Remediation of oil sands naphthenic acids by activated persulfate oxidation and biodegradation

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Abstract

Bitumen extraction from surface mines in Alberta produces oil sands process-affected water (OSPW) that contains toxic organic contaminants such as naphthenic acid fraction compounds (NAFCs). Due to the large volumes of OSPW generated, cost-effective remediation strategies are vital. One option is coupling chemical oxidation with biodegradation, where limited amounts of oxidant are used to break down NAFCs into more bioavailable compounds which microorganisms can further degrade into non-toxic end products. Sodium persulfate is a low cost, powerful oxidant that may be less damaging to microorganisms compared to other oxidants. Coupling unactivated (21°C) and activated (30°C) persulfate with biodegradation for the remediation of commercially produced Merichem naphthenic acids (NAs) was previously studied. Results demonstrated that persulfate was primarily responsible for NA reduction while bacteria removed degradation by-products, leading to a significant decline in water toxicity.

This study utilises OSPW from an active settling basin and Merichem NAs. Preliminary trials were conducted to determine the conditions of persulfate activation. Persulfate was added to OSPW at concentrations of 250, 500 and 1,000 mg/L and activated by heating to 40–60°C. NAFC removal was limited at 40°C, suggesting ineffective persulfate activation for the concentrations tested. At 60°C, 250 mg/L of persulfate removed 42.4% of OSPW NAFCs compared to 20.3% of Merichem NAs after 8 hours. OSPW NAFCs appear to be more reactive with persulfate than Merichem NAs, indicating a preference for oxidising the more complex, branched species. Increasing the persulfate concentration to 1,000 mg/L improved OSPW NAFC removal to 78.6% after 8 hours at 60°C. Despite increased NAFC removal at higher persulfate concentrations, it is more costly and previous results showed that increasing persulfate concentration past 250 mg/L led to declining microbial viability. Persulfate is a promising oxidant for NAFC remediation and coupling oxidation with biodegradation can provide more efficient and extensive clean-up than either option alone.

Keywords: *oil sands, bioremediation, oxidation, persulfate, tailings, naphthenic acids*

1   Introduction

Alberta, Canada has one of the largest oil reserves in the world, where the extraction of surface mined bitumen generates substantial volumes of oil sands process-affected water (OSPW) that is stored in above-ground tailings ponds, along with sand, silt, clay, and unrecovered bitumen (Allen 2008; Brown & Ulrich 2015; Finkel 2018). Companies must prepare for reclamation throughout the lifecycle of an oil sands mine, however the toxicity of OSPW remains a key challenge in planning for mine closure. Naphthenic acids (NAs) are a complex mixture of organic compounds in bitumen that are solubilised during the extraction process and considered a primary cause of OSPW toxicity (Morandi et al. 2017). Classical NAs refer to cyclic and acyclic alkanes with a single carboxylated side chain and the formula $C_nH_{2n+z}O_2$, where n represents the carbon number, and Z represents the hydrogen loss due to ring and double bond formation. The more general term naphthenic acid fraction compounds (NAFCs) includes classical NAs (O_2^- species), oxidised compounds with three or more oxygen atoms, and compounds containing sulphur and nitrogen (Bauer et al. 2015).

There is currently no standardised method for NAFC removal from OSPW. Chemical oxidation of NAFCs (Afzal et al. 2015; Meshref et al. 2017; Pérez-Estrada et al. 2011; Scott et al. 2008; Song et al. 2022; Wang et al. 2013) and biodegradation of NAFCs (Ahad et al. 2018; Del Rio et al. 2006; Han et al. 2008, 2009; Herman et

al. 1994; Johnson et al. 2013; Ruffell et al. 2016; Whitby 2010) have both been widely studied, however each have distinct disadvantages. Complete mineralisation via chemical oxidation is expensive (Gamal El-Din et al. 2011; Pérez-Estrada et al. 2011), and biodegradation cannot remove the recalcitrant portion of NAFCs (Scott et al. 2005; Quagraine et al. 2005). A combined treatment strategy coupling chemical oxidation and biodegradation overcomes each disadvantage by using the chemical oxidant to break down the bulk of the contaminant while the microorganisms further degrade the more bioavailable oxidation by-products. Sodium persulfate is an ideal oxidant to use for large-scale coupling with biodegradation as it is a low cost, persistent and powerful oxidant (E° = +2.1 V) that may be less damaging to microorganisms compared to other oxidants (Tsitonaki et al. 2010). Persulfate can be activated using heat, ultraviolet (UV) light, transition metals or alkaline conditions, thus creating sulphate radicals (E° = +2.6 V) and/or hydroxyl radicals (E° = +2.8 V).

