



Understanding the similarities and differences between ozone and peroxone in the degradation of naphthenic acids: Comparative performance for potential treatment



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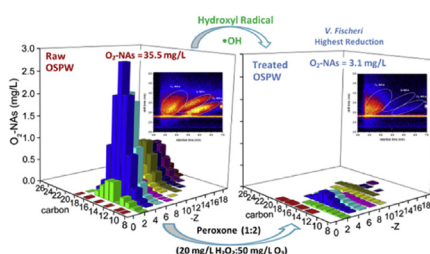
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HIGHLIGHTS

- Molecular ozone pathway was responsible for degrading around 40–50% of the O₂-NA.
- $|-Z| \geq 10$ isomers in ozone treatments were significantly degraded by molecular O₃.
- Structure reactivity is related individually to n and Z and their combined effect.
- Peroxone ratio's effectiveness: (1:2) for degradation vs (1:1) for oxidant utilization.
- At n = 9–11; peroxone (1:1) achieved similar or better degradation than 50 mg/L O₃.

GRAPHICAL ABSTRACT



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ABSTRACT

Ozonation at high doses is a costly treatment for oil sands process-affected water (OSPW) naphthenic acids (NAs) degradation. To decrease costs and limit doses, different peroxone (hydrogen peroxide/ozone; H₂O₂:O₃) processes using mild-ozone doses of 30 and 50 mg/L were investigated. The degradation efficiency of O_x-NAs (classical O₂-NAs + oxidized NAs) improved from 58% at 30 mg/L ozone to 59%, 63% and 76% at peroxone (1:1), 50 mg/L ozone, and peroxone (1:2), respectively. Suppressing the hydroxyl radical (•OH) pathway by adding *tert*-butyl alcohol did significantly reduce the degradation in all treatments, while molecular ozone contribution was around 50% and 34% for O₂-NAs and O_x-NAs, respectively. Structure reactivity toward degradation was observed with degradation increase for both O₂-NAs and O_x-NAs with increase of both carbon (n) and hydrogen deficiency/or $|-Z|$ numbers in all treatments. However, the combined effect of n and Z showed specific insights and differences between ozone and peroxone treatments. The degradation pathway for $|-Z| \geq 10$ isomers in ozone treatments through molecular ozone was significant compared to •OH. Though peroxone (1:2) highly reduced the fluorophore organics and toxicity to *Vibrio fischeri*, the best oxidant utilization in the degradation of O₂-NAs (mg/L) per ozone dose (mg/L) was observed in the peroxone (1:1) (0.91) and 30 mg/L ozone treatments (0.92). At n = 9–11, peroxone (1:1) had similar or enhanced effect on the O₂-NAs degradation

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compared to 50 mg/L ozone. Enhancing $\bullet\text{OH}$ pathway through peroxone versus ozone may be an effective OSPW treatment that will allow its safe release into receiving environments with marginal cost addition.

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1. Introduction

The enormous economical processes of bitumen extraction in the Canadian oil sands (ERCB, 2012) have led to the generation of large volumes of oil sands process-affected water (OSPW), which may cause environmental impacts on the surrounding region (Kelly et al., 2010). OSPW is stored on site in tailings that expand in footprint as the industry grows. OSPW is known to have acute and chronic toxicity to a variety of organisms (Gosselin et al., 2010) which has been attributed mostly to naphthenic acids (NAs) (Headley and McMartin, 2004; Han et al., 2009). NAs are a group of alicyclic and aliphatic compounds with a general formula of $\text{C}_n\text{H}_{2n+Z}\text{O}_x$, where n represents the carbon number ($7 \leq n \leq 26$), Z (0 or negative even integer from 0 to -18) the hydrogen deficiency number while decreasing Z number from $Z = 0$ to $Z = -18$ refers to increasing the hydrogen deficiency and increasing the number of rings, and x the number of oxygen atoms present ($x = 2$ for classical NAs (currently O_2 -NAs) and $x \geq 3$ for oxidized NAs (oxy-NAs)) while their sum (classical and oxidized) is denoted as O_x -NAs. Nyakas et al., (2013) reported that O_x -NAs represent 64% of the organic acid-extractable fraction (AEF) in OSPW among other organic compounds found in OSPW (Grewer et al., 2010).

