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Performance Characterization of Coagulation Pretreatment for Two Industrial Effluents

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Abstract

In this work, performances of coagulation and flocculation were tested for two different industrial effluents. Coagulation-Flocculation and activated carbon adsorption were applied for the remediation of oil sands process-affected water (OSPW), generated from oil sands operations in Alberta, Canada. OSPW is a complex mixture of suspended solids, various suspended and dissolved organic compounds. Alum and natural coagulant *Opuntia ficus-indica* (OFI) were used as the coagulants, and the process was optimized to improve the removal of turbidity and dissolved organic carbon (DOC). The maximum removal of 98% and 63% in turbidity and DOC from OSPW, respectively occurred at pH=6.32, with an alum dosage of 190.44 mg/L and activated carbon at 0.28 g/L. Whereas a comparable removal of turbidity and DOC from OSPW occurred at similar pH and carbon loading at a much higher dosage of 780 mg/L for natural coagulant. Adsorption on polymer seems to be the mechanism of removal of DOC from OSPW during coagulation. Natural coagulant increases the DOC of water due to dissolution of sugars and carbohydrates from natural coagulant, but these compounds are highly biodegradable and should not be a problem when treated water is disposed of in natural environment.

Large volumes of bilge water are generated by the ships across the world. Due to the abundance of saline water on-board, performance of sodium chloride/ calcium silicate as a coagulant for oily waste water was determined and compared with that of alum/ calcium carbonate. Almost 93% of the oil was recovered at the top and bottom when 100 mg alum/L and 1 g calcium carbonate/L was used, and a very clear effluent was produced in the middle section of the treatment vessel. 5 wt% of NaCl was effective in coagulating the bilge water, but at a much higher dosage than alum.

Keywords

Oil sands process-affected water (OSPW), Bilge water, Coagulation-Flocculation, Natural coagulant, Adsorption

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List of Acronyms and Symbols

BOD	Biochemical Oxygen Demand
CCD	Central Composite Design
CFS	Coagulation-Flocculation-Sedimentation
COD	Chemical Oxygen Demand
DOC	Dissolved Organic Carbon
EPA	The United States Environmental Protection Agency
FT-IR	Fourier Transform Infrared
GAC	Granular Activated Carbon
HEM	n-Hexane Extractable Material
NAs	Naphthenic Acids
NC	Natural Coagulant
NTU	Nephelometric Turbidity Unit
O&G	Oil and Grease
OFI	<i>Opuntia ficus-indica</i>
OSPW	Oil Sands Process-affected Water
RSM	Response Surface Methodology
SGT-HEM	Silica Gel Treated Hexane Extractable Material
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
b	Sips adsorption constant
C_e	Equilibrium concentration of adsorbate in solution (mg/L)
C_o	Initial concentration of adsorbate in solution (mg/L)
K_f	Freundlich adsorption constant
K_L	Langmuir adsorption constant
n	Freundlich exponent
pH_{pzc}	pH value at the point of zero charge
q_e	Adsorption capacity at equilibrium (mg/g)
q_m	Maximum adsorption capacity (mg/g)

Chapter 1

1 INTRODUCTION

This thesis deals with the treatment of two large volume wastewater effluents generated in two sectors: oil sands process-affected water and bilge water generated in marine industry and naval ships. A brief introduction to the two effluents is provided below.

1.1 Oil Sands Process-affected Water (OSPW)

Water plays a critical role in the development of oil sands. Net fresh water use in oil sands production in 2010 averaged about 3 barrels of water per barrel of oil produced by mining operations. Oil sands process water and tailings contain a significant amount of organics, i.e., naphthenic acids (NAs) 50-100 mg/L, and bitumen and aromatic hydrocarbons 25-7500 mg/L (Allen, 2008a; Rogers et al., 2002). Among the various organics present in process water and tailings, NAs are the major group of organics in terms of both concentration and toxicity. NAs are complex mixtures of predominantly alkyl-substituted cycloaliphatic carboxylic acids (containing cyclopentane and cyclohexane rings) and small amounts of acyclic acids (Scott et al., 2005). The NAs are corrosive to equipment during the extraction process from oil sands. They become concentrated in the tailings pond water, and a major source of toxicity in tailings pond water has been linked to naphthenic acids.

Therefore, treatment of the process water is becoming a critical issue and an expensive task for the oil sands industry to sustain oil production and protect freshwater resources. For example, Syncrude employs the centrifuging technology for remediating mature fine tailings (MFT) at an estimated cost in the range of \$2.10 - \$2.75/m³ of water, which could cost the company as high as \$1.3 - \$1.7 billion for centrifuging treatment of its MFT inventory (approx. 620 million m³) in the end pit lakes.

Many technologies for oil sands process water treatment have been proposed and studied, including adsorption, membrane processes, biological treatment, advanced oxidation and treatment wetlands. Among these technologies, adsorption has shown promise for

industrial applications as it is a well established and scalable technology, effective, and relatively inexpensive (Adhoum, Monser, Bellakhal, & Belgaied, 2004). However, due to the presence of high concentration of suspended particles, pretreatment of OSPW is required to remove majority of the suspended and colloidal particles before adsorption can be used to remove the dissolved organics. The objective of this thesis is to evaluate a series of treatment technologies involving coagulation and flocculation and adsorption for the treatment of real OSPW.

1.2 Bilge Water

Bilge is the lowest compartment of a ship where two sides of the ship meet where bilge water is accumulated. Bilge water is a mixture of fresh water, sea water, free oil and stable oil-in-water emulsion, sludge, chemicals and particulates. More specifically, bilge water contains oil and grease, detergents, aluminum shavings, plastic shreds/shards, dissolved heavy metals and suspended solids. It also contains organic additives such as fatty acid and amide mixture, and petroleum sulfonate. These components form chemical oxygen demand (COD) when the bilge water is discharged in the environment. In addition, heavy metals dissolved from rust in tanks and process piping can be another serious problem causing toxicity in biota. Sea water and fresh water in the bilge water is due to leakage in the system, from various machineries, propulsion system, over flowing of tanks and even due to accidental spills. Oil finds its way to the bilge well mainly from the fuel oil purifiers, leakage in fuel line and oil spills. Navy ships produce millions of gallons of bilge water each year, comprising one of the Navy's largest waste streams. Regulated by MARPOL 73/78 bilge water needs to be treated before discharging it to the open sea (International Maritime Organization, 1991).

Many solutions exist for treating bilge water (Asselin et al., 2008; Benito et al., 2007; Sun et al., 2009, 2010; Tipton, 2005), however, almost all of them use some form of gravity separation and froth flotation for removal of oil from water, which have limitations such as (i) oil particles that are twenty micrometers or smaller do not get separated, (ii) variety of oily wastes in bilge water can limit removal efficiency, especially when very dense and highly viscous oils such as bunker oil are present. Electrochemical methods for froth flotation are effective but expensive (Holt, Barton, &

Mitchell, 2005). Bioremediation of oily-water is economically viable, but an on-board application is impractical due to requirement of large holding time. The objective of present work is to evaluate the coagulation performance inexpensive common salt to remove suspended oil. This will be a cost-effective solution for bilge water as sodium chloride is abundant in the sea.

1.3 Thesis Organization

Chapter 1 describes the background of the research problems and an overview of the possible treatment processes for organic and inorganic compounds removal from OSPW and bilge water. The literature review, the objectives and scope of the research are presented in Chapter 2.

Chapter 3 presents the application of the coagulation-flocculation-sedimentation process as a pretreatment of the removal of the suspended solids and partial removal of organic compounds from OSPW using different coagulants. The performance of the combined process includes acidification and adsorption are also presented.

In Chapter 4, the treatment processes for oil removal from bilge water are discussed using coagulation-flocculation-sedimentation process as the pretreatment. The feasibility of using sodium chloride as coagulant was determined and its removal efficiency were compared with conventional coagulant alum.

In Chapter 5, conclusions of the research conducted and recommendations for the future work are presented.

Some of the experimental methodologies and supplementary graphs and tables to support the obtained results are presented in the Appendices of the Thesis.

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Chapter 2

2 Literature Review and Research Objectives

Oil sands, or more technically bituminous sands, are a type of unconventional petroleum deposit. Oil sands are either loose sands or partially consolidated sandstone containing a naturally occurring mixture of sand, clay, water and bitumen (Bitumina, 2016; Suryakanta, 2015). The oil sands deposits in Alberta, Canada, are estimated to be the third largest oil reserves in the world after Venezuela and Saudi Arabia (GEAB, 2016). They are mainly located in Cold Lake, Athabasca, and Peace River. It is estimated that about 172 billion barrels of oil can be produced from the above oil sands deposit sites (U.S. EIA, 2016). In 2006, oil sands production reached 1.126 million barrels per day; by 2020 oil production is expected to grow to 3 million barrels per day (Oil Sands Discovery Centre, 2016).

As a vital role in Canadian economy, oil sand development has numerous positive socio-economic impacts on the communities, including employment, economic benefits, economic stability, government revenue, and investment in research and development. (National Energy Board, 2006). Although economic potential of Canada's oil sands is undisputed, the large scale of its development has considerable environmental impacts on ecological systems. These include water consumption and conservation for oil sands operation; the impacts on surface water and groundwater quality; greenhouse gas (GHG) emissions and impacts on air quality; land disturbance; waste management; and the impacts on wildlife. To minimize these environmental impacts, solutions are needed to ensure sustainable development of oil sands reserves.

Unlike conventional crude oil, oil sands are comprised of 80-87 wt % of inorganic materials (sand, silt, and clay), 6-16 wt % of bitumen, and 1-8 wt % of water (Kannel & Gan, 2012; Liu, Xu, & Masliyah, 2015). Bitumen in Alberta's oil sands is a thick, tar-like viscous mixture of hydrocarbons that contains high levels of sulfur and nitrogen compounds. Some bitumen is found within 70 meters (200 feet) of the surface, but the majority is located deeper underground (Dusseault, 2001). Bitumen must be heated or diluted with lighter hydrocarbons to flow through a well. Furthermore, bitumen must also

be upgraded into crude oil which can be further refined to produce gasoline, aviation fuel, or other products (Government of Alberta, 1997). The Clark hot water process is used for bitumen extraction from the oil sands at alkaline pH ~8 (Kannel & Gan, 2012; Vincent V Rogers, Wickstrom, Liber, & MacKinnon, 2002). During the extraction process, sodium hydroxide (NaOH) solution at 80 °C is mixed with the oil sands resulting in the recovery of bitumen from the sands and clays (Allen, 2008a; Kannel & Gan, 2012).

Both mining and in situ operations use large volumes of water for extracting bitumen from the oil sands. Approximately 2 to 4.5 m³ of fresh water is withdrawn, primarily from the Athabasca river, to produce each m³ of synthetic crude oil (SCO) in a mining operation (Pembina Institute, 2006). As a result of the extraction process, approximately 4 m³ of the oil sands process-affected water (OSPW) is generated for each m³ of SCO. The OSPW contains water, sands, clay fines, silts, unrecoverable bitumen, heavy metals, and inorganic and organic compounds. Under the “zero discharge policy” imposed by provincial environmental legislation (Alberta Environmental Protection and Enhancement Act, 1993), the potentially toxic OSPW is not allowed to be released into ground or surface water, and must be managed by means of storing in tailings ponds. The approximate surface area of the tailings ponds now exceeds 70 km² (Allen, 2008b). The volume of OSPW in the tailings ponds in Athabasca region is estimated to reach more than 1 billion cubic meters by 2025 (Herman, Fedorak, MacKinnon, & Costerton, 1994). Despite some recycling (Suncor Energy Inc., 2009; Syncrude Canada Limited, 2015), almost all of the water withdrawn for oil sands operations ends up in tailings ponds. In 2007, six approved and operation oil sands mining projects are licensed to divert 414 million cubic meters of freshwater per year from the Athabasca river (Schindler, 2007). Although less than 3% of the annual river flow is currently taken from the Athabasca River, and the water use is reduced according to the sustainability reports written by mining companies, it is still of concern that the OSPW is accumulating in tailings ponds and waiting for treatment, raising the risk of affecting nearby waterways and aquatic environment.

2.1 OSPW Water Quality and Toxicity

Oil sands process-affected water is a complex mixture of water, sands, clay, silts, unrecoverable bitumen, heavy metals, and inorganic and organic compounds. The composition of OSPW varies with oil sands ore quality, source, extraction processes, and age, but generally it contains 70-80 wt % of water, 20-30 wt % of solids (i.e., sand, silt and clays) and 1-3 wt% of bitumen (Allen, 2008a).

2.1.1 Organic Compounds

Tailings pond water is like a soup with thousands of organic and inorganic compounds. The organic compounds detected in OSPW include residual bitumen, naphthenic acids (NAs), polycyclic aromatic hydrocarbons (PAHs), benzene, toluene, asphaltenes, phenols, creosols, humic and fulvic acids, and phthalates (Gulley, 1992; M. D. MacKinnon & Retallack, 1981; M MacKinnon & Sethi, 1993; Madill, Orzechowski, Chen, Brownlee, & Bunce, 2001; Vincent V Rogers, Liber, et al., 2002; Strosher & Peake, 1978) in a wide range of concentration, depending on the source of oil sands, extraction processes, and the age of tailings pond water.

Among the organic compounds detected in OSPW, the aromatic compounds are the toxicants of concern include PAHs, benzene, toluene, and phenols. The reported concentrations of benzene and toluene in Suncor process water are >0.6-6.3 and 1-3 mg/L, respectively (Gulley, 1992). These concentrations exceeded the levels for benzene and toluene in Canadian Council of Ministers of the Environment (CCME) guidelines for protection of aquatic life, which are 0.37 and 0.002 mg/L, respectively (CCME, 1999). Natural and biodegradation have caused total phenol concentrations in Mildred Lake Settling Basin (MLSB) to decline over time, ranging from 0.3 mg/L in 1981, to 0.15 mg/L in 1985, 0.02–0.04 mg/L in 1992, and 0.008 mg/L in 1998 (M. D. MacKinnon & Retallack, 1981; MD MacKinnon & Benson, 1985; Nelson, MacKinnon, & Gulley, 1993; V. V. Rogers, Wickstrom, Liber, & MacKinnon, 2002). Bitumen, measured as oil and grease was also detected in a wide range of concentrations.

Naphthenic acids (NAs) are a group of polar carboxylic acids naturally present in crude oil. The NAs in OSPW comprise of a mixture of alkyl-substituted cyclic and aliphatic

carboxylic acids and are removed from bitumen during the extraction process.

Concentrations of NAs range from 40 to 70 mg/L in tailings ponds, but can be as high as 130 mg/L in fresh tailings water (Holowenko, MacKinnon, & Fedorak, 2002; M. D. MacKinnon, 2004). Naphthenic acids are the main source of acute toxicity in OSPW and depending on their composition and age, can have toxic effects at relatively low concentrations. Although the concentration and acute toxicity of NAs have been shown to degrade naturally over time in tailings ponds and experimental pits, long residence time is required for degradation which may not be practical where the direct discharge of water is required (Allen, 2008a).

2.1.2 Inorganic Compounds

OSPW is moderately hard (15-25 mg/L Ca^{2+} , 5-10 mg/L Mg^{2+}) with pH in the range of 7.9-8.5 and a high alkalinity of 800-1000 mg/L HCO_3^- (Allen, 2008a). The total dissolved solids (TDS) concentration in tailings ponds is around 200-2500 mg/L and substantially higher than in the Athabasca River. The major ions of the dissolved solids are sodium (500-700 mg/L), bicarbonate (700-1000 mg/L), chloride (75-550 mg/L), and sulphate (200-300 mg/L). The concentration of these solids, as well as ammonia (4-14 mg/L), is significantly higher than in the Athabasca River (Vandermeulen & Hrudey, 1987). The high chemical and biochemical oxygen demands (COD & BOD) result in low dissolved oxygen concentration in the river. Trace metals such as aluminum, copper, zinc, nickel, or even some non-metals like arsenic, which are present in the oil sands, could also be released into OSPW during the extraction process.

2.1.3 Toxicity

Many toxicological studies have outlined the acute and chronic toxicity of OSPW. Various aquatic organisms, including *Salmo gairdneri* and *Pseudokirchneriella subcapitata* (formerly *Selenastrum capricornutum*), are adversely affected by unaged OSPW at environmentally relevant concentrations (M. D. MacKinnon & Boerger, 1986; Warith & Yong, 1994). Among the complex organic and inorganic components in OSPW, naphthenic acids (NAs), ranging in concentration from 40-120 mg/L in OSPW,

have been identified as the major contributor to OSPW toxicity (Dokholyan & Magomedov, 1983; M. D. MacKinnon & Boerger, 1986).

Due to complexity and variability of OSPW, the toxicity analysis of OSPW might not be accurate enough for inter-lab comparison. The toxicity of OSPW was investigated by exposing various organisms to the fractions of naphthenic acids isolated from OSPW (Frank et al., 2009) and individual naphthenic acids (Jones, Scarlett, West, & Rowland, 2011). Many studies with naphthenic acids have shown them to have inhibitory or toxic effects on a variety of organisms including plants, algae, fish, zooplankton, rats and luminescent bacteria (Table 2.1).

Table 2.1 Summary of toxicity studies with naphthenic acids

Organism	Reference	Comments
Aspen (<i>Populus tremuloides</i>)	(Kamaluddin & Zwiazek, 2002)	Aspen (<i>Populus tremuloides</i> Michx.) seedlings grew in culture containing 75, 150, or 300 mg/L naphthenic acids. Exposure of roots to NAs for 3–5 weeks significantly decreased root water flux, root respiration, leaf stomatal conductance, photosynthesis, chlorophyll concentration and leaf size.
Wistar rats	(Vincent V Rogers, Wickstrom, et al., 2002)	Adult female Wistar rats were given single dosages of naphthenic acids at either 3, 30, or 300 mg per kg body weight (mg/kg), while adult male rats received 300 mg/kg for 14 days. Acute effects including organ damage and increased organ weight were observed in the high-dose group of both sexes. In subchronic tests, naphthenic acids were administered to female Wistar rats at 0.6, 6, or 60 mg/kg, 5 days per week for 90 days. Results suggested that the liver was a potential target organ.

<p>Fish Fathead minnow <i>(Pimephales promelas)</i></p>	<p>(Kavanagh et al., 2012)</p>	<p>Fathead minnows (<i>Pimephales promelas</i>) exposed to a 10 mg/L naphthenic acid extract (NAE) for 21 days spawned fewer eggs and males had reduced expression of secondary sexual characteristics. Male fathead minnows exposed to a 5 mg/L NAE had lower plasma levels of 11-ketotestosterone whereas those exposed to a 10 mg/LNAE had lower concentrations of both testosterone and 11-ketotestosterone.</p>
<p>Microalgae <i>(Pseudokirchneriella subcapitata)</i></p>	<p>(Debenest, Turcotte, Gagné, Gagnon, & Blaise, 2012)</p>	<p>This study compared the toxicity of OSPW and oil sands lixiviate water (OSLW) with a baseline (oil sands exposed to water; OSW) on a microalga, <i>Pseudokirchneriella subcapitata</i>, at different concentrations (1.9, 5.5, 12.25, 25 and 37.5%, v/v). The toxicity of OSPW on cells with optimal intracellular esterase activity and chlorophyll autofluorescence (viable cells) (72 h-IC 50% < 1.9%) was 20 times higher than the one of OSW (72 h-IC 50% > 37.5%, v/v). OSLW was 4.4 times less toxic (IC 50% = 8.5%, v/v) than OSPW and 4.5 times more toxic than OSW.</p>
<p>Bacteria <i>(Vibrio fischeri)</i> (Microtox)</p>	<p>(Frank et al., 2009)</p>	<p><i>V. fischeri</i> was exposed 15 min to serially diluted (100%, 50%, 25% and 12.5%) solution of NA-like surrogates. Significant differences existed between all of the EC50 values (ranging from 0.07 to 627 mM) derived for the monocarboxyl NA-like surrogates. The acute toxicity of the NA-like surrogates increased with increasing MW for both the monocarboxyl</p>

		and dicarboxyl compounds, and the monocarboxyl NA-like surrogates elicited significantly greater toxic responses than dicarboxyl NA-like surrogates of similar MWs.
	(Jones et al., 2011)	Thirty-five pure individual acids were either synthesized or purchased for measuring the toxicity of some individual acids to the bioluminescent bacterium, <i>Vibrio fischeri</i> . Effective concentrations for 50% response (EC50) range from 0.004 to 0.7 Mm, which reveal the toxicity of the individual naphthenic acids to <i>V. fischeri</i> . The influence of hydrophobicity and aqueous solubility on the toxicity was also determined.

2.2 Water Treatment Technologies for OSPW

Since the tailings pond water contains a complex mixture of contaminants, a single unit may not be able to remove all the contaminants efficiently and economically in order to meet the goal of reuse and safe discharge. The choice of the treatment method heavily depends on the constituents of OSPW, industry processes, cost, and reuse or release regulations and demands. Several physico-chemical water treatment processes such as coagulation-flocculation, sedimentation, filtration, adsorption, ion-exchange, and biological degradation, as well as advanced treatment options like ozonation and membrane filtration, and a certain combination of some of these unit operations could possibly provide a relatively high efficiency treatment for OSPW. The advantages, disadvantages and possibilities of these water treatment technologies are discussed in the following section.

2.2.1 Physico-Chemical Treatments

Physico-chemical treatments are widely used to remove suspended and dissolved solids, organic and inorganic compounds in municipal and industrial wastewater treatment (AWWA, 1999; Metcalf & Eddy, 2003).

Coagulation-flocculation

The coagulation-flocculation (CF) process is widely used as a pretreatment to other processes including advanced oxidation, membrane filtration, adsorption, or ion exchange processes (Alpatova, Kim, Dong, & Sun, 2014; Crittenden, Trussell, Hand, Howe, & Tchobanoglous, 2012; Pourrezaei et al., 2011) to remove suspended and colloidal particles. Additionally, it can be used to reduce dissolved organic matter concentration (Jarvis, Jefferson, & Parsons, 2005). Because of their small size and negative surface charge, the suspended particles and colloids are difficult to settle by gravity in a reasonable time. The negative charges on the surface create repulsion forces, and therefore prevent the agglomeration and settling. Using coagulant chemicals, particles can aggregate and settle out of solution through four basic mechanisms: double layer compression, sweep flocculation, adsorption and charge neutralization, and adsorption and interparticle bridging (Crittenden et al., 2012; Nazaroff & Alvarez-Cohen, 2001). The presence of salts can cause compression of the double layer, resulting in destabilization of particles overcoming the repulsive electrostatic interactions by attractive van der Waals forces. Sweep flocculation, or enmeshment in the precipitate, occurs when precipitating coagulant traps suspended particles within a colloidal floc as it forms or settles (Crittenden et al., 2012; Gregory & Duan, 2001; Packham, 1965). Destabilization of particles through charge neutralization can occur when suspended particles in solution sorb to oppositely charged ions. Bridging can occur when a coagulant forms a polymer chain that can attach to multiple particles so that particles are bound to the coagulant and need not contact one another.

Inorganic metallic salt, especially iron and aluminum salt derivatives and lime, are the predominant coagulants widely used in industry. A trivalent metallic ion salt can be 700-1000 times more effective as coagulant than a monovalent ion salt in same dosage (Black & Riddick, 1960). This is why commonly used coagulants are trivalent aluminum salts (Al^{3+}) and iron salts (Fe^{3+}) instead of sodium (Na^+) or magnesium (Mg^{2+}) (AWWA, 1999).

Coagulation-flocculation-sedimentation (CFS) process was found to be effective for pretreatment of petroleum refining wastewater and tailings pond water (Demirci, Erdogan, & Ozcimder, 1998; Pourrezaei et al., 2011; Santo et al., 2012; Verma, Prasad, & Mishra, 2010; Y. Wang, 2011). In the study by Santo et al. (2012), the highest chemical oxygen demand (COD) removal of 87% from petroleum refining wastewater was achieved by CFS using 27.2 mg/L of polyaluminum chloride. Approximate COD removals of 87% and 85% were achieved by higher coagulant dosage of 40 mg/L alum and 56 mg/L ferric sulfate, respectively. The total organic carbon (TOC) removals of 84%, 83%, and 82% were similar by same dose of polyaluminum chloride, alum and ferric sulfate, respectively. In the study by Demirci et al. (1998), approximately 90% COD and turbidity removals from a petroleum refining wastewater were obtained by adding 100 mg/L of alum in combination with 100 mg/L of clay as coagulant aid. The BOD/COD ratio increased by CFS treatment, which indicated that the treated wastewater was suitable for biological treatment. Wang (2011) and Pourrezaei (2013) investigated the remediation of oil sands process-affected water. Wang (2011) optimized jar-test operation conditions for alum and ferric sulfate, and achieved 96% total suspended solids removal. Pourrezaei (2013) concluded that with the addition of 250 mg/L alum, about 96%, 10-37%, and 64-86% removals of turbidity, naphthenic acids, and oxidized naphthenic acids from OSPW were obtained, respectively.

However, the conventional chemical-based coagulants and flocculants have been shown to increase the toxicity of treated water (Al-Mutairi, 2006; Fort & Stover, 1995; Pourrezaei et al., 2011). Pourrezaei et al. (2011) showed that the toxicity of the alum-treated (250 mg alum/L) OSPW towards *Chironomus dilutus* (75% survival), but this was not significantly different ($p = 0.05$) from the survival in the freshwater control or OSPW.

