



## Research article

# Coagulation/flocculation process with polyaluminum chloride for the remediation of oil sands process-affected water: Performance and mechanism study



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## ABSTRACT

This study investigated the application of polyaluminum chloride (PACl) for the treatment of the oil sands process-affected water (OSPW). These coagulants are commonly used in water treatment with the most effective species reported to be Al<sub>13</sub>. PACl with 83.6% Al<sub>13</sub> was synthesized using the slow base titration method and compared with a commercially available PACl in terms of aluminum species distribution, coagulation/flocculation (CF) performance, floc morphology, and contaminant removal. Both coagulants were effective in removing suspended solids, achieving over 96% turbidity removal at all applied coagulant doses (0.5–3.0 mM Al). The removal efficiencies of metals varied among different metals depending on their pK<sub>a</sub> values with metal cations having pK<sub>a</sub> values (Fe, Al, Ga, and Ti) below OSPW pH of 6.9–8.1 (dose dependent) being removed by more than 90%, while cations with higher pK<sub>a</sub> values (K, Na, Ca, Mg and Ni) had removals of less than 40%. Naphthenic acids were not removed due to their low molecular weights, negative charges, and hydrophilic characteristics at the OSPW pH. At the highest applied coagulant dose of 3.0 mM Al, the synthetic PACl reduced *Vibrio fischeri* inhibition effect to 43.3 ± 3.0% from 49.5 ± 0.4% in raw OSPW. In contrast, no reduction of toxicity was found for OSPW treated with the commercial PACl. Based on water quality and floc analyses, the dominant CF mechanism for particle removal during OSPW treatment was considered to be enmeshment in the precipitates (i.e., sweep flocculation). Overall, the CF using synthesized PACl can be a valuable pretreatment process for OSPW to create wastewater that is more easily treated by downstream processes.

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## 1. Introduction

The recovery of bitumen through the oil sands mining operations in northern Alberta, Canada, has rapidly increased in recent years with over 2 million barrels per day of oil being produced in 2013 (Alberta Government, 2014). The hot-water bitumen recovery, and following upgrading processes, use about 3 m<sup>3</sup> of water for each m<sup>3</sup> of crude oil production (Holowenko et al., 2002) which generates large volumes of oil sands process-affected water (OSPW). OSPW is highly saline water with a range of organic and inorganic constituents, including metals, anions, organic compounds, and suspended particles (Allen, 2008). Some metals and

organic compounds make OSPW toxic with known negative impacts on aquatic organisms including algae, fish, invertebrates and mammals (Garcia-Garcia et al., 2011; He et al., 2011; Pourrezaei et al., 2011; Wiseman et al., 2013). Due to this toxicity, OSPW is currently stored in tailing ponds near mining sites awaiting adequate treatment prior to being released into receiving environments (Speight, 2000).

The coagulation/flocculation (CF) process is widely used as a pretreatment to other processes including advanced oxidation, membrane filtration, adsorption, or ion exchange processes (Alpatova et al., 2014; Crittenden et al., 2012; Pourrezaei et al., 2011). Commonly used coagulants are trivalent aluminum salts, Al<sup>3+</sup> (e.g., alum; polyaluminum chloride: PACl), iron salts, Fe<sup>3+</sup> (e.g., ferric sulfate; ferric chloride), and organic polymers (e.g., cationic polydiallyldimethylammonium chloride (polyDADMAC); polyacrylamide) (American Water Works Association, 1999). Using the CF process for OSPW treatment has recently been investigated using alum alone and/or organic polymers (Alpatova et al., 2014;

