 5.5 % but mid to high basicity of 70 %, and as coagulation pre-treatment of 5.0 mg/L was able to effectively remove NOM at pH 6.5, leading to particularly low SUVA values of 1.0 L/mg•m . PAC-B was extremely effective in reduction of colour and UV_{254}, demonstrating percent removals of 100.00 (SD < 0.001) % and 81.85 ± 0.64 %, respectively.

PAC-C contains high Al % w/w of 10.62 % and high basicity of 75 %, but did not reduce UV_{254} as effectively as PAC-A or PAC-B at its optimal dose of 1.0 mg/L at pH 6.5. Furthermore, PAC-C-1.0 did not remove all humic NOM from water at pH 6.5, as indicated by a final SUVA value of 2.4 L/mg•m . However, PAC-C had excellent colour reduction of 96.33 ± 1.15 %.

PAC-D has very high Al % w/w of 12.4 % and the highest basicity of 82.85 %, and is classified as ACH. PAC-D-5.0 had the lowest overall percent removal of NOM characteristics at pH 6.5, demonstrating an overall average removal of 70.21 ± 20.66 %, and a higher SUVA value than PAC-A and PAC-B at 6.5, with a final value of 1.7 L/mg•m . At the same dose of 5.0 mg/L Al as PAC-B, it performed slightly less effectively, but not enough to create a statistically significant difference.

4.3.4 Alum

Percent removal of UV_{254} by alum-5.0 and alum-10.0 at pH 5.5 and pH 5.8 was used to determine at which pH these optimal doses of alum were most effective at reducing UV_{254}. Mean values of UV_{254} by alum-5.0 at pH 5.5 and pH 5.8 were 0.037 ± 0.001cm^{-1}

and 0.034 ± 0.001 cm_{-1}, respectively (Figure 25). Mean values of UV_{254} by alum-10.0 at pH 5.5 and pH 5.8 were 0.028 ± 0.004 cm_{-1} and 0.022 ± 0.001 cm_{-1}, respectively.

Using paired t-tests, alum doses at each pH were compared to establish at which pH the alum doses more effectively reduced UV_{254}. For alum-5.0, it was determined that dosing at pH 5.8 was more effective, with a significant mean difference of -0.003 (95% CI, 0.001 to 0.004) cm_{-1}, $t(2) = 8.00$, $p = 0.015$.

Alum-10.0 demonstrated no significant change between pH 5.5 and pH 5.8, with an insignificant difference of 0.006 (95% CI, -0.004 to 0.017) cm_{-1}, $t(2) = 2.63$, $p = 0.119$.

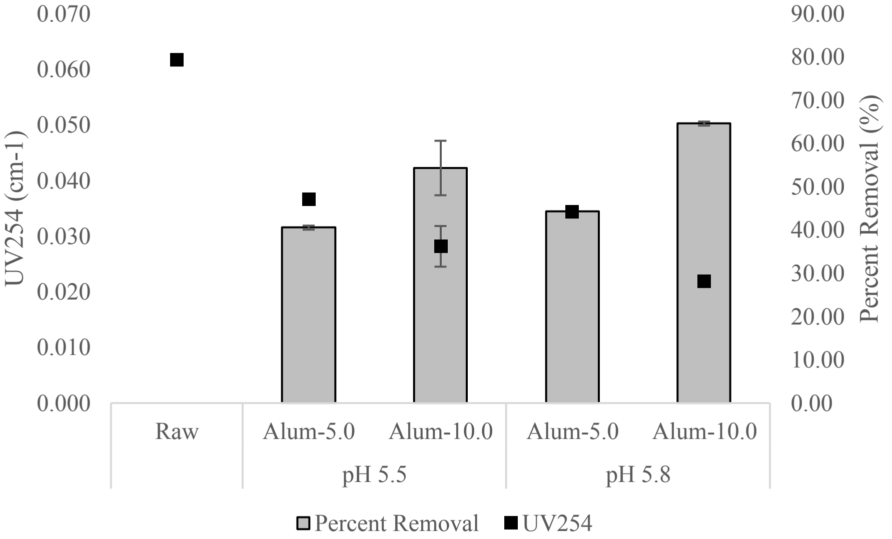

Figure 25 **Percent removal and UV254 values from alum-5.0 and alum-10.0 at pH 5.5 and pH 5.8.**

This data indicates that pH 5.8 is slightly more effective for alum than pH 5.5 for reduction of UV_{254}; since alum-5.0 was more effective at the higher pH of 5.8, and there was no significant advantage to coagulating alum-10.0 at the lower pH of 5.5.

Colour values both pH 5.5 and 5.8 by alum-5.0 and alum-10.0 were then analysed. Mean colour values of alum-5.0 at pH 5.5 and pH 5.8 were 4.3 ± 0.6 units PtCo and 2.3 ± 0.6 units PtCo, respectively (Figure 26). Mean colour values of alum-10.0 at pH 5.5 and pH 5.8 were 5.2 ± 0.6 units PtCo and 2.2 ± 0.3 units PtCo, respectively.

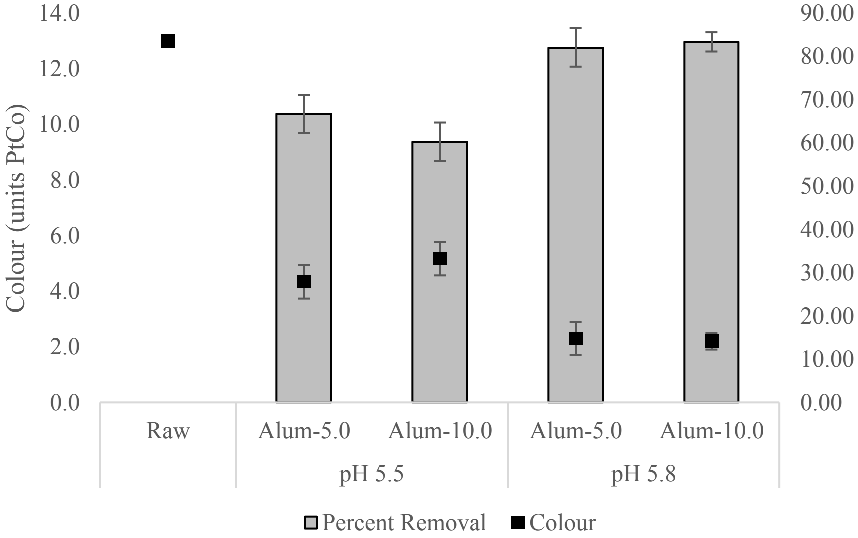

Figure 26 **Percent removal and average colour values by alum-5.0 and alum-10.0 at pH 5.5 and pH 5.8.**

Paired t-tests determined that for alum-5.0, there was no significant change between colour values at pH 5.5 and pH 5.8, showing an insignificant difference of 2.0 (95% CI, -0.5 to 4.5) units PtCo, $t(2) = 3.46$, $p = 0.074$.

However, paired t-tests determined that alum-10.0 performed significantly better at pH 5.8 (2.2 ± 0.3 units PtCo) than at pH 5.5 (5.2 ± 0.6 units PtCo), a significant difference of -3.0 (95% CI, -1.8 to 4.2) units PtCo, $t(2) = 10.39$, $p = 0.009$.