However, the survival of *C. dilutus* exposed to OSPW treated with alum and cationic polymer was 42.5%, indicating the increased toxicity of treated OSPW by adding poly DADMAC. Although alum does not significantly increase the toxicity of water, it produce large sludge volumes (James & O'Melia, 1982), react with natural alkalinity present in the water causing pH reduction (Ndabigengesere & Narasiah, 1998), and demonstrate low coagulation efficiency in cold waters (Haarhoff & Cleasby, 1988). There is also a concern for using aluminum salts that may induce Alzheimer's disease (Gupta et al., 2005).

The concerns of chemical coagulant have led to the recent growing interest in using plant-based natural coagulants because of their abundance, biodegradability and innocuousness. Research demonstrates that the plant-based materials such as *nirmali* seeds, *M. oleifera*, tannin and cactus can remove turbidity from water (Corsaro et al., 1995; Graham et al., 2008; Miller et al., 2008). If proven technically practicable, these natural coagulants such as *Opuntia.spp* and *Moringa oleifera*, may become a good alternative for the conventional chemical coagulants once their performance is established.

Activated Carbon Adsorption

Adsorption is the process of removing dissolved organic substances from a solution using an adsorbent. Among all the adsorbents, carbonaceous materials such as activated carbon, carbon black, and zeolites are the most commonly used adsorbent in the treatment of water, municipal wastewater, and organic industrial wastewaters, because of its ability to adsorb a wide variety of organic compounds, as well as the economic feasibility (Allen, 2008b; L. K. Wang, Hung, & Shammas, 2005). Activated carbon was used to remove naphthenic acids and other organic contaminants from OSPW. Martinez-Iglesias (2015) studied the feasibility of using granular activated carbon (GAC) to absorb various naphthenic acids in synthetic OSPW. GAC showed a good adsorption capacity for all three model compounds and the maximum adsorption occurred at pH 4.

During the oil upgrading process, huge amount of petroleum coke (PC), a by-product is produced (DiPanfilo & Egiebor, 1996). DiPanfilo and Egiebor (1996) proposed that

petroleum coke can be activated to produce activated carbon because of its high carbon content. Zubot (2010) investigated the effect of PC adsorption for NAs removal from OSPW. High removal of the NAs (64%-96%) was achieved by adding 9-39% wt. of PC to OSPW and mixing for 4 hr. Niasar et al. (2016) modified the surface of petroleum coke by introducing $-NH_3$ group on the surface. Both modified activated carbon (AC) and petroleum coke-derived activated carbon (PAC) showed excellent capacity for model NAs and OSPW at low pH. The ammonia and amination modified PAC had 967-1024 m^2/g of total surface area, significantly higher than the 5.7 m^2/g surface area of non-activated PC (Allen, 2008b) and 494 m^2/g of steam activated PC (Small, Ulrich, & Hashisho, 2012).

Membrane Filtration

Membrane filtration is a robust treatment technology and enjoys numerous industrial applications because of its high selective separation, good adaptability for existing production processes, continuous and automatic operation at ambient temperature with low energy consumption (Mudler, 1996). The most common membrane filtration processes are pressure-driven processes such as nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), reverse osmosis (RO), or gas separation (GS). Peng et al. (2004) reported that nanofiltration (NF) had been successfully applied for the removal of NAs from OSPW. The removal of NAs was achieved using a bench-scale flat sheet membrane system with various commercial NF membranes. The result indicated that over 95% of water hardness and NAs was removed after membrane filtration treatment, which implied a potential discharge feasibility. Sierka and King (1986) studied a two-stage RO process for organic and inorganic contaminants removal from OSPW with four types of membrane. After a sequence of pretreatments including coagulation, adsorption and ozonation, the RO process resulted in a maximum of 98% organic rejection and 97% of inorganic rejection. Although membrane filtration shows an excellent capability to removal both inorganic and organic components in OSPW, this technology is expensive due to the fouling of membrane causing frequent membrane replacement, and might not be suitable for treatment for huge amount of wastewater.

2.2.2 Biodegradation

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, Peterson, & Headley, 2005). Clemente et al. (2004) investigated the biodegradability of NAs in aerobic cultures. Within 10 days of incubation, the NAs concentrations dropped from about 100 to <10 mg/L. This was accompanied by the release of about 60% of carbon from the NAs as CO₂ and the reduction of toxicity of the culture supernatant, as measured by the Microtox assay. However, biodegradation of NAs is very slow in oil sands tailings ponds.

2.3 Bilge Water Overview

Oil is a common pollutant of wastewaters, and it can be found in a wide range of industries such as petrochemicals, food manufacturing, metal-finishing, leather tanning, etc. Besides industries, marine transportation is also responsible for the oil pollution in aquatic environment. The bilge water that is stored at the bottom of ship is a mixture of fresh water, sea-water, free oil and stable oil-in-water emulsion, sludge, chemicals and particulates. More specifically, it contains oil and grease, detergents, aluminum shavings, plastic shreds/shards, dissolved heavy metals and suspended solids.

In the United States, bilge water production is estimated over 5 million of cubic meters per year. When disposed, oil and grease are mixed with the sea water, which affect many marine species. Because of the vulnerability of planktons, which are a basic food source for aquatic lives in the seas, the species can be harmed by the presence of oil and grease, which will ultimately have adverse effects on all the other links in the food chain, and eventually affecting many marine species. Appropriate treatment methods of bilge water are needed for the purpose of meeting marine discharged standards MARPOL 73/78 (oil concentration less than 15 ppm).

2.4 Treatment Methods for Oily Wastewater

2.4.1 Floatation

The floatation process, when applied to wastewater treatment, small air bubbles (<0.1mm) which are adhered with the suspended oil particles are generated and injected in the water. As the density of oil is less than that of water, the formation of a scum layer separated from the water occurs (Moosai & Dawe, 2003). Currently, the most commonly used floatation methods are dissolved air floatation, electro-floatation, induced air floatation, nozzle floatation, column floatation, centrifugal floatation and jet floatation. Floatation agents are added to improve the process efficiency by mechanisms such as bridging adsorption, and colloidal particles, which can gather together while bubbles float (Tang and Liu, 2006). Floatation is a well-developed method for oily wastewater treatment, the separation of oil and water is stable and obvious. The drawback of floatation is that the scum generated during the process contains concentrated oil content which is intractable. Zhu and Zheng (2002) used MAF (microbubble air floatation) in refinery wastewater treatment, where the removal of oil and suspended particles was 81.4% and 69.2%, respectively. Floatation can also be combined with other pretreatment or post-treatment processes. For instance, Al-Shamrani, James, and Xiao (2002) conducted a dissolved air floatation separation of oil and water with coagulation-flocculation as pretreatment. The coagulant they used was aluminum sulfate, and the result showed that the oil base can be removed by floatation when the initial oil concentration was 100 mg/L.

2.4.2 Coagulation Treatment

Coagulation is a widely-used method because of its effectivity, inexpensiveness and adaptability. Coagulation-flocculation are usually applied as a pretreatment method for municipal and industrial wastewater, as well as drinking water treatment. It can remove suspended solids, organic matters and even some heavy metal from water body. For oily wastewater, the role of coagulant is to break the oil-in-water emulsion and make the oil droplets agglomerate together. According to the study by Ahmad, Sumathi, and Hameed (2005), the emulsified oil, dissolved oil and some non-biodegradable organic matters are

removed by coagulation. Multi-valent metallic salts such as aluminum sulfate, ferric sulfate and ferric chloride are the conventional coagulants, which are currently widely used in industry. Besides, many composite coagulants are studied to achieve better efficiency and less environmental issues. Lin and Wen (2003) developed a composite coagulant CAX for treating oily wastewater from oil refinery industry. The original oil concentration and COD was 207 mg/L and 600 mg/L, respectively. After coagulation, oil and COD removal efficiency reached 98% and 80%, respectively. Zeng et al. (2007) used zinc silicate and anionic polyacrylamide (A-PAM) as composite flocculants for oily wastewater treatment, and improved oil removal efficiency up to 99% with a low suspended solids residue of 5 mg/L. Cong, Liu, and Hao (2011) studied another composite coagulant poly-aluminum zinc silicate chloride. The optimization showed the optimal molar ratio of zinc, aluminum and silicon is 1:1:2, with best coagulation conditions were achieved at 35 mg/L dosage at pH of 7-8. The removal of turbidity, color and COD was 98.9%, 91.3%, and 71.8%, respectively. Comparison of performance between poly-aluminum zinc silicate chloride (PAZSC) and poly-aluminum silicate chloride (PASC) indicated that PAZSC was able to achieve higher removal when same dosage was applied. Although plenty of studies showed the excellent removal using composite coagulants, due to the complexity of oily wastewater composition, the optimal coagulation conditions including coagulant type and dosage are not universal. It is difficult to theoretically predict the best coagulant and treatment condition; some empirical models can be applied based on practical experience.

2.4.3 Electrochemical Treatment

Electrochemical method is one of the most effective oily wastewater treatment techniques in recent years. Several electrochemical technologies have been applied to treat oily wastewater from different sources. These electrochemical technologies include electrochemical oxidation processes and electro-Fenton using several electrodes. Electrode materials such as iron, aluminum, boron doped diamond, platinum–iridium, and titanium–ruthenium have been tested. Körbahti and Artut (2010) studied the influence of operating conditions (current density and reaction temperature) on the treatment of bilge water using platinum–iridium electrodes in a batch electrochemical reactor. Their

results demonstrated that a current density of 12.8 mA/cm² and 32°C reaction temperature removed 99.2%, 93.2%, and 91.1% of COD, oil and grease, and turbidity, respectively with an average energy consumption of 33.25 kWh/kg COD. Sekman et al. (2011) investigated the capability of electrocoagulation in the treatment of oily wastewater generated from port waste reception facilities using aluminum electrodes. They indicated that 98.8% removal of suspended solids was obtained at current density of 16 mA/cm² and electrolysis time of 5 min. In addition, 90% removal of COD was reported at current density of 12 mA/cm² and electrolysis time of 20 min. However, 80% removal of oil and grease was observed at all tested current densities after an electrolysis time of 10 min.

2.4.4 Membrane Filtration

Recently, membrane filtration has been widely applied for oily wastewater treatment. The performance of several membrane technologies for the removal of pollutants from oily wastewater has been investigated. Some of the tested membrane materials include polyvinylidene fluoride (PVDF), polysulfone (PS), polyacrylonitrile (PAN), ceramic materials, mullite, mullite-alumina ceramic material, TiO₂/carbon, and ceramic–polymeric composites. Sun et al. (2010) studied the treatment of shipboard wastewater including gray water, black water, and bilge water using a biofilm membrane bioreactor and flat sheet ceramic membrane using dead-end and recycle side stream configurations. Their results demonstrated that a good permeate quality was obtained in both configurations with oil content of 5 mg/L. Soltani et al. (2010) also investigated the treatment of oily water using a membrane bioreactor (MBR). They showed that the bacteria consortium could degrade hydrocarbons, hexadecane, and phenanthrene, in the presence of salts. In addition, their results showed that the hydraulic retention time (HRT) to biodegrade oil was about 10 to 15 hours, reporting 100% removal efficiency. Ghidossi, Veyret, Scotto, Jalabert, & Moulin, (2009) studied different membranes (0.1 µm and 300 kDa) with the ability to separate hydrocarbons. Their results showed that the 300 kDa membrane was very efficient, with permeate flux more than 100 L/(hr·m²·bar) having less than 1 mg/L of hydrocarbon concentration (97% removal).

2.4.5 Combined Technologies

The combined technology here refers to the integration of different oily wastewater treatment technologies, with the purpose of observing the overall impact of the combined technologies on the removal efficiencies of pollutants. Otadi et al. (2010) analyzed the oily compound removal of Pars Oil Refinery wastewater using a dissolved air flotation (DAF) system and activated sludge reactor and clarifier (ASR). They concluded that the physical treatment, DAF, removed 29.7%, 49%, and 27.8% of oil, COD, and BOD respectively. In addition, the biological treatment, ASR, removed 73.4% and 84.7% of COD, and BOD, respectively suggesting that the biological treatment had great efficiency in the removal of COD and BOD. Santo et al. (2012) optimized the coagulation–flocculation and flotation processes in order to reduce the organic matter and oil and grease content. PAX-18 (17% Al_2O_3), aluminum sulfate, and ferric sulfate were chosen for the primary treatment of coagulation-flocculation. NALCO 71408 was used as flocculant. Their results indicated that a combination of 28.6 mg/L of PAX-18 and 4.5 mg/L of NALCO 71408 removed more than 80% of COD, total organic carbon, and turbidity in a continuous mode of operation. In addition, a flotation test showed a removal of 95% of total petroleum hydrocarbons at a 0.6 kg air/kg of air/solid ratio, suggesting the potential implementation of coagulation–flocculation and flotation for the removal of hydrocarbons from oily wastewater at optimal design and operating parameters. The removal efficiencies by various treatment methods are summarized in Table 2.2.

Table 2.2 Removal efficiencies of pollutants from oily wastewater by various treatment methods

Treatment techniques	Source of oily wastewater	Removal efficiencies of pollutants	Reference
Coagulation-CAX	Oil industry- oil in water concentration was 207 mg/L, COD concentration was 600 mg/L	Oil removal is more than 98%	Lin and Wen (2003)
Coagulation- zinc silicate and anionic polyacrylamide	Heavy oil wastewater from industry with oil content 400-1000 mg/L	Oil removal is 99%	Zeng et al. (2007)
Coagulation- Poly-aluminum zinc silicate chloride	Oily wastewater from industry	COD removal is 71.8%	Cong et al. (2011)
MAF (microbubble air floatation)	Oil refinery wastewater	Oil removal is 81.4%	Zhu and Zheng (2002)
Dissolved air floatation	Synthetic oily wastewater	Oil removal is more than 90%	Al-Shamrani et al. (2002)
Electrochemical treatment	Synthetic bilge water prepared in synthetic 50/50% seawater/fresh water with 3,080 mg/L COD and 2,000 mg/L oil/grease	99.2% COD, 93.2% oil, and 91.1% turbidity	Körbahti and Artut (2010)

Electrochemical treatment	Oily wastewater port waste reception facilities in Turkey with 13.3–660 mg/L suspended solids, 240–2,783 mg/L COD, 6.5–736 mg/L oil/grease	98.8% suspended solids, 90% COD, and 80% oil/grease	Sekman et al. (2011)
Membrane separation	Shipboard wastewater including gray water, black water, and bilge water with 80 mg/L oil	95.96%–98.9% oil	Sun et al. (2010)
Membrane separation	Produced water and sea sediment in Iran with 10–22 mg/L oil/grease	100% oil removal	Soltani et al. (2010)
Membrane separation	Effluents from ships in France with 20–200 mg/L hydrocarbons	97% removal of hydrocarbons	Ghidossi et al. (2009)
Combined technologies	Refinery wastewater in Iran with 13.3–58.3 mg/L oil, 256–1,800 mg/L COD, 27–400 mg/L BOD	29.7% oil, 49% COD, and 27.8% BOD by dissolved air flotation (DAF). 73.4% COD and 84.7% BOD by activated sludge reactor (ASR)	Otadi et al. (2011)
Combined technologies	Refinery wastewater in Portugal with COD up to 580 ± 4 mg/L	More than 80% COD	Santo et al. (2012)

2.5 Objectives and Scope of the Present Research

2.5.1 Trends and Needs in OSPW Research

Limited research is available on OSPW pretreatment, especially pretreatment by coagulation-flocculation. Based on the literature review above, the trends and needs in current OSPW research are summarized as follows:

- Most of the present OSPW treatment research investigated stand-alone innovative treatment technologies for the removal of NAs and heavy metals. However, OSPW is a complex mix of organic and inorganic compounds requiring a train of technologies for the removal of most of the pollutants. Research on the pretreatment processes and the effect of pretreatment on other treatment processes need to be assessed.
- In OSPW pretreatment studies, most of the chosen coagulants were chemical-based coagulants, including multivalent metallic salts, cationic polymers and other innovative synthetic coagulants, which increases toxicity of water. The plant-based coagulants have never been investigated in treating oil sands tailings pond water.
- A feasible and cost-effective combination of water treatment processes based on waste material is needed for the oil sands industry.

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 sub-objectives of the research are as following:

- To investigate *Opuntia ficus-indica* as a natural coagulant to remove suspended solids, hydrocarbons, and some dissolved constituents such as NAs from OSPW. To verify the impact of pretreatment on the adsorption of dissolved organic carbon from OSPW.

- To optimize the coagulation-flocculation (CF) process and find out the optimal conditions including dosage and pH for each coagulant in terms of removal of turbidity and dissolved organic carbon for OSPW.
- To establish a CF-adsorption combined treatment process to remove the toxicity in OSPW.

2.5.2 Trends and Needs in Bilge Water Treatment

The conventional methods widely used for bilge water treatment are physical processes such as floatation, centrifugation and filtration, which are expensive and require large footprint, which often is difficult on board treatment. As the major part of the oil in bilge water is emulsified, the physical methods often fail to satisfy the targeted treatment levels (Caplan, Newton, and Kelemen 2000; Woytowich, Dalrymple, and Gilmore 1993). Their studies indicated that emulsified oil droplets smaller than 20 μm were not removed by means of conventional oil/water separation processes. Hence, demulsification by chemical coagulation is important before any physical treatment can be applied.

The conventional coagulants widely used in municipal wastewater and industrial oily wastewater are multi-valent salts such as alum (Al_2SO_4), ferric chloride and ferric sulfate. Due to the increase in ionic strength of oily wastewater by dosing a multi-valent salt, the double layer around oil droplet becomes thinner, which reduces the repulsion force between droplets increasing the Van der Waal's attraction force, allowing the droplets to coalesce together to form larger droplets. This double layer compression can be achieved by inexpensive common salt (NaCl), but it is not a practical coagulant for municipal wastewater and drinking water treatment as it will cause very high concentration of salt into water stream and make water brackish. However, for bilge water treatment, the effluent is discharged into open sea or ocean making it easier to use NaCl as a coagulant. Unlike surface water, for sea water, the influence of salt loading in bilge water is negligible. Moreover, the presence of sodium chloride in sea water itself makes it an abundant and easily available source of coagulant. Some studies investigated the effect of salt concentration on the stability of oil-in-water. Binks et al.(2006) investigated the effects of pH and sodium chloride concentration on the stability of oil-in-water emulsion using aqueous microgel emulsifier. It was found that the diameter of oil droplets

increased with increasing salt concentration, hence inducing coalescence of oil drops in water. The volume of oil-in-water emulsion in the study by Binks was below 100 ml, which was not a comparable magnitude to the large volume in industry. The study of coagulation-flocculation or similar process using sodium chloride as coagulant for bilge water or oily wastewater treatment was rarely seen.

The objectives of this research were to i) investigate whether sodium chloride is a feasible coagulant for oil removal from bilge water, ii) determine the optimal conditions including dosage of coagulant, jar test condition, sedimentation time to remove oil, iii) compare the performance between sodium chloride and conventional coagulant, such as alum.

2.6 References

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Chapter 3

3 Combined Treatment of Oil Sands Process-Affected Water using Coagulation and Adsorption

3.1 Introduction

Oil sand process affected water treatment is a critical issue for Canada's oil sand industry. Under the "zero discharge policy", large amount of oil sands process-affected water is stored in tailings ponds on-site. While oil sands producers have made significant improvements in water use efficiency and have invested in reclamation research, the industry still faces several hurdles related to water use. Recycling of tailings pond water (TPW) has slowed the increase in freshwater withdrawals, but has contributed to a long-term decline in process water quality that threatens to affect bitumen recovery through disruption of extraction chemistry and scaling and corrosion of extraction facilities. Tailings treatments such as consolidated tailings (CT), whereby calcium sulphate is added to mature fine tailings and sand, enhance the salinity and hardness of process water. As producers become increasingly dependent on process water recycling, the decline in water quality may reduce bitumen recovery rates, leading to increased demand for water.

Maintaining good water quality and ensuring more efficient and limited use of fresh water are the most important challenges that must be met in the oil sands sector. Therefore, it is very important to develop a strategy to treat oil sand process affected water (OSPW).

In conventional pretreatment techniques of wastewater, chemical coagulants such as alum and ferric compounds are used to remove suspended and colloidal particles. Although these compounds have excellent coagulation performance and availability, they also have a negative impact on the environment and health. Negative effects of chemical coagulants have increased the interest in the use of natural coagulants because of their abundance, innocuousness and biodegradability.

The genus *Opuntia* is the largest under the *Cactaceae* family, and varieties of *Opuntia* can be found from Western Canada to the tip of South America. Although, *Opuntia* has been used extensively for coagulation of drinking water (Young, 2006), this has never been tested in treating industrial effluents such as OSPW, which is the objective of this work. The *Opuntia* species selected as the natural coagulant source for this project is *Opuntia ficus-indica*, also known as nopal or prickly pear, is commonly found and cultivated. The mucilage of *Opuntia ficus-indica* is a thick, gummy substance, which provides the cacti's natural ability to store large amounts of water. When in water, the mucilage swells, producing unique surface-active properties seen in many natural gums, giving the mucilage coagulation ability to precipitate particles and ions from aqueous solutions.

Several researchers have conducted research on extraction and purification method for mucilage of *Opuntia* spp. Most of them homogenize the cactus pads with water and use ethanol for the precipitation of *Opuntia* polymers (Cárdenas, Higuera-Ciapara, & Goycoolea, 1997; Paulsen & Lund, 1979; Trachtenberg & Mayer, 1981). Medina-Torres et al. (2000) modified the extraction procedure reported by McGarvie and Parolis (1981); the authors macerated the pulp obtained from the stems, which was then centrifuged, decanted and precipitated it in acetone. The precipitation was washed with 2-propanol and finally dried. Some other researchers used mucilage from cactus juice without precipitation, which simplify the procedure. Miller et al. (2008) studied the coagulation activity of fresh and dry *Opuntia* spp. pads. Maceration was performed on the fresh pads using a blender; and dry *Opuntia* spp. was prepared by drying at ~60 °C for 24 h and grinding into particulates. The application of dry powder could lengthen the storage time and reduce the transportation cost of *Opuntia* spp., but the additional energy used to dry the fresh pads should also be considered to the cost of pretreatment.

In this work, the performance of *Opuntia ficus-indica* is compared with that of alum for treating real OSPW for the removal of suspended and colloidal particles. The effect of coagulation on the removal of dissolved organic carbon from OSPW was also determined. In addition, activated carbon adsorption was used for further removal of

organic compounds from OSPW. The effect of coagulation as the pretreatment on the adsorption was also investigated.

3.2 Materials and Methods

3.2.1 Materials

Raw OSPW was obtained from Syncrude's tailings pond located in Alberta, Canada. OSPW samples (pH \approx 8.2, initial turbidity = 80-200 NTU, initial DOC = 160-250 mg/L) were fresh and collected from the top 3 m of the tailings pond. The initial turbidity and DOC values of OSPW samples were higher than typical OSPW mentioned in other studies (Pourrezaei, 2013; Y. Wang, 2011). *Opuntia ficus-indica* fresh pads were obtained from the greenhouse, Department of Biology, Western University. All chemicals used in this project were of analytical reagent grade. All working solutions were prepared using Milli-Q water (Millipore SAS, 67120 Molsheim, France). Alum (aluminum sulfate hydrate, degree of hydration, 14-18) was purchased from Sigma-Aldrich Canada Co. (Oakville, Ontario, Canada). The granular activated carbon Norit ROW 0.8 SUPRA (CAS Number: 7440-44-0) was purchased from Sigma-Aldrich Canada Co. (Oakville, Ontario, Canada). 1 M H₂SO₄ and 1 M NaOH solutions were used to adjust the pH of water.

3.2.2 Preparation of Coagulants

Natural Coagulant - Opuntia ficus-indica Mucilage

In this study, an earlier method (Miller et al., 2008) was modified to accommodate both simplicity of preparation and stability of mucilage of the cactus.

Figure 3.1 demonstrates the procedure that was adopted in natural coagulant preparation. *Opuntia ficus-indica* pads were cut from the plant and rinsed thoroughly with tap water followed by distilled water. Fresh cactus pads were used within two days and stored in a freezer at -18 °C for up to 2 weeks (without sacrificing the effectiveness of the coagulant). Dissections of fresh cactus pads were performed: skin was peeled from the

pad, the outer pad was considered the outer layer of bright green tissue composed of chlorenchyma, and the inner pad was considered the inner layer of off-white tissue composed of aerenchyma (Lerdau et al., 1992). After removing outer layer, the inner pads were sliced into small pieces. Mortar-pestle was used to make a paste of sliced cactus. The resulting mixture of solid and gel were separated by centrifuging at 3700 rpm for 15 min. The resulting supernatant and mucilage were collected and stored in refrigerator at 4 °C. The yield of dried mucilage was 1.82% and 0.58% with reference to liquid mucilage and fresh cladodes, respectively. The experimental yield is close to 0.5% from stem (fresh weight) as reported by Srivastava and Pande (1974). The mucilage was applied as natural coagulant without any pretreatment. The efficiency of prepared mucilage in removal of turbidity is shown in Figure 3.2, which decreased with time and dropped to 90% within ten days. Thus, new coagulant was prepared every ten days to maintain consistency of the experiments.

