

INTEGRATED COAGULATION-ADSORPTION DISSOLVED AIR FLOTATION
TREATMENT FOR OILY WASTEWATER

by

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Dedication

To my parents, for a lifetime of love and encouragement of all my pursuits, academic and otherwise. And to my older siblings, Andrew and Kathryn, to whom I can never catch up. You will always be much smarter than me (but now you have to call me Doctor).

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Abstract

Produced water is the largest wastewater stream generated by the petroleum industry, and contains a range of petroleum hydrocarbons in free, dispersed and dissolved form. In the offshore environment, produced water management often consists of treatment and discharge into the ocean. The most common treatment technologies in use only target the free and dispersed phase, despite environmental concerns arising from the discharge of dissolved aromatic compounds. Thus, the primary objective of this research was to investigate a produced water treatment train which incorporates dissolved aromatics removal into a gravity separation process. Specifically, this research investigated an integrated adsorption-coagulation pre-treatment process for dissolved air flotation (DAF), which is a common gravity separation technology used for offshore produced water treatment.

This thesis reports the results of bench-scale jar test or batch adsorption experiments conducted on a synthetic saline, oily wastewater containing two soluble aromatic compounds, phenol and naphthalene. The first experimental study focused on coagulation alone as a pre-treatment for DAF, and demonstrated that this treatment was not effective for the removal of the dissolved aromatics, particularly phenol. These findings confirmed the premise of this thesis that additional pre-treatment would be necessary for enhanced dissolved aromatics removal. The second study compared the proposed integrated adsorption-coagulation pre-treatment to separate adsorption and coagulation treatments. The results of this study indicated that the integrated pre-treatment could combine the high naphthalene removals observed in the adsorption treatment with the high dispersed oil removals provided by the coagulation treatment. However, the adsorbent material used in this study was not effective for phenol removal. Thus the objective of the third study was to identify an appropriate adsorbent for both phenol and naphthalene removal. This research concluded that powdered activated carbon (PAC) and an aromatic-containing organoclay (BTMA) were both effective adsorbents for both phenol and naphthalene. Finally, experiments were conducted to investigate the impact of adsorption addition on downstream clarification. It was concluded that both sedimentation and DAF were appropriate clarification processes for adsorbent-floc aggregates in oily-saline wastewater.

List of Abbreviations and Symbols Used

$\mu\text{g/L}$	micrograms per litre
μ_w	kinematic viscosity of water
1/n	Freundlich intensity factor
AC	activated carbon
Al^{3+}	aluminum
ANOVA	analysis of variance
b	Langmuir adsorption constant (L/mg)
BAT	best available technology
BET	Brunauer-Emmet-Teller, refers to eponymous method of surface area measurement
BTEX	benzene, toluene, ethylbenzene, xylene
BTMA	benzyltrimethyl ammonium, refers to BTMA-modified organoclay in experimental results
Ca^{2+}	calcium
C_D	drag coefficient
C_e	equilibrium concentration of adsorbate in solution (mg/L)
cm	centimeters
CNSOPB	Canada-Nova Scotia Offshore Petroleum Board
COD	chemical oxygen demand
CSTR	completely stirred tank reactor
CX	refers to alkyl chain containing X number of carbons (eg. C4 refers to a 4-carbon alkyl chain)
DAF	dissolved air flotation
d_b	bubble diameter
d_f	floc diameter

d_{fb}	diameter of floc-bubble aggregates (g/cm ³)
DI	distilled/deionized water
DLVO	Derjaguin, Landau, Verwey and Overbeek, refers to eponymous model for colloidal stability
d_p	particle diameter (m)
Fe(OH)^{2+}	iron hydroxide (di-cationic)
Fe(OH)_2^+	iron hydroxide (mono-cationic)
Fe(OH)_3	iron hydroxide (electrically neutral)
Fe(OH)_4^-	iron hydroxide (anionic)
Fe^{3+}	iron
FeCl_3	ferric chloride (coagulant)
g	gravitational constant (9.81 m/s ²)
g/L	grams per litre
G-value	velocity gradient
H^+	hydrogen cation
HCl	hydrochloric acid
IR	infrared
K	shape factor
KCl	potassium chloride
K_F	Freundlich adsorption capacity factor (mg/g)/(L/mg)
km	kilometers
K_{ow}	octanol-water partition coefficient
M	molar concentration (moles per litre)
m/h	meters per hour
meq	milliequivalents

mg/g	milligrams per gram
mg/L	milligrams per litre
mS	millSiemens
mV	millivolts
N	number of bubbles attached per floc
Na ⁺	sodium
NaCl	sodium chloride
NaHCO ₃	sodium bicarbonate
NaOH	sodium hydroxide
NEB	National Energy Board
N _{max}	maximum number of bubbles that can attach to a floc
NOM	natural organic matter
NSERC	Natural Science and Engineering Research Council of Canada
NTU	nephelometric turbidity units
O&G	oil and grease
OC	organoclay, refers to commercial organoclay (Cetco) in experimental results
OH ⁻	hydroxide anion
OSPAR	Oslo-Paris Convention
p	statistical probability value
PAC	powdered activated carbon
PACl	polyaluminum chloride
PAH	polycyclic aromatic hydrocarbons
pKa	acid dissociation constant
PRAC	Petroleum Research Atlantic Canada
PSD	particle size distribution

psi	pounds per square inch
PW	produced water
q_e	adsorbent phase concentration (mg adsorbent/g adsorbate)
Q_M	maximum solid phase adsorbate concentration (i.e., when surface is saturated) mg adsorbate/g adsorbent)
rpm	revolutions per minute
SED	sedimentation
SEM	scanning electron microscope
Si^{4+}	silica
USEPA	United States Environmental Protection Agency
UV-VIS	ultraviolet-visible
v_s	settling velocity (m/s)
ZP	zeta potential
ρ_{fb}	density of floc-bubble aggregates (g/cm^3)
ρ_p	particle density (g/cm^3)
ρ_w	water density (g/cm^3)

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CHAPTER 1. Introduction

Produced water is the largest wastewater stream generated by the petroleum industry, and contains a range of petroleum hydrocarbons in free, dispersed and dissolved form. In the offshore environment, produced water management often consists of treatment and discharge into the ocean. The most common technologies used for produced water treatment, including plate separators, hydrocyclones, centrifuges and flotation, work by gravity separation, which exploit the density difference between oil and water to separate the free and dispersed organics from the aqueous phase (van de Broek et al, 1998). However, these approaches to produced water treatment are not effective for the removal of dissolved hydrocarbons, the aromatic fraction of which may be harmful to marine organisms.

The primary objective of this research was to investigate a novel produced water treatment train which incorporates dissolved aromatics removal into a gravity separation process. Specifically, this research investigated an integrated adsorption-coagulation pre-treatment process for dissolved air flotation (DAF). While adsorption, coagulation, and DAF have all been extensively used in drinking water and industrial wastewater treatment industries, research studies of these technologies for produced water treatment are relatively rare. Produced water contains constituents which are not typically found in drinking water sources, such as high levels of both salinity and dispersed oil droplets, which may affect the efficacy of coagulation, adsorption and DAF clarification treatment processes. Therefore, the secondary objective of this research was to address the existing research gap concerning the effect of salinity and dispersed oil on the treatment effectiveness of adsorption, coagulation and DAF clarification.

1.1 Thesis Objectives and Approach

The two major objectives of this research were:

- (1) To address the existing technology gap in the offshore oil and gas industry by investigating an integrated adsorption-coagulation pre-treatment for DAF to incorporate dissolved aromatics removal into a gravity separation process
- (2) To address the existing research gap concerning the use of established drinking water treatment technologies in oily industrial wastewater by investigating the effect of salinity and dispersed oil on the treatment effectiveness of adsorption, coagulation and DAF clarification

Bench-scale experiments were conducted to address the following specific objectives:

- (1) Evaluate ferric chloride (FeCl_3) coagulation and DAF for the removal of dispersed oils, naphthalene, and phenol from a synthetic produced water
- (2) Determine the impact of salinity on oily wastewater coagulation under several different pH and coagulant dose conditions
- (3) Investigate an integrated adsorption-coagulation-DAF treatment for the simultaneous removal of dispersed oil, naphthalene and phenol from synthetic produced water, and determine the impact of coagulant dose, adsorbent dose, hydraulic retention time and mixing velocity gradients on treatment efficacy

- (4) Evaluate powdered activated carbon (PAC), a commercial organoclay (OC) and a lab-synthesized aromatic organoclay (BTMA) as adsorbents for the removal of naphthalene and phenol from synthetic produced water in batch adsorption equilibrium experiments
- (5) Determine the impact of salinity and dispersed oil on adsorption of naphthalene and phenol by PAC, OC and BTMA in batch adsorption equilibrium experiments
- (6) Investigate the impact of adsorbent addition on the particle size distribution, strength and regrowth of FeCl_3 flocs in fresh water
- (7) Evaluate the impact of adsorbent addition into FeCl_3 flocs on downstream DAF and sedimentation clarification in fresh water and synthetic produced water

1.2 Thesis Outline

Chapter 1 outlines the objectives, experimental approach, and organization of this thesis.

Chapter 2 provides background information on produced water, including its chemical characteristics, the existing regulatory environment concerning the discharge of offshore produced water and the potential environmental concerns associated with its discharge. An overview of the treatment technologies currently used for produced water treatment, as well as the technologies comprising the proposed integrated pre-treatment (i.e., coagulation and adsorption) studied in this work is also provided.

Chapter 3 presents results of experiments that evaluated coagulation and DAF treatment for the removal of dispersed oil and dissolved aromatics from synthetic produced water, and investigated the impact of salinity on coagulation. Bench-scale jar tests were conducted following a factorial design which tested the removal of dispersed oil, naphthalene and phenol by

coagulation with ferric chloride (FeCl_3) and DAF at high and low ferric chloride doses (i.e., 10 and 50 mg/L), pH levels (i.e., 6 and 8), and salt concentrations (i.e., 0 and 32 g/L). This chapter has been published as a journal article in *Water Quality Research Journal of Canada*.

Chapter 4 presents results of experiments that investigated an integrated adsorption-coagulation-DAF treatment process for the removal of dispersed oil and dissolved aromatics from synthetic produced water. Bench-scale jar tests were conducted to evaluate the following treatment trains: (1) adsorption-DAF, (2) coagulation-DAF, and (3) adsorption-coagulation-DAF. Ferric chloride was the coagulant used in this study, and a commercial organoclay was used as the adsorbent. The impact of operating parameters on treatment efficacy were also studied, using factorial design of high and low values of ferric chloride dose (i.e., 10 and 50 mg/L), adsorbent dose (i.e., 300 and 1000 mg/L), hydraulic retention time (i.e., 15 and 45 minutes), and mixing velocity gradient (i.e., 20 and 110 s^{-1}). This chapter has been published as a journal article in *Journal of Environmental Chemical Engineering*.

Chapter 5 presents results of experiments conducted to examine the performance of three different adsorbent materials, a commercial organoclay (OC), a lab-synthesized aromatic organoclay (BTMA), and powdered activated carbon (PAC) for the removal of naphthalene and phenol. Batch adsorption tests were performed in fresh, saline, and oily-and-saline water to assess the impact of salinity and dispersed oil on adsorption, as well as in single- and multi-solute conditions. Results were compared using the Freundlich adsorption isotherm, and discussed in the context of the adsorption mechanisms exhibited by each adsorbent material. This chapter has been published as a journal article in the *Journal of Hazardous Materials*.

Chapter 6 presents results of experiments designed to investigate the potential impact of adsorbent addition on ferric chloride floc properties and downstream clarification efficacy. Flocs and floc-adsorbent aggregates were characterized by optical microscopy, particle size distribution determination, and analysis of floc strength and recoverability. The impact of adsorbent addition on DAF and sedimentation was estimated using modified Stokes Law modeling, and determined experimentally using turbidity measurements of clarified effluent. The impact of dispersed oil on clarification was also assessed by performing DAF and sedimentation tests on both fresh water and synthetic produced water.

Chapter 7 summarizes the findings of the research and presents conclusions in the context of the original thesis objectives. Recommendations for further research are also supplied.

1.3 Originality of Research

Integrated adsorption and coagulation treatment is a novel process for the application to produced water treatment. While combining PAC adsorption and coagulation is not uncommon in the drinking water treatment industry, this study represents a novel application of this technology in the following areas:

- Applying an integrated adsorption-coagulation process to oily industrial wastewater
- Investigating organoclay as an adsorbent material for integrated adsorption-coagulation processes
- Evaluating DAF as a clarification for adsorbent-coagulated floc aggregates, and determining the impact of adsorbent addition on clarification processes
- Investigating the impact of adsorbent addition on the properties of coagulated flocs formed in integrated process

Furthermore, in contrast to removal of dissolved components as a polishing step following dispersed oil removal, this process is unique in that it provides simultaneous removal in one unit operation of dispersed oils and dissolved aromatics from an industrial wastewater stream.

CHAPTER 2. Literature Review

2.1. Produced Water

Produced water is the largest wastewater by volume produced in the oil and gas industry (Utvik, 1999; Veil et al, 2004). Subsurface rock formations containing hydrocarbon resources, such as oil or gas, are also permeated with water, which is brought to the surface during the extraction process (Veil et al, 2004). Typically, water is also injected into the reservoir in order to maintain pressure during production (Ahmadun et al, 2009). World-wide production of produced water is around 250 million barrels per day (Ahmadun et al, 2009). While the ratio of produced water to oil production in any given well increases with the age of the extraction operation, the world average water to oil ratio is estimated to be 3:1 (Veil et al, 2004).

The organic composition of produced water includes petroleum hydrocarbons in free, dispersed and dissolved forms. Both free and dispersed oils are composed of insoluble hydrocarbons, such as high molecular weight aliphatic hydrocarbons, heavy polycyclic aromatic hydrocarbons (PAHs), or phenols substituted with long alkyl chains. Free oils are insoluble hydrocarbons which are present in large droplets and can be easily separated from water by gravity separation (Veil et al, 2004). Dispersed, or emulsified, oils are insoluble hydrocarbons which are present in small droplets which do not coalesce or quickly float to the surface of the water. Some partially soluble organics, such as lower molecular weight PAHs and C4-C5 alkylphenols have also been observed to partition into the dispersed oil phase (Faksness, 2004).

Dissolved oils are organic compounds which are soluble in water. The aromatic fraction of dissolved oils may include partially soluble compounds, such as low molecular weight PAHs (i.e., naphthalene) and C2-C3 alkylphenols, as well as highly soluble compounds, such as phenols, and BTEX (i.e., benzene, toluene, ethylbenzene, and xylene) (Faksness, 2004). While a broad range of

compounds in each of these classes has been observed in produced water, there is generally a higher concentration of the low molecular weight forms of each constituent—for example, the majority of phenols found in produced water are in the form of phenol, while the majority of BTEX are in the form of benzene (Utvik, 1999).

Non-hydrocarbon organics also comprise a large part of the organic fraction, with organic acids (i.e., such as formic, acetic acid, etc.) present in concentrations of up to 800 to 1000 mg/L (Strømgren et al, 1995; Utvik, 1999).

Table 1 summarizes results of other studies that have characterized the hydrocarbon fraction of produced water samples from offshore oil producing platforms in the North Sea. The major constituent measured in these studies was total oil and grease, which was found at concentrations up to hundreds of mg/L (Tibbets et al, 1992; Utvik, 1999). Dissolved aromatics were present in the form of BTEX, phenols and PAH. BTEX and phenols were measured at concentrations on the order of 10 mg/L, with a concentration range between 0.39 to 35 mg/L and 0 to 23 mg/L, respectively (Tibbets et al, 1992; Strømgren et al, 1995; Utvik, 1999; Faksness, 2004). PAH were measured at concentrations on the order of 1 mg/L, with a concentration range between 0.193 to 1.60 (Tibbets et al, 1992; Strømgren et al, 1995; Utvik, 1999; Faksness, 2004).

Table 2.1 Characteristics of Produced Water

	(Tibbets et al, 1992)	(Strømgren et al, 1995)	(Utvik, 1999)	(Faksness, 2004)
Total oil and grease (mg/L)	2-565		33-60	
BTEX (mg/L)	0.39-35	0.041-0.347	2.4-9.0	8.350-8.900
Phenols (mg/L)	0-23	0.8-7.8	0.58-11.45	3.260-3.629
PAH (mg/L)		0.193-0.774	0.93-1.60	1.144-1.182

Dissolved aromatic hydrocarbons have been identified as a potential source of environmental toxicity from produced water. Dissolved organics are typically more difficult to remove from wastewater streams and are also more readily absorbed by organisms through contact with the marine environment (Veil et al, 2004; Ekins et al, 2007). Of particular concern are the water soluble fraction of PAHs and alkylated phenols (Utvik et al, 2002; Bakke, 2013), both of which have been measured at elevated levels within 2 km of oil platform discharge points in the Norwegian North Sea sector (Harman et al, 2009).

Phenol toxicity is thought to occur primarily through hormone disruption, as phenols with substituted alkyl chains (i.e., alkylphenols) have been shown to act as estrogen receptor agonists (Thomas et al, 2004). Alkylphenols have been demonstrated to reduce plasma levels of both male and female sex hormones, interfere with sexual development and sex cell production and delay spawning time in Atlantic cod in *in vivo* studies (Meier et al, 2007). Of particular concern are C4-C9 alkylphenols (phenols with substituted alkyl chains of 4 to 9 carbons in length), of which C4-C5 are soluble enough to be resistant to typical oil separation technologies, and would

thus require advanced treatment (Ekins et al, 2007). These compounds have been found in produced water at concentrations up to 70 µg/L, though alkylphenol concentration is highly variable and location-dependent (Boitsov et al, 2007). In Canada, there is currently guideline for phenol concentration in marine waters. However, the guideline for phenol concentration in fresh waters is 4.0 µg/L, as determined by the Canadian Council of Ministers of the Environment (CCME, 1999a).

PAHs have also been implicated as environmental toxins through a number of mechanisms, including hormone disruption (as androgen receptor antagonists) (Thomas et al, 2009), oxidative stress and embryotoxicity (Bakke et al, 2013). Lower molecular weight PAH compounds (i.e., naphthalenes) are partially soluble in water, while higher molecular weight compounds (i.e., 2 to 6 ring PAHs) associate primarily with dispersed oil (Tollefsen et al, 2007; Faksness et al, 2004). The Canadian guidelines for naphthalene concentration is 1.1 µg/L in fresh waters and 1.4 µg/L in marine waters (CCME, 1999b).

Inorganic constituents of produced water include dissolved salts, heavy metals and radioactive materials. Salt concentration is highly variable in produced water, and can range from a few parts per million (ppm) to over 300,000 mg/L (Ahmadun et al, 2009). A study of onshore and offshore oil and gas wells in the US determined that total dissolved solids concentration in US wells ranges from 1,000 mg/L to over 400,000 mg/L, with a median value of 32,300 mg/L, with sodium chloride (NaCl) as the dominant salt present in most wells (Benko and Drewes, 2008). Produced water can also contain heavy metals, such as cadmium, chromium, copper, lead, mercury, nickel, silver, zinc (Ahmadun et al, 2009), barium, lead, and manganese (Veil et al, 2004). Naturally occurring

radioactive materials may also be present in produced water, primarily as radium isotopes (Ahmadun et al, 2009).

In addition to the naturally-occurring materials found in the hydrocarbon reservoir, produced water may also contain process chemicals used in the extraction activities. These may include scale inhibitors, corrosion inhibitors, demulsifiers, coagulants and solvents (Ahmadun et al, 2009; Veil et al, 2004).

2.1.1 Produced Water Discharge Regulations

Discharge of offshore produced water is regulated in Canada under the National Energy Board (NEB), Canada-Newfoundland Offshore Petroleum Board, or Canada-Nova Scotia Offshore Petroleum Board (NEB/CN & CNSOPB, 2002). These regulations limit the oil concentration in produced water to 30 mg/L (as a 30 day volume-weighted rolling average) with a 24-hour maximum oil concentration of 44 mg/L (NEB/CN & CNSOPB, 2010). Similar discharge standards exist in the United States under the US Environmental Protection Agency (USEPA) and in the North Sea under the Oslo-Paris Convention (OSPAR). In the US, oil in produced water discharges is limited to a 29 mg/L monthly average limit, with a 42 mg/L daily maximum (USEPA, 1993), while North Sea discharges are required to have oil concentrations under 30 mg/L (OSPAR, 2001).

These discharge standards are technology-based, meaning that the required residual pollutant levels are determined by the level of treatment that the industry can economically achieve with the current “best available technology” (BAT). The USEPA considers gas flotation with

upstream gravity separation and chemical addition to be the BAT for oil removal from produced water (USEPA, 1993).

Although produced water contains a wide range of organic contaminants, the discharge requirements for both North America and the North Sea sector in Europe are largely based on a single water quality parameter—"Oil and Grease". This parameter is used as an indicator pollutant, under the assumption that the process of removing oil and grease will also remove other toxic constituents (USEPA, 1993). Oil and grease is a methodologically defined term for the organic fraction which can be extracted from water by an organic solvent (typically Freon or hexane) and measured by the test method, which in Canada is specified by the regulating body as Standard Method 5520 (ASTM, APHA and WEF, 2005). Soluble hydrocarbon compounds have been shown to not be correlated with oil and grease concentration in field characterization studies of produced water (Utvik, 1999), and to not partition into the dispersed oil phase in lab characterization studies of produced water (Faksness, 2004). Thus, removal of oil and grease may not indicate removal of the full extent of water-soluble hydrocarbons present in produced water, leading to concerns that this potentially harmful fraction is essentially unregulated in produced water discharges (Ynnesdal and Furuhold, 1994; Utvik and Hasle, 2002).

To address the issue of dissolved hydrocarbons in produced water, OSPAR has recently adopted new standards for produced water discharge which require the specific measurement of BTEX compounds, in addition to Total Oil and Grease measurement (OSPAR, 2011). In that standard, the sum of BTEX concentrations and Total Oil and Grease must be within the 30 mg/L discharge

limit. In addition to the existing discharge standards, OSPAR has also implemented a risk based management approach, which requires all discharging platforms to determine whether predicted environmental concentrations (i.e., outside of the immediate discharge area) of produced water constituents are below the established “predicted no effect concentration” (OSPAR, 2012). In Canada, offshore producers are also required to report some manner of annual chemical characterization and/or toxicity testing of produced water discharges, although the exact reporting requirements are not specified (CNSOPB, 2010).

In summary, while produced water discharges have traditionally been regulated based on oil and grease measurements alone, new regulations in Europe’s North Sea sector have been promulgated which specifically target dissolved hydrocarbons. Existing requirements for toxicity testing or environmental risk assessments in both Europe and North America may also indicate the need for treatment technologies which can reduce the dissolved hydrocarbon fraction of produced water discharges. Thus, there may be an immediate or future industrial demand for technologies which can remove this fraction, despite there currently being no direct regulations requiring its removal in Canada or the US.

2.2. Produced Water Treatment Technologies

2.2.1. Currently Available Treatment Technologies

The currently available treatment technologies for offshore produced water treatment are based on gravity separation processes, which separate oil droplets from water based on the difference in density between the two phases (Descousse et al, 2005; Walsh, 2015). Common gravity separation techniques include plate separators, hydrocyclones, centrifuges and gas flotation.

Plate separators allow free oil to separate from water, while providing a surface for oil to adhere to and coalesce, with plates closely spaced to minimize space requirements (Reis, 1996; Ahmadun et al, 2009). Hydrocyclones use a vortex to separate oil and water based on their different densities, with denser water forced to the outside of the cyclone and less dense oil remaining in the middle (Reis, 1996). Centrifuges use the same separation mechanism as hydrocyclones; however, while hydrocyclones simply use the inlet velocity of the water from a pressurized inlet to induce the spinning motion, centrifuges use mechanical spinning (Reis, 1996). Gas flotation works by introducing small bubbles of gas into the wastewater, which attach to oil droplets and rise to the surface of the water where the oil can be skimmed off (USEPA, 1993). One method of gas flotation introduces bubbles to the water by blending gas and liquid streams or introducing mechanical shear into the water, in a process called induced gas flotation (IGF) (USEPA, 1993). The other method of gas flotation, called dissolved air flotation (DAF) produces bubbles by introducing a pressurized, supersaturated air-water solution into the process tank, from which air bubbles precipitate (USEPA, 1993). DAF typically produces small bubbles, ranging from 10 to 100 µm in diameter (with a typical bubble size around 40 µm) (Edzwald, 1995), in contrast to IFG, which produces larger bubbles, up to 1000 µm in diameter (USEPA, 1993). Chemical addition is considered to be a necessary pre-treatment for DAF, in order to neutralize the surface charge on particles and provide hydrophobic sites for bubble attachment (Edzwald, 1995). Treatment of oily wastewater by chemical addition (typically coagulation) and DAF has been widely shown to be effective for the removal of oil and grease from industrial wastewaters (Rattanapan et al, 2011; Santo et al, 2012) and synthetic oily wastewaters (Zouboulis and Avranas, 2000; Al-Shamrani et al, 2002).

The two most common treatment technologies used for produced water are hydrocyclones and gas flotation, which are commonly used in series, with hydrocyclones used as the primary treatment, followed by flotation (often with the addition of flocculant chemicals) (Walsh, 2015). These separation processes can be highly effective for removing free or dispersed oils, as hydrocyclones can reliably remove oil droplets 20 µm in diameter or larger (Van de Broek et al, 1998), while gas flotation with chemical addition can remove oil droplets 3 to 5 µm in diameter (Veil et al, 2004). However, since traditional gravity separation technologies work by removing the free/dispersed oil phase from the water, they are typically unable to remove the dissolved species (Descousse et al, 2004). Highly water-soluble dissolved aromatics (such as C0 to C3 phenols) are minimally removed (i.e., < 20%) by gravity separation treatments, while only partial removal (i.e., 20 to 60%) of partially water-soluble aromatics such as naphthalenes and C4 to C5 phenols can be achieved by these treatments (Descousse et al, 2004). Therefore, physical separation processes alone are not sufficient to reduce all of the hydrocarbon fractions, and chemical addition may be necessary for enhanced removal of the dissolved aromatic compounds.

Several new treatment methods have been investigated in field studies in the North Sea offshore sector for enhanced oil-water separation and aromatics removal. The CTour process uses liquid condensate from field produced compressed natural gas as a solvent to extract hydrocarbons from produced water (Descousse et al, 2004; Knudsen et al, 2004). Field trials showed that including the CTour process upstream of hydrocyclone treatment removals by 70% for naphthalenes and 2-6 ring PAH, by 60% for C6-C9 phenols, and by 20% for C4-C5 phenols, but showed no reduction of C0-C3 phenols (Knudsen et al, 2004). The Epcon compact flotation unit is an oil/water/gas separator which uses both centrifugal forces and gas flotation, which has been

shown to also provide 17% removals of naphthalene, 32% removals of 2-3 ring PAHs, 47% removals of 4-7 ring PAHs, and 33% removals of C6-C9 phenols, but no removals of smaller alkylated phenols (Knudsen et al, 2004). The Cetco CrudeSorb process, which is an adsorption column with organoclay media used as a tertiary treatment, has been shown to provide enhanced removals of all target aromatic compounds, including C0-C3 phenols (Descousse et al, 2004).

Several other advanced treatment technologies for offshore produced water have been investigated by researchers or applied in the field. High pressure membrane filtration (i.e., by either nanofiltration (NF) or reverse osmosis (RO)) has been shown to reduce organic content and overall toxicity from treated (i.e., prior to discharge) produced water samples (Alzahrani et al, 2013a; Alzahrani et al, 2013b). However, this treatment method would be limited to tertiary (i.e., post-conventional treatment), due to the potential for membrane fouling (Alzahrani and Mohammad, 2014). Enhanced removal of dissolved aromatic compounds, phenol and benzoic acid, has also been achieved through biodegradation (Piubeli et al, 2012). However, the long incubation period of 12 days required for treatment may indicate that this method would not be feasible given the space restrictions in the offshore environment. Catalytic oxidation on a membrane surface impregnated with a platinum-based catalyst has been shown to remove up to 97% of C2-alkylated phenols from a synthetic produced water (Kumakiri et al, 2011). In general, the options for field-tested produced water treatments capable of removing dissolved aromatics, particularly small phenols and small alkylated phenols (i.e., C0-C3 phenols) are limited.