Although both doses of alum at both pH 5.5 and 5.8 reduced colour effectively according to the AO of 15 TCU, alum-10.0 performed better at pH 5.8, and alum-5.0 did not perform more effectively at either pH. Due to this, pH 5.8 is determined to be the optimal pH for these alum coagulation bench-scale tests.

Percent removal and average turbidity values were compared for alum-5.0 and alum-10.0 at both pH 5.5 and 5.8. Turbidity values generally increased after treatment with optimal alum doses (Figure 27). This is to be expected, as there was no settling period between addition of coagulant and filtration through the 0.45 µm PES filter. The increase in turbidity is likely due to the presence of aluminum hydroxide, but this may be reduced if filtered through an ultrafiltration membrane. Turbidity would also be expected to reduce if a sedimentation period followed flocculation, as flocs created by aluminum hydroxide and NOM would settle further. As turbidity did not contribute to NOM removal data by alum, these results were excluded from optimal alum considerations.

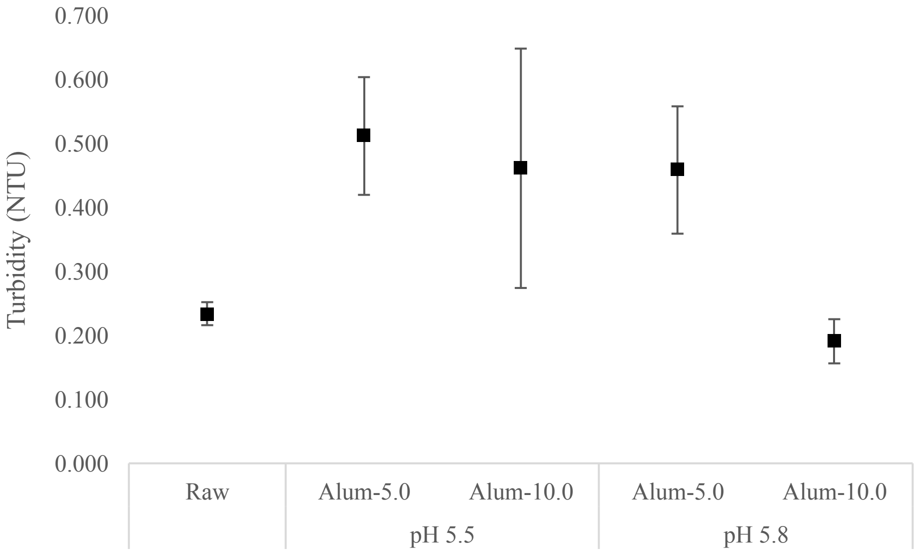

Figure 27 **Turbidity values after treatment with alum-5.0 and alum-10.0 at pH 5.5 and pH 5.8.**

SUVA values from alum-5.0 and alum-10.0 were considered as part of the analyses for determination of optimal alum dose and pH (Table 10). At pH 5.5, neither alum-5.0 or alum-10.0 were able to reduce SUVA to below 2.0 L/mg•m , indicating that some humic material remains in the water. Alum-5.0 at pH 5.8 had a similar result, but alum-10.0 was able to reduce SUVA to 1.8 L/mg•m at the higher pH of 5.8.

Table 10 SUVA values from alum-5.0 and alum-10.0 at pH 5.5 and pH 5.8.

Dose	SUVA (L/mg•m)
pH 5.5; alum-5.0	2.1
pH 5.8; alum-5.0	2.2
pH 5.5; alum-10.0	2.2
pH 5.8; alum-10.0	1.8

4.3.5 Optimal alum

There was no significant advantage to reducing pH of alum coagulation beyond pH 5.8 as shown from the characterization tests. Therefore, WTPs may not need to lower pH as far as pH 5.5 in order to achieve effective reduction of NOM by alum. This can reduce operating costs, adding to myriad reasons that alum is a common choice for many WTPs. However, the inflexibility of alum's zero basicity could lead to higher effort by operators, as constant monitoring and careful buffering of pH is critically important to proper function of alum as pre-treatment for NOM removal.

It was determined through averaging overall percent removal of NOM there was no significant difference between the overall percent removal of alum-5.0 (46.65 ± 34.30 %)

and alum-10.0 (58.86 ± 27.80 %). This result indicates that the lower dose of alum-5.0 is statistically just as effective at reducing NOM as alum-10.0 and increasing the dose beyond 5.0 mg/L is not necessary. The reduced dose is ideal for WTPs concerned about SWR production or filter fouling, as a low dose of alum can reduce strain on the WTP by mitigating these issues. Therefore, the optimal dose of alum for removing NOM from this source water is 5.0 mg/L, and the optimal pH is 5.8.

4.3.6 Optimal overall coagulant

Though all PACl tested performed equally well at reducing NOM, PAC-A-1.8 was selected as the optimal PACl for its effective removal of UV_{254}, colour, and SUVA. Furthermore, it was one of the lowest doses, and still achieved excellent results.

The overall percent removal of alum-5.0 was based on the same NOM characteristics as PAC-A-1.8 except for turbidity and demonstrated an overall percent removal of 58.86 ± 27.80 % compared to PAC-A with an average removal of 86.69 ± 7.76 %. A one-way ANOVA comparing percent removal of UV_{254} and colour for PAC-A and alum-5 found no significant difference between the two coagulants, $F(1, 2) = 1.40$, $p = 0.358$.

This result demonstrates that there is no advantage to coagulating with alum over PAC-A for NOM removal, as the optimal dose of PAC-A performed just as well as the optimal alum dose.

Furthermore, the benefit of dosing PACl into raw water with little to no pH buffering includes a decrease in chemical costs, as well as less operator management and monitoring of the treatment process. Therefore, PAC-A can be considered the optimal coagulant between PACl and alum for reducing NOM in small WTPs where cost of treatment is a consideration.

One thing to note is that bench-scale coagulation tests using alum were performed earlier in the year than PACl, so these results should be used as a general comparison instead of a direct comparison as there may be variation in raw water characteristics.

In UF membrane plants, NOM is not completely removed by mere filtration, as the molecular weight of most NOM compounds is less than what can be removed by the pores of UF membranes (Siddiqui, 2000). While membrane treatment is one key to reducing DBP precursors in drinking water plants, it may not always be sufficient to adequately remove NOM, as demonstrated by elevated DBP concentrations from PLWTP in recent years.

As such, coagulation is a promising accompaniment to UF for appropriate removal of NOM in drinking water, with just small doses of aluminum-based coagulant proving sufficient to significantly improve reduction of NOM in some cases (Walsh et al, 2009; Dong, 2007).

The results from this study indicating that low PACl and alum doses were sufficient for adequate removal of NOM are promising for operators of UF plants; low coagulant doses paired with UF would be an ideal method for removing DBP precursors from raw water and producing finished water with low health risks associated with NOM. With average overall NOM removal of 86.69 ± 7.76 % by PAC-A-1.8 and overall NOM removal of 58.86 ± 27.80 % by alum-5.0 being demonstrated with filtration by 0.45 μm, it is assumed that NOM removal would increase when low doses of these coagulants are paired with UF, as demonstrated by Walsh et al (2009).