Oxidation of NAFCs via activated persulfate has been investigated using various activation methods such as UV (Fang et al. 2018, 2019, 2020; Liang et al. 2011), heat (Xu et al. 2016, 2018, 2019), and iron (Aher et al. 2017; Drzewicz et al. 2012). The potential for combining persulfate oxidation with subsequent biological treatment has recently been examined (Balaberda & Ulrich 2021; Ganiyu et al. 2022). Solar activated persulfate oxidation followed by biofiltration showed 60% overall mineralisation of dissolved organic carbon (DOC) and removal of toxicity (Ganiyu et al. 2022). Activated persulfate partially mineralised the NAFCs in OSPW, with the remaining organics consisting of short chain, biodegradable compounds, thus making the effluent suitable for biological treatment.

Coupling unactivated (21°C) or activated (30°C) persulfate with biodegradation for the remediation of commercially produced Merichem NAs was previously studied by our lab (Balaberda & Ulrich 2021). Persulfate was primarily responsible for Merichem NA reduction while bacteria degraded the by-products, improving chemical oxygen demand (COD) removal up to 6.7× in the coupled system compared to persulfate oxidation alone. Comparing the persulfate concentrations tested (100, 250, 500 and 1,000 mg/L), the highest microbial density was observed in bottles containing 250 mg/L of persulfate (Balaberda & Ulrich 2021). It is likely that at this concentration the persulfate provided more bioavailable carbon sources for the bacteria, while increasing the concentration further led to declining microbial density due to increased oxidative stress.

The ability of heat activated persulfate oxidation coupled with biodegradation for OSPW NAFC remediation has not yet been studied and is the primary focus of this research project. The objective of this study is to investigate if persulfate that has been briefly heat activated and then inoculated with bacteria is a feasible in situ remediation method for NAFCs.

2   Methodology/materials and methods

2.1   Source of bacteria

To create a controlled system, a single bacteria isolate will be chosen to test the biodegradation potential of the coupled treatment. Four isolates that represent bacteria commonly found in oil sands tailings ponds are currently being compared in preliminary tests. *Pseudomonas fluorescens* LP6a was obtained from Dr. Julia Foght and had been isolated from an enrichment culture derived from petroleum condensate-contaminated soil. *Rhodococcus* sp. and *Brevundimonas diminuta* were isolated from OSPW by our lab and have shown tolerance to growing in the presence of high concentrations of NAFCs (1,200–9,600 mg/L) (Miles et al. 2019). *Rhodococcus* sp. ATCC 29671 was also used for comparison as it is a known hydrocarbon degrade (Beam & Perry 1974).

To determine which isolate has the strongest NAFC biodegradation ability, each isolate was inoculated into Bushnell Haas (BH) media (Table 1, pH adjusted to 8.2) containing 50 mM of sodium acetate trihydrate (99%, Thermo Fisher Scientific, Waltham MA, USA) and 50 mg/L of Merichem NAs.

Table 1 Bushnell Haas media recipe

Component	Concentration (g/L)
K_2HPO_4	1
KH_2PO_4	1
NH_4NO_3	1
$MgSO_4 \cdot 7H_2O$	0.2
$CaCl_2 \cdot 2H_2O$	0.02
$FeCl_3$	0.05

Once reaching exponential growth (optical density ~0.7) 1% v/v bacteria were transferred into fresh media with acetate and Merichem. This transfer was completed three times to acclimate the bacteria to NAs. Each bacteria strain was then transferred onto BH agar plates containing only Merichem NAs as the sole source of carbon so visible growth could be observed and compared.

2.2 Preliminary experimental setup

Preliminary trial experiments were completed to determine the persulfate activation temperature and reaction time that would be further investigated in the large-scale coupling treatment experiment. OSPW was obtained from an active settling basin containing 44.1 ± 0.5 mg/L of NAFCs and stored at 4°C until use. Commercial NAs gifted from Merichem Chemicals and Refinery Services LLC (Houston, TX) were also used for comparison. In addition, as limited volumes of OSPW are available, investigating Merichem NAs allow for a greater number of conditions to be tested.