2.2.2 Coagulation-Flocculation

Coagulation-flocculation is a widely used technology in drinking water and wastewater treatment that can remove a broad range of contaminants, including turbidity, taste and odour, colour, microorganisms, disinfectant by-products (DBP) precursors and arsenic (Wang et al, 2005).

Coagulation is the addition of chemicals to water to allow for enhanced removal of contaminants with physical separation technologies (Crittenden et al, 2012). Flocculation is the aggregation of precipitated material and destabilized particles resulting from coagulant addition into larger clusters of material known as “flocs.” The resulting floc material is amenable to removal by physical separation methods, such as sedimentation, dissolved air flotation (DAF) or filtration (Crittenden et al, 2012).

Colloids acquire surface charge in water due to interaction of water with polar or ionized functional groups. Aluminosilicate minerals have negative surface charge due to Al^{3+} replacing Si^{4+} in the crystal lattice. Natural organic matter (NOM) present in surface waters often contains polar or ionisable functional groups (i.e., carboxylic acids, $\text{R}-\text{COOH}$), which can donate a proton (H^+) to water at certain pH levels to become negatively charged (i.e., $\text{R}-\text{COO}^- + \text{H}^+$) (Crittenden et al, 2012). Oil droplets also have a negative surface charge in water, due to adsorption of hydroxyl ions (i.e., OH^-) at the oil-water interface (Marinova et al, 1996). While surface charge is highly dependent on the pH of the water, many common water contaminants are negatively charged at neutral pH (Crittenden et al, 2012, Marinova et al, 1996).

The presence of this net negative surface charge stabilizes colloidal particles in water, reducing interactions between them, and causing them to stay in suspension for long periods of time

without aggregating (Verwyne, 1934). The surface charge on material in water is balanced by the presence of counter-ions called the “electrical double layer,” as illustrated in Figure 2.1. A particle with a negative surface charge will acquire a fixed, tightly bound layer of cations on its surface (called the “Stern layer”) (Kruyt and Overbeek, 1940). This layer of cations will not entirely overcome the negative surface charge, leaving a residual net negative charge on the particle/cation surface, which then attracts an additional layer of loosely bound cations (called the “diffuse layer”) (Kruyt and Overbeek, 1940). This second layer of cations extends out to the point where all of the negative charge from the particle has been counteracted. This point marks the end boundary of the electrical double layer.

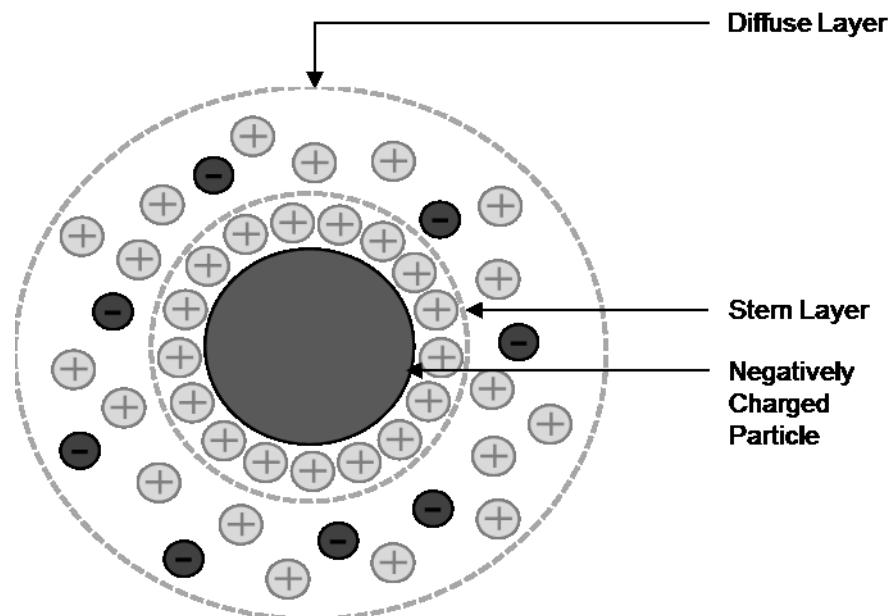


Figure 2.1 The electrical double layer surrounding a negatively charged particle in water

The stability of a colloidal system can be described as a function of the two main interparticle forces in solution—the electrostatic force, which is repulsive (between particles with the same type of surface charge), and van der Waals forces, which are attractive (Verwey and Overbeek, 1946). This model is illustrated in Figure 2.2 which represents attractive van der Waals forces as

V_A , repulsive electrostatic forces as V_{R1} and V_{R2} , and the sum of these forces as V_1 and V_2 (Bratby, 2006).

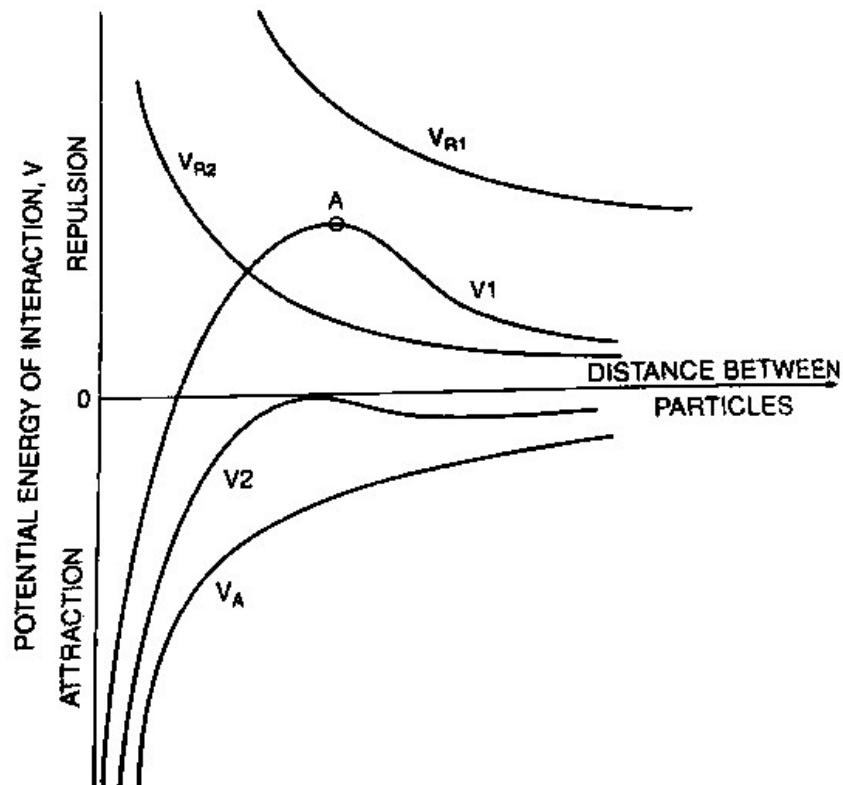


Figure 2.2 Net interaction energy between colloids as described by DVLO theory where V_A represents attractive van der Waals forces and V_R represents repulsive electrostatic forces
 (Bratby, 2006)

The mechanisms for coagulation include double layer compression, adsorption and charge neutralization, entrapment or sweep coagulation, and polymeric bridging.

In double-layer compression mechanism, the addition of electrolytes into a solution creates a denser, and thus smaller, electrical double layer, allowing for particles to move closer together

before experiencing electrostatic repulsion (Crittenden et al, 2012). At a closer distance, the attractive van der Waals forces are stronger, and can overcome the repulsive effect of the electrostatic charge, allowing for particle agglomeration (Wang et al, 2005). In saline environments, such as seawater, mineral particles have been found to be destabilized by the high ionic strength, and to be prone to aggregation as a result (Edzwald et al, 1974). This effect is particularly pronounced in the presence of multivalent cations. According to the Shultz-Hardy rule, the destabilizing effect of an ion increases with increasing valence charge, such that the destabilizing effect of a divalent cation (i.e., Ca^{2+}) is 30 times the effect of a monovalent cation (i.e., Na^+), while the effect of a trivalent cation (i.e., Fe^{3+}) is 1000 times that of a monovalent cation (Wang et al, 2005).

With adsorption and charge neutralization mechanisms, positively charged hydrolysis products (both mononuclear and polynuclear species) adsorb to the surface of the negatively charged colloid, neutralizing the surface charge (Stumm and O'Melia, 1968). This removes the electrostatic repulsion between particles, allowing the attractive van der Waals forces between them to dominate, promoting aggregation and attachment to solid surfaces. An excess of cation adsorption to the surface could result in reversal of colloid charge (to positive) and re-stabilization (Wang et al, 2005).

Entrapment/sweep coagulation processes are based on the application of high doses of metal salts (i.e., oversaturating the aqueous phase with metal hydroxide) to result in rapid and extensive coagulant precipitate formation. Colloids can become enmeshed, or “swept” out of the water, in this precipitate during or after precipitate formation (Wang et al, 2005). Particles in the

water can provide nucleation sites for precipitate formation, thus aiding the coagulation process (Wang et al, 2005).

In polymeric bridging mechanisms, polymers are added to water that contain several reactive groups, each of which can adsorb to a colloid, bridging the particles together (Wang et al, 2005).

Coagulation chemicals include natural or synthetic polymers or metal (typically aluminum or iron) salts (Bratby, 2006). In water, metal salts dissociate to form trivalent cations (i.e., Fe^{3+} and Al^{3+}), which are surrounded by coordinated water molecules (Stumm and Morgan, 1962). These hydrated metal complexes are hydrolyzed (i.e., the coordinating water molecules are converted to OH^-) to form a range of mono- and poly-nuclear hydrolysis products. Figure 2.3 illustrates the speciation of mononuclear hydrolysis products formed with ferric based coagulants as a function of pH (Stumm and O'Melia, 1968). For ferric based coagulants added to water below pH 7, the soluble iron species are in cationic form (i.e., Fe(OH)_2^+ , Fe(OH)_3^+ , and Fe^{3+}), increasing in concentration and valence at lower pH levels. Cationic metal hydroxide species can undergo complexation reactions with negatively charged dissolved NOM, allowing these resulting complexes to be removed by adsorption or precipitation onto solid surfaces (Edzwald, 1993). Between pH 7 and 9, the vast majority of ferric coagulant is precipitated as $\text{Fe(OH)}_3(s)$, however Fe(OH)_2^+ and Fe(OH)_4^- are both present in the soluble phase in trace amounts. Coagulation in this pH range is typically associated with excellent particle removal, due to the rapid formation of amorphous metal hydroxide precipitate which can enmesh particulate matter (Duan and Gregory, 2003). Ferric based coagulants are more insoluble than aluminum based coagulants, and precipitate over a wider pH range. The pH of minimum solubility for iron in water is pH 8.

(i.e., where the insoluble/neutral hydrolysis product, Fe(OH)_3 dominates) (Crittenden et al, 2012). Above pH 9, the soluble iron present exists as the anionic hydrolysis product Fe(OH)_4^- .

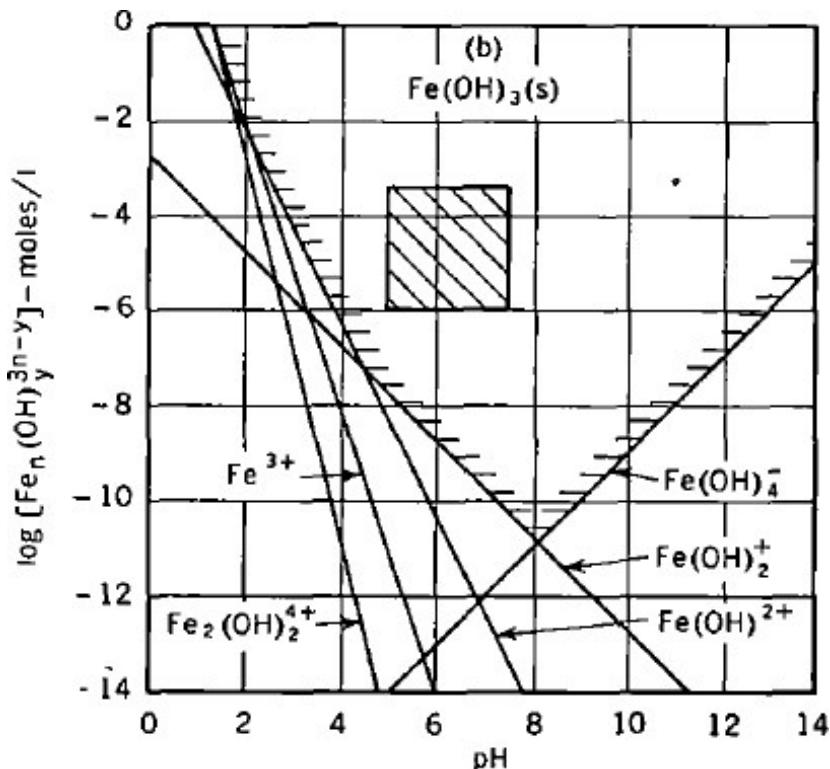


Figure 2.3 Mononuclear ferric hydrolysis species formed as a function of pH (Stumm and O'Melia, 1968)

The two coagulation mechanisms associated with metal salt addition are charge neutralization and entrapment/sweep coagulation (Pernitsky and Edzwald, 2006). The dominant mechanism largely depends on pH and coagulant dose. At very low doses of coagulant (i.e., insufficient to counteract surface charge) colloids are still stable and coagulation does not occur (Stumm and O'Melia, 1968). Once sufficient doses of coagulant has been added to counteract the surface charge, colloids are destabilized and coagulation occurs through a charge neutralization mechanism (Stumm and O'Melia, 1968). If excess coagulant has been added, a positive surface charge is applied to the colloid surface, and charge reversal and restabilization occurs, preventing

coagulation (Stumm and O'Melia, 1968). However, if enough coagulant has been added that the solution is supersaturated with the metal hydroxide species, causing widespread precipitation and sweep coagulation to occur (Stumm and O'Melia, 1968). The restabilization phenomenon does not occur for ferric coagulants above pH 6 because ferric hydroxide species are so insoluble under this condition that precipitation happens rapidly, enabling sweep coagulation conditions, and too low a concentration of soluble species is present in the water for restabilization to occur (Stumm and O'Melia, 1968).

In addition to the removal of colloidal material, metal salt coagulation has also been used to remove dissolved natural organic matter (NOM) from drinking water sources by complexation of negatively charged dissolved NOM with positively charged metal hydroxide species, followed by adsorption or precipitation of these complexes onto solid surfaces (Edzwald, 1993). . However, not all dissolved organics are amenable to removal by coagulation (Edwards, 1997). In general, higher molecular weight, and more highly hydrophobic organics are more amenable to removal by coagulation, while lower molecular weight and more hydrophilic compounds are less likely to be removed in this process (Collins et al, 1986).

2.2.3 Adsorption

Adsorption is the process of transferring a substance (i.e., the *adsorbate*) from liquid phase to a solid surface (i.e., the *adsorbent*) and is thus an important process for the removal of dissolved materials in water and wastewater treatment (Crittenden et al, 2012). Adsorption can be driven by a variety of interparticle forces, particularly dispersion forces, electrostatic interactions and hydrophobic bonding, depending on the nature of the adsorbent substance, the adsorbate surface, and the dispersant medium.

Dispersion forces, or van der Waals forces, are attractive forces between particles which arise from the polarization of their molecular structure. These forces exist between both polar and non-polar molecules, including interactions between two permanent dipoles (i.e., between two polar molecules), between a permanent dipole and an induced dipole (i.e., between a polar and a non-polar molecule), and between two induced dipoles, which are known as London dispersion forces (i.e., between two non-polar molecules) (Adair et al, 2001). The strength of the dispersion forces governed by a strong inverse relationship to the distance between the interacting particles (Adair et al, 2001). Therefore, materials such as activated carbon, which have a microporous structure, facilitate these interactions by allowing small molecules to be in close contact with the pore walls, resulting in a stronger adsorption force (Abe et al, 2001).

Specific dispersion forces arising from the polarization of electron-rich pi bonds are responsible for attraction between pi-bond containing structures, such as aromatic rings (Moreno-Castilla, 2004). This pi-pi bond interaction drives the adsorption of aromatic compounds, such as phenol, onto activated carbon (Hamdaoui and Naffrechoux, 2007; Ania et al, 2007) and onto minerals modified with aromatic surfactants (Shen, 2002).

Adsorption can also occur when the adsorbent and adsorbate acquire opposite surface charges in water. Cationic dye molecules were observed to adsorb strongly to activated carbon in the pH range where the carbon's surface was negatively charged (Dai, 1998). Acid treatment of activated carbon has been used to increase the concentration of acidic surface oxygen groups

which can ionize to become negatively charged in water, enhancing uptake of metal cations (Yin et al, 2007).

Certain aluminosilicate minerals, such as zeolites and clays, have a net negative surface charge caused by the substitution of Al^{3+} for Si^{4+} in the crystalline structure. This negative surface charge is offset by cations adsorbed to the surface by electrostatic attraction, which can be exchanged with larger cations in the context of water treatment processes (Dyer, 2007). A class of water treatment materials called “organoclays” are clay minerals which have been modified by exchanging surface cations with surfactant molecules, rendering the clay surface hydrophobic. When these organoclays are manufactured with relatively small surfactant molecules, the negatively-charged surface of the clay, as well as the cationic head of the surfactant is left exposed, and can adsorb polar molecules via electrostatic attraction (Groisman et al, 2004).

Adsorption from aqueous solution can also be driven by hydrophobic bonding, in which hydrophobic, or non-polar, molecules are rejected from water and adhere to a non-polar surface (Moreno-Castilla, 1994). Adsorption of certain hydrophobic molecular structures by activated carbon can be due to bonding of the solute to hydrophobic sites on the activated carbon surface (Chen et al, 2003).

Hydrophobic bonding is also an important mechanism for adsorption by organoclays, particularly for clays modified with surfactant molecules containing a long alkyl chain. Rather

than adsorbing to a hydrophobic spots on an adsorbent surface, these organoclays provide a layer of non-polar solvent into which hydrophobic solutes are able to partition (Groisman et al, 2004).

Adsorption Isotherms

An adsorption isotherm describes the relationship between the amount of adsorbate adsorbed onto an adsorbent surface and remaining in the water at equilibrium (Crittenden et al, 2012).

While numerous adsorption isotherm models exists, two of the most common are the Langmuir and Freundlich isotherms.

The Langmuir isotherm is a theoretically-based model which describes adsorption as a reversible chemical equilibrium, with the following assumptions (Crittenden et al, 2012):

- (1) The adsorbent contains a fixed number of adsorption sites. Once all these sites are occupied by the sorbate, an additional increase in aqueous-phase sorbate cannot drive additional adsorption past this fixed maximum solid-phase concentration.
- (2) Adsorption occurs in a monolayer, meaning that only one molecule of adsorbate can adsorb per adsorption site. This assumes that there are no favorable sorbate-sorbate interactions.
- (3) All of the adsorption sites are energetically similar.

The Langmuir isotherm is presented in Equation 2.1.

$$q_e = \frac{Q_M b C_e}{(1 + b C_e)} \quad [\text{Equation 2.1}]$$

Where: q_e = adsorbent phase concentration (mg adsorbent/g adsorbate)

b = Langmuir adsorption constant (L/mg)

C_e = equilibrium concentration of adsorbate in solution (mg/L)

Q_M = maximum solid phase adsorbate concentration (i.e., when surface is saturated) mg adsorbate/g adsorbent)

The linearized form of the Langmuir equation is presented in Equation 2.2. The Langmuir constants, b and Q_M , can be calculated by plotting C_e/q_e versus C_e . This gives a slope of $1/Q_M$ and y-intercept of $1/(bQ_M)$.

$$\frac{C_e}{q_e} = \frac{1}{bQ_M} + \frac{C_e}{Q_M} \quad [\text{Equation 2.2}]$$

The Freundlich isotherm is the most commonly used adsorption isotherm, and fits to a wide variety of adsorbent-adsorbate systems. It is an empirical equation which does not yield the strict requirements of surface homogeneity and monolayer coverage found in the Langmuir isotherm (Crittenden et al, 2012). The Freundlich isotherm is given in Equation 2.3.

$$q_e = K_F C_e^{1/n} \quad [\text{Equation 2.3}]$$

Where: K_F = Freundlich adsorption capacity factor (mg/g)/(L/mg)

$1/n$ = Freundlich intensity factor

The linearized form of the Freundlich equation is presented in Equation 2.4. The Freundlich constants, K_F and $1/n$, can be calculated by plotting q_e versus C_e on a log-log plot. This gives a slope of K_F and y-intercept of $1/n$.

$$\log(q_e) = \log(K_F) + (1/n)\log(C_e) \quad [\text{Equation 2.4}]$$

CHAPTER 3. Coagulation and Dissolved Air Flotation for Produced Water Treatment¹

3.1 Abstract

Produced water is a major wastewater stream in the oil and gas industry which typically consists of dispersed and dissolved oils, and high levels of salinity. Despite concerns that dissolved aromatics in produced water may be detrimental to marine life, discharge regulations and treatment technologies for produced water largely focus on dispersed oil and grease removal. The purpose of this research project was to investigate coagulation with ferric chloride (FeCl_3) and dissolved air flotation (DAF) at bench-scale for the removal of both dispersed and dissolved oils from synthetic and offshore produced water samples, with a specific focus on the impact of salinity on the coagulation process. Coagulation and DAF treatment of the produced water samples achieved high removals of dispersed oil and grease, but had limited impact on dissolved aromatics. Coagulation process in the saline produced water samples reduced dispersed oil and grease concentrations from 100 mg/L to below North American discharge limits (i.e., 30 mg/L in Canada, 29 mg/L in the US) under all conditions tested, while the effectiveness of coagulation treatment in the fresh water synthetic samples was highly dependent on coagulation pH.

KEYWORDS: coagulation, dissolved air flotation, offshore, oil and grease, produced water, wastewater treatment

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3.2 Introduction

Produced water is the water present in hydrocarbon-containing subsurface rock formations which is brought to the surface during extraction activities (Veil et al., 2004). While the composition of produced water is highly variable, its organic fraction tends to be largely composed of aliphatic dispersed oils, but typically also includes dissolved hydrocarbons, such as benzene, toluene, ethylbenzene and xylene (BTEX), soluble polycyclic aromatic hydrocarbons (PAHs) and phenols (Ahmadun et. al., 2009; Fraser et al., 2006; Utvik, 1999). Typically, another major constituent in produced water is salinity, with total dissolved solids (consisting primarily of sodium and chloride) concentrations ranging from 1,000 mg/L to over 400,000 mg/L (Benko and Drewes, 2008).

Common treatment technologies for produced water include gravity separation processes, such as gas flotation and hydrocyclones (USEPA, 1993), which are not able to remove the dissolved organic constituents which may contribute to the toxicity of produced water (Veil et al., 2004). Dissolved phenols and PAHs are considered to pose the greatest toxicity risk from produced water to marine life (Ekins et al., 2007). Total oil and grease concentration in discharged water is limited to 30 mg/L as a monthly average in Canada, and 29 mg/L in the United States (NEB/CN & CNSOPB, 2002; Veil et al., 2004). Although there are no discharge standards for dissolved aromatics, the reduction of these contaminants may reduce the potential environmental impact of discharged waters from the oil and gas sectors.

Dissolved air flotation (DAF) involves supersaturating water with air under high pressures, which precipitates into gas bubbles when released into water under atmospheric pressure (Gregory and Edzwald, 2011). DAF systems produce bubbles between 10 and 100 μm in diameter, depending on saturation pressure, and have been shown to be highly effective at removing hydrophobic particles in this size range (Edzwald, 1995). Produced water consists largely of dispersed oil in a stable emulsion with droplet size between 3 and 20 μm in diameter (Moosai and Dawe, 2003), suggesting DAF treatment alone would not be effective. Furthermore, oil droplets in water tend to acquire a negative surface charge (Metcalf and Eddy, 2003), making them stable in water and not hydrophobic enough for effective bubble attachment.

Several studies have found coagulation with ferric and aluminum metal salts combined with DAF to be an effective treatment for oily wastewaters to achieve over 90 % removal of oil and grease (Zouboulis and Avranas, 2000; Al-Shamrani et al., 2002; Rattanapan et al., 2011; Santo et al., 2012). However, there is no guidance in literature on how coagulation of oily wastewater may be impacted by varying levels of salinity. Several studies in this area have been conducted within the drinking water industry (Hilal et al., 2008; Duan et al., 2002; Edzwald and Haarhoff, 2011). Overall, these studies have concluded that destabilization and coagulation of particles can be achieved at lower coagulant doses in saline water than in fresh water. This is due to the compressing effect of salinity on the electrical double layer which surrounds charged particles in water.

The purpose of this research was to address the following research gaps through bench-scale laboratory testing: (1) compare coagulation of produced water in fresh and salt water conditions and (2) determine the effectiveness of coagulation and DAF for removing dissolved petroleum oils (phenol and naphthalene) from synthetic produced water. Coagulation-DAF treatment tests were also performed on a produced water sample from an offshore gas platform in the North Atlantic Ocean, and results were compared to the results of the synthetic saline produced water treatments.

3.3 Materials and Methods

3.3.1 Synthetic Produced Water

A stock solution of synthetic produced water was generated by emulsifying crude oil into distilled (DI) water at a concentration of approximately 2 g/L by shearing the oil-water mixture in a blender for three minutes using 100 μ L of Triton-X (Sigma-Aldrich) surfactant as an emulsifier. The emulsion was left to sit for 15 minutes to allow any residual free oil to float to the surface before the stable emulsion was recovered and synthetic produced water samples with 100 mg/L of oil and grease target concentration were prepared. Fresh water synthetic produced water was prepared by diluting the stock solution with DI water and adding 5 mg/L of sodium bicarbonate (NaHCO_3) to aid in pH adjustment. Salt water synthetic produced water was prepared by diluting the stock solution with DI water containing 32 g/L sea salt (H₂Ocean, D-D, Essex, UK).

Since the crude oil sample did not contain appreciable amounts of phenols or PAHs, 5 mg/L of phenol (Sigma Aldrich) and 1 mg/L of naphthalene (Fisher Scientific) were added to the synthetic produced water within the concentration ranges reported in other studies (Stromgren et al., 1995; Utvik et al., 1999). Table 3.1 reports the molecular weights, octanol-water partition coefficient, solubility and Henry's law constants of naphthalene and phenol. Produced water samples were also taken from an offshore natural gas platform south of Nova Scotia, Canada in the North Atlantic Ocean. The produced water was in transit for approximately two weeks after sampling before arriving at the lab for testing.

Table 3.1 Physical properties of naphthalene and phenol

	Naphthalene	Phenol
Molecular weight (g/mol) ^a	128.171	94.111
Partition coefficient ($\log K_{ow}$) ^b	1.49	3.35
Solubility in water at 25°C (g/kg) ^a	0.0316	91.7
Henry's law constant at 25°C (Matm ⁻¹)	2.4 ^a	501 ^c

^aHaynes and Lide, 2010

^bKamlet et al, 1988

^cFeigenbrugel et al, 2004

3.3.2 Experimental Design

Jar tests were performed at bench-scale in a DAF batch test apparatus with six 1-L jars (EC Engineering, Edmonton, Canada). The pH of the produced water samples were adjusted to coagulation pH targets of 6 and 8 by adding pre-determined volumes of hydrochloric acid (0.5 M HCl) or caustic (0.5 M NaOH) solutions. Coagulant was added in the form of 10 g/L ferric chloride ($FeCl_3$) solution. Ferric coagulants are generally preferred for salt water coagulation

since iron is less soluble than aluminum under a wide range of pH conditions (Edzwald and Haarhoff, 2011).

Immediately after coagulant addition, the solutions were rapid mixed at a velocity gradient (G-value) of 110 s^{-1} (80 rpm) for 2 minutes, then slow-mixed at a G-value of 20 s^{-1} (20 rpm) for 15 minutes, following the optimal mixing rates for coagulating oil-water emulsions as determined by Al-Shamrani et al. (2002). Flocs formed during the flocculation stage were then floated for 10 minutes using dissolved air in DI water at a saturator pressure of 75 psi and recycle rate of 10 %. At the end of the flotation period, clarified water was sampled using the sample ports located 10 cm from the base of the jar units.