Low doses of coagulant are also responsible for reducing membrane fouling of UF membranes (Park, 2014), an important consideration for both large and small WTPs. This is thought to be due to coagulation removing fractions of NOM that would otherwise be caught by the small pore size of UF membranes (Dong, 2007). In-line coagulation, as demonstrated most closely by the bench-scale coagulation experiments in this study, is also associated with more constant permeate flux than without coagulation in an UF membrane plant (Wang, 2006). This is an important consideration, as there is no settling or sedimentation of flocs in a treatment train of this style.

As such, the low coagulant doses determined to be effective at reduction of NOM in this study would be excellent candidates for pre-treatment of water in an UF membrane plant.

4.4 Conclusions and Recommendations

The first objective of this chapter was to determine an ideal operating pH and dose for each of PAC-A, PAC-B, PAC-C, and PAC-D, at which each coagulant effectively removed NOM from raw water in bench-scale coagulation experiments.

The second objective was to compare the five aluminum-based coagulants in terms of their NOM removal capabilities for use as pre-treatment in direct filtration plants, taking the optimal PACl data and comparing it to optimal alum data to establish an ideal coagulant treatment from the available options.

The results of the PACl optimization determination analysis are as follows:

1. From the initial percent removal of UV_{254} calculations, the optimal dose of each PACl at pH 5.5 was established to be PAC-A-1.8, PAC-B-5.0, PAC-C-1.0, and PAC-D-5.0. These were the doses that had the highest percent removal of UV_{254}, with two exceptions. PAC-A-3.6 had a percent removal of 81.85 % compared to PAC-A-1.8 at 81.11 %. It was decided that to double the dose of coagulant and achieve less than 1 % improvement in removal of UV_{254} was not worth the cost of the higher dose. As well, in literature, PACl are able to effectively remove NOM at low doses, so PAC-A-1.8 was selected as an optimal dose to test if this was true in practice. PAC-C was determined to have similar results as PAC-A; PAC-C-2.0 achieved a reduction of 62.59 %, while PAC-C-1.0 had a percent removal of UV_{254} of 57.04 %. The same determination of doses was applied to PAC-C as PAC-A, and the lower dose was chosen as optimal to assess if a low coagulant dose could effectively remove NOM characteristics from raw water in bench-scale coagulation tests.

   For all four PACl, there were either no significant improvements between pH 5.5 and 6.5, or there was a significant improvement at pH 6.5. Due to these analyses, it was determined that the optimal pH for coagulation with PACl in this research study was pH 6.5. This aligns with literature that suggests PACl are less susceptible to pH fluctuations than other aluminum-based coagulants such as alum due to higher basicity and are able to operate effectively at a higher pH. It also increases the affordability of PACl for WTP operators; though the upfront cost of coagulant may be higher than that of alum, the reduction in costs associated with requiring little to no buffering chemical or constant pH monitoring could certainly outweigh the initial cost.

Results from characterization of PACl coagulants and comparison to optimal alum dose are below:

2. The optimal alum dose was determined through average overall percent removals to be alum-5.0 at pH 5.8. The optimal PACl was established to be PAC-A-1.8 at pH 6.5. These two coagulants were compared through their average percent removal of NOM characteristics in order to conclude that there was no significant difference between PACl and alum. Though alum-5.0 achieved good NOM removal through bench-scale coagulation tests, coagulating with alum requires stringent pH monitoring of raw water and adjustment prior to addition of coagulation, as discussed previously. The determination of PACl to be an optimal choice of coagulant for NOM removal can be confirmed by the overall percent removals of all four optimal doses of PACl demonstrating performance just as effective as alum. However, as previously noted, alum coagulation tests were performed earlier in the year than PACl coagulation tests, so direct comparison of these results is discouraged. Instead, these should be viewed as a general comparison, and future research may directly compare alum and PAC-A from the same time of year in order to provide a concrete assessment of the two.

Further research with optimal of PACl and alum paired with UF for this source water would be beneficial to corroborate literature stating that low doses of coagulant are most effective when paired with UF.

CHAPTER 5 COMPARISON OF POLYALUMINUM CHLORIDE COAGULANTS OF VARYING CHEMICAL PROPERTIES

5.1 Introduction

Polyaluminum chlorides are a class of polymerised coagulants with high basicity that are often overlooked for WTPs in favour of more commonly used, less expensive aluminum sulfate. This may be due to their higher purchasing cost, or a lack of extensive research on their abilities in varied source waters. The other potentially limiting factor is simply the wide range of PACl available on the market, with little discernible variation outside of standard chemical properties. In many cases, engineers and municipal planners responsible for designing WTPs may hesitate to select one PACl from a list of available coagulants due to the uncertainty around its exact capabilities. In these decisions, the more universally used aluminum sulfate may be chosen.

One main characteristic of PACl is the range of Al present by weight in the solution. This value is often given in technical data sheets as Al % w/w and generally indicates how powerful a coagulant will be. PACl with low Al % w/w will need to be dosed at higher volumes to achieve the same concentration of Al in mg/L as PACl with a higher Al % w/w.

Residual aluminum is one component of coagulation with aluminum-based coagulants that WTP operators must monitor. This is the concentration of aluminum remaining in treated water after coagulation with aluminum-based coagulants and filtration. Though there is no concrete evidence that aluminum in drinking water can lead to health concerns, it is an analyte that is monitored nonetheless. Some research suggests high residual aluminum may be linked to Alzheimer's disease (Nilsson, 1990) but Health Canada has not confirmed this. From the Canadian drinking water standards, there is an operational guidance value (OG) of 0.1 mg/L residual aluminum permitted from conventional treatment plants, and 0.2 mg/L from other types of treatment plants, such as direct filtration (Health Canada, 2019b). The OG value is based on an annual average of monthly samples, so it allows for some months to have higher Al values than others, permitting that the average of the year's samples is below 0.2 mg/L or 0.1 mg/L.

Production of residual aluminum is generally considered to be due to the presence of $Al(OH)_3$, formed by the coagulation reaction of aluminum-based coagulants, that becomes soluble at low pH and does not precipitate out of solution as is desired. Above pH 5.5, $Al(OH)_3$ is formed as a solid, and becomes SWR in the coagulation process. Low pH can also cause soluble polymeric Al species to form, which then pass through filters and can lead to higher residual aluminum values (Zhao et Al, 2009).

In general, PACl coagulants contain mid-range basicity of 12 – 70 %, while high basicity PACl of up to 85 % is known as ACH (Pernitsky and Edzwald, 2003). Basicity is an indication of a coagulant's ability to buffer acid and determines how a coagulant will affect the pH of water once added. The relationship between basicity of PACl and impact on pH of raw water is inversely proportional, with high basicity PACl triggering little change in water's pH once dosed with the coagulant. Conversely, lower basicity is attributed to a higher reduction in pH of water dosed with PACl.