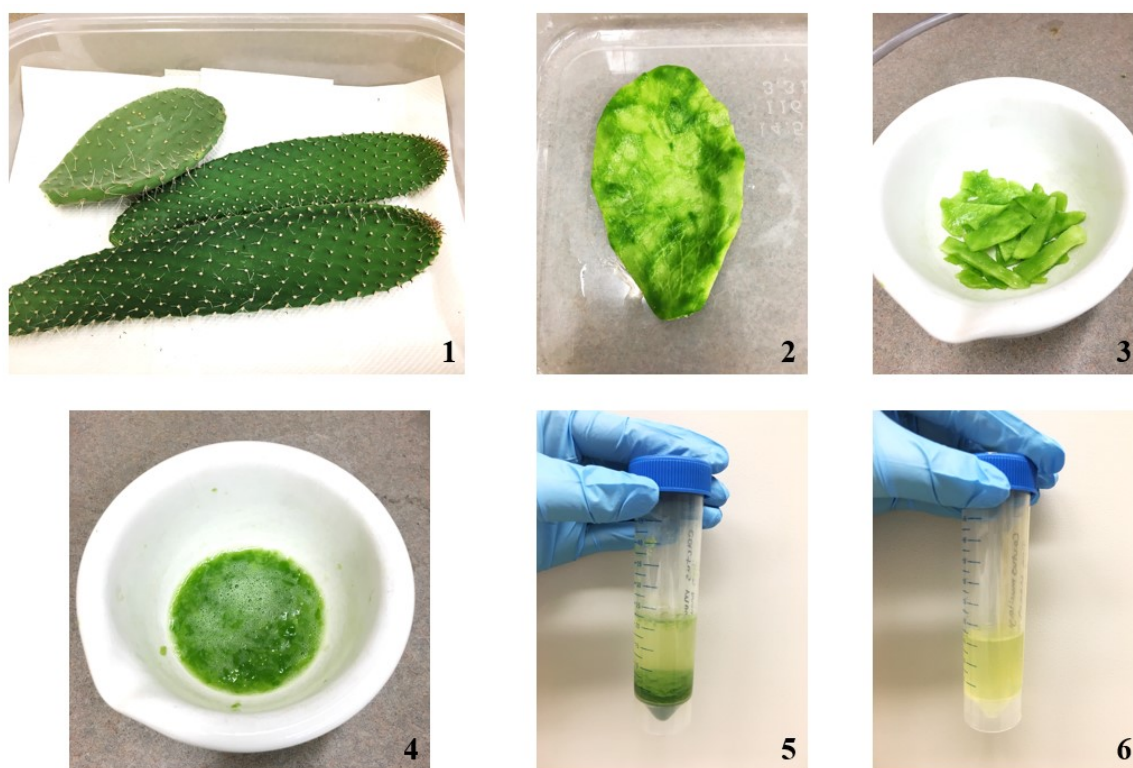


Figure 3.1 Preparation of *Opuntia ficus-indica* mucilage

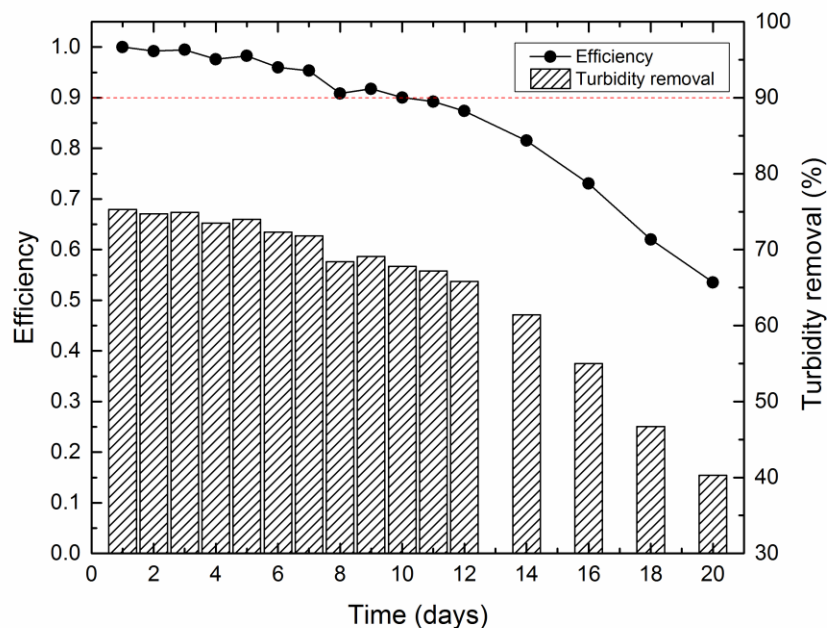


Figure 3.2 *Opuntia ficus-indica* mucilage coagulation efficiency variation with time (Raw OSPW with constant initial turbidity of 180 NTU and pH \approx 8, constant OFI mucilage dosage = 200 mg/L).

Alum Coagulant

10.00 g of aluminum sulfate hydrate was dissolved in 1 liter milli-Q water to make a 1 % alum solution. The concentrations of aluminum sulfate hydrate, aluminum sulfate anhydrous, aluminum ion were calculated to be 10^4 mg/L, 0.576×10^4 mg/L, and 9.1×10^2 mg/L, respectively (the degree of hydration was assumed to be 14). The dosage used in this dissertation was aluminum sulfate hydrate. The calculation of the dosage is presented in Appendix A.

3.2.3 Batch Coagulation-Flocculation Experiments – Jar Tests

A Phipps & Bird PB-900 programmable jar tester (Richmond, VA, USA) (shown in Figure 3.3) was used to perform bench-scale batch jar tests using 500 ml of OSPW at

room temperature (23 ± 1 °C). The rapid mixing and slow mixing were used to perform coagulation and flocculation process, respectively. The speed and time of rapid and slow mixing were determined using G-value calculation and also from literature (Vishali & Karthikeyan, 2014).

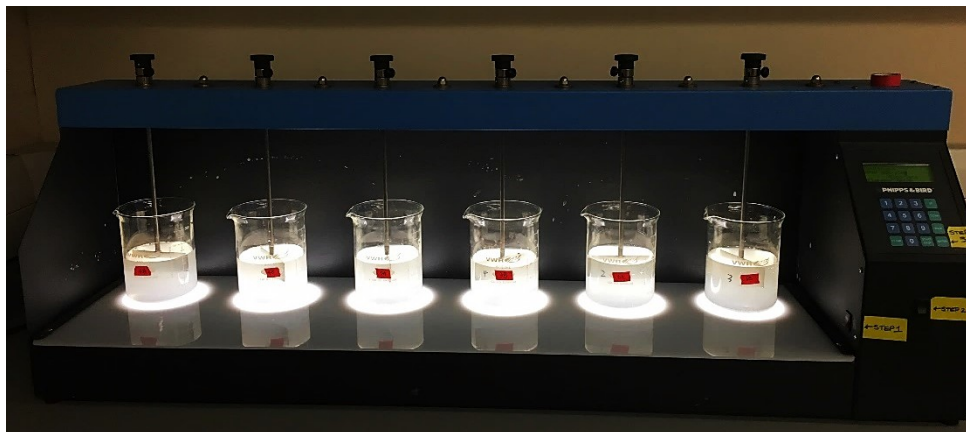


Figure 3.3 Phipps & Bird PB-900 programmable jar tester

The degree of mixing is measured by velocity gradient (G), which is the relative velocity of the two fluid particles/distance. The velocity gradient is calculated using equation 1 as below. In the flocculator design, Gt (also known Camp No.); a product of G and t is commonly used as a design parameter.

$$G = \left[\frac{P}{\mu V} \right]^{1/2} \quad \text{(Equation 1)}$$

G= velocity gradient, s^{-1} ;

P = Power input, W;

V = Tank volume, m^3 ;

μ = Dynamic viscosity, (Pa·s).

The typical G value and mixing time for coagulation and flocculation are shown in Table 3.1 (L. K. Wang et al., 2005). The velocity gradient vs. agitator speed for a 600-ml beaker was plotted by converting the graph for a 2-liter Square Beaker (B-KER2)

(Source: Water and Air Research Inc.). The original graph and transformation calculation were present in Appendix C.1.

From the theoretical appropriate range of G-value (Table 3.1) and the G-curve shown in Figure 3.4, the jar test conditions for coagulation and flocculation were selected with a certain combination of agitator paddle speed and mixing time. First, a combination of G value and mixing time in the appropriate range from Table 3.1 was selected. Then the approximate agitator paddle speed corresponding to the selected G value was read from Figure 3.4, which determines the jar condition. Conversely, a jar test condition can be examined whether if it is within the theoretical appropriate range. In this study, for coagulation, the jar tester was set as rapid mixing with 150 rpm of paddle speed for 1.5 minutes; and for flocculation, the jar tester was set as slow mixing with 25 rpm of paddle speed for 20 minutes.

Table 3.1 Parameters with appropriate range for coagulation and flocculation

Process	Jar test status	G value (s^{-1})	Mixing time	Gt (Camp. No.)
Coagulation	Rapid mixing	300-1500	30-120 s	10,000-40,000
Flocculation	Slow mixing	20-80	20-30 min	2×10^4 - 10^5

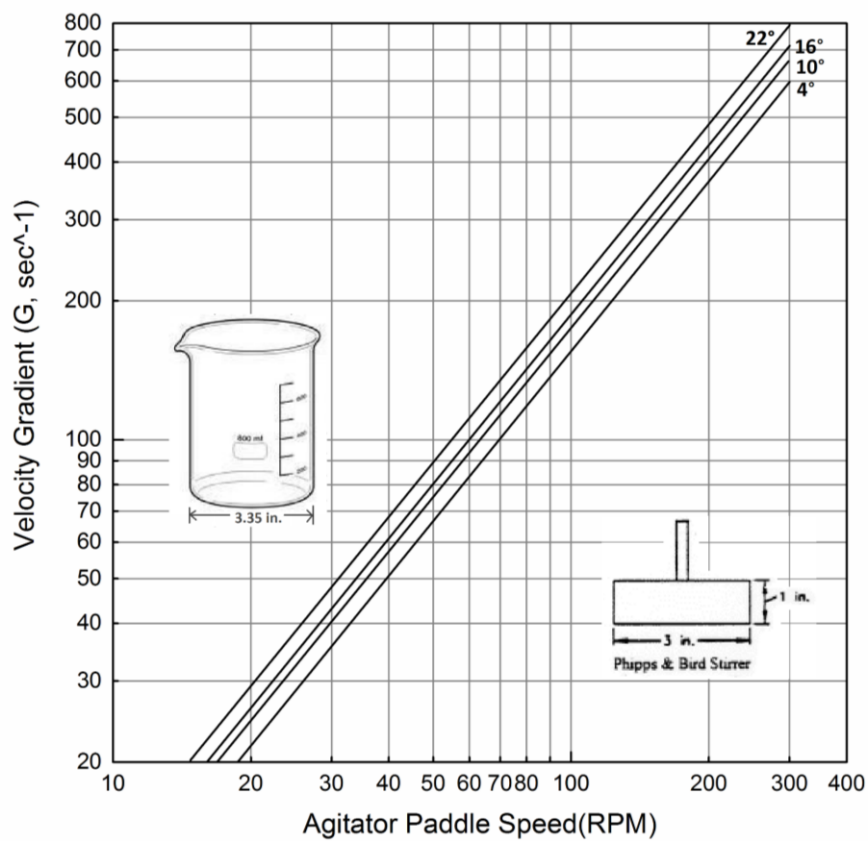


Figure 3.4 Velocity Gradient vs. Agitator Speed for a 600-ml beaker, Using a Phipps & Bird Stirrer. (Converted from the G-curve for a 2-liter Square Beaker (B-KER2)).

After jar testing, the agglomerated particulates were allowed to settle down. Preliminary sedimentation experiments indicated that no additional decrease in turbidity occurred after 60 minutes. This duration was used for all the subsequent sedimentation experiments.

After flocculation and sedimentation, 100 ml of the supernatant was collected using a syringe from 3 cm below the water surface to determine water quality parameters such as turbidity and dissolved organic carbon.

3.2.4 Preparation of adsorbent

Granular activated carbon (GAC) (total surface area \approx 1400 m²/g, mesopore=634 m²/g, micropore=766 m²/g, total pore volume=0.7 cm³/g, pore size=2 nm) was applied as the adsorbent in batch adsorption experiments. In order to remove some fines on the carbon surface, the GAC was washed and subsequently dried. The washing was performed by agitating a mixture of 2 g of GAC with 400 ml milli-Q water in a one liter Erlenmeyer flask for 15 minutes using a MaxQ 4000 Bench-top Orbital Shaker (Thermo Scientific) set to 170 rpm. The supernatant with fines of activated carbon was discarded. The whole washing process was repeated two more times, and the GAC was placed in an oven at 110 °C for 3 hours to dry the water. The hot GAC was transferred to a capped glass jar, and stored in a desiccator. The carbon dosage for adsorption experiments was considered as dry mass.

3.2.5 Batch Adsorption Experiments

Batch adsorption experiments were performed using a MaxQ 400 Bench-top Orbital Shaker (Thermo Scientific). The experiments were carried out using 500 ml Erlenmeyer flasks containing 175 ml of solution and washed and dried activated carbon. The shaker unit was operated at room temperature (23 °C) and 200 rpm of agitation speed.

Preliminary adsorption experiments indicated that the adsorption equilibrium was reached within 24 hours, and this duration was selected for all the adsorption experiments.

For further polishing the OSPW after coagulation using *Opuntia ficus-indica* or alum, the dosage of granular activated carbon was fixed at 0.4 g/L, i.e., 70 mg GAC in 175 ml of OSPW. For building adsorption isotherm of DOC value, in order to maintain the solid-liquid ratio of adsorbent and solution (i.e., 0.4 g/L), the OSPW was diluted with milli-Q water by ratio of 1:0, 5:1, 2:1, 1:1, 4:11, 1:14. The pH of solution was adjusted using 1 M H₂SO₄ or 1 M NaOH after dilution. 12 ml of solution was collected for DOC measurement from each flask before and after batch adsorption.

3.2.6 Analytical Methods

Turbidity in water is usually caused by the existence of sand, mud, silt, bacteria, germs, chemical precipitates, etc. In most cases, total suspended solids (TSS) in the water is the dominant constituent of turbidity. The efficiency of the coagulation-flocculation process can be evaluated by determining the turbidity of water before and after treatment.

Turbidity of the samples was measured using a Hach 2100N Laboratory Turbidimeter (Hach, USA). The equipment was calibrated using Stablcal® Turbidity Standards Calibration Kit (Hach, USA) before each use.

Total organic carbon (TOC) is the amount of carbon contained in organic compounds and is often used as an indicator of water quality. It can be divided into dissolved organic carbon and particulate organic carbon (POC). The dissolved organic matter present in OSPW is mainly a mixture of carboxylic acids, known as naphthenic acids (NAs). These compounds are naturally occurring surfactants that are hydrolyzed and released from the bitumen during processing (Schramm, Stasiuk, & MacKinnon, 2000). Because there are hundreds of NAs present in OSPW, it is difficult to evaluate the removal of NAs by analytical methods such as GC-MS. Therefore, dissolved organic carbon (DOC) was used as the surrogate parameter to evaluate the concentration of NAs. All the samples were filtered using 0.45 μm Acrodisc® syringe filters (PALL Corporation, USA) before being analyzed in a TOC analyzer (TOC-V series, Shimadzu, Japan). The pH and conductivity values of samples were measured using Hach HQ40d multimeter (HACH, USA). The Axioskop 40 microscope (Carl Zeiss Microscopy, LLC, United States) was used to analyze the size and shape of the flocs generated by *Opuntia ficus-indica* and alum. The dried OSPW solids and dried flocs generated by *Opuntia ficus-indica* were analyzed by PerkinElmer Fourier transform infrared (FTIR) spectroscopy, for their functionality changes in the range of 500–4000 cm^{-1} (resolution: 1 cm^{-1}).

3.3 Results and Discussion

3.3.1 Optimization of Coagulant Alum

The turbidity variation of OSPW with various alum dosage at different settling time is shown in Figure 3.5. The residual turbidity of OSPW and synthetic turbid water using

kaolin did not change after 60 min, and also the maximum removal of turbidity occurred at the dosage of 40 mg/L. No charge reversal occurred above 60 mg/L. Hence, for all the jar tests using alum as coagulant in this work, the settling time was fixed at 60 minutes.

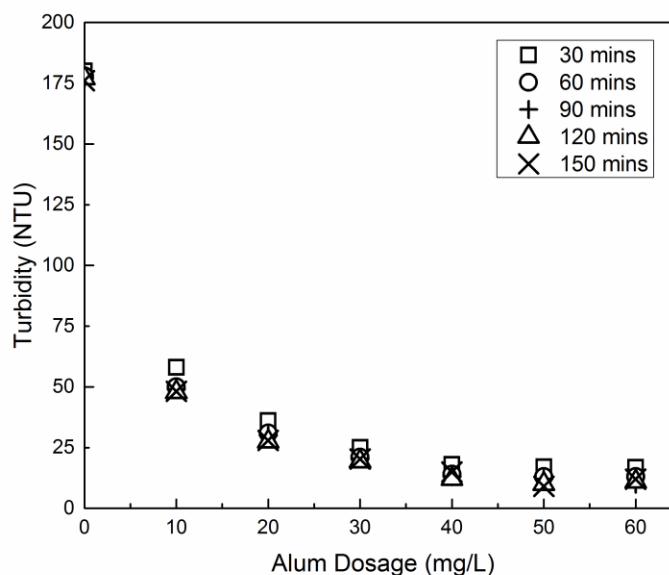


Figure 3.5 Turbidity (NTU) variations of raw OSPW after coagulation with alum (settling time ranging from 30 to 150 minutes at room temperature (20 ± 2 °C)).

Alum also has the ability to remove dissolved organic compounds from water. In order to apply alum as a coagulant on OSPW as pretreatment, the process must be optimized in terms of turbidity and dissolved organic carbon removal.

The statistical design of experiments (DoE) is a structured and systematized method of experimentation in which all factors are varied simultaneously over a set of experimental runs in order to determine the relationship between input variables (factors) affecting the output variable (response) of the process. The relationship between the response (turbidity and organics removal) and input variables (coagulant dosage and pH) cannot be modeled well by a first-order model. Hence, in this study, the central composite design (CCD) and response surface methodology (RSM), which are very efficient design tool for

fitting the second-order models, were applied to optimize the two most important operating variables: coagulant dosage and pH.

A central composite design is made rotatable by the choice of α . The value of α depends on the number of factors in the design (D. Montgomery, 2001). A value of $\alpha= 1.414$ for 2 factors in the study assured rotation of the CCD. A CCD containing 13 experiments with 4 cube points, 4 axial points, and 5 replicates at the center point was designed. The range of alum dose was chosen based on the usual range 10 - 200 mg/L. The pH was varied from 5 to 11, which is the realistic pH value in environment. The levels of the factors are given in Table 3.2 and the CCD of this work is presented in Table 3.3 and Figure 3.6. The 13 experiments were conducted in a random manner in order to minimize the effect of uncontrolled variables on the responses.

Table 3.2 Actual and coded values of independent variables used for experimental design

Variable	Symbol	Real values of coded levels				
		Lowest	Low	Center	High	Highest
		$-\alpha^a$	-1	0	+1	$+\alpha^a$
Dosage(mg/L)	X_1	10	37.8	105	172.2	200
pH	X_2	5	5.88	8	10.12	11

^a $\alpha= 1.414$ (star or axial point for CCD in the case of 2 independent variables).

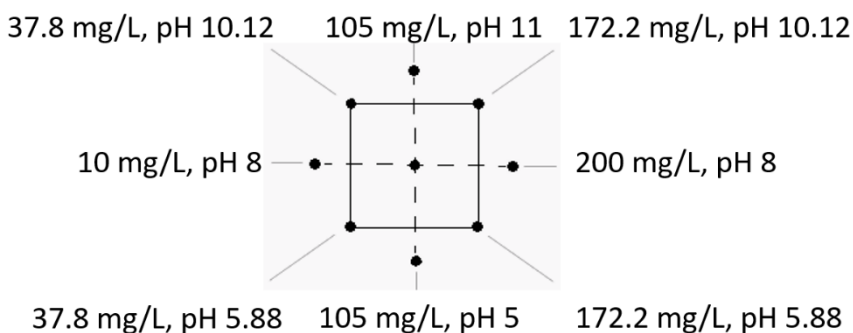


Figure 3.6 Central composite design (CCD) points of experiment

Table 3.3 CCD experimental design (DoE) for turbidity and DOC removal of OSPW by coagulation/flocculation (initial turbidity = 80 ± 2 NTU, initial DOC ≈ 230 mg/L)

Std. Order	Run Order	CCD				Results (removal (%))	
		Dosage (X ₁)	Actual Dosage (mg/L)	pH (X ₂)	Actual pH	Turbidity (Y ₁)	DOC (Y ₂)
4	1	+1.000	172.2	+1.000	10.12	91.74	-3.94
13	2	0.000	105	0.000	8	96.75	6.08
2	3	+1.000	172.2	-1.000	5.88	95.00	32.74
11	4	0.000	105	0.000	8	96.66	6.48
8	5	0.000	105	+1.414	11	72.77	-15.28
6	6	+1.414	200	0.000	8	98.80	13.64
3	7	-1.000	37.8	+1.000	10.12	56.70	-2.37
9	8	0.000	105	0.000	8	96.86	8.30
5	9	-1.414	10	0.000	8	59.00	2.34
1	10	-1.000	37.8	-1.000	5.88	73.62	10.60
12	11	0.000	105	0.000	8	96.51	7.27
7	12	0.000	105	-1.414	5	86.43	16.32
10	13	0.000	105	0.000	8	96.68	11.70

^a Experiments response are shown as means of three replicates (n=3).

By superimposing the experimental points on the aluminum hydrolysis speciation diagram (Figure 3.7a and b), it can be concluded that the experimental condition included the optimal sweep coagulation zone in the central composite design. The theoretical optimal sweep coagulation is defined in terms of its performance of removing suspended particulates. However, in this study, the aim of optimization was to find the experimental condition that maximizes both turbidity and DOC removal.

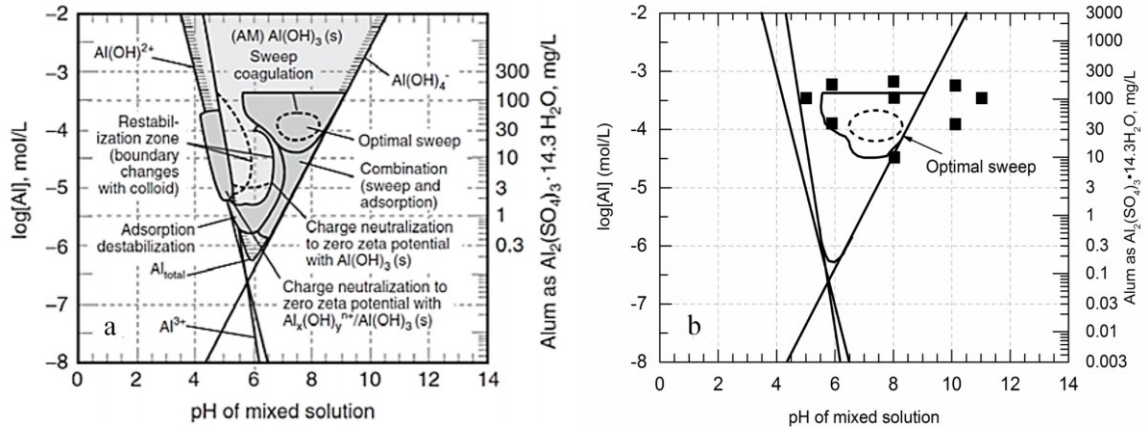


Figure 3.7 (a) Diagram from MWH showing aluminum hydrolysis speciation and operational coagulation regions (b) Jar test data for all experimental conditions plotted with aluminum hydrolysis speciation

It is interesting to note that pH had a significant effect on the DOC removal. The initial DOC significantly decreased after adjusting solution pH to acidic values. The possible reason is that the addition of sulfuric acid promoted the hydrolysis of naphthenates to form naphthenic acids, which have poor solubility in water. The precipitation resulted in reducing DOC concentration in water. The impact of pH adjustment, using sulfuric acid, for the removal of the extractable organic fraction (EOF) from the consolidated tailings (CT) water was studied by Marr et al., (1996), who also found that precipitation of the naphthenates occurred at $pH < 5$. The turbidity removal increased with increasing alum dose and a combination of 105 mg/L of alum and pH 8.0 caused the highest removal (around 97%) of turbidity. The possible explanation for the negative DOC removal at high pH is probably due to the existence of aluminum hydroxide at $pH > 10$, which could form aluminum naphthenate which are more soluble than naphthenic acids giving rise to higher DOC.

Based on the CCD experimental design results shown in Table 3.3, the RSM was applied to develop the polynomial regression equations relating the output response and the input factors. The response surface model of second-order is expressed as follows:

$$Y = f(x) = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \sum_{j=i+1}^k \beta_{ij} X_i X_j + \sum_{i=1}^k \beta_{ii} X_i^2 \quad (2)$$

where Y is the predicted response (turbidity percentage removal and DOC percentage

removal); k is the number of factors; X_i , and X_j are the factors which influence the predicted response Y ; β_0 is the constant coefficient; β_i , β_{ij} , and β_{ii} are the coefficients of linear, interaction, and quadratic term, respectively.

The results of the fitted models for turbidity removal and DOC removal are presented in Eqs. (3)-(4).

