



Potential for *in situ* chemical oxidation of acid extractable organics in oil sands process affected groundwater



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HIGHLIGHTS

- The persistent oxidants, Na₂S₂O₈ and KMnO₄, oxidize AEOs found in OSPW.
- Na₂S₂O₈ and KMnO₄ oxidized 100% and 90% of 2-oxygen NAs in 110 d (22 °C), respectively.
- Na₂S₂O₈ oxidation yields complete mineralization. KMnO₄ mainly transforms AEOs.
- Initial oxidation produced different distributions of NAs by the two oxidants.
- Although testing was inconclusive, oxidation appears to reduce Microtox toxicity.

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ABSTRACT

The process of bitumen extraction from oil sands in Alberta, Canada leads to an accumulation of toxic acid-extractable organics (AEOs) in oil sands process water (OSPW). Infiltration of OSPW from tailings ponds and from their retaining sand dykes and subsequent transport towards surface water has occurred. Given the apparent lack of significant natural attenuation of AEOs in groundwater, remediation may be required. This laboratory study evaluates the potential use of unactivated persulfate and permanganate as *in situ* oxidation agents for remediation of AEOs in groundwater. Naphthenic acids (NAs; C_nH_{2n+2}O₂), which are a component of the acutely toxic AEOs, were degraded by both oxidants in OSPW samples. Permanganate oxidation yielded some residual dissolved organic carbon (DOC) whereas persulfate mineralized the AEO compounds with less residual DOC. Acid-extractable organics from oxidized OSPW had essentially no Microtox toxicity.

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1. Introduction

Canada has the third largest proven reserves of oil with 14% of global reserves (CAPP, 2013), 97% of which is in the oil sands of Alberta. In 2013, oil sands surface mining produced approximately $1.3 \times 10^5 \text{ m}^3 \text{ d}^{-1}$ of bitumen (CAPP, 2013).

Hot-water extraction of bitumen from oil sands leads to an accumulation of the naturally-occurring, bitumen-derived, acid-extractable organics (AEOs) in oil sands process water (OSPW). The AEOs are responsible for the acute toxicity of OSPW (Schramm et al., 2000). AEOs contain a prominent class of acids, namely naphthenic acids (NAs), which are a complex class of aliphatic and cycloaliphatic monocarboxylic acids, represented by the general formula C_nH_{2n+2}O₂, in which *n* and *z* represent the number of carbon atoms, and the number of hydrogen that are lost due to the presence of double bonds or rings in the molecule, respectively

(Ross et al., 2012). Recent studies demonstrated that these classical NAs are only a fraction of the AEOs in OSPW and that molecules with a higher number of oxygen as well as sulfur and nitrogen atoms are present in the mixture (Pereira et al., 2013).

OSPW is retained in tailings ponds and is recycled back into the bitumen extraction process. It is estimated that about $830 \times 10^6 \text{ m}^3$ of fluid fine tailings exist within tailing ponds covering more than 176 km² (AESRD, 2013). Clarification of tailings pond water is extremely slow and, since all companies which mine oil sands agreed not to release any OSPW, the footprint of tailings ponds has grown steadily.

Infiltration of OSPW from tailings ponds and their retaining dykes into the subsurface and subsequent transport towards surface water is a consequence of this on-site tailings storage (Oiffer et al., 2009). Reduction in NA concentration and OSPW toxicity have been reported in experimental surface water ponds and wetlands over years of observation (MacKinnon and Boerger, 1986) due, at least in part, to aerobic biotransformation (Herman et al., 1994). NAs in groundwater appear to be somewhat recalcitrant

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to natural degradation (Scott et al., 2005; Oiffer et al., 2009), so with the continued growth in tailings being retained in potentially “leaky” tailings ponds and dykes, the potential need for technologies to remediate AEOs in groundwater is evident.

While process affected (PA) groundwater could conceivably be pumped out and treated *ex situ*, *in situ* treatment is attractive as it forgoes this expensive and often time consuming groundwater extraction (Adamson et al., 2011). Given the lack of significant sorptive retardation, or natural transformation of NAs, noted in the above groundwater studies, chemical degradation reactions are being pursued as a basis for *in situ* remediation of PA groundwater. Several oxidants have been examined to treat PA water in ponds and processing operations: e.g., ozone (Scott et al., 2008), UV/H₂O₂ (Afzal et al., 2012), Fenton's reagent (Lu et al., 2010), and activated persulfate (Drzewicz et al., 2012).

For *in situ* chemical oxidation (ISCO), the mixing of injected oxidant solution with PA groundwater is very slow (days to months) and so the oxidant must be both reactive with AEOs and persistent in the aquifer (Brown, 2010). Chemical oxidation using ozone or peroxide is impractical in this case because these oxidants quickly decompose *in situ*. Activation is problematic *in situ* because of the short lifespan of radicals and the need to transport activators (e.g. Fe⁰, peroxide) with the oxidant for months. This paper evaluates the potential for ISCO of PA groundwater, using the unactivated, persistent oxidants, persulfate and permanganate, which persist in the groundwater for weeks to months, to reduce AEOs and the associated acute toxicity of OSPW. Since maintaining activation *in situ* is problematic, only unactivated oxidants were investigated here. While most applications of persulfate have employed an activation agent (heat, pH, Fe(II), etc., (Drzewicz et al., 2012), recent research demonstrates that unactivated persulfate can still be effective, as in the *in situ* oxidation of fuel hydrocarbons (Sra et al., 2013).