Basicity of PACl can also determine residual aluminum concentrations, with Kimura et al, 2013 determining that higher basicity PACl can yield treated water with lower dissolved residual aluminum (Kimura et al, 2013). However, there is conflicting discussion in literature surrounding the production of residual aluminum in water treated with PACl, with some sources stating that using PACl can lead to higher residual aluminum (Lin and Ika, 2019) while others have found the opposite effect (Wei et al, 2015; Yang et al 2011).

The primary objective of this chapter is to prepare a comparison of the four PACl studied in this research in practical terms for use in future experiments and by WTP operators.

A secondary objective of comparing Al analyses and effect of basicity on PACl will also be pursued in order to provide concrete distinctions between all four PACl studied.

5.2 Materials and Methods

Aqueous PACl was used for bench-scale coagulation experiments, and solutions were stored at room temperature. Coagulants were dosed according to methods previously described, and characterization work took place after filtration of treated water.

Samples of each PACl were taken directly from bottles and diluted up to 10_6 for Al analysis by inductively coupled plasma mass spectrometry (ICP-MS). This analysis was performed using a Thermo Scientific X-Series 2 Inductively Coupled Plasma Mass Spectrometer, and data produced was used to establish the exact Al concentration in each PACl being studied, compared to information given from the manufacturer’s technical data sheets (TDS). Samples were also submitted for ICP-MS analysis from filtrate of each treated water sample in order to determine residual aluminum present in water after filtration by a 0.45 µm PES filter. Each sample was analysed in triplicate by the ICP-MS, and an average Al in ppb value is given. Data produced from ICP-MS analysis was given in parts per billion (ppb), but converted to µg/L for ease of conversion to mg/L, as 1 ppb = 1 µg/L. The concentration of Al in µg/L was converted to mg/L for analysis. In order to appropriately compare ICP-MS data to the data from TDS, average Al in mg/L was used in a modified Gebbie (2006) equation, as seen in Figure 28.

$$\boldsymbol{Al}\ \%\frac{\boldsymbol{w}}{\boldsymbol{w}} = \frac{\boldsymbol{Al}\frac{\boldsymbol{mg}}{\boldsymbol{L}}}{\mathbf{10\ 000} * \boldsymbol{SG}}$$

Figure 28 Modified Gebbie (2006) equation for determining Al % w/w from Al mg/L and SG.

Appropriate adjustment of pH for coagulation was determined by placing 1.0 L of raw water in a beaker on a stir plate, and a standard laboratory pH probe was calibrated and placed into the beaker. A magnetic stir stick was added to the beaker and the stir plate turned on low. A previously calculated dose of PACl was pipetted into the water, and a pH reading was taken and recorded once the device had stabilized. If the pH had to be increased, 0.1 N NaOH was added in small increments until the desired pH was reached. If the pH needed to be lowered, 0.1 N H_2SO_4 was instead added. The volume of chemical required to reach the proper pH was recorded for each PACl studied and subsequently used to prepare water in jars for bench-scale coagulation experiments.

5.3 Results and Discussion

5.3.1 Al analysis

Samples from each coagulant were submitted for ICP-MS analysis of aluminum concentration in order to confirm information listed on the TDS for each coagulant. Filtrate from bench-scale coagulation experiments were also submitted to provide information on residual aluminum after coagulation and filtration. All samples were diluted according to ICP-MS standard operating procedures, and data produced was given in average Al ppb.

From ICP-MS data for PAC-A and PAC-D, it was determined that the actual amount of Al % w/w is more than double what is stated on the TDS (Table 11). PAC-B contained less Al % w/w than even the low end of the range given, and PAC-C had approximately 6 % more Al than reported.

Table 11 Aluminum analysis by ICP-MS and Gebbie (2006).

Sample	ICP-MS (mg/L)	Gebbie (mg/L)	ICP-MS % w/w	TDS % w/w range	TDS % w/w (av)
PAC-A	153633	65 880	12.59	5.10 - 5.70	5.40
PAC-B	60147	68 200	4.85	5.20 - 5.80	5.50
PAC-C	216933	138 060	16.69	10.22 - 11.02	10.62
PAC-D	300433	164 900	22.59	12.10 - 12.70	12.40

These results indicate that Al % w/w data given by manufacturers may not always be accurate, and random analysis of Al concentration in coagulant by WTP operators may be beneficial to having as much information about the chemical as possible. As well, unknowingly dosing with a higher volume of Al could lead to inadequate reduction of residual Al. Though there are no confirmed adverse health effects from intake of Al, research is ongoing and minimizing residual Al concentration in treated water is good practice.

ICP-MS data from Al analysis of filtrate of water treated with PACl at pH 5.5 demonstrated that not coagulation and filtration by 0.45 μm filter did not reduce residual Al of all coagulants to the federal OG (Table 12). Only filtrate of PAC-A-1.8 was close to the guidelines, presenting an average Al value of 0.12 mg/L, which would meet the OG of < 0.2 mg/L for a direct filtration plant. PAC-B had the highest residual aluminum at pH

5.5, with a concentration of 8.84 mg/L. The high concentrations of Al remaining in treated filtrate from coagulation at pH 5.5 is most likely due to the presence of soluble Al(OH)$_3$, which generally precipitates out of solution at a slightly higher pH, as well as polymeric species of Al that are formed at lower pH and pass through filters.

Table 12 ICP-MS Aluminum Analysis for PACl samples at pH 5.5.

Sample	Average ICP-MS (mg/L)
Raw	0.02
PAC-A-1.8	0.12
PAC-B-5.0	8.84
PAC-C-1.0	1.91
PAC-D-5.0	1.41

ICP-MS analysis of Al from coagulation at pH 6.5 shows more promising results in terms of residual aluminum (Table 13). PAC-A, PAC-B, and PAC-C all met the federal OG of < 0.2 mg/L residual aluminum, but PAC-D did not, demonstrating an average residual aluminum value of 0.60 mg/L. This is much lower than the result of coagulation at pH 5.5, but still not low enough to properly meet the OG.

Table 13 ICP-MS aluminum analysis of PACl at pH 6.5.

Sample	Average ICP-MS (mg/L)
PL Raw	0.02
PAC-A-1.8	0.03
PAC-B-5.0	0.10
PAC-C-1.0	0.04
PAC-D-5.0	0.60

This result indicates that at pH 6.5, most of the $Al(OH)_3$ produced is insoluble and would precipitate out of solution instead of remaining soluble and passing through the filter. Furthermore, the results from this analysis of Al demonstrate that hydrolysis of Al at pH 6.5 did not produce as many soluble polymeric Al species as at pH 5.5. This is additional evidence that PACl perform optimally at pH 6.5 than at pH 5.5.

5.3.2 Effect of basicity

In general, pH of raw water decreases with addition of coagulant. Basicity of coagulant determines by how much the pH will decrease, as low basicity leads to a large drop in pH and high basicity is less impactful on the pH. Basicity, Al % w/w, aluminum dose, and percent decrease of pH are shown for all for PACl in Table 14.

Table 14 Properties of PACl studied.