Turbidity removal Y_1 (%):

$$Y_1 = -29.914 + 0.43142X_1 + 25.567X_2 - 0.001969X_1^2 - 1.9008X_2^2 + 0.023971X_1X_2 \quad (3)$$

DOC removal Y_2 (%):

$$Y_2 = -21.7 + 0.342X_1 + 7.61X_2 + 0.000280X_1^2 - 0.550X_2^2 - 0.0416X_1X_2 \quad (4)$$

To interpret the ANOVA results, there are some important test indices that need to be checked. If a model is significant, it means that the model contains at least one important term for the response. The lack-of-fit test measures the failure of adequate description of functional relationship between the experimental factors and the response variable. In addition, the coefficient of determination (denoted R^2) as a measure of the model's overall performance must be considered. Besides, the residual plots can be used to determine whether the model is adequate and meets the assumptions of the analysis. The models of Y_1 and Y_2 are both found to be significant at 95% confidence level by the F-test as shown in Table 3.4, with all p-values of regression ≤ 0.05 . In addition, there is no lack-of-fit exhibited in either model (p-values > 0.05). The R-squared and adjusted R-squared for turbidity removal are 99.99% and 99.97% respectively, which are high and not significantly different. For DOC removal, the R-squared and adjusted R-squared are 95.11% and 91.62% respectively, which are also high.

Table 3.4 ANOVA results for the two responses: Y_1 (Turbidity removal) and Y_2 (DOC removal)

Source	DF	Adj SS	Adj MS	F-Value	P-Value
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Y ₁ (Turbidity removal)					
Model	5	2765.37	553.07	24107.57	0.000
Total Error	7	0.16	0.02		
Lack-of-Fit	3	0.10	0.03	1.96	0.262
Pure Error	4	0.07	0.02		
Total	12	2765.37			
$R^2 = 99.99\%$, $R^2_{\text{adjusted}} = 99.97\%$					
Y ₂ (DOC removal)					
Model	5	1480.32	296.06	27.24	0.000
Error	7	76.08	10.87		
Lack-of-Fit	3	55.76	18.59	3.66	0.121
Pure Error	4	20.32	5.08		
Total	12	1556.4			
$R^2 = 95.11\%$, $R^2_{\text{adjusted}} = 91.62\%$					

In the normal probability plots (Figure 3.8 (a)(b)), the residuals appear follow a straight line, which indicates that the residuals are normally distributed. The normality assumption is satisfied, no outlier or other unidentified variables were exhibited. In the residual versus fits plots (Figure 3.8 (c)(d)), the points appear randomly scattered. None of the groups appears to have substantially different variability and no outliers are apparent. The residuals versus order plot can be used to verify the assumption that residuals are independent from one another. In the residuals versus order plots (Figure 3.8 (e)(f)), the residuals fall randomly around the centerline as the ideal independent residuals, which should show no trends or patterns when displayed in time order.

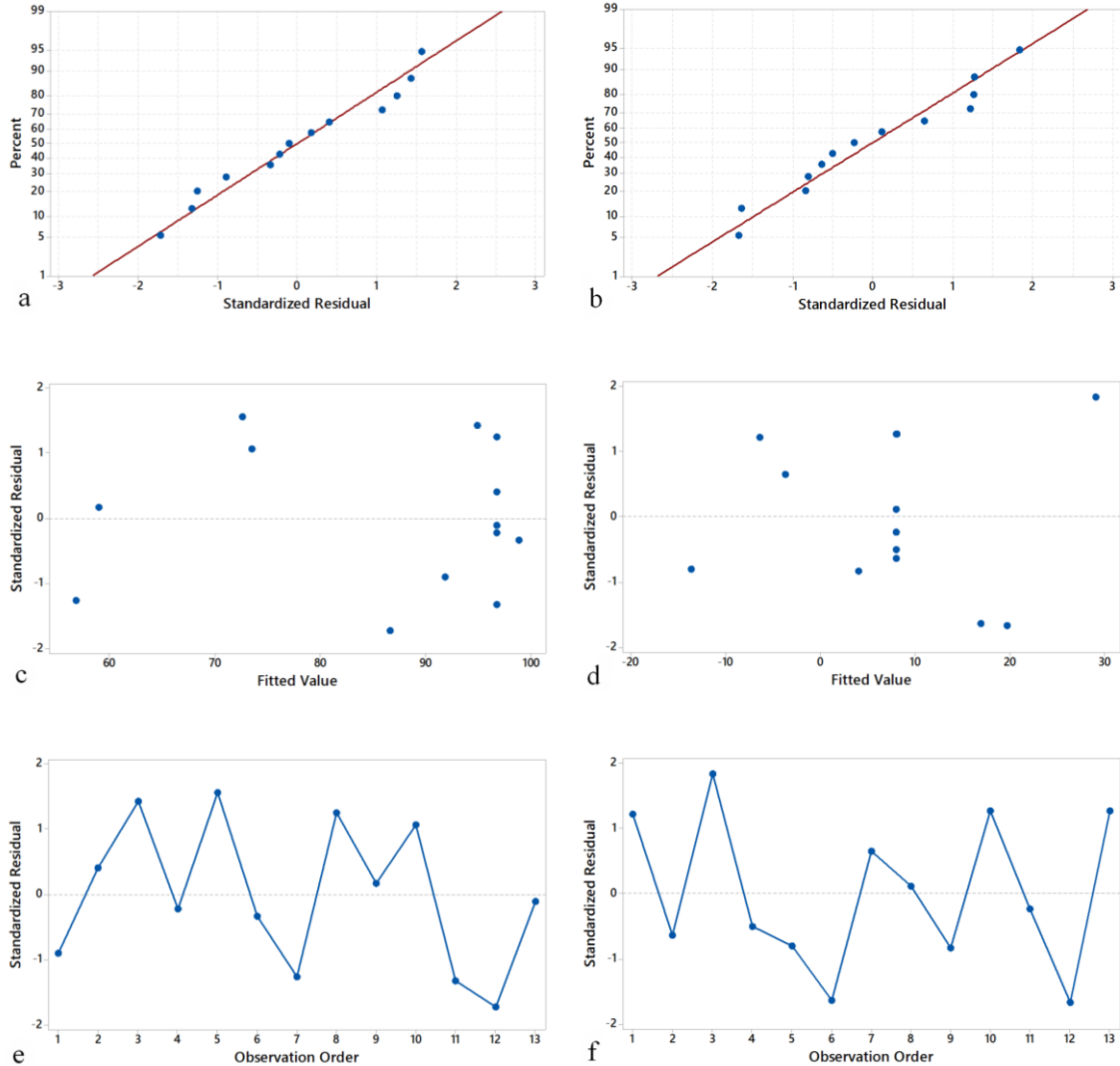


Figure 3.8 Response surface design residual plots: response turbidity removal (a) normal probability plot, (c) residual versus fits and (e) residual versus order; response DOC removal (b) normal probability plot, (d) residual versus fits and (f) residual versus order

By combining the ANOVA results and residual plots, it can be concluded that both second-order models for turbidity removal and DOC removal are significant and adequate.

The 3D response surface and 2D contour plots of the quadratic models for turbidity and DOC removal are presented in Figure 3.9 and Figure 3.10, respectively. As shown in

Figure 3.9 (a), increased turbidity removal was observed with increasing alum dose and pH, but started to decrease at $\text{pH} \geq 8$, which indicates the overdosing of coagulant. Charge reversal could occur when coagulant is overdosed into water, resulting in restabilization of the suspended solids. The contour plot in Figure 3.10 (a) shows that the turbidity removal response has a single optimum point, and the optimal condition was located inside the design boundary. The optimum turbidity removal greater than 95% was obtained with alum dose range from 120 - 190 mg/L, corresponding to pH range from 6.5 - 8.5.

Figure 3.9 (b) illustrates that alum dosage and pH value played important roles in DOC removal. Increased DOC removal was observed with increasing alum dose and decreasing pH value. The contour plot (Figure 3.10 (b)) shows the optimum DOC removal of $\geq 30\%$ occurred for alum dosage of 15-200 mg/L and pH ranging from 5 - 6.5.

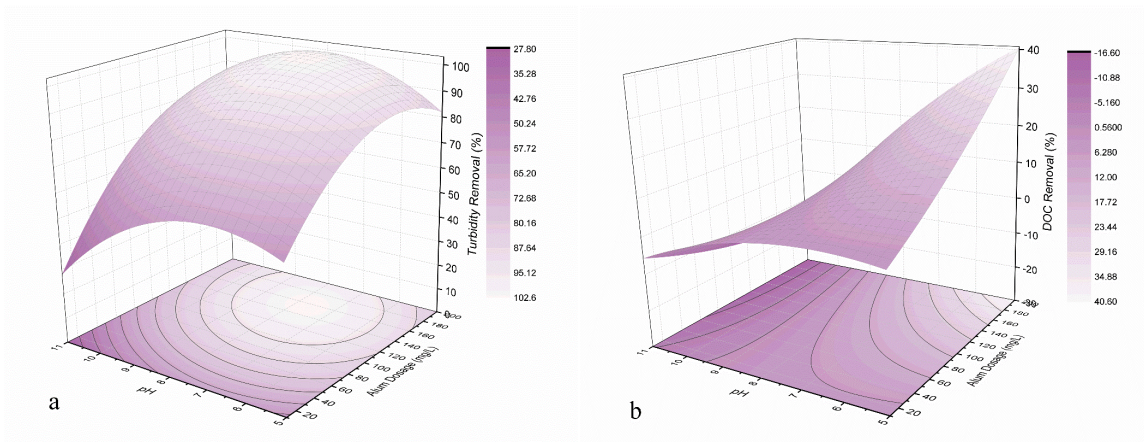


Figure 3.9 Response surface plot for (a) turbidity removal (%) and (b) DOC removal (%) of OSPW after coagulation process by alum. Data fitted by two-factor central composite design

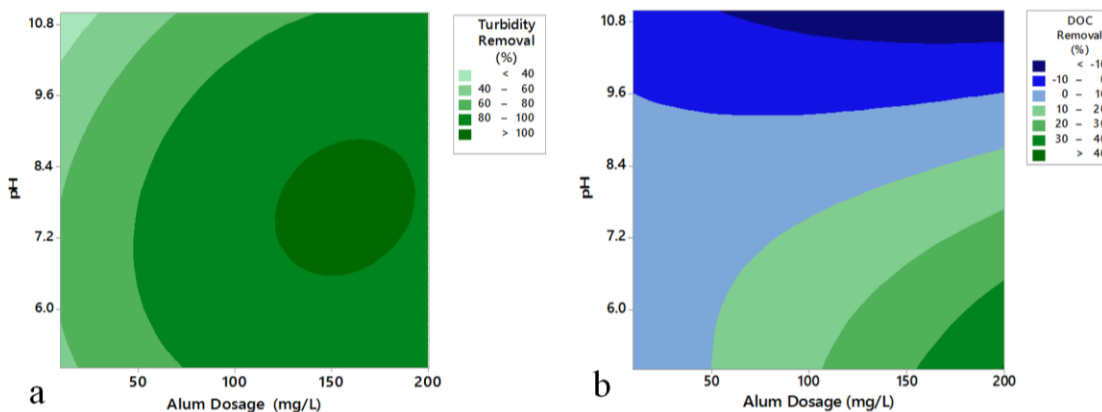


Figure 3.10 Contour plot for (a) turbidity removal (%) and (b) DOC removal (%) of OSPW after coagulation by alum. Data fitted by two-factor central composite design

The turbidity removal and DOC removal are two individual responses, and they have different optimal conditions for maximizing their respective responses. The optimal pH for turbidity removal was higher than that for DOC removal. This is in accordance with the some other studies (Edwards & Amirtharajah, 1985; Trinh & Kang, 2011), where authors observed higher DOC removal at lower pH. Thus, it is necessary to make a compromise between the optimum conditions for both responses. The highlighted area in Figure 3.11 displays the optimum condition which fits the optimization criteria for both responses. The optimum region was visualized graphically to roughly determine whether a condition is suitable for the removal of turbidity and DOC.

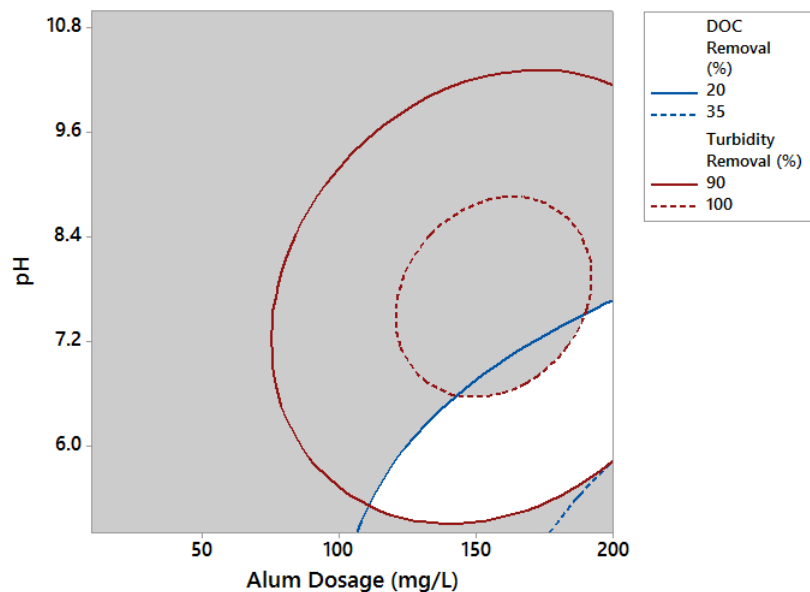


Figure 3.11 Overlaid contour plot for turbidity removal (%) and DOC removal (%) of OSPW after coagulation process by alum. Data fitted by two-factor central composite design

A more precise optimization was conducted using the built-in optimizer in software Minitab 17. The optimization goals and weights for two responses are shown in Table 3.5, and the results are presented in Table 3.6. The optimized condition for maximizing turbidity removal and DOC removal by 1:1 weight is 190.44 mg/L alum and pH 6.32, which achieved the composite desirability by 0.9265. The predicted turbidity and DOC removal was $95.42 \pm 0.92\%$ and $29.58 \pm 0.93\%$, respectively. By repeating the experiments under the optimized condition, as shown in Table 3.7, the actual response was found to be $98.29 \pm 0.16\%$ and $28.46 \pm 0.52\%$ for turbidity and DOC removal, respectively. The optimal dose of alum is higher than the optimal dose of 94.57 mg/L for drinking water treatment reported by Trinh and Kang (2011), but lower than 0.802 g/L for leather dye removal reported by Khayet et al., (2011) and 9.5 g/L for leachate treatment by Ghafari et al., (2009).

Table 3.5 Response Optimization: DOC Removal (%), Turbidity Removal (%)

Response	Goal	Lower	Target	Weight	Importance
DOC Removal (%)	Maximum	-15.28	32.74	1	1
Turbidity Removal (%)	Maximum	57.00	98.80	1	1

Table 3.6 Solution for response optimization

			DOC Removal (%)	Turbidity Removal (%)	
Solution	Alum Dosage	pH	Fit	Fit	Composite Desirability
1	190.436	6.31993	29.5803	95.4134	0.926559

Table 3.7 Predicted response vs. experimental response at optimized condition

Optimized Condition		Turbidity Removal (%)		DOC Removal (%)	
Alum Dosage (mg/L)	pH	Predicted	Experimental	Predicted	Experimental
190.44	6.32	95.42 ± 0.92 %	98.29 ± 0.16 %	29.58 ± 0.93 %	28.46 ± 0.52 %

3.3.2 Natural Coagulant and Optimization

As shown in Figure 3.12 (a), cactus (*Opuntia ficus-indica*) was able to significantly reduce turbidity with removal ranging from 92% to 99%. Residual turbidity levels are between 5 and 7 NTU. The plot of residual turbidity versus coagulant dosage showed that turbidity removal increased with the increased dosage of *Opuntia* mucilage, and there was no overdose in the range of 1000-1300 mg/L. The optimum turbidity removal achieved by natural coagulant is approximately the same achieved by alum proving the coagulation potential of *Opuntia* mucilage.

However, *Opuntia ficus-indica* mucilage could not remove dissolved organic carbon in the preliminary experiments, rather, as shown in Figure 3.12 (b), the DOC of OSPW increased with the increasing *Opuntia ficus-indica* dose. The increase in DOC is due to the fact that mucilage of *Opuntia ficus-indica* contains complex carbohydrate compounds, which will dissolve in water. However, the increase in DOC with increasing dosage of mucilage was marginal. The DOC variation by adding various concentrations of *Opuntia ficus-indica* mucilage in milli-Q water is shown in Figure 3.13. The DOC increase in water follows a linear relationship with the concentration of *Opuntia ficus-indica* mucilage in water. The slope 0.0133 indicated that the increase of DOC is around 10 mg/L per 1000 mg/L OFI mucilage. The DOC value of OSPW after coagulation had a net increase around 7 mg/L per 1000 mg/L OFI mucilage dosed. Although natural coagulant will increase the DOC of OSPW, the percentage increase is not significant because of the high initial DOC of OSPW.

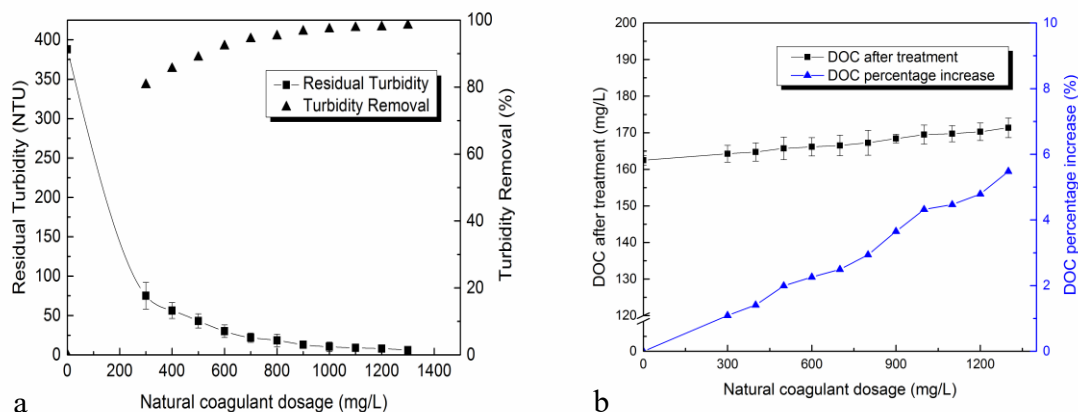


Figure 3.12 (a) Turbidity (NTU) and (b) DOC variation of raw OSPW after coagulation with natural coagulant (*Opuntia ficus-indica*) dosage ranging from 0 to 1300 mg/L and 60-minute settlement at room temperature (20 ± 2 °C) (Standard deviations of triplicate experiments are represented by error bars).

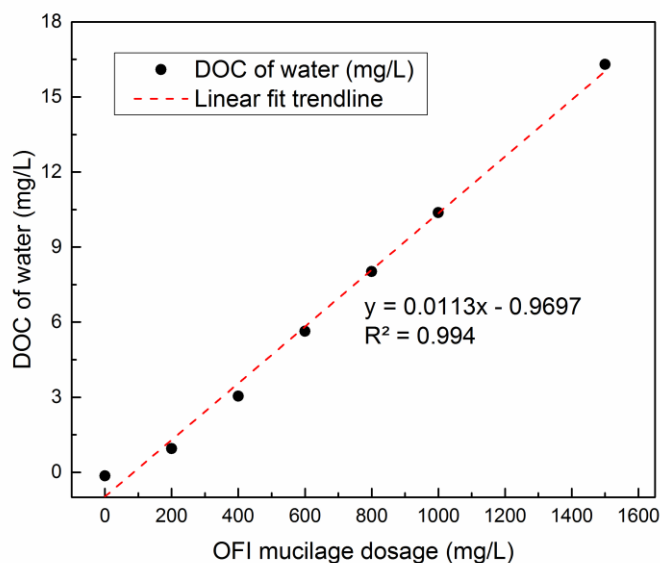


Figure 3.13 DOC variation of Milli-Q water with various *Opuntia ficus-indica* mucilage dosage

FT–IR spectroscopy was used to characterize the surface functional groups present in the OSPW and flocs. The spectra of dried OSPW and flocs formed after treatment with 800 mg natural coagulant are presented in Figure 3.14. The observed spectra of the dried OSPW and OSPW treated with natural coagulant were similar, which indicated the removal of the particulates and compounds from the OSPW into the flocs. The broad absorption band in the region of $3700\text{--}3000\text{ cm}^{-1}$ indicates the presence of -OH functional groups (Stuart, 2004). These might be related either to water in the samples or the hydroxyl groups. Although samples were air dried, the absorption band may be related to the presence of trapped water inside the flocs. Alternatively, the broad absorption band indicating hydroxyl groups may be due to the presence of the oxidized NAs in the dried OSPW and flocs. Spectra for carboxylic acids consist of three absorption bands (Stuart, 2004). An absorption band near 1400 cm^{-1} is characteristic of C–O stretching vibration and the one near 1700 cm^{-1} , is characteristic of C=O stretching vibration. These observations, together with the absorption band of OH groups in the region of $3300\text{--}2500\text{ cm}^{-1}$ indicated the presence of the carboxylic groups in the floc. It also confirmed the presence of NAs and oxidized NAs in the samples.

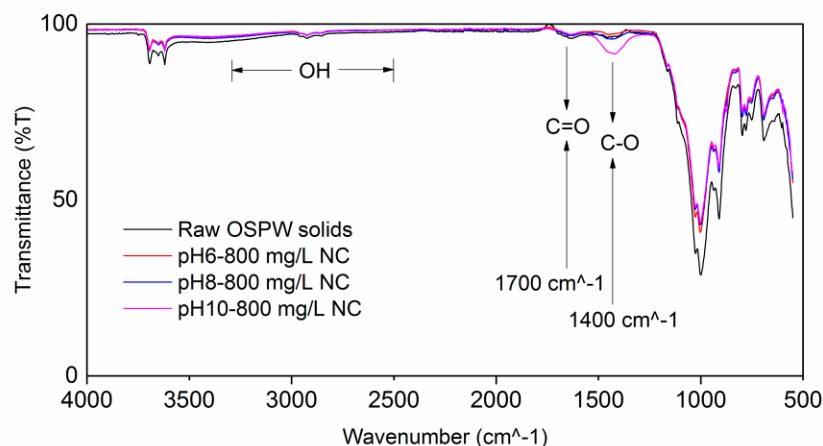


Figure 3.14 FT-IR spectroscopy of raw OSPW solids and floes generated by natural coagulant (NC) after coagulation at different initial solution pH (pH=6, 8, 10), 800 mg/L dosage and 60-minute settling at room temperature (20 ± 2 °C)

The coagulation ability of *Opuntia ficus-indica* mucilage is most likely due to the presence of the complex carbohydrate stored in cactus inner pads having great water retention function (Yin, 2010). Various researchers have studied the chemical composition of the mucilage of *Opuntia ficus-indica*. In general, the mucilage contains variable amounts of L-arabinose, D-galactose, L-rhamnose, and D-xylose, as the main neutral polysaccharide. The presence of D-galacturonic acid is also indicated (McGarvie & Parolis, 1981; Paulsen & Lund, 1979; Sáenz, Sepúlveda, & Matsuhira, 2004). The neutral sugars were found by Trachtenberg and Mayer (1981) in the following ratio: arabinose, 24.6 %; galactose, 40.1 %; rhamnose, 13.1 %; and xylose, 22.2 %. The uronic acid was present as galacturonic acid and determined as 10.7 – 19.5 % content of the purified mucilage by different methods. Miller et al. (2008) conducted the experiment by adding individual components mentioned above to turbid water in isolation and in combination to determine their coagulation ability. The results suggested that galacturonic acid is possibly the major active agent for coagulation capability as it was able to reduce turbidity by more than 50 % independently.

Though not extensively reported in literature, it is highly possible that galacturonic acid exists predominantly in polymeric form that provides the “bridging” between particles

(Okuda, Baes, Nishijima, & Okada, 1999). The possible dominant molecular interactions of adsorption and bridging between polygalacturonic acid and particles in aqueous solution are shown in Figure 3.15 (Yin, 2010). Chemisorption between the partially deprotonated carboxylic functional group and charged particles may occur although this requires further empirical substantiation. The existence of -OH groups along the polymeric chain also implies the possibility of intra molecular interactions which may distort the chain (M. Miller, Fugate, Smith, & Haven, 2008).

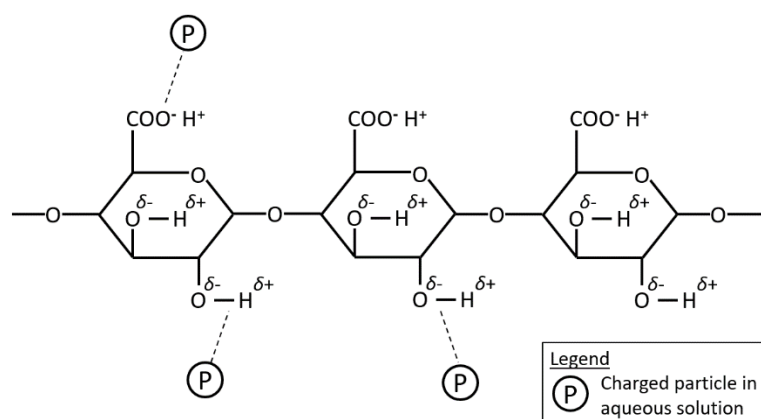


Figure 3.15 Schematic representation of polygalacturonic acid in aqueous solution and possible dominant molecular interactions associated with adsorption and bridging (Yin, 2010)

Because OSPW in tailings ponds is like a soup with complex contaminants, the distribution of the suspended particles is not always uniform. Usually the turbidity of OSPW increases with the depth of tailings pond because of gravity settling. Although the initial turbidity of OSPW involved in treatment usually ranges from 80 to 200 NTU, which is also the range of initial turbidity of the OSPW in this study, it is still necessary to see the effect of initial turbidity. The influence of the initial turbidity on the coagulation efficacy of *Opuntia spp.* was investigated by some researchers. Miller et al. (2008) reported that the residual turbidity levels for water treated with *Opuntia spp.* is between 5 -7 NTU, regardless of initial turbidity. However, each coagulant has an optimal dose that results in the greatest turbidity removal and that varies depending on the water's initial turbidity. As shown in Figure 3.16, the performance of *Opuntia ficus-*

indica at initial turbidity of OSPW at 200 and 300 NTU OSPW was similar, but at 400 NTU, the coagulant dose required to achieve same turbidity removal was much greater than that required for 200 and 300 NTU OSPW.