Several treatment processes are currently being investigated at the bench-scale level to reduce/eliminate the OSPW toxicity to allow its eventual release into the environment. Ozonation (O_3) has been shown to be effective in degrading OSPW NAs, resulting in a partial (Martin et al., 2010; He et al., 2010) or complete toxicity reduction to *Vibrio fischeri* (Garcia-Garcia et al., 2011). Wang et al. (2013) found reduced toxicity of OSPW after ozonation for *in vitro* mice assays and complete toxicity removal to *V. fischeri*. However, previous studies used high and wide ranges of ozone doses from 20 mg/L (Sun et al., 2014) to 100 (Wang et al., 2016; Afzal et al., 2014; Perez-Estrada et al., 2011) and 360 mg/L (Wang et al., 2013), with the high doses (≥ 80 mg/L) not being cost-effective for the treatment of large volumes. Anderson et al. (2011) found a negative influence of ozonated OSPW with 80 mg/L based on increasing toxicity to *Chironomus dilutes* despite the NA reduction, indicating the formation of toxic by-products post ozonation. Additionally, high ozone doses result in reduced NA degradation efficiency (e.g., lower degradation with higher doses). Gamal El-Din et al. (2011) reported that 0.6 mg/L AEF were oxidized per mg/L ozone for doses ≤ 80 mg/L; however, at O_3 doses ≥ 100 mg/L, the degradation declined to only 0.3 mg/L. Similarly, Wang et al. (2013), found that for O_3 doses below 50 mg/L the degradation efficiency was 0.5 mg/L O_x -NAs degraded per mg/L utilized ozone, while 0.05 mg/L NAs per mg/L ozone was for O_3 doses exceeding 50 mg/L. Similar findings in the decrease of AEF were reported by Islam et al. (2014a) while the removal reached a plateau by increasing the ozone dose ≥ 100 mg/L. Likewise, the authors found that the removal efficiency of various NA species decreased considerably from 50 up to 170 mg/L (Islam et al., 2014b). Beside the negative impact of high ozone doses on the degradation, it extends to the influence of the structure reactivity compared to the low doses (i.e., the structures with higher carbons and Z showed higher reactivity at ozone < 50 mg/L) (Wang et al., 2013). Clearly, the optimization of the ozonation

process is required in order to achieve the required levels of removal, especially in complex water matrices such as OSPW given the high costs of ozonation, coupled with inefficient degradation at high doses (Ternes et al., 2003).

The limiting factor of the ozonation process is the production of $\bullet\text{OH}$ to increase degradation (Lee et al., 2013). The $\bullet\text{OH}$ increase can be accomplished by introducing hydrogen peroxide (H_2O_2) in the ozonation process (an advanced oxidation process or AOP) (Afzal et al., 2014; Oh et al., 2014). Afzal et al. (2014) investigated the feasibility of the peroxone ($\text{H}_2\text{O}_2:\text{O}_3$) process, using O_3 dose of 85 mg/L, to degrade model NA compounds including limited experiments for OSPW. The authors found that the peroxone process may be useful for OSPW treatment, but warranted further research.

Given the limitations of the previous research due to the lack of comprehensive studies for peroxone applications in OSPW, a significant step forward is taken with this research in determining the peroxone feasibility for OSPW treatment and considerations about using minimum oxidant doses. The typical ozone dose for wastewater in terms of chemical oxygen demand (COD) is 0.23–0.8 mg ozone per mg COD (Di Iaconi, 2012; Jagadevan et al., 2013). While the raw COD in our OSPW sample is 216 mg/L, therefore our typical range of ozone dose is 49.7–172.8 mg/L. Interestingly, Pocostales et al. (2010) showed that the H_2O_2 addition to ozone doses increased the $\bullet\text{OH}$ yield, while the typical applied molar peroxone ratio for wastewaters applications is 1:2 ($\text{H}_2\text{O}_2:\text{O}_3$) (Pocostales et al., 2010; Paillard et al., 1988; Pisarenko et al., 2012). Similarly, Rosenfeldt et al. (2006) examined the 1:2 ratio, in addition to 1:1, in their investigation. Thus, it can be hypothesized that combining 50 mg/L utilized ozone with specific amount of H_2O_2 at specific ratio might be beneficial for the OSPW remediation.

In the present study, we assessed peroxone (1:2) treatment by the addition of 20 mg/L of H_2O_2 to 50 mg/L utilized ozone. The same H_2O_2 concentration was used for the peroxone (1:1) treatment that was conducted using 30 mg/L ozone. Both ozone doses were also conducted alone (i.e., without H_2O_2) to compare the results with peroxone treatments. The main objective of this study was to investigate the impact of the peroxone treatment on the degradation of NA species and OSPW toxicity reduction toward *Vibrio fischeri*. The specific objectives were as follows: (i) to assess the relative efficacy of ozone and peroxone in terms of NA degradation; (ii) to grasp the significance of H_2O_2 addition to ozone by elucidating the degradation pathways with/without $\bullet\text{OH}$ scavenger; (iii) to study the individual impact of carbon and Z as well as to examine, for the first time, their combined effect on the structure reactivity toward O_2 -NA, and O_x -NA degradation; and (iv) to determine the best ozone and H_2O_2 doses as well as resulting peroxone molar ratio (mol H_2O_2 /mol O_3) using several metrics, including degradation of NAs concentrations per oxidant utilization, ion-mobility spectroscopy (IMS), and toxicity assessment of the treated OSPWs.

2. Materials and methods

2.1. Chemical and reagents

Hydrogen peroxide (H_2O_2 ; 30% w/w), sulfuric acid (H_2SO_4 ;

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