University of Alberta

Application of Coagulation-Flocculation Process for Treating Oil Sands Process-Affected Water

by

Yingnan Wang

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DEDICATION

This work is dedicated to my husband, Dr. Bingyan Fang, for his love and encouragement keeping me motivated in the whole process of my education; to my mom, who always supports and stands behind me during the difficult time; to my dad, I can feel his great love always with me in my whole life.

ABSTRACT

Oil Sands Process-Affected Water (OSPW) is generated from oil sands operation processes such as mining, extraction, and upgrading. Currently, accumulated OSPW is temporarily stored in tailings ponds which are toxic to the environment and must be treated for either reuse or safe discharge in the future. In this project, coagulation-flocculation as a conventional physico-chemical treatment process was investigated to remove suspended solids and some organic carbons from OSPW. Aluminum sulfate (alum) and ferric sulfate were studied as coagulants in bench-scale experiments using jar-test apparatus, in combination with selected coagulant aids including cationic, anionic and non-ionic polymers. Experiments were carried out to optimize jar-test operating conditions for each coagulant. Based on the results, more than 96% total suspended solids were removed from OSPW after treatment.

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LIST OF SYMBOLS, NOMENCLATURE, ABBREVIATIONS

µm	micrometer
µS/cm	microsiemens per centimeter
° C	degree centigrade
·OH	hydroxyl radicals
$\leq$	less than or equal to
$\geq$	greater than or equal to
Ag_2SO_4	silver sulfate
$Al(OH)_3$	aluminum hydroxide
alum	aluminum sulfate
AOPs	Advanced Oxidation Processes
AOX	Adsorbable Organic Halogens
BOD	Biochemical Oxygen Demand
$CaCO_3$	calcium carbonate
cm	centimeter
CO_2	carbon dioxide
COD	Chemical Oxygen Demand
DI Water	Deionized Water
DOC	Dissolved Organic Carbon
EPA	Environmental Protection Agency (United States)
G	velocity gradient
g	gram
GAC	Granular Activated Carbon
GC-MS	Gas Chromatography – Mass Spectrometry
H_2SO_4	sulfuric acid

HRMS	High Resolution Mass Spectrometer
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
L	litre
M	Molarity
m	meter
Max.	Maximum
MF	Microfiltration
mg	milligram
min	minute
ML	megalitre
mL	milliliter
MMH	Monomethylhydrazine
NAs	Naphthenic Acids
NF	Nanofiltration
NREF	Natural Resources Engineering Facility
NTU	Nephelometric Turbidity Units
OSPW	Oil Sands Process-affected Water
PACl	Polyaluminum Chloride
ppb	parts per billion
ppm	parts per million
ppq	parts per quadrillion
ppt	parts per trillion
RO	Reverse Osmosis
rpm	round per minute
s	second

t	time
TDS	Total Dissolved Solids
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
TSS	Total Suspended Solids
UDMH	Unsymmetrical Dimethylhydrazine
UF	Ultrafiltration
UPLC	Ultra Performance Liquid Chromatography
v/v	volume per volume
WIP	West Inpit Pond

CHAPTER 1 INTRODUCTION

At least 85% of the world's total bitumen reserves are deposited in Alberta and play a vital role in the Canadian economy (Government of Alberta 2009). The environmental impacts of oil sands production on ecological systems are a major concern in Alberta. For oil sands deposits near the surface, thermal extraction (oil sands are mixed with warm water) is often used to recover bitumen which is converted to synthetic crude oil in the upgrading process (Government of Alberta 2006). Large volumes of fresh water are needed to support oil sands surface mining, extraction and upgrading processes. Approximately 179 million m^3 of oil sands fresh water was used in 2009. Meanwhile, large volumes of oil sands process-affected water (OSPW) are generated from operation processes such as mining, extraction, and upgrading. Water management is critical for the sustainable development of the oil sands in Northern Alberta. According to current environmental regulations, all fluid wastes generated from oil sands operations must be retained on-site and oil sands tailings cannot be released into ground or surface water supplies. Therefore, OSPW is accumulated and temporarily stored in tailings ponds, which is eventually expected to be remediated for reuse or safe release. However, with oil production steadily increasing, these tailings ponds are growing much faster and are exceeding containment capacity. Suitable water treatment processes for the oil sands industry to increase reuse and recycle to lower river water intake, as well as to detoxicate in order to possibly discharge in the future, are needed.

The major constituents of concern in OSPW are suspended and dissolved solids, hydrocarbons, salts, metals and organic acids (NAs) (Zubot, personal communication, 2009) such as naphthenic acids which are considered to be one of the most toxic components in OSPW. In order to reuse or safely discharge tailings pond water, a single water treatment method may not be efficient or economical to remove all the contaminants in OSPW. Certain combined water treatment processes like coagulation-flocculation, sedimentation, filtration, adsorption and biological degradation, as well as advanced treatment options such as ozonation and membrane filtration, are possible candidates for OSPW treatment. In this project, a physico-chemical treatment method, coagulation-flocculation, was employed as a pretreatment process for OSPW to remove suspended solids, some hydrocarbons and NAs. This research will contribute to a better understanding of the treatment and water management of OSPW in the oil sands industry.

The objectives of this study were:

- To investigate coagulation-flocculation as a pretreatment process for the removal of suspended solids, hydrocarbons, metals, and some dissolved constituents such as NAs from OSPW.
- To select the suitable coagulants and coagulant aids (cationic, anionic and non-ionic polymers) for OSPW treatment.
- To optimize the coagulation-flocculation process and find out the best jar-test conditions for each coagulant.
- To assess treatment performance at optimized jar-test conditions in terms of the removal of total organic carbon (TOC), turbidity, total suspended solids (TSS), total dissolved solids (TDS), sludge volume, ions and elements, alkalinity, conductivity and NAs.
- To estimate the cost and to evaluate the applicability of various treatment options.

- To provide recommendations regarding the application of coagulation-flocculation process in oil sands industry.

CHAPTER 2 LITERATURE REVIEW

2.1 Alberta's Oil Sands

Oil sands are a mixture of sand, clay, water and bitumen. Oil sands deposits in Alberta, Canada, are estimated to be the second largest oil reserves in the world. They are located in three geological regions: Athabasca, Cold Lake, and Peace River. It is estimated that about 315 billion barrels of oil can be recovered from these three oil sands deposit sites (Oil Sands Ministerial Strategy Committee 2006), enough to satisfy the world's demand for petroleum for the next century.

Unlike conventional crude oil, bitumen in Alberta's oil sands is a thick, tar-like viscous mixture of hydrocarbons that contains high levels of sulphur and nitrogen compounds. Further, bitumen cannot flow through a well unless it is heated or diluted with lighter hydrocarbons. Bitumen must also be upgraded into crude oil which is used to produce gasoline, aviation fuel, or other products by further refineries (Government of Alberta 1997). Typically about 10% by weight of oil sands is bitumen. Currently, two tonnes of oil sands produce one barrel of oil based on current techniques. Oil sands production is increasing drastically. In 2006, oil sands production reached 1.126 million barrels per day; by 2020 oil production will increase to 3 million barrels per day; and 5 million barrels per day are estimated by 2030 (Government of Alberta 2006). The oil sands industry is and will continue to be an important driver of economic development in Alberta, Canada.

Oil sands development provides significant economic benefits to Canada including employment, economic stability, government revenue, and investment in research and development (National Energy Board 2005). However, the oil sands industry must deal with numerous environmental and social impacts associated to their mining and upgrading operations. These include river water consumption for the oil sands operation; the impacts on the quality of surface and groundwater; greenhouse gases and other air emissions produced; land disturbance; land remediation and reclamation, and the impacts on wildlife. To minimize these environmental impacts, solutions are needed to ensure sustainable development of oil sands reserves.

2.2 Oil Sands Process-Affected Water and Environmental Issues

Water is an essential resource for oil sands operations. Large volumes of water are needed to support oil sands mining and upgrading processes. Calculations show that for every cubic meter of mined oil sands, a volume of 3 m^3 of water is required; and approximately 4 m^3 of slurry waste consisting of sands, clays, organic residual bitumen, and process-affected water is produced as a by-product of oil sands production - mainly from the bitumen extraction process (Holowenko et al. 2001). Currently, approximately 85% of the water taken from the river can be recycled to satisfy bitumen extraction, process cooling and hydrotransport requirements. Under current operational scenarios, no oil sands tailings are allowed to be released into ground or surface water supplies. Accumulated quantities of OSPW are acutely toxic to aquatic organisms and are temporarily stored in tailings ponds. These tailings ponds will eventually be treated for reuse or safe release in the future. Water management is vital to continue to sustainably develop oil sands deposits in Northern Alberta. Water treatment options for increasing reuse and recycle achieving to lower imports of river water, as well as remediation of current tailings pond water for safe discharge are required.

The major constituents of concern in the OSPW are suspended and dissolved solids, hydrocarbons, salts, metals and organic acids such as NAs. The major components in OSPW are bicarbonate, sodium, chloride, sulfate, calcium, magnesium, and ammonia (Zubot, personal communication, 2009). Ecological damage may occur if untreated OSPW is discharged into surface water or soil. Although currently more than 85% of OSPW is recycled, the quality of OSPW has impacts on some operation processes and equipment. It is known that divalent ions such as calcium and magnesium impact the ability of the extraction process to recover bitumen. Ammonia concentrations should be low enough to mitigate industrial hygiene concerns within the extraction plant (caustic is added which can liberate ammonia gas) and copper or copper alloy corrosion. In addition, from a corrosion and reclamation perspective, it is desirable to lower the overall recycle water salinity. Higher quality water is still needed to be imported from the river to feed the boiler, cooling tower, firewater, potable water and various miscellaneous uses (i.e. equipment washing, pump seal water, etc.) (Zubot and MacKinnon, personal communication, 2007). The oil sands industry's goal is to minimize the amount of water withdrawn from the river, to reduce water usage, and to reuse process-affected water more effectively. With water conservation being the highest priority, new technologies are urgently needed. New technologies currently being developed are looking at how to remove suspended solids, salts, organic acids, hydrocarbons; how to break stable heavy oil-water emulsions in order to reuse OSPW without damaging production equipment, producing formations, and how to discharge OSPW without harming the environment (Neff and Hagemann 2007). The objective of OSPW treatment is to improve water quality to efficiently recycle in the production processes; to reduce the amount of river water withdrawals by reuse OSPW for utilities and other equipment uses; to remove toxicities to meet the guidelines for the protection of aquatic ecosystems; and to release treated water in the future to avoid large storage on-site (Allen 2008).

2.3 Possible Water Treatment Technologies for OSPW

Several conventional water treatment technologies such as physico-chemical treatment including coagulation-flocculation, sedimentation, adsorption, ion-exchange, membrane filtration, chemical oxidation and biological treatment have been recently studied as possible OSPW treatment technologies for the oil sands industry. The choice of the treatment method utilized is heavily dependent on the constituents of OSPW, industry processes, cost, and reuse or release regulations and demands. It is highly likely that a combination of conventional and advanced treatment technologies will achieve these challenging goals. The advantages, disadvantages and possibilities of these water treatment technologies are discussed as follows.

2.3.1 Physico-Chemical Treatment

Basically, physico-chemical treatments such as coagulation-flocculation and sedimentation, adsorption, ion-exchange, filtration, and chemical oxidation, have been widely used in municipal and industrial water and wastewater treatment. These processes can be used to effectively remove suspended and dissolved solids, to oxidize inorganic species and organic compounds, and to decrease the toxicity of the wastewater to meet the needs of high quality effluent (AWWA 1999; Metcalf and Eddy 2003).

2.3.1.1 Coagulation-flocculation

Coagulation-flocculation is a low cost and easy-to-operate water and wastewater treatment process. It is used primarily for the removal of tiny particles or colloids, which are too small to settle by gravity in a reasonable time. Small particles in water are also difficult to settle down because they have negative charges on the surface that create repelling forces, and therefore prevent agglomeration and settling - making it a stable system. Coagulation-flocculation is a process that causes colloidal particles less stable to settle out or “destabilization” (AWWA 1999; Metcalf and Eddy 2003). The mechanisms by which coagulants actually cause the removal of colloids in water are primarily charge neutralization and sweep floc. Charge neutralization is when coagulants counteract the surface charges on particles in order to encourage initial aggregation of colloids and form particles large for gravity settling. Sweep floc simply postulates that the added coagulants form precipitates which collide with and drag colloids down. Flocculation is a process that enhances contact of destabilized particles to form a large and dense agglomeration of floc and enhances the settlement of particles in water (U.S. Army Corps of Engineers 2001). It is expected that flocs drag-out the colloids during settling. Furthermore, the addition of a polymeric coagulant aid can reduce the amount of coagulant required. The coagulation-flocculation process used in this project was predicted to remove the suspended solids and some hydrocarbons in OSPW.

From an operational point of view, the coagulation-flocculation process is divided into three steps: (1) rapid (or flash) mixing; (2) slow mixing and (3) settling. During rapid mixing, the coagulant is added into a liquid sample and thoroughly mixed to be distributed evenly in the water. During slow mixing, the water-colloid-coagulant mixture is stirred in order to enhance contact. The flocs grow bigger and heavier in this process. Once the flocs have grown large enough, they will settle down and be removed from the water.

Jar test, a bench-scale test, is typically used to simulate the desired conditions for coagulation, flocculation and sedimentation processes. It consists of rapid mixing for coagulation followed by the slow mixing with lower intensity for flocculation. After the mixing period, the formed flocs are allowed to settle. The most important factors that need to be optimized during the jar-test procedure are pH; types of coagulants and coagulant aids and their concentrations; and coagulation and flocculation mixing intensities and time (Metcalf and Eddy 2003). The optimum conditions for coagulation-flocculation processes and chemical dosages are determined through laboratory experiments.

Inorganic compounds, typically iron and aluminum derivatives and lime, are commonly used as coagulants. Table 1 lists the advantages and disadvantages of several common inorganic coagulants. A trivalent ion in an inorganic coagulant can be as much as 1000 times more effective than a monovalent ion (U.S. Army Corps of Engineers 2001). This is why aluminum sulfate (alum), iron salts (i.e. ferric sulfate or ferric chloride) and lime are extremely efficient coagulants and are most commonly used in water and wastewater treatment plants. Lime was not used in this project because it is extremely pH dependent, produces large volumes of sludge, and creates an additional level of difficulty in operations since overdosing can result in poor effluent quality.

Table 1: Advantages and disadvantages of inorganic coagulants
(adapted from (U.S. Army Corps of Engineers 2001))

Coagulant	Advantage	Disadvantage
Alum $Al_2(SO_4)_3 \cdot 18H_2O$	● Most commonly used; ● Produce less sludge than lime; ● Most effective between pH 5.8 and 7.7 (Metcalf and Eddy 2003)	● Adds dissolved solids (salts) in water; ● Effective over a limited pH range
Sodium Aluminate $Na_2Al_2O_4$	● Effective in hard waters; ● Usually small dose needed	● Often used with alum; ● High cost; ● Ineffective in soft waters
Polyaluminum Chloride (PAC) $Al_{13}(OH)_{20}(SO_4)_2 \cdot Cl_{15}$	● In some applications, floc formed is denser and faster settling than alum	● Not commonly used; ● Little full scale data compared to other aluminum derivatives
Ferric Sulfate $Fe_2(SO_4)_3$	● Effective between pH 5.2 and 8.8 (Metcalf and Eddy 2003)	● Adds dissolved solids (salts) to water; ● Usually need to add alkalinity
Ferric Chloride $FeCl_3 \cdot 6H_2O$	● Effective between pH 4 and 11	● Adds dissolved solids (salts) to water; ● Consumes twice as much alkalinity as alum
Lime $Ca(OH)_2$	● Commonly used; ● Very effective; ● May not add salts to effluent	● Very pH dependent; ● Produces large quantities of sludge; ● Overdose can result in poor effluent quality

Polymers are often used in water and wastewater treatment as coagulant aids. These polymers are referred to as organic polyelectrolytes because they dissociate into positively and negatively charged species in water and increase the conductivity of the solution. Long-chained polymeric molecules with charges along their structure are able to bridge or enmesh suspended solids into a large matrix and enhance settling. A coagulant aid is usually added after the addition of a coagulant to enhance floc formation and to increase the strength of the floc structure. Sometimes coagulant aids may also be called flocculants. Depending how and where it is used, a coagulant sometimes is a flocculant. The terminology is not standardized (AWWA 1999; Dentel et al. 1993). In this thesis, no distinction is made between coagulant and flocculant. Polymers are classified as cationic (positively charged), anionic (negatively charged) and nonionic (overall neutrally charged). Cationic polymers can also be used as primary coagulants or coagulant aids (Reynolds and Richards 1996), since they can enhance the coagulation and deposition of negatively charged particles by adsorption and charge neutralization. The advantage of polymer as a primary coagulant is that it's safe to handle and biodegradable (Sievers 1989; Sievers et al. 1994; Zhu 2003). Anionic and nonionic polymers are usually added during the flocculation process to increase the size and strength of particle aggregates. They are able to bridge particles because of their high molecular weight and appreciable length (AWWA 1999). Polymers can also be used to increase filter performance as filter aid and to increase the efficiency during the sludge dewatering process (AWWA 1999).

In this project, alum and iron salts were selected and investigated as coagulants for OSPW treatment. These coagulants were chosen based on their effectiveness, low cost, reduced sludge production and the wide pH ranges of ferric chloride and ferric sulfate. Selected cationic, anionic and nonionic polymers were studied during the coagulation-flocculation process as coagulant aids combined with coagulants.

A number of parallel and sequential reactions occur when inorganic metallic coagulants are added. Initially, they dissociate to yield charged ions. The chemistry reactions of alum and ferric sulfate coagulations in water are as follows.

$$Al_2(SO_4)_3 \rightleftharpoons 2Al^{3+} + 3SO_4{}^{2-} \tag{1}$$

$$Fe_2(SO_4)_3 \rightleftharpoons 2Fe^{3+} + 3SO_4{}^{-} \tag{2}$$

The trivalent ion can hydrate to form the aquometal complex, $Me(H_2O)_6{}^{3+}$, in which Me stands for metallic ions, such as Al^{3+} or Fe^{3+}. These aquometal complexes then pass through a series of hydrolytic reactions and form solid precipitates as shown in Equations 3 and 4 (Metcalf and Eddy 2003).

$$Al(H_2O)_6{}^{3+} \xrightleftharpoons[+H^+]{-H^+} Al(OH)_3(s) \xrightleftharpoons[+H^+]{-H^+} Al(OH)_4{}^{-} \tag{3}$$

$$Fe(H_2O)_6{}^{3+} \xrightleftharpoons[+H^+]{-H^+} Fe(OH)_3(s) \xrightleftharpoons[+H^+]{-H^+} Fe(OH)_4{}^{-} \tag{4}$$

$Al(OH)_3$ and $Fe(OH)_3$ are precipitates. At 25 °C, Al^{3+} forms precipitate $Al(OH)_3$ at pH of 5.8 to 7.7, and Fe^{3+} forms precipitate $Fe(OH)_3$ at pH of 5.2 to 8.7. Different coagulants yield different effective pH ranges.

USEPA requires the use of a natural organic material removal strategy “enhanced coagulation” to limit the formation of all disinfection by-products for conventional water treatment facilities. Enhanced coagulation requires the TOC removal based on the raw water alkalinity to avoid adding high dosages of hydrolyzing metal salt coagulants to reduce the pH lower than the coagulant most efficient pH range which often appear between 5 and 6. Performing jar tests on at least a quarterly basis for one year can be an alternative for the determination of the TOC removal requirement (AWWA 1999).

Coagulation was investigated as a pretreatment process for *in situ* tar sand process water by McTernan et al. (1987). Ferric chloride was found to be the most effective coagulant compared to aluminum sulfate and lime. After treatment, more than 98% of the emulsion was removed as total organic carbon (TOC) and more than 99% of the emulsion was removed as suspended solids. However, this increased toxicity levels. Therefore, as a further treatment process, activated carbon adsorption was studied to remove toxic compounds.

2.3.1.2 Activated carbon adsorption

Thousands of tones of petroleum coke – a byproduct of the oil upgrading process – is produced everyday by the oil sands industry and is presently considered waste (DiPanfilo and Egiebor 1996). How to utilize the huge storage in oil sand plants as well as the associated environmental impacts are major concerns of petroleum coke (Bryers 1993; Majid et al. 1988; Zamora et al. 2000). Due to its high carbon content, coke can be activated to produce activated carbon which is a common adsorbent in water and wastewater treatment (DiPanfilo and Egiebor 1996; Zamora et al. 2000). Zamora et al. (2000) assessed the feasibility of reusing petroleum coke for water treatment. The study showed that it was a highly promising process to produce an activated carbon for the heavy metals removal from wastewater. Syncrude Canada has initiated a pilot study to assess using activated coke adsorption in OSPW treatment. Utilizing petroleum coke for the production of activated carbon can provide an excellent treatment option for OSPW. At the same time, it provides a low-cost and valuable activated carbon, and a way to address consumption of coke storage in the upgrading plants (Shawwa et al. 2001).

Activated carbon adsorption removes dissolved organics and heavy metals which are attributed colours in an aqueous environment. Ramírez Zamora et al. (2000)

studied the activation process in a Mexican petroleum refinery. The process they used was highly promising for the production of the activated carbon which can be applied to the removal of heavy metals in wastewater. Shawwa et al. (2001) evaluated the activated petroleum coke for colour and chlorinated organic reduction in pulp mill wastewater. Colour, chemical oxygen demand (COD), dissolved organic carbon (DOC) and adsorbable organic halogens (AOX) were significantly removed (> 90%) when the activated coke dose exceeded 15000 mg/L. Martienssen and Simon (1996) studied the effect of activated carbon on the biological treatment of oil-water emulsions which contained high concentrations of emulsified mineral oil, stabilizers and different additives. An activated sludge reactor was used to remove biodegradable substances, and about 60% of the influent TOC was reduced during the first activated carbon treatment process. Sierka and King (1986) applied activated carbon adsorption after the coagulation process for the treatment of wastewater obtained from two different extraction techniques for the tar sands in Utah, USA: (1) sequenced reverse-forward combustion (TS-2C) and (2) steam flooding (TS-1S). 91.6 % of TOC in TS-1S wastewater and 19.5 % of TOC in TS-2C wastewater were removed by 1000 mg/L of activated carbon after 350 mg/L of ferric chloride coagulation pretreatment. Wiessner et al. (1998) studied activated carbon and activated coke adsorption for the treatment of a deposited lignite pyrolysis wastewater with a wide molecular size distribution of organic compounds. The results showed that the amount of lignite compounds adsorbed by the activated coke was higher than the activated carbon. The organic compounds in the completely autoxidized surface water were nearly 94% adsorbed based on TOC analysis. Due to its large number of macropores and mesopores, it was concluded that activated coke was more suitable for wastewater treatment and cheaper than activated carbon.

2.3.1.3 Membrane filtration

Membrane filtrations including nanofiltration (NF), reverse osmosis (RO), ultrafiltration (UF), and microfiltration (MF) are able to remove a wide range of constituents such as suspended solids, colloidal organic matters, hydrocarbons, NAs, dissolved solids, salts, trace metals, and hardness. However, since it requires membrane replacement, this technology is more costly than granular media filtration.

Nanofiltration is capable of concentrating sugars, divalent salts, bacteria, proteins, particles and other constituents that have a molecular weight greater than 1000 Dalton. Monovalent ions, such as Na^+ and $C1^-$ can pass through the membrane, while divalent ions such as Ca^{2+}, Mg^{2+}, CO_3^{2-}, and SO_4^{2-} and other polyvalent ions are rejected into the retentive volume - allowing divalent ions to be removed from an aqueous environment. It was reported that NF had been applied successfully for treatment of oil sands waters particularly for water softening and the removal of toxic components such as NAs (Peng et al. 2004). A bench-scale flat sheet membrane system with several commercially available NF membranes was applied to remove hardness and NAs from both imported and potential discharge waters. It was found that after membrane filtration more than 95% of water hardness and NAs were reduced.

Reverse osmosis can remove all the dissolved solids with the exception of water and its associated ions. It can effectively lower dissolved solids and produce high quality water, but pretreatment is required. Once the wastewater flows through a reverse osmosis membrane, almost all the contaminants are left behind except H_2O, H^+ and OH^-. However, because reverse osmosis filters have exceptionally fine pores, prefiltration is needed to minimize membrane fouling. But the major drawbacks of reverse osmosis are its high cost associated to the RO process combined with membrane fouling and concentrate disposal. Sierka and King (1986) investigated four membrane types: cellulose acetate, poly-ether amide, poly-ether urea, and noncellulose on a poly-sulfone base, with a two-stage RO process for wastewater treatment from the oil sands extraction process. In the RO process, a maximum of 98% organic rejection and 97% of inorganic rejections were achieved after a sequence of pretreatments that include: coagulation, activated carbon adsorption and ozonation.

2.3.1.4 Chemical oxidation

Chemical oxidation is used to: reduce inorganic species, reduce hazardous organic compounds, destroy taste- and odor-causing compounds, and eliminate colour. The most common chemical oxidants used in water treatment are chlorine, chlorine dioxide, ozone, peroxide and permanganate. Advanced oxidation processes (AOPs) are based on the generation and the use of highly reactive hydroxyl radicals ($\cdot OH$) to oxidize organic and inorganic substances, which are otherwise very recalcitrant to conventional oxidation processes (AWWA 1999; Lee 2006). Chemical oxidation technologies are capable of degrading petroleum contaminants. Advanced oxidation techniques are investigated as a complementary technology to current biodegradation remediation to accelerate the OSPW remediation rate. NAs are a major concern for OSPW toxicity, since they are poorly degraded by natural biodegradation in tailings ponds. There has been some evidence that advanced oxidation techniques can selectively remove the biologically persistent fraction of NAs and reduce the overall toxicity of NA mixtures (Fu et al. 2008; Scott et al. 2008).

Ozonation: Due to its high reactivity and instability, ozone, as a gas, typically needs to be generated on-site and close to the treatment area. Ozone can oxidize contaminants directly or through the formation of hydroxyl radicals (·OH). It is one of the strongest chemical oxidants and it is capable of rapidly reacting with a myriad of organic or inorganic compounds. Chemical oxidation using ozonation has been investigated as an option for mitigation of the toxicity of the OSPW (AWWA 1999; Scott et al. 2008). The results showed that the NAs' concentration decreased by 70% after 50 minutes of ozonation; and it decreased to 2 mg/L or less than 5% of the initial concentration after 130 min of ozonation. Fu et al. (2008) conducted a semi-batch study on the degradation of NAs in OSPW using a non-optimized ozonation process. In relation to ozone doses ranging from 50 to 1500 mg/L, 70 - 90% reduction of NAs was achieved. The dissolved organic carbon (DOC) and chemical oxygen demand (COD) decreased by 32% and 53% respectively. Meanwhile, the biochemical oxygen demand (BOD_5) increased from 4 mg/L to 24 mg/L, which indicated that the biodegradability of OSPW significantly increased after ozone treatment.

2.3.2 Biological Treatment

2.3.2.1 Biodegradation

Microbiological degradation of petroleum organic acids, especially NAs, is an important issue in oil sands tailings remediation. The natural aging process of oil sands tailings degrades organic acids and reduces the toxicity. Currently, the degradation rate of NAs is very low in oil sands tailings ponds, and it is extremely difficult to bring the NAs' concentration levels lower than 19 mg/L by nature biodegradation. This is difficult even under a process of more than 10 years. Uncompleted degradation may be caused by the lack of specific enzymes or bacteria to further biodegradation (Quagraine et al. 2005a).

Bioremediation is the application of normal metabolic processes of microorganisms to alter the chemical structures of organic materials to reduce the toxicity of compounds to humans and the surrounding living environment (Quagraine et al. 2005b). In order to apply bioremediation technology on site, an understanding of the mechanisms of biodegradation of NAs is necessary and required. Some conditions are critical for microbial growth and metabolism such as salinity, temperature, dissolved oxygen, pH, redox potential, and sediment structure. However, these conditions are very difficult and usually expensive to be optimized in the field (Quagraine et al. 2005b).

