Application of Coagulation/Flocculation followed by Sedimentation for Treating Urban Combined Sewer Overflows

by

Mohammed Zakee Shaikh

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Department of Civil and Environmental Engineering University of Alberta

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ABSTRACT

Combined Sewer Systems are commonplace in the United States and the major cities in Canada. These systems consist of both sanitary and stormwater lines which, when combined, create the potential for large surges of wastewater during storm conditions known as Combined Sewer Overflows (CSOs). CSOs have been identified by the USEPA and the European Parliament as damaging to the receiving environment by introducing protozoans such as *Cryptosporidium* and *Giardia* into fish as well as extra nutrients that may result in algal blooms in lakes downstream. As a result, the treatment of CSOs is an area of concern in the field of water treatment. CSOs can be treated via physical-chemical processes such as coagulation/flocculation alongside rapid/slow mixing. In Edmonton, the local wastewater treatment plant uses Aluminium Sulfate (Alum) along with coagulant aid to treat CSO flows. This process is known as Enhanced Primary Treatment.

The current study's objectives were to determine the optimum mixing conditions using a jar test apparatus for removal of common wastewater parameters such as chemical oxygen demand, pH, turbidity, alkalinity, total suspended solids, total volatile suspended solids and phosphorus. The coagulants used for this study were Alum, ferric chloride and polyaluminum chloride (PAC1). Each coagulant was given a low dose and a high dose while the mixing speed and times were varied on a high/low basis as well. The mixing speeds and times were 1 minute/150 RPM and 3 minutes/300 RPM for rapid mixing and 10 minutes/15 RPM and 20 minutes/30 RPM for slow mixing.

Six jars were chosen for the two-level, three-factor factorial design with two levels of dosages for each of the three coagulants with equivalent Al levels ranging from 4.05 mg Al/L to 10.14 mg Al/L. Four sampling campaigns took place between May 2016 and March 2017. The results of the final sampling campaign were analysed in detail. Through factorial design and ANOVA analysis, it was determined that the two most statistically significant factors in this study were slow mixing speed/time and coagulant dosage. The contaminant removal ratios and percent removal indicated that both Alum and PACl were the most effective in the removal of contaminants. The low dose, 4.05 mg Al/L, of both were more effective per mg of coagulant at removal with both removing an average of 23 mg contaminant per mg Al. The high level of slow mixing, 20 minutes/30 RPM, was determined to be the most effective mixing level with an average 9% improvement in contaminant levels over the low level of slow mixing. Alum was determined to be the most cost effective coagulant due to the cost per metric tonne for Alum being \$400 as opposed to \$800 to \$950 for PACl. The benefits of removal between PACl and Alum were not significant enough to warrant being the coagulant of choice. Ferric chloride did not perform well in contaminant removal, possibly due to the high relative molecular weight of iron compared to aluminium as well as the higher amount of iron required in the form of ferric chloride in order to maintain equivalence with the active aluminium in the other coagulants, resulting in less efficient contaminant removal.

PREFACE

This thesis is the original work of Mohammed Zakee Shaikh. No part of this thesis has been previously published. A presentation that summarizes the results of this thesis has been presented at the annual Civil Society for Civil Engineering (CSCE) Conference in Vancouver, Canada, on May 31, 2017. Under the supervision of Dr. Mohamed Gamal El-Din and the help of colleagues Abdul Rahim Al Omairi and Mirna Alameddine, Mohammed Zakee Shaikh conducted all research, designed and performed all laboratory experiments, analyzed the data, and prepared this manuscript. In addition to supervising the project, Dr. Mohamed Gamal El-Din provided all instructions and reviewed all material prepared. The experiments were conducted in Dr. Mohamed Gamal El-Din's laboratories and all materials and equipment were used from his laboratories. Dr. Selamawit Messele, Dr. Mingyu Li and Dr. Pamela Chelme-Ayala also contributed by assisting Mohammed Zakee Shaikh, through revisions of the data analysis and content prepared.

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ABBREVIATIONS

GBWWTP	Gold Bar Wastewater Treatment Plant
USEPA	United States Environment Protection Agency
CSO	Combined Sewer Overflow
EPT	Enhanced Primary Treatment
Alum	Aluminium Sulfate
FeCl ₃	Ferric Chloride
PAC1	Polyaluminium Chloride
TSS	Total Suspended Solids
TVSS	Total Volatile Suspended Solids
COD	Carbonaceous Oxygen Demand
OP	Ortho-Phosphate
BOD	Biochemical Oxygen Demand
ТР	Total Phosphorus
VOC	Volatile Organic Carbon
TKN	Total Kjeldahl Nitrogen
NH ₄	Ammonium
DOC	Dissolved Organic Carbon
MLD	Megalitres per day
PI	Primary Influent
OSPW	Oil Sands Process Water
NOM	Natural Organic Matter
NS	Not Specified
DI	Deionized
KHP	Potassium hydrogen phthalate
IC	Ion Chromatography
USB	Universal Serial Bus
Ν	Normality
ANOVA	Analysis Of Variance
RR	Removal Ratio
NTU	Nephelometric Turbidity Units
TOC	Total Organic Carbon
RPM	Revolutions Per Minute
MT	Metric Tonne
DLVO	Derjaguin, Landau, Verwey and Overbeek

Chapter 1. Introduction

1.1 Project Background

Combined Sewer Overflows present a problem to most urban centres around the world that experience significant amounts of rainfall on a yearly basis. According to the USEPA, approximately 40 million people are served by Combined Sewer Systems in the United States of America (Irvine et al., 2005). In 1989, the USEPA issued a national strategy in order to control the negative impacts of CSOs due to the potential harmful effects of CSOs on the receiving environment (Irvine et al., 2005). CSOs come about due to the combination of an old sewer system consisting of sewage lines that accept both domestic and stormwater. When a rain event occurs, the excess stormwater entering these sewage lines mixes with the domestic wastewater and makes its way to the local wastewater treatment plant (USEPA, 2017). It is often the case that the excess flows from such rain events exceed the total treatment capacity of the plant and thus, a portion of the primary influent has to be diverted to the receiving environment with little to no treatment.

At the EPCOR Gold Bar Wastewater Treatment Plant (GBWWTP), the company introduced a solution known as Enhanced Primary Treatment (EPT) which applies a set dose of aluminium sulfate (Alum) to these CSO events along with coagulant aid in order to settle out as many suspended solids as possible before discharging the treated effluent to the North Saskatchewan River (Stantec, 2004).

CSOs often have adverse effects on the receiving environments. They have been found to potentially elevate the levels of harmful bacteria such as *Giardia* and *Cryptosporidium* (Gibson et al., 1998) as well as reduce the oxygen saturation of the receiving waters (Hvitved-Jacobsen, 1980). CSOs have also been proven to contain a large quantity of priority pollutants, according to one study performed in Paris (Gasperi et al., 2008). Among these priority pollutants are various

heavy metals such as cadmium, chromium, copper, mercury, nickel, lead and zinc as well as organic compounds such as organotins, chlorobenzenes, volatile organic compounds and polycyclic aromatic hydrocarbons among others (Gasperi et al., 2008). A priority pollutant is chemical or substance that is found at some level in surface waters that contributes to a need for surface water pollution control (Gasperi et al., 2012). Out of these, there is some indication that zinc contributes to elevated levels of toxicity in phytoplankton found downstream of CSO discharges in the Seine River (Seidl et al., 1997).

A study performed in Korea revealed that stormwater runoffs carry the most pollutants when originating in a high density residential area, followed by low density residential, industrial and undeveloped watershed (Woong Bang and Ho Lee, 2000). Another Korean study found that the total suspended solids (TSS) loading was 14 times higher during rainfall events as compared to dry weather flow (Kwon et al., 2014). Similar studies in Spain have discovered that CSO flows contributed to very high loadings of suspended solids, nitrogen and zinc entering the receiving environment upon discharge (Diaz-Fierros, 2002).

In terms of CSO composition, between 27% and 56% of CSO flow comes from sanitary sewers, with the balance being mostly made up from stormwater. The stormwater contribution carries most of the TSS and metals while the sanitary sewage consists mainly of biochemical oxygen demand (BOD₅), ammonia and phosphorus (Soonthornnonda and Christensen, 2008).

1.2 Problem Statement

As noted earlier, CSO flows are commonplace in populous countries such as the United States. This leads to the need for CSO treatment and management in order to mitigate their harmful effects on the receiving environment. The main form of treatment practiced by most treatment plants is chemical treatment with coagulants and coagulant aids along with physical settling. Some common

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coagulants that are used in treatment plants are iron or aluminium based. Organic coagulants do also exist but are not in widespread use. At EPCOR Gold Bar WWTP, the company uses Alum as a coagulant to treat CSO flows in their EPT system. In order to assess their choice of coagulant and provide potential alternatives that may be more cost effective. To this end, this study explored three common coagulants found in industry in the form of aluminium sulfate, ferric chloride and polyaluminium chloride (PACI).

1.3 Hypothesis

While Alum is the coagulant of choice for many WWTPs, there remain other coagulants that could be more cost efficient and equally, if not more, effective at contaminant removal. Some common coagulants are PACl and ferric chloride. These coagulants may be better at contaminant removal, more cost effective or both.

1.4 Objectives

The objectives of this study were to:

- (1) Determine the important factors affecting the removal efficiency for important parameters such as BOD5, chemical oxygen demand (COD), pH, turbidity, alkalinity, total suspended solids, total volatile suspended solids and phosphorus
- (2) Determine the best performing coagulant out of the three mentioned by observing the effect on the parameters mentioned above.

1.5 Significance of Research

CSOs are a significant environmental hazard to receiving environments. This research aims to determine a coagulant that would minimize the contaminants present in CSO flows while at the same time be cost effective in order to be used commercially in a WWTP. This research would allow WWTPs to continue to operate in a manner that is responsible from an environmental as

well as a public health standpoint.

1.6 Thesis Outline

This thesis consists of six main sections. The first section discusses the background of the project, the importance and relevance of CSO flows in the modern context and the objectives of this study. The second section examines the surrounding literature around the subject of CSOs and CSO treatment including the impact of CSOs and their characterisation, common treatment practices, specific treatment practices in Edmonton, the processes behind coagulation and a review of the legislation in various countries with respect to relevant CSO contaminants. The third section describes the materials and methods used to perform the laboratory analyses during this study along with the kind of experimental design utilized. The fourth section discusses the results of the data analysis, analyzing the contaminant removal ratios, percentage removal values, correlation between TSS and turbidity, impact of varying coagulant dosage on pH, the effect of natural settling, precision of tests carried out across the nine months of sampling, a short comparison with EPCOR data, effects of slow and rapid mixing, pH and alkalinity values for all tests and a short cost-benefit analysis based on the price of each coagulant. The fifth and sixth sections discuss the conclusions of this study and recommendations for future studies in this field.

Chapter 2. Literature Review

2.1 Impact and Characterisation of Combined Sewer Overflows

CSOs are a well-known occurrence throughout major urban centres around the globe. Studies from various corners of the world such as Korea, France, Spain and North America focusing on the constituents of CSO flows have been performed in order to better understand and mitigate the risks of CSOs. A combined sewer system is one in which all flows are accepted into a sewage line in order to prevent the backing up of sewer lines into homes and basements during storm events (City of Edmonton, 2017). These sewage mains eventually end up at the local wastewater treatment plant, where the plant capacity may be exceeded by a large margin during storm events. Since the influent CSO water contains both regular domestic wastewater and debris washed out from streets and open soil, direct ejection into the receiving environment without treatment can result in the build-up of harmful toxins in the receiving environment.

A study conducted at a wastewater treatment plant revealed that CSOs generally consisted of the following contaminants: TSS, Ammonia, nitrogen, phosphorus compounds and heavy metals. The study concludes that the event loads were "very considerable" when it came to TSS, nitrogen, phosphorus, lead and zinc loadings with loadings of 2600-9500 kgs, 300-900 kgs, 3-71 kgs, 0.003-041 kgs and 0.37-0.62 kgs respectively (Diaz-Fierros et al, 2002).

A similar study examined the constituents of urban stormwater runoff from CSO structures as well as the effects of a first flush in urban areas. The parameters that were measured in this study included biochemical oxygen demand (BOD), carbonaceous oxygen demand (COD), total suspended solids (TSS), total Kjeldahl nitrogen, nitrite/nitrate, orthophosphate, total phosphorus (TP), lead and iron. Also examined were the relative effects of undeveloped land, residential and industrial watershed areas to the pollutants unit loading rate. According to the mass loadings observed during the study, the highest pollutant mass loadings were found in high density residential followed by low density residential, industrial and undeveloped watershed in that order. (Ho Lee and Woong Bang, 2000). This indicates that cities with high numbers of high density residential areas would experience higher plant pollutant loadings during CSO events, especially in areas with combined sewage systems.

Another study compared non-rainfall runoff events with stormwater runoff events. Although the non-rainfall event runoff contaminant concentration fluctuated along with the sewer discharge flow, it was observed that the stormwater runoff events had higher Event Mean Concentrations for contaminants such as BOD, TSS, TP, total nitrogen and COD were significantly higher than that of non-rainfall events. In particular, the suspended solids loading rate during the stormwater events was 14 times higher than the non-rainfall events (Kwon et al., 2013).

A study examined the composition of urban stormwater runoff from three separate storm sewers in order to determine what priority pollutants were making their way into the receiving environment untreated. It was observed that out of the 88 chemical substances the researchers were looking for, 55 were found in the stormwater. Of note are the concentrations of metals, polyaromatic hydrocarbons, polychlorinated biphenyls, organotins, alkyl-phenols, phthalates, pesticides and VOCs. Figure 1 shows the location of the Paris sewers where the study was conducted. It was noted that there was a risk of sediment contamination occurring from the metals and PAHs in the water if these flows were to be released untreated into the River Seine after comparison with the Canadian Sediment Quality Guidelines (Zgheib et al., 2012). Table 1 shows the chemicals that were measured but not detected at any site, detected at one site at least and detected at all three sites.



Figure 1: Sampling Site Locations. Clichy refers to the largest CSO outfall located in the Paris conturbation (adapted from Zgheib et al, 2012)

Detected in	Contaminants
Not in stormwater on any site	Cd, Hg, Ni, Pt, dichloroethane, benzene compounds, polychlorinated biphenyls, DDT, chloroform, endosulfan, alachor, isodrin, lindane, chlopyrifos, trifluralin, atrazine
Stormwater on at least one site	Cr, aldrin, chlorfenvinphos, desethylsimazine, simazine, endrin, ethylbenzene, toluene, xylene, tetrachloroethylene, methylene chloride, pentachlorophenol, dieldrin, desethylatrazine
Stormwate on all sites	3 metals, 6 pesticides, 2 organotins, 3 alkylphenols, 16 polyaromatic hydrocarbons, 7 polychlorinated biphenyls, DEHP

Table 1: Detected and Undetected substances in measured stormwater (reproduced from Zgheib et al, 2012)

A follow-up to this study was performed for the case of combined sewer systems in order to evaluate the quality of CSOs in comparison with urban stormwater and regular wastewater. The study once again focused on 88 substances out of which 49 Priority Pollutants (PPs) were detected in the CSOs sampled. The study was performed using the Clichy CSO outfall shown in Figure 1. such COD, Routine wastewater parameters were also tested as TSS, BOD, NH₄, TKN, TP and orthophosphates. Table 2 shows the detected and measured but not detected PPs found in the CSO samples. In order to compare the levels of PPs found in the CSO samples with the levels found in wastewater and stormwater, the study presented a chart with ratios of CSO/WW and CSO/Stormwater levels. This can be seen in Figure 2 below. As shown in the Figure and confirmed by the conclusions of the study, "most hydrophobic organic pollutants", namely PAHs, and some metals that were bound to particulate solids such as lead and copper, were observed at higher concentrations in the CSO as compared to regular wastewater and stormwater. Furthermore, it was discovered that CSO discharges posed "significant environmental risk" as per a comparison done with European Standards. (Gasperi et al., 2012)



Figure 2: Ratios between CSO and median wastewater (adapted from Gasperi et al., 2012)

Detected in	Contaminants
Not in CSO, wastewater and runoff, or with an occurrence of <15%	Cd, Hg, Ni, Pt, dichloroethane, benzene compounds, PCB 192, DDT, carbon tetrachloride, hexachlorobutadiene, hexachlorocyclohexane, endosulfan, alachlor, isodrin, lindane, chlorfencinphos, desethylatrazine, endrin, trifluralin, BDEs, phenols
Not in CSO, but in wastewater and runoff	Chloromethylphenol, benzene, chloroform, dichloromethane, chlorpyrifos, simazine, metaldehyde, PCB 52, pentachlorophenol
CSOs	4 metals, 5 COVs, 9 pesticides, 3 organotins, 3 alkylphenols, 16 polyaromatic hydrocarbons, 7 polychlorinated biphenyls, DEHP, chloroalkanes, deca-BDE

Table 2: Detected and Undetected substances in CSO samples (Gasperi et al., 2012)

Out of the contaminants mentioned in Tables 1 and 2, the ones that would could potentially be removed via Enhanced Primary Treatment would be heavy metals and large organic molecules that would be adsorbed onto the surface of colloids. The results of the aforementioned studies were reinforcement of a study conducted in 2008, which had found the occurrence of 40 out of 66 PPs measured in wet weather effluents (Gasperi et al., 2008).

The presence of PAHs in CSO flows and stormwater was further confirmed by a study where a sampling campaign between four stormwater discharge location and one CSO location revealed that PAHs were present in levels of up to 500 times the Environmental Quality Standards for stormwater and 2000 times for the CSO location (Birch et al., 2011).

A study conducted to determine the role of two wastewater parameters, COD and ammonium, and six organic pollutants with regards to CSO flows both in dry and wet weather. The study concluded that "emissions from CSOs are significant for both pollutants from surface runoff and dry weather flow". Figure 3 shows the percentage of annual loads for each pollutant that is derived from either dry weather, wet weather or CSO flow (Welker, 2007).



Figure 3: Percentage of annual pollution loads of COD, NH4, PAH, DEHP, EE2, E2, EDTA and NTA calculated by pollution load simulation (adapted from Welker, 2007)

A study conducted examined the potential sources of CSOs and which sources affected which groups of contaminants that were found in the CSOs. The study concluded that out of the three sources considered for CSOs, the most significant contributor to CSOs was domestic wastewater, between 27% and 56%, while the remainder was mostly made up by stormwater and some groundwater infiltration. The stormwater contributed mainly TSS and metals while the domestic wastewater contributed large portions of the BOD, ammonium and TP (Soonthornnonda & Christensen, 2007)

As mentioned previously, metals seems to be a common contaminant in CSOs. This was further confirmed by a study where researchers examined the behaviour of various heavy metals during wet weather flows. Figure 4 shows the catchment areas of individual collectors and locations of sampling points. The results of the analysis performed indicated that the concentrations of As, Cr, Cd, Pb, Mn and Fe increased during wet weather flows while the sewage system also demonstrated a considerable degree of nonhomogeneity (Drozdova et al., 2015). Table 3 shows the average daily mass loadings of some metals to a WWTP during dry weather flow and wet weather flow. A study conducted in Paris in 1998 found that the heavy metals found in CSOs may be partially toxic to phytoplankton (Seidl et al., 1998).

*Table 3: The daily pollutant loads in inflow to CWWTP during Dry Weather Flow and Wet Weather Flow in kg day*¹ (reproduced from Drozdova et al., 2015)

Elements	Load (kg/day)	
Hg	DWF 0.023	WWF 0.031
Pb	1.5	2.7
Cu	2.3	2.8
Zn	17	23



Figure 4: Location of WWTP, catchments of individual collectors and locations of 12 sampling points in Ostrava (adapted from Drozdova et al., 2015)

A significant factor that produces CSOs is abundant rainfall. However, not all rain events will

cause enough surface runoff to trigger a CSO event. The relationship between CSOs and rainfall events across over 4000 overflow structures in Quebec was examined in a study. A simple threshold model was utilised in order to correlate rainfall intensity with the occurrence of CSO events. Although each overflow structure exhibited a threshold that was a function of the local conditions and pipe configurations, a general model was able to be developed for the various structures. When validated, the model predicted with a significance of 91.3% the occurrence of CSO events. This proved that there was a simple correlation between the occurrence of CSO events and rainfall intensity which can be measured by means of a simple threshold model (Mailhot et al., 2015).