Trial experiments were completed in 250 mL flasks containing 100 mL of either OSPW or 50 mg/L of Merichem NAs in water with 250, 500, or 1,000 mg/L of sodium persulfate (>98%, Sigma Aldrich). Flasks were left on an incubator shaker (150 rpm) at 40°C, 50°C or 60°C for up to 24 hours. OSPW trials were completed using single flasks and Merichem trials were done in duplicate.

2.3 Analytical methods

To determine the degradation of NAFCs and Merichem NAs, the persulfate reaction was quenched with excess sodium thiosulphate, filtered using 0.22 μm nylon filters and stored at 4°C until analysis. NA content in samples was then determined using Fourier transform infrared (FTIR) spectroscopy (Brown & Ulrich 2015). Briefly, 8 mL of filtered samples were acidified to pH 2.0 by adding concentrated HCl, exchanged three times with approximately 5–6 mL of HPLC grade dichloromethane (DCM), passed through a sodium sulphate column to remove trace water, and then dried overnight. The dried samples were reconstituted in a known amount of DCM and measurement was completed on a Spectrum 100 FTIR (Perkin Elmer, Waltham, MA) using a 3 mm-spaced, potassium bromide window cell (International Crystal, Garfield, NJ). Data was collected with Spectrum software (V10, Perkin Elmer, Waltham, MA) using 32 scans with a spectral resolution of 4 cm^{-1}. Absorbance at 1,743 cm^{-1} (for monomers) and 1,706 cm^{-1} (for hydrogen-bonded dimers) were summed to calculate total NA concentration. Standard solutions were prepared using known concentrations of Merichem NAs (Merichem Chemicals and Refinery Services, Houston, TX) in DCM.

COD was immediately measured after sampling with HACH COD High Range (HR; limits of 20–1,500 mg/L) digestion solution vials (product 2125915, Fisher Scientific, Fair Lawn, NJ) following method 8000, using a HACH digestor reactor and UV-Vis HACH DR/4000 spectrophotometer (HACH, Loveland, CO).

3 Preliminary results

To determine the persulfate activation temperature and reaction time to be used in the coupling experiments, preliminary trials were conducted using both OSPW and Merichem NAs. The degradation of

NAFCs and Merichem NAs was investigated along with the COD to estimate the extent of mineralisation. Figure 1 displays the results of OSPW NAFC degradation with 250 mg/L and 1,000 mg/L of persulfate, activated at 40°C, 50°C and 60°C. The summarised results, demonstrating the percent decrease of NAFCs after 24 hours of reaction with persulfate are shown in Table 2.
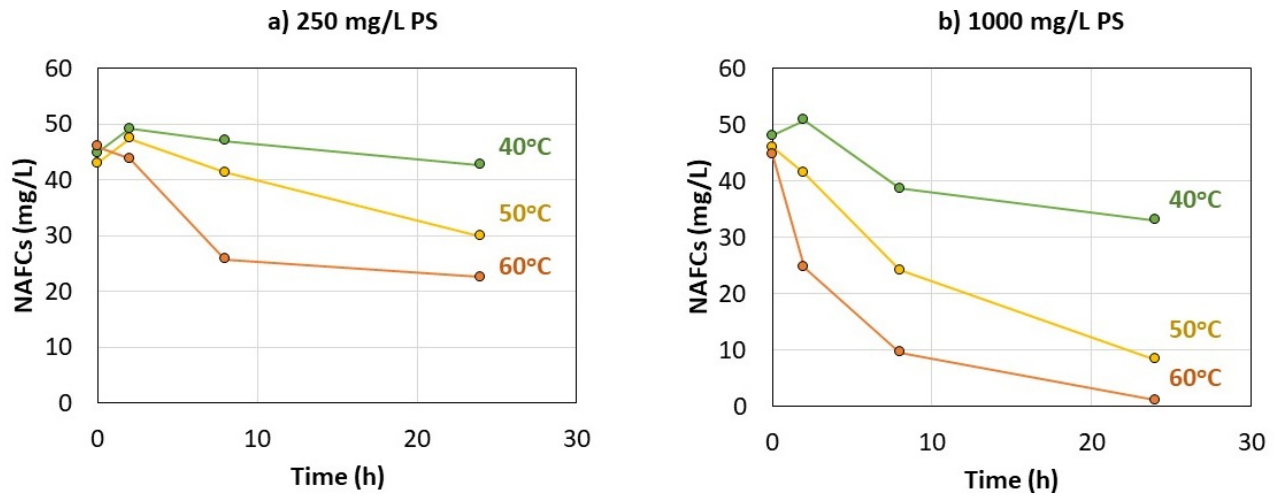
Figure 1 Degradation of naphthenic acid fraction compounds (NAFCs) in oil sands process-affected water (OSPW) with: a) 250 mg/L of persulfate (PS); and b) 1,000 mg/L PS activated at various temperatures