A 2^3 factorial design was conducted to test the effect of salinity, pH and coagulant (FeCl_3) dose on the removal of oil and grease, phenol and naphthalene from the synthetic produced water generated in this study. Each factor was tested at a low and high value (Table 3.2). Control runs in both salt and fresh water were conducted to evaluate the effectiveness of DAF alone (without coagulant addition). All synthetic produced water tests were run in triplicate. Samples of field produced water were tested in duplicate trials of treatment with 10 and 50 mg/L of FeCl_3 . The produced water samples were adjusted from their natural pH level of 6.3 to a coagulation target of 6.0 for comparison with the synthetic samples. Significance of factors to treatment outcomes was determined with Analysis of Variance (ANOVA) testing using Minitab. Independent t-tests were used to compare coagulation-DAF treatment with the control trials (i.e., DAF only). All error bars or \pm values displayed in figures and tables represent one standard deviation.

Table 3.2 Factorial design parameters

Factor	Low Value	High Value
Salinity (g/L)	0	32
pH	6	8
FeCl ₃ dose (mg/L)	10	50

3.3.3 Analytical Methods

Total oil and grease was determined by IR spectroscopy (Bruker Optics, Ettlingen, Germany) using Standard Method 5520C (APHA, AWWA, and WEF, 2005). Tetrachloroethylene was used as the extraction solvent, determined by Farmaki et al. (2007) to be a suitable substitute for the ozone-depleting Freon 113 specified by the standard method. Phenols concentration was analyzed by 4-aminoantipyrine indicator method and a UV-VIS spectrometer (Hach Company, Loveland, USA) using Standard Method 5530 (APHA, AWWA, and WEF, 2005). Naphthalene concentrations were determined by headspace analysis of a 0.8 mL sample by adsorption onto and desorption from solid phase micro extraction polydimethylsiloxane fibres using a 3800 Varian gas chromatograph (Agilent Technologies, Santa Clara, USA) with flame ionizing detection. Turbidity was measured using a turbidimeter (Hach Company, Loveland, USA) and zeta potential was measured on flocculated water samples using a Malvern Zetasizer (Malvern Instruments, Worcestershire, UK).

3.4 Results and Discussion

3.4.1 Synthetic Produced Water Characterization

Table 3.3 compares the characteristics of the synthetic produced water generated for this study with the produced water sampled from the offshore gas platform in the North Atlantic. The offshore produced water sample was found to have a very high conductivity (187 mS) and sodium concentration of 40 g/L. It was found to contain 21 mg/L of oil and grease, most of which was hydrocarbons (17 mg/L). The offshore sample had a high concentration of phenols (17 mg/L) which falls within the reported range of 0.58 to 23 mg/L for phenols concentration in produced water (Strongram et al., 1995; Tibbets et al., 1992; Utvik, 1999). However, the sample had negligible levels of naphthalene (0.13 mg/L), which is slightly lower than the reported concentrations of naphthalene, phenanthrene and dibenzothiophene, which have been shown to range from 0.21 to 1.6 mg/L (Strongram et al., 1995; Utvik, 1999).

Table 3.3 Synthetic and field produced water characterization

Analyte	Synthetic Sample (n=2)	Field Sample (n=2)
pH	6 or 8	6.3 ± 0.11
Conductivity (mS)	Salt Water: 44.75 ± 3.46 Fresh Water: 0.017 ± 0.011	187 ± 1.41
Oil and Grease (mg/L)	100	21.2 ± 0.70
Hydrocarbons (mg/L)		17.5 ± 0.98
Turbidity (NTU)	78.4 ± 18.1	223 ± 3.53
Phenols (mg/L)	5	17.1 ± 1.36
Naphthalene (mg/L)	1	0.13 ^a

^an=1 sample

3.4.2 Dispersed Oil Removal

Figure 3.1 presents the total oil and grease concentrations in the raw and clarified synthetic produced water samples. All coagulation-DAF experiments conducted on the saline synthetic produced water reduced total oil and grease to concentrations below discharge standards (i.e., < 30 mg/L), and significantly improved ($p < 0.05$) oil and grease removal with respect to the control treatment of DAF without coagulation pretreatment. The clarified samples of the fresh water synthetic produced water at pH 8 showed oil and grease concentrations near or below discharge standards (i.e., 7 to 30 mg/L), and also represented a significant reduction ($p < 0.05$) in residual oil and grease removal with respect to the control treatment. However, coagulation pretreatment in fresh water at pH 6 did not show significant ($p > 0.05$) reduction of oil and grease.

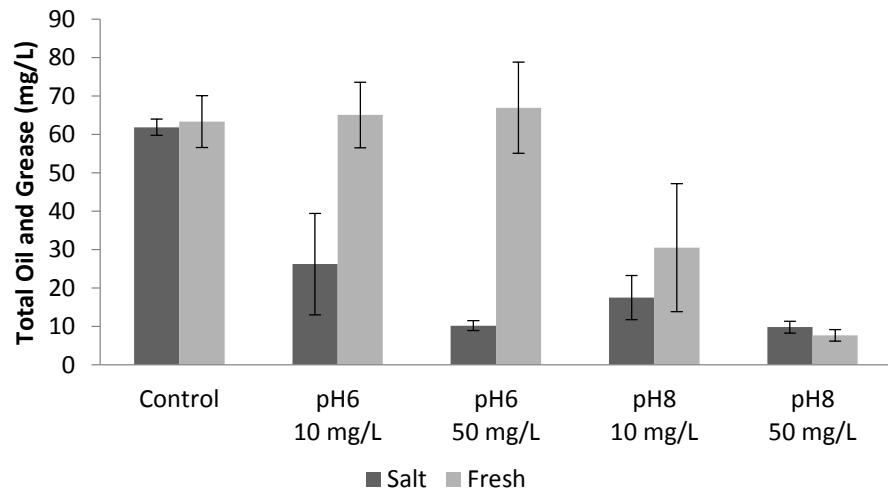


Figure 3.1 Clarified total oil and grease concentration at variable pH and FeCl_3 dose

The primary goal of coagulation is to overcome the negative electrical double layer which surrounds colloids in water and “stabilizes” the colloids, preventing them from adhering to each other and forming larger particles. Coagulation with metal salts is generally understood to occur through two distinct mechanisms: charge neutralization by adsorption of positively charged dissolved metal hydroxide species and enmeshment in solid metal hydroxide precipitate (Pernitsky and Edzwald, 2006). Coagulation through charge neutralization occurs when positively charged iron or aluminum hydroxide ions adsorb onto negatively-charged colloids in water, neutralizing their surface charge (Stumm and O’Melia, 1968). These neutrally-charged particles are “destabilized” (i.e, no longer electrostatically repulsed by each other) and thus can combine to form larger aggregates which are more easily removed from solution. However, if too much coagulant is added to the water, excess metal hydroxide will adsorb to the colloids, causing them to have a positive surface charge, and thus be “re-stabilized” (Duan and Gregory, 2003).

Charge neutralization typically occurs with lower doses of coagulant in neutral or slightly acidic pH levels because colloids have a weaker negative charge than at higher pH levels (Pernitsky and Edzwald, 2006; Sieliechi et al., 2008; Wang et al., 2011). Furthermore, Fe(OH)_2^+ , which is present at pH 6, has a higher positive surface charge than the fully hydrolyzed Fe(OH)_3 , which comprises the majority of ferric hydroxide at pH 8 (Edzwald and Haarhoff, 2011).

Zeta potential (ZP) measurements of the raw and flocculated produced water test samples are displayed in Figure 3.2. At pH 6, there was a marked difference between the removal of oil in

salt and fresh water, with good removals (i.e., 70 to 90%) of oil occurring in salt water, and poor removals (i.e., 35%) occurring in fresh water. In fresh water, an overdose of coagulant could have resulted in a restabilization of the colloids, and the positive ZP measurements observed in this study (+16 and +23 mV) support this theory. The presence of electrolytes in solution can decrease the repulsion between colloids by compressing the electric double layer, thus destabilizing the colloids and improving coagulation (Masliyah and Bhattacharjee, 2006). ZP measurements in salt water during these experiments remained within the range of -10 to +5 mV, which is considered to be optimal for removal of natural organic matter in drinking water (Matilainen et al., 2010). These results demonstrate that salt water is less sensitive to colloid restabilization effects of coagulant overdose, since the high ionic strength of the water kept the colloids destabilized at a wider range of coagulant doses. Similarly, Zhang et al (2014) found that adding Na^+ or Ca^{2+} cations to solution widened the optimal dose range of alum for fullerene removal. An excess dose of alum caused restabilization and poor removals in solution with no added cations, but in the presence of Na^+ or Ca^{2+} , the electrical double layer was compressed and high fullerene removals were achieved (Zhang et al, 2014).

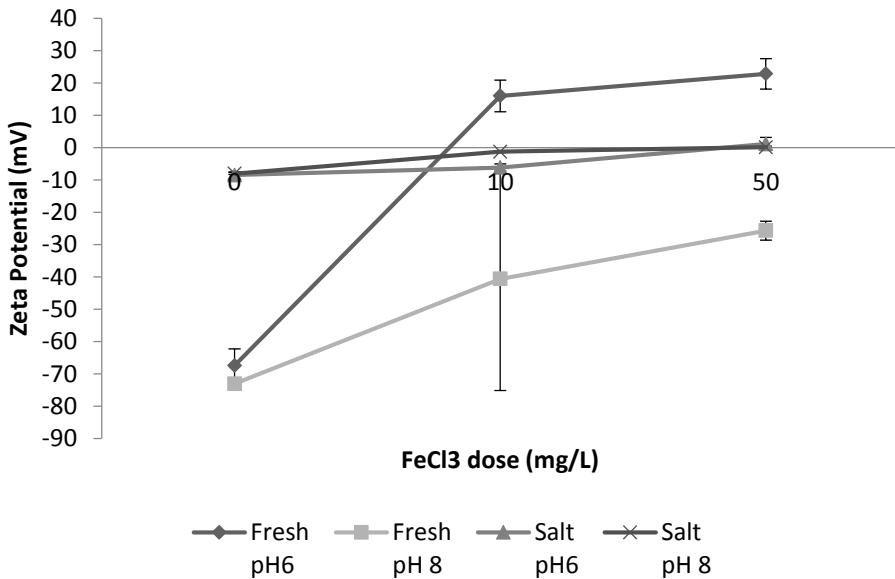


Figure 3.2. Zeta potential (mV) in salt and fresh water at pH 6 and 8

The extent of the destabilizing effect of electrolytes increases with increasing ionic strength of the solution and increased valence of the electrolyte (Edzwald et al, 1974). Edzwald et al (1974) found that increasing the strength of a NaCl solution from 0.05 M to 0.3 M (i.e., from 3.9 to 23.4 g/L) increased the destabilization of clay particles. Hilal et al (2008) reported increased removal of humic acid from a 25 g/L NaCl solution, as compared to a 10 g/L NaCl solution. However, increasing the NaCl concentration to 35 g/L did not provide an additional increase in removal, suggesting that the destabilizing effect of NaCl reached a maximum at a concentration between 25 and 35 g/L. Thus, the concentration of electrolytes used in the current study (i.e., 32 g/L) may represent the maximum level of destabilization by electrolytes.

Alternatively, coagulation can occur through enmeshment in metal hydroxide precipitate when large doses of coagulant are added to the water and large amounts of metal hydroxide precipitate

are formed rapidly. These precipitated solids provide a large surface area to which colloids can adsorb, thus sweeping the colloids out of solution. Higher pH levels, near 8 (i.e., at the point of minimum solubility for iron hydroxide), favours coagulation by enmeshment in ferric hydroxide precipitate.

At pH 8 in both salt and fresh water, coagulation is likely occurring through the mechanism of precipitation and enmeshment, since the minimum solubility of iron hydroxide occurs at pH 8, enabling large-scale precipitation. As shown in Figure 3.2, the ZP of coagulated fresh water at pH 8 was found to be strongly negative (between -30 and -40 mV), indicating that charge neutralization did not occur. However, excellent removals (i.e., 70 to 90%) of dispersed oil occurred in both salt and fresh water at pH 8.

The results of this study demonstrate that for treatment of oily wastewater in fresh water, coagulating at the pH of minimum solubility is preferred in order to avoid coagulant overdose and colloidal restabilization. However, several researchers have demonstrated effective treatment of oily wastewater with ferric chloride coagulation at pH 6 and lower, where more highly positively-charged species are present. Zoubloulis and Avranis (2000) found oil removals of greater than 90 % with FeCl_3 at coagulation pH between 6 and 9 for the treatment of a synthetic wastewater containing emulsified n-octane in water. The authors in that study reported ferric hydroxide precipitate formation with FeCl_3 at coagulation pH above 4.0. However, these authors prepared their synthetic wastewater with 0.02 M of NaCl solution, which may have contributed to destabilization of the oil at lower pH levels. Rattanapan et al. (2011) evaluated oil

and grease removal in a biodiesel wastewater sample with FeCl_3 (0.5 to 2.5 g/L) at pH levels between 5 and 7. That study showed coagulation at pH 6 resulted in the best oil and grease and chemical oxygen demand (COD) removal at the lowest FeCl_3 dose of 0.5 g/L. El-Gohary et al. (2010) found two optimal pH levels for FeCl_3 coagulation of an emulsified oil wastewater (170 mg/L O&G) at 4.6 and 8.2. The authors speculated that the optimal acidic pH value was a result of Fe(OH)_2^+ being the dominant dissolved iron species, which was able to neutralize the negative surface charge on the emulsified oil droplets. These two studies were performed on industrial wastewater, of which the ionic strength is unknown. The experimental results in the current study also show that the high ionic strength of salt water destabilizes colloids at a wider range of pH and coagulant dose conditions, so that restabilization does not occur at either pH 6 or 8.

3.4.3 Dissolved Oil Removal

Raw and clarified water concentrations of naphthalene and phenol are displayed in Figures 3.3 and 3.4, respectively. The removal of dissolved aromatic contaminants as modelled with phenol and naphthalene concentrations were found to be much lower than those of dispersed oil and grease. Coagulation has been shown to be effective for removing dissolved natural organic matter (NOM) from drinking water sources, through complexation of the dissolved NOM with dissolved coagulant species, adsorption onto metal hydroxide precipitate, or a combination of these mechanisms (Pernitsky and Edzwald, 2006).

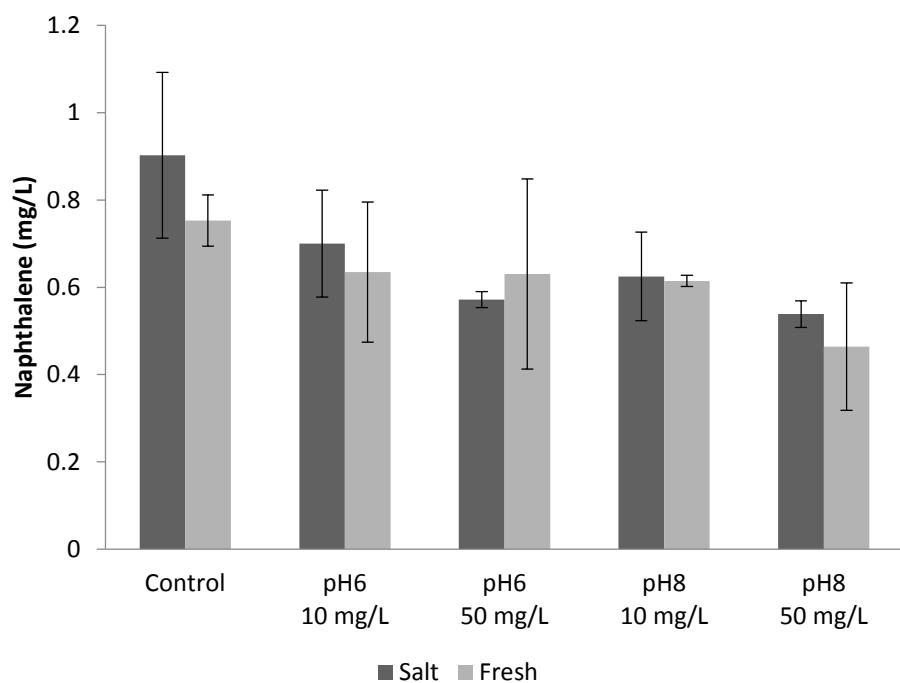


Figure 3.3 Clarified naphthalene concentration at variable pH and FeCl₃ dose

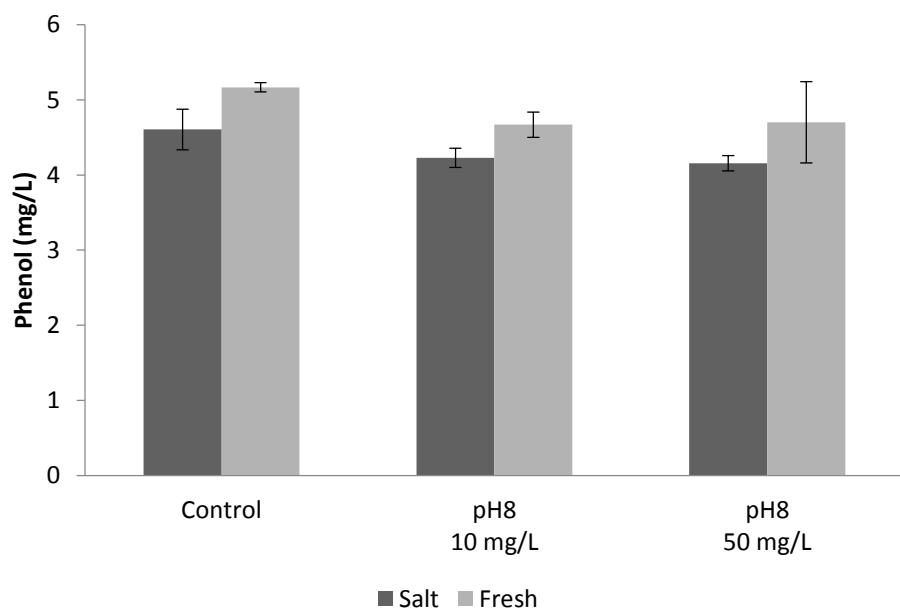


Figure 3.4 Clarified phenol concentration at pH 8

The control trials showed minimal losses of naphthalene due to volatilization, with a residual naphthalene concentration of 0.9 mg/L in the saline water control and 0.75 mg/L in the fresh water control. Low removal of naphthalene through volatilization is consistent with the work of Tansel and Pascuel (2011) who also observed poor naphthalene removals through air stripping.

Naphthalene removals with coagulant addition ranged from 19 to 47%. While none of the factors (i.e., salinity, pH, coagulant dose) were significant at a 95 % confidence level, coagulant dose was close with a p value of 0.063. This suggests that a coagulation mechanism may be responsible for some removal of naphthalene. However, coagulation did not achieve high removals of naphthalene, with the lowest residual naphthalene concentration of 0.46 mg/L occurring at pH 8, with 50 mg/L of FeCl₃ in fresh water.

Phenol removal was found to be less than 20% for fresh and salt water at both coagulant doses. Salinity was found to be a significant factor ($p < 0.05$) for phenol removal. However, coagulant addition did not significantly improve phenol removal when compared to the control trial in saline water. This suggests that any improvement in phenol removal in saline water, compared to fresh water, was due to increased volatilization rather than through a coagulation mechanism. Organic compounds are known to ‘salt out’, or have reduced solubility in saline water, which increases partitioning into the air phase. Peng and Wan (1998) determined that seawater levels of salinity (i.e., 36 g/L—which is similar to the salt concentrations in this study) increased the

Henry's law constants of several volatile organic compounds by up to 40%.

Coagulation is not typically used for the removal of phenol from water. Tomaszowska et al. (2004) conducted a study on synthetic wastewater made with 8 mg/L humic acid and 1 mg/L of phenol and found no removal of phenol by coagulation with polyaluminum chloride (PACl) and sedimentation. This is likely because phenol is a relatively small, hydrophilic compound, which is similar to the fraction of natural organic matter which is widely accepted to be recalcitrant to removal by coagulation (Collins et al., 1986). Tansel and Eifert (1999) treated a brackish synthetic petroleum wastewater with 10 g/L sea salt and 3 g/L of oil from unleaded gasoline, diesel oil and jet fuel by coagulation with a polymer/alum mixture and sedimentation. Most of the compounds remaining in the water after treatment were low molecular weight aromatic compounds, including benzenes and naphthalene, while most of the larger aliphatic hydrocarbons were removed completely by the treatment. In general, the poor removal of phenol and naphthalene found is consistent with the literature, suggesting that additional treatment steps may be necessary for the removal of these dissolved constituents.

3.4.4 Treatment of Produced Water Sample

Figure 3.5 displays the removal rates for oil and grease and phenol from the offshore produced water sample with FeCl_3 coagulation and DAF at pH 6 (near the natural pH of the produced water sample). Oil and grease removal was significantly ($p < 0.05$) improved by the addition of coagulant, with oil and grease concentrations reduced to 5 mg /L with the high coagulant dose (i.e., 50 mg/L). Similar to the synthetic produced water experiments, poor removal of phenol

(i.e., < 10%) was found for all conditions, and was not improved by coagulant addition. Coagulant addition did not impact removal of naphthalene; however, initial concentrations of naphthalene in the sample were already very low at 0.13 mg/L.

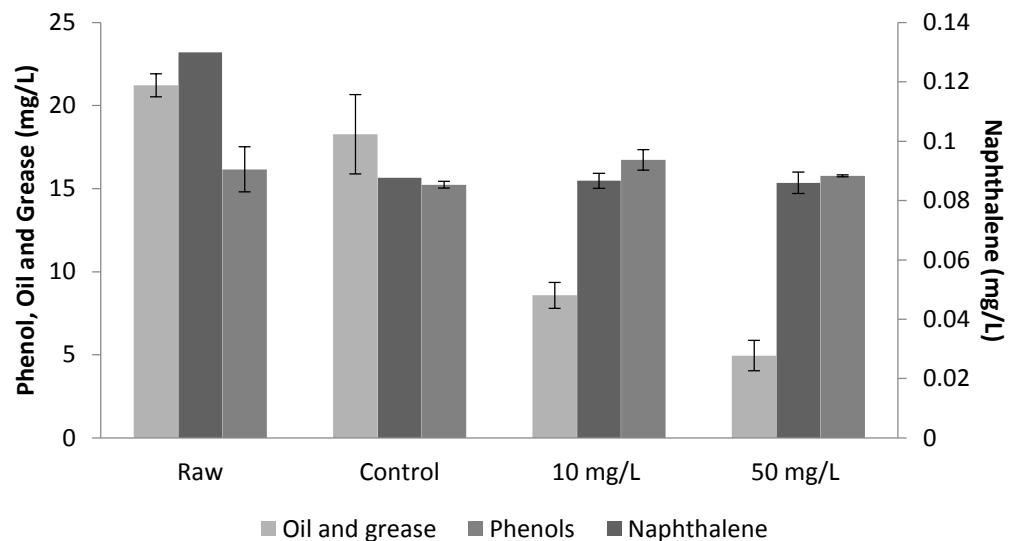


Figure 3.5 Treatment Results of Field Produced Water Experiments

The offshore produced water sample and the synthetic produced water showed similar responses to the coagulation-DAF treatment. High removals of oil and grease were achieved, with ferric chloride coagulant addition being an important factor in the removal of these constituents. With the high dose of FeCl₃ (i.e., 50 mg/L), 90% removals of oil and grease were achieved for salt water synthetic produced water, with a residual of 10 mg/L, while oil and grease in the offshore produced water sample was reduced by 76% to 5 mg/L. For both the synthetic and offshore produced water samples, the removal of dissolved aromatic constituents, especially phenol, was low and not improved by coagulant addition. These data suggest that the laboratory-made synthetic produced water is a suitable model of offshore field produced water samples.

3.5 Conclusions

The objective of this study was to investigate coagulation with ferric chloride and DAF treatment for removal of dispersed and dissolved oils from synthetic and field produced water, as well as to highlight the differences between coagulation treatment in fresh and saline oily wastewater conditions. The results of this study showed that:

- Experiments conducted with both synthetic and field produced water samples showed that coagulation with FeCl_3 and DAF can achieve high removals of oil and grease. When used to treat synthetic produced water with 100 mg/L of emulsified oil and grease, this process produced a clarified effluent which meets the North American produced water treatment standards of 29 or 30 mg/L total oil and grease concentration. Coagulation with 50 mg/L of FeCl_3 reduced oil and grease in salt water synthetic produced water to 10 mg/L, a 90% reduction, and in field produced water samples to 5 mg/L, a 76% reduction.
- In fresh water, coagulation with FeCl_3 at the pH of minimum solubility (i.e., pH 8) is preferred in order to avoid coagulant overdose and colloidal restabilization. However, the high ionic strength of salt water was found to destabilize colloids at a wider range of pH and coagulant doses, with restabilization found not to occur at either pH 6 or 8.
- Poor removal of dissolved aromatic constituents (i.e., phenol and naphthalene) was observed in the experiments in both synthetic and field produced water samples. High concentrations of phenol in the offshore produced water sample indicate that dissolved aromatics can be a major constituent of produced waters. Thus, enhanced treatment

should include capacity for phenol removal in addition to the process evaluated in this study.

- The synthetic produced water generated in the lab is a satisfactory substitute for field samples, as it contained similar constituents as the field sample, and displayed a similar response to the treatment process.

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CHAPTER 4. Integrated Adsorption-Coagulation-Dissolved Air Flotation Process for Produced Water Treatment²

4.1 Abstract

In oil and gas extraction operations, water from the hydrocarbon reservoir is brought to the surface along with the oil or gas. This “produced water” contains organics which may be free, dispersed, or dissolved in the water. While certain dissolved compounds may contribute to environmental risk from produced water, current North American discharge regulations only address the dispersed fraction of oil and grease (29 mg/L in the US, 30 mg/L in Canada). The purpose of this research was to investigate, at bench scale, chemical coagulation with ferric chloride (FeCl_3) and adsorption with organoclay (OC) in a completely stirred tank reactor (CSTR) configuration as pre-treatment for dissolved air flotation (DAF) for the removal of dissolved and dispersed oils from produced water. The integrated process was evaluated and compared to the individual processes of coagulation-DAF, adsorption-DAF and DAF without pre-treatment for the removal of dispersed oil, naphthalene and phenol from synthetic produced water. Concentrations of dispersed oil in clarified water were reduced, from an initial concentration of 100 mg/L, to concentrations as low as 10 ± 1.6 mg/l after coagulation with FeCl_3 (FeCl_3 -DAF), 15 ± 1.2 mg/L after adsorption with OC (OC-DAF), and 7 ± 1.4 mg/L after the integrated process (OC- FeCl_3 -DAF). From an initial naphthalene concentration of 1 mg/L, both the adsorption (OC-DAF) and integrated process (OC- FeCl_3) achieved clarified naphthalene concentrations of 0.11 ± 0.01 mg/L, representing a significant improvement over the 0.53 ± 0.03

² Note: This work has been published in *Journal of Environmental Chemical Engineering* Younker, J.M., Walsh, M.E., 2014. Bench-scale investigation of an integrated adsorption-coagulation-dissolved air flotation process for produced water treatment. *Journal of Environmental Chemical Engineering* 2 (1), 692-697.

mg/L achieved by coagulation treatment (FeCl_3 -DAF). However, none of the processes evaluated in this study were found to be effective for phenol removal.

KEYWORDS: adsorption; coagulation; dissolved air flotation; organoclay; produced water

4.2 Introduction

Produced water is the name given to the co-produced wastewater stream generated when water from underground reservoirs is brought to the surface during oil or gas extraction (Veil et al, 2004). Offshore platforms often discharge this wastewater into the open ocean after treatment is applied to reduce total oil and grease concentrations. Oil and grease is limited to 30 mg/L as a monthly average in Canada (NEB and CN & CNSOPB, 2002) and North-East Atlantic Europe (OSPAR, 2001), while in the United States, this limit is 29 mg/L (Veil et al, 2004). However, concentrations of dispersed oil and grease are not necessarily correlated to concentration of dissolved aromatics, which are considered to be the main contributors to produced water toxicity (Utvik, 1999; Utvik and Hasle, 2002). Recent changes to the Oslo-Paris Commission (OSPAR) discharge guidelines reflect these concerns by including BTEX concentrations in the calculations for oil and grease levels (OSPAR, 2011). However, North American discharge regulations currently address only the free and dispersed fractions of oil and grease in produced water.