The ISCO technology has been employed to remediate aquifers contaminated by many hazardous organic contaminants including petroleum hydrocarbons and chlorinated solvents (Siegrist et al., 2011). Our study is the first to examine the feasibility of ISCO for *in situ* remediation of groundwater containing OSPW. For effective *in situ* application three requirements must be met: (1) the oxidant must react with AEOs, (2) the proportion of ineffective oxidant consumption through interaction with aquifer components must be minimal, and (3) intimate contact between the injected oxidant and the AEOs in the PA groundwater must be realized within the timeframe of oxidant activity. The last issue depends on the hydrogeological processes of advection and dispersion for the required mixing of injected oxidant solution with PA groundwater. These are slow, weak processes (Payne et al., 2008) and so ISCO will require oxidants which remain effective for weeks at least. This requirement eliminates peroxide and ozone, but persulfate and permanganate are sufficiently persistent (Siegrist et al., 2011). Preliminary laboratory studies by the authors have estimated that persulfate and permanganate will persist for months in sandy aquifer material (issue 2, above), while pilot scale field experiments are planned to evaluate issue 3, above. In this paper, we focused on the first issue: reactivity of these two persistent oxidants, employed without activation, with AEOs in PA groundwater. High resolution mass spectrometry was employed to confirm the oxidation process.

2. Materials and methods

2.1. OSPW

OSPW samples were collected from a siphon site at the South Tailings Pond on the Suncor property, 35 km northeast of Fort

McMurray. The site is the discharge area of fresh tailings and OSPW into the pond. The OSPW samples were kept on ice and transferred to the University of Waterloo. Here, they were centrifuged at 10000 rpm for 30 min to remove fine particles and then stored in 4-L amber jars. The initial carboxylic acid concentration, including NAs, was about $56.5 \pm 0.2 \text{ mg L}^{-1}$ (by Fourier Transform Infrared (FTIR), see 3. below).

2.2. Oxidation experiments

Analytical grade oxidants, potassium permanganate (KMnO₄, purity 99+%, A.C.S. reagent) and sodium persulfate (Na₂S₂O₈, Sigma Ultra, purity minimum 98%) were purchased from Sigma Aldrich. Two parallel experiments were conducted; one using permanganate and the other using persulfate. Oxidants were added to separate volumetric flasks with 12 L of OSPW and stirred for 90 min to ensure that oxidants were dissolved. The final concentrations were 5 and 10 g L⁻¹ of potassium permanganate and sodium persulfate, respectively. The final solutions were split into triplicate 4-L amber jars and a 4-L jar of centrifuged OSPW, without oxidant, was retained as an un-oxidized control. Jars were incubated in the dark, at room temperature (about 22 °C) and sampled periodically.

2.3. Sample preparation and analysis

Samples for all analyses, except dissolved organic carbon (DOC), were first acidified to pH ~ 2, extracted with dichloromethane (DCM), and dried under nitrogen (Holowenko et al., 2002). This isolated the AEOs, including NAs, from residual oxidant. Specific preparation was then carried out for each analysis.

Potassium permanganate and sodium persulfate concentrations in water were measured by spectrophotometer (Milton Roy, Spectronic 20D) at various sampling times (APHA, 1995). The spectrophotometer was calibrated before and during concentration measurements using fresh standards prepared from the analytical grade oxidants. Samples were diluted by factors of 100 or 10 and analyzed at 525 and at 450 nm for permanganate and persulfate concentrations, respectively. Concentrations were determined using the linear plot for standard solutions multiplied by the appropriate dilution factor.

Samples for DOC analysis were quenched by addition of saturated sodium bisulfite (Fisher Chemicals, S654-500) solution in order to stop the oxidation reaction (Forsey, 2004) and then stored in the dark at 4 °C before analysis. Unoxidized controls were treated similarly. The reported DOC values are the average of two injections with $\pm 0.3 \text{ mg L}^{-1}$ reproducibility.

FTIR analysis was used for quantification of total carboxylic acid concentrations (including NAs) as per Jivraj et al. (1995) and Holowenko et al. (2001). Dried extracts were re-dissolved in 6–8 g of DCM and analyzed by FTIR. Quantification of NA concentration was done by comparing the absorbance peak heights of the C=O functional group at 1743 and 1706 cm⁻¹ for monomer and dimer compounds of commercial Merichem NA solutions (Merichem Chemicals and Refinery Services, Houston, TX) of known concentrations.

Ultra-performance liquid chromatography quadrupole time-of-flight mass spectrometry (UPLC-QTOF/MS) analysis was also applied to characterize select control and oxidized samples based on the number of carbon atoms (*n*) and rings/double bonds (*Z*). The method is similar to that described by Ross et al. (2012). Dried extracts were reconstituted in 4 mL DCM, from which 80 μL was removed and added to a glass autosampler vial and allowed to evaporate to dryness in a fume hood. Samples were spiked with 50 μL of 8 $\mu\text{g mL}^{-1}$ ¹³C-tetradecanoic acid (internal standard), and diluted with 950 μL of 50:50 acetonitrile/H₂O. All samples were analyzed on a Waters Aquity UPLC coupled to an AB Sciex Triple

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