Clemente et al. (2004) studied the biodegradation of commercial preparations of NAs in aerobic cultures. After 10 days of incubation, the NAs concentration decreased to levels less than 10 mg/L from approximately 100 mg/L. Sixty percent of the carbons from NAs were transferred to carbon dioxide (CO_2), releasing from the tailings pond, which contributed to the reduction of toxicity of the culture supernatant. By using gas chromatography - mass spectrometry (GC-MS) analysis, decomposition and destruction of NA mixtures occurred during the biodegradation process, and lower molecular weight acids were degraded more readily than the higher molecular weight acids.

2.3.2.2 Physico-biological treatment

The Granular Activated Carbon (GAC) filtration is an economical and effective process for the removal of dissolved solids in water by adsorption. Because of its large surface area, GAC filters provide an excellent medium for bacteria growth, which enhances a fraction of organics degradation and eventually removal. It was found that pre-oxidation prior to GAC filtration could significantly enhance the biological activity on GAC (Antonelli et al. 2003). Therefore, GAC filtration is commonly placed after the ozonation process to achieve the biological activated carbon process or biologically enhanced activated carbon process. Antonelli et al. (2003) investigated biologically enhanced granulated activated carbon filtration as a post-treatment to produce a purified effluent suitable for reuse in the textile industry. According to the study - carried-out on three small pilot-scale filters - biomass contributed significantly to COD removal but not to colour abatement. Adachi and Fuchu (1991) applied the biological aerated filter process for the reclamation and reuse of domestic wastewater in an office building, for the castor oil containing industrial wastewater in an aluminum rolling mill, and for the industrial wastewater in a paper mill. Their results showed that biological aerated filtration was a feasible process for various sources of wastewater treatment according to BOD and suspended solids removal. Yao et al. (2003) studied the feasibility of the reuse of non-biodegradable organic wastewater by utilizing immobilized biological technology as a possible process for petrochemical wastewater treatment. It was found that the immobilized biological activated carbon filter could remove COD, oil and ammonia nitrogen more than the granular activated carbon filter. The effluent can be reused in the system as circulating cooling water.

2.3.3 Combined Treatment Processes

2.3.3.1 Evaluation of treatment technologies for OSPW

The applicability of possible physical, chemical and biological treatment technologies for OSPW is summarized in Table 2. The advantages and limitations are listed in Table 3.

Table 2: Applicability of various water treatment technologies for OSPW
(Crittenden 2005)

Class	Unit treatment process	Typical application in water treatment
Physico-chemical	Coagulation-flocculation-sedimentation	Removal of suspended solids, some colloidal organic matters, colours, metals
	Activated carbon Adsorption	Removal of dissolved organics or dissolved solids
	Ozonation	Decomposition and destruction of hydrocarbons, organic acids; control of odors; removal of ammonia
	Nanofiltration	Removal of dissolved submicrometer particles (0.001 to 0.01 μm) by size exclusion, removal of natural organic matter, NAs, hardness, ammonia, bacteria and protozoa in OSPW
	Reverse osmosis	Removal of dissolved submicrometer particles (0.0001 to 0.005 μm) by size exclusion, removal of salts, everything except water in OSPW
Physico-biological	Biological activated carbon filtration	Dual purpose of particle removal by filtration and removal of biodegradable organic matter by biological oxidation; removal of hydrocarbons, naphthenic acids, ammonia in OSPW
Biological	Microbiological degradation	Decomposition and destruction of organic matter; degradation of organics and NAs in OSPW

Table 3: Advantages and limitations of various water treatment technologies (adapted from (Sorgini 2007))

Technology	**Advantages**	**Limitations**
Coagulation-flocculation-sedimentation	● Removes major suspended solids, turbidity and color ● Easy to operate ● Low cost	● Chemicals required ● Temperature affected ● More labor needed
Media filtration	● Simple, easy to operate ● Cheap ● few labor required ● Media can last longer time	● Effluent quality varies ● Feed water conditions affected ● Large volumes of wastewater during backwash
Membrane filtration	● Physical barrier to pathogens, biosolids and turbidity ● Simple and automated operation ● Few labor required	● Requires pretreatment ● Higher cost than granular media filters ● Will require membrane replacement at some point
Reverse osmosis	● Reduces total dissolved solids, salts ● Provides water suitable for disinfection ● High-quality water treatment method	● Requires pretreatment ● Fouling by suspended solids ● costly
Ozonation	● Chemical-free method ● No labor required	● Health, safety, and environmental issues with chemical handling ● Produces disinfection by-products
Biodegradation	● Low cost ● Easy to operate	● Slow degradation rate ● incomplete degradation

None of single cost-effective water treatment technologies can remove all the constituents from OSPW to achieve the requirements for reuse and safe discharge to the environment. It is necessary to set-up an effective, feasible and economical strategy by combining different water treatment processes for industrial OSPW management. Based on the evaluation of the various water treatment technologies available, the possible combined treatment processes for OSPW is proposed as:

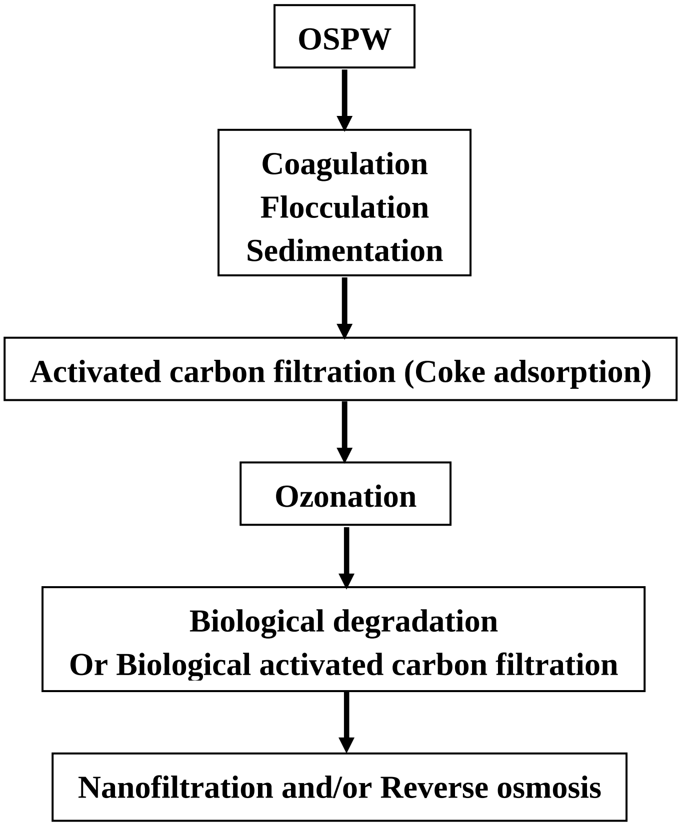


Figure 1: Proposed combined OSPW treatment processes

2.4 Trends and Needs in OSPW Research

Based on the literature review above, the trends and needs in current OSPW research are summarized as follows:

Limited research is available on OSPW treatment. OSPW management is critical for sustainably developing the Athabasca Oil Sands in Northern Alberta, which are increasingly gaining public and government interest. An objective evaluation of the feasibility of various treatment options for oil sands water management must be conducted.

- The majority of OSPW treatment research conducted looked at new innovative treatment technologies. No research on the pretreatment processes to remove suspended particles has been conducted.
- In the pretreatment study, more detailed information of the coagulation-flocculation process used for OSPW treatment needs to be addressed such as: identifying the optimized operational conditions including rapid and slow mixing intensity and time; coagulant type and dose; and coagulant aid type and dose. Based on the treatment results and cost analysis, the suitable options of coagulants and coagulant aids and the associated optimum process conditions for the industry need to be selected.
- A proposal of feasible and cost-effective combination of water treatment processes is needed for the oil sands industry.

2.5 Current Study Objectives

The objective of this research is to evaluate the feasibility of the coagulation-flocculation process as a pretreatment process for OSPW. The treatment process was optimized to achieve the best operation conditions that would yield the highest removal efficiency in TOC and turbidity, and meet the requirements of further OSPW treatment processes for its reuse and safe discharge into the environment. The detailed research strategy for the coagulation-flocculation processes are summarized as follows:

- Coagulant type selection
- Coagulant aid selection
- Process optimization including rapid and slow mixing intensities and time
- Comparison of treatment performances using different coagulants and coagulant aids, cost analysis
- pH investigation
- Provide the suitable options of the coagulation-flocculation and optimum process conditions for industry application
- Discussion of the possible mechanisms of the coagulation-flocculation process

CHAPTER 3 MATERIALS AND METHODS

3.1 Materials

Raw OSPW was obtained from Syncrude's West Inpit Pond (WIP) located in Fort McMurray, Alberta, Canada. OSPW samples were fresh and surface water collected at the top 3 m zone of the WIP tailings pond by Syncrude's staff. The samples were then delivered to the Natural Resources Engineering Facility (NREF) at the University of Alberta.

All chemicals were of analytical reagent grade conforming to specifications of the Committee of Analytical Reagents of the American Chemical Society. Deionized (DI) water was used in all the experiments.

3.2 Experimental Methods

3.2.1 Sample Collection and Storage

All the OSPW samples were reserved in plastic barrels (200 L) or small plastic barrels (20 L) in a cold room maintained at 4 ºC. The samples in 200 L barrels were mixed evenly using a LIGNTNIN Model L mixer before being transferred to 20 liter plastic barrels. The samples were then moved out of the cold room one night prior to conducting experiments, so the OSPW could reach room temperature. The OSPW samples were mixed again before being transferred to each jar. All standard sampling methods were used in this research. Labwares were rinsed with DI water and dried before use.

3.2.2 Experiment Location

Jar-test experiments, temperature, turbidity, TSS, TDS and pH measurements were performed and taken in the NREF Environmental Central Service Lab 6-001 at the University of Alberta.

TOC, TC and COD analyses were conducted in NREF Ozone/Water Research Lab 5-024 at the University of Alberta.

Ion chromatography (IC), inductively coupled plasma - mass spectrometry (ICP-MS), conductivity and alkalinity measurements were performed in NREF Geochemistry Lab L1-016 at the University of Alberta.

3.2.3 Jar Test

3.2.3.1 General

Jar test was carried out to simulate coagulation-flocculation and sedimentation processes, and to determine the type of chemicals (coagulants and coagulant aids), dosages, and operational conditions required to achieve optimum results. The primary variables to be investigated include, but are not limited to:

a. pH
b. Coagulant type and dosage
c. Coagulant aid type and dosage
d. Order of addition and mixing conditions
e. Settling time

3.2.3.2 Apparatus

The jar-test apparatus (Phipps & Bird PB-700^{TM} JarTester) shown in Figure 2 was used in experimental work.

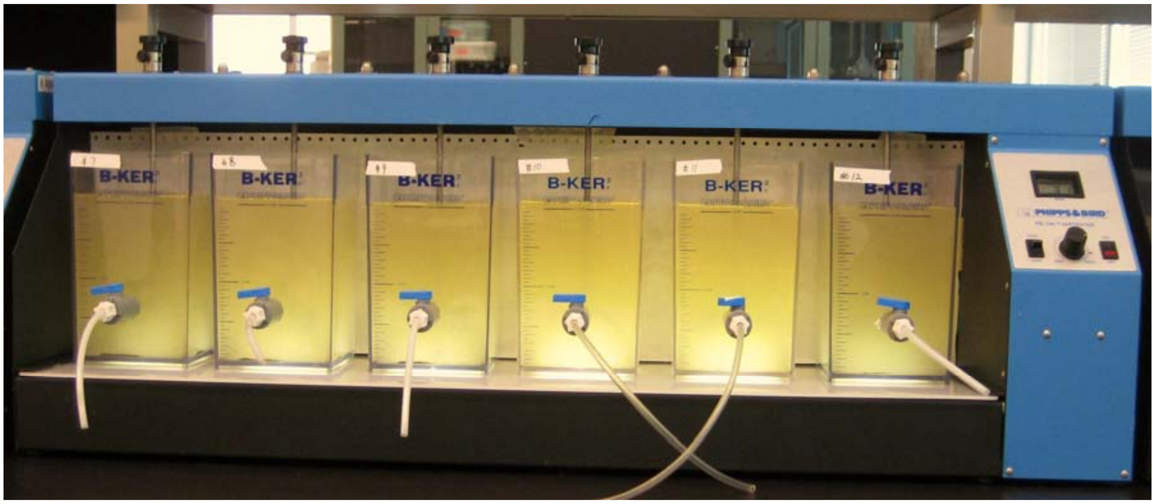


Figure 2: Jar-Test Apparatus: Phipps & Bird PB-700^{TM} JarTester

a. Multiple stirrer: A multiposition stirrer with continuous speed variation from 0 to 300 rpm can be selected. The stirring paddles are of light gage corrosion-resistant materials all of which have the same configuration and size.
b. Jars (B-KER): 2 liter, all have the same size, shape and materials.

3.3 Analytical Methods

All equipment and solutions were calibrated before use.

3.3.1 pH and Temperature

3.3.1.1 General consideration

pH is a measure of the acidity or basicity of a solution, which is one of the most important characters of water chemistry. Every phase of water/wastewater treatment is pH dependent. pH affects not only the treatment efficiency, but also the treated water quality. The ideal pH level of drinking water is between 6 and 8.5. For the reason of safe discharge, the pH of treated OSPW has to follow the environmental regulations associated with certain environment or pathways. Therefore, the pH of each OSPW sample was monitored before and after treatment.

Water chemistry is also temperature dependent. The sample temperatures were adjusted to room temperature before any experiments were conducted. Temperatures were also monitored before and after treatment.

3.3.1.2 Apparatus

Accumet Research AR20 pH/Conductivity Meter, Fisher Scientific
Thermometer, 0 - 120 °C

3.3.1.3 Procedure

Refer to Standard Method (American Public Health Association 2005), 4500-H^+

3.3.2 Turbidity

3.3.2.1 General consideration

Turbidity is the amount of cloudiness in the water. Practically, turbidity refers to how clear the water is. The more the total suspended solids (TSS) in the water, the higher the measured turbidity. Turbidity can be caused by silt, sand, mud, bacteria, germs, chemical precipitates, and etc. It is suitable to measure the cleaning efficiency of wastewater treatment processes, since it can quantitatively determine the remaining undissolved, suspended particles in a liquid phase. The coagulation-flocculation process is designed to remove turbidity. To evaluate the efficiency of the coagulation-flocculation process, the turbidity levels of the samples need to be determined before and after treatment.

In this project, turbidity was measured using a turbidity meter in nephelometric turbidity units (NTU). This is not a direct measure of the suspended particles, but a measure of their scattering effect on light. Since it can scatter more light than clear water, cloudy water has higher NTU.

3.3.2.2 Apparatus

Orbeco-Hellige 965 Digital Direct-Reading Turbidimeter, Orbeco Analytical Systems Inc.

3.3.2.3 Procedure

Refer to Standard Method (American Public Health Association 2005), 2130 Turbidity

3.3.3 Alkalinity

3.3.3.1 General consideration

Alkalinity is a measure of the capacity of water to neutralize acids. Alkalinity is an indicator of carbonates, bicarbonates and hydroxides contents. It may include borates, phosphates and silicates when they are present in water. Alkalinity describes the buffering capacity of water against pH change from the addition of acid. The higher the alkalinity, the greater the neutralizing capacity and the ability to resist pH changes. Alkalinity values provide guidance in applying proper doses of chemicals to water and wastewater treatment processes, particularly in coagulation, softening and operational control of anaerobic digestion (Department of Civil & Environmental Engineering 2007c).

The total alkalinity, bicarbonate alkalinity and carbonate alkalinity (as mg $CaCO_3$/L) can be determined and compared to theoretical values using the following calibration methods (Department of Civil & Environmental Engineering 2007c):

$$\text{Total Alkalinity} = V_t \times N \times 50000 \div V_s \tag{5}$$

$$\text{Carbonate Alkalinity} = 2 \times V \times N \times 50000 \div V_s \tag{6}$$

$$\text{Bicarbonate Alkalinity} = \text{Total Alkalinity} - \text{Carbonate Alkalinity} \tag{7}$$

Where: V_t = the total volume (mL) of titrant used at pH = 4.5

N = the normality of the titrant (0.02N H_2SO_4)

V_s = the volume (mL) of the sample being titrated

V = the volume (mL) of the titrant used at pH = 8.3

3.3.3.2 Apparatus

Graduated buret (50 mL)

Stirring plate and magnetic stirring bar

Thermo-Orion 290A$^+$ with Orion 9107BN electrode

pH meter

Graduate cylinder

Beaker (100 mL)

3.3.3.3 Procedure

a. Calibrate pH meter using buffer solutions (pH = 4.01, 7.00 and 10.01)
b. 50 mL of the sample was measured and transferred into a 100 mL beaker

containing a magnetic stirring bar. The buret was filled-up with 0.02 N of sulfuric acid (H_2SO_4). An initial volume of titrant and pH of the sample were recorded, and a constant stirring rate was achieved without turbulent before beginning the titration. The sample was titrated with 0.02 N H_2SO_4. There are two key inflection points at pH = 8.3 and 4.5. The amount of acid needed to reach pH = 8.3 was recorded, which is required for the calculation of Phenolphtalein Alkalinity. Then the Bromocresol Green Indicator was added, and the color would change from green to light pink at pH = 4.5. The titration continued, and the amount of the acid used to reach pH = 4.5 was recorded. This was needed to calculate the Total Alkalinity of the sample (American Public Health Association 2005; Burkus 2007b; River Watch Network 1992).

3.3.4 Conductivity

3.3.4.1 General consideration

Conductivity is a measure of the ability of water to pass an electrical current. Conductivity in water is mainly affected by the presence of inorganic dissolved solids such as: chloride, nitrate, sulfate and phosphate anions; or sodium, magnesium, calcium, iron and aluminum cations. Organic compounds have low conductivities in water, because they do not conduct electrical currents very well. Conductivity is affected by temperature. The warmer the water, the higher the conductivity is. Therefore, conductivity is reported at 25 °C. In this project, conductivity was measured in microsiemens per centimeter (µS/cm).

3.3.4.2 Apparatus

Thermo Orion Portable 130A Conductivity Meter

Thermo Orion 013010A Conductivity Cell

3.3.4.3 Procedure

Refer to EPA Method 9050A (EPA 1996) which is used to measure the conductivity of drinking, ground, surface, saline waters, domestic and industrial aqueous waters (Burkus 2007a).

3.3.5 Total Organic Carbon (TOC)

3.3.5.1 General consideration

Total organic carbon (TOC) is a direct expression of total organic content in the solution. Unlike the biochemical oxygen demand (BOD) or chemical oxygen demand (COD), TOC measurement is independent of the oxidation state of the organic matter in water. It is also not affected by other organically bond elements such as nitrogen, hydrogen and inorganics, which can contribute to the oxygen demand measured by BOD and COD. The presence of organic contaminants can degrade ion-exchange capacity, serve as a nutrient source for undesired biological growth, or be detrimental to the process in which the water is utilized (American Public Health Association 2005). Therefore, TOC measurement is important for the operation in wastewater treatment plants.

Total Inorganic Carbon (TIC) includes the carbonate, bicarbonate and dissolved CO_2; and Total Organic Carbon refers to all carbon atoms covalently bonded in organic molecules. Inorganic carbon interference can be eliminated by acidifying samples to $pH \leq 2$, and inorganic carbon species can be converted to CO_2 which can be easily removed from liquid samples by purging with a purified gas. The high-temperature combustion method was used for the TOC analyzer. Organic carbons were oxidized to CO_2 by combustion at 680 °C and were continually flushed with pure oxygen. All the samples were analyzed in reference to a blank (DI water).

3.3.5.2 Apparatus

Apollo 9000 TOC Combustion Analyzer, FOLIO Instruments Inc.

3.3.5.3 Procedure

It was found that lots of bubbles formed in the OSPW when purging took place by the TOC analyzer automatically and it caused the sample to overflow in its container. Therefore, the actual TOC measurement procedures were adjusted. The samples were acidified with 85% phosphoric acid and purged by compressed air for 3 minutes before placing them into an auto sampler, so inorganic carbons in OSPW were transferred to CO_2 and removed from the aqueous sample. The software was then set-up for TC measurement which gave the same results as the TOC measurement with auto sample acidification by the TOC analyzer. The instrument was calibrated using blank and KHP standards before measuring samples were taken. The standard curve and calculations were accomplished using Apollo software: TOC Talk. The calibration and sample analysis procedures referred to the Apollo 9000 TOC System Manual (Department of Civil & Environmental Engineering 2007b).

All the samples were analyzed in triplicates to ensure quality assurance. The average of triplicates was taken as the final result.

3.3.6 Chemical Oxygen Demand (COD)

3.3.6.1 General consideration

COD is used as a nonspecific measure of the organic matter content of a liquid sample (American Public Health Association 2005).

3.3.6.2 Apparatus

COD Reactor, Bioscience Inc., Analytical Products

Spectrophotometer Pharmacia Biotech Novaspec Π

3.3.6.3 Procedure

The closed reflux COD method was used in this project. 3.5 mL of digestion reagent (35 mM potassium dichromate and 3.0 M sulfuric acid) and 2 mL of Micro-COD reagent (add Ag_2SO_4 to concentrated sulfuric acid at the rate of 5.5 g Ag_2SO_4/kg H_2SO_4) (American Public Health Association 2005) were added to a 10 mL sealed test tube with 2 mL of the sample. The tightly closed test tubes including samples, standards and blanks were mixed and then placed in the COD reactor for 2-hour-digestion at 140 °C. After samples were cooled, the spectrophotometer was used to measure the absorbance at 600 nm. Standards and blanks were used to prepare a Standard Curve to determine COD of the sample. All the samples were analyzed in duplicates and their average was recorded as the final result.

3.3.7 Total Suspended Solids (TSS)

3.3.7.1 General consideration

Gravimetric analysis was used to determine TSS. The solids in a well-mixed sample were separated by filtration with a weighed standard TSS filter. The residue retained on the filter was dried to a constant weight at 103 ~ 105 °C and the water evaporated. Total suspended solids are the portion of total solids retained by the filter. Total dissolved solids (TDS) are the portion that passes through the filter. The amount of solids is expressed as the ratio of mass per volume (mg/L). (Department of Civil & Environmental Engineering 2007a)

The calculation equation is (American Public Health Association 2005):

$$\text{mg TSS/L} = \frac{(A - B) \times 1000}{Sample\ volume,\ mL} \tag{8}$$

where: A = weight of filter + dried residue, mg

B = weight of filter, mg

3.3.7.2 Apparatus

Gooch crucibles: wide-open 25 mL

Glass fibre filters (specially cut A/E glass fiber, 1 μm pore size and 33.8 mm diameter), Pall corporation

Analytical balance: APX-60 (Max. 60g; d = 0.1 mg), Denver Instrument

Isotemp oven, Fisher Scientific

Desiccator

Vacuum filtration system

3.3.7.3 Procedure

a. Preparation of glass-fiber filter disk: All the gooch crucibles were washed and rinsed using DI water. A filter was added to each crucible, and soaked with DI water in order to seat it and remove bubbles. The crucibles with filters were dried at 105 ± 2 °C overnight (at least 1 hour). They were then placed in a desiccator to cool them to ambient temperature before being weighed. The cycle of drying, cooling, desiccating and weighing was repeated until the weight change was less than 4% of the previous reading. They were stored in the desiccator until needed.

b. Sample analysis: The initial weight of the crucibles with a filter was recorded before filtration. The crucible was placed on a vacuum filtration system and the filter was wetted with a small volume of reagent-grade water to seat it. The sample was mixed and then filtered through the crucible. 100 mL of the raw OSPW sample without treatment was used for the filtration, and 500 mL of treated OSPW was used during filtration. The sample volume was adjusted to yield between around 2.5 and 200 mg dried residue for quality control and assurance as the standard method. Since fewer residues were left in the treated OSPW, the volume of sample used for the filtration was increased. When filtration was completed, the filter was washed with reagent-grade water, and suction was continued for about 3 min. The crucibles were dried in an oven at 103~105 °C for one night (more than 12 hours). The crucibles were then cooled to an ambient temperature in a desiccator before weighed on the same analytical balance. The cycle of drying, cooling, desiccating and weighing was repeated until a constant weight or weight change of less than 4% of the previous reading was achieved.

All the samples were analyzed in 5 replicates. The average value or the range was taken as the final result.

3.3.8 Total Dissolved Solids (TDS)

3.3.8.1 General consideration

TDS is the portion of total solids that have passed through a standard glass fiber filter (nominal pore size of 2.0 μm or smaller) (American Public Health Association 2005; Department of Civil & Environmental Engineering 2007a). In practice, a well-mixed sample was filtered through a standard glass fiber filter. The filtrate was evaporated in a weighed evaporating dish and dried to a constant weight at 105 ± 2 °C. The increase in the dish weight was TDS. The amount of solids is expressed as the ratio of mass per volume (mg/L) (American Public Health Association 2005)

The calculation equation is (American Public Health Association 2005):

$$\text{mg TDS/L} = \frac{(A-B)\times 1000}{Sample\ volume,\ mL} \qquad (9)$$

where: A = weight of dried residue + dish, mg

B = weight of dish, mg

3.3.8.2 Apparatus

Evaporating dishes: 50 mL

Desiccator

Isotemp oven, Fisher Scientific

Furnace: Type 30400, Thermolyne

Analytical balance: APX-60 (Max. 60g; d = 0.1 mg), Denver Instrument

Graduate cylinder

Glass fibre filters (specially cut A/E glass fiber, 1 μm pore size and 33.8 mm diameter), Pall corporation

Vacuum filtration system

3.3.8.3 Procedure

a. Preparation of evaporating dish: Evaporating dishes were cleaned and heated at 550 °C for 30 min in a furnace. The dishes were stored in a desiccator to cool down and were weighed immediately before use.
b. Sample analysis: The initial weight of the evaporating dishes was recorded and samples were mixed before filtration. Approximately 50 mL of the samples was filtered through a glass-fiber filter with applied vacuum. When filtration was completed, the suspended solids were removed. A 35 mL aliquot of the filtrate was measured using a graduate cylinder and transferred to a clean, pre-weighed evaporating dish and evaporated to achieve dryness in an oven at 103~105 °C for one night (more than 12 hours). The evaporating dish was then cooled to an ambient temperature in a desiccator before being weighed on the same analytical balance. The cycle of drying, cooling, desiccating and weighing was repeated until a constant weight or weight change of less than 4% of the previous reading was achieved.

All the samples were analyzed in triplicates or more, and the average value or TDS range was taken as the final result.

3.3.9 Naphthenic Acids (NAs)

3.3.9.1 General consideration

NAs are a broad group of alkyl-substituted saturated cyclic and non-cyclic carboxylic acids with a general formula of $C_nH_{2n+z}O_2$, where n is the number of carbons, and z is zero or the negative even integer number of rings in a molecule. For example, no ring is $z = 0$; 1 ring is $z = -2$. NAs are natural constituents of bitumen and are released during the oil sands extraction process. They are concentrated in tailings ponds (20-120 mg/L) and largely contribute to the toxicity of OSPW.

3.3.9.2 Apparatus

Waters Acquity Ultra Performance Liquid Chromatography (UPLC) System with a High Resolution QStar Pulsar i Mass Spectrometer (HRMS) equipped with a TurboIon Spray source, Applied Biosystems/MDS Sciex, Concord, ON, Canada

All the instruments were located at Dr. Jonathan W. Martin's lab in the Department of Laboratory and Pathology, Division of Analytical and Environmental Toxicology at the University of Alberta.