Alkylphenols and PAHs are specific classes of aromatic hydrocarbons which have been identified as endocrine disruptors (Tollefsen et al, 2007). These compounds may be highly soluble in water, partially soluble or may partition primarily into the dispersed oil phase, depending on molecular weight (Tollefsen et al, 2007; Faksness et al, 2004). Substances which partition partially or primarily into the water phase are of particular concern as they are not

removed with dispersed oils (Utvik, 1999; Faksness et al, 2004). Alkylphenols and PAHs have been confirmed in produced water discharges (Tollefsen et al, 2007) and within 2 km of discharge points (Harman et al, 2009). While these concentrations are below acute harm levels for marine organisms, the chronic effects of these compounds are not well understood (Harman et al, 2009).

Flotation is a common technology for offshore produced water treatment, but is not considered to be an effective treatment for dissolved components, suggesting that pre-treatment processes may be necessary (Ynnesdal and Furuholt, 1994; USEPA, 1993). Organoclay is clay which has been modified with quaternary ammonium cations to be organophilic, and thus is able to sorb organic compounds from water. Organoclay adsorption in packed-bed adsorption columns has been implemented as a treatment for produced water and gas plant wastewater (Doyle and Brown, 2000; Alther, 2001). This technology has been shown to achieve some removal of dissolved compounds from water, such as phenols and BTEX (Doyle and Brown, 2000; Rawajfih and Nsour, 2006).

Organoclay adsorption is typically implemented in fixed-bed adsorption columns, although several studies have been conducted to evaluate the efficiency of this adsorbent in a completely stirred tank reactor (CSTR) design. Moazed and Viraraghavan (2005) demonstrated up to 89% removal of oil from a produced water sample using batch adsorption with powdered organoclay. Organoclay adsorption in a CSTR with sedimentation as the clarification step was also investigated for oil refinery wastewater treatment, demonstrating that organoclays were amenable to removal by sedimentation after adsorption of oil had taken place (Yang et al, 2002).

Organoclay adsorption in a CSTR combined with alum coagulation and sedimentation was shown to simultaneously remove phosphate and phenanthrene from synthetic wastewater (Ma et al, 2010). Similarly, combining chemical coagulation with powdered activated carbon (PAC) adsorption has been shown to improve both organics removal and subsequent clarification in synthetic wastewater containing humic acid and phenol (Tomaszewska et al, 2004). However, no studies have investigated dissolved air flotation (DAF) as the clarification step for organoclay alone or in combination with a coagulant, or have evaluated an integrated coagulation-adsorption-DAF process for produced water treatment.

The overall purpose of this research was to investigate the efficacy of an integrated organoclay-coagulation CSTR process followed by DAF for produced water treatment. The treatment capacity of this integrated process was compared to the individual unit processes of FeCl₃ coagulation and organoclay adsorption followed by DAF.

4.3 Materials and Methods

4.3.1 Synthetic Produced Water

Table 4.1 summarizes the characteristics of the synthetic produced water used in this study. A stock solution of synthetic produced water was generated by emulsifying crude oil into distilled (DI) water at a concentration of approximately 2 g/L by shearing the oil-water mixture in a blender for three minutes using 100 µL of Triton-X (Sigma-Aldrich) surfactant as an emulsifier. The emulsion was left to sit for 15 minutes to allow any residual free oil to float to the surface before the stable emulsion was recovered and synthetic produced water samples with 100 mg/L

of oil and grease target concentration were prepared. As offshore produced water is typically saline (Benko and Drewes, 2008), 32 g/L sea salt was added to synthetic produced water samples. Since the crude oil sample did not contain appreciable amounts of phenols or PAHs, 5 mg/L of phenol (Sigma Aldrich) and 1 mg/L of naphthalene (Fisher Scientific) were added to the synthetic produced water which are within the concentration ranges reported for offshore produced water in other studies (Utvik, 1999; Strømgrn et al, 1995).

Table 4.1 Characteristics of synthetic produced water

Parameter	Value	Unit
Oil and Grease	100	mg/L
Phenol	5	mg/L
Naphthalene	1	mg/L
Salinity	32,000	ppm
pH	8.3	
Conductivity	46	mS/cm

4.3.2 Bench-Scale Experimental Design

Three different treatments for produced water were tested: (1) ferric chloride coagulation-DAF (FeCl_3 -DAF), (2) organoclay adsorption-DAF (OC-DAF) and (3) integrated coagulation-adsorption-DAF (OC- FeCl_3 -DAF). Figure 4.1 presents a process flow diagram of the integrated OC- FeCl_3 -DAF process evaluated in this study. A control trial of DAF without pretreatment was also conducted. All tests were performed at bench-scale in a DAF batch jar test apparatus (EC Engineering, Edmonton, Canada). Raw water was adjusted from its natural pH of 8.3 to pH 8 by adding pre-determined volumes of 0.5 M hydrochloric acid (HCl) or sodium hydroxide (NaOH)

solution to achieve pH of minimum solubility for FeCl_3 coagulation. Coagulant was added in the form of 10 g/L ferric chloride (FeCl_3) solution. Granular organoclay (PM-199, Cetco, Hoffman Estates, Illinois) was pulverized and sieved through a 200 mesh sieve to produce a powdered product which could be easily dispersed into the water during mixing. This powdered organoclay was added to the jar tester prior to the addition of FeCl_3 coagulant.

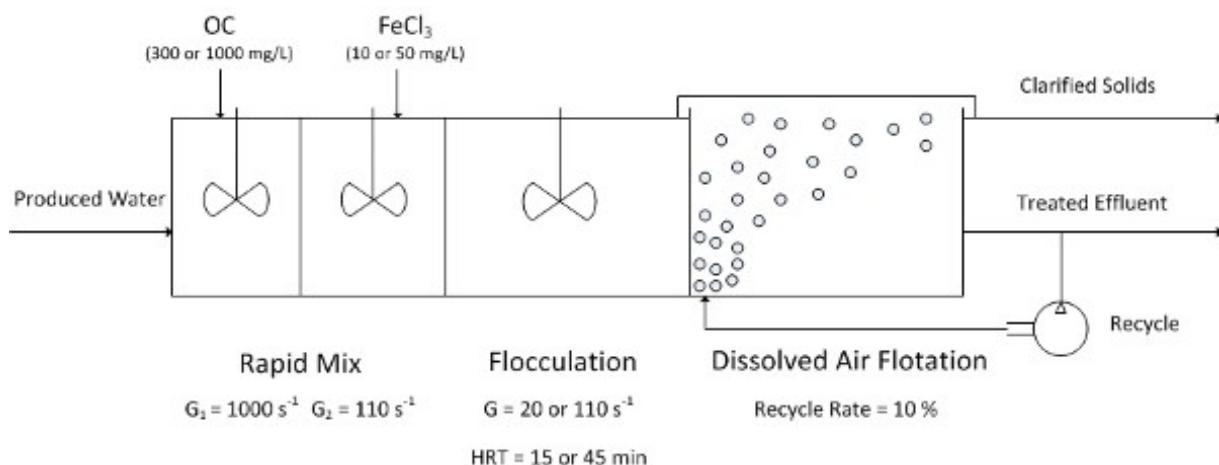


Figure 4.1 Integrated adsorption-coagulation-DAF treatment train for produced water

A factorial design was developed to investigate the impact of coagulant dose, adsorbent dose, flocculation mixing time and velocity gradients as outlined in Figure 1. All tests were performed in triplicate, and conducted at room temperature. Table 4.2 summarizes mixing velocity gradients (G-values) and durations for each treatment type. Coagulation tests (FeCl_3 -DAF) consisted of a 2 minute rapid mix at 110 s^{-1} , followed by a 15 minute slow mix at 20 s^{-1} . Adsorption tests (OC-DAF) consisted of an initial 1 minute mix at 1000 s^{-1} to fully suspend the organoclay, followed by a 15 or 45 minute mix at 110 s^{-1} . Integrated tests (OC- FeCl_3 -DAF) in the low mixing time condition consisted of a 1 minute rapid mix at 1000 s^{-1} to fully suspend the

organoclay, followed by coagulant addition, a 2 minute rapid mix at 110 s^{-1} and a 15 minute slow mix at 20 s^{-1} . Integrated tests (OC- FeCl_3 -DAF) in the high mixing time condition consisted of a 1 minute rapid mix at 1000 s^{-1} , followed by a 30 minute mix at 110 s^{-1} , coagulant addition, and a 15 minute slow mix at 20 s^{-1} . After all treatments, particles were floated for 10 minutes after injecting dissolved air in DI water at a saturator pressure of 75 psi and recycle rate of 10%.

Table 4.2 Mixing duration and G-value for each treatment

Treatment	Low HRT			High HRT		
	Rapid Mix 1	Rapid Mix 2	Flocculation	Rapid Mix 1	Rapid Mix 2	Flocculation
FeCl ₃ -DAF	---	2 min 110 s^{-1}	15 min 20 s^{-1}	---	---	---
OC-DAF	1 min	---	15 min	1 min	---	45 min
		1000 s^{-1}	110 s^{-1}	1000 s^{-1}		110 s^{-1}
OC- FeCl_3 -DAF	1 min	2 min	15 min	1 min	30 min	15 min
	1000 s^{-1}	110 s^{-1}	20 s^{-1}	1000 s^{-1}	110 s^{-1}	20 s^{-1}

4.3.3 Analytical Methods

Total oil and grease concentrations were determined by IR spectroscopy (Bruker Optics, Ettlingen, Germany) using Standard Method 5520C (APHA, AWWA and WEF, 2005), with tetrachloroethylene substituted as the extraction solvent, as described by Farmaki et al (2010). Phenols concentrations were analyzed by 4-aminoantipyrine indicator method and UV-VIS spectroscopy (Hach Company, Loveland, USA) using Standard Method 5530 (APHA, AWWA, and WEF, 2005). Naphthalene concentration was determined by headspace analysis of a 0.8 mL sample by adsorption onto and desorption from solid phase micro extraction

polydimethylsiloxane fibres using a 3800 Varian gas chromatograph (Agilent Technologies, Santa Clara, USA) with flame ionizing detection. Floc size was measured using a Malvern Mastersizer (Malvern Instruments, Worcestershire, UK). Statistical significance of treatment factors were determined using analysis of variance (ANOVA) with Minitab. Error bars and \pm values throughout the manuscript represent one standard deviation.

4.4 Results and Discussion

4.4.1 Dispersed Oil and Grease Removal

Figure 4.2 displays clarified water oil and grease concentrations after the control treatment of DAF with no pretreatment, as well as coagulation (FeCl_3 -DAF), adsorption (OC-DAF), and integrated (OC- FeCl_3 -DAF) treatments. DAF with no pretreatment (i.e., control treatment) produced a finished water oil and grease concentration of 65 ± 18 mg/L, which is considerably above discharge standards (i.e., 30 mg/L). The FeCl_3 -DAF, OC-DAF, and OC- FeCl_3 -DAF treatments all reduced oil and grease concentrations to below the 30 mg/L discharge standard, with the exception of the OC-DAF treatment with the low organoclay dose (i.e., 300 mg/L) and the low mixing time (i.e., 15 minutes). These results demonstrate that chemical pre-treatment for DAF is necessary for effective removal of oil and grease from produced water.

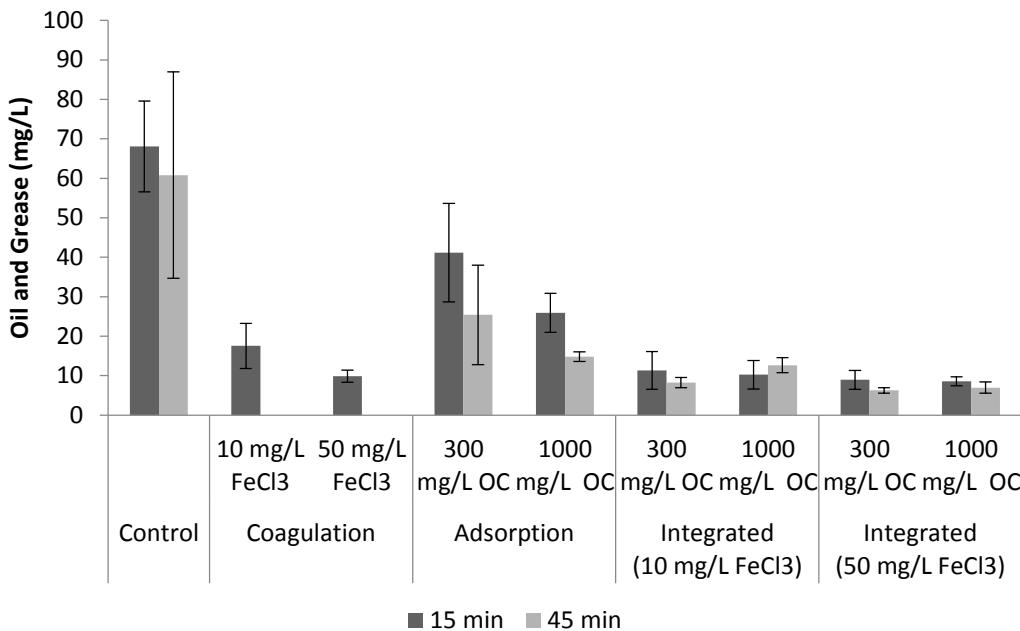


Figure 4.2 Clarified oil and grease concentrations after coagulation, adsorption and integrated treatments

In the FeCl_3 -DAF trials, both coagulant doses (i.e., 10 and 50 mg/L) reduced total oil and grease concentrations below discharge standards (i.e., 30 mg/L). Increasing the coagulant dose from 10 to 50 mg/L was not found to significantly ($p > 0.05$) improve oil and grease removal, indicating that coagulation is very effective for dispersed oil removal even at relatively low FeCl_3 doses. Several studies have found coagulation with ferric and aluminum metal salts combined with DAF to be an effective treatment for oily wastewaters to achieve over 90 % removal of oil and grease (Zouboulis and Avranas, 2000; Al-Shamrani et al, 2002; Rattanapan et al, 2011; Santo et al, 2012).

In the OC-DAF trials, the low dose of organoclay (i.e., 300 mg/L) with the low mixing time (i.e., 15 minutes) treatment did not result in a clarified water oil and grease concentration below

discharge standards. However, increasing either the organoclay dose to the high level (i.e., 1000 mg/L) or the mixing time (i.e., 45 minutes), resulted in a significant improvement ($p < 0.05$) in oil and grease removal, and reduced the concentration to below discharge standards. These results demonstrate that OC-DAF treatment can achieve high removals of dispersed oil, but its efficacy is highly dependent on the OC dose and mixing time.

Several studies have investigated the treatment of industrial wastewater or produced water using organoclay as a medium in adsorption columns. Moazed and Viraraghavan (2001) used a 30 % organoclay and 70 % anthracite mixture as a filter medium in column adsorption tests for the removal of oil from synthetic wastewaters with mineral oil or cutting oil at starting concentrations of 46 to 69 mg/L of oil and grease. Similar to the results of this study, higher oil removals were achieved with higher organoclay doses and increased contact time, with the highest bed depth and lowest flow rate achieving up to 69 % oil removal (Moazed and Viraraghavan, 2001). Another study reported high removals of oil (85 to 99 %) from produced water with initial oil and grease concentrations of 35 to 218 mg/L with organoclay column adsorption (Doyle and Brown, 2000). Moazed and Viraraghavan (2005) performed batch adsorption tests with a blend of 30 % organoclay and 70 % anthracite to remove 87 % of oil and grease from a produced water sample containing 231 mg/L of emulsified oil. The results of the present work show similar levels of removal, with the high organoclay dose (i.e., 1000 mg/L) and high retention time (i.e., 45 minutes) achieving 85 % removal of oil and grease from wastewater with an initial concentration of 100 mg/L of oil and grease. These results demonstrate that mixing organoclay in a CSTR followed by DAF clarification is a suitable application for organoclay adsorption.

The results of the OC-FeCl₃-DAF integrated treatment was shown to reduce oil and grease concentration to below 30 mg/L. Increasing the FeCl₃ dose from 10 to 50 mg/L significantly ($p < 0.05$) improved oil and grease removals in the integrated trials. However, increasing the organoclay dose or mixing time was not shown to have a significant ($p > 0.05$) impact on oil and grease removal. This indicates that coagulation, rather than adsorption, was the main mechanism for dispersed oil removal in the integrated treatment process.

4.4.2 Dissolved Aromatic Hydrocarbons Removal

Figures 4.3 and 4.4 present clarified naphthalene and phenol concentrations in the clarified water sample, respectively, after coagulation, adsorption and integrated process treatments. Some removal of naphthalene was observed in the coagulation treatments, with 50 mg/L of FeCl₃ reducing naphthalene concentration to 0.53 mg/L, as compared to 0.81 mg/L in the control treatment (i.e., DAF alone). Negligible removal of phenol was observed, with less than 15 % removal achieved in the coagulation treatment, as compared to the control treatment.

Increasing the coagulant dose from 10 to 50 mg/L did not have a significant ($p > 0.05$) effect on either naphthalene or phenol removal. Small, hydrophilic compounds, such as phenol, are not generally considered to be amenable to removal by coagulation (Collins et al, 1986).

Tomaszowska et al. (2004) found no removal of phenol by coagulation with polyaluminum chloride (PACl) and sedimentation from synthetic wastewater containing 1 mg/L of phenol. The poor removal of phenol and naphthalene found with coagulation is consistent with the literature, suggesting that additional treatment steps may be necessary for the removal of these dissolved constituents.

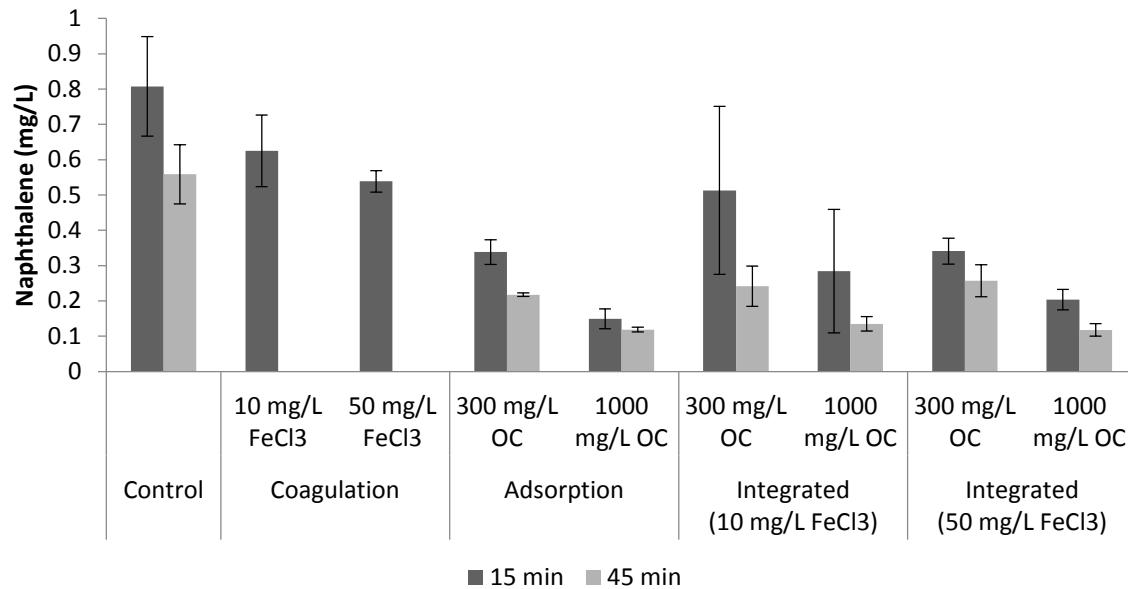


Figure 4.3 Clarified naphthalene concentrations after coagulation, adsorption and integrated treatments

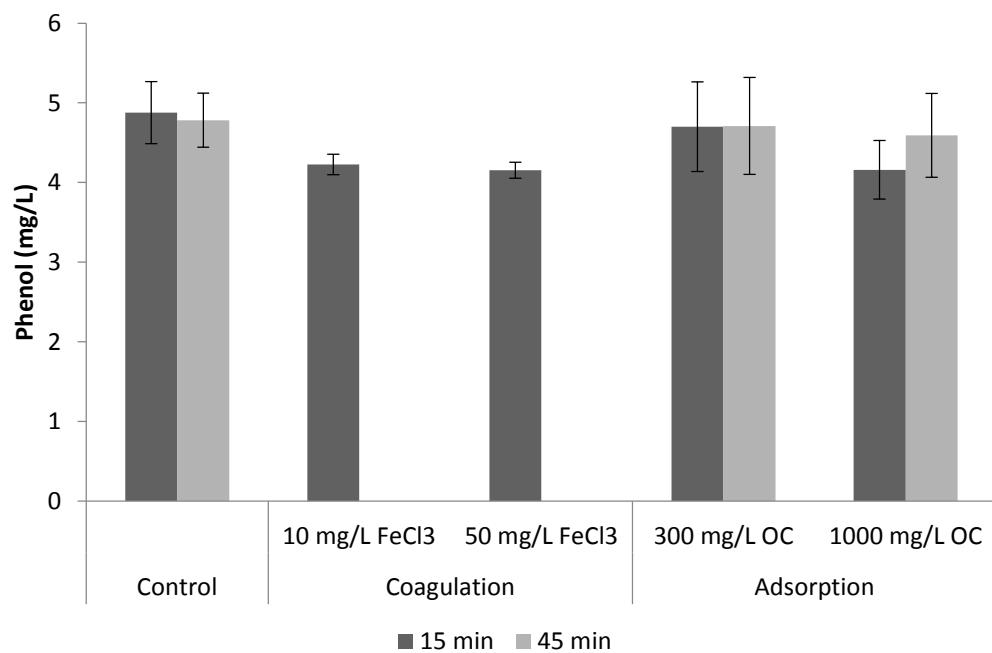


Figure 4.4 Clarified phenol concentrations after coagulation and adsorption treatments

Adsorption with organoclay was found to perform better than coagulation for naphthalene removal at all test conditions. The low dose (i.e., 300 mg/L) of organoclay at the low mixing time (i.e., 15 minutes) reduced naphthalene to 0.34 ± 0.04 mg/L, as compared to 0.53 ± 0.03 mg/L with the high dose of coagulant. Increasing the organoclay dose from 300 mg/L to 1000 mg/L significantly ($p < 0.05$) improved naphthalene removal. The high organoclay dose (i.e., 1000 mg/L) at the high mixing time (i.e., 45 minutes) reduced naphthalene concentrations to 0.12 ± 0.01 mg/L. Similar to the FeCl₃-DAF experiments, negligible removal of phenol was observed in the OC-DAF experiments.

The difference in removal between naphthalene and phenol in this study is likely a result of the higher solubility of phenol in water compared to naphthalene. Organoclays are often produced with surfactants containing a long alkyl chain ‘tail’, which form a solvent layer surrounding the clay into which organic molecules can partition (Groisman et al, 2004). Several studies comparing the adsorption of solutes with varying hydrophobicities onto long-chain surfactant based organoclays have confirmed that hydrophobic molecules are more amenable to partitioning into the solvent layer, and thus being removed by organoclays (Rawajfih and Nsour, 2006; Groisman et al, 2004; Zhu et al, 1998). Naphthalene, with a log K_{ow} of 3.35, is much more hydrophobic than phenol, which has a log K_{ow} of 1.49 (Kamlet et al, 1988). Naphthalene has been observed to adsorb to organoclays produced with long alkyl chain surfactants (Lee et al, 2004; Changchaivong and Khaodhiar, 2009). Higher naphthalene sorption was found to be achieved with longer chain surfactant-based organoclay than with shorter chain surfactant-based organoclay suggesting that a partitioning mechanism was responsible for naphthalene removal (Lee et al, 2004). Several researchers have observed poor phenol removal (< 30%) with long

aliphatic chain surfactant based organoclays (Mortland et al, 1986; Yapar et al, 2005; Lin and Cheng, 2002). However, several studies have indicated that organoclay made with aromatic surfactants (i.e., trimethylphenyl ammonium, benzyltrimethyl ammonium, benzyltriethyl ammonium) may act as efficient adsorbents for phenol, achieving up to 90% removal of phenol from water (Mortland et al, 1986; Shen, 2002; Shen, 2004; Yapar et al, 2005). This may be a result of attraction between phenol and the aromatic structure present in these organoclays (Shen, 2002). The results of this study suggest that the OC used was produced with a long alkyl chain surfactant, and that both dispersed oils and naphthalene were removed by a partitioning mechanism. However, the phenol was not hydrophobic enough to be removed by this mechanism, but may be able to be removed by an aromatic surfactant based organoclay, or an alternative adsorbant, such as powdered activated carbon (PAC), which has been found to be an effective adsorbent for phenol (Ahmaruzzaman and Sharma, 2005; Ozkaya, 2006; Anirudhan et al, 2009).

Since phenol was not found to be removed in either the FeCl_3 -DAF or OC-DAF processes, phenol removal was not tested with the integrated OC- FeCl_3 -DAF treatment. After integrated treatment, clarified naphthalene concentrations ranged from 0.34 ± 0.04 mg/L (with low organoclay dose and mixing time) to 0.12 ± 0.02 mg/L (with high organoclay dose and mixing time). These results are very similar to the naphthalene removal results for the OC-DAF process (i.e., 0.34 ± 0.04 mg/L with low OC dose and low mixing time, and 0.12 ± 0.01 with high OC dose and high mixing time). Increasing organoclay dose or mixing time significantly ($p < 0.05$) improved naphthalene removal, while increasing the coagulant dose did not significantly ($p > 0.05$) improve naphthalene removal, which indicates that adsorption, rather than coagulation was

the main mechanism for naphthalene removal in the integrated treatment process. However, naphthalene removal observed in control trials (i.e. DAF alone) was found to be significantly ($p < 0.05$) improved with increased mixing time (i.e. 15 to 45 minutes), suggesting that the improved naphthalene removal in high mixing time integrated treatment trials may have been due to volatilization or sorption to jar test equipment, rather than adsorption by the organoclay.

An analysis of variance (ANOVA) test was performed on the results of coagulation and integrated trials to determine if organoclay addition had a significant effect on removal of naphthalene. This ANOVA considered three levels of organoclay addition—0 mg/L (i.e., coagulation-DAF alone), 300 mg/L (i.e., integrated trials with the low organoclay dose) and 1000 mg/L (i.e., integrated trials with the high organoclay dose). Organoclay addition was found to be a significant factor ($p < 0.05$) for naphthalene removal, meaning that the integrated process with coagulation and organoclay adsorption resulted in enhanced naphthalene removal when compared to coagulation alone.

4.4.3 Effect of G-Value on treatment

During the integrated coagulation-adsorption trials, the lower velocity gradient applied during the flocculation stage (i.e., 20 s^{-1}) compared to the G-value applied during organoclay addition (i.e., 110 s^{-1}) was found to result in some organoclay particles settling out during this mixing stage. The velocity gradient of a slow mix stage has a direct effect on ultimate floc size since increased shear forces tend to fragment flocs (Spicer et al, 1998), so lower velocity gradients of

10 to 80 s⁻¹ are generally targeted to allow for floc growth in the flocculation stage of coagulation processes (Crittenden et al, 2005). However, DAF can remove smaller particles from water than sedimentation, and it has been shown that floc sizes of 100 µm are sufficient for good bubble attachment and clarification with DAF (Edzwald, 1995). The effect of velocity gradient on the water quality after coagulation, adsorption and the integrated process, as well particle size, was therefore investigated in this study to determine if slow mix speed could be optimized for adsorbent suspension and flocculation simultaneously.

Figures 4.5 and 4.6 present clarified oil and grease and naphthalene concentrations, respectively, for the four different treatments tested (control, FeCl₃-DAF, OC-DAF and integrated OC-FeCl₃-DAF) under low and high velocity gradients (i.e., 20 and 110 s⁻¹, respectively) in the slow mix flocculation stage. Adsorption treatment with organoclay was found to be significantly ($p < 0.05$) impacted by the flocculation stage velocity gradient, with improved oil and grease and naphthalene removals occurring at the high velocity gradient (i.e., 110 s⁻¹). Neither oil and grease or naphthalene removal was found to be significantly impacted ($p > 0.05$) by the velocity gradient in coagulation and integrated coagulation-adsorption treatments. These results suggest that higher G-values improved suspension of OC particles, allowing for improved contact time for adsorption reactions.