Table 2 Percent decrease of naphthenic acid fraction compounds (NAFCs) in oil sands process-affected water (OSPW) after 24 hours of reaction with persulfate

Temperature (°C)	% Decrease of NAFCs	
	250 mg/L persulfate	1,000 mg/L persulfate
40	4.7	26.2
50	33.2	81.5
60	49.7	97.6

The activation temperatures were chosen to reflect the temperatures already utilised during bitumen extraction (Foght et al. 2017). The above results indicate that 40°C did not provide adequate persulfate activation over 24 hours when using 250 mg/L of persulfate. Increasing the persulfate concentration to 1,000 mg/L showed an increase in NAFC degradation, however degradation was notably lower when compared to when the temperature was increased to 60°C. Conversely, Drzewicz et al. (2012) found that heating OSPW at 40°C with 2000 mg/L of persulfate for only 2 hours led to >80% NAFC removal and there was little change when increasing the temperature to 60°C. It is likely that the higher persulfate concentration used by Drzewicz et al. (2012) created more rapid radical propagation reactions leading to faster NAFC removal. However, the goal of this research project is to reduce the bulk NAFC concentration using only limited amounts of persulfate to create a more favourable environment for the biological stage of the treatment, so the focus of future experiments will be on 250 mg/L of persulfate. The bulk NAFC content was removed after 8 hours of reaction at 60°C, with 250 mg/L and 1,000 mg/L of persulfate removing 42.4% and 78.6% of NAFCs, respectively. In addition, with 250 mg/L of persulfate, further increasing the time to 24 hours did not lead to notable improvement in NAFC removal. Therefore, 8 hours of reaction at 60°C chosen as the activation conditions for future experiments.

Figure 2 displays the COD results at 60°C for 250 mg/L and 1,000 mg/L of persulfate in OSPW. After 8 hours of persulfate activation, there is an 8.8% increase and a 28.7% decrease in COD for 250 mg/L and 1,000 mg/L

of persulfate, respectively. These results indicate incomplete mineralisation of NAFCs by persulfate oxidation, which is ideal as there will be ample carbon sources for the microorganisms to utilise.
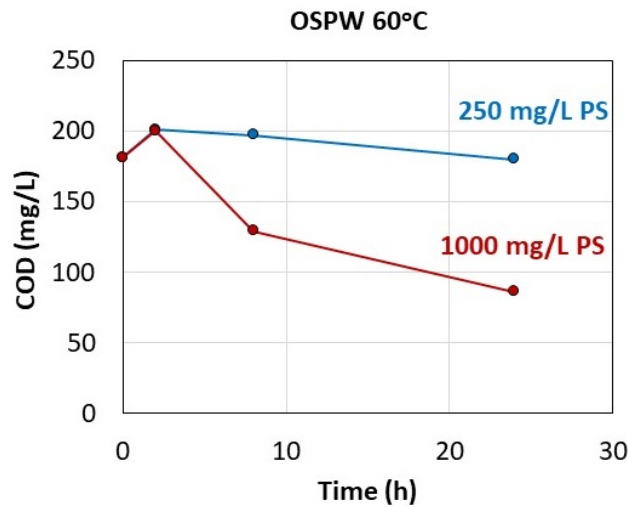
Figure 2 Chemical oxygen demand (COD) of oil sands process-affected water (OSPW) reacted with 250 mg/L and 1,000 mg/L of persulfate (PS) activated at 60°C