3.3.9.3 Procedure

a. The samples were filtered through 0.45 μm filter, and the filtrates were then collected for instrumental analysis.
b. Samples were sent to Dr. Martin's lab and analyzed by Dr. Leonidas Perez. The Waters Acquity UPLC system was employed for rapid and efficient chromatographic separation of NAs. Detection was performed in-line with a high resolution QStar Pulsar i mass spectrometer equipped with a TurboIon Spray source operated in negative ion mode. Chromatographic separations were run on a Waters UPLC phenyl BEH column (150×1 mm, 1.7 μm) using a gradient mobile phase of (*A*) 10 mmol/L ammonium acetate solution prepared in Optima-grade water and (B) 10 mmol/L

ammonium acetate in 40% acetone and 60% methanol. Gradient elution was > 1% of (*B*) by 2 min, ramped to 60% of (B) by 3 min, to 70% of (B) by 7 min, to 95% of (*B*) by 13 min, holding it until 14 min and finally returned to 1% of (B) followed by an equilibration time of 5.8 min. The flow rate was 0.110 mL/min and column temperature was 50°C (Han et al. 2009).

3.3.10 Ionic Chromatography (IC)

3.3.10.1 General consideration

Ion chromatography is capable for water chemistry analysis. It is able to measure concentrations in parts-per-millions (ppm) quantities of major anions such as: fluoride, chloride, nitrate, nitrite, and sulfate, as well as major cations such as lithium, sodium, ammonium, potassium, calcium, and magnesium. Concentrations of organic acids can also be measured by IC. The chromatography has the capability to analyze aqueous samples in parts-per-billion (ppb) quantities of hydrazine, monomethylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH). Ion chromatography measures concentrations of ionic species by separating them based on their interaction with a resin. The separated anions in their acid form are measured using an electrical conductivity cell and identified based on their retention times compared to known standards. Quantification is determined by measuring the peak height or area and comparing it to a standard calibration curve. (American Public Health Association 2005; EPA 1993; EPA 2007); (Weiss and Weiss 2005)

In this project, some ions were introduced in the sample during the chemicals addition. In order to assess the treatment performance and impacts from the chemical addition, ion chromatography was used to investigate the difference of the concentrations of major ions in the supernatant of OSPW before and after treatment.

3.3.10.2 Apparatus

Dionex 2500 and 2000 IC system equipped with AS50 auto-sampler with 25 μL injection loop, GP50 gradient pump, CD25 conductivity detector, NG1, AG14A, AS14A columns, ASRS Ultra Π suppressor, eluent reservoir with 4×2L suitable plastic containers, and nitrogen 4.8 compressed gas.
Socorex pipetter with disposable pipet tips
10 mL Dionex sample vials
Volumetric flasks (10 mL, 1 mL) and beakers
20 mL luer-lok syringes, syringe tips, 0.22 μm filters
10 mL Dionex IC vials

3.3.10.3 Procedure

Both straight samples and 10 × dilutions were tested in order to have detectable results. Measuring sample conductivity is a way to predict the dilution factor.

The procedure refers to Instrumentation Training Material: Determination of Inorganic Anions by Ionic Chromatography-SOP (Burkus 2009).

3.3.11 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

3.3.11.1 General consideration

ICP-MS is a relatively novel technique used for trace element determination. One of the advantages is its low detection limits for a wide variety of elements. Most elements can be detected and measured at parts per trillion (ppt) levels, and some can even be measured at parts per quadrillion (ppq) levels. ICP-MS has been used in various areas, including water systems, geology, soil science, metallurgy, food sciences, medicine, etc.

In the ICP-MS system, the sample solution is sprayed into a flowing argon and passed into an inductively heated plasma torch at a high temperature (approximately 10000 °C), which causes sample atomization followed by ionization. The ions are sorted according to their mass to charge ratios and are quantified with a channel electron multiplier. `

In this project, concentrations of the various elements in OSPW were measured before and after treatment in order to evaluate the coagulation-flocculation treatment.

3.3.11.2 Apparatus

Elan 9000 ICP Mass Spectrometer, PerkinElmer SCIEX

Ethos SEL Microwave Solvent Extraction Labstation, Milestone Microwave Laboratory System

3.3.11.3 Procedure

a. Microwave assisted acid digestion: For the total recoverable metals analysis, a 5 mL of sample was digested with 10 mL of concentrated nitric acid for 10 min using microwave heating in a laboratory microwave unit. Then the sample was cooled to room temperature, and the digest was transferred to a 100 mL volumetric flask. The sample was prepared for the ICP-MS analysis by 10 times dilution using 1 % HNO_3 (*v*/*v*). So, it would be a 200 times dilution in total from the straight sample. (EPA 1992; EPA 1994a)

b. Standards preparation: Standard solutions were prepared by diluting the stock standard solutions (purchased) to specific concentration: 0.2, 2, 10, 50, 100, and 200 ppb in a solvent consisting of 1 percent (*v*/*v*) HNO_3 in DI water.

c. Blanks preparation: There were three types of blanks prepared (EPA 1994b):

    i. The calibration blank was used to establish the calibration curve. It was the same solvent used to prepare the final dilution of the calibrating solution of the analyte, which was 1 % HNO_3 (*v*/*v*) in DI water.

    ii. The preparation (or reagent) blank was used to monitor for possible contamination resulting from the sample preparation. It contained the same volume of reagent as the sample solution.

    iii. The rinse blank was used to flush the system between samples and standards. It consisted of 1 to 2 % HNO_3 (*v*/*v*) in DI water.

d. Sample analysis: refers to ICP/MS Operation Overview (materials from ICP/MS operation training) (Department of Civil & Environmental Engineering 2009)

3.3.12 G Value

G value is a root-mean-square (rms) velocity gradient proposed by Camp and Stein (1943). It is calculated as equation 10.

$$G = \left(\frac{P}{V\mu}\right)^{1/2} \tag{10}$$

Where P is the power input to the fluid, V is the volume of water in the vessel, and μ is the absolute viscosity of the water (AWWA 1999). G value is obtained from Figure 3. The sample calculation for Gt (t is the mixing time) is shown as below:

Case I: rapid mixing for sample at 20 °C with mixing speed at 120 rpm and mixing time for 30 s. G value is 121 s^{-1} gained from Figure 3 at 120 rpm and 20 °C. So

$$Gt = G \times t = 121 \times 30 = 3630$$

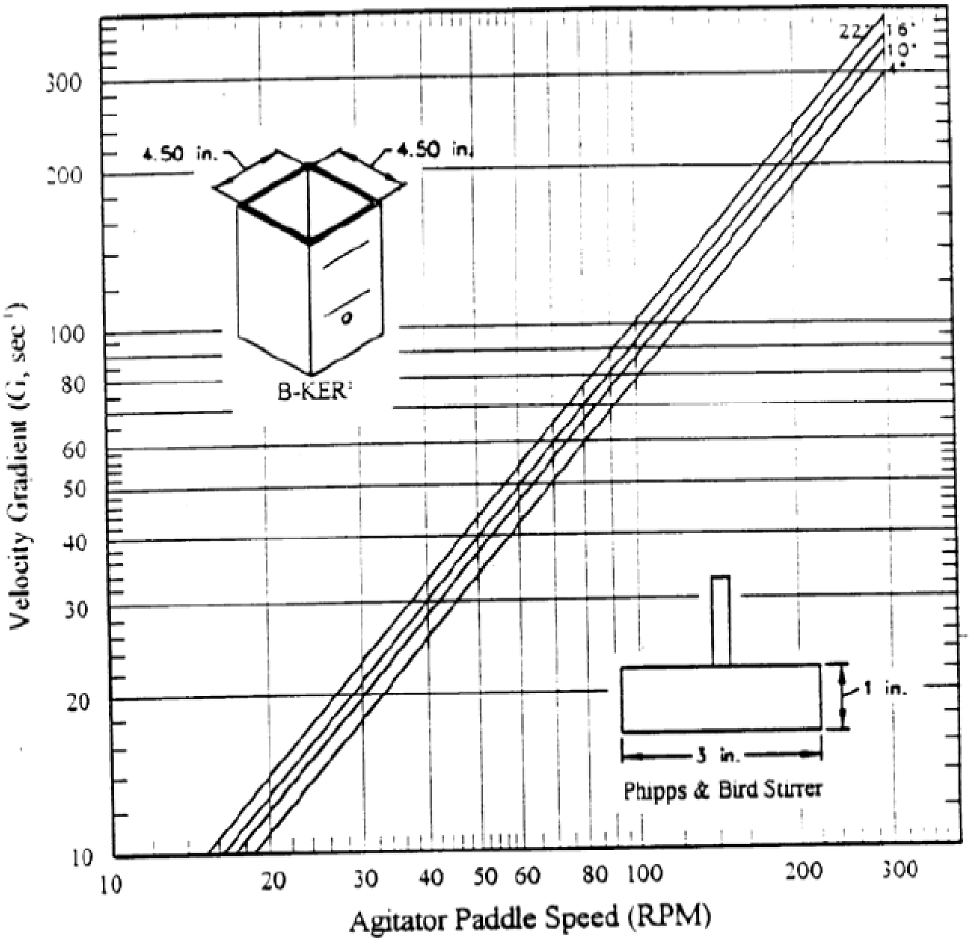


Figure 3: Velocity gradient (G) vs. agitator speed for a 2-liter square beaker (B-KER^2), using a Phipps & Bird stirrer. Water samples are at various temperatures (°C).
(Source: Water and Air Research Inc.)

G value could be used as a design parameter for flocculation facilities and reactor scale-up tool. It became a widely adopted standard used by engineers for assessing energy input in all kinds of mixing processes, particularly flocculation. *G* value is the parameter which is used to characterize mixing energy in this study (Metcalf and Eddy 2003).

CHAPTER 4 RESULTS AND DISCUSSION

4.1 OSPW Characterization

Oil sands process-affected water characteristics vary significantly depending on seasonal conditions, recycle times, sampling position, water use, operation processes, and etc. In this project, the experiments were conducted lasting more than one-and-a-half years. The OSPW samples were collected and supplied by Syncrude Canada four different times: (1) November 2007; (2) December 2008; (3) March 2009; and (4) October 2009. Each sample was taken from the top of Syncrude West Inpit Pond (W.I.P.) located in Fort McMurray, Canada, and was then delivered to the University of Alberta a couple of weeks later. The samples were preserved in a cold room at 4 °C until used. It is noted that OSPW characteristics varied from sample to sample and from barrel to barrel - especially the turbidity, TSS, TDS, TOC, conductivity and pH. Table 4 summarizes raw OSPW characteristics observed in these samples. Table 5 compares the properties of raw OSPW sampled at four different times. Table 6 shows the major ions analyzed using ion chromatography in OSPW. Table 7 shows the major elements analyzed using ICP-MS in OSPW. If the following data had more than three replicates, a Q-test was conducted to determine if a data point was different from the other data points in a set (statistical outlier). The statistical outliers would then be rejected from the data set. A sample calculation is shown in Appendix B.

Table 4: Properties of OSPW from the surface of Syncrude W.I.P.

Properties	Number of samples	Minimum	Maximum	Average	Standard deviation
pH	42	7.7	8.8	8.4	0.3
Turbidity (NTU)	42	76	255	150	46
TSS (mg/L)	30	44	141	98	26
TDS (mg/L)	30	1989	2524	2322	140
TOC (mg/L)	42	38.2	68.5	50.9	6.7
COD (mg/L)	8	226	243	235	7
Conductivity @ 25 °C (µS/cm)	8	2670	3880	3815	88
Alkalinity (mg/L)	8	518	626	590	52
NAs (mg/L)	1	23.6	23.6	23.6	0

Table 5: Properties of OSPW sampled at different times from the surface of Syncrude W.I.P.

Properties	Batch Sampling Date	Value	Average	Standard deviation
pH	November 2007	8.5-8.8	8.7	0.1
	December 2008	7.7-8.1	7.9	0.2
	March 2009	8.2-8.7	8.5	0.1
	October 2009	8.1-8.4	8.3	0.1
Turbidity (NTU)	November 2007	112-179	134	22
	December 2008	147-177	162	13
	March 2009	76-255	133	59
	October 2009	158-211	186	17
TOC (mg/L)	November 2007	49.4-55.5	53.0	1.8
	December 2008	47.9-60.2	54.1	6.2
	March 2009	38.2-68.5	51.4	9.1
	October 2009	43.7-48.5	46.7	1.9

Table 6: Major ions in OSPW from the surface of Syncrude W.I.P. (sampled on October 6, 2009)

Major ions	Concentration (mg/L)
Ammonium (NH_4^+)	21.89
Calcium (Ca^{2+})	19.12
Lithium (Li^+)	0.21
Magnesium (Mg^{2+})	11.68
Potassium (K^+)	17.86
Sodium (Na^+)	827.61
Chloride (Cl^-)	515.50
Fluoride (F^-)	2.71
Sulfate (SO_4^{2-})	513.27

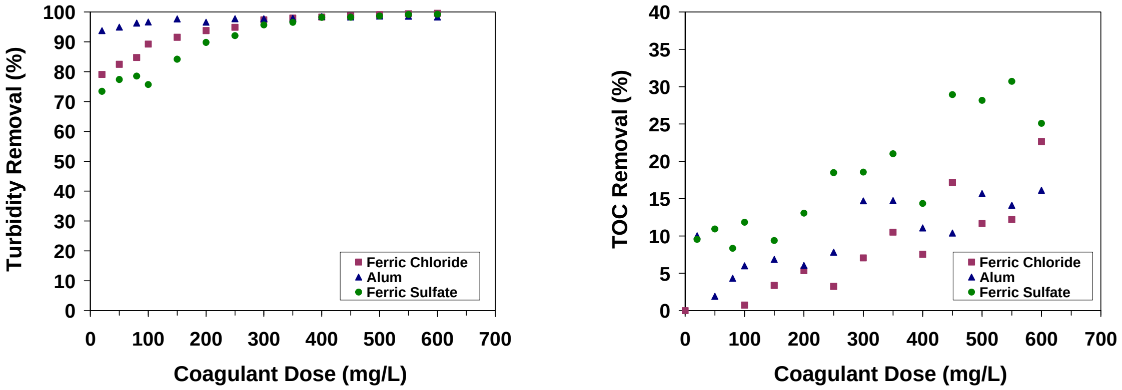
Table 7: Major elements in OSPW from the surface of Syncrude W.I.P. (sampled on October 6, 2009)

Major elements	Concentration (mg/L)
Boron (B)	2.170
Aluminum (Al)	8.481
Silicon (Si)	14.821
Phosphorus (P)	0.117
Vanadium (V)	0.018
Iron (Fe)	3.240
Zinc (Zn)	0.144
Strontium (Sr)	0.772
Molybdenum (Mo)	0.140
Barium (Ba)	0.345
Cobalt (Co)	0.004
Copper (Cu)	0.121
Nickel (Ni)	0.017
Selenium (Se)	0.007
Lead (Pb)	0.003
Uranium (U)	0.007
Zinc (Zn)	0.144

Note: Microwave digestion was used for preparation of the samples for total ions analysis by ICP-MS. The elements less than 0.001 mg/L in OSPW were not presented in the above table.

4.2 Coagulant Selection

Typically, iron and aluminum derivatives are commonly used as coagulants. A trivalent ion in an inorganic coagulant can be 1000 times more effective than a monovalent ion (U.S. Army Corps of Engineers 2001). This is why alum and iron salts (i.e. ferric sulfate or ferric chloride) are extremely efficient coagulants. In this project, a screening experiment was conducted to select suitable coagulants for OSPW from alum, ferric sulfate and ferric chloride. The jar-test was applied to simulate the coagulation-flocculation process. The treatment performance was determined mainly according to TOC and turbidity removal ratios. Figure 4 compares TOC removal ratios from OSPW using ferric chloride, alum and ferric sulfate as a coagulant in 2-litre jars at concentrations of 20, 50, 80, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550 and 600 mg/L, respectively. The initial rapid mixing speed was at 120 round per minute (rpm) (G = 121 s^{-1} at 20 °C) for 30 s, and the initial slow mixing speed was at 30 rpm (G = 23 s^{-1} at 20 °C) for 30 min. Settling time was noted between 50 to 60 min.



(a) (b)

Figure 4: TOC removal ratio (a) and turbidity removal ratio (b) vs. coagulant dose of ferric chloride, alum and ferric sulfate
(initial pH: 8.0; initial turbidity: 177 NTU; initial TOC: 47.9 mg/L; temperature: 20±1 °C. average values of triplicate TOC analyses were presented; ferric chloride, alum and ferric sulfate from 20 to 600 mg/L; experimental conditions: rapid mixing at 120 rpm for 30 s, slow mixing speed at 30 rpm for 30 min, settling for 50-60 min.)

Figure 4 shows TOC and turbidity removal ratios increased each dose of coagulant from 20 to 600 mg/L. Comparing these three coagulants, alum and ferric sulfate had better TOC removal ratio than ferric chloride. Alum gave better turbidity removal when lower dose of coagulant was applied. In this project, alum and ferric sulfate were selected as coagulants for further study.

4.3 Alum as a Coagulant

4.3.1 Dose Measurement

Triplicate jar tests were conducted to investigate the effects of alum dosage on TOC and turbidity removals from OSPW. Experiments were performed at natural pH (original pH) of raw OSPW at room temperature. Alum concentrations in a 2-litre jar were applied at 100, 250, 300, 400 and 500 mg/L. The average results of triplicate jar tests are shown in Figure 5. The error bar represents the standard deviation of the triplicate experiments in the following figures.

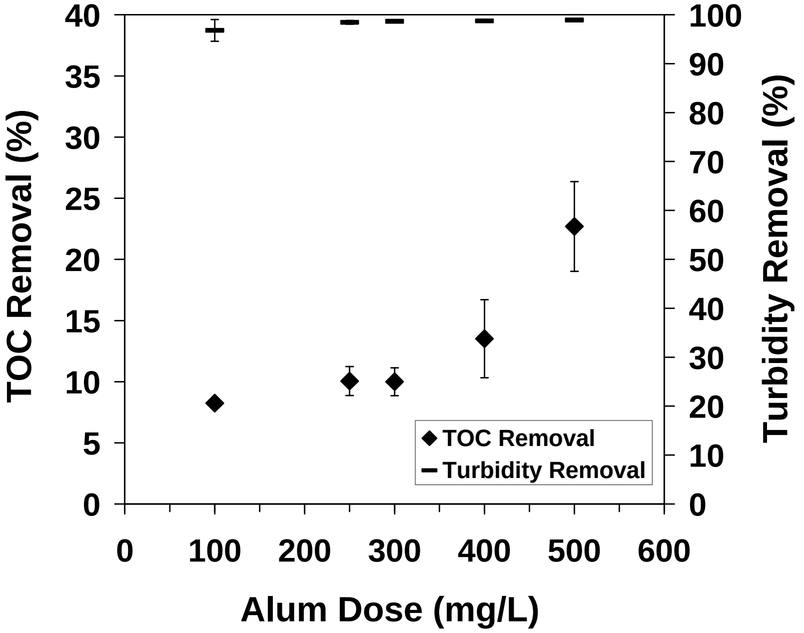


Figure 5: Alum dosage measurement at natural pH of OSPW (initial pH: 7.7; initial turbidity: 165 NTU; initial TOC: 58.5 mg/L; temperature: 20±1 °C. triplicates of jar-test experiments; experimental conditions: rapid mixing at 120 rpm for 30 s, slow mixing speed at 30 rpm for 30 min, settling for 50-60 min.)

In reference to industry applicability, coagulant doses higher than 500 mg/L were not investigated. The TOC removal ratio increased from 8% to 23% and the turbidity removal ratio increased from 97% to 99% with the alum dose increasing from 100 to 500 mg/L. Variance analysis between treatments was conducted by single factor ANOVA, which is shown in Appendix B. Based on statistical analysis, there was a significant difference between TOC removal ratios of treatments that used different doses of alum. It can be safely assumed that the alum dose affected the TOC removal from OSPW. Since the optimum dose was not observed in this concentration range, the treatment performance with low, medium and higher coagulant concentrations of 100, 250 and 500 mg/L were investigated, in the following study.

4.3.2 Polymer Selection Combined with Alum

The effects of cationic, nonionic and anionic polymers combined with alum for OSPW treatment of coagulation-flocculation were investigated in terms of TOC and turbidity removals. Polymer selection is empirical because of the complex interactions among polymers, coagulants and particles as well as the uncertain influence of water quality on these interactions (Crittenden 2005).

4.3.2.1 Cationic polymer

Two cationic polymers, CTI TL and Praestol 858BS (supplied by ClearTech, Edmonton), were studied with 250 mg/L alum in the coagulation-flocculation process for OSPW. Alum was added at the beginning of the rapid mixing process, and the cationic polymer was added in the middle of rapid mixing (15s after the start) because the positive charge on the cationic polymer is commonly used to enhance the coagulation process (AWWA 1999; Metcalf and Eddy 2003). Figure 6 shows the effects of the CTI TL dose on TOC and turbidity removals. Concentrations of CTI TL in a 2-L jar were applied at 0, 0.5, 0.8, 1, 2, 5, 10, 20 and 30 mg/L. Figure 7 shows the effects of the Praestol 858BS dose on TOC and turbidity removals from OSPW. The concentrations of Praestol 858BS in a 2-L jar were applied at 0, 2, 5, 10, 20, and 30 mg/L.

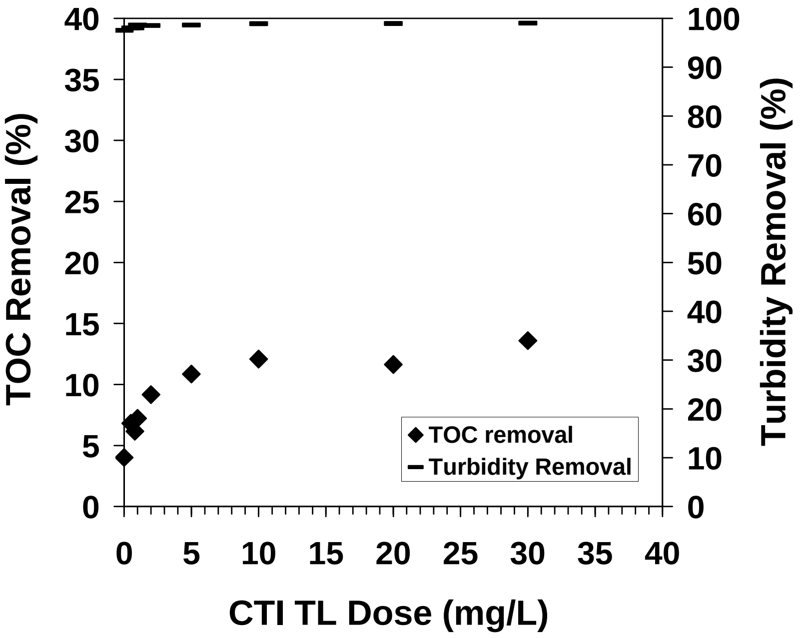


Figure 6: Effects of CTI TL dose on TOC and turbidity removal ratios from OSPW

(initial pH: 8.8; initial turbidity: 136 NTU; initial TOC: 53.6 mg/L; temperature: 20±1 °C. triplicates of TOC analysis; experimental conditions: alum dose: 250 mg/L, rapid mixing at 120 rpm for 30 s, 15 s rapid mixing for cationic polymer, slow mixing speed at 30 rpm for 30 min, settling for 50-60 min)

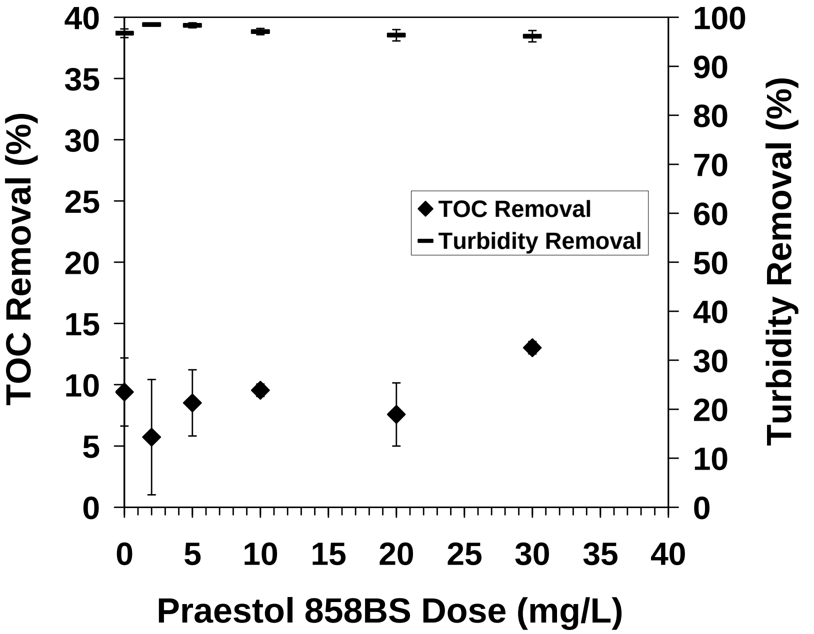


Figure 7: Effects of Praestol 858BS dose on TOC and turbidity removal ratios from OSPW
(initial pH: 8.7; initial turbidity: 170 NTU; initial TOC: 52.1 mg/L; temperature: 20±1 °C. triplicates of jar-test experiments; experimental conditions: alum dose: 250 mg/L, rapid mixing at 120 rpm for 30 s, 15 s rapid mixing for cationic polymer, slow mixing speed at 30 rpm for 30 min, settling for 50-60 min.)

In Figure 6, the cationic polymer CTI TL enhanced the treatment performance with alum in terms of TOC and turbidity removals. Both the TOC and turbidity removal ratios increased along with the CTI TL dose from 0 to 10 mg/L. In Figure 7, compared with the TOC removal using alum only, there was no positive contribution from Praestol 858BS to the TOC removal when the polymer dose was under 20 mg/L. Based on the above analysis, 10 mg/L of cationic polymer CTI TL was selected with 250 mg/L alum in the further study.

It was found that the flocs after treatment became sticky if more than 2 mg/L of Praestol 858BS was applied. The flocs stayed on the walls and the stirrer inside the jar during the experiment, which were difficult to be removed and cleaned-up. It became a challenge for equipment maintenance if a higher dosage of Praestol 858BS was applied in the industry. Figure 8 shows the phenomenon. Therefore, a concentration more than 2 mg/L of Praestol 858BS is not suggested to be applied in the coagulation-flocculation treatment for OSPW.

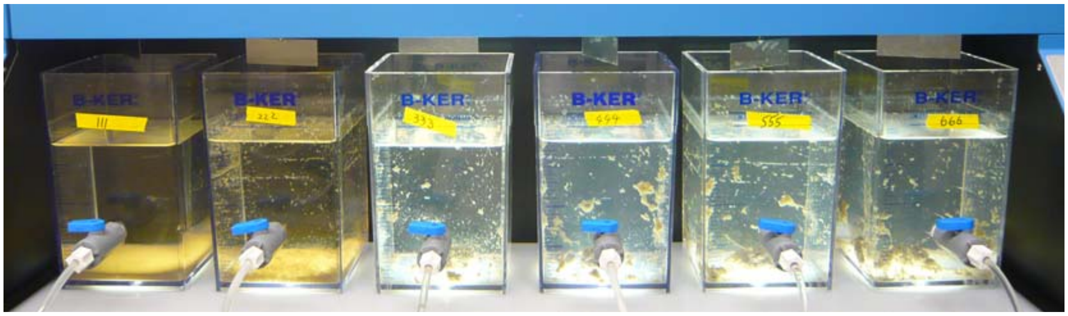


Figure 8: Observation of treated OSPW after the coagulation-flocculation and sedimentation processes using 250 mg/L of alum with different doses of Praestol 858BS at 0, 2, 5, 10, 20, and 30 mg/L (left to right)

4.3.2.2 Nonionic polymer

The effects of nonionic polymer - LT20 on the coagulation-flocculation treatment of OSPW using alum as a coagulant were investigated. Alum was added at the beginning of the rapid mixing process, and nonionic polymer was added in the middle of the rapid mixing process (15s after the start). Figure 9 shows the effects of the LT20 dose on TOC and turbidity removals from OSPW. The concentrations of LT20 in a 2-L jar were applied at 0, 1, 2, 5, and 10 mg/L, respectively.