A comprehensive literature review conducted in 1995 showed that the quality of stormwater is an important parameter in the water treatment process and the variety and concentration of contaminants contained within stormwater pose a significant risk to the receiving environment if released untreated (Makepeace et al., 1995). In the literature review, the authors compared various chemical, physical and biological contaminants with relevant guidelines in order to come to this conclusion. The most critical parameters identified with respect to human health were TSS, aluminum, chloride, chromium, iron, lead, manganese, mercury, total polycyclic aromatic hydrocarbons, benzo(a)pyrene, tetrachloroethylene, fecal coliforms, fecal streptococci, and *Enterococci*. The most critical parameters with respect to aquatic life and health included total solids, TSS, aluminum, beryllium, cadmium, chloride, chromium, copper, iron, lead, mercury, nitrogen, silver, zinc, dissolved oxygen, polychlorinated biphenyl, bis(2-ethylhexyl) phthalate, y-BHC, chlordane, heptachlor, and heptachlor epoxide (Makepeace et al., 1995).

A significant impact of CSO releases to the environment has been the depletion of dissolved oxygen in the receiving waters. Studies have indicated at least the presence of a depletion in DO immediately after the CSO has been released, while some also show an effective depletion of DO for up to a day after the release of DO due to the settled out organic matter at the bottom of rivers (Hvitved-Jacobsen, 1982. Miskewitz and Uchrin, 2013.). However, one study indicated that the hydraulics of the receiving environment may have more of a hand in the depletion of DO than discharges from CSOs (Irvine et al., 2005). The depletion of DO from receiving waters is a concern because almost all aquatic life depend on oxygen for their survival and a depletion in DO could result in the eventual death of multiple life forms in the affected areas. Aside from the immediate depletion of DO at the outfall location, one study suggests that the water column DO would also be depleted up to 5.6 kilometers downstream of the discharge site (Miskewitz and Uchrin, 2013). The major mechanism of removal of organic matter discharged during CSO events appears to be transfer to the bottom of the receiving waters via sedimentation (Hvitved-Jacobsen, 1982).

Another way CSO discharges affect receiving waters is by increasing the levels of harmful bacteria such as *Escherichia Coli*, Fecal Coliforms, *Giardia Lambia* and intestinal enterococci. These bacteria are of particular concern when they are found at drinking water intakes (DWIs). According to some estimates by the WHO, 13 million people die each year from waterborne infections with the majority of these deaths taking place in developing countries. However, the US sees approximately 900,000 cases of waterborne illnesses and 900 deaths resulting from these illnesses each year (Arnone and Walling, 2007). A study indicated that wet weather effluents caused a 1.5 log increase in E. Coli concentrations at these DWI structures while the impact was somewhat lesser at the centre of the river in question with a 0.5 log increase in *E. Coli* concentration (Madoux-Humery et al., 2016). In Paris, a study conducted on a particularly intense CSO event on the bacterial concentration downstream of CSO outlets revealed that directly after the event, E. Coli and intestinal enterococci levels had exceeded normal dry weather flow levels by two orders of

magnitude, decreasing by 66% and 79% respectively after 13-14 hours (Passerat et al., 2011). These two bacteria are considered today to be the best indicator organisms to predict sanitary risk associated with freshwaters (Passerat et al., 2011). A different study also pointed to the fact that simultaneous CSO discharges in a short period of time could lead to elevated levels of *E. Coli* at DWIs (Jalliffier-Verne et al., 2016). The apparent high loadings of harmful bacteria by CSO discharges is further confirmed in a study from the USA where dry weather *Cryptosporidium* and *Giardia* concentrations were compared with CSO end-of-pipe concentrations. The concentrations increased dramatically during CSO discharges, going from 5-105 oocysts/100L to 250-40000 oocysts/100L for *Cryptosporidium* and from 13-6579 cysts/100L to 9000-283000 cysts/100L for *Giardia*. Oocysts are cysts that contain the zygotes needed to form viable bacteria. The study suggested that there was a potential for CSOs to contribute significantly to bacterial loadings to receiving environments (Gibson et al., 1998)

In addition to excess levels of pathogens and heavy metals being found in CSOs, they can also be a source of hormones, micro pollutants and pharmaceuticals. Evidence has shown that CSOs can potentially carry up to 10 times higher concentrations of estrogens, androgens and micro pollutants (Phillips et al., 2012). Some pharmaceutical products such as acetaminophen and nicotine have also been shown to persist in CSO flows even after dilution is taken into account (Benotti and Brownawell, 2007).

Numerous models have been put forth in order to predict the impact CSOs have on receiving waters. One such model links the frequency of overflow events and their volumes to the impact on receiving water quality. The study concluded that the two factors are linked to each other and may be used to predict the quality of receiving waters. However, the subtle relationships involved with other factor limits the applicability of such a model and it must be used with considerable care

(Lau et al., 2002).

2.2 Common Practices in the Treatment of Combined Sewer Overflow

In order to mitigate the risks associated with high CSO flows, water treatment strategies have been developed around the world. These can be divided into three broad categories; physical treatments, chemical treatments and a combination of both.

The majority of CSO treatment strategies rely on a combination of chemical and physical treatments. A few purely physical strategies come in the form of plate settling and gravity settling after the removal of coarse solids in the screening processes found earlier in a WWTP (Metcalf & Eddy, 2003). Another physical treatment is mixing, both rapid and slow. Rapid mixing is generally employed in order to mix chemicals such as coagulants instantaneously into the water stream while slow mixing is utilised in order to encourage floc formation and growth (Metcalf & Eddy, 2003). A few common examples of mixers are static inline mixers, high speed induction mixers, pressurized water jets, turbine and propeller mixers, pumps and paddle mixers (Metcalf & Eddy, 2003).

Chemical treatments are primarily based on a class of chemicals known as coagulants. Coagulants are chemicals that are added to the water matrix in order to destabilize the negatively charged colloidal particles found in the wastewater and allow them to stick to each other and form large flocs. Common coagulants include metal salts, such as aluminium chloride, ferric chloride, polyaluminium chloride, and organic polymers. Flocculation refers to the physical process that takes place after the addition of chemical coagulants where the small colloidal particles mesh together and create large flocs (Metcalf & Eddy, 2003).

The majority of CSO treatments rely on a combination of these two treatment techniques, i.e. chemical coagulants are used in conjunction with rapid and slow mixing in order to settle out

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colloidal solids in the form of flocs.

A unique treatment alternative that has been used in the past are constructed storm treatment reed beds. These reed beds are constructed using naturally reeds and are useful in removing particulate matter, phosphorus and nitrogen from incoming wastewater. Wetlands are generally useful in areas where there is a smaller volume of waste to be treated as higher volumes and flowrates would not be sufficiently treated by the action of the reeds and reed bed. A study performed in the Klamath Basin by CH2M HILL examined the literature surrounding reed beds as wastewater treatment options and found that the general body of literature around this technology seems to show mixed results for both natural and constructed wetlands when it comes to their effectiveness in reducing pollutants from wastewater (CH2M Hill, 2012).

2.2 Treatment of Combined Sewer Overflow in Edmonton

Edmonton is the only major city in Alberta that experiences the phenomenon of CSOs (EPCOR, 2015). The North Saskatchewan River is the city's lifeline and is used for multiple purposes, including as the source of drinking water for the city inhabitants. Another key function performed by the river is that it receives treated wastewater discharge from the GBWWTP as well as storm sewer outfalls. In order to move towards a city with no combined sewers the City of Edmonton government had requested EPCOR to improve the treatment of CSOs before being discharged to the River as well as reduce the amount of sewage that would enter the River during CSO events. As a result, EPCOR commissioned and created the Enhanced Primary Treatment (EPT) initiative whereby existing primary clarifiers would be modified in order to receive 600 MLD of CSO flows over and above the 910 MLD capacity. In addition, extra channels were created in order to bypass CSO flows around the rest of the treatment at the plant and go directly into the River following the EPT steps. The EPT steps consist of addition of aluminum sulfate, also known as Alum, along with

a coagulating agent consisting of polymer to the modified primary clarifiers during CSO events. This is followed by flocculation of the wastewater by the formation and enlargement of clumps of solid material that bind colloidal particles in the wastewater. The flocculated wastewater then flows upward through a series of inclined plates in the primary clarifiers where a great degree of solidliquid separation is achieved. The solid sludge falls to the bottom of the clarifier and is raked out into a sludge collection network while the effluent is discharged into the River (Stantec, 2004). Figure 5 below shows a simplified representation of how the EPT system operates currently at GBWWTP.



Figure 5: Simplified Representation of EPT System at EPCOR Gold Bar WWTP (adapted from Stantec, 2004)

The overflow structure serves as a failsafe in case plant influent flows exceed capacity. Excess flow is then diverted via overflowing over the weirs into a channel that goes straight to the North Saskatchewan River. The screens remove large debris and flotsam from the influent stream. The grit tanks remove large, coarse solids while the primary clarifiers reduce the solids further by gravity settling. If the plant influent flow exceeds the capacity of the bioreactors, the excess flow is diverted to the EPT clarifiers where alum and polymer is added before being sent to the EPT clarifiers. The chemicals are mixed into the water using turbine type mixers with flat blades in a separate chemical addition building (Stantec, 2004). Here, flocs form and settle via inclined plate settling. The Primary Clarifiers differ from the EPT Clarifiers in that the EPT Clarifiers include a section for slow mixing and flocculation after chemical addition while the Primary Clarifiers only

have space for sedimentation to occur. The supernatant is release to the river while the solids join the solids treatment train.

2.3 Coagulation Processes

Coagulation is a process that involves the interactions and collisions between destabilized colloidal particles such that they clump together and grow in size and collective mass (Metcalf and Eddy, 2003). Coagulants are chemicals that neutralize the charged particles that are usually found in colloidal form in wastewater. These are frequently found in the form of inorganic salts containing aluminium or iron. Coagulation is closely followed by the process of flocculation which involves the clumping of the smaller colloidal particles into larger conglomerates that can be easily separated out of solution via gravity. These larger collections of solids are known as flocs (Metcalf and Eddy, 2003). The coagulation process can be affected by temperature through the lowering of the water viscosity as well as the chemical solution viscosity. A lower viscosity value would result in a lower number collisions as well as a lowered velocity gradient resulting in an overall slower rate of floc formation. This is illustrated in a simple formula below in Equation 1:

$$G = \sqrt{\frac{P}{uV}}$$
(Eq 1)

Where G is the velocity gradient, P is the power input, u is the dynamic viscosity and V is the tank volume. A decrease in dynamic viscosity would cause the velocity gradient required to increase unless the power input in also increased proportionally.

Examples of these processes are found in multiple studies performed all across the globe, a sampling of which is presented below.

A coagulant survey carried out by Environment Canada in order to determine the effectiveness and robustness of conventional inorganic coagulants and organic polymeric flocculants as well as coagulants. This effectiveness was measured by means of the TSS removal as well as DOC removal. One of the side effects observed from the chemicals studied was the tendency of overdosing when it came to addition to CSO flows. This overdosing often resulted in a drop in pH. The organic and inorganic coagulants were seen to produce good to excellent removals of both TSS and DOC while the polymeric flocculants showed good TSS removal with low DOC removal (Exall and Marsalek, 2013).

The aqueous chemistry of ferric was explored in a paper from 1983 where a few statements are made regarding the nature of ferric chloride's coagulating activity. The Fe(III) ion is not present in natural environments. Instead, the ion exists as a part of aquocomplexes such as $Fe(H_2O)_6^{3+}$. Additionally, the addition of ferric chloride to water below its solubility limit causes the formation of mono, di and polymeric complexes that assist in the formation of flocs. Figure 6 shows the pC-pH curve for Fe(III) coagulation, indicating concentrations and pH ranges where sweep coagulation occurs. The study also examined the effectiveness of using both Alum and ferric chloride as a dual coagulant, although the conclusion was that using both is not more effective than separate usage (Johnson and Amirtharajh, 1983).



Figure 6: Fe (III) Coagulation pCpH diagram indicating sweep coagulation ranges in the shaded area (adapted from Johnson and Amirtharajh, 1983)

A study similar to this thesis was undertaken in Malaysia in order to determine which out of three coagulants, PACl, ferric chloride and alum was most effective in the treatment of Automotive Wastewater. Jar test apparatus was used during this study with sample pH adjustment with addition of 0.5% concentration anionic polymer. Each coagulant had a wide range of dosages in order to determine the optimum dosage. The samples taken from each sample were analyzed for COD, TSS and heavy metals. It was determined that PACl was the most effective coagulant out of the three with a dosage level of 70 mg/L with 2 mg/L of anionic polymer. The removal levels for COD, TSS and heavy metals were superior for PACl compared to ferric chloride and alum, while the addition of the polymer improved performance for automotive wastewater (Abu Bakar and Abdul Halim, 2013).

Among the different types of wastewater that coagulation and coagulants can be utilised for is

tannery wastewater. Tannery wastewater is usually high in organic, solids and chromium content. In one study, this type of wastewater was treated with alum in conjunction with cationic and anionic polymeric coagulant aids. A control was used in the form of alum alone during the treatment process. The parameters investigated were turbidity, TSS, COD and chromium levels. It was determined that a cationic polymer with a charge density of 40% and MW of 6 million Dalton was most effective along with alum with respect to chromium, turbidity and TSS removals greater than 95% while also achieving good COD removal of around 40% (Haydar and Aziz, 2009). In Windsor, Ontario, a study was carried out to determine the treatability of CSO flows with four different kinds of cationic polymers. Polymers are generally used as coagulant aids and the purpose of the study was to determine the effect of these polymers with respect to the settleability of the sewage that made up CSO flows and the TSS removal ratio. As a secondary finding, it was determined that the CSO flows being received at the reclamation plant had similar characteristics as the flows seen at actual overflow site along the riverfront. Overall, the addition of these polymers had a significant positive impact on the settle ability of CSO sewage (Li et al., 2003). Many of the coagulants mentioned can be used to treat different kinds of wastewater. Some of the aforementioned literature covers treatment of tannery wastewater as well as automotive wastewater. Another type of wastewater that is of specific concern to Alberta is Oil Sands Processaffected Water (OSPW). OSPW is mainly the byproduct of Steam Assisted Gravity Drainage oil sands recovery projects, wherein steam is injected into a well deep below the ground in order to warm and extract the bitumen present in the soil. The condensate from this process is pumped and partially recycled. However, there is always a waste stream of OSPW present. OSPW differs from municipal wastewater in the fact that it is usually highly saline and contains both organic and inorganic materials such as heavy metals. Some of the metals and organic constituents contribute

to the toxicity of OSPW and thus are targets for removal during treatment. A jar test apparatus was used during this study in order to determine the turbidity removal efficiency as well as any toxicity reduction potential of two types of PACl coagulant. One type was chemically synthesized to be 83.6% AL¹³ whereas the other was a commercially available sample. Both coagulants achieved high percentage removals with over 96% turbidity removed. Toxicity was reduced using the chemically synthesized PACl but not with the commercially available PACl (Wang et al., 2016).

Another practical application of coagulation is for the removal of natural organic matter (NOM) during drinking water treatment. Many types of coagulants are used for this purpose, some of which have already been mentioned previously. These include aluminium based coagulants, ferric based coagulants, organic polyelectrolytes, composite organic-inorganic coagulants and electrocoagulation. Figure 7 shows the possible removal mechanisms for NOM during coagulation. Aluminum based coagulants include aluminium sulfate, one of the most common commercial coagulants in use today, as well as aluminum chloride and polyaluminum silicate chloride. Ferric coagulants come in a wide range including ferric chloride, ferric sulfate, polyferric sulfate, polymeric iron chloride, polysilicate ferric and polyferric silicate sulfate. The polymeric coagulants tend to work in a wide range of pH ranges and perform better than their non-polymeric counterparts. Other coagulants include polyelectrolytes, which is a term used for a polymer whose monomeric unit contains an ionisable group. Examples of such coagulants are polydiallyldimethyl ammonium chloride, cationic polyacrylamides and natural cationic polymers. Another potential option for NOM removal has proven to be electrocoagulation, whereby two electrodes of soluble aluminum and iron are used to form polymeric hydroxides, which then cause coagulation to occur (Matilainen et al., 2010).



Figure 7: Possible removal mechanisms for NOM during coagulation (Matilainen et al., 2010)

Important factors in the overall coagulation process are mixing speed and time. Every wastewater and water treatment plant employs both rapid and slow mixing in some manner in order to mix coagulants into the water being treated efficiently. A study was performed in order to determine effectiveness of mixing conditions with respect to TOC and turbidity removal. Jar test apparatus were used to investigate the effect of the G value, indicative of mixing intensity, on water with high organic content. The results showed that between 110 s⁻¹ and 450 s⁻¹, the effective removal of both TOC and turbidity were achieved, whereas anything higher than 450 s⁻¹ showed negligible improvements in TOC removal. These findings were presented as an opportunity for plant operators to reduce their energy input while maximizing removal and treatment efficiencies (Vadasarukkai and Gagnon, 2015).

2.4 Mechanisms of contaminant removal

Wastewater is made up of two major components, inorganic contaminants and organic
contaminants. Inorganic contaminants include parameters such as TSS, TP, OP. Organic contaminants consist of humic and fulvic acids and are largely responsible for the colour observed in untreated, and treated, wastewater (AWWA Committee Report, 1979). The inorganic contaminants are often found in suspension in the form of colloidal particles that are difficult to settle out naturally due to their small size, about 0.001 to 1 micron in diameter (Metcalf & Eddy, 2003). As a result, coagulants are needed in order to destabilize these stable, negatively charged colloidal particles and induce their clumping and eventual forming into flocs of solids. Once these flocs are formed, they are able to be removed by gravity or accelerated gravity settling via inclined plates.

The mechanism behind the destabilization of these particles is best described by the DLVO theory which explains the aggregation of colloidal particles as a combination of the overcoming of repulsive double layer forces between two similarly-charged particles until the attractive particle-particle Van Der Waals forces take over and cause two particles to stick together (Trefalt and Borkove, 2014; Teh et al., 2016). Under normal conditions, the energy barrier that particles are required to overcome in order to coalesce is too high to overcome via Brownian motion. The kinetic energy of the particles need to be increase, or the energy barrier is required to be decreased. The energy barrier can be lowered by four main mechanisms. These are double layer compression, charge neutralization, colloid entrapment and intraparticle bridging (Teh et al., 2016). Other mechanisms that play a role are adsorption of polymeric metal hydroxide species and the formation of metal-hydroxide floc formations known as sweep flocs (Dentel and Gossett, 1988).

According to Dentel and Gossett, iron and aluminium ions at low pH are surrounded by water molecules. As the pH is raised, or more coagulant is added to the water matrix, hydrolysis takes place which releases hydrogen ions into the water and lower the net charge on the metal ions. During this process, dimerization and polymerization may occur, although their formation mechanisms are poorly understood (Dentel and Gossett, 1988). Ultimately, the charged colloidal particles are neutralized by the addition of metal-based coagulants, particularly aluminum, by deposition/adsorption of positively charged metal-hydroxide onto these particles (Dentel and Gossett, 1988; Teh et al., 2016). This would lead to the lowering of the energy barrier by compression of the electric double layers that keep particles in stable suspensions apart from each other and promote the overcoming of the energy barrier and consequent aggregation of particles. Once these particles have been destabilized, the cloud of metal hydroxide particles grows around them and effectively entraps them via this action as well as other colloids once the hydroxide precipitate begins to settle out of solution. These particles are enmeshed and removed regardless of their origin, be it biological in nature or inorganic. However, this process is prone to produce large amounts of sludge (Teh et al., 2016).

The final mechanism of coagulation is intraparticle bridging which increases the rate at which particles are settled out of solution. The addition of linear, long chained polymers is involved in this step with these long particles attaching to particle surfaces by physical attraction or chemical bonding and catching other such "bridges" of polymers, intertwining with them and growing the overall mass of solids into a floc (Teh et al., 2016).

Flocculation occurs in parallel, or very soon after, the first stage of coagulation. Once colloidal particles have been destabilized, the thermal environment present in the water matrix along with concentration gradients cause destabilized particles to move towards each other via Brownian motion. This is known as perikinetic flocculation (Metcalf & Eddy, 2003; Teh et al., 2016). The second stage of flocculation, known as orthokinetic flocculation, involves the addition of shear forces and gentle mixing in order to increase the probability of particle collisions (Metcalf & Eddy,

2003; Teh et al., 2016).

It is worthwhile to note that the solids removed during these processes also contain organic matter which is adsorbed onto their surface pores (AWWA Committee Report, 1979). The removal of some viruses is also helped by perikinetic flocculation due to their small size, smaller than 1 micron (Teh et al., 2016).