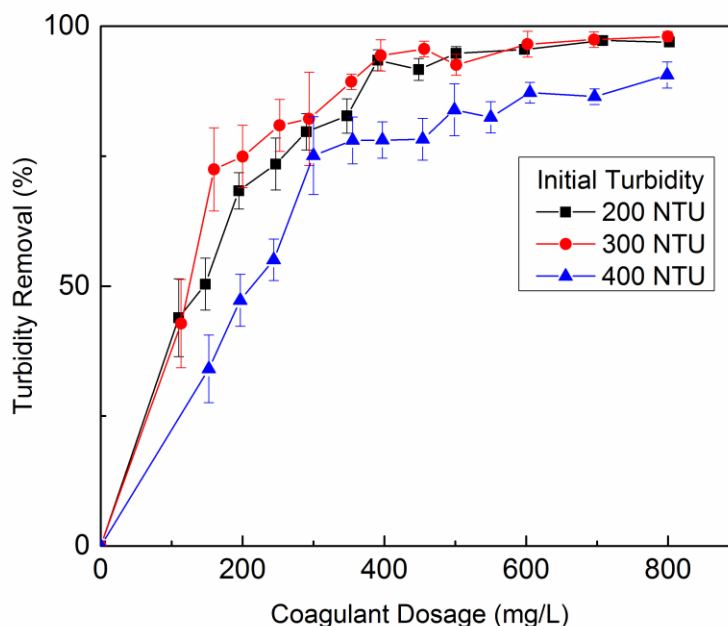


Figure 3.16 Turbidity removal efficiency of raw OSPW with different initial turbidity (turbidity = 200, 300, 400 NTU) after coagulation with natural coagulant (*Opuntia ficus-indica*) dosage ranging from 0 to 800 mg/L and 60-min set settling at room temperature (20 ± 2 °C) (Standard deviations of triplicate experiments are represented by error bars).

The initial pH of water plays an important role in coagulation-flocculation. More than that, since *Opuntia ficus-indica* is a plant-based coagulant, it may also respond to the variation of surrounding pH. The effect of initial pH on the turbidity removal by OFI mucilage is shown in Figure 3.17. The result shows that the maximum turbidity removal occurs at pH=7.5. Both higher and lower pH would reduce the turbidity removal. However, the effect of pH is insignificant on turbidity removal because the variation is within 1%.

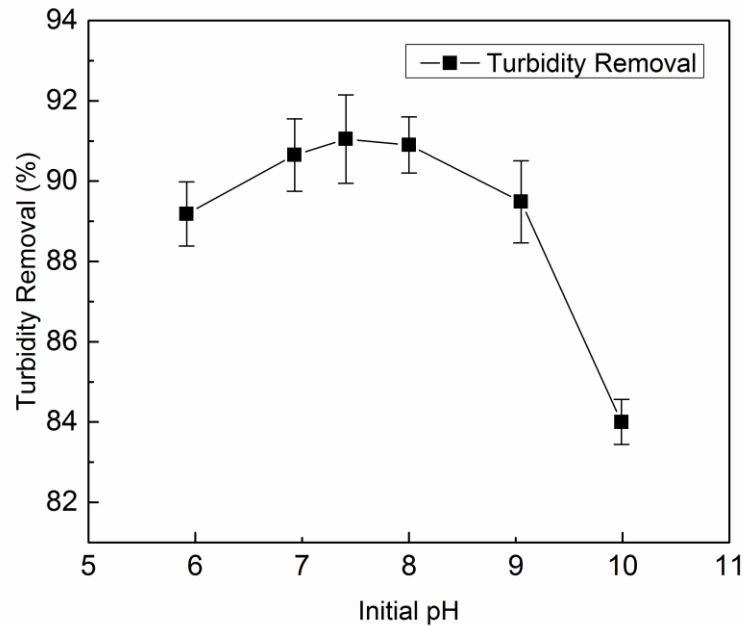


Figure 3.17 Optimal turbidity removal efficiency of raw OSPW with different initial solution pH (pH = 6, 7, 8, 9, 10) after coagulation with 600 mg/L natural coagulant (*Opuntia ficus-indica*) dosage and 60-minute settling at room temperature (20 ± 2 °C) (Standard deviations of triplicate experiments are represented by error bars).

In order to evaluate the effects of dosage and pH, and their interaction on turbidity and DOC removal, a two-factor three-level general full factorial experiment design was applied. Two-factor factorial experiment is the simplest type of factorial experiment. There are a levels of factor A and b levels of factor B. The experiment has n replicates, and each replicate contains all ab treatment combinations. The observation in the ij th cell for the k th replicate is denoted by Y_{ijk} . The observations may be described by the linear statistical model:

$$Y_{ijk} = \mu + \tau_i + \beta_j + (\tau\beta)_{ij} + \epsilon_{ijk} \begin{cases} i = 1, 2, \dots, a \\ j = 1, 2, \dots, b \\ k = 1, 2, \dots, n \end{cases} \quad (5)$$

where μ is the overall mean effect, τ_i is the effect of the i th level of factor A, β_j is the effect of the j th level of factor B, $(\tau\beta)_{ij}$ is the effect of the interaction between A and B,

and ϵ_{ijk} is a random error component having a normal distribution with mean zero and variance σ^2 (D. C. Montgomery, 2003).

The design and data analyses were conducted using software Minitab 17. The variable parameters are pH and natural coagulant dosage; the levels of factors are presented in Table 3.8. As shown in Table 3.9, a total of 18 experiments was conducted in random order to minimize the effect of uncontrolled variables on the responses.

Table 3.8 Actual and coded values of independent variables used for experimental design

Factor	Symbol	Real values of coded levels		
		Low	Intermediate	High
		1	2	3
Dosage(mg/L)	A	200	500	800
pH	B	6	8	10

Table 3.9 General full factorial experimental design for turbidity and DOC removal by natural coagulant (initial turbidity = 180 ± 3 NTU, initial DOC ≈ 160 mg/L)

Std. Order	Run Order	3 ² Design		Results (removal (%))	
		Dosage (A)	pH (B)	Turbidity (Y ₁)	DOC (Y ₂)
17	1	3	2	96.34	3.49
14	2	2	2	92.39	1.31
1	3	1	1	82.63	-5.83
13	4	2	1	92.61	-8.03
16	5	3	1	95.01	-9.03
11	6	1	2	77.13	2.43
8	7	3	2	94.67	2.99
9	8	3	3	92.06	-2.00
12	9	1	3	72.80	0.96

15	10	2	3	86.99	-1.03
7	11	3	1	96.09	-10.09
18	12	3	3	93.25	-3.99
6	13	2	3	86.69	-2.62
10	14	1	1	84.96	-8.26
4	15	2	1	92.31	-7.58
3	16	1	3	69.18	0.07
2	17	1	2	74.67	0.62
5	18	2	2	92.53	2.93

The main effect plots for turbidity removal (Figure 3.18 (a)) illustrate that the turbidity removal from OSPW has a positive correlation to natural coagulant dose and a negative correlation to the initial pH of OSPW. In other words, greater turbidity removal can occur in acidic pH with higher dosage of natural coagulant. However, the main effect plots for DOC removal shows a negative correlation with the natural coagulant dosage. The correlation between DOC removal and pH is positive for the pH range from 6 - 8 and negative between pH 8 - 10.

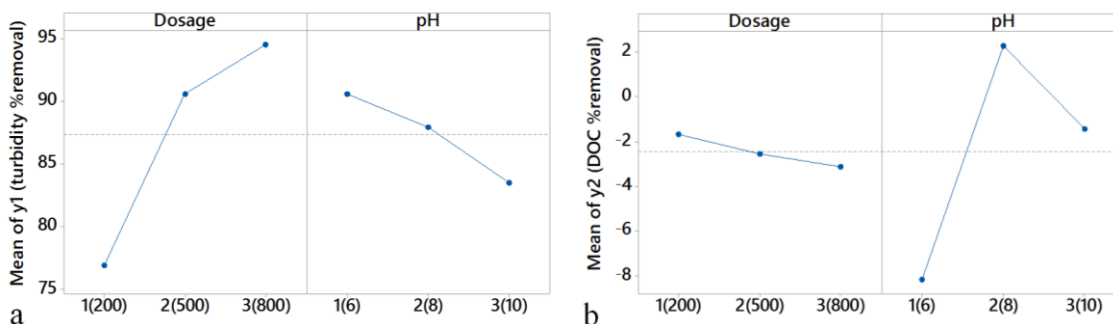


Figure 3.18 Main effects plot for turbidity removal (a) and DOC removal (b) Data fitted by two-factor three-level general full factorial experiment design for natural coagulant at room temperature (20 ± 2 °C)

The interaction plot indicates the relationship between two factors. The parallel lines in interaction plot indicate no interaction whereas nonparallel lines indicate an interaction. The more nonparallel the lines are, greater the strength of the interaction is (Minitab, 2016). In Figure 3.19, the lines are not parallel but not significantly different in slope.

This indicated that for both responses, turbidity and DOC removal, the interactions between coagulant dosage and pH exist but the degree of interactions are not statistically significant.

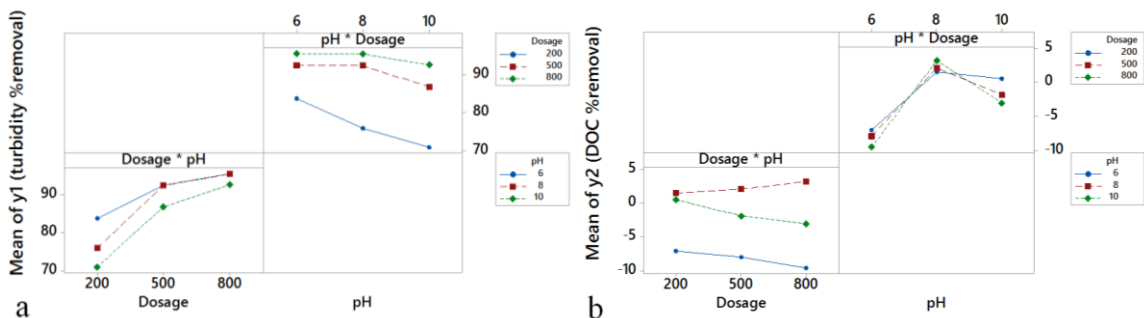


Figure 3.19 Interaction effects plot for turbidity removal (a) and DOC removal (b) Data fitted by two-factor three-level general full factorial experiment design for natural coagulant at room temperature (20 ± 2 °C)

The optimization of experimental conditions for *Opuntia ficus-indica* mucilage was conducted in two different ways. Firstly, the aim of optimization was to maximize both turbidity and DOC removal, the optimum condition was 781.8 mg/L OFI mucilage dose and pH 8.3 resulting in 94.42% turbidity removal and 2.61% DOC removal. Another way of optimization was aiming to minimize residual turbidity and DOC, in which the acidic pH is preferred because the DOC of OSPW can be reduced by lowering the pH. The solution for this objective was 500 mg/L OFI mucilage and pH 6.0, resulting in 12 NTU residual turbidity (initial turbidity ~ 180 NTU) and 75.06 mg/L residual DOC (initial DOC ~160 mg/L); this seems to be a better solution as 54% DOC removal occurred.

3.3.3 Performance Comparison of Coagulants

The comparative performance of both the coagulants is summarized in Table 3.10.

Table 3.10 Optimal conditions for coagulants and the corresponding results

	Optimal Condition		Results			
Coagulant	Coagulant Dose (mg/L)	Solution pH	Turbidity removal (%)	DOC removal after	Additional DOC removal	Total DOC

				acidification (%)	after coagulation (%)	removal (%)
Alum	190.44	6.32	98.29	36.70	28.46	58.60
<i>Opuntia ficus-indica</i>	500	6.00	93.33	55.63	-7.80	53.09

Note: Total DOC removal = 1-DOC after pH adjustment and coagulation/ Initial DOC

The total DOC removal is the fraction of DOC reduced by pH adjustment and coagulation. In this study, by adjusting the pH of OSPW from initially around 8.5 to 6, the DOC of water was reduced by around 50%. As mentioned earlier, acidification was also found to induce rapid settling, and remove a large fraction of the dissolved organic carbon (DOC) and toxicity in process water (Hall & Tollefson, 1979; M. D. MacKinnon & Retallack, 1981). Similar study by Marr et al. (1996) found that 36-38.67% of the extractable organic fraction (EOF) was removed from consolidated tailings (CT) water by acidification and sand filtration, and the removal was 44-50.67% using acidification followed by coagulation and sand filtration.

The results in Table 3.10 show that both alum and *Opuntia ficus-indica* mucilage have excellent performance on turbidity removal, however, DOC removal was insignificant by both the coagulants. The total DOC removal by coagulation using alum was slightly higher than that using OFI. Although majority of the DOC removed from OSPW was done by acidification, alum coagulation could further reduce the DOC of OSPW by 30%. Unlike alum, *Opuntia ficus-indica* did not make a significant change to the DOC of water.

The microscopy image (Figure 3.20) supports the hypothesis that the predominant coagulation mechanism for *Opuntia ficus-indica* is bridging and adsorption, whereby the particles in aqueous solution are bounded to the polymer-like material instead of directly contacting one another. Unlike the flocs formed by alum, which are somewhat spherical in shape, the flocs formed by *Opuntia ficus-indica* are long, heterogeneous in shape, distorted and threadlike. The threadlike flocs start to form and become clearly visible within one-minute of rapid mixing (150 rpm), and grow in length and circumference

during the slow mixing. By comparing their darkness, the flocs formed by *Opuntia ficus-indica* (Figure 3.20 a) are denser than those formed by alum (Figure 3.20 b).

Furthermore, the average diameter of flocs formed by *Opuntia* (Figure 3.20 a) is greater than those formed using alum (Figure 3.20 b). The bulky and dense flocs formed by natural coagulant are able to settle faster and decrease the settling time, which is another advantage of natural coagulant over the alum.

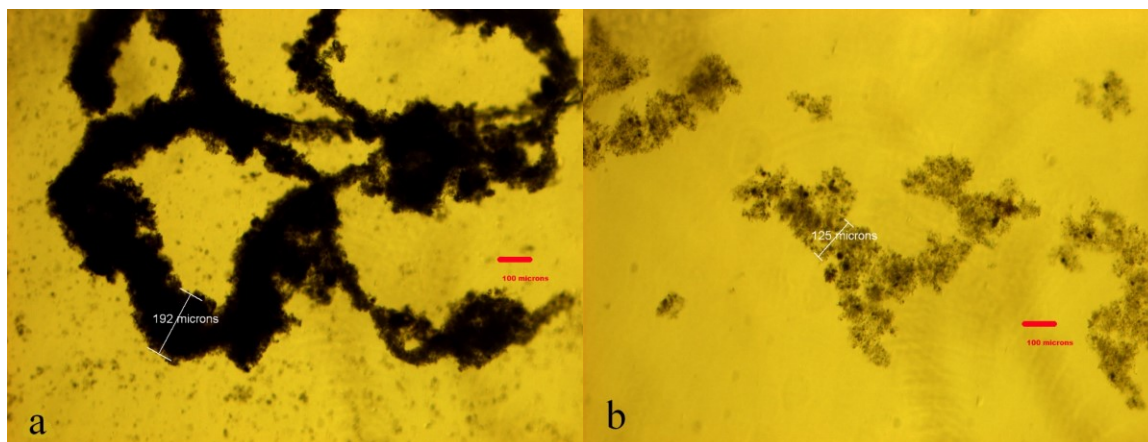


Figure 3.20 OSPW coagulation flocs formed by (a) *Opuntia ficus-indica* and (b) Alum

3.3.4 Adsorption of DOC in Coagulated Effluent

Activated carbon was shown to significantly reduce DOC concentrations in oil sands process-affected water (Hall & Tollefson, 1979). The effect of adsorption on the treatment of coagulated water is presented in this section. However, activated carbon adsorption did not show a capability to reduce turbidity of water. Thus, the turbidity variation is not discussed in this section.

The typical DOC concentration versus time plot for the adsorption of non-pretreated OSPW is shown in Figure 3.21. It can be seen that for all the adsorbent dosages, the DOC value of non-pretreated OSPW dropped drastically in 300 minutes, then slowly decreased and remained constant as adsorption equilibrium was attained. There was no obvious decrease in DOC after 1440 minutes (24 hr), which is the time applied for all the rest of

the adsorption experiments to ensure they reached the equilibrium. Rather, there is a small increase in DOC concentration after 24 hr due to the desorption of DOC from OSPW.

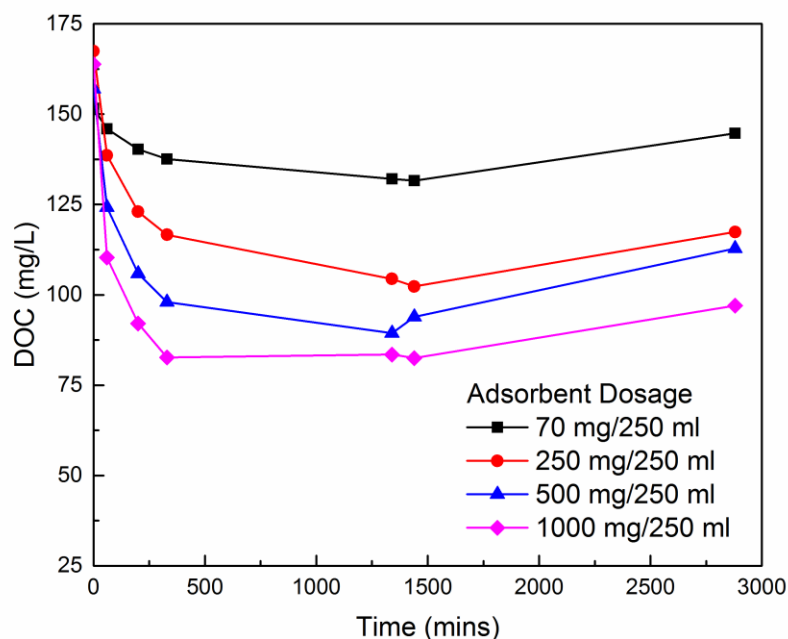


Figure 3.21 DOC change with time in typical adsorption experiment. (Non-pretreated OSPW. Granular activated carbon dosage: 0.28, 1.0, 2.0, 4.0 g/L. Sample collecting time: 0, 60, 200, 300, 1340, 1440, 2880 minutes)

Since natural coagulant was not effective in the removal of DOC from OSPW, activated carbon adsorption was conducted after bio-coagulation. The effects of both natural coagulation and adsorption on DOC of OSPW are shown in Figure 3.22, 23, and 24. The experiments were conducted with an intermediate dosage (200, 500, and 800 mg/L) of *Opuntia ficus-indica* mucilage. The DOC value reduced after adsorption, and the decrease of the coagulation-treated groups is greater than the decrease of control group. The DOC of OSPW dropped from initially around 160 mg/L to 51.40 mg/L after pH adjustment, coagulation with 500 mg/L OFI mucilage and 24-hr adsorption with 0.28 g/L granular activated carbon. Although with the addition of OFI mucilage DOC increased in

water, coagulation aids to have better activated carbon adsorption to achieve higher DOC removal. Similar trend occurred at different pH including pH 8 and 10. From Figure 3.25, it can be concluded that the advantage of coagulation was more significant when alum was used as coagulant improving the performance of activated carbon for final polishing of the effluent.

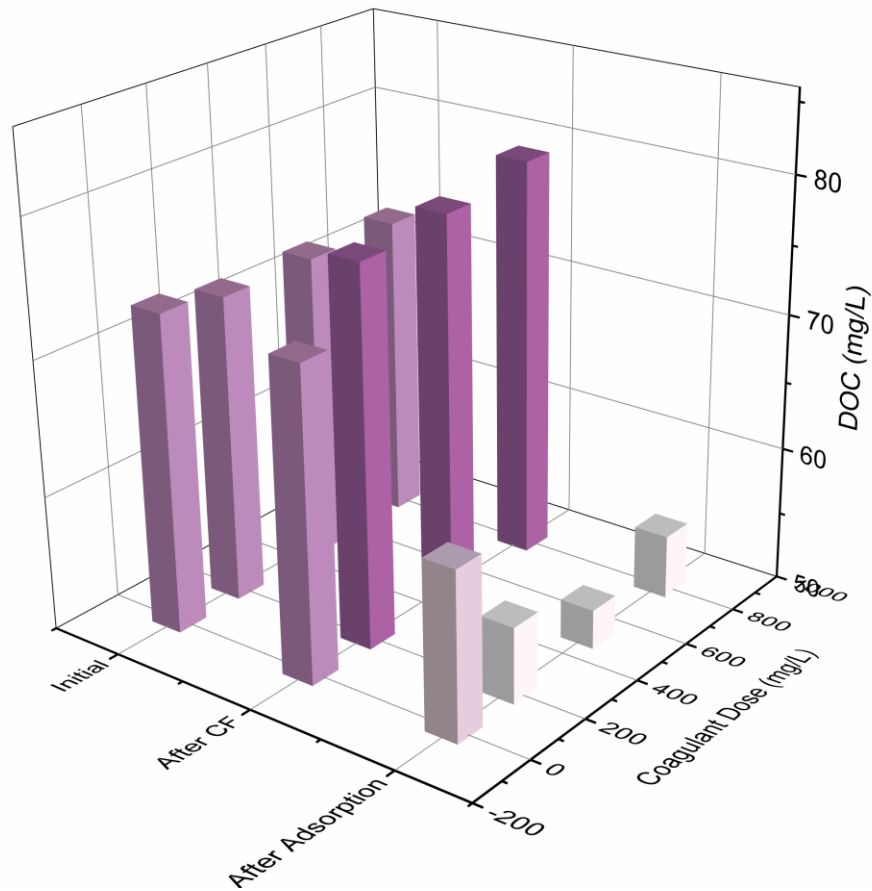


Figure 3.22 DOC variations of raw OSPW after pH adjustment, coagulation in various conditions (pH = 6, natural coagulant dosage = 0, 200, 500, 800 mg/L) and constant condition adsorption by 0.28 g/L of granular activated carbon

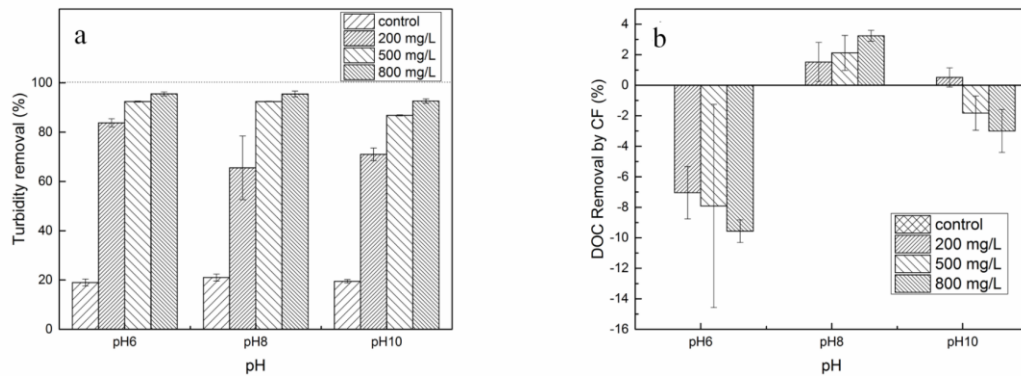


Figure 3.23 Turbidity removal (a) and DOC removal (b) of raw OSPW after coagulation in various conditions (pH = 6, 8, 10, natural coagulant dosage = 0, 200, 500, 800 mg/L)

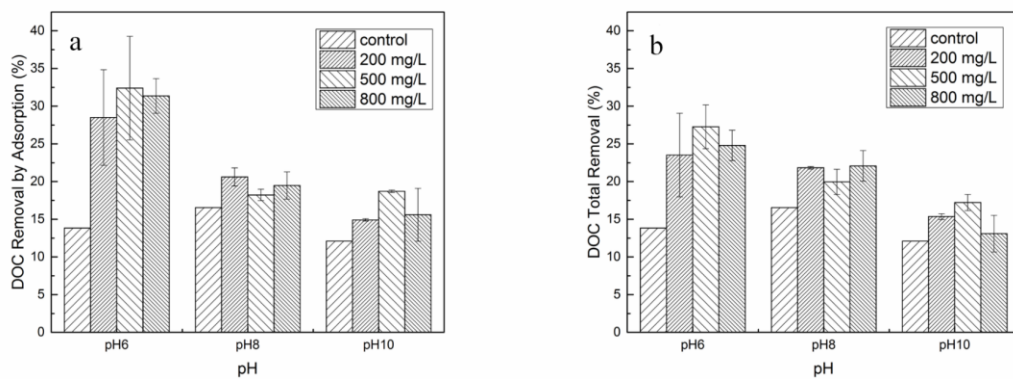


Figure 3.24 DOC removal of raw OSPW before and after adsorption (a) and total removal (b) by coagulation and adsorption

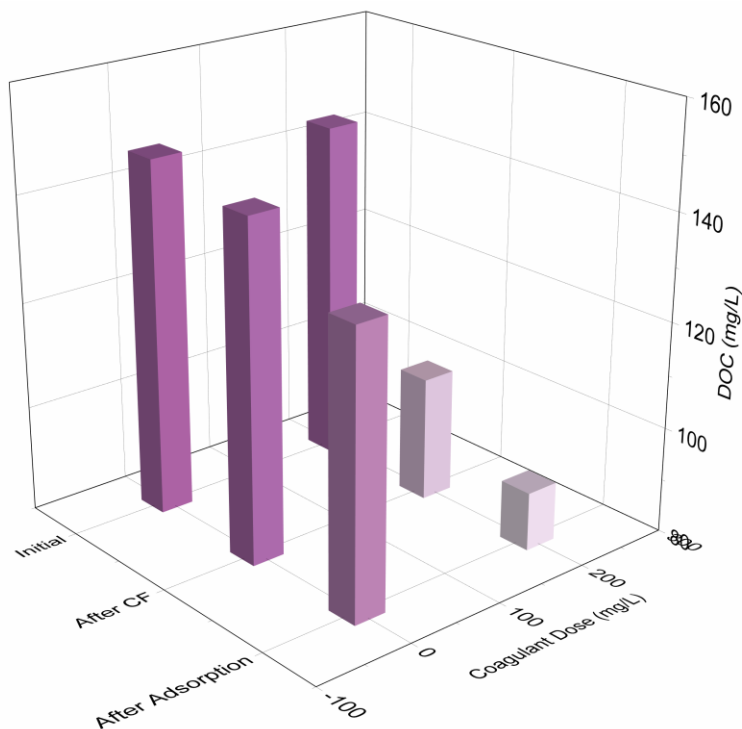


Figure 3.25 DOC variations of raw OSPW after coagulation using alum on optimal condition (pH = 6.32, alum dosage = 190.44 mg/L) and 24-hr adsorption by 0.28 g/L of granular activated carbon

The adsorption isotherm data for the dissolved organic carbon (DOC) adsorption from non-treated OSPW experiments were fitted using nonlinear regression methods in OriginPro. The model parameters were initially determined using linear form equations (as shown in Table 3.11) for the adsorption models. However, the model parameters obtained by linear regression did not fit the experimental data better than those obtained by nonlinear regression using OriginPro. Thus, linear regression results will not be discussed in this section but are attached in Appendix C.