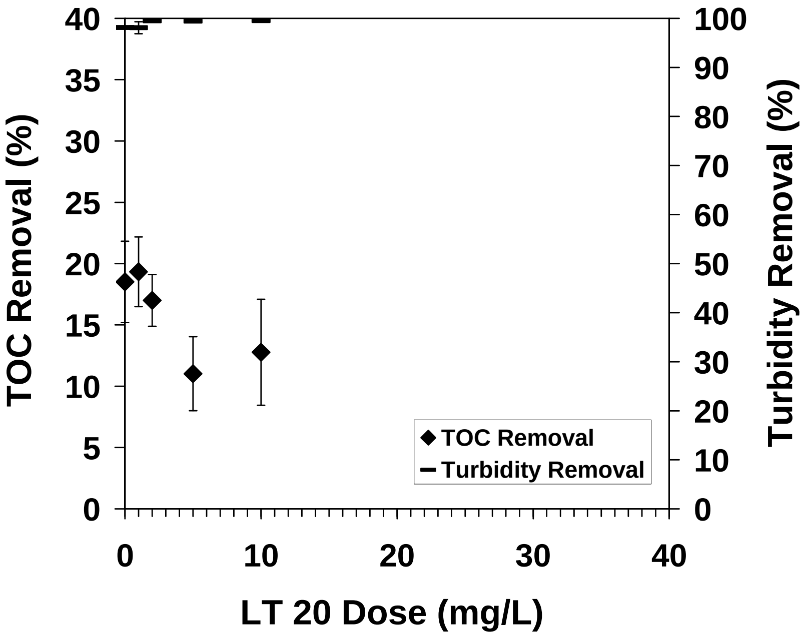


Figure 9: Effects of LT20 dose on TOC and turbidity removal ratios from OSPW (initial pH: 7.9; initial turbidity: 158 NTU; initial TOC: 60.2 mg/L; temperature: 20±1 °C. triplicates of jar-test experiments; experimental conditions: alum dose: 250 mg/L, rapid mixing at 120 rpm for 30 s, 15 s rapid mixing for nonionic polymer, slow mixing speed at 30 rpm for 30 min, settling for 50-60 min.)

Figure 9 shows that when a concentration range of 1 to 10 mg/L is applied, LT20 contributed to the TOC removal only when the concentration was applied at 1 mg/L. When compared with TOC removal using 250 mg/L of alum only, it is not necessary to add the nonionic polymer LT20 as a coagulant aid with alum in the coagulation-flocculation process. In the water treatment plant, low dose (0.005 to 0.05 mg/L) of high-molecular-weight nonionic polymer is often added as a filter aid before granular filtration to improve filter performance (Crittenden 2005).

4.3.2.3 Anionic polymer

The effects of anionic polymer - PAM A-503 (supplied by ClearTech, Edmonton) - doses on the coagulation-flocculation treatment for OSPW using alum as a coagulant were also studied. Alum was added at the beginning of the rapid mixing process, and PAM A-503 was added during the flocculation process right after rapid mixing (30s after the start) because an anionic polymer is commonly used to enhance the flocculation process. Figure 10 shows the effects of PAM A-503 doses on TOC and turbidity removals from OSPW. Concentrations of PAM A-503 in a 2-L jar were applied at 0, 0.1, 0.5, 1, and 2 mg/L, respectively. No concentrations higher than 2 mg/L was used in the experiments because the flocs become very sticky if higher concentrations of PAM A-503 are applied.

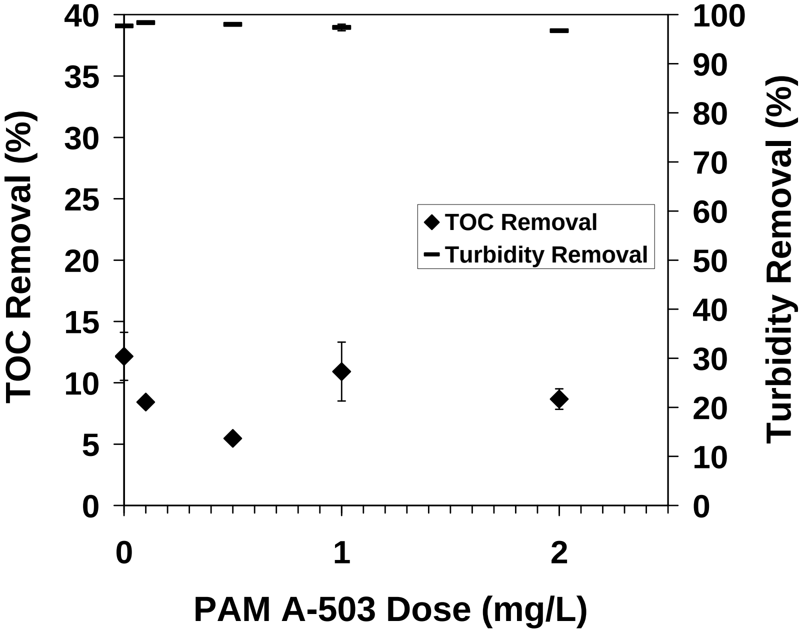


Figure 10: Effects of PAM A-503 dose on TOC and turbidity removal ratios from OSPW
(initial pH: 8.2; initial turbidity: 188 NTU; initial TOC: 48.3 mg/L; temperature: 20±1 °C. triplicates of jar-test experiments; experimental conditions: Alum dose: 250 mg/L, rapid mixing at 120 rpm for 30 s, PAM A-503 was added after rapid mixing, slow mixing speed at 30 rpm for 30 min, settling for 50-60 min.)

In Figure 10, no positive contribution was observed from PAM A-503 to the alum treatment for TOC removal.

After comparing efficiencies of TOC and turbidity removals using cationic, non-ionic and anionic polymer combined with alum, cationic polymer CTI TL was selected as a coagulant aid with alum for further coagulation-flocculation process optimization. Cationic polymers are commonly used together with metal-ion coagulants because it reduces the dosage of metallic ion coagulants by 40% to 80%. The advantage of a lower dosage of the metallic ion coagulant used in the process is that it produces less sludge and reduces alkalinity consumption. In addition, pH is not depressed as much, which maintains the metallic ion coagulation efficiency (Crittenden 2005).

4.3.3 Process Optimization

Rapid mixing speed, time and flocculation time were optimized in this section. Alum and CTI TL doses were fixed at 250 mg/L and 10 mg/L in all the jars during this study.

4.3.3.1 Rapid mixing intensity and time

Screening experiments were conducted to investigate the suitable time to add cationic polymer CTI TL during rapid mixing processes. CTI TL was added at 5, 10, 15 and 30 s, respectively, after the addition of alum during a 30 s rapid mixing process. Therefore, the actual rapid mixing times for CTI TL were 25, 20, 15 and 0 s. Figure 11 shows the effects of rapid mixing time of CTI TL on TOC and turbidity removals from OSPW. Alum was added at the beginning of the rapid mixing process.

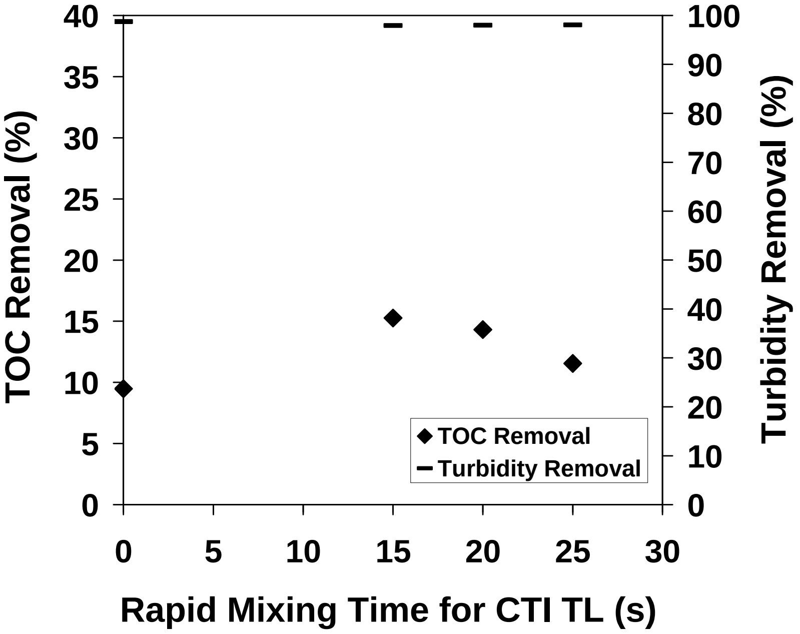


Figure 11: Effects of rapid mixing time of CTI TL on TOC and turbidity removal ratios from OSPW

(initial pH: 8.5; initial turbidity: 123 NTU; initial TOC: 49.4 mg/L; temperature: 20±1 °C. triplicates of TOC analysis; experimental conditions: Alum dose: 250 mg/L, CTI TL dose: 10 mg/L, rapid mixing at 120 rpm (G = 120 s^{-1}) for 30 s for alum, slow mixing at 30 rpm (G = 23 s^{-1}) for 30 min, settling for 50-60 min.)

In Figure 11, the optimum rapid mixing time of CTI TL was 15 s, in other words, the CTI TL should be added in the middle of the 30 s rapid mixing process. Based on the findings from the screening experiments, further investigations regarding rapid mixing intensity (at room temperature: 20 ± 1 °C, speed at 220 rpm, G = 258 s^{-1}; speed at 120 rpm, G = 120 s^{-1}; speed at 80 rpm, G = 74 s^{-1}) and time were conducted and the results are shown in Figure 12. The G values were obtained from Figure 3: Velocity gradient vs. agitator speed for a 2-litre square beaker (B-KER^2), using a Phipps & Bird stirrer. Sample calculations of Gt values are illustrated in Appendix A. Calculated Gt values are shown in Table 8: under each experimental condition. TOC vs. Gt was plotted in Figure 13.

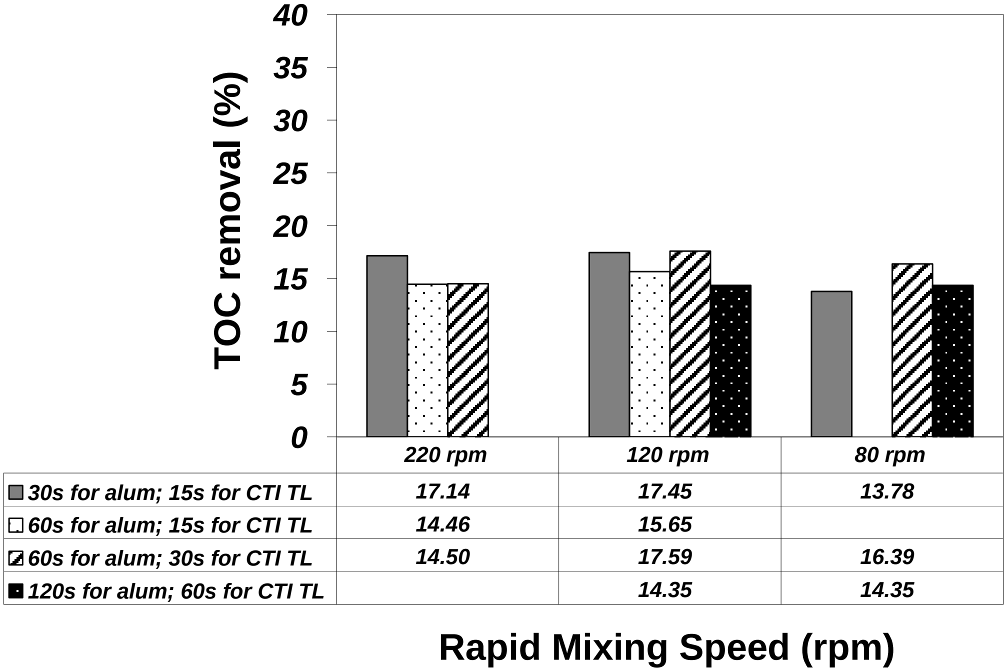


Figure 12: Rapid mixing intensity and time adjustment in terms of TOC removal (initial pH: 8.8; initial TOC: 55.5 mg/L; temperature: 20±1 °C. triplicates of TOC analysis; alum dose: 250 mg/L, CTI TL dose: 10 mg/L; experimental conditions: slow mixing at 30 rpm for 30 min, settling for 50-60 min.)

Table 8: Gt value calculations under each experimental condition (20 ± 1 °C)

Rapid mixing speed (rpm)	G (s^{-1})	t (s)	Gt	TOC removal (%)
220	258	60	15480	14.50
220	258	60	15480	14.46
220	258	30	7740	17.14
120	120	120	14400	14.35
120	120	60	7200	17.59
120	120	60	7200	15.65
120	120	30	3600	17.45
80	74	120	8880	14.35
80	74	60	4440	16.39
80	74	30	2220	13.78

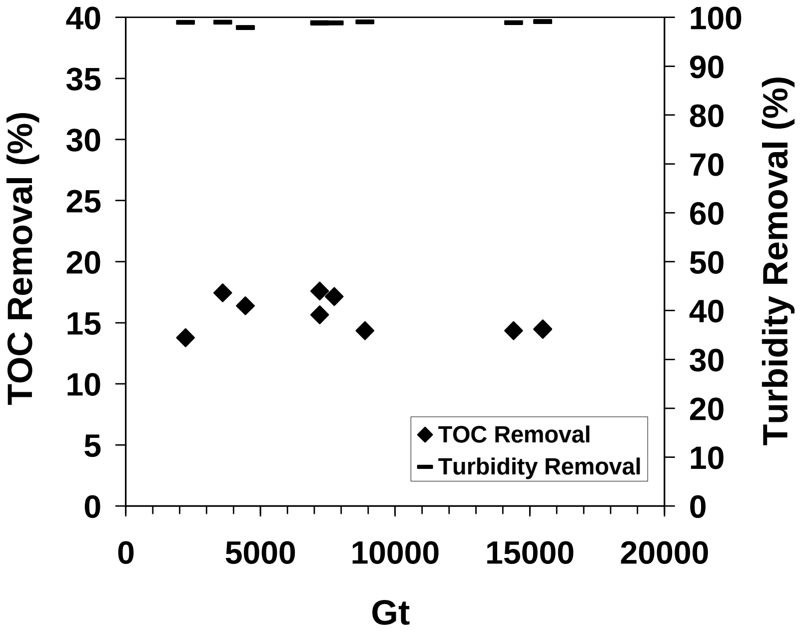


Figure 13: TOC vs. Gt under each experimental condition (20 ± 1 °C)
(initial pH: 8.8; initial turbidity: 179 NTU; initial TOC: 55.5 mg/L)

In Figure 12, TOC removal ratios were observed to be relatively high under the three different rapid mixing conditions of: (1) 30s rapid mixing for alum and 15s rapid mixing for CTI TL at 220 rpm; (2) 30s rapid mixing for alum and 15s rapid mixing for CTI TL at 120 rpm; and (3) 60s rapid mixing for alum and 30s rapid mixing for CTI TL at 120 rpm. TOC removals and turbidity removals were similar under these three rapid mixing conditions. Considering the energy saving, 30 s rapid mixing for alum and 15 s rapid mixing for CTI TL at 120 rpm (G = 120 s^{-1}) with a Gt value of 3600, was selected as the optimum rapid mixing condition, which was applied in the following study.

4.3.3.2 Flocculation time

Flocculation time was investigated at 0, 10, 20, 30, 45, and 60 minutes. The flocculation speed was applied at 30 rpm (G = 23 s^{-1}). Figure 14 shows the effects of flocculation time on TOC and turbidity removals from OSPW.

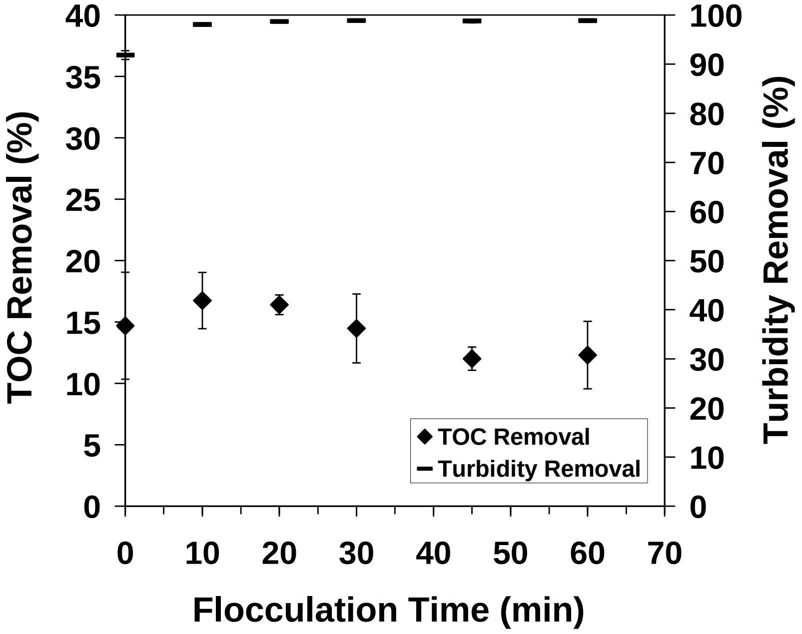


Figure 14: Effects of flocculation time on TOC and turbidity removal ratios from OSPW
(initial pH: 8.6; initial turbidity: 76 NTU; initial TOC: 53.7 mg/L; temperature: 20±1 °C. triplicates of jar-test experiments; experimental conditions: alum dose: 250 mg/L, CTI TL dose: 10 mg/L, rapid mixing at 120 rpm (G = 120 s^{-1}) for 30 s for alum, slow mixing speed at 30 rpm (G = 23 s^{-1}), settling for 50-60 min.)

In Figure 14, the TOC removal ratio increased then decreased with the increasing flocculation time. The optimum flocculation time was 10 min at 30 rpm (G = 23 s^{-1}), which would be employed in the further study.

4.3.3.3 Optimum jar-test conditions

According to the process optimization results, the optimum (or best) jar-test conditions for coagulation-flocculation using alum combined with cationic polymer CTI TL are summarized in Table 9.

Table 9: Optimum jar-test conditions for alum and cationic polymer CTI TL

Process	Speed	Time
Coagulation (Rapid mixing)	120 rpm	30 s for alum, 15 s for CTI TL
Flocculation (Slow mixing)	30 rpm	10 min

4.3.4 CTI TL Dose

The cationic polymer CTI TL doses combined with low, medium and high alum doses at 100, 250 and 500 mg/L were investigated at the optimum jar-test conditions. Figures 15 and 16 show the effects of CTI TL doses combined with 100 mg/L and 250 mg/L of alum on the TOC and turbidity removals from OSPW. The concentrations of CTI TL in a 2-L jar were applied at 0, 2, 5, 10, 20, and 30 mg/L. Figure 17 shows the CTI TL dose study combined with 500 mg/L of alum. The concentrations of CTI TL in 2-L jars were studied at 0, 1, 2, 5, and 10 mg/L. Usually, the higher the dose of coagulant applied, the lower the dose of coagulant aid needed.

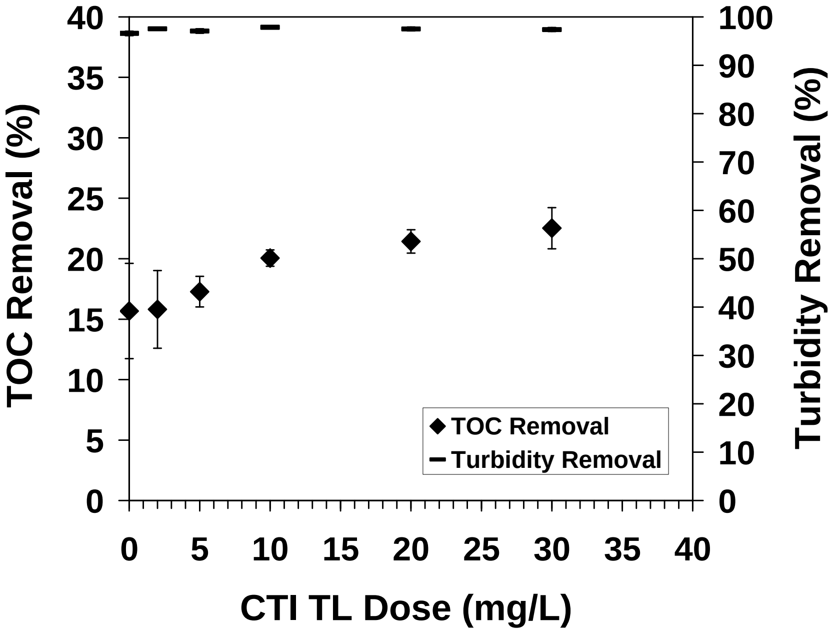


Figure 15: Effects of CTI TL dose combined with 100 mg/L alum on TOC and turbidity removal ratios from OSPW
(initial pH: 8.3; initial turbidity: 91 NTU; initial TOC: 63.6 mg/L; temperature: 20±1 °C. triplicates of jar-test experiments; Jar-test conditions: rapid mixing at 120 rpm for 30 s, 15 s rapid mixing for CTI TL, flocculation at 30 rpm for 10 min, settling for 50-60 min.)

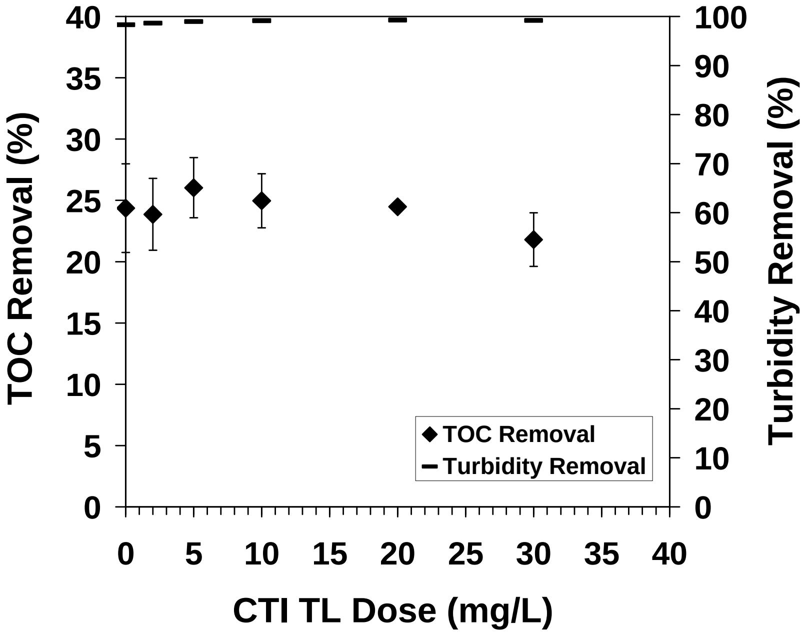


Figure 16: Effects of CTI TL dose combined with 250 mg/L alum on TOC and turbidity removal ratios from OSPW
(initial pH: 8.6; initial turbidity: 178 NTU; initial TOC: 65.0 mg/L; temperature: 20±1 °C. triplicates of jar-test experiments; Jar-test conditions: rapid mixing at 120 rpm for 30 s, 15 s rapid mixing for CTI TL, flocculation at 30 rpm for 10 min, settling for 50-60 min.)

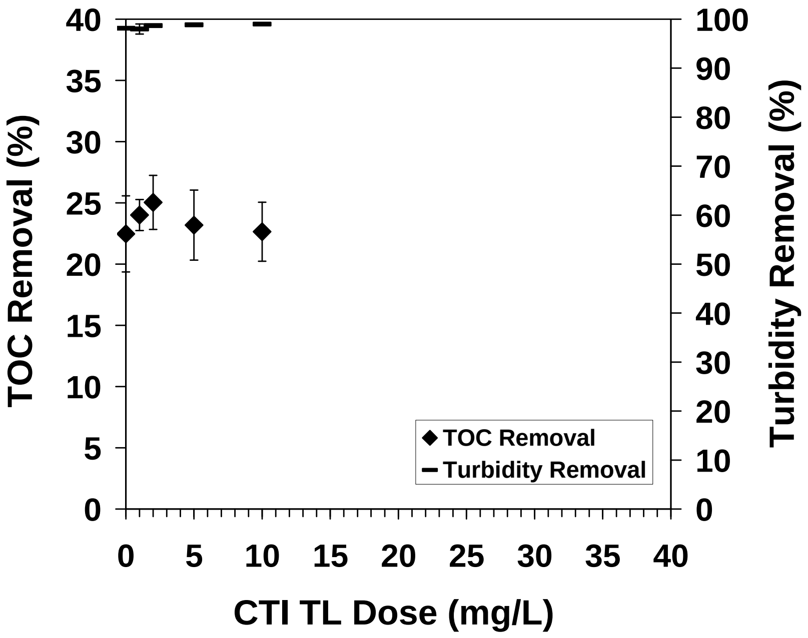


Figure 17: Effects of CTI TL dose combined with 500 mg/L alum on TOC and turbidity removal ratios from OSPW
(initial pH: 8.1; initial turbidity: 147 NTU; initial TOC: 49.7 mg/L; temperature: 20±1 °C. triplicates of jar-test experiments; Jar-test conditions: rapid mixing at 120 rpm for 30 s, 15 s rapid mixing for CTI TL, flocculation at 30 rpm for 10 min, settling for 50-60 min.)

According to Figures 15, 16 and 17, the optimum cationic polymer CTI TL dose decreased with the coagulant alum dose increasing. This is considered reasonable because the cationic polymer is a coagulant aid which has a synergistic effect with the metallic ion coagulant on enhancing the coagulation process. Usually, the higher the amount of coagulant used, the lower the dose of coagulant aid needed, and vice versa. In Figure 15, there was no optimum CTI TL dose observed while testing the concentration range from 0 to 30 mg/L with 100 mg/L alum. However, 10 mg/L CTI TL combined with 100 mg/L alum was chosen for further study, since the typical dosage rates of popular cationic polymers for sedimentation are on the order of 1 to 10 mg/L (Crittenden 2005). In Figure 16, the optimum dose of

CTI TL combined with 250 mg/L alum was observed at 5 mg/L. The optimum CTI TL dosage was verified at the optimized jar-test conditions. 5 mg/L of CTI TL was selected as the optimum dose combined with 250 mg/L alum based on the triplicate experiment results showed in Figure 16. As seen in Figure 17, 2 mg/L was selected as the optimum CTI TL dose combined with 500 mg/L of alum for the coagulation-flocculation treatment of OSPW.

Figure 18 compares the OSPW before and after coagulation-flocculation and sedimentation processes using 250 mg/L alum and 5 mg/L CTI TL in the optimum jar-test conditions. It can be seen that most suspended particles and colors in OSPW were removed after treatment.

Figure 18: Comparison of the OSPW before and after coagulation-flocculation and sedimentation processes using 250 mg/L alum and 5 mg/L CTI TL in the optimum jar-test conditions

4.4 Cationic Polymer as a Primary Coagulant

The cationic polymer CTI TL was investigated as a primary coagulant for OSPW treatment. The optimum dose, rapid mixing intensity and time, and flocculation time were investigated.

4.4.1 Coagulant Dose

TOC and turbidity removals were measured when CTI TL doses were applied at 0.5, 2, 5, 10, and 20 mg/L in a 2-L jar. The results are shown in Figure 19.