A point to note with regards to orthophosphate removal is that not all phosphate is present in particulate form in wastewater. Phosphorus is generally present in soluble and non-soluble forms with each category being further subdivided into reactive orthophosphates and non-reactive phosphorus forms (Metcalf & Eddy, 2003). As a result, simple coagulation and flocculation action may not remove most present phosphorus in wastewater. The mechanism behind orthophosphate removal is complex and involves the formation of complexes between the metal-hydroxide and orthophosphate compounds present in the water resulting in the uptake of orthophosphates onto the metal-hydroxide compound surfaces (Lijklema, 1980). However, the potential for restabilization of charge and consequent resuspension of these metal-hydroxo-phosphate complexes is always a possibility due to factors such as coagulant dose, pH, temperature and phosphate concentration (Lijklema, 1980).

2.5 Legislative Background

The need to legislate the quality of CSO discharges to receiving environment stems from their proven ability to interfere with and damage the aquatic ecosystem. As shown previously, CSO flows can be damaging to fish as well as be the cause for algal blooms in lakes downstream of discharge points. In addition, fecal bacteria and pathogens such as *Escherichia Coli* and Cryptosporidium can cause havoc with the water supply for any people and animals downstream. As a result, many municipalities and countries around the world have taken steps in ensuring that

CSO flows are regulated and treated sufficiently before release to the environment. Presented below are some summary Tables 4 to 6, of all the major wastewater guidelines currently existing around the world including guidelines for relevant CSO parameters.

							Pog	ulated D	arameters					
Guideline	pH range	Turbidit y (NTU)	BOD ₅ (mg/L)	CBOD (mg/L)	TSS (mg/L)	Residual Chlorine (mg/L)	Ammonia (mg/L)	Total Nitrog en	Nitrate-N (mg/L)	Total Phosphor us (mg/L)	Total Coliform (#/100 mL)	Fecal Coliform (#/100 mL)	E. Coli (#/100 mL)	Other (mg/L)
								(mg/L)						
Canada wide,		1	-		1	1	I	1	I	I	I	1	1	I
Not specified	NS	NS	NS	25	25	0.02	1.25 (as N, at 15°C± 1°C)	NS	NS	NS	NS	NS	NS	
Alberta, 2013	(Govern	ment of Al	berta, 20	16)				•			1		<u> </u>	•
Secondary effluent (population< 20,000)	NS	NS	NS	25	25	NS	NS	NS	NS	NS	NS	NS	NS	
Tertiary effluent (population >20,000)	NS	NS	NS	20	20	NS	NS	NS	NS	NS	1000	200	NS	
British Colum	bia, 2016	6 (Governn	nent of B	ritish Col	umbia, 2	2016)	<u> </u>	<u> </u>		1	1		<u> </u>	L
Municipal effluent to streams, rivers, estuaries for max daily flow >50m ³ /d (dilution ratio)	6-9	NS	<pre>≤ 45 (≥40: 1) ≤10 (≥10: 1)</pre>	NS	≤ 45	NS	NS	NS	NS	≤1	NS	1	NS	Orthophos phate: ≤0.5
Municipal effluent to lakes for max	6-9	NS	≤ 45	NS	≤ 45	NS	NS	NS	NS	≤1	NS		NS	Orthophos phate: ≤0.5

¹ "If discharging to shellfish bearing waters at the edge of the initial dilution zone, the median or geometric mean MPN of fecal coliform organisms must be less than 14/100 mL, with not more than 10% of the samples exceeding 43/100 mL; if discharging to recreational use waters, the geometric mean number of fecal coliform organisms at the edge of the initial dilution zone must be less than or equal to 200/100 mL"

	Regulated Parameters													
Guideline	pH range	Turbidit y (NTU)	BOD₅ (mg/L)	CBOD (mg/L)	TSS (mg/L)	Residual Chlorine (mg/L)	Ammonia (mg/L)	Total Nitrog en (mg/L)	Nitrate-N (mg/L)	Total Phosphor us (mg/L)	Total Coliform (#/100 mL)	Fecal Coliform (#/100 mL)	E. Coli (#/100 mL)	Other (mg/L)
daily flow >50m³/d														
Municipal effluent to open marine waters for max daily flow >50m ³ /d Municipal	6-9	NS	≤ 45 ≤ 45	NS	≤ 45 ≤ 45	NS	NS	NS	NS	NS	NS NS		NS NS	
effluent to embayed marine waters for max daily flow >50m ³ /d	0-9		≥ 43	NS	≥ 43		INS	113	113		INS .			
United States	2010 (U	SEPA, 201	D)											
Secondary Treatment (30 day avg)	6-9	NS	30	25	30	NS	NS	NS	NS	NS	NS	NS	NS	
Secondary Treatment (7 day avg)	6-9	NS	45	40	45	NS	NS	NS	NS	NS	NS	NS	NS	

		Regulated Parameters												
Guideline	pH range	Turbidity (NTU)	BOD ₅ (mg/L)	COD (mg/L)	TSS (mg/L)	Residual Chlorine (mg/L)	Ammonia (mg/L)	Total Nitrogen (mg/L)	Nitrate-N (mg/L)	Total Phosphorus (mg/L)	Total Coliform (#/100 mL)	Fecal Coliform (#/100 mL)	E. Coli (#/100 mL)	Other (mg/L)
Australia, 1997	(Agricu	lture and R	lesource	Manage	ment Co		ustralia and	New Zeala	and, 1997)					
Primary Effluent	NS	NS	120- 250	NS	80- 200	NS	NS	30-55	NS	6-14	NS	NS	10 ⁶ - 10 ⁷	
Secondary Effluent	NS	NS	20-30	NS	25-40	NS	NS	20-50	NS	6-12	NS	NS	10 ⁵ - 10 ⁶	
Tertiary Effluent	NS	NS	2-5	NS	2-5	NS	NS	<10	NS	<1	NS	NS	<10 ²	
EU, 2014 (Euro	pean Co	mmission,	2010)											
NS	6-9.5	1-15	10-70	70- 100	5-60	70-350	NS	15-30	NS	1-10	2	100-10000	10- 1000 00	
Ireland, 2001 (Attorney	y General o	of Ireland	l, 2001)										
Secondary Effluent (10,000-100,000 p.e.)	NS	NS	25	125	35	NS	NS	15	NS	2	NS	NS	NS	
Secondary Effluent (>100,000 p.e.)	NS	NS	25	125	35	NS	NS	10	NS	1	NS	NS	NS	
Japan, 2015 (G	overnm	ent of Japa	n, 2015)			_				-			_	
NS South Africa, 2	5-9 010 (So ı	NS u th African	160 Drinking	160 g Water A	200 Authority	NS / , 2010)	NS	120	NS	16	300	0/cm ³	NS	
NS	5.5- 9.5	NS	NS	75	25	0.25	3	NS	15	NS	NS	1000	NS	

Table 5: Wastewater Effluent Standards in selected Developed countries

							Re	gulated P	arameters	;				
Guideline	pH range	Turbidity (NTU)	BOD₅ (mg/L)	COD (mg/L)	TSS (mg/L)	Residual Chlorine (mg/L)	Ammonia (mg/L)	Total Nitrogen (mg/L)	Nitrate-N (mg/L)	Total Phosphorus (mg/L)	Total Coliform (#/100 mL)	Fecal Coliform (#/100 mL)	E. Coli (#/100 mL)	Other (mg/L)
China, 2002 (Po	eoples R	epublic of	China, 20	002)							() /			
Grade I A ²	6-9	NS	10	50	10	NS	Temp ≤ 12°C: 5 Temp ≥ 12°C: 8	15	NS	WWTP built ≤ 2005: 1 WWTP built ≥ 2006: 0.5	NS	NS	10 ³	Total Hg: 0.001 Total Cd: 0.01 Total Cr: 0.1
Grade I B ³	6-9	NS	20	60	20	NS	Temp ≤ 12°C: 8 Temp ≥ 12°C: 15	20	NS	WWTP built ≤ 2005: 1.5 WWTP built ≥ 2006: 1	NS	NS	104	Total Cr ⁶⁺ : 005 Total As: 0.1 Total Pb: 0.1
Grade II ⁴	6-9	NS	30	100	30	NS	Temp ≤ 12°C: 25 Temp ≥ 12°C: 30	-	NS	3	NS	NS	104	
Grade III ⁵	6-9	NS	60 ⁶	120 ⁷	50	NS	-	-	NS	5	NS	NS	-	
Egypt, 2010 (Eg	gyptian l	Invironme	ntal Affa	irs Ageno	cy, 2010)									
Effluent to marine environment	6-9	NS	60	100	60	NS	3	10	NS	2	1000/100 cm ³	NS	NS	Se: 0.001 Hg: 0.001 Pb: 0.01

Table 6: Wastewater effluent standards in selected developing countries

² Basic requirement for water reuse, when the WWTP discharges effluent into water body with limited dilution capacity (like small lakes and rivers)

³ When the effluent is discharged into type III surface water body (excluding area that is protected as drinking water source and swimming zone), or is discharged into type II sea waters (defined by GB3097) and enclosed/semi-enclosed water bodies such as lakes and reservoirs

⁴ When the effluent is discharged into type IV and V water bodies, or type III and IV sea waters

⁵ For WWTP in small towns that are located in non-critical conservation basin or outside the protection zone of drinking water source

⁶ When BOD₅ >160 mg/L removal should be > 50%

⁷ When COD > 350 mg/L removal should be > 60%

							Re	gulated P	arameters					
Guideline	pH range	Turbidity (NTU)	BOD₅ (mg/L)	COD (mg/L)	TSS (mg/L)	Residual Chlorine (mg/L)	Ammonia (mg/L)	Total Nitrogen (mg/L)	Nitrate-N (mg/L)	Total Phosphorus (mg/L)	Total Coliform (#/100 mL)	Fecal Coliform (#/100 mL)	E. Coli (#/100 mL)	Other (mg/L)
														Cd: 0.01 As: 0.01 Cr: 0.01 Cu: 1 Ni: 0.1 Fe: 1.5 Mn: 0.1 Zn: 1 Ag: 0.05 Pesticides: 0.2
Jamaica, 2015					1			NG	NC	NC	NG	2001401	NG	
Kingdom of Sau	6-9 Idi Arab	NS	20 bu-Rizai	NS	20	NS	NS	NS	NS	NS	NS	200MPN	NS	
	6-9	75	25	150	15	0.5	1	5 (TKN)	NS	1	1000MPN	NS	NS	
Oman, 2013 (A	RWA, 20			1				. ,						<u> </u>
Liquid effluent to marine environment	NS	NS	20	200	30	0.4	1	15	15	2	NS	1000/L	NS	
Jordan, 1991 (N	Ainistry	of Water a	nd Irriga	tion, 199	91)	•		•						
Requirement for discharges of Industrial effluents to valleys and rivers	6.5-9	NS	50	150	50	NS	5	-	12	15	-	NS	NS	SO4: 500 Cl ⁻ : 500 F: 1.5 Al: 5 As: 0.05 B: 1 Cr: 0.1 Cu: 2 Fe: 1 Mn: 0.2 Ni: 0.2 Pb: 0.1 Se: 0.02

		Regulated Parameters												
Guideline	pH range	Turbidity (NTU)	BOD₅ (mg/L)	COD (mg/L)	TSS (mg/L)	Residual Chlorine (mg/L)	Ammonia (mg/L)	Total Nitrogen (mg/L)	Nitrate-N (mg/L)	Total Phosphorus (mg/L)	Total Coliform (#/100 mL)	Fecal Coliform (#/100 mL)	E. Coli (#/100 mL)	Other (mg/L)
														Cd: 0.01 Zn: 15 Sn: 0.1 Hg: 0.001 Nematode <1
Requirement for discharges of Industrial effluents to sea	5.5-9	NS	-	200	-	NS	12	125	-	-	4	NS	NS	As: 0.1 Cr: 0.3 Cu: 0.1 Fe: 2 Mn: 0.2 Ni: 0.02 Pb: 0.1 Se: 0.02 Cd: 0.07 Sn: 1 Hg: 0.001
Requirement for discharges of Industrial effluents for groundwater recharge	6.5-9	NS	50	150	-	NS	5	-	12		-	NS	NS	SO ₄ : 500 Cl ⁻ : 500 F: 1.5 Na: 400 Al: 0.3 As: 0.05 B: 1 Cr: 0.05 Cu: 2 Fe: 1 Mn: 0.2 Ni: 0.1 Pb: 0.1 Se: 0.05 Cd: 0.02 Zn: 15 Sn: 0.1

	Regulated Parameters													
Guideline	pH range	Turbidity (NTU)	BOD₅ (mg/L)	COD (mg/L)	TSS (mg/L)	Residual Chlorine (mg/L)	Ammonia (mg/L)	Total Nitrogen (mg/L)	Nitrate-N (mg/L)	Total Phosphorus (mg/L)	Total Coliform (#/100 mL)	Fecal Coliform (#/100 mL)	E. Coli (#/100 mL)	Other (mg/L)
Requirement for discharges of Industrial effluents for reuse for irrigation	6.5-4	NS	-	-	100	NS	5	50	30	-	-	NS	NS	Hg: 0.001 SO4: 400 Cl ⁻ : 350 HCO ₃ : 500 Al: 5 As:0.1 B: 1 Cr: 0.1 Cu: 0.2 FE: 5 Mn: 0.2 Pb: 1 Se: 0.02 Cd: 0.01 Zn: 15 Sn: 0.1 Hg: 0.001 Nematode <1

Chapter 3. Materials and Methods

The chemicals used in this study were the following:

- Aluminium Sulfate (Alum)
- Ferric Chloride
- Polyaluminium Chloride (PACl)
- Praestol cationic polymer

The Alum, ferric chloride and PACl were used as coagulants whereas the polymer was used as a coagulants aid.

The Alum used in this study was close to 100% pure from Fisher Scientific (CAS: 7784-31-8) with molecular formula Al₂S₃O₁₂ · 18H₂O, molecular weight 666.42 and in a solid form. The ferric chloride was from Sigma-Aldrich (CAS: 10025-77-1) with a >98.0% purity in the form of solid chunks. The molecular weight was 270.30 and the molecular formula was FeCl₃ · 6H₂O. The PACl was a sample obtained from supplier ClearTech under the trade name "ClearPAC 180". The chemical is described by the supplier as Polyhdroxy Aluminum Chloride, a clear liquid with a slight yellowish colour. Polyaluminum chloride is the name given to the family of compounds defined by the formula: Al_m(OH)_nCl_{3m-n} where $0 \le n \le 3m$ and where $m \ge 1$. The OH to Al ratio is known as the basicity. The specific gravity of the sample was 1.37 while the Al₂O₃ w/w % is 17.2% with a basicity of 43%. The coagulant aid used was cationic and called Praestol 858 BS (CAS: 69418-26-4). The active ingredient was Ethanaminium, N,N,N-trimethyl-2-[(1-oxo-2-propenyl)oxy]-, chloride. The approximate bulk density was 650 kg/m³. A stock solution of the polymer was prepared in order to use in all experiments.

3.1 Experimental Design

3.1.1 Factorial Design

A three-factor, two-level factorial design was chosen in order to determine the ideal mixing conditions using a jar test apparatus, as well as the effectiveness of the coagulants under investigation. The coagulants investigated were aluminium sulfate, polyaluminium chloride and ferric chloride, at both a low dose and a high dose. The rapid and slow mixing conditions were chosen based on the physical limits of the apparatus used. The jar test apparatus has a lower limit of 15 RPM and an upper limit of 300 RPM. Mid points were not used in this factorial design due to the logistical difficulties in performing all the different doses for all coagulants with the requisite amount of replicates needed for statistical strength. The settling time was determined by the approximating residence time of a primary clarifier, about 1.5 hours. One hour was chosen in order to obtain maintain similar conditions as are found in a clarifier. Additional points would have been useful in determining the optimum dosage levels for each coagulant. The factorial design can be seen in Table 7 below. The factorial design was implemented between May 2016 and March 2017 in order to conduct multiple different repetitions of these experiments, with different levels used for the high and low level coagulant doses. The most complete run of experiments, the one performed in March 2017, is the one that is highlighted in this study. The rest of the raw data can be found in Appendix.

The dose levels for the March run are indicated below in Table 7. An equivalent amount of active aluminium was chosen as the basis for these dose levels as indicated in Equation 2. For ferric chloride, the following stoichiometric equations were applied in order to determine the equivalent amount of active iron needed:

$$Al_{2}(SO_{4})_{3} \cdot 18H_{2}O + 3Ca(HCO_{3})_{2} \Leftrightarrow 3CaSO_{4} + 2Al(OH)_{3} + 6CO_{2} + 18H_{2}O$$
(Eq 2)

$$2FeCl_3 \cdot 6H_2O + 3Ca(HCO_3)_2 \Leftrightarrow 3CaCl_2 + 2Fe(OH)_3 + 6CO_2 + 12H_2O$$
(Eq 3)

		Factoria	l Design						
	Experiment 1	Experiment 2	Experiment 3	Experiment 4					
	(1/1)	(1/-1)	(-1/1)	(-1/-1)					
Rapid Mixing	300 rpm - 3 min	300 rpm - 3 min	150 rpm - 1 min	150 rpm - 1 min					
Slow Mixing	30 rpm - 20 min	15 rpm - 10 min	30 rpm - 20 min	15 rpm - 10 min					
Settling	1 hr	1 hr	1 hr	1 hr					
Alum	4.05 mg A	l/L – 10.15 mg Al/L (50 mg/L Alum – 125	mg/L Alum)					
Ferric Chloride	8.38 mg Fe	/L – 20.95 mg Fe/L (2	23.4 mg/L FeCl3 – 69	mg/L FeCl3)					
PACI	4.05 mg Al/L – 10.15 mg Al/L (0.030 mL/L PACI – 0.075 mL/L PACI)								
Analyzed	рН	Turbidity	TSS	TVSS					
Parameters		Ortho-phosphate	COD						

Table 7: Factorial Design used for all experiments in this study

3.1.2 Jar Test

In order to carry out the factorial design, a B-KER² Jar Test apparatus with a 3-inch wide Phipps & Bird stirrer was used. The jars are shown below in Figure 8. Each jar held two litres of liquid and measured 11.4 cm by 11.4 cm wide at the mouth. The supernatant sample from each jar was withdrawn using 30 mL or 60 mL syringes from the top 2% of the supernatant in order to obtain the clearest supernatant possible.

At the beginning of each run, the jars were labelled with the appropriate coagulant and amount that would be added. The Primary Influent (PI) collected from the GBWWTP was tested for the TSS value. After this value was obtained, a dilution ratio was calculated to determine how much dilution water would be needed to achieve average CSO TSS levels. The PI was then mixed in a large garbage bin, shown in the Appendix, along with deionized water (DI) with a large plastic stirring rod. This solution was then carefully added to the two-litre mark in each jar. The coagulant and coagulant aid were then added simultaneously in each jar, following which the impellors were tuned to the desired RPM and length of time for each experiment. After the completion of the experiment, the jars were left to settle for one hour. Either 60 mL or 30 mL syringes were then used to withdraw supernatant samples from the top 2% of the liquid surface, taking care to disturb the settled flocs as little as possible. This supernatant was transferred to labelled dark glass bottles, capped and stored in a cold storage room at 4 °C overnight. A sample bottle of diluted PI was also stored in this manner. In order to obtain replicate data, each jar was duplicated with regards to the amount of coagulant and coagulant aid added as well as mixing conditions. The assignment for each jar can be seen in Table 8 below.

The dose levels were based on a study conducted by EPCOR in 2015 (EPCOR, 2015) where the chosen levels of Alum investigated were 50 mg/L to 75 mg/L. In order to obtain a range of doses and be as broad as possible, a range of 50 mg/L to 125 mg/L Alum was chosen for all runs. In order to remain consistent in comparison with the other coagulants, the active Al species was calculated on a molar basis for all coagulants, including the equivalent amount of active Fe for FeCl₃ on a molar basis, and the PACl and ferric chloride doses were adjusted accordingly to match the Alum levels. These molar value were converted to mass values using the atomic masses of each element.

Jar	Coagulant and Level
Blank	None
1A/B	10.14 mg Al/L Alum

Table 8: All Jars and respective coagulants with levels

2A/B	4.05 mg Al/L Alum
3A/B	61 mg Fe/L FeCl ₃
4A/B	24 mg Fe/L FeCl ₃
5A/B	10.14 mg Al/L PACl
6A/B	4.05 mg Al/L PAC1

3.2 Analytical Methods

3.2.1 Laboratory Analysis

After the refrigeration of the supernatant samples overnight at 4 °C, the samples were moved to the analysis laboratory for further analysis. For each analysis, the samples were taken directly from the sample bottle, or the relevant probe was inserted directly into the bottle. Each sample bottle was inverted a few times before proceeding with any analysis in order to ensure a homogenous sample was analysed.