	Coagulant	Average Basicity (%)	Average Al (% w/w)	Aluminum Dose (mg/L)	Percent Decrease pH (%)
Group 1	PAC-B	70	5.5	5.0 15.0 30.0	13.68 23.31 25.86
	PAC-D	82.85	12.4	5.0 15.0 30.0	4.21 12.33 16.54
Group 2	PAC-A	53	5.4	0.6 1.8 3.6	0 6.32 16.54
	PAC-C	75	10.62	0.3 1.0 2.0	1.95 2.71 3.61

5.3.2.1 Group 1 PACl

Group 1 PACl is comprised of PAC-B and PAC-D. PAC-B has low Al % w/w while PAC-D contains a high Al % w/w, and they were compared directly based on the high doses of Al mg/L determined by previous methods. Each Group 1 PACl was dosed at 5.0 mg/L, 15.0 mg/L, and 30.0 mg/L Al.

PAC-B is characterised by mid-high basicity (70%) and low Al (5.5 % w/w) and possesses the second lowest of these characteristics of all four PACl studied. It was dosed at 5.0 mg/L, 15.0 mg/L, and 30.0 mg/L aluminum. Upon addition of PAC-B doses to raw water, pH decreased by 13.68 %, 23.31 %, and 25.86 %, respectively from the raw water pH of 6.65 (Figure 29).

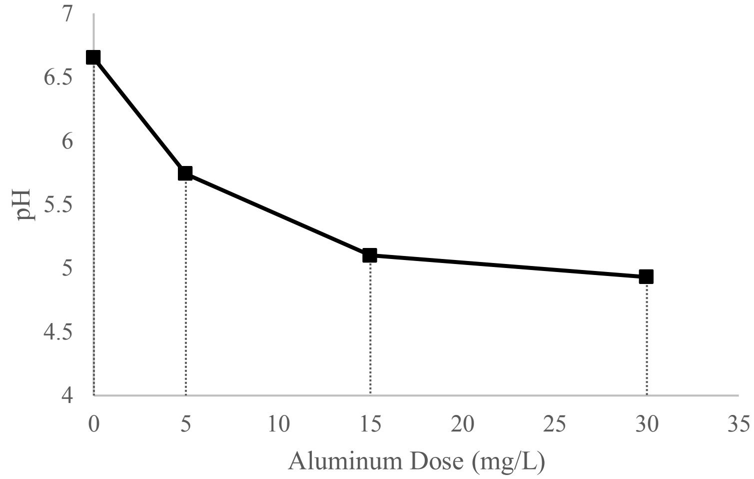

Figure 29 **Decrease in pH after addition of PAC-B at 5.0 mg/L, 15.0 mg/L, and 30.0 mg/L.**

This relatively steep decrease in pH can be attributed to the mid-range basicity value of PAC-B; though not as drastic a change in pH as could be found from a zero basicity coagulant, it is still worth taking into consideration that PAC-B can decrease pH up to 25 % at a dose of 30 mg/L aluminum. Though PACl can operate effectively at a varied range of pH, it may be beneficial to chemically adjust pH prior to coagulation with PAC-B at higher doses to ensure the pH is within the operating range of PACl.

PAC-D is classified as ACH, with extremely high basicity (82.85 %) and high Al (12.4 % w/w). It is the PACl with the highest basicity and Al % w/w in this study, and demonstrated more resilience in pH change than PAC-B. PAC-D was dosed at 5.0 mg/L, 15.0 mg/L, and 30.0 mg/L, and demonstrated a percent reduction in pH of 4.21 % for the lowest dose, 12.33 % for the middle dose, and 16.54 % for the highest dose (Figure 30).

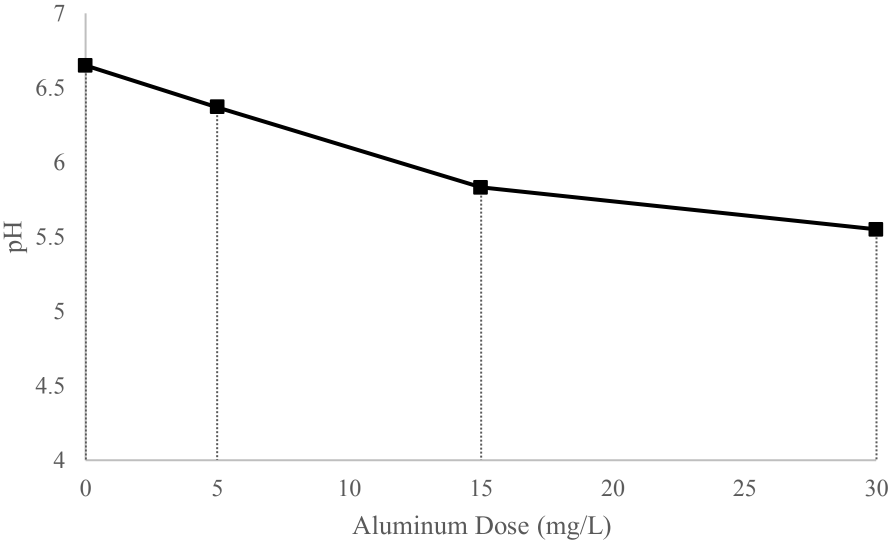

Figure 30 Decrease in pH after addition of PAC-D at 5.0 mg/L and 15.0 mg/L.

The high basicity of PAC-D allows it to have less of an effect on the pH of raw water than other PACl. In particular, compared to PAC-B, PAC-D has much less of an effect on pH even at the highest dose; demonstrating a pH reduction of 16.54 % at 30.0 mg/L compared to a pH reduction of 25.86 % by PAC-B at the same dose. PAC-D has a low impact on raw water pH and could be dosed directly into raw water at a WTP without prior pH adjustment, due to the wide range at which PACl operate effectively.

5.3.2.2 Group 2 PACl

PAC-A and PAC-C are categorized into Group 2. PAC-A contains the lowest basicity (53%) and Al (5.4 % w/w) of all PACl studied, while PAC-C has high basicity (75 %) and high Al (10.62 %). These PACl were tested at very low doses of aluminum, with PAC-A undergoing bench-scale coagulation experiments at 0.6 mg/L, 1.8 mg/L, and 3.6

mg/L aluminum, and PAC-C being evaluated at 0.3 mg/L, 1.0 mg/L, and 2.0 mg/L aluminum.

PAC-A demonstrated no change in pH at the lowest dose of 0.6 mg/L, followed by a 6.32 % reduction at 1.8 mg/L, and a 16.54 % reduction at 3.6 mg/L (Figure 31).