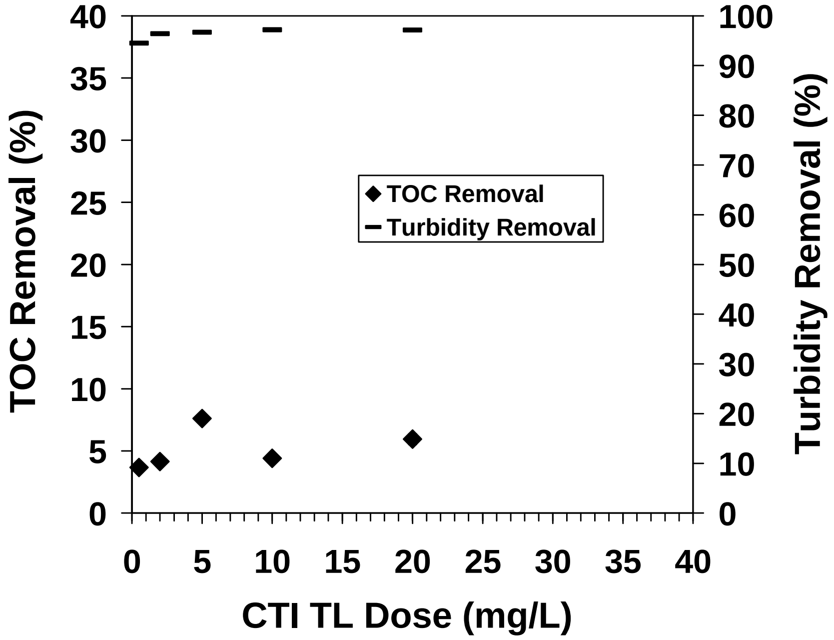


Figure 19: Effects of CTI TL dose on TOC and turbidity removals from OSPW when cationic polymer was used as a primary coagulant
(initial pH: 8.7; initial turbidity: 124 NTU; initial TOC: 53.1 mg/L; temperature: 20±1 °C. triplicates of TOC analysis; Jar-test conditions: initial rapid mixing speed at 220 rpm for 15 s, slow mixing at 30 rpm for 30 min, settling for 50-60 min.)

In Figure 19, the TOC removal ratio varied in respect to the polymer dose. The CTI TL dose ranged from 0.5 mg/L to 20 mg/L and the TOC removal ratios were between 4% and 8%. Turbidity removal increased when the CTI TL dose was increased. However, an overdose occurred when it was higher than 5 mg/L according to the TOC removal. And as a result, 5mg/L of CTI TL was selected for the following process optimization.

4.4.2 Process Optimization

Rapid mixing intensity, time and flocculation time were optimized in this section. The CTI TL dose was fixed at 5 mg/L in a 2-L jar during this study.

4.4.2.1 Rapid mixing intensity and time

The rapid mixing time for CTI TL was investigated at 0, 15, 30, 60 and 120s at speeds of 220 rpm ($G = 258\ s^{-1}$), 120 rpm ($G = 120\ s^{-1}$) and 80 rpm ($G = 74\ s^{-1}$), respectively. Figure 20 shows the effects of the rapid mixing speed and time on TOC removal from OSPW. The G values were obtained from Figure 3: Velocity gradient vs. agitator speed for a 2-litre square beaker (B-KER^2), using a Phipps & Bird stirrer. Calculated Gt values are shown in Table 10 under each experimental condition. TOC vs. Gt was plotted in Figure 21.

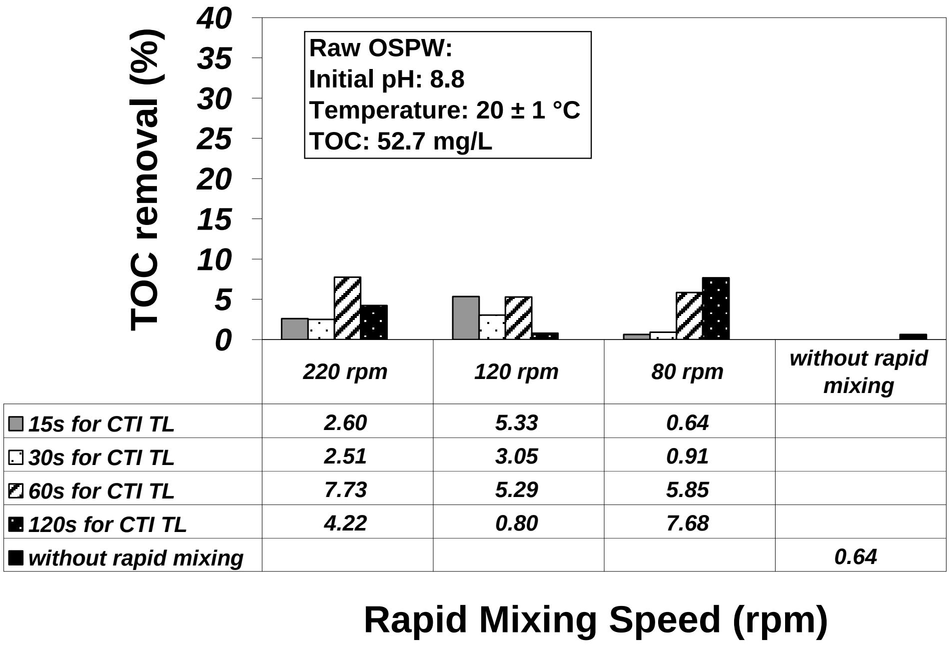


Figure 20: Rapid mixing intensity and time adjustment according to TOC removal (initial pH: 8.8; initial TOC: 52.7 mg/L; temperature: 20±1 °C. triplicates of TOC analysis; CTI TL dose: 5 mg/L. Experimental conditions: slow mixing at 30 rpm for 30 min, settling for 50-60 min.)

Table 10: Gt value calculations at each experimental condition (20 ± 1 °C)

Rapid Mixing Speed (rpm)	G (s^{-1})	t (s)	Gt	TOC Removal (%)
220	258	120	30960	4.22
220	258	60	15480	7.73
220	258	30	7740	2.51
220	258	15	3870	2.60
120	120	120	14400	0.80
120	120	60	7260	5.29
120	120	30	3600	3.05
120	120	15	1800	5.33
80	74	120	8880	7.68
80	74	60	4440	5.85
80	74	30	2220	0.91
80	75	15	1125	0.64

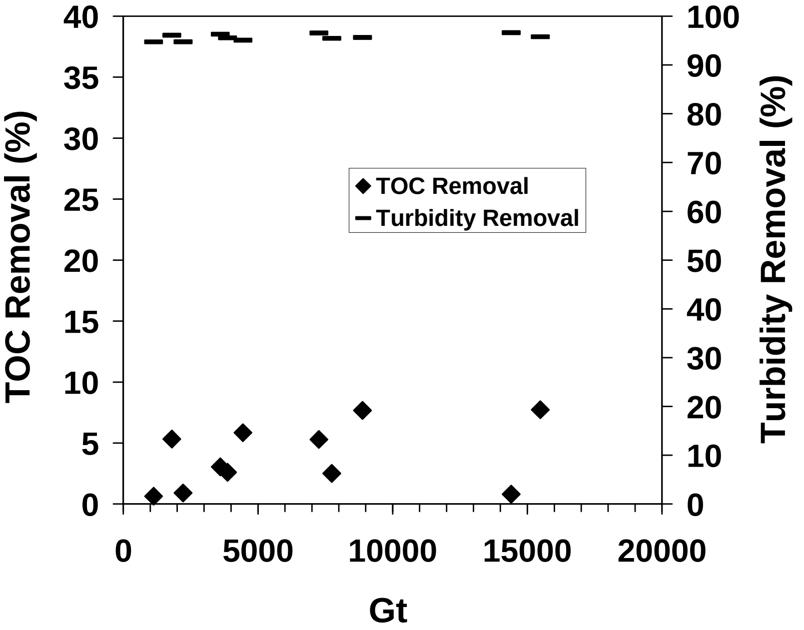


Figure 21: TOC vs. Gt under each experimental condition (20 ± 1 °C) (initial pH: 8.8; initial turbidity: 125 NTU; initial TOC: 52.7 mg/L; temperature: 20±1 °C)

In Figure 20, TOC removal ratios were recorded to be relatively high in two rapid mixing conditions: (1) 60s rapid mixing at 220 rpm (G = 258 s^{-1}); and (2) 120s rapid mixing at 80 rpm (G = 74 s^{-1}). The TOC removals were similar in these two conditions. Considering the energy saving (Gt value of 8880 at condition (2) was much lower than that of 15480 at condition (1)), condition (2) - 120 s rapid mixing at 80 rpm (G = 74 s^{-1}) - was selected as the optimum rapid mixing condition. This optimum rapid mixing condition was applied in the following study.

4.4.2.2 Flocculation time

Flocculation time was investigated at 0, 10, 20, 30, 45 and 60 min, while flocculation speed was applied at 30 rpm (G = 23 s^{-1}). Figure 22 shows the effects of flocculation time on TOC and turbidity removals from OSPW.

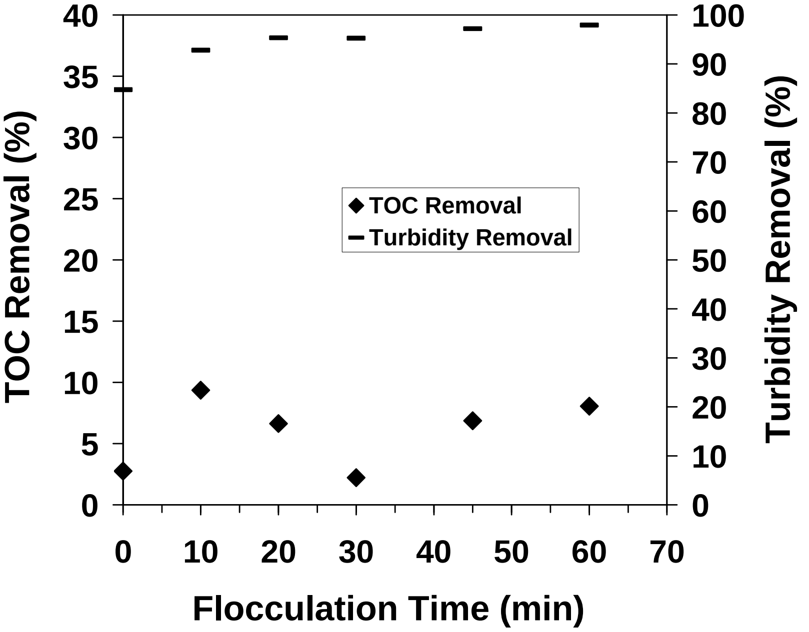


Figure 22: Effects of flocculation time on TOC and turbidity removal ratios from OSPW when CTI TL was used as a primary coagulant
(initial pH: 8.8; initial turbidity: 141 NTU; initial TOC: 53.6 mg/L; temperature: 20±1 °C. triplicates of TOC analysis; Experimental conditions: CTI TL dose: 5 mg/L, rapid mixing at 80 rpm (G = 74 s^{-1}) for 2 min, slow mixing speed at 30 rpm (G = 23 s^{-1}), settling for 50-60 min.)

In Figure 22, the highest TOC removal of 9% occurred at 10 minutes of flocculation. As the flocculation time increased between 0 to 60 minutes, turbidity removal increased as well. After 10 minutes of flocculation, the turbidity was about 10 NTU after settling and about 3 NTU after 60 min flocculation. However, even following 10 minutes of flocculation, more than 92% of the initial turbidity in OSPW was removed. The optimum flocculation time was selected as 10 minutes with a mixing speed of 30 rpm (G = 23 s^{-1}).

4.4.2.3 Optimum jar-test conditions

According to the above experiments, the optimum jar-test conditions for coagulation-flocculation using cationic polymer CTI TL as a primary coagulant are summarized in Table 11.

Table 11: Optimum jar-test conditions for cationic polymer CTI TL as a primary coagulant

Process	Speed	Intensity (G)	Time
Coagulation (Rapid mixing)	80 rpm	74 s^{-1}	120 s
Flocculation (Slow mixing)	30 rpm	23 s^{-1}	10 min

4.4.3 Comparison with Metallic Ion Coagulants

Compared with aluminum and ferric salt coagulants, cationic polymer CTI TL as a primary coagulant produced less sludge because of its known effectiveness at much lower dose than inorganic coagulant. The sludge was also denser and stickier as shown in Figure 23. However, the quality of water, in terms of TOC, turbidity and TSS removals from OSPW, obtained by using cationic polymer coagulants was not as good as that obtained by using metallic ion coagulants. Table 12 shows the comparison of TSS and TDS values in OSPW after treatment using between metallic ion and cationic polymer as a coagulant. Therefore, cationic polymers are rarely used as sole coagulants except for direct filtration (Crittenden 2005). They are commonly used together with inorganic coagulants, which can reduce the dosages of metallic ion coagulants by 40% to 80%. When lower metallic ion coagulant doses are used, sludge volume is reduced as well as alkalinity consumption. And the pH will not be depressed much, which helps to keep the metallic ion coagulation efficiency (Crittenden 2005). Figure 23 compares the treated OSPW by using between metallic ion coagulant (alum) combined with cationic polymer (CTI TL) (left) and CTI TL only (right) after coagulation-flocculation process and settling.

Table 12: Comparison of TSS and TDS values in OSPW after treatment using between metallic ion and cationic polymer as a coagulant (refer to Table 16)

Treatment	Ave. TSS (mg/L)	TSS Removal (%)	Ave. TDS (mg/L)	TDS Removal (%)
OSPW	97	--	2477	--
100 mg/L alum	2.4	97.5	2401	3.07
100 mg/L alum + 10 mg/L CTI TL	2.4	97.5	2382	3.84
250 mg/L alum	1.9	98.0	2457	0.81
250 mg/L alum + 5 mg/L CTI TL	1.0	99.0	2462	0.61
500 mg/L alum	1.8	98.1	2444	1.33
500 mg/L alum + 2 mg/L CTI TL	1.4	98.6	2408	2.79
5 mg/L CTI TL	9.5	90.2	2452	1.01

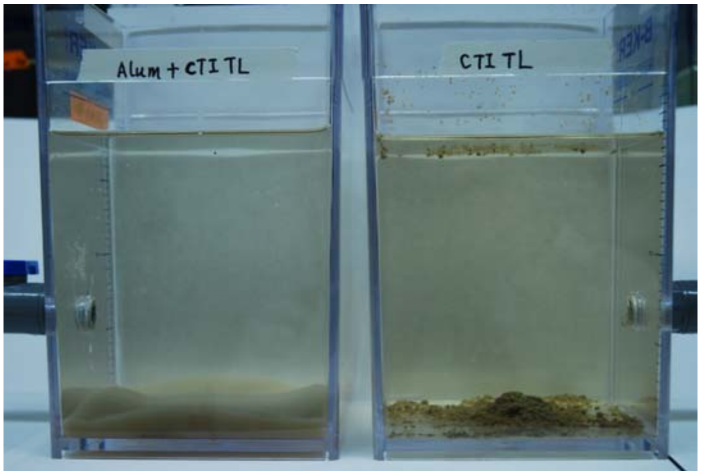


Figure 23: Comparison of the treated OSPW by using 5 mg/L CTI TL combined with 250 mg/L alum and 5 mg/L CTI TL only after coagulation-flocculation and settling

4.5 Ferric Sulfate as a Coagulant

4.5.1 Dose Measurement

Triplicate jar tests were conducted to investigate the effects of ferric sulfate dosages on TOC and turbidity removals from OSPW. Experiments were conducted at the natural pH (original pH) of the raw OSPW at room temperature. Alum concentrations in a 2-L jar were investigated at 100, 200, 250, 300, 400 and 500 mg/L. Initial jar-test conditions were applied at: rapid mixing at 120 rpm for 30s; flocculation at 30 rpm for 10 minutes. The jar-test conditions will be adjusted in the further study. The average results of the triplicate jar tests are shown in Figure 24.

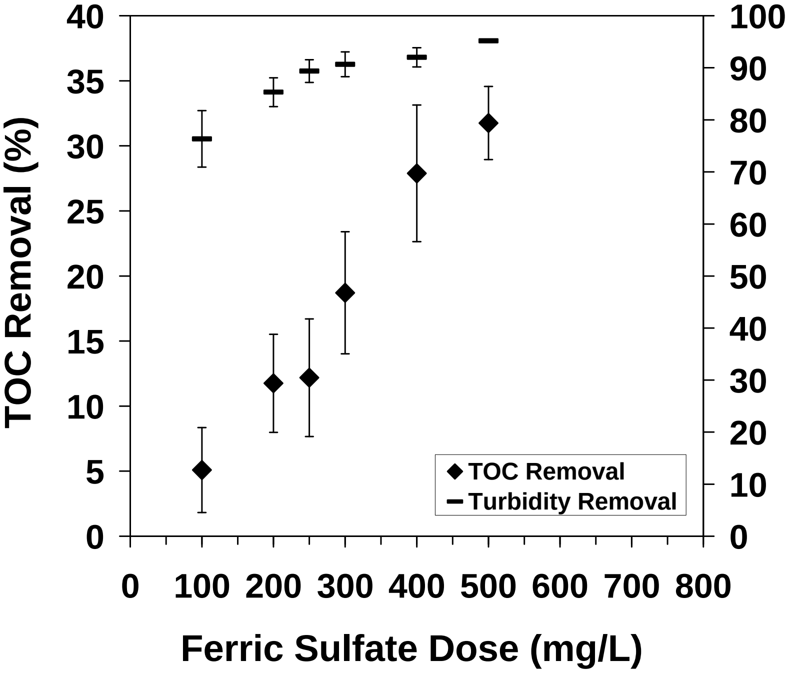


Figure 24: Effects of ferric sulfate dose on TOC and turbidity removal ratios from OSPW
(initial pH: 8.3; initial turbidity: 87 NTU; initial TOC: 46.5 mg/L; temperature: 20±1 °C. triplicates of jar-test experiments; experimental conditions: rapid mixing at 120 rpm for 30 s, slow mixing speed at 30 rpm for 10 min, settling for 50-60 min.)

Taking into consideration the industry applicability coagulant doses higher than 500 mg/L were not studied. The TOC removal ratio increased from 5% to 32% and the turbidity removal ratio increased from 76% to 95% when ferric sulfate doses increased from 100 to 500 mg/L. Compared with alum as a coagulant, the TOC removal increased sharply when low to high ferric sulfate doses were applied, however the turbidity could not be removed as much as it did with alum. Statistic variance analysis between treatments was conducted by Single Factor ANOVA which is shown in Appendix B. According to the statistic analysis, a significant difference between the means of treatments using different dosages of ferric sulfate was found. We can safely assume that ferric sulfate dose affected the TOC removal from OSPW. The standard deviations of TOC and turbidity removals shown in the error bars were all relatively high because the treatments using ferric sulfate were not as stable as those using alum. In addition, TOC analyses were conducted by MAXXAM (a commercial laboratory in Edmonton) but not in the University, and their replicate analyses results were not stable as well. Since an optimum dose was not observed in the testing concentration range, the treatment performance with lower, medium and higher coagulant concentrations of 100, 250 and 500 mg/L were investigated respectively in the following study.

4.5.2 Polymer Selection Combined with Ferric Sulfate

The effects of cationic, nonionic or anionic polymers combined with ferric sulfate and a suitable rapid mixing time in the coagulation-flocculation process were investigated in terms of TOC and turbidity removals.

4.5.2.1 Cationic polymer

The cationic polymer, CTI TL, supplied by ClearTech in Edmonton, was studied with 250 mg/L of ferric sulfate in the coagulation-flocculation treatment for OSPW. The initial rapid mixing time and flocculation time were applied at 30s and 10 minutes. A certain amount of ferric sulfate was added at the beginning of the rapid mixing process to achieve 250 mg/L in each 2-L jar. At each dosage, the polymer was added at three different moments during the rapid mixing process: at the beginning (30s rapid mixing); in the middle (15 s rapid mixing); and at the end of the rapid mixing process (approximately 2s rapid mixing). Concentrations of CTI TL in a 2-L jar were applied at 5, 10 and 20 mg/L. The triplicate treatments using 250 mg/L of ferric sulfate without any polymer were conducted as a reference. Figure 25 shows the effects of CTI TL dose and rapid mixing time combined with a coagulant of 250 mg/L ferric sulfate on TOC and turbidity removals from OSPW.

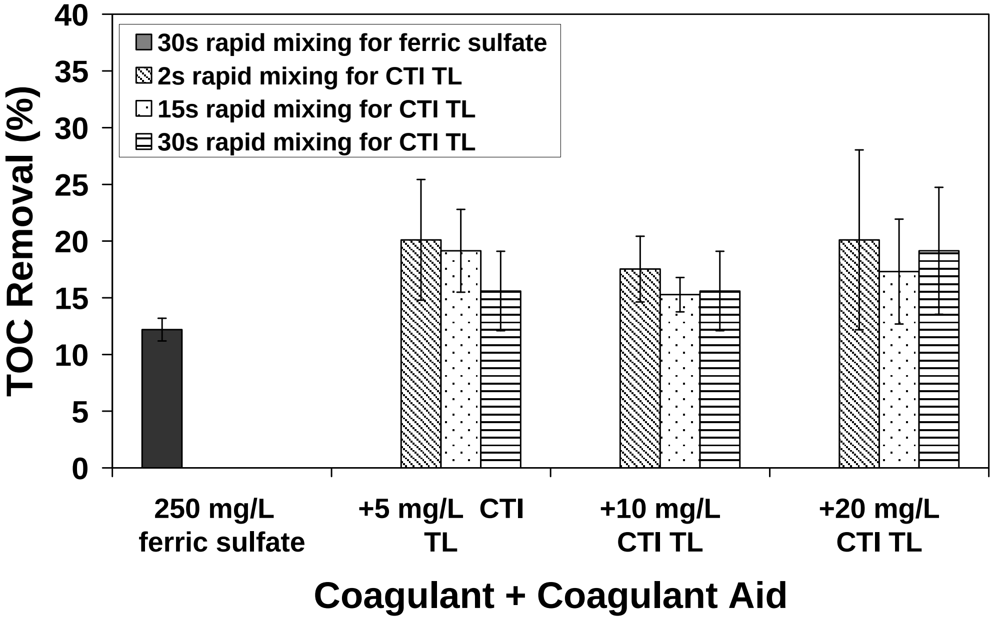


Figure 25: Effects of the dosage and rapid mixing time of CTI TL combined with 250 mg/L ferric sulfate on TOC and turbidity removal ratios from OSPW (initial pH: 8.5; initial turbidity: 85 NTU; initial TOC: 46.5 mg/L; temperature: 20±1 °C. duplicates of jar-test experiments; experimental conditions: ferric sulfate dose: 250 mg/L, total rapid mixing time: 30 s at 120 rpm, slow mixing at 30 rpm for 10 min, settling for 50-60 min.)

In Figure 25, compared with the treatment using only 250 mg/L of ferric sulfate, the treatments using cationic polymer CTI TL combined with ferric sulfate all made positive contributions to the TOC removal. All the highest TOC removal ratios at each dose happened with approximately 2s of rapid mixing time, and the lowest dose of CTI TL at 5 mg/L gave the highest TOC removal ratio. The turbidity removal ratios were similar. Therefore, the optimum rapid mixing time for CTI TL was 2s. CTI TL doses less than 5 mg/L were further investigated and are shown in Figure 26.

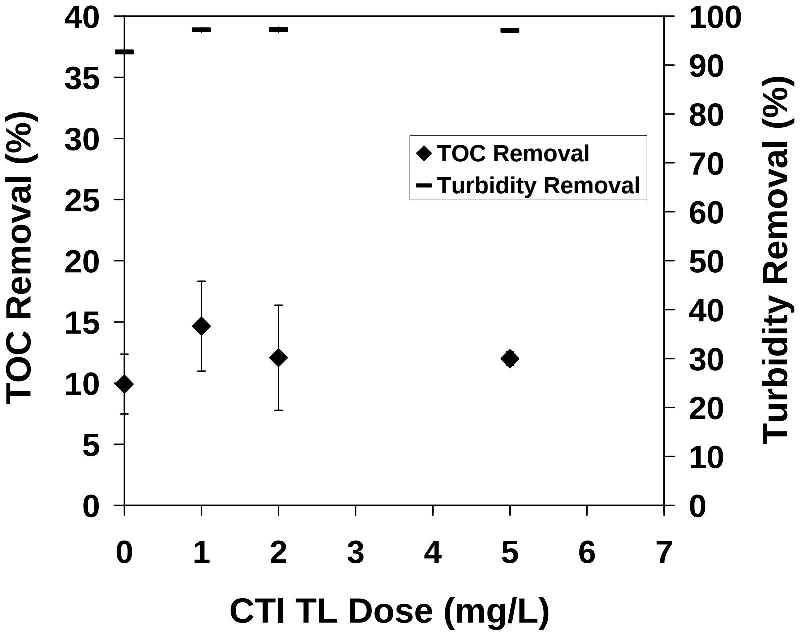


Figure 26: Effects of cationic polymer CTI TL dose combined with 250 mg/L ferric sulfate on TOC and turbidity removal ratios from OSPW
(initial pH: 8.5; initial turbidity: 194 NTU; initial TOC: 46.4 mg/L; temperature: 20±1 °C. triplicates of jar-test experiments; experimental conditions: ferric sulfate: 250 mg/L, rapid mixing at 120 rpm for 30 s, 2 s rapid mixing for CTI TL, flocculation at 30 rpm for 10 min, settling for 50-60 min.)

From Figure 26, the optimum CTI TL dose combined with 250 mg/L ferric sulfate was 1 mg/L according to TOC and turbidity removals. With the optimum dose, TOC and turbidity removal ratios were approximately 15% ± 3.7% and 97% ± 0.5%, respectively.

4.5.2.2 Non-ionic polymer

The non-ionic polymer LT20 was studied with 250 mg/L of ferric sulfate during the coagulation-flocculation treatment for OSPW. The initial rapid mixing time and flocculation time were applied at 30s and 10 minutes. Ferric sulfate was added at the beginning of rapid mixing. At each dosage, the polymer was added at three different moments during the rapid mixing process: at the beginning (30s rapid mixing); in the middle (15s rapid mixing); and at the end of the rapid mixing process (0s rapid mixing). Since the high-molecular-weight non-ionic polymers are usually used at a lower dose in water treatment, concentrations of LT20 in a 2-L jar were applied at 0.1, 0.5 and 1 mg/L in the experiments. The triplicate treatments using 250 mg/L of ferric sulfate only were conducted as a reference. Figure 27 shows the effects of LT20 dose combined with a coagulant of 250 mg/L ferric sulfate and rapid mixing time on TOC and turbidity removals from OSPW.

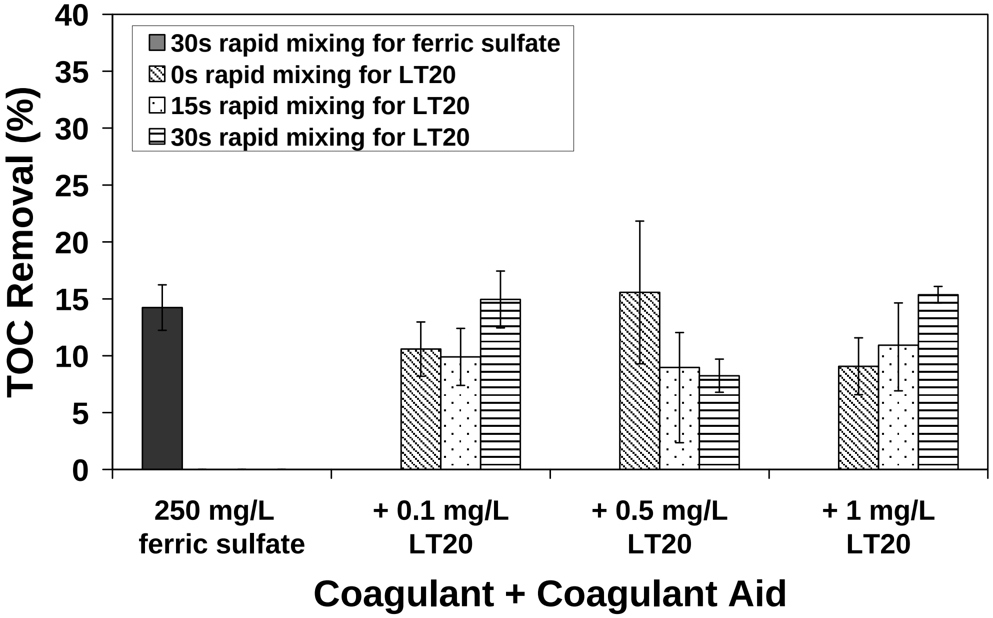


Figure 27: Effects of the dosage and rapid mixing time of LT20 combined with 250 mg/L ferric sulfate on TOC and turbidity removal ratios from OSPW (initial pH: 8.5; initial turbidity: 86 NTU; initial TOC: 48.5 mg/L; temperature: 20±1 °C. duplicates of jar-test experiments; experimental conditions: ferric sulfate dose: 250 mg/L, total rapid mixing time: 30 s at 120 rpm, flocculation at 30 rpm for 10 min, settling for 50-60 min.)