3.2.1.1 pH

A Fischer Scientific pH meter and probe were used for this analysis. The meter was calibrated using standards with pH 4, 7 and 10 before each experiment. The pH was measured in order to observe any changes in pH that may result as an unintended consequence of treatment. Each sample bottle was inverted multiple times to ensure homogeneity in the sample before removing the cap and inserting the pH probe into the bottle until partially submerged in the liquid. Some carbon dioxide may have been dissolved into the sample while inverting although the effect of this on the measurement was assumed to be negligible. A measurement was taken after the reading had stabilized. The probe was rinsed with DI water and wiped with a soft wipe. Each measurement was taken twice in order to ensure replicates.

3.2.1.2 Turbidity

Two different turbidity meters were used in the determination of turbidity. A hand held Oakton Turbidimeter field model T-100 was used from the third sampling campaign onwards while a model 965 Orbico-Hellige Digital Direct Reading Turbidimeter was used from the initial sampling campaign up until the second campaign inclusive. Each sample bottle was inverted multiple times to homogenise the sample before transferring a small amount to the clear glass turbidity bottles for testing. The glass bottles were then inverted multiple times, placed in the holder and covered with a dark cap to prevent outside light from interfering with the measurement. For the meter used in the first experiments, a measurement was recorded once a relatively stable reading was observed on the display. For the field meter used in the later experiments, the "Read" button was pressed following which the meter displayed a firm reading after a few moments. Each glass bottle was rinsed 2-3 times with DI water after usage and used again if needed. Each sample bottle was measured twice in order to obtain replicate data. Both meters were calibrated before each usage.

3.2.1.3 TSS and TVSS

The Total Suspended Solids is a measure of how many suspended solids are in a sample. The Total Volatile Suspended Solid (TVSS) is a measure of how much of the TSS is organic in nature and thus, vaporizes at 550 °C. The Standard Methods were followed for both of these tests (AWWA, 1999).

Each sample bottle was inverted multiple times to homogenise the sample. Aluminium weighing boats were prepared, marked and placed in an oven at around 120 °C for approximately 20 minutes. They were then pre-weighed along with a Whatman 47 mm diameter, 1.5 micron filter paper in each boat. All equipment such as plastic apparatus and forceps were washed with detergent and DI water beforehand. Using a plastic filtration apparatus hooked into the laboratory vacuum line, 50

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mL of each sample was filtered into a waste beaker through the filter paper placed within the plastic apparatus. The filter paper was then placed back onto the aluminium boats using forceps and dried in the oven at 120 °C for 1 hour. They were left in a desiccator to cool and then carefully weighed at the same scale as the pre-weighing. The scale was tared between each boat in order to obtain as accurate a reading as possible. Duplicates were used for each sample bottle.

Following the TSS, the filter papers and weighing boats were kept on a tray and covered up in order to lessen the impact of dust deposition. They were then placed in a Fischer Scientific Isotemp Muffle Furnace and heated up to 550 °C for one hour followed by a cooling cycle to room temperature. The boats were then weighed once more on the same weighing scale and the weights recorded. The boats and filters were then discarded.

3.2.1.4 COD

Chemical Oxygen Demand is a measure of the amount of oxygen that can be chemically oxidized by dichromate in an acid solution (Metcalf & Eddy, 2003). In the context of wastewater, it provides an indication of the amount of organic material in any given sample.

Two different methods of COD were utilised through the sampling campaigns. One is the COD HR HACH kit (TNT 822) which follows the USEPA Reactor Digestion Method and is meant for COD expected in the range of 20 to 1500 mg/L. The other is based on the AWWA Standard Methods and involves the preparation of reagents and digestion in special COD test tubes.

The HACH method involved the addition of 2 mL of sample to the pre-prepared HACH vials followed by digestion in a preheated reactor for 2 hours at 150 °C. After being left to cool at room temperature and wiped carefully without mixing the residue at the bottom of the tube, a UV Absorbance Spectrophotometer is used to measure and calculate the amount of oxygen consumed in each vial.

The AWWA Standard Method procedure involved the formulation of the following reagents: digestion solution from potassium dichromate, concentrated sulfuric acid reagent and mercuric sulfate in DI water, sulfuric acid reagent from a small amount of silver sulfate dissolved in a large quantity of concentrated sulfuric acid and stock potassium hydrogen phthalate (KHP) solution prepared from DI water and dried KHP powder. Each test tube received 3.5 mL of sulfuric acid reagent, 2 mL of digestion solution and 2 mL of either the blank, standard or sample. The tubes were all digested simultaneously at 140 °C for 1.5 hours before cooling and wiping. The Spectrophotometer was zeroed using the blank at a wavelength of 600 nm. The standards were used to create a calibration curve against which the rest of the measurements were compared.

3.2.1.5 Phosphorus

Phosphorus removal is of interest to wastewater treatment as it is an important factor in algal blooms in the receiving environment (Metcalf & Eddy, 2003). For these sampling campaigns, two different methods were employed to determine the amount of phosphorus in the sample. The first was the HACH Method 10210 to measure total phosphorus (TP) using the ascorbic acid method. The second was via anion analysis through Ion Chromatography (IC), where the phosphate ion in a filtered sample was measured and compared to 5 standards. Total Phosphorus (TP) was not measured for the final sampling campaign.

The HACH method involved the mixing of a solid reagent after addition of 0.50 mL of sample to the test vial followed by vigorous shaking and digestion at 100 °C for 1 hour. After letting the vial cool to room temperature, a different solid reagent was mixed thoroughly with the solution and allowed to react for 10 minutes before wiping and measuring in the UV Spectrophotometer.

For the IC method, approximately 1 mL from the sample bottles were filtered using 30 mm, 0.2 micron pore size syringe filters into vials for analysis. The IC system was primed and the pump

was purged of all air bubbles, which the DI water eluent bottle was filled to mark and sonicated to remove any air bubbles as well. The sample vials were placed in the autosampler and the system was switched on and allowed to run after a steady baseline conductivity was reached. After the completion of all replicates, the system automatically turned off and the data was extracted via a USB device.

3.2.1.6 Alkalinity

Alkalinity in wastewater is an important factor when it comes to chemical and biological treatment options. It also buffers the wastewater pH against the addition of any acids. In essence, it is a measure of the buffering capacity of any given wastewater stream (Metcalf & Eddy, 2003).

The alkalinity was measured via titration for all the sampling campaigns, except for the last campaign where alkalinity was not measured.

In order to measure alkalinity, the titrant solution needed to be prepared and standardized. The preparation of the solution involved the addition of boiled and cooled DI water to a small quantity of concentrated sulfuric acid in order to make a 0.02 N sulfuric acid solution. The standardization was performed by making a 0.02 N solution of sodium carbonate powder dried in a muffle furnace at 250 °C for 4 hours and then titrating this solution with the sulfuric acid solution prepared previously until the pH reaches 4.50. The following calculation yields the normality of the acid titrant: $(A \times B)/(53.00 \times C)$ where A is the weight of the dried sodium carbonate used, B is the volume of sodium carbonate solution used as the titrate and C is the total volume of the acid titrant used in the standardization.

Once the normality of the acid titrant is found, the following calculation was used to determine the alkalinity of any given sample:

$$mgCaCO_{3}/L = \frac{mL \ acid \ used \times normality \ of \ the \ acid \times 50,000}{mL \ sample}$$
(Eq 4)

This titration was performed by two different auto-titrators throughout the sampling campaigns.

3.2.2 Results Analysis

3.2.2.1 Statistical Analysis

A three-factor ANOVA analysis was performed on all relevant processed data sets in order to determine if there was a statistical significance for the factors used in the factorial design as well as their interactions. A confidence level of 95% (Alpha of 0.05) was used for this analysis. A two tailed T-test was also performed on the percent contaminant removal means for both high and low doses of Alum and PACl in order to determine if the two means were significantly different or not, with an alpha of 0.05. All tests performed in the last sampling campaign were performed in replicates in order to obtain standard deviation values and error bars. These are represented on most figures shown.

3.2.2.2 Cost Benefit Analysis

The price of three chemical coagulants was determined via a chemical supplier, ClearTech, and their unit cost was compared against the removal efficiencies obtained from each coagulant in order to determine the most cost effective coagulant.

Chapter 4. Results and Discussion

The results from four sampling campaigns, each following the two-level factorial design mentioned in the "Materials and Methods" section, are shown below. Four sampling campaigns, each with four experiments were carried out between the months of June 2016 and March 2017. The first campaign took place during the rainy season and therefore used real CSO water. The subsequent campaigns utilised dry weather flows diluted with distilled water, usually in a 50-50 ratio by volume, although some were split 25-75 with 75% distilled water.

The factorial design resulted in the following equations of best fit. Four equations with all coagulant data factored in, four each for each of the three coagulants. All the equations were determined with respect to contaminant removal ratios (RR). The equations for all coagulants are: TSS RR = 16.6 - 0.63A - 3.0B - 6.7C + 0.33AB + 0.28AC + 0.94BC - 0.13ABC (Eq 5) TVSS RR = 14.8 + 0.51A - 2.9B - 6.0C - 0.05AB - 0.25AC + 0.87BC + 0.04ABC (Eq 6) OP RR = 0.44 + 0.02A - 0.11B - 0.11C + 0.07AB + 0.00AC + 0.01BC - 0.02ABC (Eq 7) COD RR = 22.8 + 0.76A - 6.3B - 8.9C - 5.0AB + 0.22AC + 2.1BC + 2.4ABC (Eq 8) The equations for Alum are:

TSS RR = 20.6 - 0.36A - 3.8B - 8.4C + 0.37AB - 0.23AC + 1.1BC + 0.12ABC(Eq 9) TVSS RR = 18.3 + 1.1A - 3.6B - 7.4C - 0.23AB - 0.87AC + 1.0BC + 0.39ABC(Eq 10) OP RR = 0.60 + 0.03A - 0.16B - 0.18C + 0.09AB + 0.00AC + 0.03BC - 0.03ABC(Eq 11) COD RR = 27 + 1.6A - 7.0B - 11C - 5.9AB - 0.39AC + 2.5BC + 1.9ABC(Eq 12)

The equations for ferric chloride are:

TSS RR = 9.6 - 0.45A - 1.6B - 4C + 0.48AB + 0.28AC + 0.68BC - 0.23ABC(Eq 13)

 $TVSS RR = 8.5 + 0.26A - 1.5B - 3.5C + 0.23AB - 0.01AC + 0.64BC - 0.16ABC \quad (Eq 14)$

$$OP RR = 0.22 + 0.01A - 0.05B - 0.04C + 0.04AB + 0.00AC - 0.00BC - 0.01ABC \quad (Eq 15)$$

$$COD RR = 12.9 + 0.19A - 4.2B - 5.3C - 3.8AB - 0.01AC + 1.4BC + 1.7ABC$$
(Eq 16)
The equations for PACl are:
$$TSS RR = 19.6 - 1.1A - 3.6B - 7.8C + 0.14AB + 0.78AC + 1.0BC - 0.30ABC$$
(Eq 17)

 $TVSS RR = 17.7 + 0.18A - 3.7B - 7.0C - 0.15AB + 0.14AC + 0.94BC - 0.12ABC \quad (Eq 18)$

$$OP RR = 0.50 + 0.02A - 0.11B - 0.11C + 0.09AB + 0.01AC + 0.0BC - 0.02ABC \quad (Eq 19)$$

$$COD RR = 28.5 + 0.46A - 7.8B - 10C - 5.4AB + 1.1AC + 2.4BC + 3.6ABC$$
(Eq 20)

Where,

A = Rapid Mixing (-1 or +1)

B = Slow Mixing (-1 or +1)

C = Coagulant Dosage (-1 or +1)

As per the factorial design, each of these three factors had a high level and a low level. Each of the coefficients in each equation indicate the relative impact of the corresponding factor, or multiple factor interaction, on the value of the contaminant removal ratio. Three-factor ANOVA analysis was performed on each equation and data set with an alpha of 0.05, or a confidence level of 95%. Table 9 shows the groups of equations as well as the factors that were statistically significant for each group.

Coagulant group	Contaminants	Statistically significant factors and
		interactions
	TSS	B, C
All	TVSS	B, C
	OP	B, C
	COD	B, C, AB

Table 9: Statistically significant factors for contaminant removal ratios with a confidence level of 95%

Alum	TSS	B, C, AB, BC
	TVSS	A, B, C, AC, BC
	OP	A, B, C, AB, AC, ABC
	COD	B, C, AB
Ferric Chloride	TSS	A, B, C, AB, AC, BC, ABC
	TVSS	A, B, C, AB, AC, BC, ABC
	OP	A, B, C, AB, BC
	COD	B, C, AB, BC, ABC
PACI	TSS	A, B, C, AC, BC
	TVSS	A, B, C, AC, BC
	OP	A, B, C, AB, BC
	COD	B, C, AB, BC, ABC

It can be observed from Table 9 that C, or the coagulant dosage, was the most important and statistically significant factor in all the equations mentioned above. Another important factor was B, or slow mixing. The p values ranged from 0.046 for TSS to 0.005 for COD with respect to Factor B. The p values ranged from 0.028 for OP to 0.0001 for TSS with respect to Factor C. A Factor was considered statistically significant if the p value was found to be lower than 0.05. The individual coagulants showed a dependence on many factors and their interactions, however when combined, all coagulants were observed to dependent on coagulant dose and slow mixing.

4.1 Final Sampling Campaign Results

The results from the final sampling campaign are shown below. These are the most appropriate results to display as all the materials and methods used across the campaigns were pruned down

to the most effective and essential by the time this campaign was carried out. Although real CSO wastewater would have been more appropriate, the methods used in the first sampling campaign were not fully compliant with the AWWA Standard Methods and thus some of the data was not usable. The coagulant dosages were also slightly different from the final sampling campaign and not based on the equivalent Al basis used in the final sampling campaign. Some of the parameters that were not measured in the final campaign were Alkalinity and total phosphorus due to the time consuming nature of both tests while not yielding sufficiently useful data in return. Figures 11 to 15 show the turbidity, TSS, orthophosphate, TVSS and COD measured, respectively, for each experiment and each jar. Error bars were added based on the standard deviation obtained from duplicates for the experiment as well as duplicates in measurement for each data point.



Figure 8: Turbidity results with error bars for final sampling campaign

As expected, the PI turbidity was the highest measured out of all the jars. The blank jar showed significant reduction in turbidity although not as pronounced as when the coagulants were added. The high doses of PACl, 10.14 mg AL/L, were observed to have the lowest NTU values out of all

the experiments, which were approximately 3.42 NTU. The relatively low level of turbidity observed in the blank jar, 37.8 NTU on average, indicates that roughly half of the particles in the Primary Influent were large enough to be removed via natural settling. The rest were actively removed after chemical coagulants were added and flocs were formed and settled. The treatment guideline used for turbidity was found in the British Columbia Municipal Wastewater Regulation (Government of British Columbia, 2012) and was 5 NTU as the allowable turbidity of released water. This limit is meant for Class A effluent which is effluent that results from advanced treatment with the addition of disinfection and nitrogen reduction. This is much higher than the level of treatment seen in this study. The 10.14 mg Al/L dose of PACI was observed to meet and exceed this guideline, while the equivalent Alum dose also demonstrated high turbidity removal that exceeded the guideline on two occasions.



Figure 9: TSS results with error bars for final sampling campaign

As expected, the PI TSS mirrored the turbidity and was the highest measured out of all the jars. The blank jar showed significant reduction in turbidity. The high doses of both the PACl and Alum, 10.14 mg AL/L, were observed to once again have the lowest TSS values out of all the experiments although the difference from the other coagulants TSS values was marginal with the Alum 10.14 mg Al/L dosage averaging a TSS of 10.5 mg/L and the the PACl 10.14 mg/L dosage averaging a TSS of 14.6 mg/L. The other two coagulants performed with TSS in the range of 22.8 mg/L to 16 mg/L. It is likely that the high removal observed in the blank jar for TSS could be partially responsible for the relative parity between the different coagulants in terms of removal performance. This is discussed in a later section. The treatment guideline used for turbidity was found in the Alberta Wastewater Effluent Standards (Government of Alberta, 2013) and was 20 mg/L as the allowable TSS of released water. This limit is also found in the EPCOR GBWWTP Approval To Operate document. The 10.14 mg Al/L dose of Alum was observed to meet and exceed this guideline, while the other coagulants also demonstrated high TSS removal.



Figure 10: Orthophosphate results with error bars for final sampling campaign

The PI OP was the highest measured out of all the jars. The blank jar showed no significant reduction in OP. The high dose of Alum, 10.14 mg AL/L, was observed to have the lowest OP

value on average with 0.32 mg/L. The high dosage of PACI exhibited an average of 0.64 mg/L. This could potentially be due to the fact that phosphate molecules would be adsorbed onto colloidal particles that would not be removed by natural settling. Hence, the addition of chemical coagulants and subsequent settling of colloidal particles would remove the bulk of the phosphorus present in the water. The treatment guideline used for OP was found in the EPCOR EPT report (EPCOR, 2015) and was 0.4 mg/L as the minimum OP level observed during the study. The 10.14 mg Al/L dose of Alum was observed to meet and exceed this guideline, while the other coagulants did not demonstrate effective OP removal.



Figure 11: TVSS results with error bars for final sampling campaign

The PI TVSS was the highest measured out of all the jars. The blank jar showed significant reduction in orthophosphate, almost matching the coagulants in performance. The high doses of Alum and PACl, 10.14 mg AL/L, were observed to have the lowest TVSS values on average with

9.63 mg/L and 11.5 mg/L respectively, although the other coagulants performed to a close level with the next best measurement being 15.8 mg/L on average. It is likely that the high removal observed in the blank jar for TSS could be partially responsible for the relative parity between the different coagulants in terms of removal performance. This is discussed in a later section. No treatment guideline was found in the literature for TVSS removal.



Figure 12: COD results with error bars for final sampling campaign

The PI COD was the highest measured out of all the jars. The blank jar showed some reduction in orthophosphate. The high dose of PACl, 10.14 mg AL/L, was observed to have the lowest orthophosphate values on average with 71.3 mg/L, although not with a significant margin since the Alum 10.14 mg Al/L dosage resulted in a COD reading of 95.0 mg/L on average. The blank jar did not exhibit high levels of COD removal with a reading of 158 mg/L on average. This may have been due to the fact that the majority of the organic material that would take up oxygen in the water would be adsorbed onto or would be the size of colloidal particles that would remain in suspension until chemical coagulants are added and flocs are formed and settled. The treatment guideline used

for COD was found in the Alberta Water Reuse for Agriculture Guidelines (Government of Alberta, 2015) and was 150 mg/L as the maximum COD level allowed for water reuse activities. The 10.14 mg Al/L dose of PACl was observed to meet and exceed this guideline the most, while the other coagulants did also meet and exceed the guidelines, although to different levels. This guideline was used a value to compare the performance of the treatments used in this study and not as a criteria to be met by the treatments necessarily.

4.2 Contaminant Removal Ratios

The next parameter that was calculated was the contaminant removal ratio. This ratio describes the mass of contaminant removed per milligram of coagulant added in each jar. A high ratio relative to the other coagulants indicates that the coagulant in question is efficient at removing the contaminant being examined as it would require a small amount of chemical to remove a large amount of contaminant. Conversely, a low relative ratio would indicate poor removal efficiency by the coagulant used. Figure 16 below shows the contaminant removal ratio for each jar and four major parameters. The subsequent figures break Figure 17 to 20 down by the contaminants in question.



Figure 13: Contaminant Removal Ratios with error bars for four major contaminants, during the final sampling campaign

A high level scan of the above Figure 16 reveals that both Alum and PACl had the highest contaminant removal ratios, peaking at 57 mg/mg for both coagulants for the removal of COD, with the low dosage level, 4.05 mg Al/L, of each coagulant outperforming all other jars by a significant margin. The ferric chloride dosages were observed to have fared the worst in comparison to the other coagulants. Each of the following graphs, as well as Figure 16, contains error bars calculated from the standard deviation of 4 samples per data point.



Figure 14: TSS Removal Ratio for final sampling campaign

In terms of TSS removal ratio, both the Alum and PACl low dosages, 4.05 mg Al/L, were very comparable in performance, as well the high dosages of the two coagulants, 10.14 mg Al/L. Ferric chloride exhibited the worst performance out of all three coagulants.



Figure 15: TVSS Removal Ratio for final sampling campaign

In terms of TVSS removal ratio, both the Alum and PACl low dosages, 4.05 mg Al/L, were very comparable in performance, as well the high dosages of the two coagulants, 10.14 mg Al/L. Ferric chloride exhibited the worst performance out of all three coagulants.



Figure 16: Orthophosphate Removal Ratio for final sampling campaign

In terms of orthophosphate removal ratio, both the Alum and PACl low dosages, 4.05 mg Al/L, were comparable in performance with the Alum outperforming the PACl by a small margin, as well the high dosages of the two coagulants, 10.14 mg Al/L. Ferric chloride exhibited the worst performance out of all three coagulants.