Preliminary trials at 50°C and 60°C were also completed using Merichem NAs. Merichem NAs consist only of the classical O_2^- species which are considered the main contributors to acute toxicity. Therefore, the use of Merichem creates a controlled system to directly examine the reactivity of persulfate with the more toxic fraction. Figure 3 displays results of Merichem NA degradation and COD removal after 8 hours of activated persulfate reaction. 250 mg/L of persulfate decreased Merichem NA concentrations by 29.3% and 20.3% at 50°C and 60°C, respectively (Figure 3a). Increasing the persulfate concentration to 500 mg/L did not lead to increased Merichem NA removals, with only 17.5% of Merichem NAs removed at 50°C; however, there was 8.1% COD removal compared to no COD removal in the 250 mg/L flasks. The lack of COD removal when using 250 mg/L of persulfate is consistent between OSPW and Merichem. There was little change in Merichem NA degradation between 50°C and 60°C, while there was a notable difference in OSPW NAFCs.
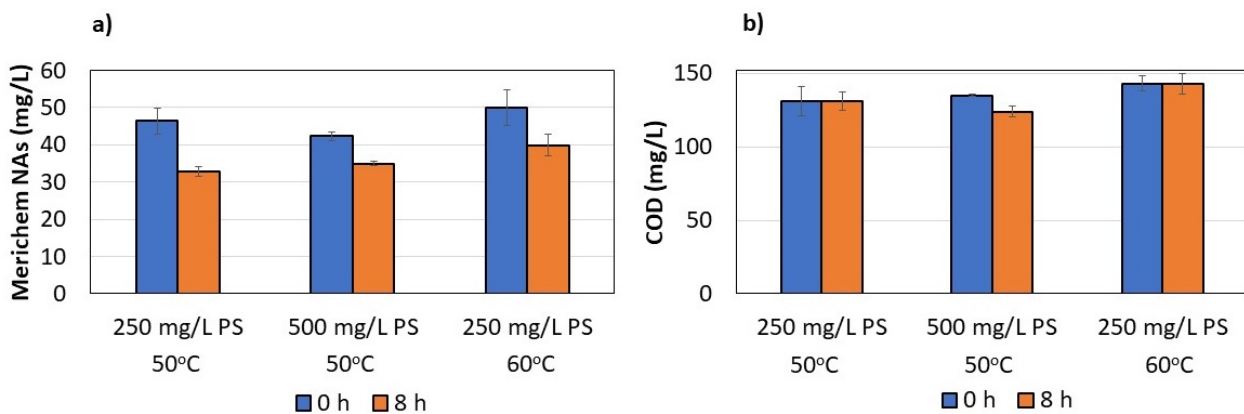
Figure 3 Removal of: a) Merichem naphthenic acids (NAs); and b) chemical oxygen demand (COD), using 250 mg/L and 500 mg/L of activated persulfate (PS) at 50°C and 60°C, over 8 hours. Error bars represent ±2 standard deviations of the averaged value

Merichem NAs appear to be less reactive with activated persulfate than OSPW NAFCs. For example, two times more NAs were removed in OSPW than for Merichem using 250 mg/L of persulfate at 60°C after 8 hours. Aher et al. (2017) similarly found that commercial Sigma NAs were less reactive than OSPW. Using a high dose of 5,000 mg/L of iron activated persulfate led to 95% NAFC OSPW degradation compared to 46% Sigma NA removal over 10 min. The difference in reactivity can be contributed to the differences in structure between commercial NAs and OSPW NAFCs. Merichem NAs are primarily linear and lower molecular weight

compounds consisting only of the O_2^- fraction (Han et al. 2009; Scott et al. 2005). While these are considered more biodegradable than the complex mixture of NAFCs in OSPW, they are less reactive with persulfate. Activated persulfate has been shown to preferentially react with higher carbon numbers and ring containing NAFCs that are more resistant to biodegradation and are not found in commercial NA mixtures (Brown & Ulrich 2015; Fang et al. 2019, 2020). Therefore, persulfate preferentially oxidises the recalcitrant portion, creating an ideal environment for the microorganisms to degrade there remaining bioavailable components.

Based on the above results from the preliminary trials, a large-scale experiment utilising OSPW and Merichem NAs is currently being setup in which 250, 500 and 1,000 mg/L of persulfate will be activated at 60°C for 8 hours. These bottles will be removed from heat and inoculated with bacteria to simulate OSPW entering tailings ponds containing indigenous microorganisms. Four bacteria isolates are currently being compared to determine which provides an adequate representation for biodegradation of NAFCs.

4 Conclusion

NAFCs are a significant contributor towards the acute toxicity of OSPW. This study established that persulfate concentrations as low as 250 mg/L can considerably reduce OSPW NAFC concentrations after 8 hours of activation time. Furthermore, COD was not reduced which indicates the remainder of abundant carbon sources for bacteria to degrade. Merichem NAs appear to be less reactive with persulfate due to their linear structure and low molecular weights, which should be taken into consideration when using commercial NAs as a surrogate for NAFCs. Remediation of NAFCs from OSPW is a key step in mine closure planning for all oil sands mines. Coupling persulfate oxidation with biodegradation allows less oxidant to be utilised, thereby significantly reducing overall treatment costs.

Acknowledgement

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