In Figure 27, compared with the treatment using 250 mg/L of ferric sulfate only, there were no much contributions to the TOC removal from the non-ionic polymer LT20. Therefore, non-ionic polymer LT20 was not selected.

4.5.2.3 Anionic polymer

Two anionic polymers, PAM A-503 and Praestol 2515TR (supplied by ClearTech, Edmonton) were studied with 250 mg/L of ferric sulfate in the coagulation-flocculation treatment for OSPW. Initial rapid mixing times and flocculation times were applied at 30s and 10 minutes. Ferric sulfate was added at the beginning of rapid mixing. At each dosage, the polymer was added at three different moments during the rapid mixing process: at the beginning (30s rapid mixing); in the middle (15s rapid mixing); and at the end of the rapid mixing process (0s rapid mixing). Since the anionic polymers are commonly used at a lower dose in water treatment, concentrations of the anionic polymers in a 2-L jar were applied at 0.1, 0.5 and 1 mg/L in the experiments. Figures 28 and 29 show the effects of the dosages of PAM A-503 and Praestol 2515TR combined with a coagulant of 250 mg/L ferric sulfate and rapid mixing time on TOC and turbidity removals from OSPW.

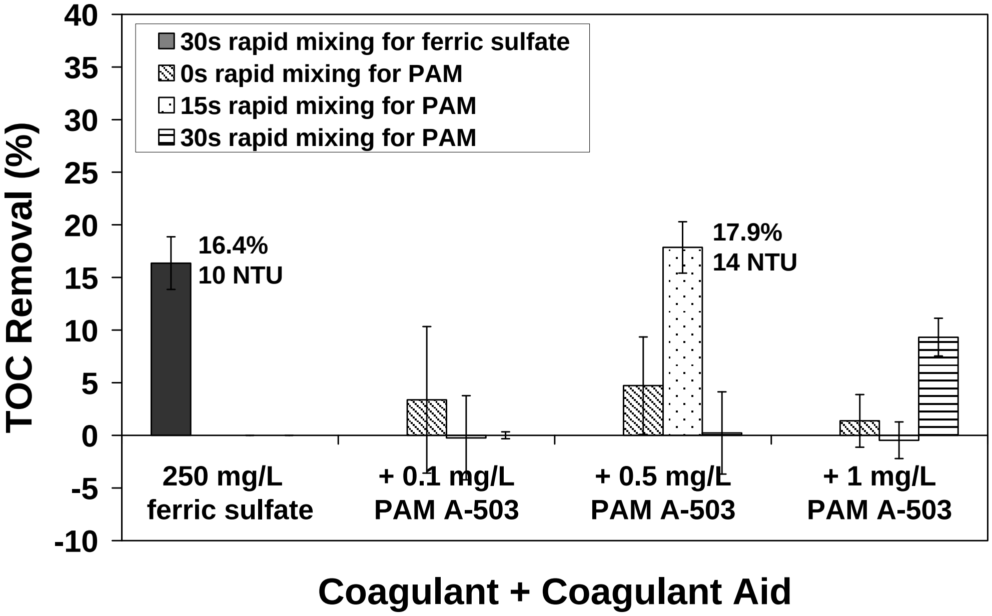


Figure 28: Effects of the dosage and rapid mixing time of PAM A-503 combined with 250 mg/L ferric sulfate on TOC and turbidity removal ratios from OSPW (initial pH: 8.5; initial turbidity: 85 NTU; initial TOC: 43.4 mg/L; temperature: 20±1 °C. duplicates of jar-test experiments; experimental conditions: ferric sulfate dose: 250 mg/L, total rapid mixing time: 30 s at 120 rpm, flocculation at 30 rpm for 10 min, settling for 50-60 min.)

In Figure 28, compared with the treatment using only 250 mg/L of ferric sulfate, the only positive contribution to TOC removal came from the anionic polymer PAM A-503 at 0.5 mg/L with 15 s rapid mixing. However, the positive contribution was minimal. Therefore, anionic polymer PAM A-503 was not selected for further study.

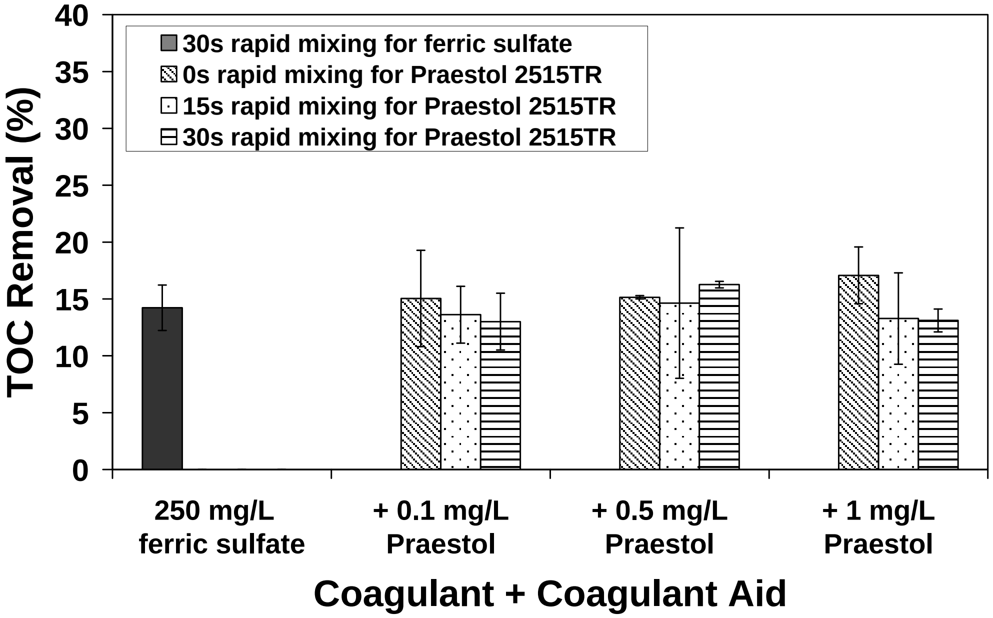


Figure 29: Effects of the dosage and rapid mixing time of Praestol 2515TR combined with 250 mg/L ferric sulfate on TOC and turbidity removal ratios from OSPW
(initial pH: 8.5; initial turbidity: 85 NTU; initial TOC: 49.2 mg/L; temperature: 20±1 °C. duplicates of jar-test experiments; experimental conditions: ferric sulfate dose: 250 mg/L, total rapid mixing time: 30 s at 120 rpm, flocculation at 30 rpm for 10 min, settling for 50-60 min.)

In Figure 29, compared with the treatment using 250 mg/L of ferric sulfate, some treatments using anionic polymer Praestol 2515TR combined with ferric sulfate showed slightly more positive contributions to the TOC removals. 1 mg/L of Praestol 2515TR added directly after the rapid mixing process showed the highest TOC removal ratio. Therefore, Praestol 2515TR was chosen to be added directly after the rapid mixing process, which supported the concept that anionic polymers commonly enhance flocculation process. Higher dosage range of Praestol 2515TR from 1 mg/L to 5 mg/L were further investigated, which are shown in Figure 30.

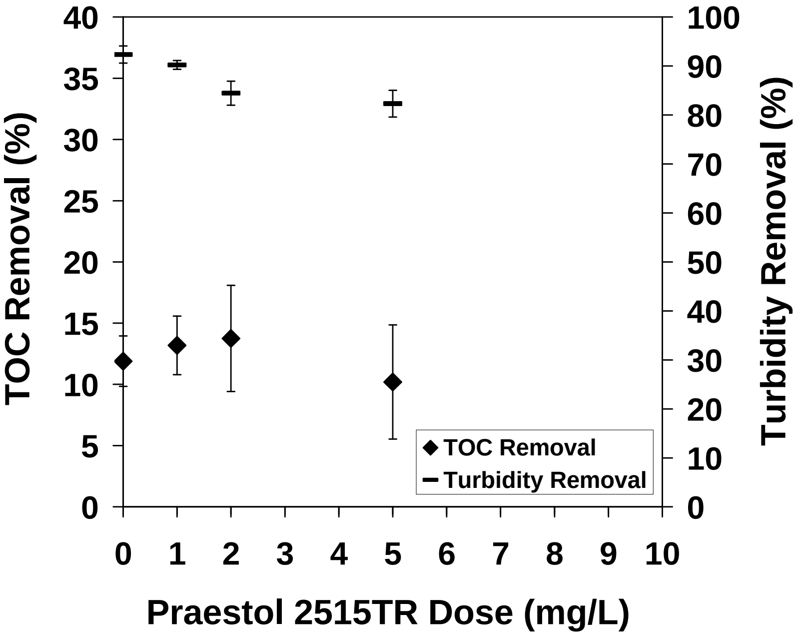


Figure 30: Effects of Praestol 2515TR dosage combined with 250 mg/L ferric sulfate on TOC and turbidity removal ratios from OSPW
(initial pH: 8.5; initial turbidity: 185 NTU; initial TOC: 41.2 mg/L; temperature: 20±1 °C. triplicates of jar-test experiments; experimental conditions: ferric sulfate: 250 mg/L, rapid mixing at 120 rpm for 30 s, polymer was added after rapid mixing, flocculation at 30 rpm for 10 min, settling for 50-60 min.)

Praestol 2515 produced bigger flocs than CTI TL. The flocs became very sticky when a dosage of more than 2 mg/L was applied. It will be a challenge for equipment maintenance if higher dosage of Praestol 858BS is applied in the industry. In Figure 30, the optimum dose of Praestol 2515TR was 2 mg/L, which increased TOC removal from OSPW by 2%. However, turbidity removal decreased sharply when the polymer dose increased. At 2 mg/L, the turbidity removal ratio was only about 84% which is less than the treatment using 250 mg/L of ferric sulfate only without the addition of any polymer. Therefore, anionic polymer Praestol 2515TR was not selected.

After comparing the efficiencies of TOC and turbidity removals using cationic, non-ionic and anionic polymer combined with ferric sulfate, cationic polymer CTI TL was selected as a coagulant aid with ferric sulfate for further process optimization. Cationic polymer CTI TL combined with ferric sulfate gave better TOC and turbidity removals than any other polymer studied.

4.5.3 Process Optimization

Total rapid mixing time and flocculation time were optimized for different dosages of ferric sulfate applied at 100, 250 and 500 mg/L. Rapid mixing and flocculation speeds were fixed at 120 rpm and 30 rpm, and the CTI TL was added about 2 s before the end of the rapid mixing process according to the above experimental findings. The optimum CTI TL dose of 1 mg/L selected in Section 4.5.2.1 was applied with 250 mg/L of ferric sulfate. The optimum CTI TL doses combined with 100 mg/L and 500 mg/L of ferric sulfate were further studied as well.

4.5.3.1 Process optimization for 100 mg/L ferric sulfate

(a) Polymer dose selection:

Optimum cationic polymer CTI TL dose combined with 100 mg/L of ferric sulfate was investigated. The concentrations of CTI TL in a 2-L jar were applied at 0, 2, 5, 10, 20 and 30 mg/L. Figure 31 shows the results of the CTI TL dose study combined with 100 mg/L of ferric sulfate in terms of TOC and turbidity removals from OSPW.

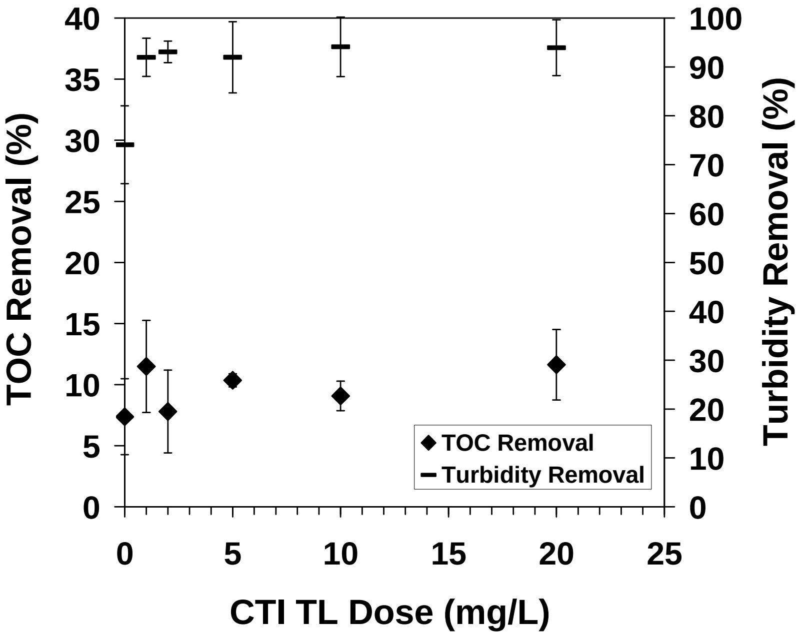


Figure 31: Effects of CTI TL dose combined with 100 mg/L ferric sulfate on TOC and turbidity removal ratios from OSPW
(initial pH: 8.4; initial turbidity: 201 NTU; initial TOC: 47.3 mg/L; temperature: 20±1 °C. triplicates of jar-test experiments; Jar-test conditions: rapid mixing at 120 rpm for 30 s, 2 s rapid mixing for CTI TL, flocculation at 30 rpm for 10 min, settling for 50-60 min.)

From Figure 31, 1 mg/L was selected as the optimum dose of CTI TL combined with 100 mg/L of ferric sulfate, which was then applied in the following process optimization.

(b) Rapid mixing time optimization:

The total rapid mixing time at 120 rpm (G = 120 s^{-1}) for the coagulation process using 100 mg/L ferric sulfate and 1 mg/L CTI TL was investigated at 0, 15, 30, 60 and 120 s, as shown in Figure 32. CTI TL was added 2 s before the flocculation process as per the previous finding.

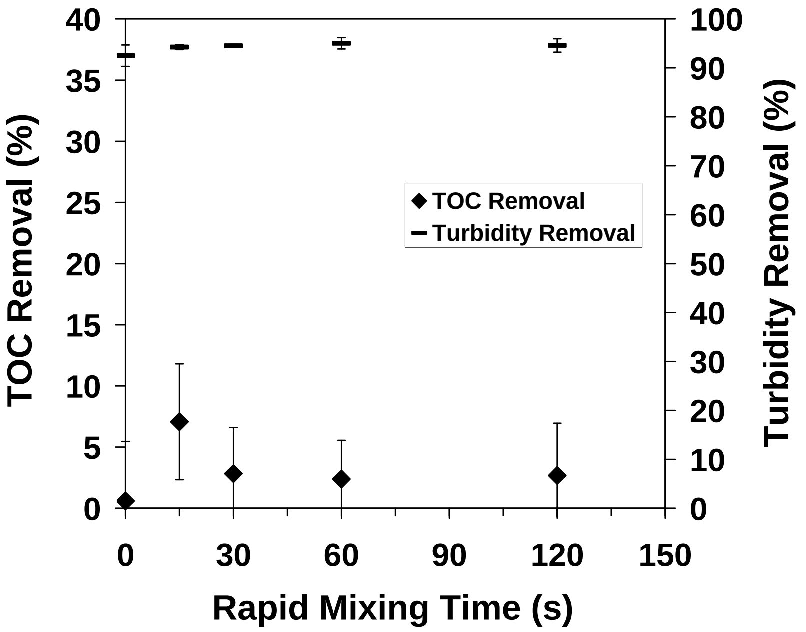


Figure 32: Effects of rapid mixing time for the coagulation process using 100 mg/L ferric sulfate and 1 mg/L CTI TL on TOC and turbidity removal ratios from OSPW

(initial pH: 8.2; initial turbidity: 170 NTU; initial TOC: 44.2 mg/L; temperature: 20±1 °C. triplicates of jar-test experiments; Jar-test conditions: rapid mixing speed at 120 rpm (G = 120 s^{-1}), 2 s rapid mixing for CTI TL, flocculation at 30 rpm for 10 min, settling for 50-60 min.)

As shown in Figure 32, the optimum rapid mixing time at 120 rpm (G = 120 s^{-1}) was 15s which was applied in the further study.

(c) Flocculation time optimization:

Flocculation time was investigated at 0, 10, 20, 30, 60 and 120 minutes, while the flocculation speed applied was 30 rpm (G = 23 s^{-1}). Figure 33 shows the effects of flocculation time on TOC and turbidity removals from OSPW.

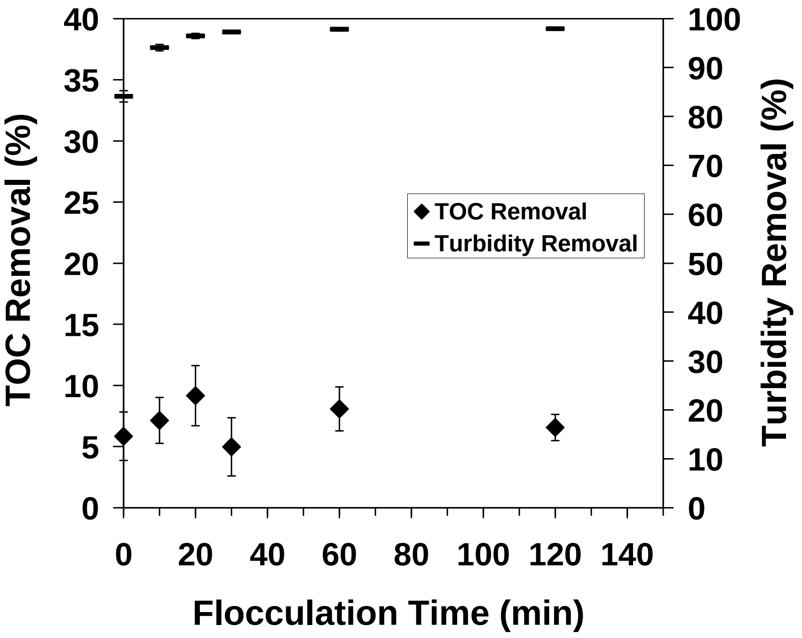


Figure 33: Effects of flocculation time on TOC and turbidity removal ratios from OSPW
(initial pH: 8.4; initial turbidity: 186 NTU; initial TOC: 46.2 mg/L; temperature: 20±1 °C. triplicates of jar-test experiments; Jar-test conditions: ferric sulfate dose: 100 mg/L, CTI TL dose: 1 mg/L, rapid mixing at 120 rpm (G = 120 s^{-1}) for 15 s, 2 s rapid mixing for CTI TL, flocculation speed at 30 rpm (G = 23 s^{-1}), settling for 50-60 min.)

As shown in Figure 33, 20 minutes was selected as the optimum flocculation time for the coagulation-flocculation process using 100 mg/L of ferric sulfate combined with 1 mg/L of cationic polymer CTI TL.

4.5.3.2 Process optimization for 250 mg/L ferric sulfate

(a) Polymer dose selection:

As discussed in Section 4.5.2.1, 1 mg/L was selected as the optimum CTI TL dose combined with 250 mg/L of ferric sulfate during the coagulation-flocculation treatment for OSPW.

(b) Rapid mixing time optimization:

The total rapid mixing time at 120 rpm (G = 120 s^{-1}) for the coagulation process using 250 mg/L ferric sulfate and 1 mg/L CTI TL was investigated at 0, 15, 30, 60 and 120 s, as shown in Figure 34, CTI TL was added 2 s before the flocculation process.

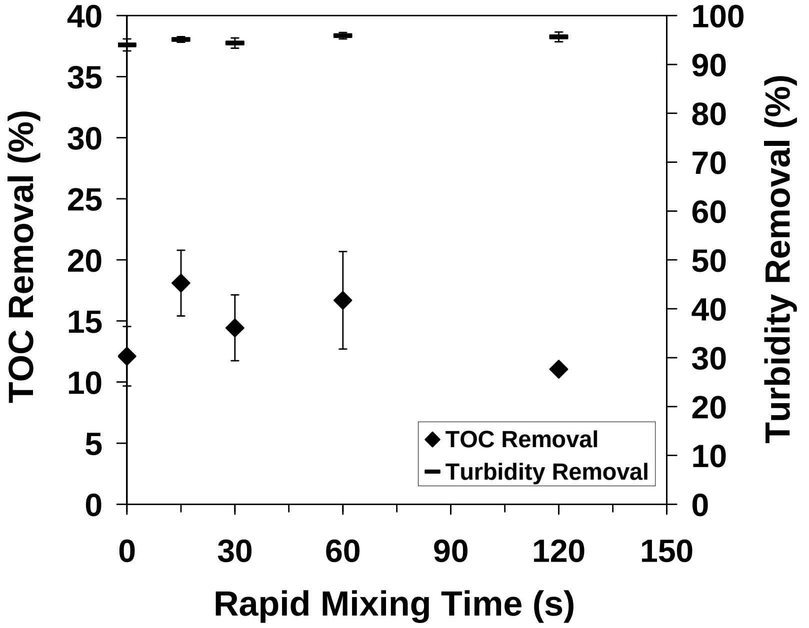


Figure 34: Effects of rapid mixing time for the coagulation process using 250 mg/L ferric sulfate and 1 mg/L CTI TL on TOC and turbidity removal ratios from OSPW
(initial pH: 8.4; initial turbidity: 211 NTU; initial TOC: 47.3 mg/L; temperature: 20±1 °C. triplicates of jar-test experiments; Jar-test conditions: rapid mixing speed at 120 rpm (G = 120 s^{-1}), 2 s rapid mixing for CTI TL, flocculation at 30 rpm for 10 min, settling for 50-60 min.)

From Figure 34, the optimum rapid mixing time at 120 rpm (G = 120 s^{-1}) was 15 s which was applied in the study further.

(c) Flocculation time optimization:

Flocculation time was investigated at 0, 10, 20, 30, 60 and 120 minutes and the flocculation speed was applied at 30 rpm (G = 23 s^{-1}). Figure 35 shows the effects of flocculation time on TOC and turbidity removals from OSPW.

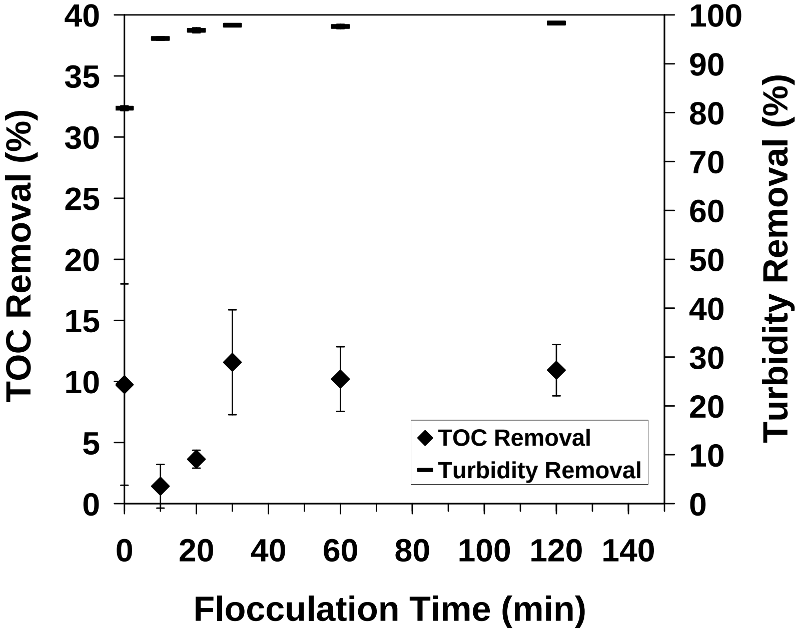


Figure 35: Effects of flocculation time on TOC and turbidity removal ratios from OSPW
(initial pH: 8.4; initial turbidity: 158 NTU; initial TOC: 43.7 mg/L; temperature: 20±1 °C. triplicates of jar-test experiments; Jar-test conditions: ferric sulfate dose: 250 mg/L, CTI TL dose: 1 mg/L, rapid mixing at 120 rpm (G = 120 s^{-1}) for 15 s, 2 s rapid mixing for CTI TL, flocculation speed at 30 rpm (G = 23 s^{-1}), settling for 50-60 min.)

In Figure 35, although TOC removal ratios were similar with 30 minutes of flocculation and without flocculation, turbidity was higher without the flocculation process. Therefore, 30 minutes was the optimum flocculation time selected for the treatment using 250 mg/L of ferric sulfate combined with 1 mg/L of cationic polymer CTI TL.

Figure 36 compares the OSPW before and after treatment with 250 mg/L of ferric sulfate and 1 mg/L of CTI TL.

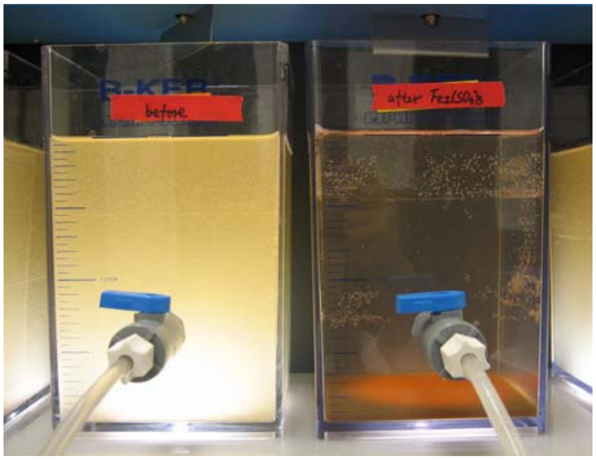


Figure 36: OSPW before and after coagulation-flocculation and sedimentation processes using 250 mg/L ferric sulfate and 1 mg/L CTI TL

4.5.3.3 Process optimization for 500 mg/L ferric sulfate

(a) Polymer dose selection:

The optimum cationic polymer CTI TL dose combined with 500 mg/L of ferric sulfate was studied. The concentrations of CTI TL in a 2-L jar were applied at 0, 1, 2 and 5 mg/L. Figure 37 shows the effects of CTI TL dose combined with 500 mg/L of ferric sulfate on TOC and turbidity removals from OSPW.

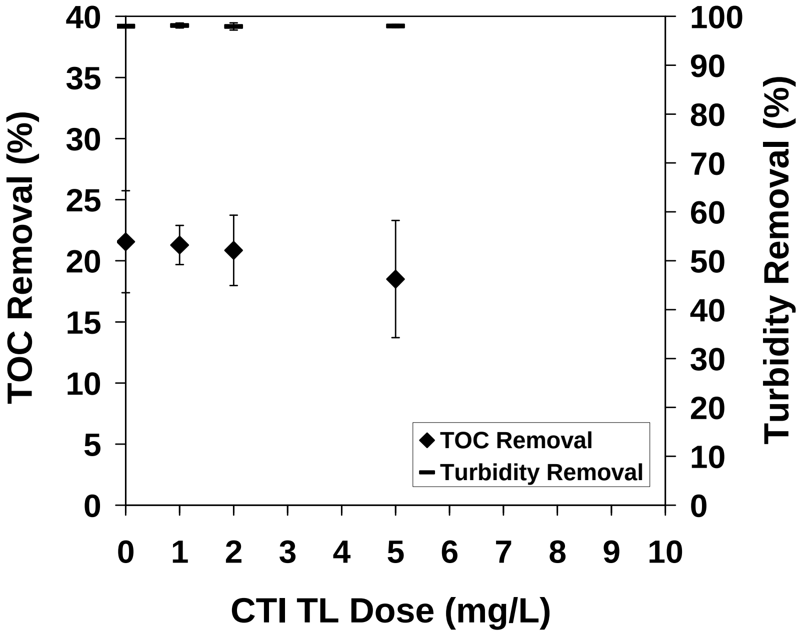


Figure 37: Effects of CTI TL dose combined with 500 mg/L ferric sulfate on TOC and turbidity removal ratios from OSPW
(initial pH: 8.5; initial turbidity: 191 NTU; initial TOC: 38.2 mg/L; temperature: 20±1 °C. triplicates of jar-test experiments; Jar-test conditions: rapid mixing at 120 rpm for 30 s, 2 s rapid mixing for CTI TL, flocculation at 30 rpm for 10 min, settling for 50-60 min.)