Figure 17: COD Removal Ratio for final sampling campaign

In terms of COD removal ratio, both the Alum and PACl low dosages, 4.05 mg Al/L, were very comparable in performance, as well the high dosages of the two coagulants, 10.14 mg Al/L. Ferric chloride exhibited the worst performance out of all three coagulants.

Counter-intuively, the 4.05 mg Al/L dosages of Alum and PACl were the best performing in terms of contaminant removal ratio. This is explained by the fact that having larger and more flocs does not necessarily result in efficient removal of contaminants. If the amounts of flocs are in excess of the quantity of contaminant present in the water, then the excess coagulant is wasted. In this study, the higher removal ratios exhibited by the lower dosages of both PACl and Alum indicate that the optimum dosage of both coagulants appears to be closer to the 4.05 mg Al/L dosage than the 10.14 mg Al/L dosage.

There are a few possible explanations behind the poor performance of ferric chloride as a coagulant. According to Johnson and Amirtharajah, ferric salt coagulants are prone to instability and can be affected by a variety of factors such as pH, age, concentration, temperature, mode of

preparation and other factors. As such, even if the same dosage level is prepared, coagulants may vary greatly in strength and coagulation ability due to natural decay or the other factors mentioned previously (Johnson and Amirtharajah, 1982). Previous coagulation performance studies involving ferric chloride have indicated that a higher dose of ferric chloride, increased pH as well as increased mixing time is needed in order to achieve substantial contaminant removal performance. In one study, a dose of 600 mg/L ferric chloride and mixing time of 25 minutes was required in order achieve 62% turbidity removal from sugar cane industry wastewater to (Thirugnanasambandham et al., 2016). One study was able to achieve greater than 90% turbidity removal with a dosage of 1.5 mg/L ferric chloride, although this was with algal turbid water that had an NTU value of 2 (Chekli et al., 2017). For comparison, the PI NTU values in this study ranged from 106 NTU to 43 NTU. As well, the water matrix in this study was more complex than in the study by Chekli et al. A Master thesis completed in Florida indicated that it required a dosage between 100 mg/L and 240 mg/L in order to achieve percentage removals of DOC up to 89%. The percentage removals would decrease once the ferric chloride dosage decreased below 80 mg/L, indicating that a higher dosage than used in the present study would be required in order to demonstrate effective contaminant removal on the part of ferric chloride. The thesis also indicated that the removal percentage decreased as the pH of the water increased from 5.0 to 7.0. The average pH of the raw CSO wastewater studied in this study was approximately 7.0. This may have contributed to the poor performance of ferric chloride as well (Yonge, 2012). Additionally, iron has almost twice the molecular weight of aluminium which would result in lower efficiency when compared to aluminium based coagulants on a mass basis.

4.3 Percent Contaminant Removal

Percent Contaminant Removal is an indicator of how much contaminant has been removed from

the wastewater sample as compared to how much was present in the raw sample. It is an indicator of the relative quantity of contaminant removed as opposed to a measure of efficiency like the Contaminant Removal Ratio. Figure 21 shows the percentage contaminant removal for the high doses of Alum and PACl for the final sampling campaign while Figure 22 shows the percentage contaminant removal for the 4.05 mg Al/L dosage levels of Alum and PACl for the final sampling campaign. The parameters observed were turbidity, TSS, TVSS, COD and orthophosphate. A breakdown of the graphs is available in the Appendix.



Figure 18: Percent Contaminant Removal for 10.14 mg Al/L Alum and PACl for four contaminants, during the final sampling campaign

Overall, it was observed that turbidity, TSS, TVSS and ortho-phosphate experienced removal percentages greater than 85% across all four experiments for the 10.14 mg Al/L PACl and Alum
dosages. COD was observed to have an overall higher percentage removal with Alum as compared to PACI although these percentages were in the range of 60% to 70%. A breakdown by contaminant along with relevant error bars can be found in the Appendix. Ferric chloride was not shown in the above Figure due to the lack of removal it demonstrated. This has already been documented in the previous sections. Table 10 below shows the p values from two tailed t-tests that were used to determine if the mean percentage removals between Alum and PACI were statistically different or not. The alpha value was 0.05. Any value in green indicates that the p-value was below 0.05 for that comparison, and thus the two means for the respective data sets were not statistically different from each other. The red values indicate that the p-value was higher than 0.05 and thus the two means were statistically different from each other. The full t-tests can be found in the Appendix.

Table 10: P-values for two tailed t-test with alpha of 0.05 for 10.14 mg Al/L doses of Alum and PACl. Value greater than 0.05 marked in red and lesser than 0.05 marked in green.

	Turbidity (NTU)	TSS (mg/L)	TVSS (mg/L)	Ortho-P (mg PO4 ³⁻ /L)	COD (mg/L)
Experiment 4 (-1/-1)	0.003	0.001	0.315	0.032	0.003
Experiment 3 (-1/1)	0.025	1.000	1.000	0.144	0.379
Experiment 2 (1/-1)	0.017	0.063	0.063	0.008	0.308
Experiment 1 (1/1)	0.012	0.168	0.168	0.391	0.155



Figure 19: Percent Contaminant Removal for 4.05 mg Al/L Alum and PACl for four contaminants, during the final sampling campaign

Overall, it was observed that turbidity, TSS and TVSS experienced removal percentages greater than 70% across all four experiments for both 4.05 mg Al/L PACI and Alum dosages. Orthophosphate was observed to have an overall slightly higher percentage removal with Alum as compared to PACI. COD was observed to have not been significantly different in terms of percentage removal between the two coagulants. A breakdown by contaminant along with relevant error bars can be found in the Appendix. Ferric Chloride was not shown in the above Figure due to the lack of removal it demonstrated. Table 11 below shows the p values from two tailed t-tests that were used to determine if the mean percentage removals between Alum and PACI were statistically different or not. The alpha value was 0.05. Any value in green indicates that the pvalue was below 0.05 for that comparison, and thus the two means for the respective data sets were not statistically different from each other. The red values indicate that the p-value was higher than 0.05 and thus the two means were statistically different from each other. The full t-tests can be

found in the Appendix.

Table 11: P-values for two tailed t-test with alpha of 0.05 for 4.05 mg Al/L doses of Alum and PACI. Value greater than 0.05 marked in red and lesser than 0.05 marked in green.

	Turbidity (NTU)	TSS (mg/L)	TVSS (mg/L)	Ortho-P (mg PO4 ³⁻ /L)	COD (mg/L)
Experiment 4 (-1/-1)	0.007	0.939	0.538	0.033	0.515
Experiment 3 (-1/1)	0.003	0.182	0.182	0.037	0.733
Experiment 2 (1/-1)	0.023	0.004	0.006	0.001	1.000
Experiment 1 (1/1)	0.793	0.077	0.067	0.069	0.509

A key component of floc formation in coagulant usage is the presence of alkalinity in the form of calcium bicarbonate as shown in Eq 1. The amount of bicarbonate needed in the water in order to react with 10 mg/L of Alum, for instance, is 4.5 mg/L (Metcalf & Eddy, 5 ed). Although alkalinity was not measured for the final sampling campaign, the range for simulated CSO wastewater alkalinity seemed to be between approximately 275 mg/L and 186 mg/L from previous campaigns. The ready availability of alkalinity seems to have accelerated the high removal rates and rapid floc formation observed with the Aluminium based coagulants. The larger the dosage of alum and PACl, the more floc was formed and therefore, the more contaminant was removed from the water matrix. This was why the 10.14 mg Al/L dosages of both Alum and PACl performed better than the 4.05 mg Al/L dosages. Alkalinity availability did not seem to have a noticeable effect on ferric chloride performance. This may have been due to the dosage levels being too low as well as the pH of the water being too high, as has been mentioned previously.

4.4 Correlation between TSS and Turbidity

Due to the frequency of the TSS and turbidity testing performed across the sampling campaigns, it was decided to determine if a correlation existed between the two parameters in the context of CSO flows. Figure 23 below shows all the collected TSS and turbidity samples from all four sampling campaigns plotted against each other.



Figure 20: All TSS and Turbidity data obtained from all four sampling campaigns

As can be seen from the above Figure, there is a strong statistical correlation, with an R-squared value of 0.88, between TSS and turbidity which is particularly strong between the ranges of 0 to 50 NTU and 0 to roughly 100 mg/L TSS. A breakdown of the TSS and turbidity correlations by Jar type is available in the Appendix. Out of the three coagulants, only Alum and ferric chloride were observed to have fair correlations between the TSS and turbidity readings. PACl is seen to have weak correlations, especially at the higher end of the scale. The other two coagulants demonstrated R-squared values between 0.74 and 0.93.

This finding confirms what is found in the literature regarding the linear correlation between turbidity and TSS. Strong correlations have been found previously between these two critical parameters (Hannouche et al., 2011; Al-Yaseri et al., 2013). A caveat seems to be present however, with dry and wet weather correlations differing in slope values while the type of wet weather event also exhibits some variability in this regard (Hannouche et al., 2011). Strong R-squared values

have been measured, usually over 0.92 whereas one study indicated that a log-linear relationship existed with the equation $\ln (TSS) = 0.979 \ln (turbidity) + 0.574$ for stormwater run-off from green roofs (Al-Yaseri et al., 2013).

4.5 Impact of varying coagulant dose on pH

A phenomenon that was observed with some PACI jars was overdosing and its effect on pH in particular. This phenomenon was also observed in a survey carried out by Environment Canada in 2013, where a drop in pH was observed when the chemicals tested in the survey were used with CSO flows (Exall and Marsalek, 2013). Throughout the four sampling campaigns, PACI high dosages were consistently found to be overdosing with respect to pH and producing an acidic final effluent. In order to determine if these were isolated scenarios or the pattern of overdosing was linked to dosage levels, an experiment was carried out with varying levels of Alum, ferric chloride and PACI dosages both with and without buffer in the matrix of pure distilled water. The pH of these sample jars was monitored either once every 20 minutes or once every 30 minutes with duplicate readings for each measurement recorded.

All three coagulants were fairly stable at low pHs between 3.50 and 4.80 when no buffer was involved.

Alum and ferric chloride were stable in their pH even after buffer was added to the system. However, PACl experienced a large dip in pH from approximately 9.50 to 7.10 at most, once the added dosage exceeded the buffering capacity that was added to the water matrix. This dip occurred at the PACl dosage of 40 mg Al/L and the pH progressively decreased as the dosage increased after this point down to a minimum of 4.80. It was also observed that some improvement in pH occurred over the course of one hour for 70 mg Al/L and above, as evidenced by the spaced out measurements although this effect was not very noticeable. Plots of the data can be found in the Appendix.

The likely mechanism of this drop in pH due to PACl overdosing is related to the linear consumption of alkalinity by the PACl, following the complete consumption of which free hydrogen ions are released in the water resulting in a lower pH (Bachand et al., 2010). This would explain why pH is approximately between 3.50 and 4.80 without any addition of buffer and why the pH increases when buffer is added. Although the hydroxyl groups present on PACl would be expected to reduce the consumption of alkalinity by the chemical, the comparatively high dose of PACl in these scenarios when compared to the alkalinity present in the raw wastewater sample would have caused the hydrolysis reactions to be incomplete and increase the concentration of hydrogen ions in solution (Greville, 1997).

4.6 Effect of natural settling on removal ratios

Each Jar test performed had a blank jar with no chemicals added in order to determine the effect natural settling would have on the process. It was observed that natural settling had a significant impact on the removal ratios of all the contaminants and parameters measured. Figure 26 shows the overall effect on removal ratios when contaminant removal by natural settling is removed from the data. Figures 27 to 30 break this data down further by contaminant type.



Figure 21: Contaminant removal ratios with contaminant removed by natural settling excluded

It is observed from the above graph that although natural settling has a big impact on the removal ratios, comparatively speaking the 4.05 mg Al/L dosages of Alum and PACl are still exhibiting the highest removal ratios, ranging from approximately 19 mg COD/mg to approximately 0.80 mg orthophosphate/mg, for all contaminants.



Figure 22: TSS removal ratios with contaminant removed by natural settling excluded

Compared to Figure 20 which includes natural settling results, the TSS removal ratios have been reduced by up to 94% indicating that chemical coagulants have little actual effect on the removal of TSS. However, compared to the other Jar Test results, both 4.05 mg Al/L dosages of Alum and PACl continue to exhibit the highest removal ratios of approximately 2.50 mg/mg to 5.80 mg/mg, although by much finer margins compared to the rest of the data. The Alum 10.14 mg Al/L dosage is particularly strong in this regard as well. Ferric chloride continues to exhibit the worst removal of the three coagulants.



Figure 23: TVSS removal ratios with contaminant removed by natural settling excluded

Compared to Figure 21 which includes natural settling results, the TVSS removal ratios have been reduced by up to 93% indicating that chemical coagulants have little actual effect on the removal of TVSS. However, compared to the other Jar Test results, both 4.05 mg Al/L dosages of Alum and PACl continue to exhibit the highest removal ratios although by much finer margins. The Alum high dosage is particularly strong in this regard as well. Ferric chloride continues to exhibit the worst removal of the three coagulants.



Figure 24: Orthophosphate removal ratios with contaminant removed by natural settling excluded

Ortho-phosphate removal seems to be the least affected when it comes to removal by natural settling with reductions only reaching 37%. This may be due to the reason that ortho-phosphate is present in higher quantities adsorbed onto colloidal and suspended solids that are too small to settle out naturally. Both 4.05 mg Al/L dosages of Alum and PACl were once again the best performing out of all the Jars.



Figure 25: COD removal ratios with contaminant removed by natural settling excluded

Compared to Figure 23 which includes natural settling results, the COD removal ratios have been reduced by up to 100% in one case indicating that chemical coagulants have little actual effect on the removal of COD. However, compared to the other Jar Test results, both 4.05 mg Al/L dosages of Alum and PACl continue to exhibit the highest removal ratios although by much finer margins. The Alum and PACl 10.14 mg Al/L dosages are particularly strong in this regard as well. Ferric chloride continues to exhibit the worst removal of the three coagulants.

The removal ratios mentioned above indicate that both Alum and PACl are the best performing coagulants out of the three coagulants investigated. They are both superior in regards to removal of COD, TSS, TVSS and orthophosphate. These results are reflected in a similar study performed on automotive wastewater where PACl was determined to be the most effective in the removal of contaminants such as COD and TSS (Abu Bakar and Abdul Halim, 2013).

These results indicate that natural settling remains an effective form of wastewater treatment, particularly for smaller communities and flowrates. Chemical requirements for wastewater that has already been allowed to naturally settle would be far lower than currently used at Gold Bar WWTP, for instance. The drawback with this approach is the unrealistic size of lagoon or settling basin that would be required to hold the large flows of CSOs flowing into the plant. Such space is at a premium in a major city such as Edmonton.

4.7 All Campaign Results

This section shows the results of all four sampling campaigns combined. Some of the parameters were measured using different methods as the campaigns progressed along with different coagulant dosages used for PACI and ferric chloride before the final campaign. Figures 31 to 36 below show all the results obtained for each contaminant from all jars and all sampling campaigns.

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Figure 26: All Phosphorus data for all four sampling campaigns and all jars tested

The measurement methodology used for phosphorus differed with each sampling campaign, which may explain the increase in measurement precision. This may also be explained by an improvement over time in the handling and sample preparation procedures by the laboratory personnel.



Figure 27: All COD data for all four sampling campaigns and all jars tested



Figure 28: All Turbidity data for all four sampling campaigns and all jars tested



Figure 29: All TSS data for all four sampling campaigns and all jars tested



Figure 30: All Alkalinity data for all four sampling campaigns and all jars tested



Figure 31: All pH data for all four sampling campaigns and all jars tested

With the exception of pH and COD, which were measured using a pH meter and pre-prepared chemicals, all other parameters mentioned in Figures to above exhibited an improvement in precision with each successive sampling campaign.

4.8 Comparison with EPCOR Data

In 2015, EPCOR compiled a report on testing performed using Jar Test apparatus to examine the effect of Alum as a coagulant on the reduction of certain parameters and contaminants found in CSO flows experienced by the Wastewater Treatment Plant where the study was carried out. Figure 37 below shows the comparison of TSS from simulated CSO flows from the EPCOR study as a function of Alum dosage in mg/L. This is presented alongside data collected in the current study across the four sampling campaigns. Although only one sampling campaign in the current study tested the effect of varying alum dosages, the EPCOR data overlapped significantly when it came to 125 mg/L of Alum (EPCOR, 2015)



Figure 32: EPCOR measured TSS values as compared to TSS values from this study as a function of Alum dosage

Table 12: Average TSS in different compositions of simulated CSO – EPCOR EPT Annual Report, 2015

	25% P + 75% W	50% P + 50% W	75% P + 25% W	100% P
Avg. TSS (mg/L)	62	127	189.5	251.4

Table 10 gives an indication as to the average TSS that was observed during the EPCOR testing for different combinations of wastewater, P, and dilution water, W. The two were used together to create a simulated CSO wastewater sample (EPCOR, 2015).

4.9 Effect of Slow Mixing

The effects of slow and rapid mixing were one of the parameters assessed during the jar tests. The factorial design incorporated into the four experiments, conditions with similar mixing speeds and times such that two experiments can be compared side-by-side in order to determine the effect of any one combination of mixing speeds and times. Table 11 shows the mixing times with the associated power imparted into the water through the impeller. The conversion chart from RPM to mixing gradient G can be found in the Appendix. Table 7 includes the different mixing speeds and times indicated by each mixing level. Figures 38 to 42 show the effect of slow mixing on each contaminant by comparison of experiments 4 and 3 from the final sampling campaign. All data has been normalized based on the contaminant load found in the PI for the sake of accurate comparison.

Mixing Levels	Time	Energy	Power
	(min)	(mW)	(mWh)
-1 (Rapid Mix)	1	57.92	0.97
+1 (Rapid Mix)	3	309.91	15.50
-1 (Slow Mix)	10	0.21	0.04
+1 (Slow Mix)	20	1.10	0.37

Table 13: Mixing times used during experiments with association Power input into water matrix



Figure 33: Normalized Turbidity values for slow mixing experiments







Figure 35: Normalized orthophosphate values for slow mixing experiments



Figure 36: Normalized TVSS values for slow mixing experiments



Figure 37: Normalized COD values for slow mixing experiments

With the exception of COD and some jars from the other Figures above, the high level of slow mixing, that is 30 RPM for 20 minutes, seems to produce the best performance in terms of contaminant removal. COD removal was not significantly impacted by the slow mixing levels, although a slight improvement was observed for the high level of slow mixing. Orthophosphate exhibited the highest decrease in contaminant levels compared to the blank jar indicating that most of the orthophosphate was adsorbed onto colloidal particles in the water that needed chemical coagulant to remove. TSS seemed to be significantly affected by the high level of slow mixing as well.

Mixing time is an important factor to consider when determining ideal or optimum conditions for coagulation and flocculation to occur. This is because of the fact that flocculation can be accelerated rapidly if mixing is applied as it bring particles destabilized by the addition of coagulants to come together quicker and stick to each other more efficiently (Metcalf & Eddy, 2003; Teh et al., 2016). The purpose of slow mixing in this respect is to provide the particles in such a suspension with just enough shear and velocity such that they are able to collide more frequently with other destabilized particles and form flocs (Teh et al., 2016). The optimum slow mixing speed is a matter of balancing the potential for increased collisions of this sort as opposed to the potential for large flocs that form from breaking up again due to excess shear forces exerted by the mixer (Subramonian et al., 2014; Teh et al., 2014; Ayoub et al., 2011).

The importance of optimizing the mixing conditions was illustrated in a study performed in 2015 where the G value was investigated in order to determine the effect on removal efficiency of TOC and turbidity. The ideal G values found in this study were between 110 s⁻¹ and 450 s⁻¹, although these values differ greatly by the type of mixing vessel involved. The end result is the optimization of the energy used towards mixing coagulants into the water while also maintaining high contaminant removal efficiencies (Vadasarukkai and Gagnon, 2015).

In the present study, it seems that the higher slow mixing time yielded the better results due to the higher slow mixing and longer slow mixing time resulting in increased opportunities for destabilized particles to interact with each other and form flocs.

4.10 Effect of Rapid Mixing

Figures 43 to 47 show the effect of rapid mixing on each contaminant by comparison of experiments 4 and 2 from the final sampling campaign. All data has been normalized based on the contaminant load found in the Primary Influent for the sake of accurate comparison.