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Pourrezaei et al., 2011). Pourrezaei et al. (2011) found that at an optimum dose of 250 mg/L alum the turbidity and total organic carbon (TOC) removals during OSPW treatment were 90% and 10%, respectively. However, the CF treatment process has been shown to increase the toxicity of treated waters (Al-Mutairi, 2006; Fort and Stover, 1995; Pourrezaei et al., 2011). Pourrezaei et al. (2011) showed that the toxicity of the alum-treated OSPW towards *Chironomus dilutes* (75% survival) increased as compared to raw OSPW (100% survival), while the addition of polyDADMAC made the treated water even more toxic (42.5% survival). For aluminum-based coagulants, the toxicity increase might be attributed to the monomeric aluminum ions ( $\text{Al}^{3+}$ ), which are more available to the organisms than polymeric aluminum compounds (Bard et al., 2009; Stumm and Morgan, 1996). The overall performance of aluminum-based coagulants has been reported with PACI resulting in higher removals of turbidity, metals and organic matter as compared to alum, especially at  $\text{pH} > 8$  (Stewart et al., 2009; Wu et al., 2012). The residual aluminum concentration in the treated water was also found to be lower using PACI versus other aluminum-based coagulants (Kimura et al., 2013). Therefore, a CF process with PACI is considered a potentially feasible process for OSPW pretreatment, which might lead to higher pollutant removal and better toxicity performance (i.e., less/no impact or even reduced toxicity) as compared with other coagulants.

PACI is a mixture of  $\text{Al}^{3+}$  and polymeric aluminum cations including,  $\text{Al}_2(\text{OH})_2^{4+}$ ,  $\text{Al}_8(\text{OH})_{20}^{4+}$ ,  $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  and other species (Crittenden et al., 2012; Yang et al., 2011). The compound  $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  is generally referred to as  $\text{Al}_{13}$  and has been reported as the most effective PACI species in the CF process (Bottero et al., 1980; Gao et al., 2005).  $\text{Al}_{13}$  is a pre-hydrolyzed coagulant with high positive charge ( $\text{Al}_{13}^{7+}$ ) making it less sensitive to pH changes and thus sustain charge neutralization capacity even in basic conditions, as compared to  $\text{Al}^{3+}$  (Hu et al., 2006). Although the physical structure of  $\text{Al}_{13}$  molecule is still debated, the Keggin structure is currently the most widely accepted model (Holleman et al., 2001). The adsorption of pollutants, especially metals, might be promoted due to the presence of hydroxyl functional groups found in the Keggin structure (Burgess, 1978). Commercially available PACI products usually contain less than 40% of  $\text{Al}_{13}$  because of their relatively high total aluminum concentration and relatively low basicity. However, products with  $>80\%$   $\text{Al}_{13}$  have been synthesized previously with lower total aluminum concentrations and higher basicity (Wang et al., 2004, 2011). Given that  $\text{Al}_{13}$  is the most effective PACI species for the CF process, the use of a synthesized PACI may have better performance for OSPW treatment versus the commercially available product.

This study is the first to consider PACI for the treatment of OSPW. To investigate PACI treatment, comparisons were made between a PACI synthesized in our laboratory having a high  $\text{Al}_{13}$  percentage and a commercial PACI with relatively low  $\text{Al}_{13}$  percentage. The objectives of this study were as follows: (1) to test and compare two PACI products for their efficiency in OSPW treatment (i.e., turbidity, organics removals, metals, naphthenic acids, and  $\text{UV}_{254}$ ); (2) to investigate the impact of PACI coagulants on OSPW toxicity using *Vibrio fischeri*; and (3) to elucidate contaminant removal mechanisms based on water quality and floc analyses.

## 2. Materials and methods

### 2.1. OSPW and chemicals

Raw OSPW was collected from an active oil sands tailings pond in Fort McMurray, Alberta, Canada, and was preserved at  $4^\circ\text{C}$  in a cold storage room prior to use. Sodium hydroxide (NaOH) and aluminum chloride ( $\text{AlCl}_3$ ) used in PACI synthesis, were purchased

from Sigma–Aldrich (St. Louis, MO, USA). All working solutions were prepared in 18 M $\Omega$  Milli-Q water (Millipore Corp., Bedford, MA, USA).