As illustrated in Figure 37, there were no positive contributions from the addition of cationic polymer CTI TL to the TOC and turbidity removals. Therefore, 500 mg/L of ferric sulfate should be used alone without any polymer in the coagulation-flocculation process. The initial TOC value for the raw OSPW was relatively low in this experiment, which resulted in lower TOC removal ratios as well.

(b) Rapid mixing time optimization:

The total rapid mixing time at 120 rpm (G = 120 s^{-1}) for the coagulation process using 500 mg/L ferric sulfate alone was investigated at 0, 15, 30, 60 and 120s, which is shown in Figure 38.

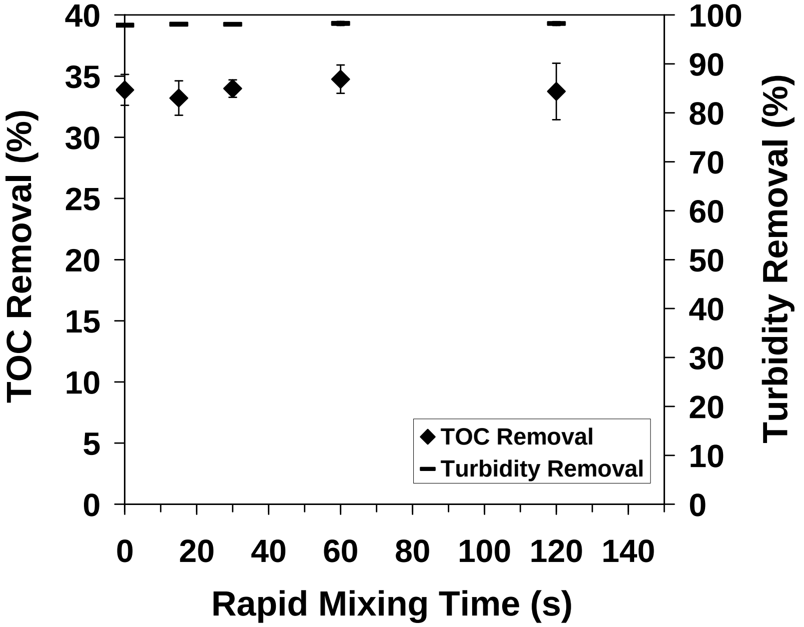


Figure 38: Effects of rapid mixing time for the coagulation process using 500 mg/L ferric sulfate alone on TOC and turbidity removal ratios from OSPW (initial pH: 8.5; initial turbidity: 255 NTU; initial TOC: 56.3 mg/L; temperature: 20±1 °C. triplicates of jar-test experiments; Jar-test conditions: rapid mixing speed at 120 rpm (G = 120 s^{-1}), flocculation at 30 rpm for 10 min, settling for 50-60 min.)

As shown in Figure 38, there was not much contribution from the rapid mixing process to the TOC and turbidity removals. t-Test analysis (in Appendix B) indicated that there was no significant difference between the TOC removals without rapid mixing and with 60 s of rapid mixing. Therefore, further in the study, no rapid mixing process was applied with 500 mg/L ferric sulfate treatment, and the coagulant (500 mg/L of ferric sulfate) was added at the beginning of flocculation process.

(c) Flocculation time optimization:

Flocculation time was investigated at 0, 10, 20, 30, 60 and 120 minutes, while flocculation speed was applied at 30 rpm (G = 23 s^{-1}). Figure 39 shows the effects of flocculation time on TOC and turbidity removals from OSPW, when 500 mg/L of ferric sulfate was applied alone.

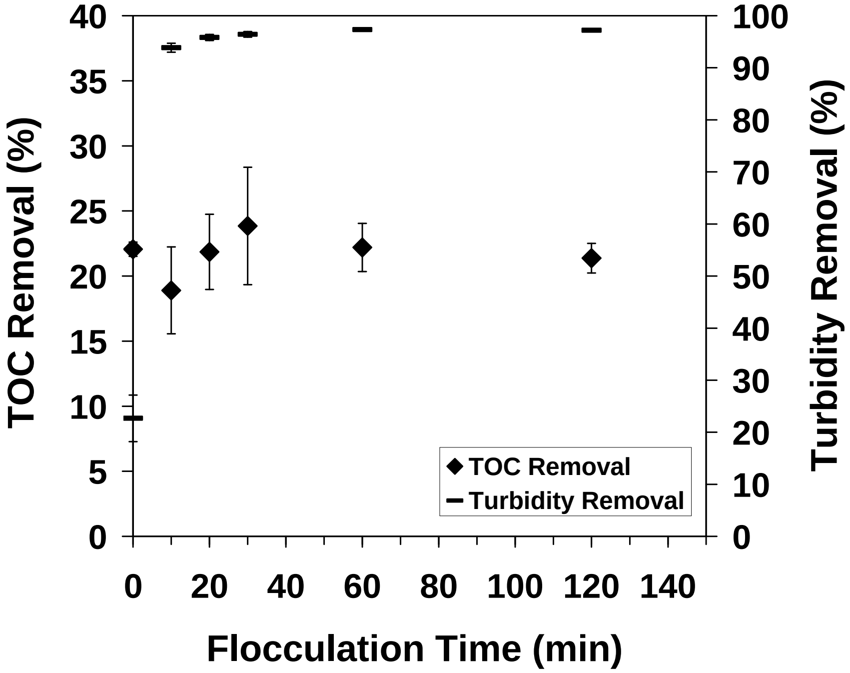


Figure 39: Effects of flocculation time on TOC and turbidity removal ratios from OSPW
(initial pH: 8.4; initial turbidity: 194 NTU; initial TOC: 48.5 mg/L; temperature: 20±1 °C. triplicates of jar-test experiments; experimental conditions: ferric sulfate dose: 500 mg/L, flocculation speed at 30 rpm (G = 23 s^{-1}), settling for 50-60 min.)

From Figure 39, 30 minutes was selected as the optimum flocculation time for the coagulation-flocculation process using 500 mg/L of ferric sulfate alone.

4.6 Best Jar-Test Conditions

The optimized jar-test conditions for alum and ferric sulfate at different dosages with or without polymers were summarized in Table 13, as well as those for the cationic polymer CTI TL as a primary coagulant.

Table 13: Summaries of optimized jar-test conditions (20 ± 1 °C)

Coagulant		Polymer		Rapid mixing				Flocculation (slow mixing)			Sedimentation
Type	Dose (mg/L)	Type	Dose (mg/L)	Speed (rpm)	Intensity (s^{-1})	Time (s)	Time for polymer (s)	Speed (rpm)	Intensity (s^{-1})	Time (min)	Time (min)
Alum	100	CTI TL	10	120	120	30	15	30	23	10	50-60
	250	CTI TL	5	120	120	30	15			10	
	500	CTI TL	2	120	120	30	15			10	
Ferric sulfate	100	CTI TL	1	120	120	15	2			20	
	250	CTI TL	1	120	120	15	2			30	
	500	--	--	--	--	--	--			30	
--	--	CTI TL	5	80	74	120	--			10	

4.6.1 Characterization of Treated OSPW

In order to assess treatment performance, the raw and treated OSPW were compared and characterized by different measurements and analytical methods, such as TOC, turbidity, TSS, TDS, conductivity, alkalinity, ions, elements, NAs, and sludge volume. In order to ensure the sampling procedures were consistent, all the OSPW was sampled at the same time and mixed in a 200-litre plastic barrel. The OSPW was pumped out from the bottom of the barrel to each 2-L jar while it was mixing. All the jar tests, five replicates for each treatment under the best jar-test conditions as listed in Table 13, were conducted within two days. OSPW samples before and after treatment were collected for analyses. The characteristics of raw and treated OSPW were compared as follows. All the analytical results below were based on the OSPW sampled at this time.

4.6.1.1 General properties

The pH, TOC, turbidity, conductivity and sludge volume values of the treated OSPW under the best jar-test conditions were summarized in Table 14, The raw OSPW (before treatment) was tested as reference. The TOC removal ratios were compared in Figure 40.

Table 14: General properties of the OSPW before and after treatment

Treatment options	pH	TOC (mg/L)	TOC removal (%)	Turbidity (NTU)	Turbidity removal (%)	Sludge Volume (cm^3/L water)	Conductivity (µS/cm)
Raw OSPW	8.1-8.2	48.34±1.70	--	188±5.73	--	--	3870
100 mg/L alum	7.4	43.76±0.79	9.48±1.64	7.68±3.29	95.78±1.81	30	3770
100 mg/L alum + 10 mg/L CTI TL	7.4	42.25±3.00	12.61±6.18	2.96±0.45	98.43±0.24	30	3720
250 mg/L alum	7.1	42.78±1.00	11.52±2.04	4.88±1.10	97.37±0.59	48	3795
250 mg/L alum + 5 mg/L CTI TL	7.0	42.22±1.13	14.09±2.34	2.10±0.61	98.89±0.33	48	3795
500 mg/L alum	6.6	41.40±3.00	14.36±1.36	4.06±0.56	97.83±0.30	67	3790
500 mg/L alum + 2 mg/L CTI TL	6.6	39.68±1.06	16.71±2.19	2.32±0.41	98.77±0.22	67	3775
100 mg/L ferric sulfate	7.4	45.10±1.03	6.71±1.21	17.65±3.57	90.19±1.98	18	3820
100 mg/L ferric sulfate + 1 mg/L CTI TL	7.4	45.03±1.66	6.85±3.44	7.44±1.34	96.16±0.69	12	3850
250 mg/L ferric sulfate	6.9	44.50±1.00	7.95±1.20	7.69±0.47	95.91±0.25	24	3845
250 mg/L ferric sulfate + 1 mg/L CTI TL	7.0	43.06±1.72	10.92±3.56	3.04±0.53	98.43±0.27	24	3870
500 mg/L ferric sulfate	6.5	39.43±3.68	18.43±1.33	3.77±0.33	98.00±0.18	54	3860

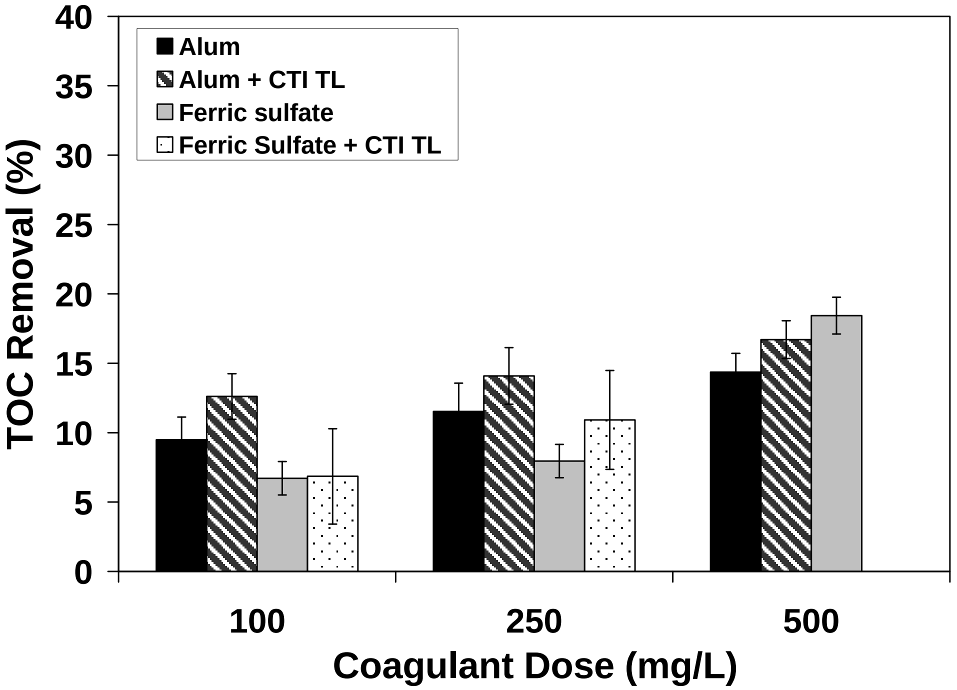


Figure 40: Comparison of TOC removal ratios from OSPW by different treatments under the best jar-test conditions
(initial pH: 8.1 - 8.2; initial turbidity: 182 NTU, SD = 5.7; initial TOC: 48.3 mg/L, SD = 1.7; temperature: 20±1 °C)

In Table 14, the pH depressed after treatment because of the addition of the acidic coagulants. The final pH after treatment depended on the coagulant dosage used in the process. The sludge volume depended mainly on the coagulant type and dosage used. Alum produced more sludge than ferric sulfate when the same doses were applied. However, alum had a better treatment performance in terms of TOC and turbidity removals when a lower coagulant dose (less than 250 mg/L) was applied. When the coagulant dose was increased up to 500 mg/L, ferric sulfate had better TOC removals than alum. The ferric sulfate solution with a strong orange colour became difficult to remove completely from the treated water and introduced colour into the sludge, as shown in Figure 36. But alum solution was transparent which was ideal for the colour removal from OSPW. Therefore, alum is good for TOC, turbidity and color removals at lower dose (≤ 250 mg/L) treatments combined with polymer. Ferric sulfate is good for higher dose (≥ 500 mg/L) treatment without polymer.

Statistic variance analysis for TOC removal ratios between different treatment options was conducted by Single Factor ANOVA as shown in Appendix B. According to the statistic analysis, significant difference between means of treatments was observed.

4.6.1.2 COD analysis

COD analysis was conducted in order to estimate the correlation between TOC and COD values of OSPW samples, which are shown in Table 15.

Table 15: COD values of OSPW and the correlations of TOC and COD (duplicate analysis)

Treatment options	COD (mg/L)	TOC (mg/L)	TOC/COD
OSPW	243.0	48.3	0.1989
100 mg/L alum	190.0	43.8	0.2303
100 mg/L alum + 10 mg/L CTI TL	191.0	42.8	0.2240
250 mg/L alum	197.0	41.4	0.2102
250 mg/L alum + 5 mg/L CTI TL	198.0	42.3	0.2134
500 mg/L alum	185.0	42.2	0.2282
500 mg/L alum + 2 mg/L CTI TL	177.0	39.7	0.2241
100 mg/L ferric sulfate	203.0	44.6	0.2197
100 mg/L ferric sulfate + 1 mg/L CTI TL	191.0	44.4	0.2326
250 mg/L ferric sulfate	166.0	41.1	0.2473
250 mg/L ferric sulfate+ 1 mg/L CTI TL	212.0	45.6	0.2149
500 mg/L ferric sulfate	200.0	43.3	0.2165

The TOC/COD correlation was around 0.21 ~ 0.23 for treated OSPW, and it was between 0.19 and 0.20 for raw OSPW.

4.6.1.3 Gravimetric analysis

Total suspended solids and total dissolved solids were measured, which are shown in Table 16. The TSS was removed from 96% to 99% according to the different treatment options. Basically, the higher the dosages of coagulant and polymer used, the more TSS was removed. 250 mg/L of alum combined with 5 mg/L of CTI TL produced the highest TSS removal ratio of 99%. However, only a few TDS were removed by the coagulation-flocculation process. It further reflected that coagulation-flocculation is a process to remove suspended solids (AWWA 1999; Metcalf and Eddy 2003)

Table 16: TSS and TDS analyses under the best jar-test conditions
(5 replicates)

Treatment options	TSS				TDS			
	Value (mg/L)	Ave. (mg/L)	Std. deviation	removal (%)	Value (mg/L)	Ave. (mg/L)	Std. Deviation	removal (%)
OSPW	67-141	97	23	--	2392-2524	2477	48.3	--
100 mg/L alum	0.6-3.2	2.4	1.0	97.5	2328-2463	2401	54.9	3.07
100 mg/L alum + 10 mg/L CTI TL	1.4-3.6	2.4	1.1	97.5	2340-2427	2382	38.1	3.84
250 mg/L alum	0.8-2.6	1.9	0.7	98.0	2415-2513	2457	43.6	0.81
250 mg/L alum + 5 mg/L CTI TL	0.2-1.6	1.0	0.6	99.0	2421-2559	2462	56.3	0.61
500 mg/L alum	1.2-2.4	1.8	0.6	98.1	2390-2504	2444	45.7	1.33
500 mg/L alum + 2 mg/L CTI TL	0.8-2.2	1.4	0.6	98.6	2381-2427	2408	17.9	2.79
100 mg/L ferric sulfate	0.8-3.8	2.5	1.1	97.4	2405-2448	2425	18.6	2.10
100 mg/L ferric sulfate + 1 mg/L CTI TL	1.4-7.4	3.5	2.3	96.4	2433-2516	2454	34.8	0.93
250 mg/L ferric sulfate	1.2-4.4	2.3	1.3	97.6	2447-2470	2458	10.1	0.77
250 mg/L ferric sulfate+ 1 mg/L CTI TL	0.2-2.6	1.0	1.0	99.0	2439-2460	2452	9.0	1.01
500 mg/L ferric sulfate	1.6-6.2	3.3	2.0	96.6	2462-2498	2475	14.1	0.08

4.6.1.4 Ions and elements analysis

Ions and elements in raw and treated OSPW were analyzed by Ionic Chromatography (IC) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The ions or elements which concentrations were changed after treatment are summarized in Table 17.

As seen in Table 17, although aluminum sulfate and ferric sulfate were added during the coagulation-flocculation process, concentrations of aluminum and iron in the supernatant of OSPW decreased after treatment. This indicated that aluminum and iron were removed from the water (OSPW) and transferred into the sludge after the treatment in a batch reactor (jar). The sample calculation of aluminum in supernatant and sludge based on mass balance was illustrated in Appendix A. The concentration of sulfate increased because more sulfate from the coagulant dissolved in water. However, the increase is not as much as the theoretically calculated value, which indicates that some sulfates originally in OSPW or coagulants have been removed from the water into the sludge. The theoretical calculation was shown in Appendix A, and the comparison of the theoretical and actual values of sulfate in water is shown in Table 18. As seen in Table 17, the concentrations of other elements such as fluoride, silicon, vanadium and barium were decreased significantly after treatment.

Table 17: Ions and elements analyses under the best jar-test conditions (duplicates)

Treatment options	Aluminum (mg/L)	Iron (mg/L)	Sulfate (mg/L)	Fluoride (mg/L)	Silicon (mg/L)	Vanadium (mg/L)	Barium (mg/L)
OSPW	8.48-10.51	3.01-3.25	506-520	2.63-2.68	15.24-19.04	0.017-0.019	0.329-0.345
100 mg/L alum	1.65-2.01	0.41-0.56	546-556	1.96-2.16	3.22-3.71	0.005	0.154-0.162
100 mg/L alum + 10 mg/L CTI TL	0.59-0.63	0.37-0.44	550-554	1.93-1.98	2.76-3.00	0.005-0.006	0.149-0.153
250 mg/L alum	1.55-2.04	0.23-1.47	628-632	1.23-1.32	2.98-3.46	0.005	0.130-0.131
250 mg/L alum + 5 mg/L CTI TL	0.58-0.67	0.30-0.39	634-640	1.26-1.29	2.54-2.63	0.005	0.127-0.129
500 mg/L alum	2.16-3.00	0.24-0.42	760-768	0.52-0.58	2.75-2.82	0.005	0.139-0.140
500 mg/L alum + 2 mg/L CTI TL	0.68-0.79	0.24-0.29	766-775	0.53-0.55	1.82-2.17	0.005	0.131-0.129
100 mg/L ferric sulfate	0.90-1.01	1.11-1.34	538-557	2.63	3.62-4.52	0.005	0.138-0.148
100 mg/L ferric sulfate + 1 mg/L CTI TL	0.57-0.77	1.17-1.44	553-558	2.64	2.89-3.33	0.005-0.006	0.131-0.150
250 mg/L ferric sulfate	0.27-0.42	1.04-1.26	631-639	2.59-2.62	2.86-3.10	0.005	0.133-0.137
250 mg/L ferric sulfate+ 1 mg/L CTI TL	0.19-0.352	1.16-1.46	633-635	2.60-2.63	2.10-2.26	0.004	0.128-0.201
500 mg/L ferric sulfate	0.27-0.39	2.33-2.44	770-773	2.55-2.60	2.33-2.53	0.004	0.131-0.157

Table 18: Comparison of the theoretical and actual increase of ferric sulfate after addition of coagulants

Treatment options	Increase of sulfate (mg/L)		
	Theoretical	Actual	Actual/Theoretical
100 mg/L alum	84	38	45%
100 mg/L alum + 10 mg/L CTI TL	84	117	139%
250 mg/L alum	211	124	59%
250 mg/L alum + 5 mg/L CTI TL	211	124	59%
500 mg/L alum	421	252	60%
500 mg/L alum + 2 mg/L CTI TL	421	256	61%
100 mg/L ferric sulfate	72	35	49%
100 mg/L ferric sulfate + 1 mg/L CTI TL	72	42	58%
250 mg/L ferric sulfate	180	122	68%
250 mg/L ferric sulfate+ 1 mg/L CTI TL	180	121	67%
500 mg/L ferric sulfate	360	258	72%

As shown in Table 18, the actual increase of the sulfate concentration was smaller than the theoretical calculation, which indicates that some sulfate ions were removed during the coagulation-flocculation and sedimentation processes.

4.6.1.5 Alkalinity

Alkalinities for the raw and treated OSPW were measured using titration method. The results are shown in Table 19.

Table 19: Alkalinity of the OSPW before and after treatment
(Initial pH of the OSPW: 8.1~8.2)

Treatment options	Carbonate alkalinity as $CaCO_3$ (mg/L)	Bicarbonate alkalinity as $CaCO_3$ (mg/L)	Alkalinity as $CaCO_3$ (mg/L)
OSPW	0	624	624
100 mg/L alum	0	560	560
100 mg/L alum + 10 mg/L CTI TL	0	552	552
250 mg/L alum	0	493	493
250 mg/L alum + 5 mg/L CTI TL	0	472	472
500 mg/L alum	0	377	377
500 mg/L alum + 2 mg/L CTI TL	0	355	355
100 mg/L ferric sulfate	0	553	553
100 mg/L ferric sulfate + 1 mg/L CTI TL	0	571	571
250 mg/L ferric sulfate	0	489	489
250 mg/L ferric sulfate+ 1 mg/L CTI TL	0	488	488
500 mg/L ferric sulfate	0	357	357

Since the initial pH of the raw OSPW was less than 8.3, no carbonates had been recorded in the OSPW samples. The bicarbonates were consumed by the addition of the acidic coagulant. The more the coagulant used, the less the alkalinity left in the OSPW. The mechanism behind the pH and alkalinity decreased after the addition of the coagulants is discussed as follows, using alum as an example coagulant:

The alum reacts with bicarbonate to form a precipitate (aluminum hydroxide) and to produce gas CO_2.

$$Al_2(SO_4)_3 \bullet nH_2O + 6HCO_3^- \rightarrow 2Al(OH)_3 \downarrow + 6CO_2 \uparrow + 3SO_4^{2-} + nH_2O \qquad (11)$$

Here, n is usually 14 or 18. Some of the CO_2 will then react with water to produce carbonic acid. The carbonic acid will partially dissociate to produce bicarbonate,

carbonate and H^+ (shown in Equation 11). Thus, the pH of water will drop after alum added (see Table 14), but not very much, since carbonic is a weak acid.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-} \qquad (12)$$

4.6.1.6 Naphthenic acids

The summary of NAs values before and after treatment is shown in Table 20.

Table 20: NAs analyses before and after treatment by selected treatment options under the best jar-test conditions

Treatment options	NAs parents		NAs mono-oxidized	
	Concentration (mg/L)	Removal (%)	Concentration (mg/L)	Removal (%)
Raw OSPW	23.6	--	31.6	--
100 mg/L alum	16.9	28.4	6.1	80.7
100 mg/L alum + 10 mg/L CTI TL	17.8	24.6	6.6	79.1
250 mg/L alum	14.9	36.9	4.3	86.4
250 mg/L alum + 5 mg/L CTI TL	14.5	38.6	4.5	85.8
500 mg/L alum	14.1	40.3	3.9	87.7
500 mg/L ferric sulfate	15.0	36.4	6.3	80.1

NAs were removed 25% to 40% after the coagulation-flocculation process within the above treatment options. Mono-oxidized compounds in NAs are related to biological activity which contributes to the toxicity. More than 79% of them can be removed after the treatment.

4.6.2 Economical Analysis

The market prices of coagulants and polymers were offered by ClearTech, Edmonton, in February 2010 (Cawson, personal communication, 2010), which also tends to bounce around with US exchange:

- Aluminum sulfate (48.5%): \$0.60/kg or \$163.80/drum (273kg);
- Ferric sulfate (45%): \$0.75/kg or \$240/drum (320 kg);
- CTI TL (pure): \$5.25/kg or \$1071/drum (204 kg)

Based on these prices, a cost analysis for the chemicals used in different treatment options was calculated, and the results were listed in Table 21. Sample calculations are shown in Appendix A. The cost of the industry application of coagulation-flocculation also includes energy, maintenance, operation and management cost.

Table 21: Chemical cost calculations for each megalitre of OSPW

Treatment options	Cost (\$/ML of OSPW)
100 mg/L alum	124
100 mg/L alum + 10 mg/L CTI TL	176
250 mg/L alum	309
250 mg/L alum + 5 mg/L CTI TL	336
500 mg/L alum	619
500 mg/L alum + 2 mg/L CTI TL	629
100 mg/L ferric sulfate	167
100 mg/L ferric sulfate + 1 mg/L CTI TL	172
250 mg/L ferric sulfate	417
250 mg/L ferric sulfate+ 1 mg/L CTI TL	422
500 mg/L ferric sulfate	833

4.6.3 Comparison of Alum and Ferric Sulfate as a Coagulant

Figure 41 compares the coagulation-flocculation processes using alum (left) and ferric sulfate (right) as a coagulant. The ferric sulfate was an orange colour which can ultimately affect the colour of sludge produced. The treated water was a slightly bright yellow colour which was resulted from the ferric sulfate. Alum is colorless, which doesn't affect the colour of treated water and sludge. Therefore taking into consideration colour removal, alum is better than ferric sulfate when higher doses are applied during the coagulation-flocculation process.

Figure 41: Comparison of the coagulation-flocculation processes process using alum and ferric sulfate as a coagulant
(left: 250 mg/L alum + 5 mg/L CTI TL; right: 250 mg/L ferric sulfate + 1 mg/L CTI TL)

6.2.4 Treatment Options for Industry Application

Taking into consideration treatment performance and cost, 10 mg/L of cationic polymer CTI TL with 100 mg/L of metallic ion coagulant alum is a cost-effective option. The polymer dose can be adjusted according to actual conditions and requirements. 5 mg/L of CTI TL with 250 mg/L alum is an option for better NAs removal of approximately 39%. The main advantages of cationic polymers combined with ion coagulants are: to reduce the dosage of coagulants; to produce less sludge; to decrease alkalinity consumption. The pH is not depressed as much as well, which helps to keep coagulation efficiency (Crittenden 2005). The low pH may also cause corrosion problems in the water and wastewater treatment plant.

The industrial application options are also dependent on combination of the treatment processes applied. Cationic polymer as a primary coagulant would be an alternative, if coagulation-flocculation followed by a filtration process because of the lower coagulant dose and filtration assistance. In this project, it is objective to evaluate different coagulants for OSPW treatment and to provide various treatment options for the industry.

Various coagulant doses were selected in the references of wastewater treatment research. McTernan et al. (1987) conducted coagulant screening studies of steam drive tar sand process water. 1000 mg/L of alum, 350 mg/L of ferric chloride and 1000 mg/L of lime were studied in their research. The doses of alum and ferric chloride were selected ranging from 800 mg/L to 2500 mg/L in Zhu's thesis work on coagulation-flocculation treatment of swine liquid manure (Zhu 2003). The coagulant dose was selected depending on the original water quality. 100 mg/L of alum is a relatively low dosage compared to other research work in wastewater treatment.