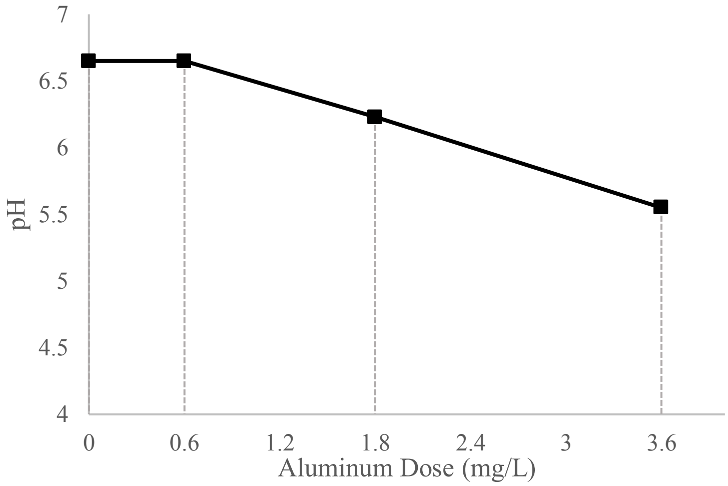

Figure 31 **Decrease in pH after addition of PAC-A at 0.6 mg/L, 1.8 mg/L, and 3.6 mg/L.**

The low basicity of PAC-A lead to a higher decrease in pH at higher doses but did not affect the raw water pH at the lowest dose. This result indicates that despite the low basicity value, low doses of PAC-A may be able to be dosed directly into raw water without chemical pH buffering. Effective NOM removal may still occur at the pH after dosing with PAC-A.

PAC-C demonstrated the least change in pH after dosing of all four PACl. This may be due in part to its high basicity concentration of 75 %. PAC-C coagulated at the lowest doses of aluminum of all PACl, and showed a percent decrease of 1.95 % at 0.3 mg/L, 2.71 % at 1.0 mg/L, and 3.61 % at 2.0 mg/L (Figure 32).

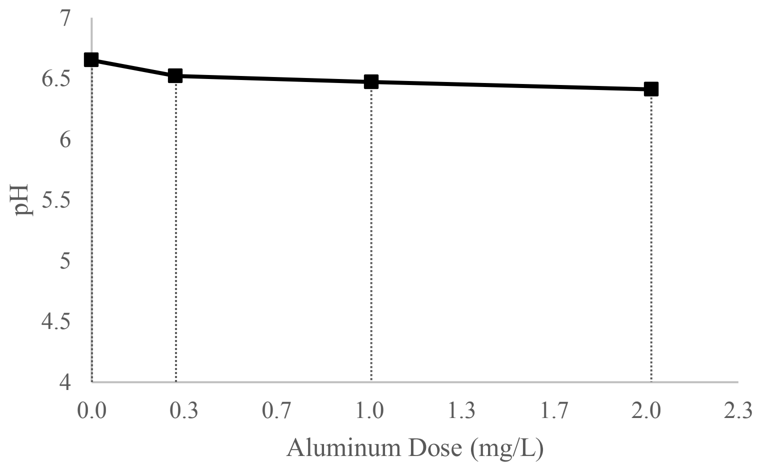

Figure 32 Decrease in pH after addition of PAC-C at 0.3 mg/L, 1.0 mg/L, and 2.0 mg/L.

The very low decrease in pH from addition of PAC-C is attributed to its high basicity, and it is possible that raw water would not need to be buffered prior to addition of PAC-C even at higher doses.

5.3.2.3 Optimal PACl

Results from the comparison of Group 1 and 2 corroborate the relationship between basicity and pH decrease; at equal doses of aluminum (mg/L), PAC-B demonstrated higher percent decreases at every dose. PAC-D contains higher basicity than PAC-B, and therefore exhibits less of an effect on the pH of raw water. PAC-C appeared to exhibit less of an effect on pH than PAC-A, but was also dosed at lower volumes.

PAC-A contains the lowest basicity of all four PACl and displays a percent decrease of 16.54 % pH at a dose of 3.6 mg/L. Comparatively, PAC-D also demonstrated a 16.54 % decrease at its highest dose, which is nearly ten times as high as the highest dose of PAC-A. This indicates that the buffering capacity of PAC-A is significantly less than that of PAC-D, and WTPs selecting this coagulant should be stringent in pH monitoring to ensure the coagulant is performing effectively.

At the optimal dose of each coagulant, pH decrease was generally low. With the exception of PAC-B, all optimal doses caused pH of raw water to drop only slightly and remain above pH 6.0 (Table 15).

Performance of PACl were tested at pH 5.5 and pH 6.5, but literature suggests the ideal operating range for coagulation with PACl begins at 6.0. Therefore, at the ideally performing dose of PAC-A, PAC-C, and PAC-D, there may be the option of not chemically buffering raw water prior to coagulating. For raw water with an approximate pH of 6.5 or above, buffering would not be required for optimal coagulation and effective NOM removal.

Table 15 Decrease in pH of optimal PACl doses.

Sample	Aluminum Dose (mg/L)	pH After Addition of PACl	Percent Decrease (%)
PAC-A	1.8	6.23	6.32
PAC-B	5.0	5.74	13.68
PAC-C	1.0	6.47	2.71
PAC-D	5.0	6.37	4.21

Though costs of purchasing PACl may be higher than alum, the benefits of coagulating with PACl include low volumes of coagulant needed to reduce NOM, more flexible pH requirements, and the ability of WTP operators to dose coagulant without buffering. The low volumes of coagulant will allow daily operating cost to be low, as well as no additional chemical requirements for buffering, and reduced pH monitoring contribute to low financial strain.

5.3.3 Overall comparison

An analysis of PAC-A, PAC-B, PAC-C, and PAC-C is below (Table 16). This comparison encompasses chemical properties, both those stated by the manufacturer and those provided through laboratory analysis; physical properties; optimal doses and their volumes; effect on pH of each PACl; NOM removal abilities; and residual aluminum values of coagulant. One-way ANOVAs and paired t-tests indicate that there was no significant difference between any PACl in terms of overall percent removal of NOM, signifying that all four coagulants performed equally well.

Table 16 Overall comparison of PACl.

	Group 1		Group 2	
	PAC-B	**PAC-D**	**PAC-A**	**PAC-C**
Average Basicity (%)	70	82.85	53	75
Average TDS Al (% w/w)	5.5	12.4	5.4	10.62
ICP-MS Al (% w/w)	4.85	22.59	12.59	16.69
Doses tested at pH 5.5	5.0 15.0 30.0	5.0 15.0 30.0	0.6 1.8 3.6	0.3 1.0 2.0
Optimal Dose (Al mg/L)	5.0	5.0	1.8	1.0
Volume of Coagulant for Optimal Dose (µg/L)	73.3	30.3	27.2	73.0
Percent Decrease in pH after Optimal Dose	13.68	4.21	6.32	2.71
Percent Removal of UV254; pH 6.5 (%)	81.85 ± 0.64	69.26 ± 0.64	79.63 ± 0.64	58.77 ± 0.64
Percent Removal of Colour; pH 6.5 (%)	100.00 (SD < 0.001)	91.33 ± 6.03	95.00 ± 8.70	96.33 ± 1.15
Percent Removal of Turbidity; pH 6.5 (%)	62.25 ± 3.19	50.04 ± 22.80	85.44 ± 5.59	83.02 ± 3.66
Overall NOM Removal; pH 6.5 (%)	82.37 ± 17.38	70.21 ± 20.66	86.69 ± 7.76	79.37 ± 19.05
SUVA; pH 5.5 (L/mg•m)	0.7	1.6	1.3	2.1
SUVA; pH 6.5 (L/mg•m)	1	1.7	1	2.4
Average Residual Al, Optimal Dose; pH 5.5 (mg/L)	8.84	1.41	0.12	1.91
Average Residual Al, Optimal Dose; pH 6.5 (mg/L)	0.10	0.60	0.03	0.04

PAC-A was determined to have the highest overall removal of NOM (86.69 ± 7.76 %) of all PACl at its optimal dose of 1.8 mg/L. PAC-A is supposed to have the lowest Al % w/w at 5.4 %, but actually contained an average of 12.59 % Al % w/w as determined through ICP-MS analysis. This coagulant also contained the lowest basicity but did not demonstrate the highest percent decrease in pH after addition, as would be expected. Finally, PAC-A exhibited the lowest residual aluminum at both pH 5.5 and pH 6.5.