In order to determine the goodness of fit, the OriginPro reports several statistical tests to measure the fit result, including reduced chi-square, residual sum of squares, adjusted r-square. When performing nonlinear curve fitting, an iterative procedure is employed that minimizes the reduced chi-square value to obtain the optimal parameter values. The reduced chi-square is obtained by dividing the residual sum of squares (RSS) by the degrees of freedom (DOF). Although this is minimized in the iteration process, this

quantity is typically not a good measure to determine the goodness of fit. For example, if the y data is multiplied by a scaling factor, the reduced chi-square will be scaled as well.

A better measure would be the r square value, which is also known as coefficient of determination and r-square close to 1 indicates goodness of fit. The adjusted r-square value accounts for the degrees of freedom and this could be a better measure of the goodness of fit. The adjusted r-square results for isotherm models are tabulated in Table 3.11 and used for comparing the fit results.

There are statistical tests that OriginPro provides, to compare the fit results to a single dataset using different models. The models resulting in a best fit for isotherms at each pH are presented in Table 3.12. The isotherm curve plots are presented in Figure 3.26.

Table 3.11 Isotherm parameters of Langmuir, Freundlich and Sips models

	Langmuir			Freundlich			Sips (Langmuir-Freundlich)			
General form	$q_e = q_m \frac{K_L C_e}{1 + K_L C_e}$			$q_e = K_f C_e^{\frac{1}{n}}$			$q_e = q_m \frac{(b C_e)^{1/n}}{1 + (b C_e)^{1/n}}$			
Linear form	$\frac{1}{q_e} = \frac{1}{q_m K_L} \frac{1}{C_e} + \frac{1}{q_m}$			$\log(q_e) = \log(K_f) + \frac{1}{n} \log(C_e)$			$\ln \frac{q_e}{q_m - q_e} = \frac{1}{n} \ln(C_e) + \ln \left(b \frac{1}{n} \right)$			
	K_L	q_m	R^2	K_f	n	R^2	b	q_m	n	R^2
pH=2	0.2409	89.74	0.874	29.77	3.433	0.882	0.0416	151.24	2.138	0.854
pH=4	0.0296	187.78	0.945	10.57	1.662	0.954	No fit			
pH=6	0.1049	39.46	0.969	10.85	3.651	0.975	0.0478	51.68	1.658	0.990
pH=8	0.0122	78.74	0.982	3.65	1.896	0.968	0.0093	88.87	1.114	0.977
pH=10	No fit			No fit			No fit			

Table 3.12 Models that provided the best fit for isotherm adsorption experiments

pH	2	4	6	8	10
Best fit model	Freundlich	Freundlich	Langmuir-Freundlich	Freundlich	No fit

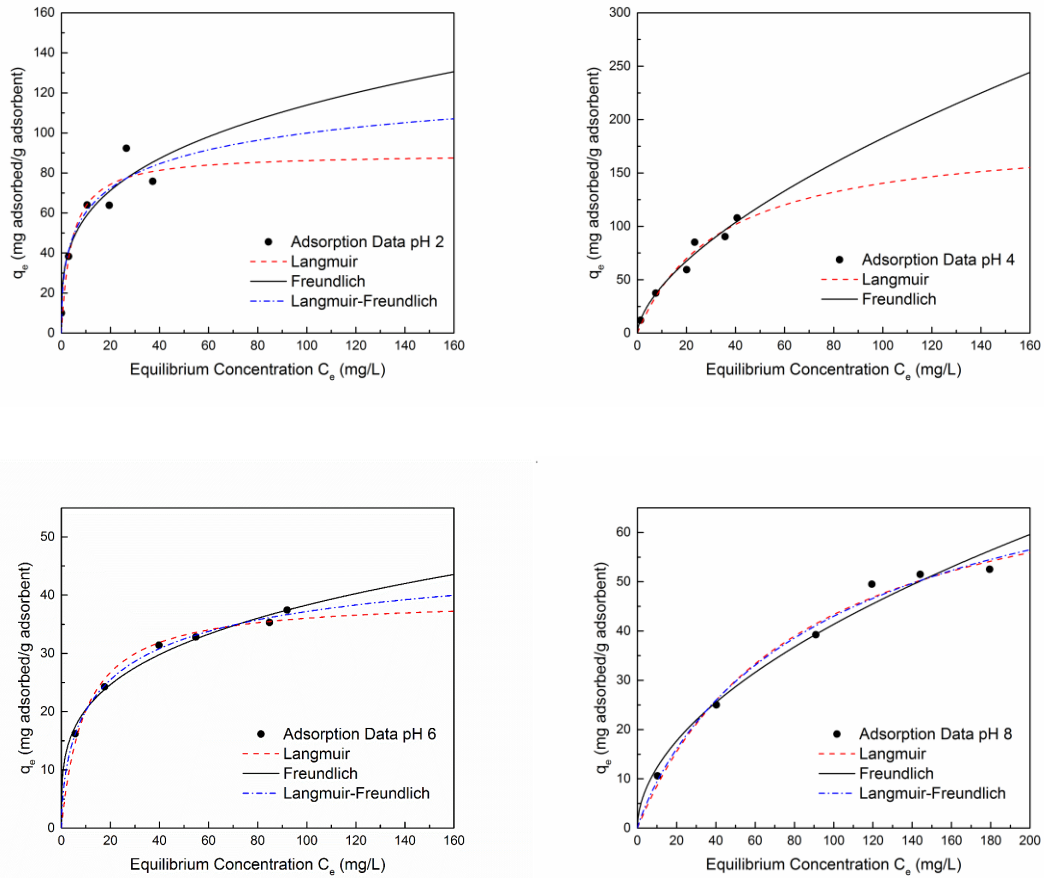


Figure 3.26 Adsorption isotherm curves of dissolved organic carbon (DOC) in non-treated OSPW – pH = 2,4,6,8

The adsorbent saturation capacity, q_m (mg DOC adsorbed/ g adsorbent), was calculated and tabulated in Table 3.13. The calculated values presented for the Freundlich and Langmuir-Freundlich models are the values of q_e at $C_e = C_0$ (the initial DOC concentrations of OSPW are different at different pH). These values are thus assumed to be the saturation capacity, q_m . The values in bold correspond to the saturation capacity of the best fit model for the respective experiment. The maximum saturation capacity q_m is much lower than the one of single compound adsorption reported by Martinez-Iglesias (2015) because of the competition of the background organics.

Table 3.13 Calculated saturation capacity q_m of Langmuir, Freundlich and Sips models

	Langmuir	Freundlich	Langmuir-Freundlich
pH	q_m	q_m	q_m
2	84.55	<i>101.57</i>	93.55
4	133.82	<i>151.77</i>	No fit
6	36.23	39.02	<i>37.62</i>
8	55.89	<i>59.77</i>	56.55
10	No fit	No fit	No fit

For all the models, the maximum adsorption saturation capacity was found at pH 4, although the Langmuir-Freundlich model did not fit the experimental data at pH 4. The finding agrees with the results found by Martinez-Iglesias (2015) that the adsorption capacity for single naphthenic acid compound was maximum at pH 4, and adsorption of DOC in OSPW decreased with increasing pH. Similar reductions in adsorbent capacities with increased pH have been found with other organic compounds (Y. S. Al-Degs, El-Barghouthi, El-Sheikh, & Walker, 2008; Newcombe, Hayes, & Drikas, 1993). It is also reported by Marr et al. (1996) that acidification is required to effectively adsorb naphthenic acids, the toxic component of DOC in process water. Thus, the pH adjustment is necessary to achieve effective activated carbon adsorption.

The reduction in adsorptive capacity with increasing pH may be explained by the surface charge of the activated carbon (Martinez-Iglesias, 2015). At $pH < pHPzc$, the net surface charge of activated carbon is positive while at $pH > pHPzc$ the surface charge is negative (Y. Al-Degs, Khraisheh, Allen, & Ahmad, 2000). It is believed that the un-dissociated acids have a preferential attraction to the positively charged surface at low pH due to hydrophobic interactions (Martinez-Iglesias, 2015). However, in this work there is an optimum pH where maximum adsorption occurs, which was not the case with pure naphthenic acids where there was a monotonic decrease in adsorption with the increase in pH. Due to the complex nature of OSPW, which is a mixture of organics with different polarity, it is natural to have an optimum pH for adsorption.

The adsorption capacities at equilibrium (q_e) of DOC in treated OSPW ($\text{pH} \approx 6$) by alum and *Opuntia ficus-indica* at their optimal conditions were calculated to be 47.43 mg/g at $C_e=92.72$ mg/L and 84.18 mg/g at $C_e=55.73$ mg/L (calculation is presented in Appendix A.2). If these two adsorption data are superimposed on the adsorption isotherm of non-treated OSPW at $\text{pH}=6$, it shows they locate above the curve, indicating the higher adsorption capacity of activated carbon when the OSPW is pre-treated. Due to coagulation, a large fraction of color, odor, turbidity and colloidal and suspended particles in OSPW are removed, reducing their competition for adsorption.

3.5 Conclusions

The results of this study demonstrate the feasibility of coagulation-flocculation-sedimentation as a pretreatment process for oil sands process-affected water. Both alum and *Opuntia ficus-indica* mucilage can be applied as effective coagulants for the removal of turbidity of OSPW, although the natural coagulant was not effective in removal of the DOC or rather there was about 1% increase in DOC due to the solubilization of carbohydrates from mucilage of *Opuntia ficus-indica*. However, acidification and subsequent treatment using activated carbon could remove the DOC by 62-67%. Alum showed good performance on both turbidity and DOC removal. The acidification, followed by coagulation using 190.4 mg alum/L and adsorption decreased DOC of OSPW by 63%. The structure of flocs generated from alum and OFI mucilage indicated that OFI mucilage has a stronger capability to capture suspended particles and form denser flocs with less sludge volume.

The adsorption isotherms conducted at different initial pH indicated that activated carbon has better performance on DOC removal at lower pH. The adsorption capacity of activated carbon for DOC was higher if the OSPW was pre-treated by coagulation.

3.6 References

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Chapter 4

4 Oil Removal from Bilge Water Using Coagulation-Flocculation Process

4.1 Introduction

The discharge of oil-containing wastewater to the environment is increasing every year due to industrial development. Oils as the common pollutant in wastewater can be found as fats, lubricants, heavy hydrocarbons (grease, crude oil, diesel oil and tars), and light hydrocarbons (gasoline, jet fuel and kerosene). The sources of oily wastewater are from a wide range of industries such as petrochemicals, food manufacturing, metal-finishing, leather tanning, etc. Besides industries, marine transportation is also responsible for oil pollution in aquatic environment. The bilge water that is stored at the bottom of ship is mixture of fresh water, sea-water, free and emulsified oil, sludge, chemicals and particulates. More specifically, it contains oil and grease, detergents, aluminum shavings, plastic shreds/shards, dissolved heavy metals and suspended solids. Unlike free or floating oil spilled in sea, bilge water contains oil-in-water emulsions among their basic contaminants. The presence of emulsified oil in wastewater is of real concern as it often results in fouling of process equipment creating problems during treatment of such wastewater.

In the United States, bilge water production is estimated over 5 million cubic meters per year. The oil and grease are mixed with the sea-water, which affect many marine species. Because of the vulnerability of planktons, which are a basic food source in the seas, the species can be harmed by the presence of oil and grease, which will ultimately have adverse effects on all the other links in the food chain, and eventually affecting many marine species. Appropriate treatment methods of bilge water are needed for meeting marine discharged standards MARPOL 73/78 (oil concentration less than 15 ppm in discharge water).

The conventional methods widely used for bilge water treatment are physical processes such as gravity separation, gas floatation, cyclone separation, centrifugation and filtration. Because major part of the oil in bilge water is present as emulsified oil, pure

physical methods often fail to satisfy the targeted treatment levels (Caplan et al., 2000; Woytowich et al., 1993). Their studies indicated that emulsified oil droplets smaller than 20 μm were not removed by means of conventional oil/water separation processes. Hence, demulsification by chemical coagulation is important before any physical treatment can be applied. Demulsification can be obtained by coagulating the suspended oil in water.

Chemical treatment can be used for the removal of suspended and colloidal oil from oily wastewater by agglomerating oil droplets. By adding chemical in oil-water emulsion system, larger oil droplets can be generated, resulting in better performance of following physical separation techniques, such as oil skimming and floatation.

A schematic diagram (Figure 4.1) illustrates the continuous process plan of coagulation. The large droplets in bilge water will either float to top layer or settle with the aids to the tank bottom after sedimentation. They can be collected by skimming and recycled as the lubricant for mechanical equipment. The residual oil present in middle layer water will be treated by additional treatment in downstream processes. The oil concentration in middle layer is measured in order to examine the performance of coagulation process.

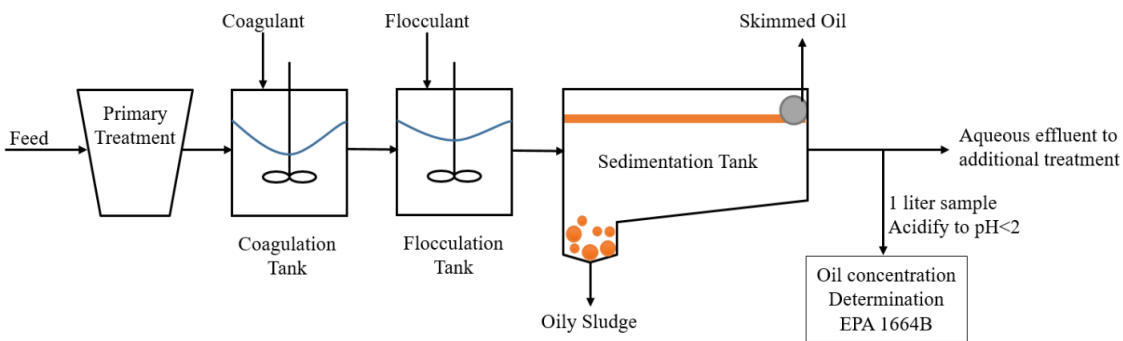


Figure 4.1 Schematic diagram of continuous coagulation design for bilge water treatment

The conventional coagulants widely used in municipal wastewater and industrial oily wastewater are multi-valent metallic salts such as AlCl_3 , $\text{Al}_2(\text{SO}_4)_3$, FeCl_3 , CaCl_2 , FeSO_4 , etc. The addition of coagulants has two main effects: (i) to compress the thickness of the

double layer around the colloids, (ii) and neutralize the surface charge. After coagulation, the larger oil droplets are formed which float to the top, which are consequently easier to be removed by physical techniques.

Theoretically, sodium chloride can achieve the same performance as high valence salts but large amount is required for the same degree of coagulation using alum, and resulting in brackish effluent. This is the reason why it is not a practical universal coagulant. However, in the case of bilge water treatment on-board of a ship, the effluent is discharged into open sea. In addition, sodium chloride is abundant and easily available in marine environment. Even the seawater can be used to coagulate oil-water emulsion due to its high salinity of about 3.5%. Sodium chloride is less harmful to the environment compared to alum and also is less expensive. However, there is no documented research on the effect of coagulation on oil-water emulsion using sodium chloride.

The objective of this study was to investigate the feasibility of sodium chloride as a coagulant to agglomerate oil droplets and determine the optimal working dose. The performances of sodium chloride and widely used coagulant alum are also compared.

4.2 Materials and Methods

4.2.1 Chemical Reagents

Three type of oil samples were provided by Aircraft Appliances and Equipment Limited, Brampton, ON. The synthetic bilge water was prepared as mentioned in section 4.2.2. Alum (aluminum sulfate hydrate, degree of hydration, 14-18), calcium silicate and calcium carbonate were purchased from Sigma-Aldrich Canada Co. (Oakville, Ontario, Canada). Sodium chloride ($\geq 99.0\%$) was purchased from Fisher Scientific (Hampton, New Hampshire, United States). All chemicals used in this project were of analytical reagent grade. All working solutions were prepared in Milli-Q water obtained from a Milli-Q Integral A10 purification system (Millipore SAS, 67120 Molsheim, France).

4.2.2 Preparation of Synthetic Bilge Water

Three oil samples MIL-PRF-16884 Diesel Fuel, MIL-PRF-17331 Steam Lube Oil, and MIL-PRF-9000 Diesel Lube Oil were provided by Aircraft Appliances and Equipment Limited (Brampton, ON). A mixture of the three oil samples called Navy Oil Mix #4 was prepared in the ratio of 50 wt% MIL-PRF-16884 Diesel Fuel, 25 wt% MIL-PRF-17331 Steam Lube Oil, and 25 wt % MIL-PRF-9000 Diesel Lube Oil in accordance with the influent requirement in an internal Engineering Report ER-2436 for Navy Bilge Water filtration systems provided by Aircraft Appliances and Equipment Limited. In order to produce a stable emulsion of oil in water, Detergent mix #4 consisting of 50% general purpose detergent and 50% commercial liquid laundry detergent was used with oil –water suspension. The Navy Oil Mix #4 and Detergent Mix #4 were sealed and stored avoiding sunlight at room temperature.

The synthetic bilge water was prepared using 100 ppm Navy Oil Mix #4 and 25 ppm Detergent Mix #4. The volume of synthetic bilge water for each preparation depends on the total amount of solution needed for each treatment. The preparation method described below is applicable for water volume from 1 to 20 liters. After loading 100 ppm Navy Oil Mix #4 and 25 ppm Detergent Mix #4 in Milli-Q water in a closed container, the mixture was mixed immediately at room temperature using a magnetic stirrer at speed of 200 ± 20 rpm. During mixing, vortex in water should be avoided. The standard mixing duration of 24 hr was determined empirically for oil with 0.1 g/L loading (Singer, Aurand, Bragin, & Clark, 2000). The synthetic bilge water should be used as soon as possible after mixing.

4.2.3 Preparation of Coagulants and Aids

Sodium chloride and coagulation aids such as calcium silicate and calcium carbonate were dosed directly into solution during the coagulation treatment.

10.00 g of aluminum sulfate hydrate was dissolved in 1 liter milli-Q water to make a 1 % alum solution. The concentrations of aluminum sulfate hydrate (the degree of hydration was assumed to be 14), aluminum sulfate anhydrous, and aluminum ion were calculated to be 10^4 mg/L, 0.576×10^4 mg/L, and 9.1×10^2 mg/L, respectively. The dosage value discussed in this dissertation was the concentration of aluminum sulfate hydrate.

4.2.4 Batch Coagulation-Flocculation Experiments – Jar Tests

Unlike the continuous process showed in Figure 4.1, the batch coagulation-flocculation and sedimentation processes were conducted in the same tank using the jar tester. The experimental procedures are presented in Figure 4.2.

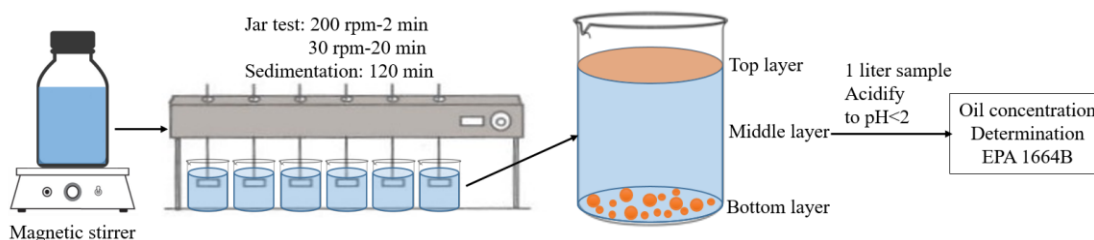


Figure 4.2 Schematic diagram of batch coagulation experiments for bilge water treatment

A Phipps & Bird PB-900 programmable jar tester (Richmond, VA, USA) was used to perform bench-scale batch jar tests using 1 liter of synthetic bilge water at room temperature (20 ± 2 °C). The rapid mixing and slow mixing were to perform coagulation and flocculation process, respectively. The rapid mixing started immediately after adding coagulants to jars. For coagulation, the jar tester was set as rapid mixing with 200 rpm of paddle speed for 2 minutes; and for flocculation, the jar tester was set as slow mixing with 30 rpm of paddle speed for 20 minutes. After flocculation, the contents of the jars were allowed for sedimentation for 120 minutes. This duration was used for all the subsequent sedimentation experiments. Middle layer of water in the jar containing residual oil was siphoned to another vessel without disturbing the top layer of floated oil and bottom layer of oil sludge. Approximately, 30 ml of middle layer water was collected for turbidity and DOC determination; the rest was collected for oil concentration determination by EPA method 1664B: n-Hexane Extractable Material (HEM) and Silica Gel Treated Hexane Extractable Material (SGT- HEM).

4.2.5 Analytical Methods

The oil and grease concentration of the synthetic bilge water samples was measured using EPA method 1664B: n-Hexane Extractable Material (HEM) and Silica Gel Treated Hexane Extractable Material (SGT- HEM). N-hexane extractable material (HEM) refers to the material that is extracted from a sample using n-hexane as extraction solvent measured gravimetrically, otherwise known by the common name “oil and grease”. This material includes relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related matter. Silica gel treated n-hexane extractable material refers to the components of n-Hexane extractable material (HEM) that are not adsorbed by silica gel and are gravimetrically determined by this method, otherwise known as non-polar material (NPM). The SGT- HEM method gives a measure of the non-volatile non-polar material present in the sample. In this method, hexane is used to extract the oil and grease from O/W emulsion, followed by the evaporation of hexane. The mass of the residual oil and grease (O&G) was measured by an analytical balance (Model AB265-S, Mettler Toledo, USA). The O&G concentration of the sample is the mass of HEM/SGT-HEM divided by the corresponding recovery efficiency and water sample volume. Thus, it is necessary to determine the recovery efficiency of the HEM/SGT-HEM method. The recovery of the HEM/SGT-HEM method was determined using initial precision and recovery (IPR) by the preparation of precision and recovery (PAR) standard and then extracting it by gravimetric method. The detailed procedures are described in EPA method 1664B and presented in Appendix, and the results are shown in Table 4.1.

Table 4.1 Initial Precision and Recovery (IPR) study for EPA 1664B

Sample	HEM concentration (mg/L)	HEM recovery (%)	SGT-HEM concentration (mg/L)	SGT-HEM recovery (%)
Sample 1	29.6	74	10.8	54
Sample 2	31.1	77.75	10.9	54.5
Sample 3	31.1	77.75	11.4	57
Sample 4	33.9	84.75	12.0	60

The average recovery (X) of HEM and SGT-HEM was $78.56 \pm 4.488\%$ and $56.38 \pm 2.75\%$, respectively. These values were used for calculating HEM and SGT-HEM for subsequent oil samples.