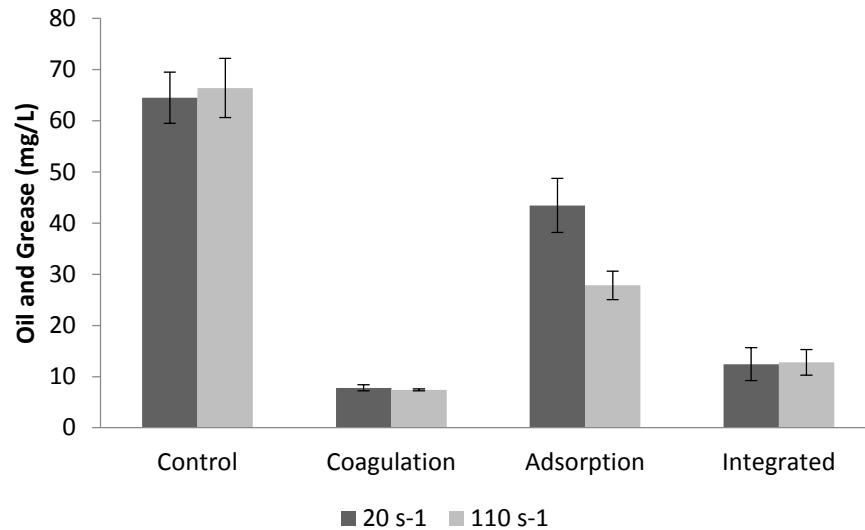


Figure 4.5 Clarified oil and grease concentrations under low and high velocity gradients

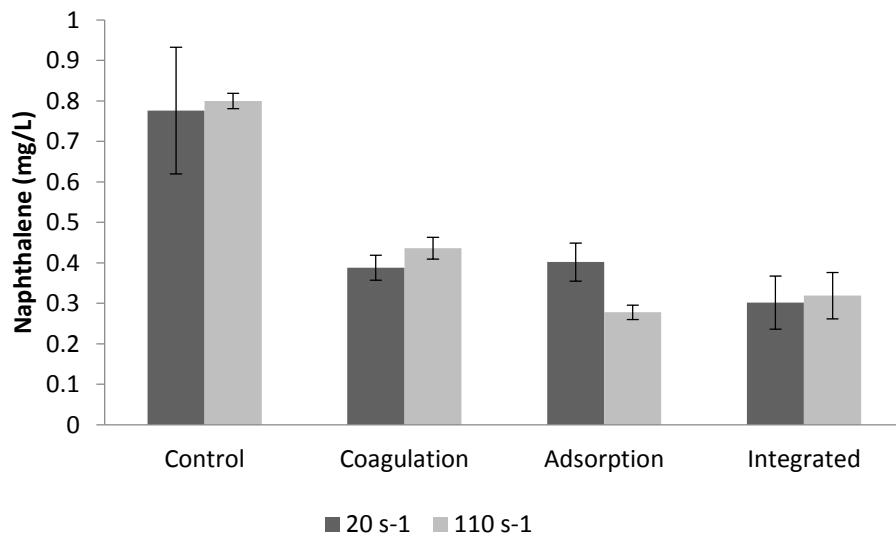


Figure 4.6 Clarified naphthalene concentration under low and high velocity gradients

Figure 4.7 displays the 50th, 90th and 10th percentile floc-particle sizes of OC-FeCl₃ aggregates formed with 300 mg/L of OC and 50 mg/L of FeCl₃ in synthetic produced water under low and high slow mix velocity gradients (i.e., 20 and 110 s⁻¹, respectively). Increasing the slow mix velocity gradient from 20 to 110 s⁻¹ significantly ($p < 0.05$) reduced the 50th and 90th percentile

floc sizes. However, at the highest velocity gradient (i.e., 110 s^{-1}), the 10th percentile floc aggregates were still over 100 μm in diameter. Thus, the smallest flocs being formed at the high G-value were still within the optimal range for DAF clarification. Therefore, increasing the mixing speed did not affect efficacy of coagulation and integrated coagulation-adsorption treatments, since adequate floc sizes were being formed even under higher velocity gradient conditions.

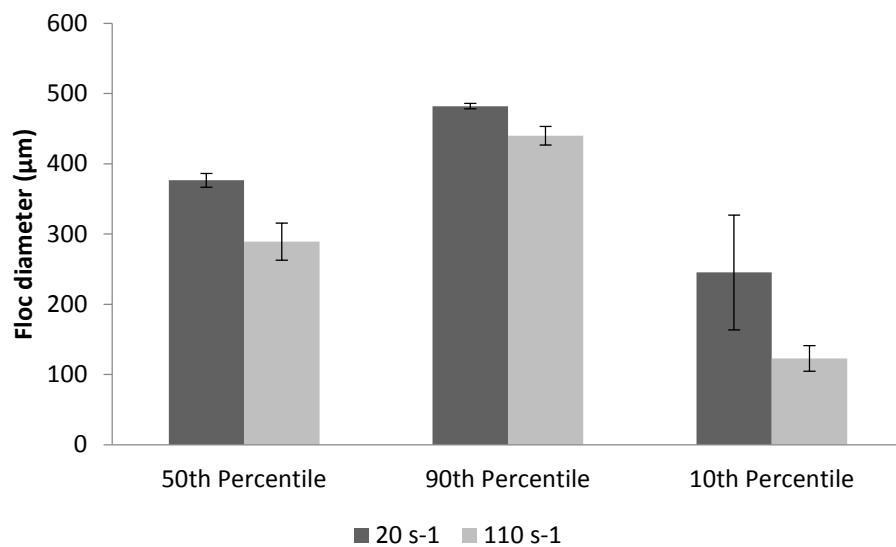


Figure 4.7 50th, 90th and 10th percentile particle sizes under low and high velocity gradients

4.5 Conclusions

- Overall, all of the processes evaluated in this study resulted in oil and grease removal from synthetic produced water samples. With the exception of the low organoclay/low mixing time adsorption trial, all chemical pre-treatments for DAF resulted in oil and grease concentrations below discharge standards (i.e., 30 mg/L).

- None of the treatment processes evaluated in this study demonstrated significant removal of phenol, possibly due to its hydrophilic nature. An alternative adsorbent, such as PAC, or an aromatic-based organoclay may be more effective for phenol removal within the CSTR-based treatment trains evaluated in this study.
- The addition of organoclay to FeCl₃-DAF process significantly improved naphthalene removal, while maintaining high oil and grease removals.
- Increasing the slow mix velocity gradient significantly improved OC treatment in the removal of both oil and grease and naphthalene, but did not impact the coagulation or integrated treatments for the removal of either contaminant. While increasing the G-value significantly decreased 50th and 90th percentile floc diameter of OC-FeCl₃ aggregates, the smallest floc size under this treatment remained above the optimal range for DAF clarification (i.e., 100 um)

4.7 References

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CHAPTER 5. Adsorption of Dissolved Aromatic Hydrocarbons by Activated Carbon and Organoclay³

5.1 Abstract

Adsorption capacity of phenol and naphthalene by powdered activated carbon (PAC), a commercial organoclay (OC) and a lab synthesized organoclay (BTMA) was studied using batch adsorption experiments under variable feed water quality conditions including single- and multi-solute conditions, fresh water, saline water and oily-and-saline water. Increasing salinity levels was found to reduce adsorption capacity of OC, likely due to destabilization, aggregation and subsequent removal of organoclay from the water column, but did not negatively impact adsorption capacity of PAC or BTMA. Increased dispersed oil concentrations were found to reduce the surface area of all adsorbents. This decreased the adsorption capacity of PAC for both phenol and naphthalene, and reduced BTMA adsorption of phenol, but did not negatively affect naphthalene removals by either organoclay. The presence of naphthalene as a co-solute significantly reduced phenol adsorption by PAC, but had no impact on adsorption b OC or BTMA. These results indicated that adsorption by PAC occurred via a surface adsorption mechanism, while organoclay adsorption occurred by hydrophobic or pi dispersion forces. In general, PAC was more sensitive to changes in water quality than either of the organoclays (i.e., OC or BTMA) evaluated in this study. However, PAC exhibited a higher adsorption capacity for phenol and naphthalene compared to both organoclays even in adverse water quality conditions.

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5.2 Introduction

The petroleum industry generates a range of wastewater streams, including co-produced water and petroleum refinery effluent, which typically contain insoluble oil and grease, high levels of salinity, and a range of dissolved organics (Utvik, 1999; Benko and Drewes, 2008). Dissolved aromatics, including BTEX (i.e., benzene, toluene, ethylbenzene and xylene), phenols and PAHs (i.e., polycyclic aromatic hydrocarbons) have been identified as major contributors to the environmental toxicity of wastewater discharges (Utvik and Hasle, 2002). While a number of adsorbent materials have been demonstrated to be effective for the removal of these compounds in pure water tests, the adsorption process may be affected by the presence of oil and grease, salinity or co-solutes. Thus, identification of an appropriate adsorbent for dissolved aromatics removal from an industrial wastewater matrix is of crucial importance.

Activated carbon is a carbon-based material with an exceptionally large surface area, which has been widely studied for the removal of dissolved organics (Snoeyink and Weber, 1967). While adsorption of petroleum organics by activated carbon has been found to generally increase with increasing molecular weight and decreasing solubility, aromatics are particularly amenable to activated carbon adsorption due to the presence of aromatic functional groups on the carbon surface (Giusti et al, 1974). Thus, the removal of phenol by activated carbon is of particular

interest to researchers, with studies demonstrating removal capacities as high as 161 mg/g (Giusti et al, 1974), 238 mg/g (Fierro et al, 2008), and 322 mg/g (Ahmaruzzaman and Sharma, 2005) from distilled water. While studies of activated carbon adsorption in industrial wastewater are rare, a few authors have noted a reduction in adsorption capacity in petroleum refinery wastewater (Anirudhan, 2009; El-Naas, 2010) and resin manufacturing wastewater (Rengaraj, 2002).

Organoclays are materials derived from clay minerals by exchanging the inorganic surface cations with organic surfactants which have been studied as alternative adsorbents for organics removal from water (Wolfe et. al., 1985). When organoclay is produced with a surfactant containing a long alkyl chain, the alkyl chains will interact to form an organic solvent phase, which can remove nonpolar organics from water through a solvent partitioning mechanism (Groisman et. al., 2004; Richards and Bouazza, 2007). Zhu et al (1997) found a strong correlation between the octanol-water partition coefficient of a compound and its affinity for organoclay, indicating that this material is best suited for the removal of hydrophobic organics.

Organoclays can also be produced using an aromatic surfactant, such as benzyltrimethylammonium (BTMA), in which case the resulting organoclay is particularly effective for removal of aromatic contaminants, such as phenol, due to a co-affinity between aromatic ring structures (El-Nahhal et al, 1998; Shen, 2002). In addition to determining the affinity of the organoclay for specific contaminants, the nature of the exchanged organic surfactant may also impact the organoclay's performance in wastewater. In a study of pesticide adsorption by organoclay, Groisman et al (2004) found that the performance short alkyl chain-

based organoclays (which are characterized by a surface adsorption mechanism) was substantially reduced in a wastewater matrix, while the performance of long alkyl-chain-based organoclays (which are characterized by a solvent partitioning mechanism) was not affected. However, it appears that this study has not been replicated in the context of petroleum wastewater, or used to evaluate the impact of wastewater on the performance of aromatic-based organoclay.

Dissolved aromatics have been shown to respond well to adsorbents characterized by surface adsorption or interactions between aromatic rings. However, adsorbents which work by these mechanisms have been shown to be sensitive to interference by other wastewater constituents. In the absence of a direct comparison between these different adsorption mechanisms in a wastewater context, it is unclear which material presents the most effective option for dissolved aromatics removal in the presence of common petroleum industry wastewater constituents. This study aims to remedy this research gap by comparing the effect of salinity, co-solutes, and dispersed oil on the adsorption of phenol and naphthalene by activated carbon (AC), a commercial organoclay (OC), and an aromatic-based organoclay (BTMA).

5.3 Materials and Methods

5.3.1 Adsorbents

Powdered activated carbon (PAC) (Sigma-Aldrich), commercial granular organoclay (OC) (PM-199, Cetco, Hoffman Estates, Illinois) crushed and sieved through a 200 mesh sieve, and a lab-synthesized organoclay made with an aromatic surfactant (BTMA-OC) were tested. BTMA-OC

was prepared following the procedure described by Shen (2004). Sodium montmorillonite clay with a cation exchange capacity (CEC) of 76.4 meq/100 g was obtained from the Source Clays Repository (Clay Minerals Society, Columbia, MO). A 25 g mass of clay was swelled in DI water overnight by mixing with a magnetic stirrer, after which 3.45 g of benzyltrimethyl ammonium (BTMA) chloride (Sigma Aldrich) was added and stirred with a mechanical mixer for six hours. The resulting organoclay was vacuum filtered and rinsed repeatedly with DI water, dried overnight in a 100°C oven, crushed and sieved through a 200 mesh (i.e., 74 µm) filter.

5.3.2 Bench-Scale Experimental Design

Bench-scale batch adsorption tests were conducted using 250 mL glass bottles capped to reduce volatilization placed on a shaker table at 150 rpm for four hours. Preliminary batch adsorption experiments showed that equilibrium was reached within three hours, which is in agreement with several other researchers (Ma and Zhu, 2007; El-Naas et al, 2010; Yang et al, 2015). Doses of the adsorbents evaluated in this study ranged from 1 to 100 mg/L for PAC, from 100 to 10,000 mg/L for OC, and from 20 to 2,000 mg/L for BTMA. Adsorption tests were conducted in four different water conditions: (1) fresh water single-solute, (2) fresh water multi-solute, (3) saline water multi-solute, and (4) oily-and-saline water multi-solute. Single-solute tests were performed in water containing either phenol or naphthalene, while multi-solute test waters contained both phenol and naphthalene. This experimental approach was followed to observe the effects of competitive adsorption. The doses of dissolved aromatics were 5 mg/L phenol (Sigma Aldrich) and 1 mg/L naphthalene (Fisher Scientific), which are within the concentration range observed in produced water samples (Stromgren et al, 1995; Utvik, 1999). For the fresh

water experiments, DI water was mixed with 5 mg/L of sodium bicarbonate (NaHCO_3) to aid in pH buffering. For the saline water experiments, DI water was mixed with 32 g/L sea salt. The oily-saline experimental water contained 32 g/L sea salt and 100 mg/L crude oil emulsified in DI water with 100 $\mu\text{g}/\text{L}$ Triton-X (Sigma-Aldrich) surfactant by shearing in a blender for three minutes , as described by Younker and Walsh (2014). All test waters were adjusted to pH 8 with predetermined volumes of 1 N sodium hydroxide (NaOH) or hydrochloric acid (HCl) solution. After shaking, the adsorbent was removed from samples by filtration through Whatman no. 4 (i.e., 20-25 μm) filter paper (Sigma-Aldrich), and the filtrate was used for water quality analysis. Oily adsorbent samples were prepared by shaking 100 mg/L of adsorbent in synthetic wastewater with 100 mg/L of crude oil on a shaker table at 150 rpm for four hours, and then filtering the sample and drying the collected adsorbent in a 100 ° C oven overnight to remove water from the material.

Data from the batch adsorption experiments were fit to the Langmuir and Freundlich models. However, only the Freundlich model results are presented as it provided a better fit for all the experimental data, allowing for direct comparisons among the three adsorbent materials studied. The Freundlich isotherm model is presented in Equation 5.1: (Crittenden and MWH, 2012):

$$q_e = K_F C_e^{1/n} \quad (\text{Equation 5.1})$$

where q_e is the mass of adsorbate sorbed per gram of sorbent (mg/L) and C_e is the liquid-phase equilibrium concentration of adsorbate (mg/L). K_F and $1/n$ are empirical constants of the model which indicate absorption capacity and adsorption intensity, respectively. McKay et. al. (1985) have stated the magnitude of the exponent ($1/n$) gives an indication of the affinity of the

adsorbate for the adsorbent surface. Values of n greater than unity indicate strong attraction between the adsorbate and adsorbent, resulting in high uptake of adsorbate even at low liquid equilibrium concentrations (Treybal, 1988). K_F and n were determined using linear regression as the y-intercept and slope, respectively, from a plot of $\log q_e$ vs $\log C_e$.

5.3.3 Analytical Methods

Phenol concentrations were analyzed by 4-aminoantipyrine indicator method and UV-VIS spectroscopy (Hach Company, Loveland, USA) using Standard Method 5530 (APHA, AWWA, and WEF, 2005). Naphthalene concentrations were determined by headspace analysis of a 0.8 mL sample by adsorption onto and desorption from solid phase micro extraction polydimethylsiloxane fibres using a 3800 Varian gas chromatograph (Agilent Technologies, Santa Clara, USA) with flame ionizing detection.

Zeta potential was measured using a Malvern Zetasizer (Worcestershire, UK) to analyze adsorbent samples at a concentration of 1 g/L dispersed in fresh and saline water at pH 8. Adsorbent particle size distributions were measured using a Malvern Mastersizer 3000 (Worcestershire, UK). Suspensions of adsorbents in fresh and saline water were produced by mixing at 150 rpm and were pumped directly to the Mastersizer flow cell using a peristaltic pump.

The following characterization tests were performed on unmodified montmorillonite clay, virgin PAC and organoclay samples, as well as adsorbent samples with crude oil adsorbed to the

surface. Brunauer-Emmet-Teller (BET) surface area was measured using a Micromeritics Flowsorb II 2300 (Norcross, GA, USA) surface area analyzer. Adsorption and desorption of N₂ gas was measured on PAC, OC and BTMA samples following sample degassing at 150 C for one hour. A Hitachi S-4700 (Tokyo, Japan) scanning electron microscope (SEM) was used to record images of adsorbents at magnifications between 300 to 30,000 X.

Analysis of variance (ANOVA) in Minitab was used to determine whether water conditions (i.e., salinity, dispersed oil) had a significant effect on removal by each adsorbent.

5.4 Results and Discussion

5.4.1 Adsorbent Characterization

Table 5.1 presents the results of characterization tests conducted on each adsorbent including zeta potential and particle size analysis for adsorbents in fresh and salt water, and BET surface area, for virgin and oil adsorbed Na-montmorillonite clay, PAC, OC and BTMA samples.

Table 5.1 Summary of Adsorbent Characterization Tests

	Median particle diameter (μm)		Zeta potential at pH 8 (mV)		BET surface area (m^2g^{-1})	
	Fresh	Salt	Fresh	Salt	Raw	Oil adsorbed
Clay			- 40.5	- 14.4	29.9	
PAC	32.4	34.1	- 21.6	- 2.6	907.7	3.8
OC	50.7	27.1	+ 26.2	+ 4.0	3.9	0.1
BTMA	49.6	45.6	- 26.0	- 11.7	41.3	0.2

Zeta Potential Measurements

In fresh water at pH 8, PAC exhibited a negative surface charge (-21.6 mV), which is likely due to the dissociation of acidic surface functional groups. BTMA-modified clay exhibited a negative surface charge (-26.0 mV), with a smaller magnitude than unmodified clay (-40.5 mV), indicating that some of the negative surface charge on the clay was neutralized by the presence of cationic surfactant. In contrast, OC exhibited a positive surface charge (+26.2 mV). Wang et al. (2004) found that organoclay produced with a relatively small surfactant retained a negative surface charge, while organoclay produced with a long alkyl chain-based surfactant had a positive zeta potential. During manufacture of long alkyl chain surfactant-based organoclays, once all cation exchange sites on the clay are occupied by surfactant molecules, additional surfactant molecules can attach to the clay by hydrophobic bonding, in which the alkyl tails of the surfactant interact with each other, leaving the cationic head groups to build up positive charge (Wang et. al., 2004; Xu and Boyd, 1995). Thus a positive surface charge indicates that OC is capable of hydrophobic bonding, which suggests that partitioning was also its main mechanism for organic contaminant removal from water.

In salt water, the zeta potentials of all three adsorbent materials were reduced to -2.6 mV, +4.0 mV and -11.7 mV for PAC, OC and BTMA, respectively. High salinity has been shown to compress the electrical double layer surrounding particles in water, reducing the repulsive forces between them (Edzwald et al, 1974).

Particle Size

As displayed in Table 5.1, In fresh water, the median particle size diameter for both organoclays was near 50 μm , which is below the maximum size cutoff of the 200 mesh sieve (i.e. 74 μm), indicating that the OC or BTMA particles were not aggregating during mixing. However, in salt water, the median particle diameter of OC was significantly ($p < 0.05$) reduced to 27.1 μm , which suggests that the larger OC particles were aggregating and settling out of solution. This result was likely due to the destabilizing effect of salt, which reduced the zeta potential of OC from +26.2 mV in fresh water to +4.0 mV in salt water. BTMA retained a stronger surface charge in salt water (i.e., ZP of -11.7 mV) from unused ion exchange sites on the clay surface. The median particle size diameter for PAC was 32.4 μm in fresh water, and was not significantly ($p > 0.05$) affected by salinity.

BET Surface Area

The BET surface area data displayed in Table 5.1 show that the specific surface area of montmorillonite clay ($29.9 \text{ m}^2\text{g}^{-1}$) increased after modification with BTMA ($41.3 \text{ m}^2\text{g}^{-1}$), while OC had a smaller surface area ($3.9 \text{ m}^2\text{g}^{-1}$) than either unmodified or BTMA-modified clay. The process of exchanging very small inorganic cations with organic cations forces the spaces between clay layers to expand in order to accommodate the larger molecule. Relatively small organic exchange cations will remain isolated in the clay interlayer, resulting in a net increase in the surface area of the clay (Wang et. al., 2004). This was observed in the present study, as the surface area of BTMA-exchanged montmorillonite was higher than that of raw montmorillonite. However, if the organic cation exchanged has a long hydrophobic tail, these molecules will interact to form a continuous phase in the clay interlayer, which ultimately results in a net

decrease in the surface area of the clay (Wang et. al., 2004). Thus the very small surface area of OC indicates that it was produced with a long alkyl chain surfactant, with a continuous organic phase in the clay interlayer, in contrast to BTMA, which had less compact packing of surfactant and more exposed surface area.

PAC had a much larger specific surface area ($907.7\text{ m}^2\text{g}^{-1}$) than either of the organoclays, which illustrates its high capacity for contaminant removal by surface adsorption. Oil adsorption reduced the surface area of all adsorbents, with the surface areas of BTMA, OC, and PAC reduced to $0.2\text{ m}^2\text{g}^{-1}$, $0.1\text{ m}^2\text{g}^{-1}$, and $3.8\text{ m}^2\text{g}^{-1}$, respectively. This was an anticipated finding, and demonstrates that oil coverage may result in a reduction of contaminant removal capacity with adsorbents that rely on a surface adsorption mechanism, such as PAC.

Scanning Electron Micrographs (SEM)

Figures 5.1.a and 5.1.b display SEM images of PAC at 30,000X magnification with and without oil adsorbed to the surface, respectively. Figures 5.1.c and 5.1.d display SEM images of OC at 30,000X magnification with and without oil adsorbed to the surface, respectively. The surfaces of virgin PAC (Figure 5.1.a) and virgin OC (Figure 5.1.b.) are markedly different, with PAC exhibiting a complex surface with numerous pore openings, in contrast to the layered structure of OC. The surface of PAC was dramatically altered after oil adsorption (Figure 5.1.b) resulting in a smooth surface with oil covering over the pore structure. While oil appeared to coat the surface of OC (Figure 5.2.d), the contrast in surface structure after oil adsorption is not nearly as stark for OC as what was observed for PAC.

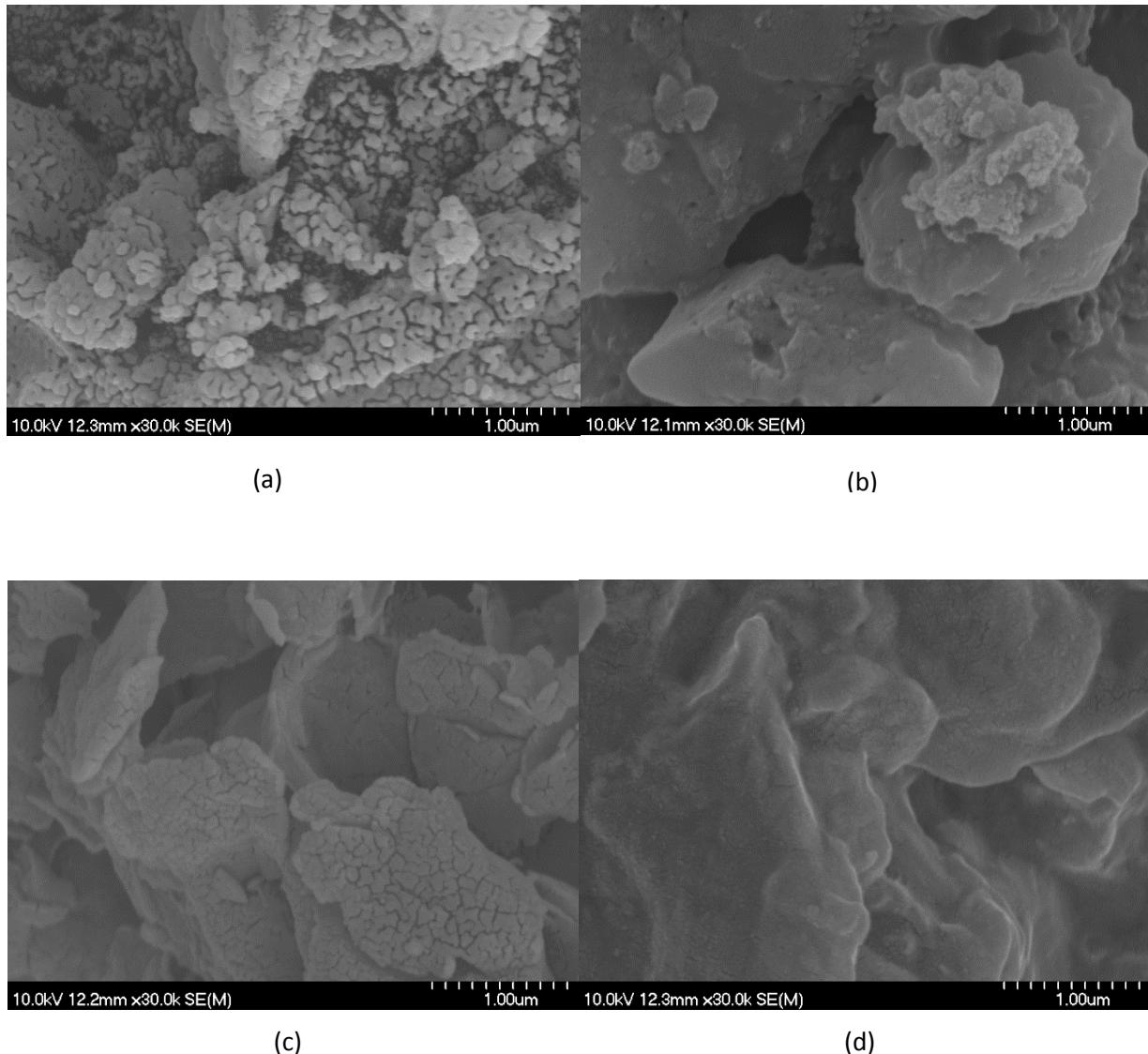


Figure 5.1 SEM image of PAC surface at 30,000x magnification before (a) and after oil adsorption (b), and OC surface at 30,000x magnification before (c) and after oil adsorption (d)

5.4.2 Adsorption Isotherm Experiments

Table 5.2 presents the Freundlich isotherm empirical constants (K_F and n) and R^2 values from the PAC, OC and BTMA batch adsorption experiments of phenol and naphthalene in fresh, salt and oily-and-salt water. In both the current study and in the literature, PAC adsorption capacities for naphthalene have been shown to be an order of magnitude higher than those of organoclays. In

fresh water trials in the current study, the adsorption of naphthalene by PAC was characterized by a Freundlich adsorption capacity value (i.e., K_F) of 294.85(mg/g)/(g/L). Other authors have found values of K_F for PAH adsorption on the order of hundreds of milligrams of sorbent per gram of PAC, with Walters and Luthy (1984) and Anbia and Moradi (2009) reporting K_F values of 277 and 170 (mg/g)/(g/L), respectively, for PAC adsorption of naphthalene, and Ahn et al (2005) reporting a K_F value of 260 (mg/g)/(g/L) for PAC adsorption of phenanthrene. K_F values for naphthalene adsorption onto organoclays has been reported to be on the order of tens of milligrams per gram. K_F values for adsorption of naphthalene by long alkyl chain organoclays were reported as $K_F = 18.9$ and 22.45 (mg/g)/(g/L) by El-Nahhal and Safi (2005) and Kaya et al (2013), respectively, as compared to 13.76 in the current study for OC. Similarly, adsorption of naphthalene by BTMA organoclay was reported with a K_F value of 33.6 (mg/g)/(g/L) (El-Nahhal and Safi, 2005), as compared to 16.42 in the current study.