Figure 38: Normalized turbidity values for rapid mixing experiments







Figure 40: Normalized orthophosphate values for rapid mixing experiments







Figure 42: Normalized COD values for rapid mixing experiments

As demonstrated earlier at the beginning of Section 4, the rapid mixing levels had little to no bearing on the final factorial design effects and model equations. Vadsarukkai and Gagnon have noted in their study into the influence of mixing energy consumption on coagulation and floc aggregation that rapid mixing appears to not be very effective in the removal of aquatic organic matter in the form of humic acids. A closer look at the metal-ligand complexes formed during coagulation and flocculation revealed that mixing energy input seemed to have no effect on the formation of these complexes. In fact, the study determined that most WWTPs were expending too much mixing energy into coagulation, in the range of 600 s⁻¹ to 1000 s⁻¹, than necessary as coagulation was able to remove dissolved organic matter at lower mixing intensities than what most plants were designed for (Vadasarukkai and Gagnon, 2017). This supports the data found in this study that indicates that rapid mixing is not as big of an influence on contaminant removal when compared to slow mixing and coagulant dosage.

4.11 pH

Out of all the parameters measured across the four sampling campaigns, pH was the parameter that demonstrated the most consistency due to stable nature of the wastewater and the high buffering capacity of municipal wastewater.



Figure 43: All pH data collected for all four sampling campaigns and for all jars tested

With the exception of the PACl high dosages, most of the pH measurements were found to be around pH 7.0. Due to the high PACl dosage overcoming the natural buffering capacity of the wastewater and the resulting chloride ions lowering the pH level of the water, most of the PACl high dosages resulted in overdosing except for the final sampling campaign. The final campaign adjusted the PACl dosages in order to make them equivalent to the other coagulant dosages in terms of active Aluminium, resulting in a significantly lowered high dosage, explaining why there were no overdoses observed in the final campaign.



Figure 44: pH values as a function of primary influent flowrates from real CSO events

Figure 49 shows the pH compared to the flowrates observed during the first sampling campaign that involved the sampling of real CSO flows. It was observed that the pH stayed consistently around 7.0 even though the flowrate into the Primary Clarifiers fluctuated from 420 MLD to nearly 1000 MLD. Dilution of the wastewater due to stormwater runoff seems to not have a significant impact of CSO pH. Most studies performed on wastewater influent into a wastewater treatment plant indicate that the natural pH of wastewater observed was between 6.0 and 8.0 (Canizares et al., 2007; Samrani et al., 2008; Yonge, 2012; Bachand et al., 2010). This trend is also observed in this study with the average PI pH measured as 7.36. All coagulants, with the exception of PAC1 overdosing mentioned earlier, did not significantly alter the natural pH of the PI wastewater.

A breakdown by Jar of all the pH measurements taken during all four sampling campaigns can be found in the Appendix.

4.12 Alkalinity

The first two sampling campaigns were used to determine the alkalinity levels both before treatment with chemical coagulants and after treatment. The test was not repeated for the final sampling campaign due to the lack of variation and observable effect on the parameter by any treatment as well as due to the amount of time it would take to obtain replicates via an auto sampling titrator. Figure 50 shows all the sampling results from all the sampling campaigns where Alkalinity was measured. Figure 51 shows the Alkalinity as compared to the flowrate for the first sampling campaign which used real CSO flows as opposed to simulated CSO. A breakdown by Jar of all the Alkalinity data can be found in the Appendix.



Figure 45: All Alkalinity values for all four sampling campaigns and all jars tested

Due to the variable nature of the CSO flows observed in the first sampling campaign, the alkalinity in this same period of time was variable as well. As simulated CSO flows were used, the alkalinity varied less.



Figure 46: Alkalinity as a function of primary influent flowrate

It was observed that an increasing CSO flowrate caused a drop in the alkalinity entering the Primary Clarifiers. This may be due to the diluting effect that stormwater runoff would have on the natural alkalinity found in municipal dry weather wastewater.

As mentioned earlier, the natural alkalinity present in wastewater plays a critical role in the formation of floc formation due to the fact that it is needed by chemical coagulants to form the insoluble hydroxides that form the basis of flocs.

4.13 Cost Benefit Analysis

A request for cost estimates for the coagulants under consideration was made to a commercial vendor known as ClearTech. They indicated that the prices of Alum, ferric chloride and PACl were CAD \$400/MT, CAD \$600/MT and CAD \$800 to CAD \$950/MT respectively. The most expensive coagulant was determined to be PACl while the least expensive was Alum. Figure 47 shows the cost in CAD\$ per MT as a function of dosages of Alum, PACl and ferric chloride.



Figure 47: Cost in CAD\$ per ML of liquid coagulant as a function of dosage level in mg/L

Chapter 5. Conclusions

The purpose of this study was to determine which of the three coagulants out of Alum, ferric chloride and PACl performed the best when it came to the removal of common wastewater parameters in a CSO setting. Alongside this determination, the effects of mixing speeds and times were also examined in relation to jar test apparatus, which was used to carry out the experiments and collect the data presented in this study. The cost of each coagulant was also taken into account in order to decide which coagulant would be most cost effective. The parameters that were measured across the four sampling campaigns included pH, turbidity, TSS, phosphorus content, TVSS, Alkalinity and COD. Other parameters that were tested include biological parameters such as BOD and *E. Coli* colony counts, but these were discarded due to procedural or quality control errors. Four sampling campaigns were carried out between the months of June 2016 and March 2017 in order to collect CSO samples and analyse for the above parameters. This study mainly presents the results of the final sampling campaign as this was the campaign with the most focus

on the most relevant parameters. A two-level, three-factor factorial design was followed which combined two levels of rapid and slow mixing conditions with two levels of coagulant dosages while using Jar test apparatus to carry out the experiments. The following results were observed:

- Out of the three coagulants measured, Alum and PACl were observed to have the highest percent contaminant removals and contaminant removal (per mg of coagulant added) ratios. Ferric chloride exhibited poor contaminant removal performance in all tests compared to the other two coagulants.
- The factorial design model equations and effects demonstrated that it was coagulant dose levels and slow mixing that were the two most statistically significant factors that affected contaminant removal.
- Out of the two dose levels tested for each coagulant, the most effective in removal of contaminants were the 10.14 mg Al/L doses of Alum and PACl.
- However, based on how much coagulant was needed to remove 1 mg of contaminant, which is reflected in the removal ratios, the lower doses of 4.05 mg Al/L were more effective with an average of 23 mg contaminant removed per mg coagulant for both Alum and PAC1. This indicates that the optimum dosage for each coagulant is likely to be closer to the low dosage as opposed to the high dosage.
- The high level of slow mixing (30 RPM for 20 minutes) was observed to be most effective

while rapid mixing was not observed to have any effect in contaminant removal with an average improvement of 9% over the contaminant levels exhibited by the low level of slow mixing. These levels represented a power output of 0.97 mWh and 0.37 mWh respectively. Notable exceptions to this trend were the COD results with respect to slow mixing levels.

• Taking into account the high cost of PACl, Alum is the most cost effective option for most operators. PACl costs between \$800 and \$950 per MT while Alum costs \$400 per MT as per a supplier, ClearTech.

This study demonstrates the applicability of Alum and PACl as coagulants in Canadian WWTPs and will assist in the continuation of operation of these plants while minimizing the health impacts and environmental risks associated with the phenomenon of CSO flows.

Chapter 6. Recommendations

An in depth study to determine the optimum Alum dosage with the determined optimum mixing conditions would be recommended as a future study. The focus of this study was on the conventional wastewater parameters, therefore a study that focuses on contaminants of emerging concern and more novel coagulants and coagulant aids would also be recommended in order to expand the knowledge base with respect to CSO treatment options. Further study into the mechanics of ferric chloride performance as well as an in-depth look at natural settling in the context of large city WWTPs is also recommended.

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Appendix



A. Individual percentage contaminant removal for 10.14 mg Al/L Alum and PACl doses

Figure A 1: % Turbidity removal for Alum and PACl 10.14 mg Al/L



Figure A 2: % TSS removal for Alum and PACl 10.14 mg Al/L


Figure A 3:% TVSS removal for Alum and PACl 10.14 mg Al/L



Figure A 4: % COD removal for Alum and PACl 10.14 mg Al/L



Figure A 5: % Orthophosphate removal for Alum and PACl 10.14 mg Al/L



B. Individual percentage contaminant removal for 4.05 mg Al/L Alum and PACI doses

Figure A 6: % Turbidity removal for Alum and PACl 4.05 mg Al/L



Figure A 7: % TSS removal for Alum and PACl 4.05 mg Al/L



Figure A 8: % TVSS removal for Alum and PACl 4.05 mg Al/L



Figure A 9: % COD removal for Alum and PACl 4.05 mg Al/L



Figure A 10: % Orthophosphate removal for Alum and PACl 4.05 mg Al/L



C. Turbidity vs TSS values for all individual jars across all sampling campaigns

Figure A 11: Primary Influent TSS vs turbidity values for all sampling campaigns



Figure A 12: Blank Jar TSS vs turbidity values for all sampling campaigns



Figure A 13: 125 mg/L Alum TSS vs turbidity values for all sampling campaigns



Figure A 14: 50 mg/L Alum TSS vs turbidity values for all sampling campaigns



Figure A 15: Ferric chloride high dose TSS vs turbidity values for all sampling campaigns



Figure A 16: Ferric chloride low dose TSS vs turbidity values for all sampling campaigns



Figure A 17: PACl high dose TSS vs turbidity values for all sampling campaigns



Figure A 18: PACl low dose TSS vs turbidity values for all sampling campaigns



D. pH values for all sampling campaigns for individual jars

Figure A 19: Blank Jar pH values for all sampling campaigns



Figure A 20: 125 mg/L Alum pH values for all sampling campaigns



Figure A 21: 50 mg/L Alum pH values for all sampling campaigns



Figure A 22: Ferric chloride high dose pH values for all sampling campaigns



Figure A 23: Ferric chloride low dose pH values for all sampling campaigns



Figure A 24: PACl low dose pH values for all sampling campaigns



Figure A 25: PACl high dose pH values for all sampling campaigns



E. Alkalinity values for all sampling campaigns and individual jars

Figure A 26: Blank Jar alkalinity values for all sampling campaigns in mg CaCO₃/L



Figure A 27: 125 mg/L Alum alkalinity values for all sampling campaigns in mg CaCO₃/L



Figure A 28: 50 mg/L Alum alkalinity values for all sampling campaigns in mg CaCO₃/L



Figure A 29: Ferric chloride high dose alkalinity values for all sampling campaigns in mg CaCO₃/L



Figure A 30: Ferric chloride low dose alkalinity values for all sampling campaigns in mg CaCO₃/L



Figure A 31: PACl high dose alkalinity values for all sampling campaigns in mg CaCO₃/L



Figure A 32: PACl low dose alkalinity values for all sampling campaigns in mg CaCO₃/L

F. Factorial Design main and interaction effects

TSS Removal Ratio								
	Main Effects			Interactions				
Run	А	В	С	AB	AC	BC	ABC	TSS RR
1	-1	-1	-1	1	1	1	-1	28.55
2	1	-1	-1	-1	-1	1	1	25.823
3	-1	1	-1	-1	1	-1	1	19.81
4	1	1	-1	1	-1	-1	-1	18.924
5	-1	-1	1	1	-1	-1	1	12.42
6	1	-1	1	-1	1	-1	-1	11.324
7	-1	1	1	-1	-1	1	-1	7.97
8	1	1	1	1	1	1	1	7.656
Effect	-1.25	-5.94	-13.43	0.65	0.55	1.88	-0.27	16.56
Coefficient	0.63	2.97	6.72	0.33	0.28	0.94	0.13	16.56
	B1	B2	B3	B12	B13	B23	B123	B0

Table A 1: Effects on TSS Removal Ratio for all 3-factor interactions and coefficients for model equation for all coagulant data

Table A 2: Effects on TVSS Removal Ratio for all 3-factor interactions and coefficients for model equation for all coagulant data

TVSS								
Removal								
Ratio								
	Main							
	Effects							
Run	А	В	С	AB	AC	BC	ABC	TVSS RR
1	-1	-1	-1	1	1	1	-1	23.72
2	1	-1	-1	-1	-1	1	1	25.415
3	-1	1	-1	-1	1	-1	1	16.35
4	1	1	-1	1	-1	-1	-1	17.697
5	-1	-1	1	1	-1	-1	1	10.60
6	1	-1	1	-1	1	-1	-1	11.160
7	-1	1	1	-1	-1	1	-1	6.58
8	1	1	1	1	1	1	1	7.084
Effect	1.02	-5.80	-11.94	-0.10	-0.49	1.75	0.07	14.83
Coefficient	0.51	2.90	5.97	0.05	0.25	0.87	0.04	14.83
	B1	B2	B3	B12	B13	B23	B123	BO

OP								
Removal								
Ratio								
	Main Effects							
Run	А	В	С	AB	AC	вс	ABC	OP RR
1	-1	-1	-1	1	1	1	-1	0.73
2	1	-1	-1	-1	-1	1	1	0.590
3	-1	1	-1	-1	1	-1	1	0.32
4	1	1	-1	1	-1	-1	-1	0.538
5	-1	-1	1	1	-1	-1	1	0.45
6	1	-1	1	-1	1	-1	-1	0.391
7	-1	1	1	-1	-1	1	-1	0.15
8	1	1	1	1	1	1	1	0.315
Effect	0.04	-0.21	-0.22	0.15	0.01	0.02	-0.03	0.44
Coefficient	0.02	0.11	0.11	0.07	0.00	0.01	0.02	0.44
	B1	B2	ВЗ	B12	B13	B23	B123	B0

 Table A 3: Effects on Orthophosphate Removal Ratio for all 3-factor interactions and coefficients for model equation for all coagulant data

Table A 4: Effects on COD Removal Ratio for all 3-factor interactions and coefficients for model equation for all coagulant data

COD								
Removal								
Ratio								
	Main Effects							
Run	А	В	С	AB	AC	BC	ABC	COD RR
1	-1	-1	-1	1	1	1	-1	32.29
2	1	-1	-1	-1	-1	1	1	48.095
3	-1	1	-1	-1	1	-1	1	30.13
4	1	1	-1	1	-1	-1	-1	16.475
5	-1	-1	1	1	-1	-1	1	14.47
6	1	-1	1	-1	1	-1	-1	21.698
7	-1	1	1	-1	-1	1	-1	11.30
8	1	1	1	1	1	1	1	7.967
Effect	1.51	-12.67	-17.89	-10.00	0.44	4.22	4.72	22.80
Coefficient	0.76	6.34	8.94	5.00	0.22	2.11	2.36	22.80

B1	B2	B3	B12	B13	B23	B123	BO

TSS								
Removal								
Ratio								
	Main							
	Effects							
Run	А	В	С	AB	AC	BC	ABC	TSS RR
1	-1	-1	-1	1	1	1	-1	34.20
2	1	-1	-1	-1	-1	1	1	33.457
3	-1	1	-1	-1	1	-1	1	23.95
4	1	1	-1	1	-1	-1	-1	24.198
5	-1	-1	1	1	-1	-1	1	15.88
6	1	-1	1	-1	1	-1	-1	13.708
7	-1	1	1	-1	-1	1	-1	9.62
8	1	1	1	1	1	1	1	9.418
Effect	-0.72	-7.51	-16.80	0.74	-0.47	2.24	0.25	20.55
Coefficient	0.36	3.76	8.40	0.37	0.23	1.12	0.12	20.55
	B1	B2	B3	B12	B13	B23	B123	B0

Table A 5: Effects on TSS Removal Ratio for all 3-factor interactions and coefficients for model equation for Alum data

Table A 6: Effects on TVSS Removal Ratio for all 3-factor interactions and coefficients for model equation for Alum data

TVSS								
Removal								
Ratio								
	Main							
	Effects							
Run	А	В	С	AB	AC	BC	ABC	TVSS RR
1	-1	-1	-1	1	1	1	-1	27.78
2	1	-1	-1	-1	-1	1	1	32.963
3	-1	1	-1	-1	1	-1	1	19.75
4	1	1	-1	1	-1	-1	-1	22.469
5	-1	-1	1	1	-1	-1	1	13.36
6	1	-1	1	-1	1	-1	-1	13.511
7	-1	1	1	-1	-1	1	-1	7.94
8	1	1	1	1	1	1	1	8.728
Effect	2.21	-7.18	-14.86	-0.46	-1.74	2.08	0.78	18.31
Coefficient	1.10	3.59	7.43	0.23	0.87	1.04	0.39	18.31

B1	B2	B3	B12	B13	B23	B123	BO

OP								
Removal								
Ratio								
	Main							
	Effects							
Run	А	В	С	AB	AC	BC	ABC	OP RR
1	-1	-1	-1	1	1	1	-1	1.05
2	1	-1	-1	-1	-1	1	1	0.877
3	-1	1	-1	-1	1	-1	1	0.43
4	1	1	-1	1	-1	-1	-1	0.741
5	-1	-1	1	1	-1	-1	1	0.58
6	1	-1	1	-1	1	-1	-1	0.510
7	-1	1	1	-1	-1	1	-1	0.19
8	1	1	1	1	1	1	1	0.385
Effect	0.06	-0.32	-0.36	0.19	0.00	0.06	-0.06	0.60
Coefficient	0.03	0.16	0.18	0.09	0.00	0.03	0.03	0.60
	B1	B2	B3	B12	B13	B23	B123	B0

Table A 7: Effects on OP Removal Ratio for all 3-factor interactions and coefficients for model equation for Alum data

Table A 8: Effects on COD Removal Ratio for all 3-factor interactions and coefficients for model equation for Alum data

COD								
Removal								
Ratio								
	Main Effects							
Run	А	В	С	AB	AC	BC	ABC	COD RR
1	-1	-1	-1	1	1	1	-1	38.03
2	1	-1	-1	-1	-1	1	1	57.425
3	-1	1	-1	-1	1	-1	1	34.42
4	1	1	-1	1	-1	-1	-1	23.015
5	-1	-1	1	1	-1	-1	1	15.12
6	1	-1	1	-1	1	-1	-1	25.574
7	-1	1	1	-1	-1	1	-1	14.03
8	1	1	1	1	1	1	1	8.463
Effect	3.22	-14.06	-22.43	-11.71	-0.78	4.95	3.69	27.01
Coefficient	1.61	7.03	11.21	5.85	0.39	2.48	1.85	27.01
	B1	B2	B3	B12	B13	B23	B123	B0

TSS								
Removal								
Ratio								
	Main							
	Effects							
Run	А	В	С	AB	AC	BC	ABC	TSS RR
1	-1	-1	-1	1	1	1	-1	17.12
2	1	-1	-1	-1	-1	1	1	14.260
3	-1	1	-1	-1	1	-1	1	11.28
4	1	1	-1	1	-1	-1	-1	11.217
5	-1	-1	1	1	-1	-1	1	6.92
6	1	-1	1	-1	1	-1	-1	6.062
7	-1	1	1	-1	-1	1	-1	4.68
8	1	1	1	1	1	1	1	4.821
Effect	-0.91	-3.09	-7.85	0.95	0.55	1.35	-0.45	9.55
Coefficient	0.45	1.55	3.92	0.48	0.28	0.68	0.23	9.55
	B1	B2	B3	B12	B13	B23	B123	B0

Table A 9: Effects on TSS Removal Ratio for all 3-factor interactions and coefficients for model equation for FeCl3 data

Table A 10: Effects on TVSS Removal Ratio for all 3-factor interactions and coefficients for model equation for FeCl3 data

TVSS Removal								
Ratio								
	Main							
	Effects							
Run	А	В	С	AB	AC	BC	ABC	TVSS RR
1	-1	-1	-1	1	1	1	-1	14.26
2	1	-1	-1	-1	-1	1	1	14.021
3	-1	1	-1	-1	1	-1	1	9.31
4	1	1	-1	1	-1	-1	-1	10.621
5	-1	-1	1	1	-1	-1	1	5.61
6	1	-1	1	-1	1	-1	-1	5.967
7	-1	1	1	-1	-1	1	-1	3.87
8	1	1	1	1	1	1	1	4.487
Effect	0.51	-2.89	-7.07	0.45	-0.02	1.28	-0.32	8.52
Coefficient	0.26	1.45	3.54	0.23	0.01	0.64	0.16	8.52
	B1	B2	B3	B12	B13	B23	B123	BO