PAC-B-5.0 had the second highest percent removal of NOM, with a removal of 82.37 ± 17.38 %. This coagulant, when analysed by ICP-MS for Al % w/w, showed the closest value to its TDS of all PACl and therefore contained the lowest amount of Al. PAC-B required the highest volume of coagulant to achieve its removal of NOM, and exhibited the highest percent decrease in pH, as well as the highest residual Al at pH 5.5. Its percent removal of colour was excellent, with an average of 100 % removal, but many of its other characteristics were highly variable.

PAC-C contained the second highest average basicity (75 %) and ranked third for overall percent removal of NOM while requiring one of the highest volumes of coagulant. The percent decrease of pH after addition of coagulant was very low, likely due to the high basicity of the PACl, and would allow for little to no chemical buffering of raw water. PAC-C reduced SUVA by the least amount and therefore indicated that it may not have removed all of the humic material from the source water as the other coagulants did. The average residual Al value at pH 5.5 was the second highest of the PACl, but PAC-C demonstrated an acceptably low residual Al value at pH 6.5.

PAC-D is classified as ACH, with high basicity and high Al % w/w, but the stated Al value on the TDS was nearly half of what was determined through ICP-MS analysis. A low percent decrease of pH was demonstrated by PAC-D upon addition to raw water, presumably due to the high basicity value. However, PAC-D exhibited the lowest overall percent removal of NOM, and some of the highest residual aluminum values at both pH 5.5 and pH 6.5.

All four PACl are not directly comparable due to differing doses, but the results from characterization with optimal doses were able to be compared. Statistical analysis indicated that there was no significant difference in overall NOM removal between any of the PACl, but there are specific characteristics that may make one PACl more useful for water treatment than another for particular conditions.

PAC-A appeared to be the most effective PACl based on various characteristics; high percent removal of NOM characteristics, low volume of coagulant required, low impact on pH of raw water, good SUVA reduction, and low residual aluminum.

PAC-D appeared to be the least effective PACl for this source water. It exhibited the lowest overall NOM removal, one of the highest residual aluminum values, and mediocre SUVA values after treatment.

Selection of a coagulant for a WTP requires careful consideration of operations, procedures, infrastructure, and source water quality. Treatment facilities may be focused on financial considerations, residual aluminum values, DBPs, or other parameters that require comparison of available options. Often, alum is chosen for its widespread availability and inexpensive purchasing price, but PACl are able to provide all the benefits of an aluminum-based coagulant while also out-performing alum in some regards. This comparison of four PACl varieties should prove useful for future research, as it provides a more detailed description of the properties of these coagulants beyond what can be found in the manufacturer-produced TDS.

The presumption of higher basicity being better for treatment of raw water and removal of NOM was proved in this study to be untrue, as it was not the highest basicity PACl that showed the best overall performance. It is true that basicity higher than zero can have benefits, which allows for all PACl to have an advantage over alum, particularly in terms of pH adjustment requirements. In bench-scale coagulation experiments, there was often no significant difference in treatment results between pH 5.5 and pH 6.5, which demonstrates that for the most part, PACl performs comparably well between the two pH values. This result indicates that when high pH source water is dosed with PACl, there is an opportunity to begin coagulation immediately without any chemical adjustment of pH.

PAC-B returned an interesting result of demonstrating the highest reduction in pH (13.68 %) despite containing the second highest basicity of 70 %. This result goes against the convention of high basicity coagulants having a lower effect on pH than their lower basicity counterparts. Where the tested Al values were so different from those stated on the TDS for each coagulant, it may be beneficial for future research to test the actual basicity of coagulants to compare against the stated value.

ICP-MS results of Al testing show that there were discrepancies between stated and actual Al values, with some PACl containing more Al than listed on TDS, while others contained less Al. WTPs dosing with PACl or any aluminum-based coagulant would certainly benefit from random Al concentration testing of their coagulant to ensure that appropriate doses are being added to raw water; too high a concentration of Al could lead to higher residual Al in finished water if the WTP is unaware of the actual concentration of Al in the coagulant.

5.4 Conclusions and Recommendations

This chapter had two objectives; to compare effects of basicity and analyses on Al concentration in PACl; and to prepare a broad comparison of all four PACl studied for future research and use by WTP operators.

The results of the basicity and Al analyses are as follows:

1. ICP-MS Al analysis indicated that Al % w/w stated on TDS provided by manufactures was incorrect. PAC-B was the only coagulant that demonstrated lower Al % w/w than that given on its TDS; all other coagulants demonstrated up to double the Al % w/w than listed. These results can be problematic, for when WTP operators expect a certain value for Al % w/w they can set operating parameters according to this value. This can include dosing a proper amount of coagulant and removing enough aluminum through coagulation and flocculation in order to minimise residual aluminum in treated water. However, if coagulants contain more aluminum than stated, calculated doses can become too high and could lead to high aluminum residuals.

   Basicity analyses studied the relationship between pH decrease after addition of coagulant and the given basicity of a coagulant. It was determined that PAC-B demonstrated the highest decrease in pH after addition of its optimal dose of all the PACl, despite its high basicity. The other coagulants followed the expected relationship; high basicity PAC-C and PAC-D demonstrated smaller changes in pH of raw water than the low basicity PAC-A.

2. The overall comparison of PACl provides information from chemical properties to demonstrated NOM removal and should aid in differentiating between ideal coagulants for specific operating conditions of WTPs. Though there was no significant difference in overall percent removal of NOM between all four PACl, the values are still useful in comparing properties.

   PAC-A required the lowest volume of coagulant, and demonstrated the highest overall percent removal of NOM. However, its low basicity can require more careful monitoring of raw water pH than its counterparts.

   PAC-B showed the greatest variation in residual aluminum, and also the highest decrease in pH of raw water. It required the highest volume of coagulant but removed the highest amount of colour and produced some of the lowest SUVA values after treatment at both pH 5.5 and pH 6.5.

   PAC-C also required a high volume of coagulant but demonstrated the lowest effect on pH of raw water. It also produced the highest SUVA values, above 2.0, and therefore did not remove all humic material from the raw water during treatment. PAC-C also removed the least amount of UV_{254}, a critical factor in reducing precursors for DBPs.

PAC-D removed the least amount of NOM overall, while also producing only mediocre results for SUVA and residual aluminum at both pH 5.5 and pH 6.5. Though it contains the highest amount of basicity as an ACH coagulant, it did not prove to be vastly superior to other PACl.