Table 5.2 Freundlich Isotherm Parameters at pH 8 and 20 °C, with \pm values representing one standard deviation.

		Naphthalene			Phenol		
		K_F	n	r^2	K_F	n	r^2
Fresh	PAC	294.85 ± 82.84	2.23 ± 0.50	0.958 ± 0.022	37.73 ± 4.21	2.21 ± 3.59	0.128 ± 0.110
	OC	13.76 ± 1.42	0.84 ± 0.05	0.975 ± 0.009	0.08 ± 0.02	0.43 ± 0.08	0.962 ± 0.012
	BTMA	16.42 ± 6.61	1.21 ± 1.04	0.860 ± 0.006	1.01 ± 0.21	0.69 ± 0.01	0.997 ± 0.002
Salt	PAC	179.24 ± 33.54	3.72 ± 1.46	0.915 ± 0.100	36.90 ± 1.54	5.97 ± 3.58	0.199 ± 0.243
	OC	4.61 ± 0.95	1.03 ± 0.06	0.970 ± 0.037	0.09 ± 0.01	0.68 ± 0.07	0.805 ± 0.152

	BTMA	14.17 ± 5.33	1.22 ± 0.97	0.844 ± 0.016	2.25 ± 0.51	0.97 ± 0.25	0.924 ± 0.053
Oil	PAC	33.70 ± 0.03	3.03 ± 0.33	0.635 ± 0.350	13.58 ± 18.34	-0.60 ± 2.14	0.486 ± 0.401
	OC	28.00 ± 5.79	0.60 ± 0.04	0.973 ± 0.032	0.10 ± 0.03	0.65 ± 0.15	0.769 ± 0.134
	BTMA	29.39 ± 37.95	1.15 ± 1.09	0.863 ± 0.071	1.74 ± 0.27	0.96 ± 0.22	0.926 ± 0.051
Single Solute (Fresh)	PAC	289.80 ± 7.60	2.31 ± 0.09	0.953 ± 0.027	48.49 ± 4.59	2.91 ± 0.10	0.921 ± 0.002
	OC	5.58 ± 0.41	0.96 ± 0.01	0.990 ± 0.004	0.17 ± 0.06	0.52 ± 0.04	0.916 ± 0.099
	BTMA	10.25 ± 0.51	0.43 ± 0.01	0.896 ± 0.041	1.19 ± 0.03	1.06 ± 0.03	0.992 ± 0.004

As displayed in Table 5.1, the PAC used in this study had a surface area over $900 \text{ m}^2/\text{g}$, which is one and two orders of magnitude higher than the surface area of BTMA ($41 \text{ m}^2/\text{g}$) and OC ($4 \text{ m}^2/\text{g}$), respectively. The large surface area of PAC allows for highly effective removal of contaminants by surface adsorption.

PAC isotherms for naphthalene adsorption also had high n-values (i.e., 2.23 to 3.72) indicating favorable adsorption over a wide range of adsorbate concentrations. In contrast, isotherms for BTMA had n-value near 1 (i.e., 1.15 to 1.22), and isotherms for OC had n-values near or below 1, (i.e., 0.60 to 1.03). Low n-values are characteristic of cooperative adsorption, in which adsorption is enhanced at higher adsorbate concentrations due to attractive forces between adsorbate molecules. This is in agreement with literature values, in which several authors report high n-values for PAC adsorption of PAH compounds in the range of 2.33 to 4.76 (Walters and Luthy, 1984; Ahn et al, 2005; Anbia and Moradi, 2009), while reported n-values for organoclay

adsorption are lower, between 0.60 and 1 (Changchaivong and Khaodhair, 2009; Kaya et al, 2013).

K_F values of phenol adsorption by PAC has also been shown, in both the current study (Table 5.2), and in the literature, to be at least one order of magnitude higher than values for organoclay. While data from fresh water adsorption (in the multi-solute condition) of phenol by PAC did not fit well to the Freundlich isotherm, the K_F value in the single-solute condition was 48.49 (mg/g)/(g/L), which was similar to findings by Hamdaoui and Naffrechoux (2007) with a K_F value of 53.9, Streat et al (1995), with K_F values between 10 and 61, and Rengaraj et al (2002), with K_F values between 9.9 and 18.3.

Adsorption of phenol was different between the two types of organoclays, as the fresh water adsorption isotherm for OC had a K_F value of 0.08 (mg/g)/(g/L), while the K_F value for BTMA was substantially higher at 1.01 (mg/g)/(g/L). This was also reflected in the literature, with Ko et al (2007) reporting K_F values of 3.064 and 0.039 for phenol adsorption by aromatic (i.e., dimethyl-benzyl-hydrogenated-tallow-montmorillonite) and non-aromatic (i.e., dimethyl-dehydrogenated-tallow-montmorillonite) organoclays, respectively. Lin and Cheng (2002) also reported a direct comparison of phenol adsorption by aromatic (i.e., benzyltriethylammonium-bentonite) and non-aromatic (i.e., hexadecyltrimethylammonium-bentonite) organoclays, yielding K_F values of 0.606 and 0.015, respectively. Nir et al (2000) also found that the aromatic herbicide, alachhor, adsorbed to aromatic-based organoclays, including BTMA, with a higher binding coefficient than to a non-aromatic-based organoclay (i.e., HDTMA). This was likely due to the co-affinity of aromatic functional groups from pi dispersion forces (Shen, 2002; El-Nahhal

and Safi, 2004). These results indicate that a partitioning mechanism (i.e., by OC) is less effective than adsorption by specific pi dispersion forces (i.e., by BTMA) for phenol removal.

5.4.3 Effect of Water Type

Effect of Salinity

Figures 5.2,5.3 and 5.4 display naphthalene and phenol adsorption results for the batch adsorption experiments with PAC, OC, and BTMA, respectively in fresh, salt and oily-salt water matrices. Salinity did not have a significant ($p > 0.05$) effect on the removal of phenol or naphthalene by PAC; however, salinity significantly ($p < 0.05$) reduced phenol and naphthalene adsorption by OC, and significantly ($p < 0.05$) improved phenol adsorption by BTMA. In general, salinity should be expected to increase the adsorption of organics due to the “salting-out” effect, in which the aqueous solubility of organics is reduced in salt solutions (Turner and Rawling, 2000; Xie et. al., 1997). Based on data provided in a review by Xie et. al. (1997), the solubility of phenol and naphthalene in artificial seawater is reduced by 12 % and 21 %, respectively, as compared to pure water. The adsorption of polycyclic aromatic hydrocarbons onto organoclay has been found to be enhanced in water with higher ionic strength (El-Nahhal and Safi, 2004), while phenol adsorption onto organoclay has been found to be slightly increased (Ma and Zhu, 2007) or not significantly affected (Shen, 2002) by salinity. Thus the reduced solubility of these organic compounds in saline solutions may be responsible for the observed increase in adsorption by BTMA. As previously discussed, salinity significantly reduced the median particle size of OC, due to destabilization and settling of the larger OC particles, reducing contaminant access to the OC surface. This may have counteracted the effects of reduced organic solubility in salt water, resulting in a significant reduction in phenol and naphthalene adsorption by OC.

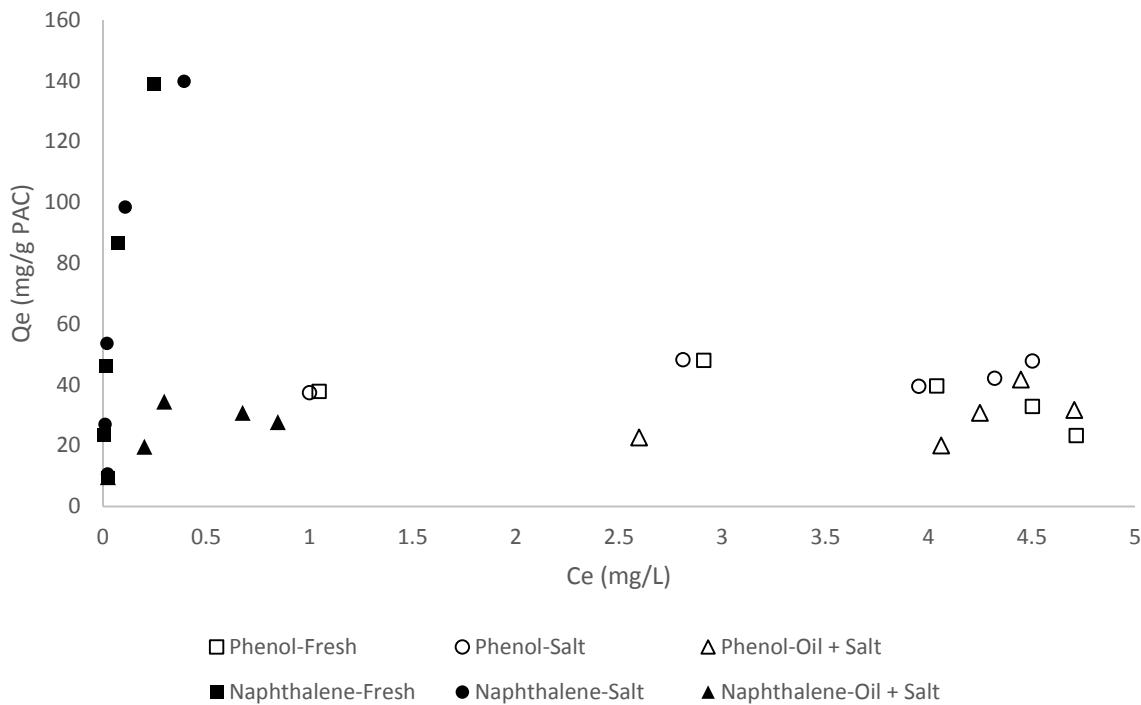


Figure 5.2 Freundlich isotherm plot of phenol and naphthalene adsorption by PAC

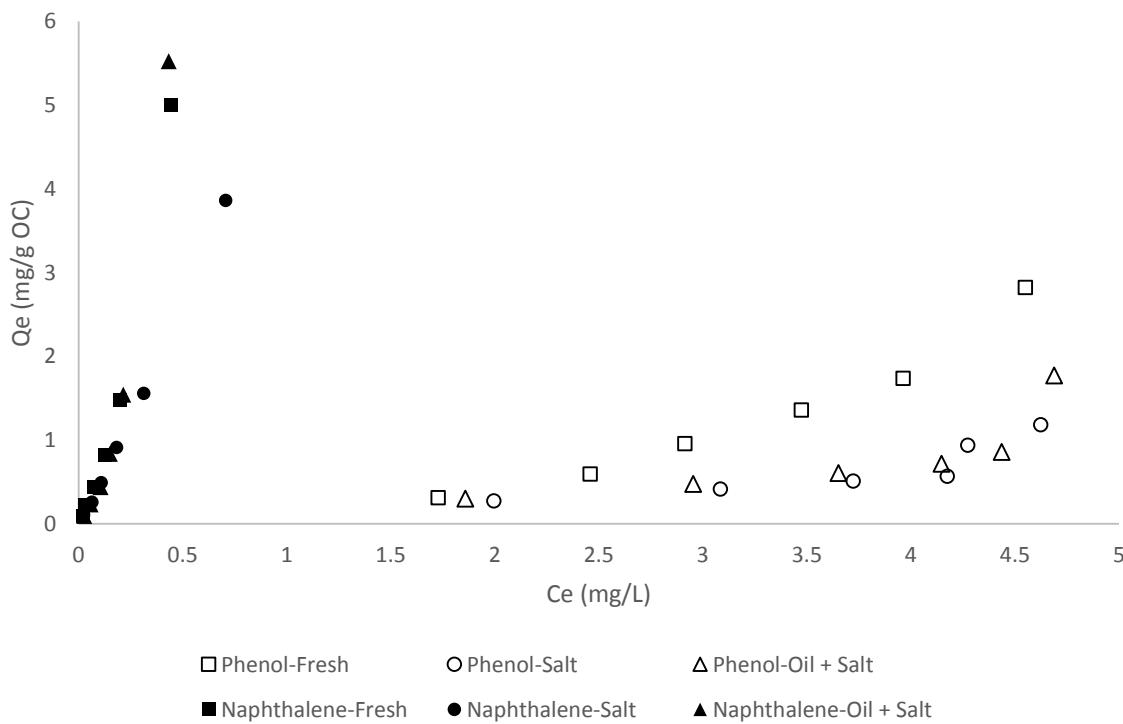


Figure 5.3 Freundlich isotherm plot of phenol and naphthalene adsorption by OC

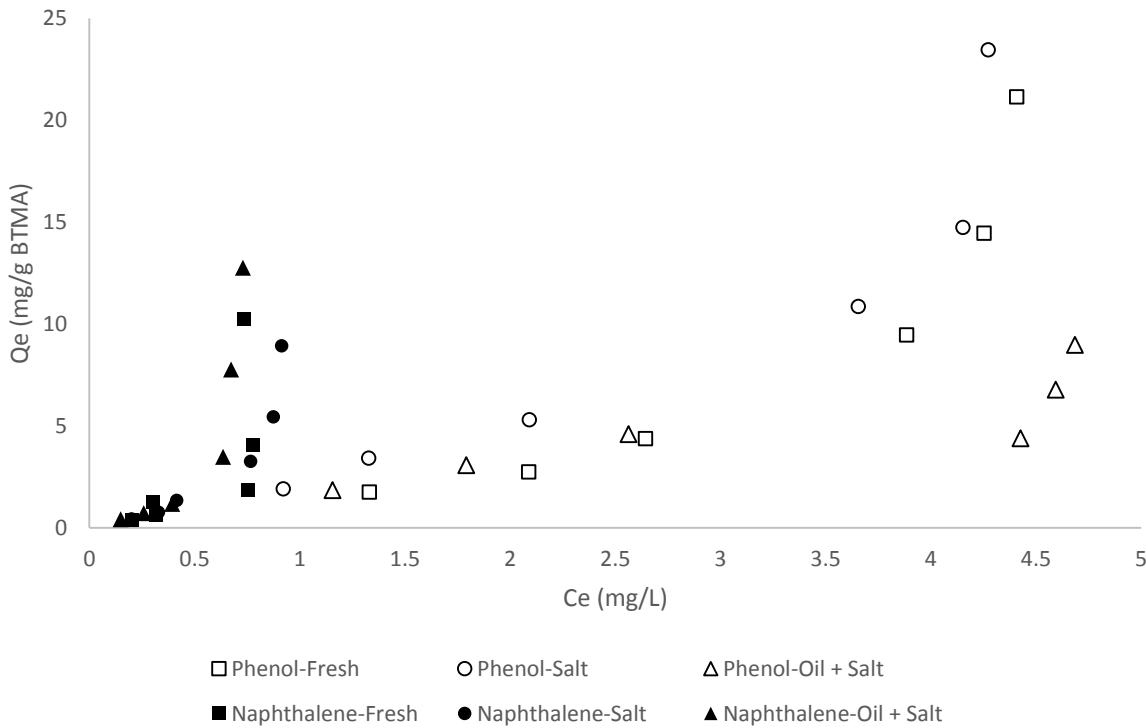


Figure 5.4 Freundlich isotherm plot of phenol and naphthalene adsorption by BTMA

While several authors have reported increased removal of natural organic matter (NOM) by PAC in saline waters, this is typically understood to be due to suppression of electrostatic repulsion between ionic moieties on the NOM and the PAC surface (Bjelopavlic et. al., 1999; Newcombe and Drikas, 1997). In a study of PAC adsorption of phenol in its anionic form at pH 11 (i.e., above the pKa of phenol), 0.05 to 0.5 M of KCl was shown to increase phenol adsorption (Arafat et. al., 1999), while other researchers reported that adsorption of phenol from its non-ionic form (i.e., at neutral pH) was not affected by salt addition (Halhouli et. al., 1997). Since all tests in the present study were conducted at pH 8, phenol was in its non-ionic form, and thus salinity would not be expected to increase adsorption of phenol. Additionally, several factors have been shown to mitigate the salting-out effect of adsorption onto PAC. Water cluster formation, in which the

oxygenated functional groups on the PAC surface closely bind water molecules which then obstruct contaminant access to the pores of the carbon, can be enhanced in saline solutions, resulting in a decrease in adsorption (Arafat et. al., 1999). Furthermore, a decrease in aqueous solubility may not result in enhanced adsorption if the organic compound has a high enough affinity for PAC to saturate the PAC surface even at low concentrations, as evidenced by a relatively flat isotherm curve (i.e., high n-value). In a study by Arafat et. al., (1999) adsorption of a very hydrophobic compound (i.e., toluene) was not enhanced in high salinity, while adsorption of a moderately hydrophobic compound (i.e., benzene) was enhanced. This may be the case in the present study, as the Freundlich isotherm n-value for PAC adsorption of naphthalene was greater than 1, indicating a strong affinity between naphthalene and the PAC surface.

Effect of Dispersed Oil

Dispersed oil significantly reduced PAC adsorption of both phenol and naphthalene ($p < 0.05$). El-Naas et al (2010) found reduced adsorption of phenol on activated carbon in refinery wastewater ($K_F = 26$), as compared to a synthetic wastewater containing only phenol ($K_F = 118$). A study conducted by Pelekani and Snoeyink (1999) found that high molecular weight natural organic matter (NOM) reduced the adsorption of smaller organic molecules on PAC. Even though the larger molecules could not penetrate into the inner micropores of the PAC surface and directly compete for adsorption sites, adsorbed NOM could block contaminant access to these micropores. Adsorption of naphthalene onto activated carbon has been found to occur mainly

within the inner micropores (Ania et. al., 2007). Since PAC works by a surface adsorption mechanism, the reduction of dissolved aromatics adsorption in the presence of dispersed oil was most likely a result of oil droplets blocking micropores on the PAC surface. As shown in Table 5.1, the BET surface area of PAC was reduced from $907.7 \text{ m}^2\text{g}^{-1}$ to $3.8 \text{ m}^2\text{g}^{-1}$ after contact with dispersed oil, indicating a dramatic decrease in available surface area for dissolved aromatics adsorption. The change in surface texture from complex and porous to smooth after oil adsorption is illustrated by the SEM images displayed in Figures 5.1 (a) and (b).

In contrast to the PAC results, dispersed oil had no effect on OC adsorption of phenol, and significantly increased OC adsorption of naphthalene ($p < 0.05$). Dispersed oil caused a significant ($p < 0.05$) reduction in phenol adsorption by BTMA, but had no effect on BTMA adsorption of naphthalene. Groisman et. al. (2004) compared sorption of organics onto organoclays from pure water solutions and industrial wastewater, and found that sorption by long-chain organoclays (i.e., characterized by a partitioning mechanism) was not affected by competition from other compounds in the industrial wastewater, while adsorption by a short-chain organoclay (i.e., characterized by surface adsorption) was reduced in the wastewater matrix. This is in agreement with phenol results in the current study; however, adsorption of naphthalene by the short-chain organoclay (i.e., BTMA) was not inhibited by the presence of dispersed oil. Faksness et al (2004) reported that naphthalene, but not phenol, may partially partition into oil droplets in produced water, resulting in enhanced removal. This phenomenon may explain the increased removal of naphthalene by OC in the presence of dispersed oil in the present study.

Effect of Mixed Adsorbate Solutions

Figure 5.5 compares Freundlich isotherm plots of phenol adsorption from fresh water with both naphthalene and phenol (i.e., ‘mixture’) to adsorption from fresh water with either naphthalene or phenol alone (i.e., ‘single-solute’). PAC adsorption of phenol from a single-solute test with only phenol was found to be significantly ($p < 0.05$) higher than phenol adsorption from a mixture of phenol and naphthalene, and also produced a more linear isotherm plot. Organic compounds of similar size have been shown to strongly compete for the finite number of adsorption sites on PAC (Newcombe et. al., 1997). This result in the current study shows that in mixed solute tests, naphthalene and phenol compete for adsorption sites. However, PAC adsorption of naphthalene was not significantly different ($p > 0.05$) in single solute and mixture tests, which shows that naphthalene was preferentially adsorbed by PAC under mixed solute conditions.

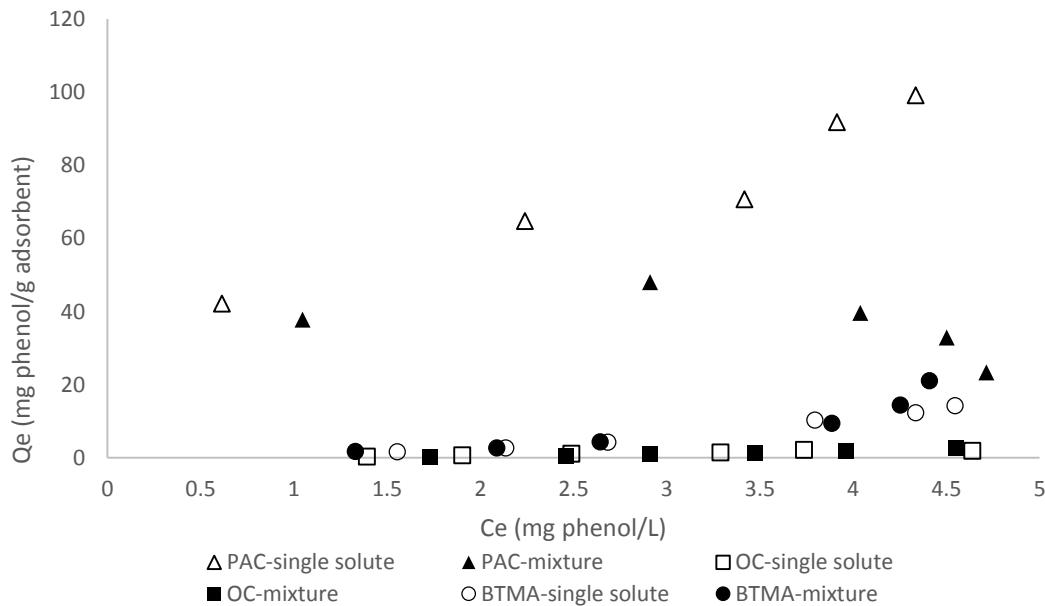


Figure 5.5 Freundlich isotherm plot of fresh water phenol adsorption by PAC, OC and BTMA in single- and multi-solute systems

Adsorption of phenol and naphthalene by both OC and BTMA organoclays were not found to be significantly different ($p > 0.05$) in single solute and mixed tests. Sorption by a long alkyl chain-based organoclay typically involves a solvent partitioning mechanism, which does not involve a fixed number of specific adsorption sites and is not characterized by competitive sorption (Smith et al, 1990). Groisman et al (2004) found similar adsorption results by a long chain organoclay from a pure solution and a mixture of solutes, which is in agreement with the results found in the current study for OC. In contrast to the results presented here for BTMA, it has typically been found that organoclays made with short-chain surfactants remove contaminants by a surface adsorption mechanism, which is subject to competitive effects (Groisman et al, 2004; Smith et al, 1990). However, strong adsorbate-adsorbate interactions may be present with aromatic solutes, such as phenol and naphthalene, due to the co-affinity between aromatic rings. Yasar et al (2005) demonstrated that phenol adsorption by organoclay is highly cooperative, as evidenced by increased phenol uptake at higher solute concentrations. Additionally, Wie and Nakato (2006) observed synergistic adsorption of phenol and chlorophenol in a binary solute system. It is thus possible that strong adsorbate-adsorbate interactions mitigated the effects of competitive sorption between naphthalene and phenol on BTMA in the current study.

5.5 Conclusions

The primary objective of this study was to compare three different adsorbents for the removal of dissolved aromatics from water, and to investigate the impacts of salinity, dispersed oil, and mixed adsorbate systems on treatment efficacy.

- PAC was found to have a higher adsorption capacity for the removal of both naphthalene and phenol in all types of water tested in this study.
- Salinity decreased adsorption of dissolved aromatics by OC, likely due to aggregation and subsequent removal from the water column, but did not negatively impact adsorption of phenol or naphthalene by PAC or BTMA.
- Dispersed oil decreased the adsorption capacity of PAC for both phenol and naphthalene, and reduced BTMA adsorption of phenol, but had no negative impact on adsorption of naphthalene by OC or BTMA.
- PAC adsorption of phenol from a mixture of two solutes (i.e., phenol and naphthalene) was significantly lower than PAC adsorption of phenol from a pure solution (i.e., phenol alone), indicating competition between phenol and naphthalene for adsorption sites. For both OC and BTMA, adsorption was similar from multi- and single-solute trials.

5.6 References

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CHAPTER 6. Effect of Adsorbent Addition on Floc Formation and Clarification

6.1 Abstract

The basis of this study was to evaluate simplifying traditional petroleum wastewater treatment by combining coagulation and adsorption processes into a single unit operation. The impact of powdered activated carbon (PAC) or clay modified with benzyltrimethyl ammonium surfactant (BTMA) addition with ferric chloride (FeCl_3) coagulant was investigated in terms of potential changes to the coagulated flocs formed with respect to size, structure, breakage and regrowth properties. The ability of dissolved air flotation (DAF) and sedimentation (SED) clarification processes to remove hybrid adsorbent-coagulant flocs was also evaluated by calculating settling velocities with Stoke's Law and through clarified water quality analysis of samples collected in bench-scale jar test experiments. The jar tests were conducted using both a synthetic fresh water and oily wastewater test waters. Results of the study demonstrated that addition of adsorbent reduced the median coagulated floc size by up to 50% but did not affect floc strength or regrowth potential after application of high shear. Stoke's Law modeling results for fresh water predicted that FeCl_3 -PAC floc aggregates would be amenable to both sedimentation and DAF clarification, while FeCl_3 -BTMA floc aggregates would settle rapidly even in a DAF clarification system. Experimental results in fresh water demonstrated that sedimentation was more effective than DAF for clarification of both FeCl_3 -PAC and FeCl_3 -BTMA floc aggregates. However, experimental tests performed on the synthetic oily wastewater showed that coagulant-adsorbent floc aggregates were effectively removed with both DAF and sedimentation treatment, with lower residual turbidity achieved in clarified water samples than with coagulation treatment alone.

KEYWORDS: Dissolved air flotation (DAF); sedimentation; adsorption; coagulation; industrial wastewater; powdered activated carbon (PAC); organoclay

6.2 Introduction

The oil and gas industry generates a range of complex wastewaters which contain a variety of contaminants. In particular, the organic composition of produced water and refinery wastewaters typically includes both dispersed and dissolved organic fractions, which may require advanced treatment for satisfactory removal. Coagulation with aluminum or ferric-based metal salts has been shown to be highly effective for the removal of emulsified oils from wastewater (Rios et al, 1998; Zouboulis and Avranas, 2000). However, coagulation has long been understood to be limited in its ability to remove dissolved organics from water (Edwards, 1997). Previous work by the authors investigating an integrated coagulation-adsorption treatment for produced water has demonstrated that coagulation can effectively remove dispersed oils, while adsorption treatment can target the dissolved fraction (Younker and Walsh, 2014).