OP								
Removal								
Ratio								
	Main							
	Effects							
Run	А	В	С	AB	AC	BC	ABC	OP RR
1	-1	-1	-1	1	1	1	-1	0.34
2	1	-1	-1	-1	-1	1	1	0.263
3	-1	1	-1	-1	1	-1	1	0.15
4	1	1	-1	1	-1	-1	-1	0.263
5	-1	-1	1	1	-1	-1	1	0.24
6	1	-1	1	-1	1	-1	-1	0.209
7	-1	1	1	-1	-1	1	-1	0.09
8	1	1	1	1	1	1	1	0.185
Effect	0.02	-0.09	-0.07	0.08	0.01	0.00	-0.02	0.22
Coefficient	0.01	0.05	0.04	0.04	0.00	0.00	0.01	0.22
	B1	B2	B3	B12	B13	B23	B123	B0

Table A 11: Effects on OP Removal Ratio for all 3-factor interactions and coefficients for model equation for FeCl3 data

Table A 12: Effects on COD Removal Ratio for all 3-factor interactions and coefficients for model equation for FeCl3 data

COD Removal								
Ratio								
	Main Effects							
Run	А	В	С	AB	AC	BC	ABC	COD RR
1	-1	-1	-1	1	1	1	-1	18.21
2	1	-1	-1	-1	-1	1	1	29.437
3	-1	1	-1	-1	1	-1	1	17.83
4	1	1	-1	1	-1	-1	-1	7.415
5	-1	-1	1	1	-1	-1	1	8.09
6	1	-1	1	-1	1	-1	-1	12.626
7	-1	1	1	-1	-1	1	-1	6.82
8	1	1	1	1	1	1	1	3.037
Effect	0.39	-8.32	-10.58	-7.49	-0.02	2.89	3.33	12.93
Coefficient	0.19	4.16	5.29	3.75	0.01	1.44	1.67	12.93
	B1	B2	B3	B12	B13	B23	B123	B0

TSS								
Removal								
Ratio								
	Main							
	Effects							
Run	А	В	С	AB	AC	BC	ABC	TSS RR
1	-1	-1	-1	1	1	1	-1	34.32
2	1	-1	-1	-1	-1	1	1	29.753
3	-1	1	-1	-1	1	-1	1	24.20
4	1	1	-1	1	-1	-1	-1	21.358
5	-1	-1	1	1	-1	-1	1	14.45
6	1	-1	1	-1	1	-1	-1	14.201
7	-1	1	1	-1	-1	1	-1	9.62
8	1	1	1	1	1	1	1	8.728
Effect	-2.14	-7.21	-15.66	0.27	1.57	2.05	-0.59	19.58
Coefficient	1.07	3.60	7.83	0.14	0.78	1.03	0.30	19.58
	B1	B2	B3	B12	B13	B23	B123	B0

Table A 13: Effects on TSS Removal Ratio for all 3-factor interactions and coefficients for model equation for PACl data

Table A 14: Effects on TVSS Removal Ratio for all 3-factor interactions and coefficients for model equation for PACI data

TVSS Removal								
Ratio								
	Main Effects							
Run	А	В	С	AB	AC	BC	ABC	TVSS RR
1	-1	-1	-1	1	1	1	-1	29.14
2	1	-1	-1	-1	-1	1	1	29.259
3	-1	1	-1	-1	1	-1	1	20.00
4	1	1	-1	1	-1	-1	-1	20.000
5	-1	-1	1	1	-1	-1	1	12.82
6	1	-1	1	-1	1	-1	-1	14.004
7	-1	1	1	-1	-1	1	-1	7.94
8	1	1	1	1	1	1	1	8.037
Effect	0.35	-7.31	-13.90	-0.30	0.29	1.89	-0.24	17.65
Coefficient	0.18	3.66	6.95	0.15	0.14	0.94	0.12	17.65
	B1	B2	B3	B12	B13	B23	B123	B0

OP								
Removal								
Ratio								
	Main							
	Effects							
Run	А	В	С	AB	AC	BC	ABC	OP RR
1	-1	-1	-1	1	1	1	-1	0.81
2	1	-1	-1	-1	-1	1	1	0.630
3	-1	1	-1	-1	1	-1	1	0.38
4	1	1	-1	1	-1	-1	-1	0.610
5	-1	-1	1	1	-1	-1	1	0.54
6	1	-1	1	-1	1	-1	-1	0.456
7	-1	1	1	-1	-1	1	-1	0.18
8	1	1	1	1	1	1	1	0.375
Effect	0.04	-0.22	-0.22	0.17	0.01	0.00	-0.03	0.50
Coefficient	0.02	0.11	0.11	0.09	0.01	0.00	0.02	0.50
	B1	B2	B3	B12	B13	B23	B123	B0

Table A 15: Effects on OP Removal Ratio for all 3-factor interactions and coefficients for model equation for PACI data

Table A 16: Effects on COD Removal Ratio for all 3-factor interactions and coefficients for model equation for PACl data

COD								
Removal								
Ratio								
	Main							
	Effects							
Run	А	В	С	AB	AC	BC	ABC	COD RR
1	-1	-1	-1	1	1	1	-1	40.64
2	1	-1	-1	-1	-1	1	1	57.425
3	-1	1	-1	-1	1	-1	1	38.13
4	1	1	-1	1	-1	-1	-1	18.995
5	-1	-1	1	1	-1	-1	1	20.21
6	1	-1	1	-1	1	-1	-1	26.893
7	-1	1	1	-1	-1	1	-1	13.04
8	1	1	1	1	1	1	1	12.401
Effect	0.92	-15.65	-20.66	-10.81	2.10	4.82	7.15	28.47
Coefficient	0.46	7.83	10.33	5.40	1.05	2.41	3.57	28.47
	B1	B2	B3	B12	B13	B23	B123	B0

G. Factorial Design three-factor ANOVA analysis tables

ANOVA				Alpha	0.05	
	SS	df	MS	F	p-value	sig
А	9.427372	1	9.427372	0.208915	0.653764	no
В	211.5673	1	211.5673	4.688422	0.045823	yes
С	1082.953	1	1082.953	23.99871	0.000161	yes
A x B	2.570282	1	2.570282	0.056959	0.814399	no
AxC	1.81934	1	1.81934	0.040317	0.843392	no
ВхС	21.22978	1	21.22978	0.470461	0.502594	no
АхВхС	0.4231	1	0.4231	0.009376	0.924064	no
Within	722.0075	16	45.12547			
Total	2051.998	23	89.21729			

Table A 17: Three Factor ANOVA Analysis via regression for all coagulant TSS RR data

Table A 18: Three Factor ANOVA Analysis via regression for all coagulant TVSS RR data

ANOVA				Alpha	0.05	
	SS	df	MS	F	p-value	sig
А	6.299786	1	6.299786	0.171139	0.684593	no
В	201.5152	1	201.5152	5.47434	0.032591	yes
С	855.6016	1	855.6016	23.24318	0.000188	yes
A x B	0.062275	1	0.062275	0.001692	0.9677	no
AxC	1.451017	1	1.451017	0.039418	0.845123	no
ВхС	18.35684	1	18.35684	0.49868	0.490237	no
АхВхС	0.030818	1	0.030818	0.000837	0.977275	no
Within	588.974	16	36.81087			
Total	1672.292	23	72.70833			

Table A 19: Three Factor ANOVA Analysis via regression for all coagulant OP RR data

ANOVA					Alpha	0.05
	SS	df	MS	F	p-value	sig
А	0.011155	1	0.011155	0.231937	0.636612	no
В	0.268563	1	0.268563	5.583949	0.031122	yes
С	0.28224	1	0.28224	5.868335	0.027653	yes
A x B	0.130202	1	0.130202	2.707166	0.119398	no
AxC	0.000236	1	0.000236	0.00491	0.945004	no
ВхС	0.002983	1	0.002983	0.062033	0.806481	no
АхВхС	0.007226	1	0.007226	0.150241	0.703413	no
Within	0.769527	16	0.048095			

Total	1.472133	23	0.064006
Within	0.769527	16	
Total	1.472133	23	

Table A 20: Three Factor ANOVA Analysis via regression for all coagulant COD RR data

ANOVA				Alpha	0.05	
	SS	df	MS	F	p-value	sig
А	13.6975	1	13.6975	0.150001	0.703637	no
В	963.7283	1	963.7283	10.55379	0.005035	yes
С	1920.003	1	1920.003	21.02596	0.000305	yes
A x B	600.2231	1	600.2231	6.573047	0.020814	yes
AxC	1.138344	1	1.138344	0.012466	0.912489	no
ВхС	106.9192	1	106.9192	1.170873	0.295261	no
АхВхС	133.8665	1	133.8665	1.465973	0.243564	no
Within	1461.053	16	91.31581			
Total	5200.629	23	226.1143			

Table A 21: Three Factor ANOVA Analysis via regression for Alum TSS RR data

ANOVA				Alpha	0.05	
	SS	df	MS	F	p-value	sig
А	4.091777	1	4.091777	4.024278	0.056247	no
В	451.7549	1	451.7549	444.3027	5.42E-17	yes
С	2256.787	1	2256.787	2219.559	3.64E-25	yes
AxB	4.380921	1	4.380921	4.308652	0.048801	yes
AxC	1.754133	1	1.754133	1.725197	0.201444	no
ВхС	40.0862	1	40.0862	39.42493	1.72E-06	yes
АхВхС	0.484849	1	0.484849	0.476851	0.496477	no
Within	24.40255	24	1.016773			
Total	2783.743	31	89.79815			

Table A 22: Three Factor ANOVA Analysis via regression for Alum TVSS RR data

ANOVA	1			Alpha	0.05	
	SS	df	MS	F	p-value	sig
А	39.05617	1	39.05617	29.2383	1.49E-05	yes
В	412.5806	1	412.5806	308.8668	3.29E-15	yes
С	1765.518	1	1765.518	1321.706	1.68E-22	yes
A x B	1.670993	1	1.670993	1.250942	0.274443	no
AxC	24.25109	1	24.25109	18.1549	0.000272	yes

ВхС	34.53983	1	34.53983	25.85727	3.35E-05	yes
АхВхС	4.836552	1	4.836552	3.620749	0.069127	no
Within	32.05891	24	1.335788			
Total	2314.513	31	74.6617			

Table A 23: Three Factor ANOVA Analysis via regression for Alum OP RR data

ANOVA				Alpha	0.05	
	SS	df	MS	F	p-value	sig
А	0.031387	1	0.031387	48.52109	3.34E-07	yes
В	0.929148	1	0.929148	1436.362	6.3E-23	yes
С	0.967883	1	0.967883	1496.242	3.89E-23	yes
A x B	0.209823	1	0.209823	324.3639	1.9E-15	yes
AxC	0.012302	1	0.012302	19.01826	0.000211	yes
ВхС	2.58E-05	1	2.58E-05	0.039817	0.843519	no
АхВхС	0.016085	1	0.016085	24.86549	4.3E-05	yes
Within	0.015525	24	0.000647			
Total	2.182179	31	0.070393			

Table A 24: Three Factor ANOVA Analysis via regression for Alum COD RR data

ANOVA				Alpha	0.05	
	SS	df	MS	F	p-value	sig
А	26.20255	1	26.20255	1.013007	0.324224	no
В	2621.107	1	2621.107	101.3336	4.32E-10	yes
С	4023.225	1	4023.225	155.5404	5.6E-12	yes
A x B	1096.055	1	1096.055	42.37417	9.87E-07	yes
AxC	38.2035	1	38.2035	1.476971	0.23607	no
ВхС	6.602626	1	6.602626	0.255262	0.618003	no
АхВхС	109.1882	1	109.1882	4.221284	0.050963	no
Within	620.7866	24	25.86611			
Total	8541.37	31	275.5281			

Table A 25: Three Factor ANOVA Analysis via regression for ferric chloride TSS RR data

ANOVA				Alpha	0.05	
	SS	df	MS	F	p-value	sig
А	1.845584	1	1.845584	15.29263	0.00066	yes
В	122.0004	1	122.0004	1010.903	3.94E-21	yes
С	492.8601	1	492.8601	4083.871	2.56E-28	yes
АхВ	7.245416	1	7.245416	60.03599	5.53E-08	yes

AxC	7.706794	1	7.706794	63.859	3.22E-08	yes
ВхС	2.332594	1	2.332594	19.32802	0.000193	yes
АхВхС	1.623439	1	1.623439	13.45192	0.001214	yes
Within	2.896429	24	0.120685			
Total	638.5108	31	20.59712			

Table A 26: Three Factor ANOVA Analysis via regression for ferric chloride TVSS RR data

ANOVA				Alpha	0.05	
	SS	df	MS	F	p-value	sig
А	7.660016	1	7.660016	54.75942	1.22E-07	yes
В	107.719	1	107.719	770.0543	9.5E-20	yes
С	399.9251	1	399.9251	2858.958	1.79E-26	yes
A x B	1.645012	1	1.645012	11.75976	0.002194	yes
AxC	1.559572	1	1.559572	11.14897	0.002738	yes
ВхС	2.057689	1	2.057689	14.70987	0.000798	yes
АхВхС	0.830481	1	0.830481	5.936885	0.022618	yes
Within	3.357238	24	0.139885			
Total	524.7541	31	16.92755			

Table A 27: Three Factor ANOVA Analysis via regression for ferric chloride OP RR data

ANOVA				Alpha	0.05	
	SS	df	MS	F	p-value	sig
А	0.008382	1	0.008382	22.52703	7.92E-05	yes
В	0.177645	1	0.177645	477.4363	2.38E-17	yes
С	0.04721	1	0.04721	126.8817	4.58E-11	yes
A x B	0.049436	1	0.049436	132.8635	2.86E-11	yes
AxC	3.01E-05	1	3.01E-05	0.080848	0.77859	no
ВхС	0.039153	1	0.039153	105.2277	2.98E-10	yes
АхВхС	1.6E-06	1	1.6E-06	0.004306	0.948227	no
Within	0.00893	24	0.000372			
Total	0.330788	31	0.010671			

Table A 28: Three Factor ANOVA Analysis via regression for ferric chloride COD RR data

ANOVA				Alpha	0.05	
	SS	df	MS	F	p-value	sig
А	2.14329	1	2.14329	0.673207	0.420011	no
В	684.372	1	684.372	214.9612	1.78E-13	yes
С	895.1195	1	895.1195	281.157	9.37E-15	yes

A x B	448.7944	1	448.7944	140.9663	1.56E-11	yes
AxC	0.09853	1	0.09853	0.030948	0.861832	no
ВхС	30.49917	1	30.49917	9.579788	0.004945	yes
АхВхС	88.70389	1	88.70389	27.86189	2.06E-05	yes
Within	76.40879	24	3.1837			
Total	2226.14	31	71.81095			

Table A 29: Three Factor ANOVA Analysis via regression for PACI TSS RR data

ANOVA				Alpha	0.05	
	SS	df	MS	F	p-value	sig
А	16.14011	1	16.14011	24.25523	5.03E-05	yes
В	429.7531	1	429.7531	645.8294	7.34E-19	yes
С	1961.729	1	1961.729	2948.071	1.24E-26	yes
A x B	0.591186	1	0.591186	0.88843	0.355295	no
AxC	41.70809	1	41.70809	62.67857	3.79E-08	yes
ВхС	29.7969	1	29.7969	44.77853	6.38E-07	yes
АхВхС	2.807077	1	2.807077	4.218453	0.051035	no
Within	15.97028	24	0.665428			
Total	2498.496	31	80.59665			

Table A 30: Three Factor ANOVA Analysis via regression for PACI TVSS RR data

ANOVA				Alpha	0.05	
	SS	df	MS	F	p-value	sig
А	22.65286	1	22.65286	20.87259	0.000124	yes
В	371.8483	1	371.8483	342.6251	1.03E-15	yes
С	1545.362	1	1545.362	1423.913	6.99E-23	yes
АхВ	0.729957	1	0.729957	0.672591	0.420221	no
AxC	21.02138	1	21.02138	19.36933	0.00019	yes
ВхС	45.30875	1	45.30875	41.74798	1.11E-06	yes
АхВхС	0.462103	1	0.462103	0.425786	0.520265	no
Within	26.04701	24	1.085292			
Total	2033.432	31	65.59458			

Table A 31: Three Factor ANOVA Analysis via regression for PACl OP RR data

ANOVA				Alpha	0.05	
	SS	df	MS	F	p-value	sig
А	0.016275	1	0.016275	5.021173	0.034559	yes
В	0.635661	1	0.635661	196.1094	4.8E-13	yes

0.349921	1	0.349921	107.955	2.32E-10	yes
0.173759	1	0.173759	53.60673	1.46E-07	yes
0.003108	1	0.003108	0.958834	0.337249	no
0.070104	1	0.070104	21.62788	0.000101	yes
0.004006	1	0.004006	1.235801	0.277294	no
0.077793	24	0.003241			
1.330627	31	0.042923			
	0.173759 0.003108 0.070104 0.004006 0.077793	0.17375910.00310810.07010410.00400610.07779324	0.17375910.1737590.00310810.0031080.07010410.0701040.00400610.0040060.077793240.003241	0.17375910.17375953.606730.00310810.0031080.9588340.07010410.07010421.627880.00400610.0040061.2358010.077793240.003241	0.17375910.17375953.606731.46E-070.00310810.0031080.9588340.3372490.07010410.07010421.627880.0001010.00400610.0040061.2358010.2772940.077793240.003241

Table A 32: Three Factor ANOVA Analysis via regression for PACI COD RR data

ANOVA				Alpha	0.05	
	SS	df	MS	F	p-value	sig
А	0.232791	1	0.232791	0.010568	0.918976	no
В	2950.683	1	2950.683	133.95	2.63E-11	yes
С	3019.187	1	3019.187	137.0598	2.08E-11	yes
A x B	733.1522	1	733.1522	33.28238	6.03E-06	yes
AxC	10.13782	1	10.13782	0.460219	0.504011	no
ВхС	111.8623	1	111.8623	5.078134	0.033639	yes
АхВхС	279.3896	1	279.3896	12.68324	0.001583	yes
Within	528.6778	24	22.02824			
Total	7633.323	31	246.2362			

H. Two tailed t-tests for percent contaminant removals

Table A 33: T-test for Turbidity, Experiment 4, 4.05 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mear	Ì		
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	84.4%	0.009						
Group 2	4	79.0%	0.008						
Difference	4	5.4%	0.016	0.008	6.612		3	3.3058	0.9674

T TEST

	<i>p</i> -				
	value	t-crit	lower	upper	sig
One Tail	0.004	2.353			yes
Two Tail	0.007	3.182	0.028	0.08	yes

Table A 34: T-test for TSS, Experiment 4, 4.05 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mean			
SUMMARY			Alpha	0.05		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	82.9%	0.057						
Group 2	4	83.2%	0.02						
Difference	4	-0.3%	0.072	0.036	- 0.08		3	0.042	0.048
T TEST									
	р-								
	value	t-crit	lower	upper	sig				
One Tail	0.4695	2.3534			no				
Two Tail	0.939	3.1824	-0.12	0.112	no				

Table A 35: T-test for TVSS, Experiment 4, 4.05 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mea	n		
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	81.5%	0.083						
Group 2	4	85.5%	0.059						
					-				
Difference	4	-4.0%	0.115	0.057	0.69		3	0.3467	0.3717
T TEST						_			
	р-					-			
	value	t-crit	lower	upper	sig	_			
One Tail	0.269	2.353			no				
Two Tail	0.538	3.182	-0.22	0.143	no				

Table A 36: T-test for Ortho P, Experiment 4, 4.05 mg Al/L percent removal

			Hyp Mean	
SUMMARY	Alpha	0.05	Diff	0

Groups	Count	Mean	Std Dev	Std Err	t	df		Cohen d	Effect r
Group 1	4	62.6%	0.024						
Group 2	4	46.9%	0.078						
Difference	4	15.7%	0.084	0.042	3.735		3	1.868	0.907

T TEST

	р-				
	value	t-crit	lower	upper	sig
One Tail	0.0167	2.3534			yes
Two Tail	0.0334	3.1824	0.023	0.292	yes

Table A 37: T-test for COD, Experiment 4, 4.05 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mear	n		
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	54.5%	0.072						
Group 2	4	58.2%	0.049						
Difference	4	-3.7%	0.102	0.051	- 0.74		3	0.3684	0.3914

T TEST

	<i>p</i> -				
	value	t-crit	lower	upper	sig
One Tail	0.257	2.353			no
Two Tail	0.515	3.182	-0.2	0.124	no

Table A 38: T-test for Turbidity, Experiment 3, 4.05 mg Al/L percent removal

						Hyp Mear	٦		
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	90.4%	0.009						
Group 2	4	92.8%	0.006						
					-				
Difference	4	-2.5%	0.006	0.003	8.56		3	4.2825	0.9802

T TEST

111231					
	р-				
	value	t-crit	lower	upper	sig
One Tail	0.002	2.353			yes
Two Tail	0.003	3.182	-0.03	-0.02	yes