CHAPTER 6 CONCLUSIONS

6.1 Summary of Conclusions

Bench-scale coagulation tests were performed on raw Pottle Lake water using four PACl coagulants that varied in their chemical properties. Following coagulation testing, characterization of treated and raw was completed through analysing UV_{254}, turbidity, and colour in order to provide an overview of NOM precursors to DBPs. Results of PACl characterization testing were compared to alum testing completed previously in the year, and it was determined that there was no significant difference between water treated with alum and water treated with any of the PACl. The advantages of coagulating with PACl instead of alum are numerous, but include lower volumes of dosing, potentially lower residual aluminum, a wider operating range of pH and associated reduction or elimination of required chemical buffering of raw water.

The four PACl studied were divided into two groups for optimization at pH 5.5; PAC-B and PAC-D comprised Group 1, dosed at 5 mg/L, 15 mg/L, and 30 mg/L Al. Group 2 included PAC-A and PAC-C, which were dosed at 0.6 mg/L, 1.8 mg/L, 3.6 mg/L and 0.3 mg/L, 1.0 mg/L, 2.0 mg/L, respectively. Using percent removal of UV_{254} at pH 5.5 as a metric, the optimal doses for each PACl were determined to be as follows: PAC-B-5.0, PAC-D-5.0, PAC-A-1.8, and PAC-C-1.0. Characterisation tests were conducted on UV_{254}, colour, and turbidity to determine whether bench-scale coagulation experiments with the optimal PACl doses removed NOM more effectively at pH 5.5 or pH 6.5. Each optimal dose performed either significantly better at pH 6.5, or had no significant change between the two pH, indicating that the higher pH was the optimal operating condition. This was a beneficial finding for WTP operators and future research, as it confirms that PACl require less pH buffering than other aluminum-based coagulants and can operate effectively at a higher pH.

At pH 6.5, PAC-B-5.0 had a percent removal of UV_{254} of 81.85 ± 0.64 %, a percent removal of colour of 100.00 (SD < 0.001) %, and a turbidity percent removal of 65.25 ± 3.19 %. PAC-D-5.0 had a percent removal of UV_{254} of 69.26 ± 0.64 %, a percent removal of colour of 91.33 ± 6.03 %, and a percent removal of turbidity of 50.04 ± 22.80 %. There was no statistically significant difference between UV_{254}, colour, or turbidity values for PAC-B and PAC-D, indicating that they each performed equally well.

PAC-A performed statistically better than PAC-C for removal of UV_{254} with a percent reduction of 79.63 ± 0.64 % compared to 58.77 ± 0.64 %, but there was no significant difference between PAC-A and PAC-C for reduction of colour, 95.00 ± 8.66 % and 96.33 ± 1.15 %, respectively. There was also no statistically significant difference between the percent reduction of turbidity for PAC-A and PAC-C, showing removal of 85.44 ± 5.59 % and 83.02 ± 3.66 %, respectively. With the exception of UV_{254}, PAC-A and PAC-C are equally effective in their removal of NOM characteristics.

Statistical analyses on PACl coagulation work determined that there was no significant difference between the final overall percent removals of any PACl, indicating that each PACl was equally effective in removing NOM.

Residual Al values were varied across PACl at pH 5.5, but at the optimal pH of 6.5 nearly all optimal doses of PACl met the federal drinking water OG of 0.2 mg/L for direct filtration plants. PAC-D was the exception, exhibiting a residual Al value of 0.60 mg/L. The low residual Al values at pH 6.5 indicate that the coagulation reaction is producing solid metal hydroxide in the form of $Al(OH)_3$, which precipitates out of solution as SWR in large-scale WTPs. Furthermore, the results indicate that soluble polymeric Al hydrolysis species are not being produced as much as at pH 5.5, where residual aluminum values were well above the OG.

Analysis of Al % w/w in PACl by ICP-MS resulted in findings that PAC-A, PAC-C, and PAC-D contained higher concentrations of Al than those listed on the TDS for each coagulant. In fact, PAC-D contained nearly twice the Al % w/w as stated. PAC-B was the only coagulant that contained less Al than stated on its TDS.

PACl are excellent coagulants for WTPs of all sizes but may be especially attractive for small WTPs that may not have the capacity, training, or financial ability to monitor pH of raw water constantly and buffer with chemical pH adjusters prior to coagulation. Though PACl can have a higher upfront cost than alum, they often require low dosing volumes and produce less SWR than alum, adding to their advantages.

For Pottle Lake source water, PAC-A-1.8 appears to be the ideal coagulant. PAC-A achieved excellent overall reduction of NOM, produced low SUVA values after coagulation at pH 6.5, and also demonstrated the lowest residual aluminum values at both pH 5.5 and pH 6.5. Current literature suggests that PACl operate effectively at pH 6.0 and above, which would allow PAC-A-1.8 to be used at PLWTP effectively without prior buffering of raw water, provided the pH of raw water was above 6.4. This is due to PAC-A-1.8 demonstrating a pH decrease of 6.32 %; if the pH of raw water was 6.4, a 1.8 mg/L dose of PAC-A would depress the pH to approximately 6.0. However, PAC-A exhibited good removal of NOM and a residual Al value of 0.12 mg/L at pH 5.5, indicating effective treatment of water would still occur even at a lower pH. This would allow PLWTP to coagulate effectively without chemical pH adjustment during times when raw water pH could be lower.

Finally, PAC-A-1.8 required the lowest volume of coagulant of any PACl. This is one further method PLWTP could use to justify the higher upfront cost of coagulating with PAC-A over alum; effective reduction of NOM would take place at a low dose, which would allow each purchase of coagulant to last longer than if a higher dose were required.

6.2 Recommendations for Future Work

Bench-scale coagulation tests were performed using water from Pottle Lake in the winter, so an annual survey of efficacy of PACl would be greatly beneficial to PLWTP and future research. Furthermore, seasonal changes in source water may lead to different PACl showing different treatment characteristics, so in order to provide a full framework of the benefits of PACl, an annual comparison would be required.

Comparison of NOM removal between alum and PACl was completed only loosely in this study due to the fact that bench-scale coagulation experiments with alum were performed earlier in the year, and thus some results may be attributed to differences in source water quality. A direct comparison of alum and PACl could be completed using source water drawn from the same time frame in order to provide improved results.

Further bench-scale coagulation experiments could be completed using variations of coagulation and flocculation times to determine the impact of a flocculation period on effective removal of NOM by PACl. In this study, PACl were coagulated with a 60 s rapid mix at 300 rpm followed by no flocculation period in order to mimic a small in-line coagulation WTP operating train. Further research on longer coagulation periods, different mixing speeds, flocculation times, and settling periods could be conducted to provide further insight into the coagulation abilities of PACl.

Finally, as this was a study on removal of precursors to DBPs, future research could be supplemented by performing DBP formation potential tests, as well as testing concentrations of THMs and HAAs in raw source water and after pre-treatment with coagulant. These tests were not able to be performed for the supplementation of this study due to research restrictions surrounding COVID-19, but future work would benefit greatly from this data.

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