Several other studies have evaluated the combination of chemical coagulation and adsorption into a single treatment step to enhance removal of target contaminants in drinking water and municipal wastewater systems. Integrating powdered activated carbon (PAC) adsorption with coagulation has been examined in drinking water treatment systems to (1) enhance removal of dissolved organic carbon (DOC) and UV254 (Kristiana et al, 2011; Szlachta and Adamski, 2009; Uyak et al, 2007), (2) target the removal of the taste and odour-causing compounds (i.e., 2-methylisoborneol (MIB) and gesomin) (Cook et al, 2001) and (3) simultaneously remove both

humic acid and phenol (Tomaszewska et al, 2004). In those studies, the coagulation process was used to target the larger, more negatively charged fraction of natural organic matter (NOM), while PAC adsorption was used to target the smaller, neutral-charged and/or aromatic organic fractions. Organoclay (OC) adsorbent coupled with coagulation has also been investigated for simultaneous removal of phosphate and phenanthrene as a tertiary treatment for municipal wastewater (Ma et al, 2010).

In addition to enhancing the finished water quality, the introduction of adsorbent material into the coagulation-flocculation process may have an impact on floc properties that could impact removal in subsequent clarification steps. In ballasted flocculation processes, microsand is added to the flocculation tank to deliberately change floc properties in order to enhance their settling rate (Desjardins et al, 2002; Ghanem et al, 2007; Young and Edwards, 2003). Addition of microsand to flocs was found to increase floc strength (Dianous and Dernaucourt, 1991) and floc density (Ghanem, 2007). Several adsorbent materials have also been investigated as ballasting agents. Demirci et al (1998) investigated the use of clay as a ballasting agent to enhance turbidity removal by sedimentation in petroleum refinery wastewater treated with alum coagulation. In that study clay addition reduced settled water turbidity by 80% compared to alum treatment alone, and also improved organics removal as measured by chemical oxygen demand (COD). Aguilar et al (2003) examined PAC as a coagulant aid for slaughterhouse wastewater treatment, and found increased particle removal (i.e., 95%) with PAC addition as compared to ferric sulfate coagulation alone (i.e., 87%). However, there is a paucity of research that has investigated the impacts of adding adsorbents and coagulants simultaneously on floc structure and DAF clarification.

The purpose of this study was to investigate the impact of PAC and organoclay (BTMA) addition on floc properties and downstream DAF and sedimentation clarification efficacy in both synthetic fresh water and oily wastewater.

6.3 Materials and Methods

6.3.1 Adsorbents

Table 6.1 presents physical characteristics of powdered activated carbon (PAC) (Sigma-Aldrich) and lab-synthesized organoclay (BTMA) used as test adsorbents in this study. BTMA was prepared following the procedure described by Shen (2004) using sodium montmorillonite clay from the Source Clays Repository (Clay Minerals Society, Columbia, MO). The clay was swelled in DI water overnight by mixing with a magnetic stirrer, after which benzyltrimethyl ammonium (BTMA) chloride solution (Sigma Aldrich) equal to 100% of the clay's cation exchange capacity was added and stirred with a mechanical mixer for six hours. The resulting organoclay was vacuum filtered and rinsed repeatedly with DI water, dried overnight in a 100 C oven, crushed and sieved through a 200 mesh filter.

Table 6.1 Physical characteristics of PAC and BTMA adsorbents

	Median particle diameter (μm) ^a	Zeta potential at pH 8 (mV) ^a		BET surface area (m^2g^{-1}) ^a	Particle density (kgm^{-3})
		Fresh	Salt		
PAC	32.4	-21.6	-2.6	907.7	1300 ^b
BTMA	49.6	-26.0	-11.7	41.3	2220 ^c

^aYounker and Walsh, 2015

^bHendricks, 2006

^cMicropycnometer (Quantachrome, Boynton Beach, Fla, USA)

6.3.2 Synthetic Wastewater

Fresh water trials were conducted using DI water with 5 mg/L of NaHCO_3 added for alkalinity.

A stock solution of synthetic produced water with 100 mg/L of emulsified crude oil, 5 mg/L phenol (Sigma Aldrich), 1 mg/L naphthalene (Fisher Scientific) and 32 g/L sea salt was generated according to procedure described by Younker and Walsh (2014). Prior to testing, both fresh water and wastewater were adjusted to a pH level of 8 using pre-determined volumes of 1 M NaOH solution, in order to maintain the water conditions near the pH of minimum solubility for FeCl_3 .

6.3.3 Jar Test Procedure

Jar tests were performed in a 1L DAF jar tester (EC Engineering, Edmonton, Canada). For coagulation tests, 50 mg/L of FeCl_3 (in a 10 g/L solution) was added to the water and rapid mixed at 200 rpm (G-value = 550 s^{-1}) for 1 minute. The test water was then mixed for 5 minutes at 50 rpm (G-value = 55 s^{-1}) to simulate the flocculation stage, followed by clarification. For adsorbent-only tests, 100 mg/L of PAC or BTMA were added to the jars and fully dispersed into the water by mixing at a high speed of 300 rpm (G-value = 1000 s^{-1}), then mixed at 50 rpm (G-

value = 55 s⁻¹) for 5 minutes, followed by clarification. For combined adsorbent-coagulation trials, PAC and BTMA adsorbents, at either a low dose of 100 mg/L or a high dose of 1000 mg/L, were added to the jars in separate experiments and fully dispersed into the water by mixing at a high speed of 300 rpm (G-value = 1000 s⁻¹) for 1 minute, followed by coagulant addition and rapid mixing at 200 rpm (G-value = 550 s⁻¹), then a 5 minute flocculation stage at 50 rpm (G-value = 55 s⁻¹), followed by clarification. DAF clarification was performed using a 10% recycle rate with DI water saturated with air at 75 psi (i.e., 517 kPa). In the sedimentation trials, the jar test apparatus mixers were turned off to allow for floc settling. Grab samples of approximately 30 mL of DAF and SED clarified water were taken at 0, 5, 10, and 30 minutes of clarification, through a sample port located 10 cm from the water surface, and analyzed for turbidity.

For floc characterization tests, the flocculation stage as described in jar test experiments was followed by a 5 minute floc breakage phase at a high shear of 200 rpm (G-value = 550 s⁻¹)) followed by a 5 minute floc regrowth phase where G-values were returned to the flocculation stage value of 50 rpm (G-value = 55 s⁻¹).

6.3.4 Analytical Methods

Particle size distribution (PSD) in flocculated water was measured using a Malvern Mastersizer (Malvern Instruments, Worcestershire, UK). Flocculated water was pumped directly from the jar tester to the sample cell by a peristaltic pump located after the sample cell, and recirculated back to the jar tester. Photographic images of flocs were taken using a Zeiss microscope with a digital camera attachment (Carl Zeiss, Jena, Germany). Microscope slides were prepared by drawing water through a wide-mouth glass pipette approximately 2 inches below the water

surface, depositing 1 mL of flocculated water on the slides, and allowing slides to dry before analysis. Zeta potential was measured in both fresh water and synthetic wastewater using a Malvern Zetasizer (Malvern Instruments, Worcestershire, UK). Turbidity measurements were performed using a Hach Turbidimeter (Hach Company, Loveland, USA).

Statistical significance of treatment factors were determined using analysis of variance (ANOVA) with Minitab at an α value of 0.05. All error bars displayed in figures represent one standard deviation.

6.3.5 Settling and rise velocity modelling procedure

Clarification models were developed using Malvern Mastersizer particle size distribution data and estimated floc, adsorbent, and floc-adsorbent aggregate densities, as displayed in Table 6.2. Density of FeCl_3 flocs was assumed to be 1006 g/cm^3 (Lagvankar, 1968), wetted particle densities of 1.3 g/cm^3 was used for PAC (Hendricks, 2006) and 2.2 g/cm^3 was used for BTMA (as measured by micropycnometer (Quantachrome, Boynton Beach, FLA, USA)). The volume of FeCl_3 floc material in the jar tests was calculated by dividing the mass of the FeCl_3 dose (i.e., 50 mg) by its density (i.e., 1006 g/cm^3) to give a volume of $4.97 \times 10^{-5} \text{ cm}^3$. Similarly, the volumes of PAC and BTMA were calculated by dividing the adsorbent dose (i.e., 100 or 1000 mg) by the adsorbent densities (i.e., 1300 and 2200 g/cm^3 for PAC and BTMA, respectively). Floc-adsorbent aggregate densities were calculated assuming a uniform distribution of adsorbent material in the flocs, and using floc and adsorbent weighted densities based on the contribution of total solids volume by floc and adsorbent material, using Equations 6.1 through 6.3.

$$\% floc = 100 * \left(\frac{floc\ volume}{total\ volume} \right) \quad [Equation\ 6.1]$$

$$\% PAC\ or\ BTMA = 100 * \left(\frac{PAC\ or\ BTMA\ volume}{total\ volume} \right) \quad [Equation\ 6.2]$$

$$Aggregate\ density = \frac{\% floc*floc\ density + \% adsorbent*adsorbent\ density}{100} \quad [Equation\ 6.3]$$

Table 6.2 Calculation of estimated densities of FeCl₃-adsorbent aggregates

Chemical doses (mg/L)	Floc density (g/cm ³)	Floc volume (cm ³)	PAC or BTMA density (g/cm ³)	PAC or BTMA volume (cm ³)	Total Volume	% floc	% PAC or BTMA	Aggregate density (g/cm ³)
FeCl ₃ (50) + PAC(100)	1006	4.97x10 ⁻⁵	1300	7.69x10 ⁻⁵	1.27x10 ⁻⁴	39	61	1185
FeCl ₃ (50) + PAC(1000)	1006	4.97x10 ⁻⁵	1300	7.69x10 ⁻⁴	8.19x10 ⁻⁴	6	94	1282
FeCl ₃ (50) + BTMA(100)	1006	4.97x10 ⁻⁵	2200	4.55x10 ⁻⁵	9.97x10 ⁻⁵	52	48	1576
FeCl ₃ (50) + BTMA(1000)	1006	4.97x10 ⁻⁵	2200	4.55x10 ⁻⁴	5.50x10 ⁻⁴	10	90	2082

Settling velocity was modeled using Stokes Law at 20°C, as described below in Equation 6.4 (Droste, 1997):

$$v_s = \left[\frac{4g}{3C_D} * \frac{(\rho_p - \rho_w)}{\rho_w} * d_p \right]^{\frac{1}{2}} \quad [Equation\ 6.4]$$

Where:

v_s = settling velocity (m/s)
 g = gravitational constant (9.81 m/s²)
 ρ_p = particle density (g/cm³)
 ρ_w = water density (g/cm³)
 d_p = particle diameter (m)
 C_D = drag coefficient

The drag coefficient, C_D , was calculated in laminar flow ($Re < 1$) using Equation 6.5, and in transitional flow ($1 < Re < 10^3$) using Equation 6.6, with the Reynold's number (Re) calculated using Equation 6.7.

$$C_D = \frac{24}{Re} \quad [\text{Equation 6.5}]$$

$$C_D = \frac{24}{Re} + \frac{3}{\sqrt{Re}} + 0.34 \quad [\text{Equation 6.6}]$$

$$Re = \frac{\rho_w v_s d_p}{\mu} \quad [\text{Equation 6.7}]$$

Where:

ρ_w = density of water (g/cm³)
 v_s = settling velocity (m/s)
 d_p = particle diameter (m)
 μ_w = kinematic viscosity of water

DAF rise velocity was modeled using a modified Stokes Law equation (Equation 6.8), as described by Edzwald (2007):

$$v_{fb} = \frac{4g(\rho_w - \rho_{fb})d_{fb}^2}{3K\mu_w} \quad [\text{Equation 6.8}]$$

Where:

g = gravitational constant (9.81 m/s²)
 ρ_w = density of water (g/cm³)
 ρ_{fb} = density of floc-bubble aggregates (g/cm³)

d_{fb} = diameter of floc-bubble aggregates (g/cm^3)

K = shape factor

μ_w = kinematic viscosity of water

The diameters and densities of floc-bubble aggregates were calculated using Equations 6.9 and 6.10 described by Edzwald (2007).

$$d_{fb} = (d_f^3 + N d_b^3)^{\frac{1}{3}} \quad [\text{Equation 6.9}]$$

Where:

d_{fb} = diameter of floc-bubble aggregate

d_f = floc diameter

d_b = bubble diameter

N = number of bubbles attached per floc

$$\rho_{fb} = \frac{\rho_f d_f^3 + N \rho_b d_b^3}{d_f^3 + N d_b^3} \quad [\text{Equation 6.10}]$$

Where:

ρ_{fb} = density of floc-bubble aggregate

ρ_f = floc density

ρ_b = bubble density

N = number of bubbles attached per floc

A shape factor, K, of 24 was assumed for flocs $< 40 \mu\text{m}$ in diameter, increasing to 45 for flocs $\geq 170 \mu\text{m}$, as described by Edzwald (2007). Bubble size was assumed to be $60 \mu\text{m}$ in diameter for saturator pressures of 500 kPa (i.e., 75 PSI) (Haarhoff and Edzwald, 2004).

Once coagulation-flocculation has produced flocs greater than 10 µm in diameter, bubble attachment to flocs is limited by the available surface area on the floc, rather than by the number of air bubbles in the system (Haarhoff and Edzwald, 2004). The maximum number of bubbles (N_{max}) of size d_b that can attach to a floc of size d_f can be described by Equation 6.11 (Haarhoff and Edzwald, 2004).

$$N_{max} = \pi \left(\frac{d_f}{d_b} \right)^2 \text{ [Equation 6.11]}$$

However, it has been shown that efficient bubble attachment can be achieved with particles as small as 10 µm in diameter (Haarhoff and Edzwald, 2004). In this study, DAF clarification was modelled with one bubble attached to all particles $\geq 10 \mu\text{m}$, and with half of N_{max} bubbles (as described by the previous equation) attached to particles $\geq 70 \mu\text{m}$.

6.4 Results and Discussion

6.4.1 Floc Characterization

Floc image analysis

Figure 6.1 displays 20x magnification photographs of the FeCl₃ coagulant flocs formed with 50 mg/ L FeCl₃ treatment, BTMA and PAC particles, and the coagulant-adsorbent floc aggregates formed with PAC and BTMA addition to the coagulation treatment step. For both the FeCl₃-PAC and FeCl₃-BTMA floc aggregates, adsorbent material was found to be incorporated into the floc structure, as evidenced by the visually darker colour of flocs formed with PAC addition and

the visible presence of clay particles in flocs formed with BTMA addition. In both sets of experiments with PAC and BTMA addition to the coagulation step, the coagulant-adsorbent floc aggregates appeared to be more heavily loaded with the test adsorbent at the higher dosage (i.e., 1000 mg/L), indicating that the capacity for FeCl_3 flocs to incorporate adsorbent was in excess of the lower adsorbent dose (i.e., 100 mg/L) evaluated in this study. However, at the higher adsorbent dosage evaluated for PAC and BTMA, there appeared to be loose adsorbent particles that were not incorporated into the coagulated flocs, suggesting a limit to the amount of adsorbent able to be incorporated into the flocs.

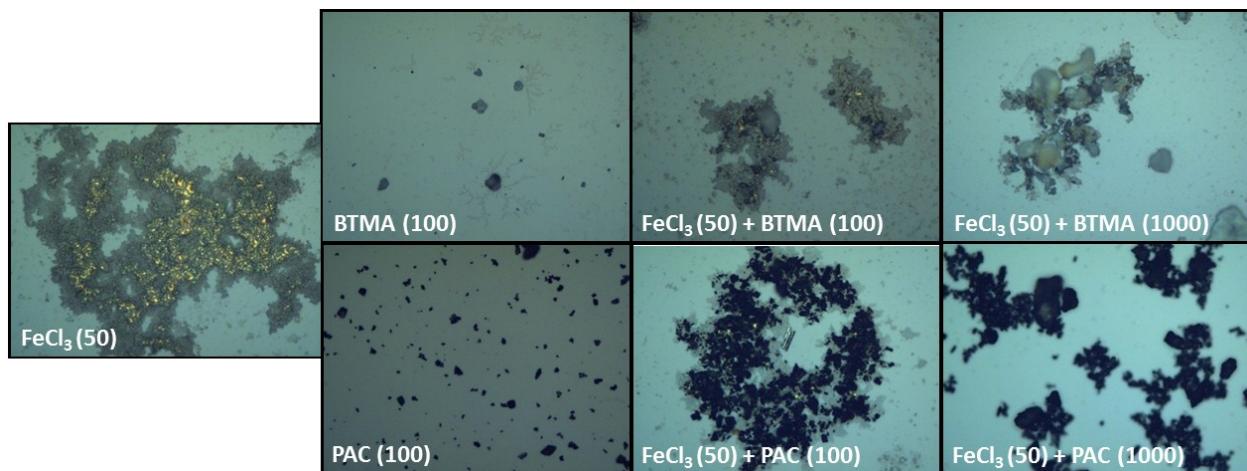


Figure 6.1 Micrographs of Flocs Formed under Different Treatments (20x magnification)

Floc size, strength and recovery

Floc strength and recovery are important characteristics of flocs due to regions of high shear in water treatment processes (i.e., DAF, pumping, close proximity to impellers in the flocculation tank) which may break up flocs prior to separation processes (Jarvis et al, 2005). Figure 6.2 displays the median particle diameter of coagulated flocs, PAC and BTMA adsorbent particles

and coagulant-adsorbent floc aggregates after growth, breakage and regrowth. Addition of 100 mg/L of BTMA or PAC to FeCl_3 flocs did not significantly (i.e., $p > 0.05$) impact particle size. However, addition of 1000 mg/L of either adsorbent significantly (i.e., $p < 0.05$) reduced floc size. FeCl_3 flocs had a median particle diameter of $320 \pm 47 \mu\text{m}$, which decreased to $160 \pm 21 \mu\text{m}$ with addition of 1,000 mg/L of PAC and $179 \pm 29 \mu\text{m}$ with 1,000 mg/L BTMA dose. This result confirms micrograph observations which showed the presence of more fragmented flocs and un-aggregated adsorbent material at the high adsorbent dose. These results are similar to results of Jarvis et al (2009) who found that the addition of glass beads as a ballasting agent reduced the median diameter of ferric sulphate flocs from $600 \mu\text{m}$ to $185 \mu\text{m}$ in a natural surface water.

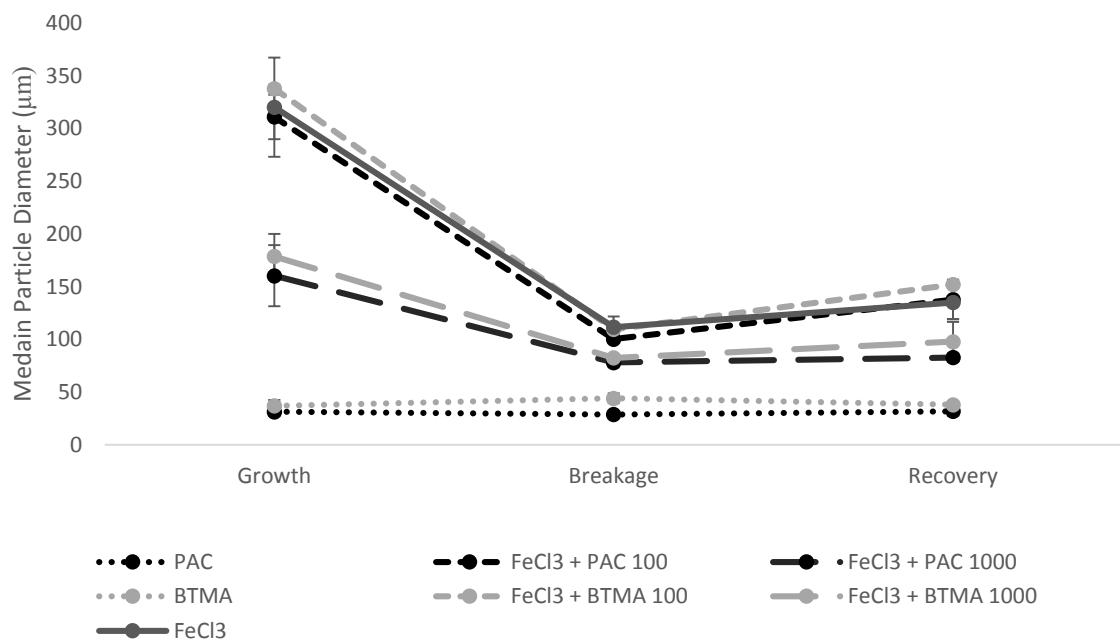


Figure 6.2 Median particle size of FeCl_3 flocs, adsorbents and floc-adsorbent aggregates after growth, breakage and recovery

Flocs formed with a high dose (i.e., 1000 mg/L) of either PAC or BTMA also had a significantly ($p < 0.05$) higher percentage of particles that measured below 76 μm in diameter, which is the size range that 90% of adsorbent particles fall into. For FeCl_3 -PAC aggregates formed with 1000 mg/L of PAC, 9.7 ± 3.1 % of particles were found to measure lower than 76 μm , as compared to 3.6 ± 2.8 % of particles at the 100 mg/L PAC dose. Similarly, FeCl_3 -BTMA aggregates formed at the high BTMA dose had 15.6 ± 4.5 % of particles with size lower than 76 μm , while only 4.9 ± 1.3 % of particles were in the size range for aggregates formed with the low BTMA dose.

These particle size measurements support the micrograph observations which indicated the presence of un-aggregated adsorbent material at the high adsorbent dose.

Collectively, the data suggests that a 1000 mg/L dose of adsorbent may somewhat exceed the capacity of the coagulated floc (at a coagulant dose of 50 mg/L) to integrate adsorbent material within the floc structure. In a study of a ballasted flocculation system with microsand particles, Young and Edwards (2003) found that a 250 mg/L dose of FeCl_3 could incorporate up to 5 g/L of ballasting agent, but further doses of microsand could not be aggregated into the floc structure. Similarly, Ghanem et al (2007) found a limit of 7 g/L of ballasting agent could be integrated into coagulant floc formed with 250 mg/L of FeCl_3 under similar flocculation conditions. The presence of un-aggregated adsorbent material may have implications for downstream clarification processes, as these particles may be too small to settle quickly or may have too high of a residual surface charge to attach to DAF bubbles for flotation.

All of the flocs formed with coagulant and coagulant-adsorbent treatment decreased in size with an increase in applied shear from 55 to 550 s^{-1} G-values (i.e., 50 to 200 rpm). FeCl_3 flocs were

reduced in size by 64 ± 8 % after 5 minutes of breakage, which was very similar to the level of breakage exhibited by flocs with 100 mg/L of either PAC or BTMA, with 62 ± 17 % and 67 ± 6 % reductions in median particle diameter, respectively. While slightly less extensive breakage was observed for flocs formed with 1000 mg/L of PAC or BTMA (i.e., 52 ± 3 % and 53 ± 5 % reduction in median particle size, respectively), the difference in floc breakage was not significant ($p > 0.05$) for either adsorbent dose or type. These results demonstrate that the addition of adsorbent to FeCl_3 flocs did not increase or reduce floc strength, suggesting that adsorbent addition would not drastically change the strength of flocs to operational shear, such as that found in a DAF system.

Returning to the lower velocity gradient of 55 s^{-1} after the breakage trials, only partial recovery or regrowth of the flocs were observed. FeCl_3 flocs only regained 58 ± 3 % of their original size, while flocs formed with 100 mg/L of PAC or BTMA recovered to 48 ± 25 % or 55 ± 7 % of the original median particle diameter, respectively. Flocs formed with 1000 mg/L of PAC or BTMA recovered 49 ± 11 % or 45 ± 6 % of the original floc size, respectively, after a 5 minute recovery period. Again, the adsorbent type or dose produced no statistically significant difference ($p > 0.05$) in the regrowth capability of the flocs. Jarvis et al (2005) found that the regrowth capability of flocs was strongly linked to their formation mechanism. Sweep flocs (as modeled by ferric hydroxide precipitates) showed limited regrowth potential. In the current study, the limited regrowth capacity of both FeCl_3 flocs and FeCl_3 -adsorbent aggregates indicates that the attachment mechanism for adsorbent material in the floc structure appears to be enmeshment in the ferric hydroxide precipitate.

Zeta Potential

Figure 6.3 displays zeta potential data for FeCl_3 flocs, PAC and BTMA adsorbent, and adsorbent-floc aggregates in fresh water and synthetic oily-saline wastewater. In the fresh water experiments, negative surface charges were observed on both PAC and BTMA adsorbent particles (i.e., -21.6 ± 7.2 and -26.0 ± 3.0 mV, respectively) and FeCl_3 flocs (i.e., -4.6 ± 3.2 mV), as well as on FeCl_3 -adsorbent aggregates (i.e., -15.9 ± 6.9 to -5.5 ± 1.9 mV). This further supports the hypothesis that adsorbent particles were attached to the flocs via an enmeshment, rather than charge neutralization mechanism, as coagulated floc-adsorbent aggregates were formed despite both the floc material and the adsorbent particles having negative surface charges.

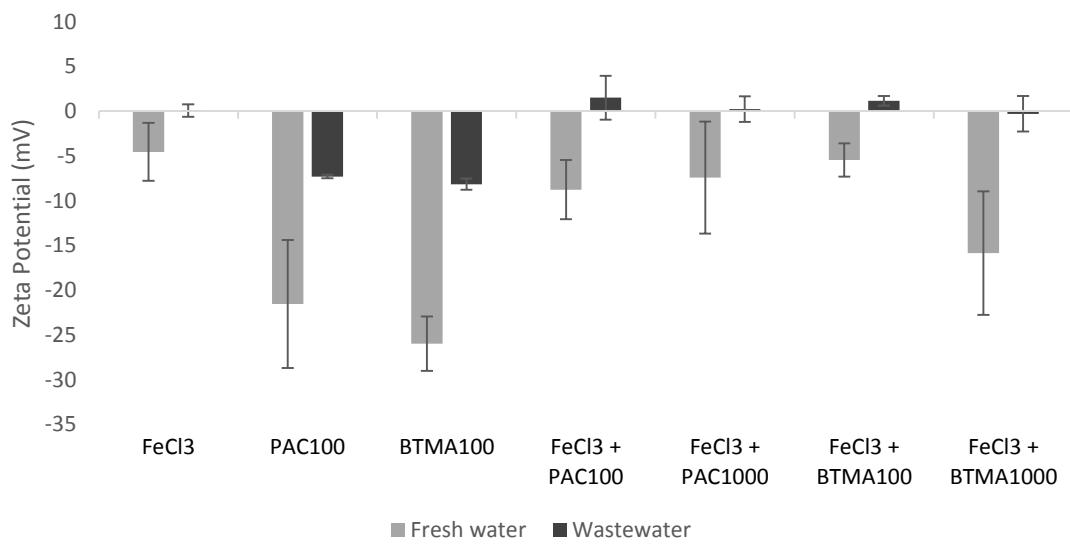


Figure 6.3 Zeta potential of flocs, adsorbent and floc-adsorbent aggregates in fresh water and wastewater at pH 8

In the synthetic wastewater experiments, FeCl₃ flocs exhibited a neutral surface charge (i.e., 0.1 ± 0.7 mV), while the surface charge of PAC and BTMA particles was greatly reduced (i.e., to -7.3 ± 0.2 and -8.2 ± 0.6 mV, respectively), as compared to fresh water conditions. The high ionic strength of seawater or saline wastewaters has been observed to compress the electrical double layer around particles in water, causing a reduction in zeta potential, as observed in the present study (Edzwald et al, 1974; Younker and Walsh, 2015). The FeCl₃-adsorbent floc aggregates formed in the synthetic wastewater experiments had neutral or near-neutral surface charges (i.e., -0.3 ± 2.0 to 1.5 ± 2.4 mV), indicating that a charge neutralization mechanism may also have played a role in adsorbent integration into the FeCl₃ flocs under the high ionic strength conditions.

6.4.2 Clarification

Modelling Results

Figure 6.4 displays settling velocities calculated with Stoke's Law for the coagulant flocs, PAC and BTMA adsorbents, and coagulant-adsorbent floc aggregates as a function of particle diameter percentile measurements taken from fresh water samples, and estimated particle densities. The modelling results predicted a substantial increase in settling velocity for all coagulant-adsorbent floc aggregates as compared to coagulant flocs with FeCl₃ treatment alone, due to the increase in floc density with the associated with the integration of the adsorbent particles in the coagulant floc. Modelling results predicted a median settling velocity for FeCl₃ flocs alone of 1.2 m/h, which is near the typical design settling rates (i.e., 1.4 to 2 m/h) for water treatment plant design (AWWA/ASCE, 2005). Settling rates were increased to 25 or 117 m/h

with the addition of 100 mg/L of PAC or BTMA, respectively. Since the median particle sizes of FeCl₃ flocs and FeCl₃-adsorbent aggregates with 100 mg/L of adsorbent were similar, this predicted increase in settling velocity can be attributed to the increase in floc density associated with the integration of the adsorbent particles in the coagulated floc.