Table A 39: T-test for TSS, Experiment 3, 4.05 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mear	۱		
SUMMARY			Alpha	0.05		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	98.0%	0.023						
Group 2	4	99.0%	0.012						
					-				
Difference	4	-1.0%	0.012	0.006	1.73		3	0.866	0.707
T TEST									
	р-								
	value	t-crit	lower	upper	sig				
One Tail	0.0908	2.3534			no				
Two Tail	0.1817	3.1824	-0.03	0.008	no				

Table A 40: T-test for TVSS, Experiment 3, 4.05 mg Al/L percent removal

						Hyp Mear	า		
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	97.6%	0.028						
Group 2	4	98.8%	0.014						
Difference	4	-1.2%	0.014	0.007	- 1.73		3	0.866	0.7071
T TEST						:			
	n								

	р-				
	value	t-crit	lower	upper	sig
One Tail	0.091	2.353			no

Table A 41: T-test for Ortho P, Experiment 3, 4.05 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mean	1		
SUMMARY			Alpha	0.05		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	83.3%	0.027						
Group 2	4	72.6%	0.046						
Difference	4	10.7%	0.06	0.03	3.576		3	1.788	0.9

T TEST

	р-				
	value	t-crit	lower	upper	sig
One Tail	0.0187	2.3534			yes
Two Tail	0.0374	3.1824	0.012	0.202	yes

Table A 42: T-test for COD, Experiment 3, 4.05 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mear	۱		
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	64.1%	0.074						
Group 2	3	71.1%	0.053						
					-				
Difference	3	-6.9%	0.305	0.176	0.39		2	0.2264	0.2672

T TEST

	p- value	t-crit	lower	upper	sig
One Tail	0.366	2.92			no
Two Tail	0.733	4.303	-0.83	0.689	no

Table A 43: T-test for Turbidity, Experiment 2, 4.05 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mear	ı		
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	84.1%	0.009						
Group 2	4	79.2%	0.02						
Difference	4	4.8%	0.023	0.011	4.283		3	2.1416	0.9271
T TEST									
	<i>p</i> -					-			
	value	t-crit	lower	upper	sig	_			
One Tail	0.012	2.353			yes				
Two Tail	0.023	3.182	0.012	0.085	yes				

Table A 44: T-test for TSS, Experiment 2, 4.05 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mean			
SUMMARY			Alpha	0.05		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	88.0%	0.012						
Group 2	4	78.2%	0.012						
Difference	4	9.7%	0.025	0.012	7.833		3	3.917	0.976

T TEST

	р-				
	value	t-crit	lower	upper	sig
One Tail	0.0022	2.3534			yes
Two Tail	0.0043	3.1824	0.058	0.137	yes

Table A 45: T-test for TVSS, Experiment 2, 4.05 mg Al/L percent removal

						Hyp Mean		
SUMMARY			Alpha	5.0%		Diff	0	
			Std	Std			Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df	d	r

Group 1	4	87.8%	0.013					
Group 2	4	78.1%	0.015					
Difference	4	9.7%	0.027	0.014	7.172	3	3.5862	0.9721

T TEST					
	р-				
	value	t-crit	lower	upper	sig
One Tail	0.003	2.353			yes
Two Tail	0.006	3.182	0.054	0.14	yes

Table A 46: T-test for Ortho P, Experiment 2, 4.05 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mear	l I		
SUMMARY			Alpha	0.05		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	64.0%	0.015						
Group 2	4	45.9%	0.039						
Difference	4	18.0%	0.029	0.015	12.25		3	6.124	0.99
T TEST									

	<i>p</i> -				
	value	t-crit	lower	upper	sig
One Tail	0.0006	2.3534			yes
Two Tail	0.0012	3.1824	0.133	0.227	yes

Table A 47: T-test for COD, Experiment 2, 4.05 mg Al/L percent removal

						Hyp Mear	ı		
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	64.4%	0.108						
Group 2	4	64.4%	0.074						
Difference	4	0.0%	0.166	0.083	-0		3	4E-05	5E-05
T TEST									
	р-								
	value	t-crit	lower	upper	sig				

One Tail	0.5	2.353			no
Two Tail	1	3.182	-0.26	0.265	no

Table A 48: T-test for Turbidity, Experiment 1, 4.05 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mear	۱		
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	84.5%	0.007						
Group 2	4	84.3%	0.008						
Difference	4	0.2%	0.014	0.007	0.286		3	0.1432	0.1631

T TEST

111231					
	р-				
	value	t-crit	lower	upper	sig
One Tail	0.397	2.353			no
Two Tail	0.793	3.182	-0.02	0.024	no

Table A 49: T-test for TSS, Experiment 1, 4.05 mg Al/L percent removal

T Test: Two Paired Samples

				Hyp Mean						
SUMMARY			Alpha	0.05		Diff		0		
			Std	Std				Cohen	Effect	
Groups	Count	Mean	Dev	Err	t	df		d	r	
Group 1	4	85.2%	0.036							
Group 2	4	75.2%	0.048							
Difference	4	10.0%	0.076	0.038	2.644		3	1.322	0.837	
T TEST										
	p- value	t-crit	lower	upper	sig					

One Tail	0.0387	2.3534			yes
Two Tail	0.0774	3.1824	-0.02	0.22	no

Table A 50: T-test for TVSS, Experiment 1, 4.05 mg Al/L percent removal
						Hyp Mear	۱		
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	84.3%	0.039						
Group 2	4	75.0%	0.047						
Difference	4	9.3%	0.066	0.033	2.81		3	1.4049	0.8513
T TEST						_			
	р-					-			
	value	t-crit	lower	upper	sig				
One Tail	0.034	2.353			yes				
Two Tail	0.067	3.182	-0.01	0.197	no				

Table A 51: T-test for Ortho P, Experiment 1, 4.05 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mean			
SUMMARY			Alpha	0.05		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	76.9%	0.055						
Group 2	4	63.5%	0.082						
Difference	4	13.5%	0.097	0.048	2.782		3	1.391	0.849

T TEST

	р-				
	value	t-crit	lower	upper	sig
One Tail	0.0345	2.3534			yes
Two Tail	0.0689	3.1824	-0.02	0.289	no

Table A 52: T-test for COD, Experiment 1, 4.05 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mean		
SUMMARY			Alpha	5.0%		Diff	0	
			Std	Std			Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df	d	r
Group 1	4	58.3%	0.201					
Group 2	4	48.2%	0.074					

Difference	4	10.2%	0.273	0.136	0.747
T TEST					
11231	n-				
	p- value	t-crit	lower	upper	sig
One Tail	0.255	2.353			no
Two Tail	0.509	3.182	-0.33	0.536	no

Table A 53:T-test for Turbidity, Experiment 4, 10.14 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mea	า		
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	94.9%	0.004						
Group 2	4	95.9%	0.002						
Difference	4	-1.0%	0.002	0.001	- 9.051		3	4.5253	0.982
T TEST									
	p-value	t-crit	lower	upper	sig	_			
One Tail	0.001	2.353			yes				
Two Tail	0.003	3.182	-0.01	-0.01	yes				

3 0.3734 0.3959

Table A 54: T-test for TSS, Experiment 4, 10.14 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mean			
SUMMARY			Alpha	0.05		Diff		0	
			Std					Cohen	Effect
Groups	Count	Mean	Dev	Std Err	t	df		d	r
Group 1	4	96.4%	0.0098						
Group 2	4	87.7%	0.0115						
Difference	4	8.7%	0.0115	0.0057	15.145		3	7.572	0.994

	р-				
	value	t-crit	lower	upper	sig
One Tail	0.0003	2.3534			yes

Two Tail 0.0006 3.1824 0.0686 0.1051 yes

Table A 55: T-test for TVSS, Experiment 4, 10.14 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mean	I		
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	98.2%	0.027						
Group 2	4	94.2%	0.039						
Difference	4	4.0%	0.066	0.033	1.2026		3	0.6013	0.57

T TEST

	p-value	t-crit	lower	upper	sig
One Tail	0.158	2.353			no
Two Tail	0.315	3.182	-0.07	0.145	no

Table A 56: T-test for Ortho P, Experiment 4, 10.14 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mean	1		
SUMMARY			Alpha	0.05		Diff		0	
			Std					Cohen	Effect
Groups	Count	Mean	Dev	Std Err	t	df		d	r
Group 1	4	88.2%	0.0157						
Group 2	4	81.1%	0.0464						
Difference	4	7.1%	0.0375	0.0187	3.7808		3	1.89	0.909
T TEST									
	р-					-			
	value	t-crit	lower	upper	sig				
One Tail	0.0162	2.3534			yes				

Table A 57: T-test for COD, Experiment 4, 10.14 mg Al/L percent removal

0.0324 3.1824 0.0112 0.1305

T Test: Two Paired Samples

Two Tail

yes

						Hyp Mean	l		
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	54.2%	0.066						
Group 2	4	72.5%	0.037						
Difference	4	#####	0.042	0.021	- 8.704		3	4.3522	0.981
T TEST									
	p-value	t-crit	lower	upper	sig	_			
One Tail	0.002	2.353			yes				
Two Tail	0.003	3.182	-0.25	-0.12	yes				

Table A 58: T-test for Turbidity, Experiment 3, 10.14 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mear	1		
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	96.1%	0.004						
Group 2	4	92.7%	0.015						
Difference	4	3.4%	0.016	0.008	4.1987		3	2.0993	0.924

T TEST

11231					
	p-value	t-crit	lower	upper	sig
One Tail	0.012	2.353			yes
Two Tail	0.025	3.182	0.008	0.06	yes

Table A 59: T-test for TSS, Experiment 3, 10.14 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mean			
SUMMARY			Alpha	0.05		Diff		0	
			Std					Cohen	Effect
Groups	Count	Mean	Dev	Std Err	t	df		d	r
Group 1	4	98.5%	0.0193						
Group 2	4	98.5%	0.0101						
Difference	4	0.0%	0.0233	0.0117	1E-14		3	5E-15	5E-15

T TEST

11231					
	р-				
	value	t-crit	lower	upper	sig
One Tail	0.5	2.3534			no
Two Tail	1	3.1824	-0.037	0.0371	no

Table A 60: T-test for TVSS, Experiment 3, 10.14 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mea	า		
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	98.2%	0.023						
Group 2	4	98.2%	0.012						
Difference	4	0.0%	0.028	0.014	0		3	0	0

T TEST

	p-value	t-crit	lower	upper	sig
One Tail	0.5	2.353			no
Two Tail	1	3.182	-0.04	0.045	no

Table A 61: T-test for Ortho P, Experiment 3, 10.14 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mean			
SUMMARY			Alpha	0.05		Diff		0	
			Std					Cohen	Effect
Groups	Count	Mean	Dev	Std Err	t	df		d	r
Group 1	4	92.9%	0.0615						
Group 2	4	85.2%	0.0501						
Difference	4	7.6%	0.0774	0.0387	1.9695		3	0.985	0.751

	<i>p</i> -				
	value	t-crit	lower	upper	sig
One Tail	0.0718	2.3534			no
Two Tail	0.1435	3.1824	-0.047	0.1993	no

Table A 62: T-test for COD, Experiment 3, 10.14 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mean			
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	65.5%	0.067						
Group 2	4	60.9%	0.041						
Difference	4	4.6%	0.09	0.045	1.0287		3	0.5144	0.511
T TEST									
	p-value	t-crit	lower	upper	sig				
One Tail	0.19	2.353			no	-			
Two Tail	0.379	3.182	-0.1	0.189	no				

Table A 63: T-test for Turbidity, Experiment 2, 10.14 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mean	1		
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	88.5%	0.032						
Group 2	4	96.2%	0.008						
Difference	4	-7.7%	0.032	0.016	۔ 4.779		3	2.3896	0.94
T TEST									
	p-value	t-crit	lower	upper	sig				
One Tail	0.009	2.353			yes				

Table A 64: T-test for TSS, Experiment 2, 10.14 mg Al/L percent removal

0.017 3.182 -0.13 -0.03

T Test: Two Paired Samples

Two Tail

						Hyp Mean		
SUMMARY			Alpha	0.05		Diff	0	
			Std				Cohen	Effect
Groups	Count	Mean	Dev	Std Err	t	df	d	r

yes

Group 1	4	90.3%	0.0249					
Group 2	4	93.5%	0.0106					
Difference	4	-3.2%	0.0225	0.0112	- 2.887	3	1.443	0.857
T TEST								
	<i>р</i> -							

	value	t-crit	lower	upper	sig
One Tail	0.0316	2.3534			yes
Two Tail	0.0632	3.1824	-0.068	0.0033	no

Table A 65: T-test for TVSS, Experiment 2, 10.14 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mean	1		
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	90.1%	0.025						
Group 2	4	93.4%	0.011						
Difference	4	-3.3%	0.023	0.011	- 2.887		3	1.4434	0.857
T TEST						_			
	p-value	t-crit	lower	upper	sig	-			
One Tail	0.032	2.353			yes				
Two Tail	0.063	3.182	-0.07	0.003	no				

Table A 66: T-test for Ortho P, Experiment 2, 10.14 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mean			
SUMMARY			Alpha	0.05		Diff		0	
			Std					Cohen	Effect
Groups	Count	Mean	Dev	Std Err	t	df		d	r
Group 1	4	93.2%	0.0173						
Group 2	4	83.3%	0.0227						
Difference	4	9.9%	0.0312	0.0156	6.3509		3	3.175	0.965

	p- value	t-crit	lower	upper	siq
One Tail	0.0039	2.3534		••	yes
Two Tail	0.0079	3.1824	0.0494	0.1488	yes

Table A 67: T-test for COD, Experiment 2, 10.14 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mean			
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	71.8%	0.022						
Group 2	4	75.5%	0.041						
Difference	4	-3.7%	0.061	0.031	- 1.224		3	0.6122	0.577
T TEST									
	p-value	t-crit	lower	upper	sig				
One Tail	0.154	2.353			no				
Two Tail	0.308	3.182	-0.13	0.06	no				

Table A 68: T-test for Turbidity, Experiment 1, 10.14 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mean	l I		
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	85.8%	0.056						
Group 2	4	95.8%	0.023						
					-				
Difference	4	#####	0.037	0.018	5.444		3	2.7219	0.953

111251						_
	p-value	t-crit	lower	upper	sig	_
One Tail	0.006	2.353			yes	
Two Tail	0.012	3.182	-0.16	-0.04	yes	

Table A 69: T-test for TSS, Experiment 1, 10.14 mg Al/L percent removal

T Test: Two Paired Samples

SUMMARY			Alpha	0.05		Hyp Mean Diff	1	0	
			Std					Cohen	Effect
Groups	Count	Mean	Dev	Std Err	t	df		d	r
Group 1	4	83.0%	0.0756						
Group 2	4	77.0%	0.1379						
Difference	4	6.1%	0.0674	0.0337	1.8074		3	0.904	0.722
T TEST									
	р-								
	value	t-crit	lower	upper	sig				
One Tail	0.0842	2.3534			no				
Two Tail	0.1684	3.1824	-0.046	0.168	no				

Table A 70: T-test for TVSS, Experiment 1, 10.14 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mear	1		
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	81.9%	0.081						
Group 2	4	75.5%	0.147						
Difference	4	6.5%	0.072	0.036	1.8074		3	0.9037	0.722

T TEST

	p-value	t-crit	lower	upper	sig
One Tail	0.084	2.353			no
Two Tail	0.168	3.182	-0.05	0.179	no

Table A 71: T-test for Ortho P, Experiment 1, 10.14 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mean		
SUMMARY			Alpha	0.05		Diff	0	
			Std				Cohen	Effect
Groups	Count	Mean	Dev	Std Err	t	df	d	r

Group 1	4	100.0%	0					
Group 2	4	97.4%	0.0513					
Difference	4	2.6%	0.0513	0.0256	1	3	0.5	0.5
T TEST								
1 1 2 3 1								
	р-							
11231	p- value	t-crit	lower	upper	sig			
One Tail	•	<i>t-crit</i> 2.3534	lower	upper	<i>sig</i> no			
	value		<i>lower</i> -0.056	<i>upper</i> 0.1072				

Table A 72: T-test for COD, Experiment 1, 10.14 mg Al/L percent removal

T Test: Two Paired Samples

						Hyp Mean			
SUMMARY			Alpha	5.0%		Diff		0	
			Std	Std				Cohen	Effect
Groups	Count	Mean	Dev	Err	t	df		d	r
Group 1	4	53.7%	0.123						
Group 2	4	78.7%	0.146						
Difference	4	#####	0.264	0.132	- 1.892		3	0.9461	0.738

T TEST

111231						_
	p-value	t-crit	lower	upper	sig	-
One Tail	0.077	2.353			no	
Two Tail	0.155	3.182	-0.67	0.17	no	

I. Miscellaneous Figures and Tables

Table A 73: Cost of coagulants as a function of dosage levels

					Ferric
			Alum	PACI	chloride
Dosage level	Mass		Cost	Cost	Cost
mg/L	MT		CAD\$	CAD\$	CAD\$
0		0	0	0	0
80	0.	.08	32	70	48
100	(0.1	40	87.5	60
120	0.	.12	48	105	72
140	0.	.14	56	122.5	84
160	0.	.16	64	140	96

180	0.18	72	157.5	108
200	0.2	80	175	120
220	0.22	88	192.5	132
240	0.24	96	210	144

Table A 74: Average standard deviation values for final sampling campaign

	Primar Y Influen t	Blank Jar	Jar 1 - Alum 10.14 mg Al /L	Jar 2 - Alum 4.05 mg Al /L	Jar 3 - FeCl₃ 20.95 mg Fe/L	Jar 4 - FeCl₃ 8.38 mg Fe/L	Jar 5 - PACL 10.14 mg Al/L	Jar 6 - PACI 4.05 mg AI/L
				Turbidi	ty (NTU)			
Experiment 4 (-1/-1)	7.071	0.071	0.336	0.499	0.240	0.035	0.095	0.035
Experiment 3 (-1/1)	5.657	0.071	0.113	0.382	0.725	0.339	0.530	0.141
Experiment 2 (1/-1)	1.061	1.131	1.001	0.902	0.315	0.460	0.827	0.092
Experiment 1 (1/1)	8.2	0.42	0.8	0.79	0.62	0.88	0.63	0.64
				TSS (mg/L)			
Experiment 4 (-1/-1)	12.728	0.000	1.414	10.607	4.243	2.121	2.121	2.828
Experiment 3 (-1/1)	9.899	0.000	2.120	0.000	1.410	0.710	0.710	0.000
Experiment 2 (1/-1)	2.83	5.660	1.410	0.710	5.660	0.710	1.410	0.710
Experiment 1 (1/1)	1.41	8.49	0.71	4.24	1.41	4.24	3.54	2.12
				TVSS	(mg/L)			
Experiment 4 (-1/-1)	11.314	1.414	3.540	10.607	2.120	6.360	4.243	7.070
Experiment 3 (-1/1)	16.971	4.243	2.120	0.000	1.410	0.000	0.710	0.000
Experiment 2 (1/-1)	4.24	2.830	1.410	0.710	5.660	0.710	1.410	0.71
Experiment 1 (1/1)	11.31	8.49	0.71	4.24	1.4	2.83	3.54	4.24
			(Orthophos	phate (mg/	/L)		
Experiment 4 (-1/-1)	0.071	0.141	0.071	0.177	0.106	0.247	0.354	0.035
Experiment 3 (-1/1)	0.000	0.212	0.071	0.071	0.035	0.071	0.127	0.035
Experiment 2 (1/-1)	0.0707	0.283	0.035	0.071	0.106	0.000	0.106	0.141
Experiment 1 (1/1)	0.1414	0.1414	0	0.2121	0.0354	0.0707	0.1414	0.2475
				COD (r	ng O₂/L)			
Experiment 4 (-1/-1)	19.983	7.993	8.992	21.981	7.993	3.997	3.997	12.989
Experiment 3 (-1/1)	8.088	2.022	17.187	17.187	6.066	5.055	5.055	16.176
Experiment 2 (1/-1)	6	25.000	5.000	0.000	13.000	0.000	12.000	0
Experiment 1 (1/1)	33	29	21	0	40	0	19	0



Figure A 33: Jar Test Apparatus velocity gradient in sec⁻¹ vs agitator paddle speed in RPM



Figure A 34: Jar Test Apparatus



Figure A 35: Mixing of Primary Influent and Distilled Water for dilution in a large waste bin



Figure A 36: pH drop for PACl, Alum and ferric chloride with time in DI water



Figure A 37: pH drop for PACl, Alum and ferric chloride with time in DI water along with added calcium carbonate buffer

1: 0 minutes3: 40 minutes (Alum, FeCl3). , 60 minutes (PACl)2: 20 minutes (Alum, FeCl3), 30 minutes (PACl)4: 60 minutes