Impact of salinity on coagulation and dissolved air flotation treatment for oil and gas produced water
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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 (FeCl₃) 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. The 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 USA) under all conditions tested, while the effectiveness of coagulation treatment in the fresh water synthetic samples was highly dependent on coagulation pH.

Key words | coagulation, dissolved air flotation, offshore, oil and grease, produced water, wastewater treatment

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, soluble polycyclic aromatic hydrocarbons (PAHs) and phenols (Utvik 1999; Fraser et al. 2006; Ahmadun et al. 2009). Typically, another major constituent in produced water is salinity, with total dissolved solids (consisting primarily of sodium and chloride) concentrations ranging from 1,000 to over 400,000 mg/L (Benko & Drewes 2008).

Common treatment technologies for produced water include gravity separation processes, such as gas flotation and hydrocyclones (USEPA 1995), 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 & 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 & Dawe 2003), suggesting DAF treatment alone would not be effective. Furthermore, oil droplets in water tend to acquire a negative surface charge (Metcalf & 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 & Avranas 2002; Al-Shamrani 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 (Duan et al. 2002; Hilal et al. 2008; Edzwald & 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.

**MATERIALS AND METHODS**

**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 5 min using 100 μL of Triton-X (Sigma-Aldrich) surfactant as an emulsifier. The emulsion was left to sit for 15 min 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 (NaHCO₃) 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 (Strømgren et al. 1998; Utvik 1999). 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 2 weeks after sampling before arriving at the laboratory for testing.

**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 (FeCl₃) 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 & 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 min, then slow-mixed at a G-value of 20 s⁻¹ (20 rpm) for 15 min, 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 min 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 1). 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).

### Analytical methods

Total oil and grease was determined by infrared (IR) spectroscopy (Bruker Optics, Ettlingen, Germany) using Standard Method 5520C (APHA AWWA & 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-aminoantipyrene indicator method and a UV-VIS spectrometer (Hach Company, Loveland, USA) using Standard Method 5530 (APHA AWWA & 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.

**Table 1** | Factorial design parameters

<table>
<thead>
<tr>
<th>Factor</th>
<th>Low value</th>
<th>High value</th>
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<tbody>
<tr>
<td>Salinity (g/L)</td>
<td>0</td>
<td>32</td>
</tr>
<tr>
<td>pH</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>FeCl$_3$ dose (mg/L)</td>
<td>10</td>
<td>50</td>
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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).

### RESULTS AND DISCUSSION

#### Water characterization

Table 2 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 (Tibbetts et al. 1992; Stromgren et al. 1995; 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 (Stromgren et al. 1995; Utvik 1999).

#### Dispersed oil removal

Figure 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. 7–30 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.
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 & 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 & 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 & 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 & 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 & Haarhoff 2011).

Zeta potential (ZP) measurements of the raw and flocculated produced water test samples are displayed in Figure 2. At pH 6, there was a marked difference between the removal of oil in salt and fresh water, with good removals (i.e. 70–90%) 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 & 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 (NOM) in drinking water (Matilainen et al. 2010). These results demonstrate that salt water is less sensitive to colloidal 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).

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 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. Coagulation by enmeshment in ferric hydroxide precipitate is easier to achieve at higher pH levels, near 8, at the point of minimum solubility for iron hydroxide.

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 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. 70–90%) 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. Zouboulis & Avranas (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$_3$ (0.5–2.5 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.

**Dissolved oil removal**

Raw and clarified water concentrations of naphthalene and phenol are displayed in Figures 3 and 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 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 & Edzwald 2006).

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 literature. Tansel & Pascual (2011) found that while petroleum hydrocarbons with low molecular weights were readily removed from water by an air stripping mechanism with DAF treatment, naphthalenes were too heavy to be efficiently removed.

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 & 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. Tomaszewska 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 NOM which is widely accepted to be recalcitrant to removal by coagulation (Collins et al. 1986). Tansel & 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.

Treatment of produced water sample

Figure 5 displays the removal rates for oil and grease and phenol from the offshore produced water sample with FeCl₃ coagulation and DAF. 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 0.15 mg/L.

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.

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 the following:

- Experiments conducted with both synthetic and field produced water samples showed that coagulation with FeCl₃ 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 FeCl₃ 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 FeCl₃ 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 laboratory 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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