These modelling results are similar to the experimental results of Young and Edwards (2003), who measured settling velocities on the order of 100 m/h for microsand-ballasted flocs of 500 μm in diameter. However, FeCl₃-adsorbent aggregates with 1000 mg/L of PAC or BTMA were predicted to have lower settling velocities (i.e., 16 and 47 m/h, respectively) than the aggregates formed with 100 mg/L of adsorbent, despite the increase in aggregate density from additional adsorbent material, due to the reduction in median particle size of the integrated coagulant-adsorbent floc observed at that dose.

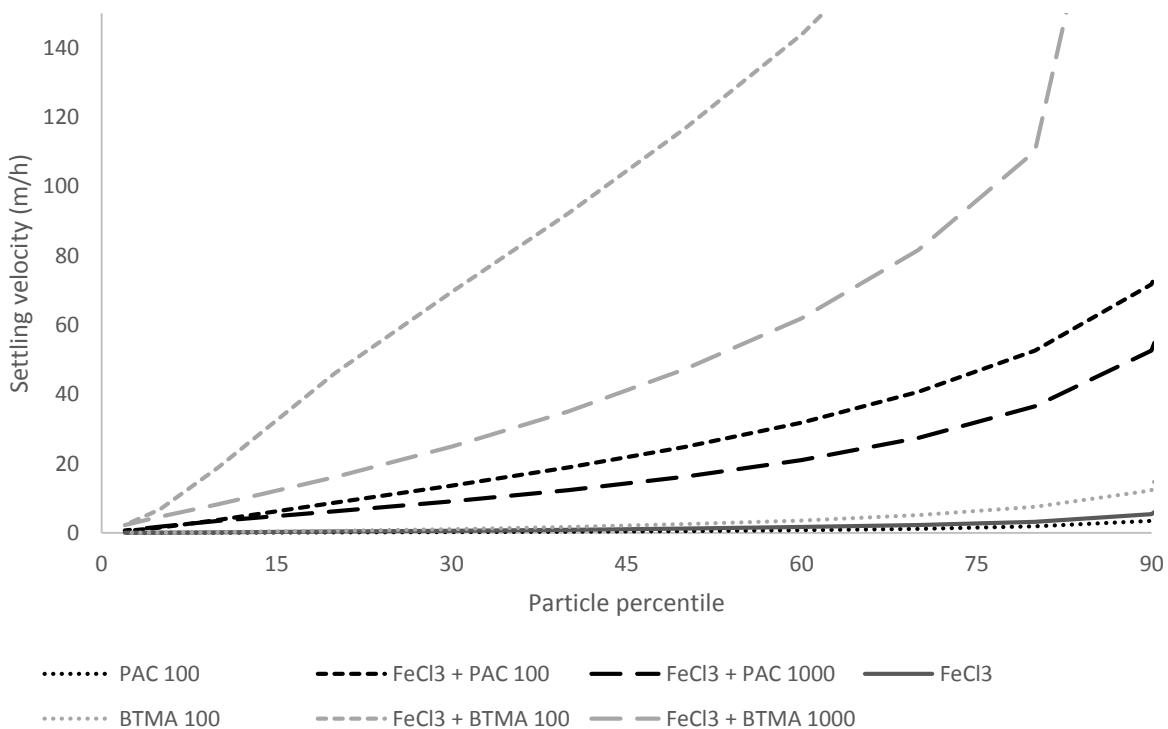


Figure 6.4 Modelled settling velocity for measured particle size distribution

As BTMA is denser than PAC, the FeCl₃-BTMA aggregates were predicted by model calculations to settle faster than FeCl₃-PAC aggregates. The difference in density between BTMA and PAC also predicted a more rapid settling rate for un-coagulated BTMA adsorbent (i.e., 2.5 m/h) than PAC (i.e., 0.5 m/h), despite their similar particle size distributions (PSD).

Figure 6.5 presents modelled DAF rise velocity for FeCl₃ flocs, adsorbents, and floc-adsorbent aggregates as a function of particle diameter percentile taken from the Malvern Mastersizer PSD results. FeCl₃ flocs were predicted to have very high rise velocities (i.e., 25 m/h for median floc size), and rise velocity was predicted to steadily increase with floc size due to an increased surface area for bubble attachment, allowing for multiple bubble attachment. Addition of adsorbent into floc particles was predicted to reduce the rise velocity under all conditions, due to the increase in density of the integrated coagulant-adsorbent flocs. FeCl₃-PAC aggregates were predicted to have moderate rise velocities (i.e., between 5 and 10 m/h) for all but the largest particles in the distribution, indicating that DAF may be a feasible method for clarifying these particles. For comparison, an optimal rise rate for DAF systems, operating with small flocs (10's of μm in diameter) attaching to one bubble each, would be approximately 20 m/h (Edzwald, 2007). In contrast, practically all FeCl₃-BTMA aggregate flocs were predicted to be too dense to be clarified by a DAF system, and would likely settle instead, with a median settling velocity of 46 and 11 m/h for aggregates formed with 100 and 1000 mg/L of BTMA, respectively.

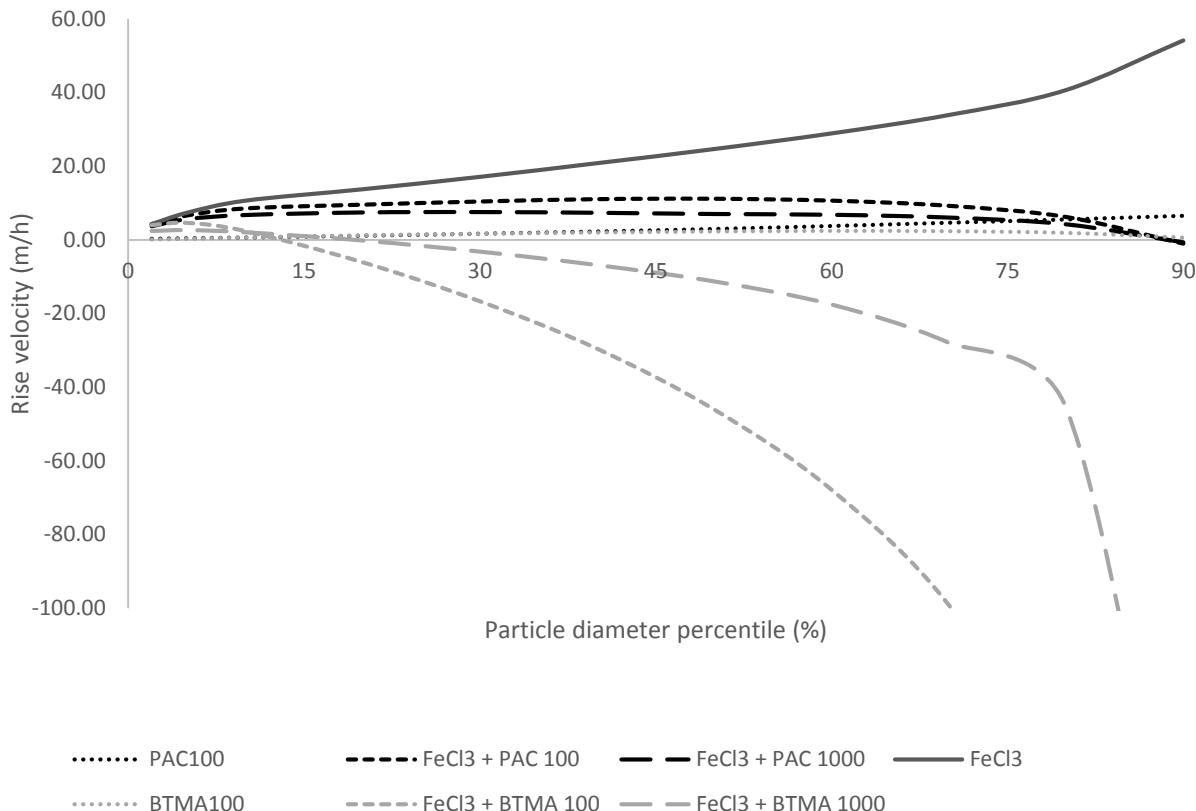


Figure 6.5 Modelled DAF rise velocity for measured particle size distribution

Fresh water clarification experiments

Figure 6.6 presents the clarified water turbidity measurements after coagulant, adsorbent and combined coagulant-adsorbent treatment with DAF and SED clarification. Following DAF clarification, the turbidity of water with 100 mg/L of adsorbent was reduced from an initial value in PAC trials of 20.0 ± 5.4 NTU to 14.2 ± 2.7 NTU, and in BTMA trials from 28.9 ± 4.7 NTU to 5.4 ± 0.6 NTU. While most of the adsorbent particles were within the optimal size range for DAF bubble attachment (i.e., $> 10 \mu\text{m}$), the particles were likely too hydrophilic for efficient bubble attachment, as evidenced by the strong negative zeta potential displayed in Figure 6.3, due to the lack of coagulation pre-treatment (Edzwald, 1995). Coagulation with FeCl_3 greatly

improved adsorbent removal by DAF clarification. The final turbidity after DAF clarification for test water coagulated and dosed with 100 mg/L adsorbent was 2.9 ± 1.5 NTU and 2.4 ± 0.7 NTU for FeCl₃-PAC and FeCl₃-BTMA tests, respectively, representing a significant ($p < 0.05$) turbidity reduction compared to adsorbent addition only-results. These data are in agreement with the microscope images which indicate that both PAC and BTMA are incorporated into the structure of the FeCl₃ flocs.

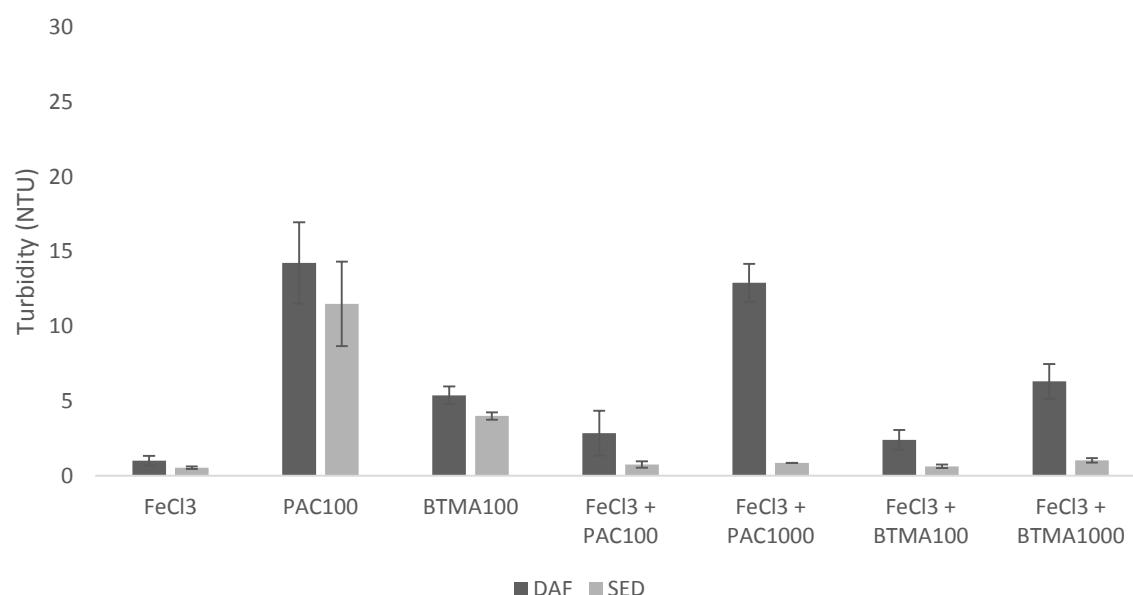


Figure 6.6 Final turbidity after 30 minutes of clarification in fresh water

DAF clarification was highly effective for removing FeCl₃ flocs alone, resulting in a final turbidity level of 1.0 ± 0.3 NTU. The addition of 100 mg/L of either BTMA or PAC adsorbent did not have a significant ($p > 0.05$) impact on final turbidity values. However, increasing the adsorbent dose to 1,000 mg/L with coagulation resulted in significantly ($p < 0.05$) higher clarified turbidity measurements for both FeCl₃-PAC aggregates (i.e., 12.9 ± 1.3 NTU) and FeCl₃-BTMA aggregates (i.e., 6.3 ± 1.2 NTU) than for FeCl₃ flocs alone. The increase in

turbidity measurements with the high PAC and BTMA doses suggests that not all of the adsorbent particles were integrated into the coagulated floc at a dose of 1000 mg/L, which was also evidenced by the micrograph and particle size distribution data as discussed previously. Furthermore, results from DAF rise velocity modelling also demonstrated that coagulant-adsorbent floc aggregates with 1,000 mg/L of PAC or BTMA would have lower rise velocities (i.e., 37 % lower velocity for the median particle size) and settling velocities (i.e., 75 % lower velocity for the median particle size), respectively, than those produced with 100 mg/L dose of adsorbent.

Sedimentation was also not able to fully remove loose adsorbent, with final turbidity values of 11.5 ± 2.8 NTU in PAC trials and 4.0 ± 0.2 NTU in BTMA trials after 30 minutes of settling. Similarly to DAF results, incorporation of adsorbent into FeCl_3 floc significantly ($p < 0.05$) improved clarification, with final turbidity values of 0.7 ± 0.2 NTU for $\text{FeCl}_3 + 100$ mg/L PAC, and 0.6 ± 0.0 NTU for $\text{FeCl}_3 + 100$ mg/L BTMA.

FeCl_3 flocs alone were removed effectively by sedimentation, resulting in a final turbidity level of 0.5 ± 0.1 NTU after 30 minutes of settling. In all of the combined FeCl_3 -adsorbent trials, the final turbidity after 30 minutes of sedimentation was at or below 1 NTU, even in trials with the high dose of adsorbent. These low final turbidity values may be the result of the floc material “sweeping” any loose adsorbent from solution during the settling period. These results are also in agreement with the sedimentation model, which predicted rapid settling of floc-adsorbent aggregates due to their high densities.

The results of this study indicated that sedimentation was a more effective clarification method than DAF for floc-adsorbent aggregates with high doses of adsorbent, either due to (1) the presence of loose adsorbent particles which may have been swept out of solution during sedimentation, or (2) the increased density of flocs when combined with the heavy adsorbent material inhibiting the flotation process.

Oily water clarification

Figure 6.7 displays final turbidity in synthetic wastewater after 30 minutes of sedimentation or flotation. Adsorbent-only trials had very high residual turbidity (i.e., >20 NTU) after both DAF and sedimentation, which was likely due to the presence of oil in the water in addition to any unclarified adsorbent particles. As in the fresh water trials, FeCl₃ flocs were able to incorporate the adsorbent particles, resulting in a significant ($p < 0.05$) turbidity reduction after both DAF and sedimentation when compared to adsorbent-only trials.

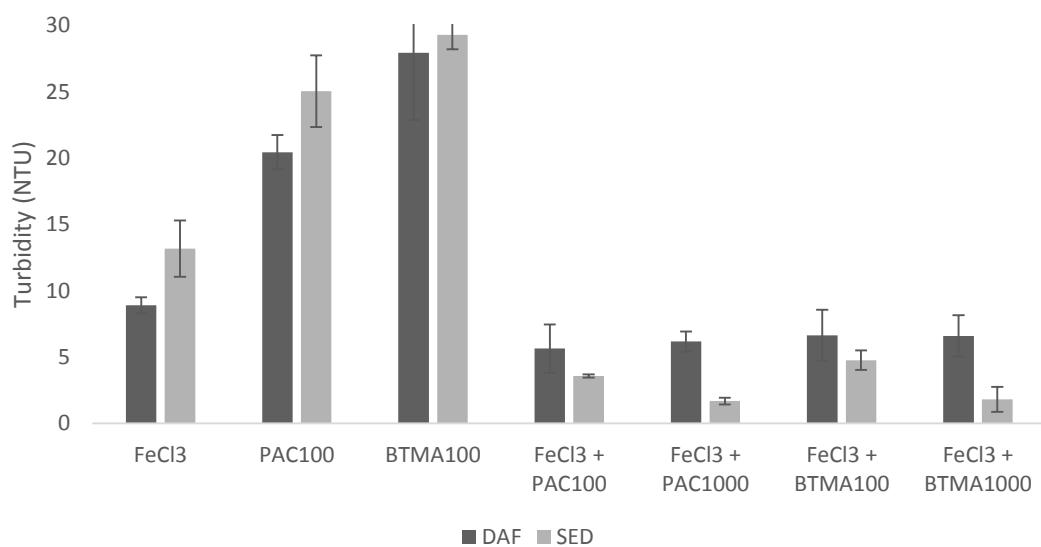


Figure 6.7 Final turbidity after 30 minutes of clarification in wastewater

After DAF clarification of FeCl_3 flocs alone, the residual turbidity was 8.9 ± 0.6 NTU. In contrast to the fresh water results, addition of adsorbent at the high dose (i.e., 1000 mg/L) did not result in an increase in final turbidity, with residual turbidity values of 6.2 ± 0.8 NTU and 6.6 ± 1.6 NTU for FeCl_3 -PAC and FeCl_3 -BTMA aggregates, respectively. This may be due to increased particle cohesion in the high ionic strength wastewater, as FeCl_3 -adsorbent aggregates were observed to have a near-neutral zeta potential in wastewater (as displayed in Figure 6.3) which may have enhanced the aggregation of adsorbent into the floc material.

Sedimentation of FeCl_3 flocs in oily wastewater resulted in a final turbidity of 13.2 ± 2.1 NTU. The high residual turbidity after sedimentation may be because the presence of oil droplets on the floc material reduced the density, and thus the settling velocity, of the flocs. However, the addition of either PAC or BTMA to the flocs significantly ($p < 0.05$) improved final turbidity levels. Sedimentation of FeCl_3 -adsorbent aggregates with 100 mg/L of PAC or BTMA resulted in final turbidity levels of 3.6 ± 0.1 NTU or 4.8 ± 0.7 NTU, respectively. Increasing the adsorbent dose to 1000 mg/L resulted in a further reduction in final turbidity to 1.7 ± 0.2 NTU for FeCl_3 -PAC trials and 1.8 ± 0.9 NTU for FeCl_3 -BTMA trials. Demirci et al (1998) also observed high residual turbidity in refinery wastewater treated with metal salt coagulation and settling, and found that addition of clays as a coagulant aid resulted in substantial improvements in water clarity. The findings of the present study also suggest that the addition of adsorbent material into coagulation processes may ballast the resulting floc sufficiently to make sedimentation a feasible treatment option for oily wastewater.

6.5 Conclusions

- Addition of adsorbent into FeCl₃ flocs reduced floc size, but did not affect floc strength or recovery. Floc strength and recovery factors indicated that adsorbent particles incorporated into FeCl₃ via an enmeshment mechanism.
- Stokes Law sedimentation models predicted very high settling velocities for floc-adsorbent aggregates, similar to those observed in ballasted flocculation studies. DAF models predicted that most FeCl₃-PAC aggregates would achieve rise velocities between 5-10 m/h, but FeCl₃-BTMA aggregates would largely settle, even after DAF bubble attachment, due to their high particle densities.
- Experimental clarification results showed that, in fresh water, adsorbent addition increased final water turbidity after DAF clarification, but had little impact on final turbidity after sedimentation, indicating that sedimentation is a more appropriate clarification method for removing floc-adsorbent aggregates in fresh water.
- In contrast to the fresh water clarification results, adsorbent addition to FeCl₃ flocs in oily water improved clarified water turbidity in either DAF or sedimentation trials.

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CHAPTER 7. Conclusions

7.1 Research Summary

Chapter 3 investigated ferric chloride (FeCl_3) coagulation followed by DAF clarification for the removal of dispersed oil and dissolved aromatics from synthetic produced water. Experimental results showed that coagulation with FeCl_3 and DAF can achieve high removals of dispersed oil and grease, such that synthetic produced water with an initial oil concentration of 100 mg/L would meet the North American discharge standards of 29 or 30 mg/L of oil and grease. However, poor removals of dissolved aromatics, particularly phenol, were achieved by coagulation-DAF, which is consistent with the literature which states that coagulation is better suited to removing the hydrophobic, high molecular weight fraction of dissolved organics, and is largely unable to remove small, hydrophilic compounds from water. These results demonstrated the need for the application of additional treatment technology which would specifically target the dissolved aromatic fraction typical of produced water.

This chapter also evaluated the impact of salinity on coagulation of oily wastewater. It was found that salinity facilitated effective coagulation over a wider range of coagulant dose and pH conditions than was possible in fresh water, as the high ionic strength of saline water was able to prevent the charge reversal and re-stabilization caused by excessive coagulant dose below the pH of minimum solubility for FeCl_3 .

Chapter 4 presented a proof-of-concept study for integrating adsorption and coagulation as a pre-treatment for DAF. This study found that the integrated process was able to combine the high naphthalene removals provided by OC adsorption with the high O&G removals provided by FeCl₃ coagulation in a single process step. This result suggested that the proposed integrated treatment may be a viable option for incorporating dissolved aromatics removal into a commonly-used gravity separation process. However, the OC adsorbent used in this study was not able to achieve high removals of phenol, indicating that it would be necessary to investigate alternative adsorbents to target the hydrophilic fraction of dissolved aromatics.

Chapter 5 evaluated three different adsorbents, powdered activated carbon (PAC), commercial organoclay (OC) and a lab synthesized, aromatic-containing organoclay (BTMA) for the removal of naphthalene and phenol from synthetic produced water. Both PAC and BTMA were found to be suitable adsorbents for the removal of both phenol and naphthalene from the wastewater, while OC was limited to the adsorption of hydrophobic organics (i.e., naphthalene).

This study also investigated the impact of salinity and dispersed oil on adsorption. Salinity was found to decrease the adsorption of phenol by OC, likely due to aggregation and subsequent removal from the water column, but did not negatively impact adsorption of phenol or naphthalene by PAC or BTMA. Dispersed oil dramatically reduced the adsorption capacity of PAC for both phenol and naphthalene, but had a limited impact on adsorption by the organoclays. However, despite this negative impact, PAC was found to have a higher adsorption

capacity than either of the organoclays for the removal of both naphthalene and phenol, even under adverse water conditions.

Chapter 6 investigated the impact of adsorbent (i.e., PAC or organoclay (BTMA)) addition on the structure of FeCl_3 flocs and downstream clarification in pure water conditions. Addition of adsorbent into FeCl_3 flocs reduced floc size, but did not affect floc strength or recovery.

Modelling results predicted very high settling velocities for FeCl_3 -PAC and FeCl_3 -BTMA aggregates in sedimentation clarification, as well as moderate rise velocities for FeCl_3 -PAC in DAF clarification. However, it was predicted that FeCl_3 -BTMA aggregates would largely settle, even after DAF bubble attachment, due to their high particle densities. Experimental clarification results showed that adsorbent addition increased final water turbidity after DAF clarification, but had little impact on final turbidity after sedimentation, indicating that sedimentation is a more appropriate clarification method for removing floc-adsorbent aggregates in fresh water.

In order to determine the impact of wastewater constituents on clarification processes, the sedimentation and DAF experiments were repeated in synthetic produced water. In contrast to the fresh water clarification results, adsorbent addition to FeCl_3 flocs in oily water improved clarified water turbidity in either DAF or sedimentation trials, suggesting that either clarification process would be suitable for removing floc-adsorbent aggregates. Furthermore, the addition of adsorbent particles appeared to have a ballasting effect on oily floc material, providing the potential for the use of a low-energy process for the clarification of coagulated oily wastewaters, which has typically been limited to DAF clarification.

7.2 Conclusions

The primary objective of this work was to address the existing technology gap in the offshore oil and gas industry by investigating an integrated adsorption-coagulation pre-treatment for DAF to incorporate dissolved aromatics removal into a gravity separation process. With respect to this objective, this research:

1. Demonstrated that coagulation-DAF treatment alone was not sufficient to remove the potentially harmful dissolved aromatic fraction, illustrating the need for advanced treatment
2. Established that integrated adsorption-coagulation pre-treatment can simultaneously provide the treatment benefits of both processes as practiced separately
3. Identified two adsorbent materials (PAC and BTMA-organoclay) which are effective for both hydrophobic and hydrophilic dissolved aromatics removal.
4. Showed that both sedimentation and DAF are appropriate technologies for clarifying adsorbent-floc aggregates from oily-saline wastewater.

The secondary objective of this work was to address the existing research gap concerning the use of established drinking water treatment technologies in oily industrial wastewater by investigating the effect of salinity and dispersed oil on the treatment effectiveness of adsorption, coagulation and DAF clarification. With respect to this objective, this research:

1. Showed that salinity had a positive effect on coagulation of oily wastewater, in that it prevented charge reversal and re-stabilization in non-optimal coagulant dose/pH conditions

2. Indicated that high salinity could promote the aggregation and settling of some types of adsorbent material in a CSTR configuration, reducing this effectiveness of the adsorption process
3. Demonstrated that dispersed oil droplets can adsorb to the surface of adsorbent particles, reducing their surface area. This process had a profound impact on adsorption by PAC; however, the impact of dispersed oil on organoclay adsorption was limited.
4. Indicated that oily-saline water promoted adsorbent aggregation into flocs, and improved the DAF clarification process for adsorbent-floc aggregates, as compared to fresh water trials

7.3 Recommendations for Further Research

The following are recommendations for further research on the integrated adsorption-coagulation-DAF treatment process with the aim of developing this process for implementation at full-scale in the offshore environment.

1. *Treatment evaluation with HRT/flow rate constraints*

In the present research, all batch adsorption experiments were conducted to equilibrium, with a contact time of several hours, while integrated adsorption-coagulation experiments were conducted with an adsorption contact time between 15 and 45 minutes. On an offshore oil and gas platform, high flow rates and space constraints are likely a large factor in treatment design, which would limit the adsorption contact time available. Thus, further study on adsorption kinetics would be necessary to evaluate adsorbent performance under realistic time constraints.

Similar hydraulic retention time constraints would likely be placed on the clarification process as well. DAF processes in offshore platforms tend to have relatively short retention times, ranging from 30-60 seconds to several minutes (Walsh, 2015). Thus evaluation of the clarification process under these time constraints would also be beneficial.

2. Validation in field produced water samples

The present research was conducted on a synthetic, lab-generated wastewater, rather than on an actual field sample. The constituents of the synthetic sample were limited to emulsified oil, phenol, naphthalene, and a mix of salts, while actual produced water is a complex mix of organic and inorganic components. As such, the processes studied may be affected by some un-accounted for material. For instance, produced water often contains extremely high levels of organic acids, often on the order of hundreds to a thousand mg/L (Strømgren et al, 1995; Utvik, 1999). It would be necessary to determine what, if any, effect such a high concentration of dissolved materials would have on adsorption, particularly by a competition-sensitive material such as PAC.

3. Impact of adsorbent addition on sludge properties

The addition of adsorbent to the coagulation process may have an effect on the properties of the resulting sludge. Adsorbent material would increase the amount of solids entering the system; however, the addition of ballasting material into flocs has been shown to reduce the water content of flocs, and may thus actually be beneficial for residual solids management (Ghanem et al, 2007). Further study should be conducted to determine the overall effect of adsorbent addition on sludge properties.

4. Comparison of adsorption as pre- and post-treatment

Finally, this research has shown that integrated adsorption-coagulation could be a viable pre-treatment for DAF which can result in enhanced removal of dissolved aromatics. However, adsorption treatment is typically considered a polishing treatment, which could be applied to the effluent of the DAF system in an adsorption column configuration. In this configuration, adsorption would take place after dispersed oil removal, which would improve the performance of some adsorbents (i.e., PAC), as determined in this research. Thus a comparison of adsorption as a pre-treatment in a CSTR configuration and as a post-treatment in a column configuration would be necessary to determine which configuration would be more practical in terms of balancing materials costs with space constraints.

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