4.6.5 Factors Affecting Treatment

4.6.5.1 Initial pH of OSPW

The initial pH of the OSPW was adjusted to pH = 6.5 using 2% hydrochloric acid. The comparison of the TOC removal ratios from OSPW after the coagulation-flocculation treatments at natural pH and pH = 6.5 is shown in Figure 42. The TOC, turbidity, sludge volume and conductivity analyses are presented in Table 22. TSS and TDS analyses are shown in Table 23. Ions and elements analyses are shown in Table 24, and alkalinity analyses are shown in Table 25.

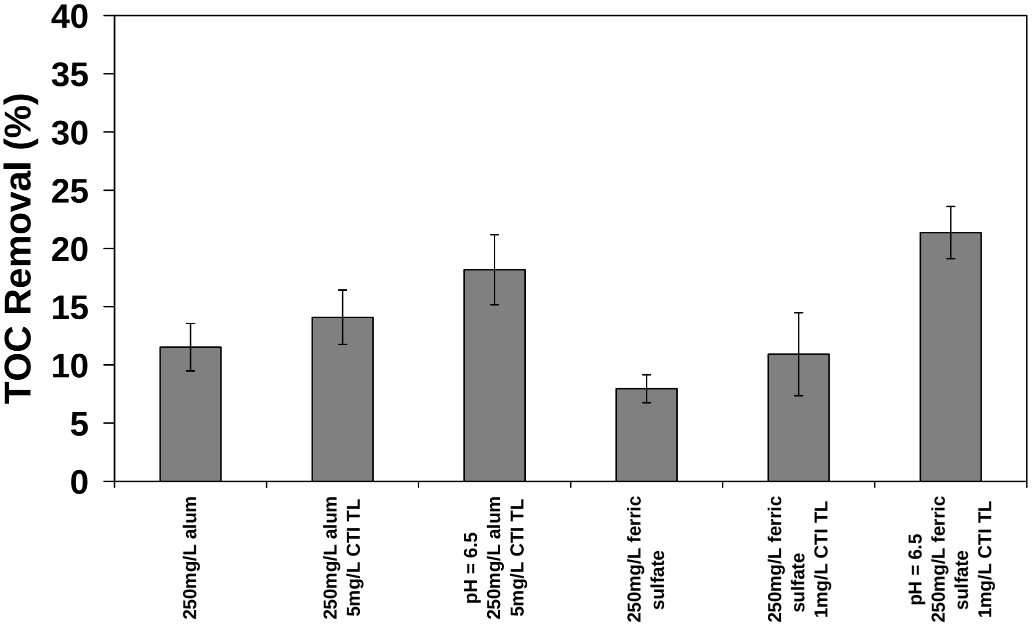


Figure 42: Comparison of TOC removal ratios after treatments at natural pH (8.1-8.2) and adjusted pH (6.5)
(initial TOC: 48.3 mg/L, SD = 1.7; temperature: 20±1 °C)

Table 22: Properties of the OSPW before and after treatments at natural pH and pH = 6.5

Treatment options	pH	TOC (mg/L)	TOC removal (%)	Turbidity (NTU)	Turbidity removal (%)	Sludge Volume (cm^3/L water)	Conductivity (µS/cm)
Raw OSPW	8.1-8.2	48.34±1.70	--	188±5.73	--	--	3870
Raw OSPW, pH=6.5	6.5	46.00-48.10	--	194	--	--	4020
250 mg/L alum + 5 mg/L CTI TL	7.0	42.22±1.13	14.09±2.34	2.10±0.61	98.89±0.33	48	3795
250 mg/L alum + 5 mg/L CTI TL, pH=6.5	6.5	38.50±1.41	18.17±3.01	2.42±0.33	98.75±0.17	54	4000
250 mg/L ferric sulfate + 1 mg/L CTI TL	7.0	42.22±1.13	14.09±2.34	2.10±0.61	98.89±0.33	24	3870
250 mg/L ferric sulfate + 1 mg/L CTI TL, pH=6.5	6.5	37.00±1.05	21.36±2.24	2.82±0.46	98.55±0.24	36	4020

Table 23: TSS and TDS analyses before and after treatments at natural pH and pH = 6.5
(5 replicates)

Treatment options	TSS				TDS			
	Value (mg/L)	Ave. (mg/L)	Std. deviation	removal (%)	Value (mg/L)	Ave. (mg/L)	Std. Deviation	removal (%)
Raw OSPW	67-141	97	23	--	2392-2524	2477	48.3	--
250 mg/L alum + 5 mg/L CTI TL	0.2-1.6	1.0	0.6	99.0	2421-2559	2462	56.3	0.61
250 mg/L alum + 5 mg/L CTI TL, pH=6.5	2.2-3.4	2.8	0.8	97.1	2472-2479	2476	5.2	0.04
250 mg/L ferric sulfate+ 1 mg/L CTI TL	0.2-2.6	1.0	1.0	99.0	2439-2460	2452	9.0	1.01
250 mg/L ferric sulfate + 1 mg/L CTI TL, pH=6.5	1.6-4.4	3.3	1.5	96.6	2447-2464	2455	8.7	0.89

Table 24: Ions and elements analyses before and after treatments at the natural pH and pH = 6.5 (duplicates)

Treatment options	Aluminum (mg/L)	Iron (mg/L)	Sulfate (mg/L)	Fluoride (mg/L)	Silicon (mg/L)	Vanadium (mg/L)	Barium (mg/L)
Raw OSPW	8.48-10.51	3.01-3.25	506-520	2.63-2.68	15.24-19.04	0.017-0.019	0.329-0.345
Raw OSPW, pH=6.5	8.66	2.68	500	2.59	15.69	0.018	0.342
250 mg/L alum + 5 mg/L CTI TL	0.58-0.67	0.30-0.39	634-640	1.26-1.29	2.54-2.63	0.005	0.127-0.129
250 mg/L alum + 5 mg/L CTI TL, pH=6.5	1.41-1.66	0.49-0.50	583-625	1.02-1.42	2.51-3.33	0.007	0.171-0.172
250 mg/L ferric sulfate+ 1 mg/L CTI TL	0.19-0.352	1.16-1.46	633-635	2.60-2.63	2.10-2.26	0.004	0.128-0.201
250 mg/L ferric sulfate+ 1 mg/L CTI TL, pH=6.5	0.38-0.04	2.39-2.98	625-639	2.54-2.55	2.17-3.04	0.005	0.124-0.166

Table 25: Alkalinity of the OSPW before and after treatment at natural pH and pH = 6.5

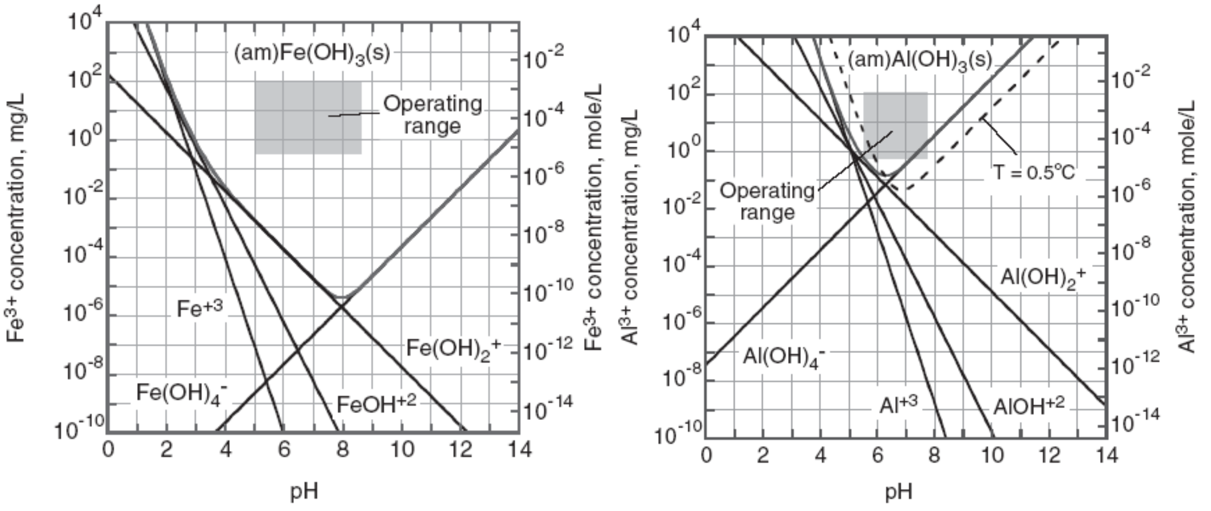
Treatment options	Carbonate alkalinity as $CaCO_3$ (mg/L)	Bicarbonate alkalinity as $CaCO_3$ (mg/L)	Alkalinity as $CaCO_3$ (mg/L)
OSPW	0	624	624
OSPW, pH=6.5	0	398	398
250 mg/L alum + 5 mg/L CTI TL	0	472	472
250 mg/L alum + 5 mg/L CTI TL, pH=6.5	0	285	285
250 mg/L ferric sulfate+ 1 mg/L CTI TL	0	488	488
250 mg/L ferric sulfate+ 1 mg/L CTI TL, pH=6.5	0	278	278

Based on the above analysis, the TOC removal ratio increased significantly when the initial pH of the OSPW was adjusted from the natural pH (8.1~8.2) to pH = 6.5. At pH = 6.5, the TOC removal ratio increased from 14% to 18% when 250 mg/L of alum and 5 mg/L of CTI TL were applied. The TOC removal ratio increased from 11% to 21% when 250 mg/L of ferric sulfate and 1 mg/L of CTI TL were applied. TSS and TDS removal ratios slightly decreased when the initial pH was adjusted to 6.5, but not by very much. Residual ions and elements were not depended on the initial pH of the OSPW. pH is a factor affecting alkalinity. Since the initial pH of the OSPW was less than 8.3, no carbonates had been recorded. The alkalinity decreased when the initial pH of the OSPW was adjusted to 6.5.

The pH affects the coagulant performance because of the solubility of the metal hydroxide precipitate. The most commonly used pH range during coagulation in the water treatment was between 5.5 and 8. The solubility of the metal hydroxide precipitate must be considered to maximize coagulant performance and minimize the amounts of residuals in treated water (AWWA 1999). The boxes shown in Figure 43 (a) and (b) correspond to the operating pH and dosage ranges normally used in water treatment when alum and iron coagulants are applied (Crittenden 2005). Approximately, aluminum hydroxide precipitates at a pH range of 5.5 to 7.7 at 25 °C, and iron precipitates at a wider pH range of 5 to 8.5. Based on all the samples used in this project, the initial pH of the OSPW was between 7.7 to 8.8. The pH of the OSPW decreased to 7.0 (see Table 22) which is in the precipitation range when 250 mg/L of coagulant (alum or ferric sulfate) was added. When the initial pH of the OSPW was adjusted to 6.5, the pH of the OSPW after treatment using 250 mg/L of coagulant (alum or ferric sulfate) was stable at 6.5 (see Table

22), which is close to the minimum solubility pH (approximately 6.3 as shown in Figure 43 (b)) of aluminum hydroxide precipitate at 25 °C. pH of 6.5 contributed to a better coagulant performance for alum. According to the literature, pH between 5 and 6 is the range where hydrolyzing metal salt coagulants frequently appear to be most efficient (AWWA 1999).

Although lower pH can increase TOC removal ratios, it is more complicated and costly for the industry to adjust the pH of a large volume of OSPW before the coagulation-flocculation process. Therefore, it is recommended to treat the OSPW at natural pH.



(a)　　(b)

Figure 43: Solubility diagram for Al(Ш) (a) and Fe(Ш) (b) at 25 °C
(Only the mononuclear species have been plotted)
(typical operating ranges for aluminum and iron are indicated by shade boxes; adapted from (Crittenden 2005).)

4.6.5.2 Raw water quality

The minimum and maximum TOC removal ratios obtained in the entire research period have been summarized in Table 26.

Table 26: Summary for the range of historical TOC removal ratios and $\frac{\Delta TOC\ (mg/L)}{\Delta Coagulant\ dose\ (mg/L)}$ under the best jar-test conditions based on all the experiments in the project

Treatment options	Historical min. ~ max. TOC removal (%)	Historical $\frac{\Delta TOC\ (mg/L)}{\Delta Coagulant\ dose\ (mg/L)}$
Raw OSPW	--	--
100 mg/L alum	8.25 ~ 15.67	0.048 ~ 0.100
100 mg/L alum + 10 mg/L CTI TL	12.61 ~ 20.05	0.061 ~ 0.128
250 mg/L alum	9.76 ~ 24.37	0.047 ~ 0.158
250 mg/L alum + 5 mg/L CTI TL	14.09 ~ 26.03	0.068 ~ 0.169
500 mg/L alum	14.36 ~ 22.69	0.069 ~ 0.133
500 mg/L alum + 2 mg/L CTI TL	16.71 ~ 25.03	0.081 ~ 0.124
100 mg/L ferric sulfate	5.09 ~ 7.38	0.237 ~ 0.349
100 mg/L ferric sulfate + 1 mg/L CTI TL	6.85 ~ 11.49	0.331 ~ 0.543
250 mg/L ferric sulfate	7.95 ~ 12.19	0.384 ~ 0.567
250 mg/L ferric sulfate + 1 mg/L CTI TL	10.92 ~ 18.09	0.527 ~ 0.856
500 mg/L ferric sulfate	18.43 ~ 33.87	0.089 ~ 0.191

TOC removal ratios were not consistent at each experiment. It varied depending on the water quality of raw OSPW, experimental conditions, operation consistency and TOC analyzer accuracy. Higher TOC removal ratio is commonly associated with higher initial TOC value in the raw OSPW.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

In this project, physico-chemical treatment (coagulation-flocculation) was investigated on oil sands process-affected water from Syncrude's West Inpit Pond (WIP) located in Fort McMurray, Alberta, Canada. A series of jar-test experiments for the coagulation-flocculation process optimization, chemical selection and treatment performance evaluation were carried out in the Environmental and Geochemistry Laboratories located in the Natural Resources Engineering Facility (NREF) at the University of Alberta. The following conclusions are drawn from this study:

- OSPW characteristics vary from sample to sample, especially the turbidity, TSS, TDS, TOC, conductivity and pH.
- Alum and ferric sulfate were investigated as inorganic coagulants for the OSPW treatment. TOC and turbidity removal ratios increased when the dosage of coagulant was increased from 20 to 600 mg/L. Considering industry applicability, coagulant dosages for alum and ferric sulfate were studied up to 500 mg/L, and an optimum dose was not observed in this concentration range.
- Cationic, anionic and non-ionic polymers were investigated to assist the coagulant during the coagulation-flocculation process. The cationic polymer CTI TL was chosen as a coagulant aid which contributed to TOC and turbidity removal, reduced the coagulant dosage in order to produce less sludge, decreased alkalinity consumption to keep the coagulation efficiency.
- The cationic polymer CTI TL was also investigated as a primary coagulant for OSPW treatment. It was not as effective as metal-ion coagulants, but it

produced less and denser sludge due to its effectiveness at low dosages. Polymers used as a primary coagulant would be an alternative, if the pretreatment is objected to produce small, high density aggregates for direct filtration (AWWA 1999).

- The coagulation-flocculation processes were optimized at certain doses of coagulants: 100, 250, and 500 mg/L, respectively. pH decreased after the addition of coagulants and the final pH after treatment depended on the amount of coagulant applied. The sludge volume produced depended on the coagulant type and dosage used. Based on observation, alum produced more sludge than ferric sulfate.
- TSS can be removed by more than 96% after the coagulation-flocculation process. However, only a small amount of TDS was removed during the coagulation-flocculation process.
- Aluminum and iron within coagulants can be removed completely from the supernatant of OSPW into sludge after treatment. Only some sulfate ions within the coagulant can be removed, and the concentration of sulfate in OSPW increased after the addition of coagulants (aluminum sulfate or ferric sulfate). The concentrations of some elements such as fluoride, silicon, vanadium and barium decreased significantly after treatment.
- The bicarbonate concentration and alkalinity decreased when the coagulant dose was increased during the treatment.
- NAs can be removed 25 to 40% after the coagulation-flocculation process based on different treatment options. More than 79% of mono-oxidized compounds in NAs can be removed after treatment.
- Alum is good for TOC, turbidity and color removals at lower dose (less than 250 mg/L) treatment combined with polymer; and ferric sulfate is good for

higher dose treatment (500 mg/L) without polymers.

- pH and raw OSPW water quality are the factors that affect treatment performance. TOC removal ratio increased when the initial pH of OSPW was adjusted to lower pH (6.5). The TOC removal ratio was not consistent with each experiment and varied with the water quality of OSPW, experimental conditions, operation consistency and TOC analyzer accuracy.
- Based on experimental observation, results and literatures, the possible mechanisms of the coagulation-flocculation process are charge neutralization, interparticle bridging and sweep floc. The coagulants with positive charges neutralize negative charges on particles' surface to encourage the initial aggregation of colloids. Combined with polymer, particles bridge together and grow large for gravity settling. Sweep floc happened when the precipitates collide with and drag colloids down with them.

The following recommendations need to be considered for further investigations:

- Because of the difficulty to pre-mix the sample evenly before transferring it into each jar, therefore designing a big sample mixing container combined with a constantly sampling pump is suggested.
- Sludge analysis is needed to understand the sludge composition and to verify the removals of ions and elements from the supernatant of OSPW to the sludge.
- In order to figure out the removed TOC during the coagulation-flocculation process mainly from the suspended or dissolved organic carbons (DOC), the DOC in OSPW should be monitored before and after treatment.
- In order to determine the predominant mechanisms of the

coagulation-flocculation process, surface area and zeta potential are recommended to be measured.

- It is always good to test more coagulants and new products for OSPW treatment in order to find out the most efficient, economical and environment-friendly products. Synthesized polymer may be more efficient for specific water sources. On the other hand, it could cost more than hydrolyzing metal salts. Prehydrolyzed metal salts are the coagulants neutralized with base when they are manufactured, which avoid the consumption of alkalinity during the hydrolysis reaction. In addition, Polymeric coagulant from natural organic compounds, such as chitin from crustacean shells, may be an option for OSPW as well. Its main advantages are low cost and biodegradable. However, it may not be as efficient as commercial coagulants (AWWA 1999).
- A pilot plant study is recommended after the bench-scale investigation.

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APPENDICES

Appendix A: Sample Calculation

Sample calculation of the theoretical value of sulfate concentration

Case I: 250 mg/L of alum (aluminum sulfate) was added into the OSPW sample whose original sulfate concentration was 513 mg/L, the theoretical increase of sulfate was calculated as follow:

Increase of SO_4^{2-} concentration =

$$\frac{\text{concentration of } Al_2(SO_4)_3 \text{ added}}{\text{molecular weight of } Al_2(SO_4)_3} \times 3 \times \text{molecular weight of } SO_4^{2-} \quad \text{(A-1)}$$

Increase of SO_4^{2-} concentration after addition of 250 mg/L of $Al_2(SO_4)_3$ =

$$\frac{250\ mg/L}{342.13} \times 3 \times 96.056 \ = 211 \text{ mg/L}$$

Case Π: 250 mg/L of ferric sulfate was added into the OSPW sample whose original sulfate concentration was 513 mg/L, the theoretical increase of sulfate was calculated as follow:

Increase of SO_4^{2-} concentration =

$$\frac{\text{concentration of } Fe_2(SO_4)_3 \text{ added}}{\text{molecular weight of } Fe_2(SO_4)_3} \times 3 \times \text{molecular weight of } SO_4^{2-} \quad \text{(A-2)}$$

Increase of SO_4^{2-} concentration after addition of 250 mg/L of $Fe_2(SO_4)_3$ =

$$\frac{250\ mg/L}{399.862} \times 3 \times 96.056 \ = 180 \text{ mg/L}$$

Mass balance calculations on aluminum mass in supernatant and sludge

Case I: Verify the aluminum concentration in the sludge after jar test for coagulation-flocculation process based on mass balance. For example, the initial aluminum concentration in OSPW was 8.24 mg/L. Certain amounts of alum (aluminum sulfate) and cationic polymer CTI TL were added into a 2-liter jar during the coagulation-flocculation process to achieve the dosages as 100 mg/L of alum and 10 mg/L of CTI TL. After the coagulation-flocculation and sedimentation, the aluminum concentration in the supernatant was 0.36 mg/L and the sludge volume was approximately 30 cm^3 per liter of water. Calculate the aluminum concentration in the sludge after jar test based on mass balance.

Mass balance in a 2-liter jar:

Aluminum mass before jar test = aluminum mass after jar test

Aluminum mass before jar test:

1) Initial aluminum mass in 2 liter raw OSPW = 8.24 mg/L × 2L = 16.48 mg
2) Addition of the aluminum mass = $100 \text{ mg/L} \times \frac{2Al}{Al_2(SO_4)_3} \times 2 \text{ L}$

$$= 100 \text{ mg/L} \times \frac{2 \times 27}{342} \times 2 \text{ L} = 31.58 \text{ mg}$$

Total aluminum mass before or during 2-L jar test = 16.48 + 31.58 = 48.06 mg

Aluminum mass after jar test:

1) Aluminum mass in the supernatant = 0.36 mg/L × 2 L = 0.78 mg
2) Assume the aluminum concentration in the sludge is X mg/L,

Aluminum mass in the sludge = X mg/L × 30 cm^3/L × 2 L × $\frac{1L}{1000cm^3}$

Mass balance: 48.06 mg = X mg/L × 30 cm^3/L × 2 L × $\frac{1L}{1000cm^3}$

So, X = 801 mg/L

Sample calculation for chemical cost

Case I: 100 mg/L of alum combined with 10 mg/L of CTI TL for 2 liter of OSPW treatment.

Aluminum sulfate (48.5%): $0.60/kg or $163.80/drum (273kg);

CTI TL (pure): $5.25/kg or $1071/drum (204 kg)

For one mega liter of OSPW,

Aluminum sulfate needed: $\frac{100 mg/L}{10^6 mg/kg} \times 10^6 L =$ 100 kg

Aluminum sulfate (48.5%) needed: $\frac{100 kg}{48.5\%} =$ 206.19 kg

Cost of aluminum sulfate: $163.80 \times \frac{206.19 kg}{273 kg} = \$123.71$

CTI TL needed: $\frac{10 mg/L}{10^6 mg/kg} \times 10^6 L =$ 10 kg

Cost of CTI TL: $1071 \times \frac{10 kg}{204 kg} = \$52.5$

So, the total cost of chemicals are: $123.71 + $52.5 = $176.21

Appendix B: Statistic Analysis

1. Q-test

Q-test is used for identification or rejection of statistical outliers in a set of data. To arrange the data in order of increasing values and calculate Q as defined Equation (B-1):

$$Q = \frac{|outlier - value\ closest\ to\ the\ outlier|}{|highest\ value - lowest\ value|} \qquad \text{(B-1)}$$

Table B-1: Critical Q values at 95% confidence

Number of replicates:	3	4	5	6	7	8	9	10
$Q_{95\%}$	0.970	0.829	0.710	0.625	0.568	0.526	0.493	0.466

If $Q_{calculated} > Q_{critical}$, the outlier can be discarded with 95% confidence.

For example, the TOC values of OSPW after 5 replicate jar tests were 43.1, 45.4, 40.7, 43.2 and 44.1, respectively. In order to identify if 40.7 is an outlier in the data set, arrange the data in order of increasing values and calculate Q as defined Equation (B-1).

Arranged data in increasing order: 40.7, 43.1, 43.2, 44.1, 45.4

$$Q = \frac{|40.7 - 43.1|}{|45.4 - 40.7|} = 0.5106$$

From Table B-1, $Q_{critical}$ is 0.710 at 95% confidence.

Since $Q_{calculated} > Q_{critical}$, 40.7 is not an outlier in this data set with 95% confidence.

2. Variance Test: ANNOVA

Table B-2: ANOVA analysis of TOC removal ratios (single factor, α = 0.05) for alum dose measurement from 100 to 500 mg/L (triplicates)

Summary

Groups	Count	Sum	Average	Variance
100	3	0.209366	0.069789	0.000487
250	3	0.301487	0.100496	0.000139
300	3	0.381473	0.127158	0.00228
400	3	0.405401	0.135134	0.001019
500	3	0.680738	0.226913	0.001347

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.041713	4	0.010428	9.890712	0.001669	3.47805
Within Groups	0.010544	10	0.001054			
Total	0.052257	14				

$F > F_{crit}$, reject the null hypothesis. So, at lease one of the means is different.

Table B-3: ANOVA analysis (single factor, α = 0.05) of TOC removal ratios for ferric sulfate dose measurement from 100 to 500 mg/L (triplicates)

Summary

Groups	Count	Sum	Average	Variance
100	3	0.152688	0.050896	0.001065
200	3	0.352688	0.117563	0.006032
250	3	0.365591	0.121864	0.002041
300	3	0.56129	0.187097	0.005915
400	3	0.836559	0.278853	0.008557
500	3	0.952688	0.317563	0.000788

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.158057	5	0.031611	7.773602	0.001802	3.105875
Within Groups	0.048798	12	0.004066			
Total	0.206854	17				

$F > F_{crit}$, reject the null hypothesis. So, at lease one of the means is different.

Table B-4: ANOVA analysis (single factor, α = 0.05) of TOC removal ratios for different treatment options at the best jar-test conditions
(3 to 5 replicates)

Summary

Groups	Count	Sum	Average	Variance
100 mg/L alum	5	0.474144	0.094829	0.000269
100 mg/L alum + 10 mg/L CTI TL	4	0.504252	0.126063	0.003824
100 mg/L ferric sulfate	4	0.276718	0.069179	0.000145
100 mg/L ferric sulfate + 1 mg/L CTI TL	5	0.28798	0.057596	0.00118
250 mg/L alum	4	0.460814	0.115203	0.000418
250 mg/L alum + 5 mg/L CTI TL	5	0.633418	0.126684	0.000546
250 mg/L ferric sulfate	4	0.355321	0.08883	0.000144
250 mg/L ferric sulfate + 1 mg/L CTI TL	5	0.521719	0.104344	0.001269
500 mg/L alum	3	0.430935	0.143645	0.000184
500 mg/L alum + 2 mg/L CTI TL	5	0.896116	0.179223	0.000478
500 mg/L ferric sulfate	3	0.552976	0.184325	0.000177

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.068888	10	0.006889	8.469716	6.78E-07	2.106054
Within Groups	0.029281	36	0.000813			
Total	0.098169	46				

$F > F_{crit}$, reject the null hypothesis. So, at lease one of the means is different.

3. t-Test

The t-test is used to assess whether the means of two groups are statistically different from each other.

For example, t-test analysis was used to assess whether the means of TOC removals in OSPW treated using 500 mg/L of ferric sulfate without rapid mixing and with 60s rapid mixing are significant different.

TOC removal ratios (triplicates) without rapid mixing were: 34.99%, 34.10%, 32.50%

TOC removal ratios (triplicates) with 60 s rapid mixing were: 34.81%, 35.88%, 33.57%

Table B-5: t-Test (Microsoft Excel: paired two sample for means) for TOC removal ratios of the OSPW treated using 500 mg/L of ferric sulfate between without rapid mixing and with 60 s rapid mixing.

	Variable 1	Variable 2
Mean	0.347533	0.338633
Variance	0.000134	0.000159
Observations	3	3
Pearson Correlation	0.666292	
Hypothesized Mean Difference	0	
df	2	
t Stat	1.553455	
P(T<=t) one-tail	0.130265	
t Critical one-tail	2.919986	
P(T<=t) two-tail	0.26053	
t Critical two-tail	4.302653	

Since $t_{stat} < t_{critical}$, there is no significant difference between the means of TOC removal ratios in OSPW treated using 500 mg/L of ferric sulfate without rapid mixing and with 60 s rapid mixing.