PACI with high  $\text{Al}_{13}$  content was prepared using the modified slow base titration method at room temperature ( $23 \pm 1.0^\circ\text{C}$ ) (Wang et al., 2002; Wu et al., 2012). A 187.5 mL of 0.5 M NaOH solution was added to 75.0 mL of 0.5 M  $\text{AlCl}_3$  solution ( $\text{OH}^-/\text{Al}$  molar ratio of 2.5) at a rate of 1.5 mL/min controlled by a Master Flex L/S peristaltic pump (Cole–Parmer, Chicago, IL, USA). After titration, the PACI solution was diluted to a concentration of 0.1 M as Al and aged for 24 h to allow structure rearrangement prior to use in experiments (Wang et al., 2011). The commercial PACI was provided by Cleartech Industries Inc. (Edmonton, AB, Canada) and used as received.

### 2.2. Coagulation and flocculation test

A Phipps & Bird PB-700™ JarTester (Richmond, VA, USA) was used to perform the jar tests using 2L of OSPW at a room temperature ( $23 \pm 1.0^\circ\text{C}$ ). Coagulants were added to the jars immediately after the start of rapid mixing. After flocculation and sedimentation, 200 mL of the supernatant was collected using a syringe from about 2 cm below the water surface. In order to optimize the mixing time and rapid and slow mixing speeds, a  $2^4$  factorial design study was carried out at the dose of 1.0 mM Al, with two rapid mixing times (20 s and 120 s), two rapid mixing speeds (80 rpm and 220 rpm), two slow mixing times (30 min and 120 min), and two slow mixing speeds (15 rpm and 30 rpm). Based on the TOC and turbidity removals in the initial study, the optimum condition used for all the current experiments included 30 s rapid mixing at 80 rpm, 30 min of slow mixing at 15 rpm, and 60 min of settling. After CF optimization, triplicate jar tests for each PACI were performed with doses including 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 mM Al. The 3.0 mM Al was chosen as a maximum value given that higher doses may not be feasible for full-scale treatment processes due to cost considerations (Crittenden et al., 2012).

### 2.3. Water quality analysis

Treated water samples were preserved in amber glass bottles at  $4^\circ\text{C}$  prior to analysis of each sample in triplicate (unless otherwise stated). The pH was measured using an Accumet Research AR20 pH/conductivity meter (Fisher Scientific, Ottawa, ON, Canada) and turbidity was measured with an Orbeco–Hellige 965 Digital Nephelometric Turbidimeter (Orbeco Analytical Systems Inc., Sarasota, FL, USA). The color was determined using EPA Method 110.2; alkalinity according to the Standard Method 2320-B (Eaton et al., 2005); and chemical oxygen demand (COD) by the Standard Colorimetric Method 5220-D (Eaton et al., 2005). A  $0.45\ \mu\text{m}$  nylon filter (Supelco Analytical, Bellefonte, PA, USA) was used to filter OSPW samples prior to determining soluble COD and DOC (TOC was measured without filtration) (Apollo 9000 TOC Combustion Analyzer, FOLIO Instruments Inc., Kitchener, ON, Canada); and  $\text{UV}_{254}$  with a UV/visible spectrophotometer (Varian Inc., Santa Clara, CA, USA). An Elan 6000 ICP mass spectrometer (PerkinElmer, Waltham, MA, USA) was used to quantify the concentration of metals after the samples were filtered through  $0.45\ \mu\text{m}$  nylon filter (Supelco Analytical, Bellefonte, PA, USA).

Naphthenic acids (NAs) were quantified by ultra performance liquid chromatography (Waters Corp., Milford, MA, USA) equipped with a Phenyl BEH column ( $15 \times 1\ \text{mm}$ ,  $1.7\ \mu\text{m}$ ) (Waters Corp., Milford, MA, USA). The detection of NAs was performed with a high resolution Synapt G2 HDMS mass spectrometer (Waters Corp., Milford, MA, USA) equipped with an electrospray ionization source (Waters Corp., Milford, MA, USA) operating in the negative ion

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