The non-treated synthetic bilge water containing 100 ppm Navy Oil Mix #4 was extracted gravimetrically (Appendix, step 1-8 Extraction of PAR Standard) and both HEM and SGT-HEM were measured.

Table 4.2 shows that the average initial concentration of HEM and SGT-HEM in synthetic bilge water is 68.48 mg/L and 71.21 mg/L, respectively. Thus, out of 100 mg of Navy Oil Mix#4 dosed in water, 68.48 mg was measured as n-hexane extractable material and 71.21 mg was measured as silica gel treated n-hexane extractable material. The calculated SGT-HEM concentration is around the same amount as measured HEM concentration, indicating the major fraction of the extractable oil in the sample is petroleum hydrocarbon. Numerically, SGT-HEM mass cannot be greater in value than HEM, the slight variation is due to experimental error. Since these two methods give approximately same O&G concentration, HEM method was adopted for the subsequent measurement due to ease of analysis.

Table 4.2 Initial O&G concentration in synthetic bilge water measured by EPA 1664B

Sample	HEM mass in 1 liter sample (mg)	Calculated HEM concentration (mg/L)	SGT-HEM mass in 1 liter sample (mg)	Calculated SGT-HEM concentration (mg/L)
Sample 1	53	67.46	41.5	73.61
Sample 2	54.1	68.86	39.6	70.24
Sample 3	54.3	69.12	40.2	71.30
Sample 4	53.8	68.48	39.3	69.71

Turbidity is a measure of the cloudiness of a fluid, which refers to how clear the fluid is. In the synthetic bilge water, the turbidity of water is caused by the existence of fine suspended oil droplets. In the preliminary study, it was found that the higher the turbidity,

the more oil droplets in the water. The synthetic bilge water was turbid after 24-hr mixing, and became relatively clear after coagulation treatment. Although the turbidity measurement does not determine the actual oil concentration, the efficiency of the coagulation process can be evaluated by determining the turbidity of samples before and after treatment.

In this study, the turbidity of samples was measured using Hach 2100N Laboratory Turbidimeter (Hach, USA). The equipment was calibrated using Stablcal® Turbidity Standards Calibration Kit (Hach, USA) before each use. The oil and grease matters in synthetic bilge water are from the diesel fuel and lubricating oil, which are mainly petroleum fractions. The measured total organic carbon (TOC) of synthetic bilge water is the amount of carbon found in different hydrocarbons. Total organic carbon (TOC) was used as a quick substitute to evaluate the concentration of oil and grease. The total organic carbon values of all the samples before and after treatment were measured using a TOC analyzer (TOC-V series, Shimadzu, Japan). The pH and conductivity of the samples were measured using Hach HQ40d multimeter (HACH, USA).

4.3 Results and Discussion

4.3.1 Effects of Sodium Chloride Dose on Bilge Water Quality Before and After Treatment

Because the monovalent ion salt NaCl is 700-1000 times less effective as coagulant than a trivalent metallic ion salt in same dosage (Black & Riddick, 1960), the required NaCl dose for oil removal is usually in magnitude of g/L. In the preliminary study, it was found that there was no significant oil removal from synthetic bilge water if the dose was less than 10 g/L (salinity 1%). Thus, the sodium chloride doses for further experiments was 3%, 5%, 10% and 15%.

Figure 4.3 shows that the turbidity removal increases with the increasing NaCl dosage. The highest turbidity removal of 75.85% occurred with a dosage of 15 wt% of sodium chloride. Figure 4.4 illustrates the TOC removal after coagulation. The TOC removals in the same coagulant dose are approximately same with or without sedimentation, which indicates the TOC removal occurs during coagulation-flocculation process. Unlike TOC,

the turbidity of synthetic bilge water decreases during the 120-min sedimentation. Thus, it is necessary to let the jars to settle 120 min if the relatively clear effluent is required. The TOC removal (Figure 4.4) also increases with the increasing sodium chloride dose and the highest removal is 78.5%. It increases drastically from 0 to 3% dose but the rate of removal reduces at dose above 3%. The similar trend of HEM removal is shown in Figure 4.5. The oil and grease removal increases to 63.48% at 5% dose but there is no significant increase for the dose above 5%. By comparing the performance of sodium chloride at a dose 5% and 10%, doubling the dose did not increase the percent removal proportionately. Since there were no particulates in the synthetic bilge water, the percent removals of turbidity, TOC, and HEM were comparable and mainly due to the removal of emulsified and dissolved oil.

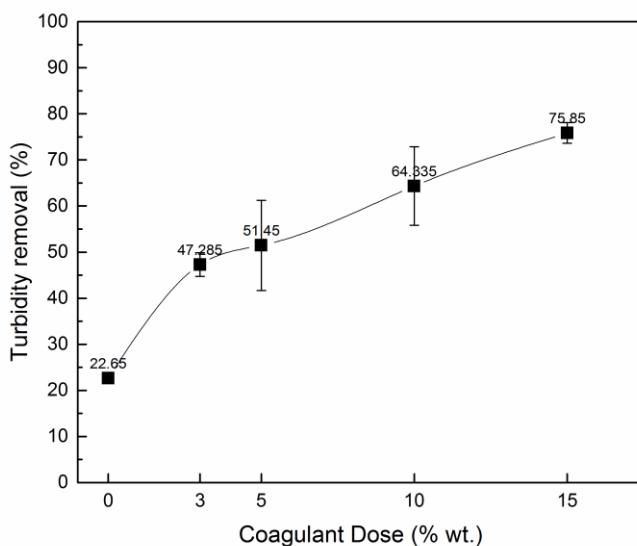


Figure 4.3 Effects of sodium chloride dose on turbidity removal from synthetic bilge water (initial pH: 6.97; initial turbidity: 59.33 ± 3.11 NTU; temperature: 20 ± 2 °C. Triplicates of jar-test experiments; Jar-test conditions: rapid mixing at 200 rpm for 2 min, slow mixing at 30 rpm for 20 min, settling for 120 min.)

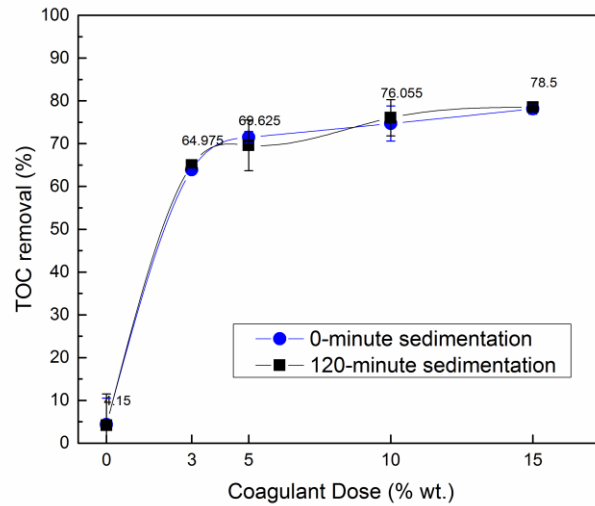


Figure 4.4 Effect of sodium chloride dose on TOC removal from synthetic bilge water (initial pH: 6.97; initial TOC: 30.55 ± 3.84 mg/L; temperature: 20 ± 2 °C. Triplicates of jar-test experiments; Jar-test conditions: rapid mixing at 200 rpm for 2 min, slow mixing at 30 rpm for 20 min, settling for 120 min.)

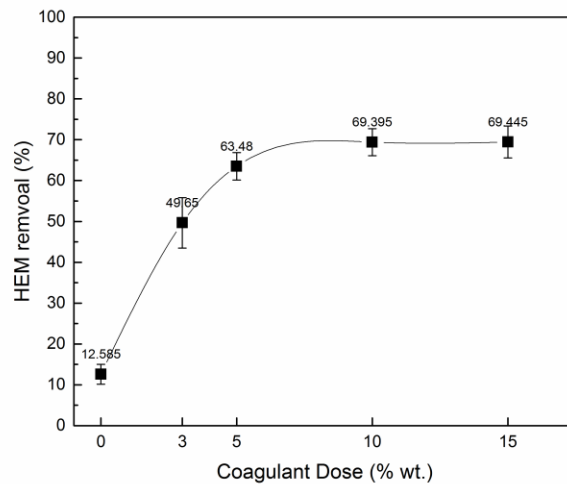


Figure 4.5 Effect of sodium chloride dose on HEM removal from synthetic bilge water (initial pH: 6.97; initial HEM concentration: 68.48 ± 0.73 mg/L; temperature: 20 ± 2 °C. Triplicates of jar-test experiments; Jar-test conditions: rapid mixing at 200 rpm for 2 min, slow mixing at 30 rpm for 20 min, settling for 120 min.)

Oil droplets in an O/W emulsion exhibit a net charge at the droplet surface. It is usually a negative charge, and as described by the double layer model, the negative charges are aligned or closely bound to the interface (Coca, Gutiérrez, & Benito, 2011). As shown in Figure 4.6, the attraction from these negative charges causes some of the positive ions from the bulk solution to form a layer around the colloid surface. This layer of counter ions is known as the Stern layer. Additional positive ions are still attracted by the negative colloid particles, but are repelled by the positive Stern layer. During the coagulation using Na^+ ion, the negative charges of the oil droplets are neutralized allowing the droplets to come closer and coalesce, which is further explained below.

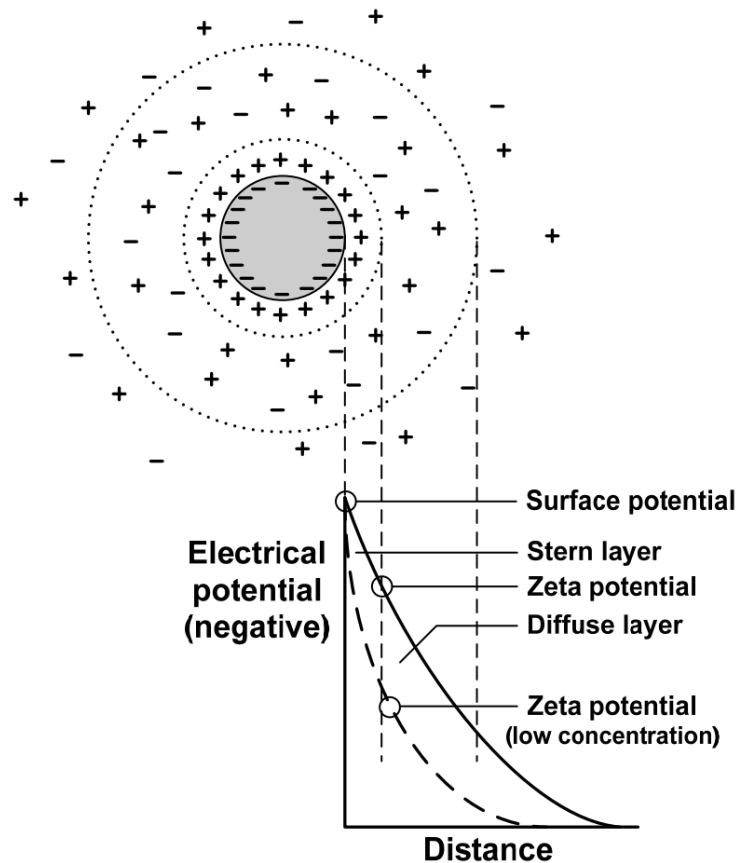


Figure 4.6 Electrical double layer around a negatively charged oil droplet and the distribution of electrical potential around it (Coca et al., 2011)

Stability of oil droplets can be explained by DLVO theory (named after Derjaguin, Landau, Verwey and Overbeek). The theory looks at the balance between electrostatic

repulsive forces and the attractive forces (van der Waals forces) that normally act between particles or droplets. The combined curve of electrostatic repulsion and van der Waals is called net interaction energy (Figure 4.7). The net interaction curve can shift from attraction to repulsion and back to attraction with increasing distance between particles. In order to agglomerate, the energy barrier must be lowered so that the net interaction is attractive. This can be achieved by compressing the double layer or reducing the surface charge. In oily wastewater treatment, this usually is accomplished during coagulation and flocculation.

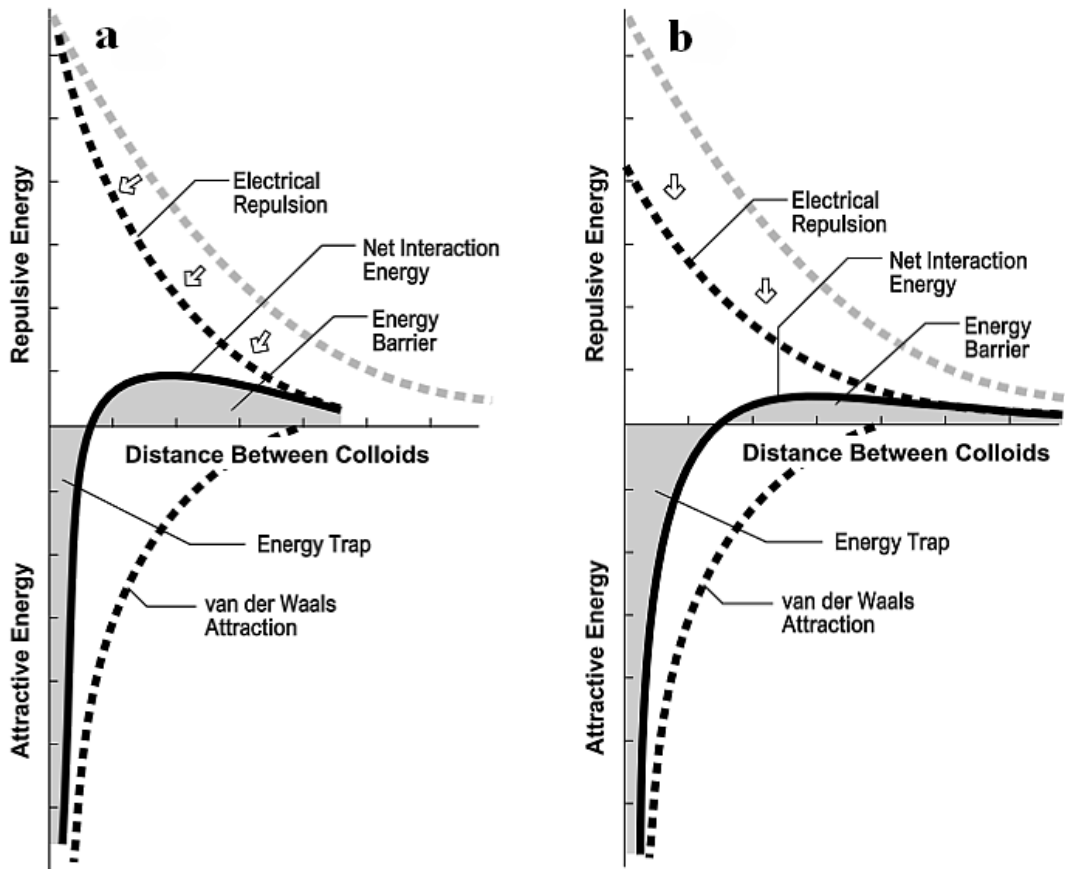


Figure 4.7 Potential energy of interaction between colloids and energy barrier reduction by (a) double layer compression and (b) charge reduction (Ravina & Moramarco, 1993)

Double layer compression reduces the energy barrier by adding salts to the system. As the ionic concentration increases, the thickness of the double layer reduces, causing the lower energy barrier. This salting out method usually requires massive amount of salt, hence it is not a practical technique for water treatment, but has application toward wastewater flocculation in brackish waters (Ravina & Moramarco, 1993). Charge reduction reduces energy barrier by adding coagulants to neutralize the surface charge of colloids.

In this study, the two main mechanisms of oil coagulation as mentioned above are double layer compression and charge reduction. Double layer compression reduces the energy barrier by adding salts to the system. As the ionic concentration increases, the thickness of the double layer reduces, causing lower energy barrier. This salting out method usually requires large amount of salt, hence it is an impractical technique for drinking and wastewater treatment, but has application toward wastewater flocculation in brackish waters (Ravina & Moramarco, 1993). Charge reduction reduces energy barrier by adding coagulants to neutralize the surface charge of colloids.

4.3.2 Performance of Sodium Chloride Combined with Coagulation Aid

The coagulation of synthetic bilge water using sodium chloride alone increases the size of the oil droplets allowing them to float on the surface. Large oil droplets cannot settle to the bottom of jar because of the lighter density of oil. Coagulation aid can be used to increase the settling velocity and strengthen the floc to make it easier to be separated. Inorganic coagulant aids such as calcium silicate and calcium carbonate are used because they are inexpensive and non-toxic compared to polymer aids.

Figure 4.8 shows that the water treated with coagulant aid was clearer than the one treated with the same dose of coagulant alone. No oil floc was generated from bilge water treated with only sodium chloride, conversely, water sample treated with 49 g/L sodium chloride and 1 g/L calcium silicate indicated the presence of oil in the surface, in the middle section (effluent water) and in the floc. The floc with milky white color was generated which precipitated on the bottom of the jar. For further discussion, the top 1 cm

height of water combined with the thin layer of oil droplets is defined as “top layer”; the bottom 1 cm height of water combined with the floc is defined as the “bottom layer”; and the rest of water is defined as “middle layer”.

The middle layer of water was collected for the determination of turbidity, TOC and HEM concentration. The results in Table 4.3 show that the removal efficiencies increased by adding coagulant aid. It is found that higher oil removal from the middle water layer occurred with increasing calcium silicate dosage. The highest turbidity, TOC and HEM removals were 72.55%, 75.02% and 87.92% respectively, whereas for the same dosage of NaCl, the corresponding percent removals were 51.45%, 69.63% and 63.48%, respectively. However, considering the cost of coagulant aid, 1 g/L of calcium silicate would be the proper dosage for the treatment.

The improvement in the removal performance caused by particulate coagulant aid calcium silicate is due to the increased collision due to increased particulate concentration (L. K. Wang et al., 2005). Calcium silicate also produces denser and better settling floc. As shown in Figure 4.9, the flocs in the bottom layer are the mixture of calcium silicate powder and the captured oil droplets that resulted in the milky white color. For the samples coagulated without addition of coagulant aid, no floc was observed.

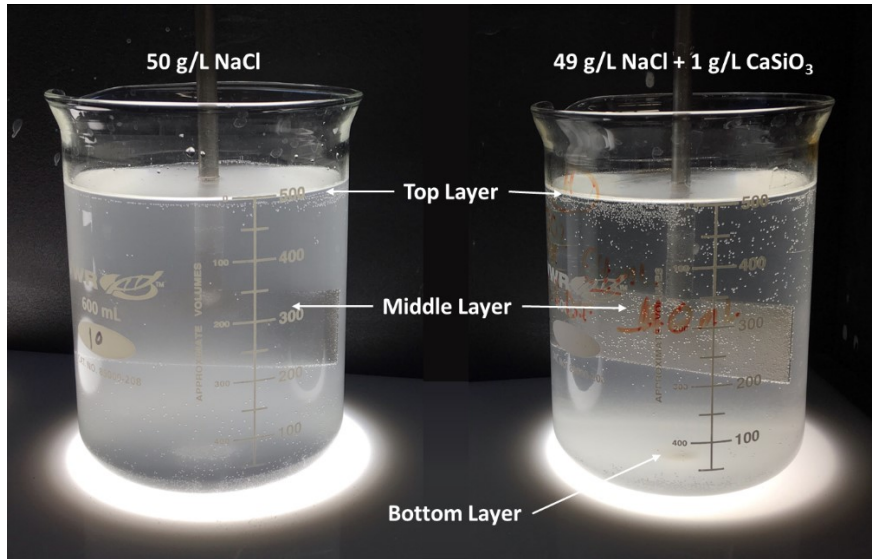


Figure 4.8 The synthetic bilge water samples after coagulation-flocculation using 50 g/L NaCl and 49 g/L NaCl + 1 g/L CaSiO₃ and sedimentation (Temperature: 20 ± 2 °C. Jar-test conditions: rapid mixing at 200 rpm for 2 min, slow mixing at 30 rpm for 20 min, settling for 120 min.)

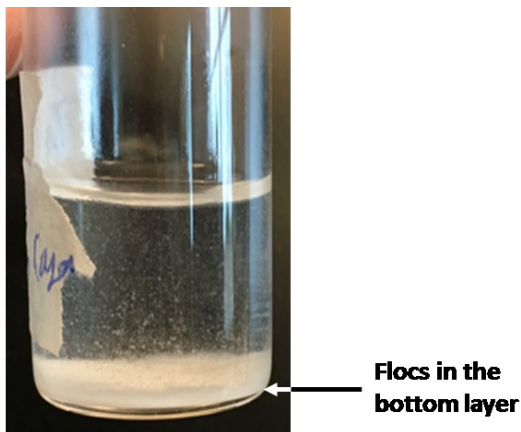


Figure 4.9 The flocs in the bottom layer collected from the synthetic bilge water sample after coagulation-flocculation using 49 g/L NaCl + 1 g/L CaSiO₃ and sedimentation (Temperature: 20 ± 2 °C. Jar-test conditions: rapid mixing at 200 rpm for 2 min, slow mixing at 30 rpm for 20 min, settling for 120 min.)

Table 4.3 General properties of the synthetic bilge water before and after treatment

Treatment coagulant	Turbidity (NTU)	Turbidity removal (%)	TOC (mg/L)	TOC removal (%)	HEM concentration (mg/L)	HEM removal (%)	pH
Raw bilge water	59.33 ± 3.11	-	30.55 ± 3.84	-	68.48 ± 0.73	-	6.97
Control	48.95 ± 0.78	22.65 ± 0.92	29.94 ± 3.17	4.15 ± 6.15	59.08 ± 1.65	12.58 ± 2.44	7.05
3% (30 g/L) NaCl	31.1 ± 1.41	47.29 ± 2.57	9.87 ± 0.50	64.98 ± 0.30	33.98 ± 4.13	49.65 ± 6.15	7.65
5% (50 g/L) NaCl	28.08 ± 2.29	51.45 ± 9.75	8.71 ± 0.99	69.63 ± 5.93	24.97 ± 2.74	63.48 ± 3.35	7.41
10% (100 g/L) NaCl	22.43 ± 2.23	64.34 ± 8.53	7.34 ± 0.07	76.06 ± 4.23	20.67 ± 2.22	69.40 ± 3.33	7.59
15% (150 g/L) NaCl	19.15 ± 0.78	75.85 ± 2.23	7.26 ± 0.61	78.50 ± 0.98	20.63 ± 2.63	69.45 ± 3.92	7.86
49.5 g/L NaCl+ 0.5 g/L CaSiO ₃	23.81 ± 1.13	59.44 ± 1.78	14.47 ± 0.32	51.77 ± 0.97	22.73 ± 1.34	66.57 ± 3.15	7.77
49 g/L NaCl+ 1 g/L CaSiO ₃	19.23 ± 1.76	67.79 ± 3.05	10.72 ± 0.10	64.27 ± 0.31	12.18 ± 0.07	82.18 ± 1.12	7.67
47.5 g/L NaCl+ 2.5 g/L CaSiO ₃	15.92 ± 0.98	72.55 ± 1.52	7.49 ± 0.09	75.02 ± 0.25	8.27 ± 0.13	87.92 ± 1.09	7.87
50 mg/L alum	45.65 ± 2.08	27.88 ± 3.28	20.90 ± 1.41	32.57 ± 2.07	37.66 ± 2.81	45.02 ± 4.02	5.71
100 mg/L alum	37.86 ± 1.29	39.90 ± 2.05	19.64 ± 0.89	35.42 ± 1.67	34.61 ± 2.11	49.47 ± 3.75	5.65
500 mg/L alum	39.34 ± 1.06	37.75 ± 1.71	19.66 ± 1.28	33.36 ± 2.62	38.02 ± 1.87	44.50 ± 3.43	4.41
100 mg/L alum + 1 g/L CaCO ₃	1.49 ± 0.02	97.51 ± 0.03	18.16 ± 2.13	39.47 ± 4.16	4.54 ± 0.90	93.37 ± 1.25	6.66

4.3.3 Oil Distribution

The goal of coagulation process was to minimize the oil content of the middle layer of water, as this is the effluent from the coagulation and flocculation. The coagulated oil on the water surface and in the flocs are separated from water by skimming and sludge removal. Thus, it is necessary to investigate the oil distribution in the sedimentation tank. The different layers were collected separately, then the oil was extracted from water according to EPA method 1664B. The oil distribution in different layers is presented in Figure 4.10.

Figure 4.10 illustrates the oil mass distribution in synthetic bilge water samples after treatment with different coagulant conditions. Since, no floc was generated in the water treated with sodium chloride alone, therefore no bottom layer was collected in these treatments. The coagulated oil was mainly distributed in the top layer (63.48%), rest of the oil (36.52%) remained in water because the size of oil droplets were too small to agglomerate and float to the surface. With addition of coagulant aid, part of the oil (28.51%-71.22%) was trapped by the calcium silicate particulate. It is interesting to see with the increase of calcium silicate dosage, there is a corresponding increase in oil collection at the bottom floc, causing much cleaner effluent from the middle section.

Figure 4.11 shows the effect of flocculation time on oil distribution. In the same coagulant dose and rapid mixing condition, the proportion of oil in the bottom layer increased with increasing flocculation time from 10 to 20 minutes. Also, the proportion of oil remained in the middle layer was lower with increasing flocculation time. During the flocculation process, the contact and coalescence between coagulant aid and oil droplets are enhanced by the slow mixing. The coagulant aid cannot have the optimal performance if the flocculation time is not sufficient enough (L. K. Wang et al., 2005).

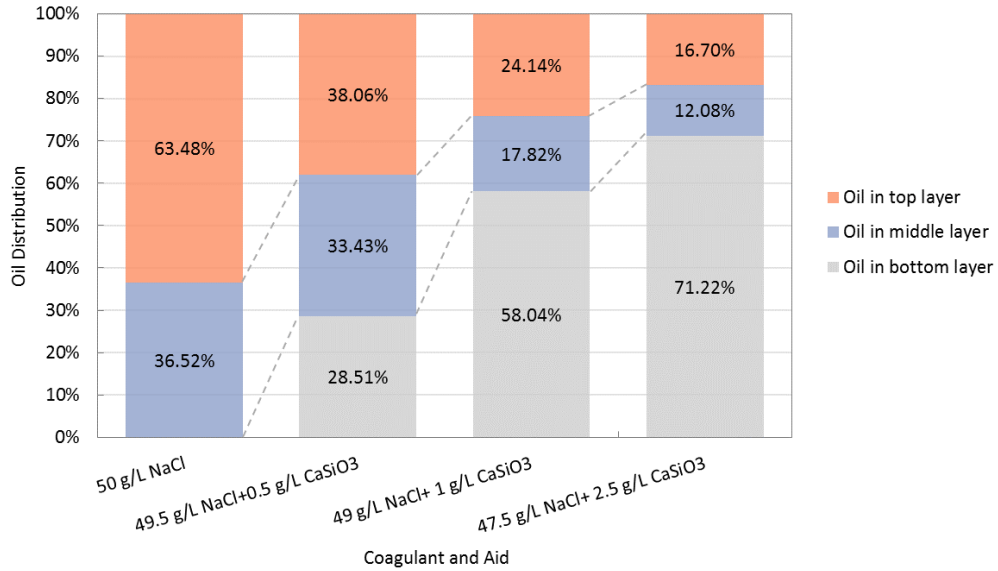


Figure 4.10 Oil mass distribution in synthetic bilge water samples after treatment with different coagulant conditions (Total mass of oil recovered from 1 L sample: 53.8 ± 1.0 mg. Temperature: 20 ± 2 °C. Jar-test conditions: rapid mixing at 200 rpm for 2 min, slow mixing at 30 rpm for 20 min, settling for 120 min.)

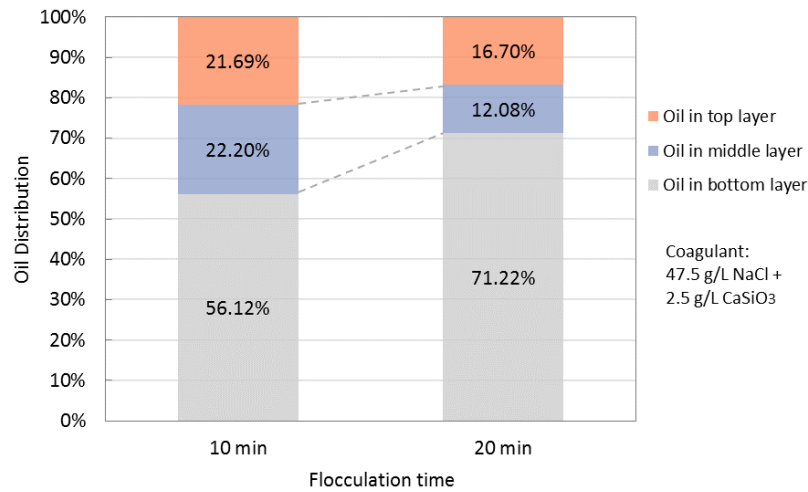


Figure 4.11 Oil mass distribution in synthetic bilge water samples after treatment with different flocculation time (Total mass of oil recovered from 1 L sample: 53.8 ± 1.0 mg. Temperature: 20 ± 2 °C. Coagulant: 47.5 g/L NaCl + 2.5 g/L CaSiO₃. Jar-test conditions: rapid mixing at 200 rpm for 2 min, slow mixing at 30 rpm for 10, 20 min, settling for 120 min.)

4.3.4 Performance Comparison of Coagulants

The performance of different combinations of coagulant and aid are presented in Table 4.3. As can be seen that performance of alum was comparable to NaCl at a much lower dosage due to higher charge (Al^{3+}) than NaCl (Na^+). This shows charge neutralization is the dominant mechanism of coagulation of oil droplets. As before, the performance of alum improved significantly with the addition of calcium carbonate, a common inorganic coagulant aid. The highest turbidity and HEM removals are 97.51% and 93.37% respectively, which occurred at treatment with 100 mg/L alum and 1 g/L CaCO_3 . The residual turbidity in water was 1.49 ± 0.02 NTU, which is very low and meets the turbidity standard for tap water (as shown in Figure 4.12). The highest TOC removal of 78.50% was achieved by treatment with 15 wt% NaCl.

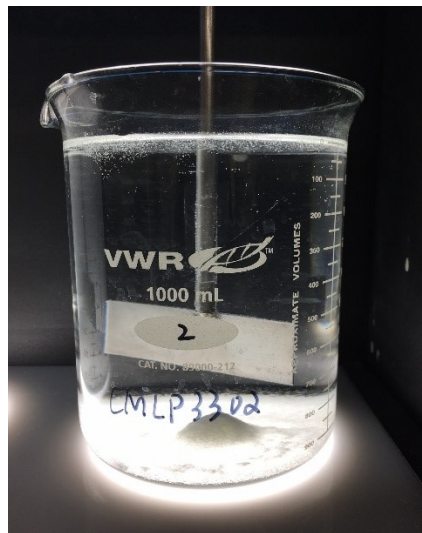


Figure 4.12 The synthetic bilge water samples after coagulation-flocculation using 100 mg/L alum + 1 g/L CaCO₃ and sedimentation (Temperature: 20 ± 2 °C. Jar-test conditions: rapid mixing at 200 rpm for 2 min, slow mixing at 30 rpm for 20 min, settling for 120 min.)

Both 49 g/L NaCl+ 1 g/L CaSiO₃ and 100 mg/L alum + 1 g/L CaCO₃ as the coagulant options show good overall removal performance. Considering the cost of coagulant, alum would be the best option because of the small dosage required compared to NaCl. However, NaCl would still be feasible to act as the coagulant in bilge water treatment, especially if seawater can be brought into the process to raise the ionic concentration and reduce the required addition of sodium chloride. In addition, the application of sodium chloride has no influence to the marine ecosystem after discharge of the treated water. As shown in Table 4.4, the prices of calcium silicate and calcium carbonate are approximately the same. The coagulant aid dosage of 1g/L is relatively high, the investigations on performance of aid with lower dosage and other types of coagulant aid are needed.

Table 4.4 Prices of coagulants and aids (industrial grade)

Coagulant	Coarse salt (NaCl)	Alum (Al ₂ (SO ₄) ₃ · 14~18 H ₂ O)	Calcium silicate (powder)	Calcium carbonate (powder)
Price	USD 25-50 /ton	~ USD 400 /ton	~ USD 150 /ton	~ USD 150 /ton

4.4 Conclusions

The results of this study demonstrate the feasibility of coagulation-flocculation-sedimentation as the pretreatment to remove part of the emulsified oil from bilge water. Both sodium chloride and alum can be applied as effective coagulants for the removal of turbidity, DOC and HEM from bilge water. Although the required dosage of sodium chloride is large compared to that of alum, the salinity of treated bilge water is close to the salinity of seawater. The amount of sodium chloride would be reduced if sea water can be brought into the process to raise the ionic strength. In addition, the application of sodium chloride has no influence to the marine ecosystem after bilge water is discharged because sodium chloride is originally present in the ocean. Almost 93% of the oil can be recovered at the top and bottom when alum and calcium carbonate was used which can be reused after removal of water.

The coagulant aids significantly improved the performance of coagulation-flocculation. Calcium silicate and calcium carbonate are common inorganic coagulant aids. They served as weighting agents and increased the particulate concentration that produced denser and faster settling floc. The oil distribution investigation proved the function of coagulant aids, as most of the oil was partitioned in the flocs when aids were added.

4.5 References

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Chapter 5

5 General Conclusions and Recommendations

5.1 Conclusions

Based on the experimental results and analysis obtained in this study, the following conclusions were drawn:

1. Alum as a conventional inorganic coagulant, showed good performance on both turbidity and DOC removal from OSPW. The optimal coagulation condition with a dosage of 190.44 mg alum/L and pH = 6.32 was obtained using response surface methodology, resulting in 98.29% turbidity removal and 28.46% DOC removal by coagulation.
2. Natural coagulant *Opuntia ficus-indica* showed the same good performance on turbidity removal but it increased the DOC of OSPW by 1-3%. The increased DOC was from the dissolution of carbohydrate naturally present in *Opuntia ficus-indica*. The flocs formed by *Opuntia ficus-indica* were denser and bulkier than the flocs formed by alum, resulting in faster settling speed with lower sludge volume.
3. Acidification of OSPW to pH <6 significantly reduced the DOC by around 50%. Acidification was also found to be necessary for better coagulation and adsorption performance.
4. Adsorption using granular activated carbon can further reduce the DOC of OSPW. Low pH was beneficial for adsorption, the maximum saturation capacity occurred at solution pH=4.
5. The adsorption capacity of activated carbon to adsorb DOC from pretreated OSPW was higher than the one from non-treated OSPW. This indicates the positive effect of coagulation-flocculation on adsorption to remove DOC.
6. Sodium chloride was able to coagulate oil droplets in synthetic bilge water. The appropriate dose of sodium chloride was 5 wt%, resulting in 63.48% oil removal.

7. The application of calcium silicate and calcium carbonate as coagulation aids was able to significantly increase the oil removal from bilge water by coalescing with oil droplets and settling to the bottom. The coagulated oil droplets floated to the water surface, and settled to form oily sludge if coagulant aid was present.
8. Almost 93% of the oil can be recovered at the top and bottom when 100 mg alum/L and 1 g calcium carbonate/L was used which can be reused after removal of water.

5.2 Recommendations

Based on the obtained results and drawn conclusions, the following recommendations are made for future research:

1. Natural coagulant *Opuntia ficus-indica* could generate bulkier and denser flocs from colloids of OSPW, which increase the settling speed. The effect on sedimentation time and sludge volume reduction could be investigated further to quantify the effect.
2. The adsorption study could use petroleum coke-derived activated carbon as adsorbent to establish a green process by recycling the by-product from oil sands refining industry.
3. The effect of pretreatment by coagulation-flocculation on other secondary treatment techniques could be investigated, such as membrane filtration, chemical oxidation and biodegradation.
4. The toxicity analysis of the effluents from the individual and combined processes could be performed.
5. The coagulation studies of synthetic bilge water could introduce seawater as the provider of coagulant to reduce the addition of sodium chloride. The toxicity analysis of non-treated bilge water and the effluent using marine algae or other marine organism can be conducted to ensure the reduction of toxicity.

6. The performance of other types of coagulation aids including natural and synthetic polymers could be investigated.
7. The design of continuous process including coagulation-flocculation and further treatments such as skimming and oil recycling are necessary because coagulation-flocculation dose not generate separation by itself.

Appendices

Appendix A: Sample Calculation

Appendix A.1: Sample calculation of the aluminum concentration in stock solution

10.00 g of aluminum sulfate hydrate (the degree of hydration was assumed to be 14) was dissolved in 1 liter milli-Q water to make a 1 % alum solution. The concentrations of aluminum sulfate hydrate, aluminum sulfate anhydrous, aluminum ion are calculated as follow:

$$\text{Concentration of aluminum sulfate hydrate (Al}_2\text{(SO}_4\text{)}_3 \cdot 14 \text{H}_2\text{O)} = \frac{\text{mass of Al}_2\text{(SO}_4\text{)}_3 \cdot 14 \text{H}_2\text{O added (mg)}}{\text{volume of stock solution (L)}} = 10^4 \text{ mg/L}$$

$$\text{Concentration of aluminum sulfate anhydrous (Al}_2\text{(SO}_4\text{)}_3) = \frac{\text{concentration of Al}_2\text{(SO}_4\text{)}_3 \cdot 14 \text{H}_2\text{O in stock solution}}{\text{molecular weight of Al}_2\text{(SO}_4\text{)}_3 \cdot 14 \text{H}_2\text{O}} \times \text{molecular weight of}$$

$$\text{Al}_2\text{(SO}_4\text{)}_3 = \frac{10^4 \text{ mg/L}}{594.43 \text{ g/mol}} \times 342.15 \text{ g/mol} = 0.576 \times 10^4 \text{ mg/L}$$

$$\text{Concentration of aluminum ion (Al}^{3+}\text{)} = \frac{\text{concentration of Al}_2\text{(SO}_4\text{)}_3 \cdot 14 \text{H}_2\text{O in stock solution}}{\text{molecular weight of Al}_2\text{(SO}_4\text{)}_3 \cdot 14 \text{H}_2\text{O}} \times 2 \times \text{atomic weight of Al}^{3+} =$$

$$\frac{10^4 \text{ mg/L}}{594.43 \text{ g/mol}} \times 2 \times 26.98 \text{ g/mol} = 9.1 \times 10^2 \text{ mg/L}$$

Appendix A.2: Calculation of the adsorption capacity at equilibrium of DOC in treated OSPW

Case I: OSPW was treated by coagulation using 190.44 mg alum/L at pH=6.32, resulting in the decrease of DOC from 250.2 mg/L to 106.0 mg/L (C_0). The DOC of treated OSPW was further reduced to 92.72 mg/L (C_e) by adsorption using 0.28 g/L activated carbon.

The adsorption capacity at equilibrium is calculated as follow:

$$q_e \text{ (at } C_e = 92.72 \text{ mg/L)} = \frac{(C_0 - C_e) \times V}{W} = \frac{106.0 \text{ mg/L} - 92.72 \text{ mg/L}}{0.28 \text{ g/L}}$$

$$= 47.43 \text{ mg DOC adsorbed/g adsorbent}$$

Case II: OSPW was treated by coagulation using 800 mg *Opuntia ficus-indica* mucilage/L at pH=6, resulting in the decrease of DOC from 160.3 mg/L to 79.3 mg/L (C_0). The DOC of treated OSPW was further reduced to 55.73 mg/L (C_e) by adsorption using 0.28 g/L activated carbon. The adsorption capacity at equilibrium is calculated as follow:

$$q_e \text{ (at } C_e = 55.73 \text{ mg/L)} = \frac{(C_0 - C_e) \times V}{W} = \frac{79.3 \text{ mg/L} - 55.73 \text{ mg/L}}{0.28 \text{ g/L}}$$

$$= 84.18 \text{ mg DOC adsorbed/g adsorbent}$$

Appendix B: Experimental Procedures

Appendix B.1: EPA Method 1664, Revision B Essential Procedures

Preparation of precision and recovery (PAR) Standard

- (1) Hexadecane (98% purity) and stearic acid (98% purity) were mixed in 1:1 ratio in acetone. 200 mg each of stearic acid and hexadecane were placed in 100 ml volumetric flask which was then filled to mark with acetone. The solution was warmed for complete dissolution of stearic acid, followed by cooling. This formed the spiking solution having concentration of 2 mg/mL each of hexadecane and stearic acid.
- (2) The PAR Standard was then prepared by dissolving 10 ml of the spiking solution into 1000 ml of reagent water to give an approximate concentration of 20 mg/L each of hexadecane and stearic acid.

Extraction and gravimetry of precision and recovery (PAR) Standard

- (1) Sample (original volume recorded as V_s) was acidified with sulphuric acid solution (1 part concentrated sulphuric acid in 3 parts reagent water) so that the sample pH becomes less than 2.
- (2) The acidified sample was poured in a 2 L separatory funnel.
- (3) 30 ml of hexane was added to the empty sample bottle, shaken to rinse the entire interior surface including the lid of the bottle cap. The hexane was then poured into the separatory funnel.
- (4) Sample was extracted by vigorously shaking the funnel for 2 minutes. This was followed by allowing the organic phase to separate from the aqueous phase for minimum 10 minutes.

- (5) The lower aqueous layer was drained into the original sample bottle. The n-hexane layer (upper layer) was drained through a filter containing 10 g of sodium sulphate into a pre-weighed boiling flask.
- (6) Steps 3 to 5 were repeated twice more with fresh 30 ml of hexane, combining the extracts into the boiling flask. Rinse the tip separatory funnel, the filter paper, and the funnel with 2-3 small (3-5 ml) portions of n-hexane. Collect the rinsings in the boiling flask.
- (7) If only SGT-HEM is to be determined, proceed to step (11).
- (8) The flask containing the extract was placed in a vacuum oven (model OV-11, Jeio Tech, South Korea) at 70 °C to evaporate the hexane leaving the dried residue in the boiling flask. Cool the flask to room temperature in a desiccator for 30 minutes minimum.
- (9) While at room temperature and without additional heating, repeat the cycle of desiccating and weighing until the weight loss of the flask and dried residue is less than 4 % of the previous weight or less than 0.5 mg, whichever is less. The final weighing should be used for determining the value for HEM or SGT-HEM as appropriate. If the extract was from the HEM procedure, determine the HEM (W_h) by subtracting the tare weight (step 5) from the total weight of the flask. If the extract was from the SGT-HEM procedure (step 13), determine the weight of SGT-HEM (W_s) by subtracting the tare weight from the total weight of the flask.
- (10) Add 100 ml to the boiling flask to redissolve the HEM. If necessary, warm the solution to completely redissolve the HEM.
- (11) Add 3.0 ± 0.3 g of anhydrous silica gel to the boiling flask for every 100 mg of HEM. Add a fluoropolymer-coated stirring bar to the flask and stir the solution on a magnetic stirrer for a minimum of 5 minutes.

- (12) Filter the solution through n-hexane moistened filter paper into a pre-dried, tared boiling flask containing several boiling chips. Rinse the silica gel and filter paper with several small amounts of n-hexane to complete the transfer.
- (13) Distill the solution and determine the weight of SGT-HEM as step 8 and 9.
- (14) N-Hexane extractable material—Calculate the concentration of HEM (“oil and grease”) in the sample per the following equation:

$$HEM (mg/L) = \frac{W_h (mg)}{V_s (L)}$$

Silica gel treated n-hexane extractable material—calculate the concentration of SGT-HEM (“nonpolar material”) in the sample per the equation above, substituting WS for Wh.

- (15) Calculate the percent recovery (X) of HEM or SGT-HEM in each PAR standard aliquot using the following equation:

$$\text{Percent recovery (X)} = \frac{100 A}{T}$$

A = measured concentration of HEM or SGT-HEM

T = True concentration of the spiked sample in PAR standard (40 mg/L for HEM; 20 mg/L for SGT-HEM).

Extraction and gravimetry of experimental samples

The HEM concentrations in experimental samples were determined by following the same extraction and gravimetry procedures of PAR standard (step 1 to 14).

Note: Only essential procedures are described above. For complete detailed procedures and quality control requirements, see the original file of EPA method 1664B at https://www.epa.gov/sites/production/files/2015-08/documents/method_1664b_2010.pdf

Appendix C: Supporting Figures

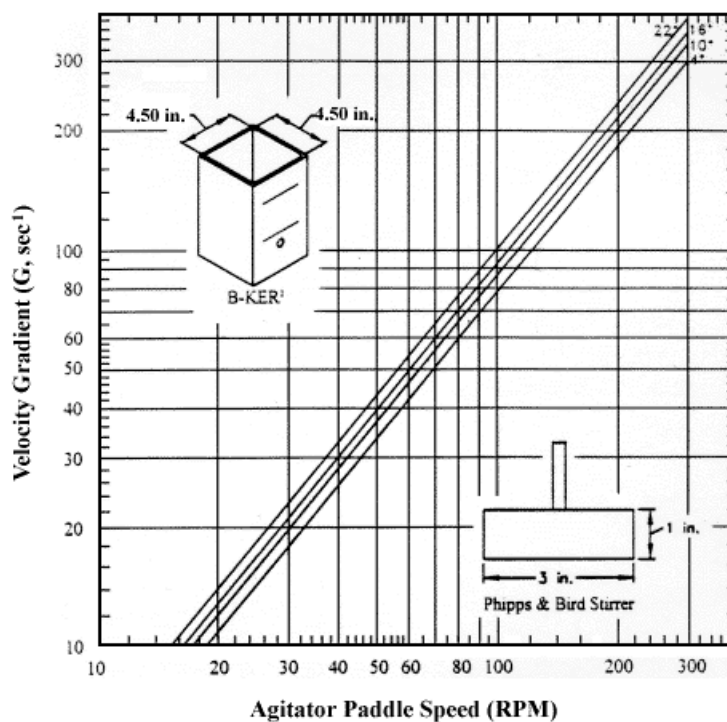


Figure C.1. Velocity Gradient vs. Agitator Speed for a 2-liter Square Beaker (B-KER2), Using a Phipps & Bird Stirrer

For a 500-ml beaker, the G value (velocity gradient) curve is different. The transformation was calculated as follow:

$$G = \left[\frac{P}{\mu V} \right]^{1/2}$$

$$\frac{G_1}{G} = \left[\frac{P_1/\mu_1 V_1}{P/\mu V} \right]^{1/2} ; \mu = \mu_1; P = P_1$$

$$\frac{G_1}{G} = \left[\frac{V}{V_1} \right]^{1/2} = \left[\frac{2 \text{ liter}}{0.5 \text{ liter}} \right]^{1/2} = 2$$

Hence, the function transformation would be vertically stretched by multiplying each of its y-coordinates by 2. The slope in log-log plot remains constant as it stands for the exponential relation between input power (P) and agitator paddle speed (N).

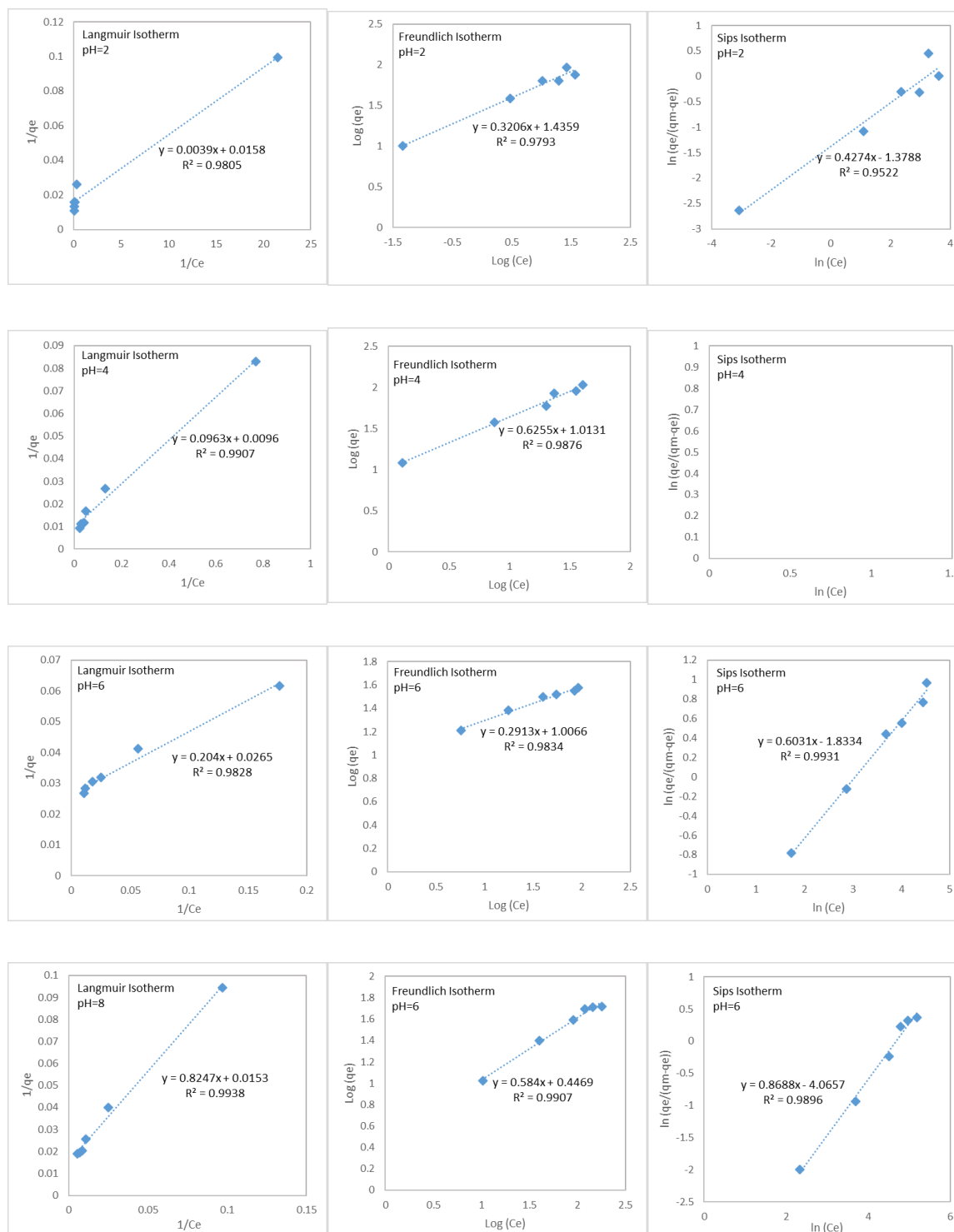


Figure C.2. Langmuir, Freundlich and Sips isotherm linear plots for GAC at pH 2,4,6,8.

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