Removal and toxicity reduction of naphthenic acids by ozonation and combined ozonation-aerobic biodegradation

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HIGHLIGHTS

- Ozone reacted preferentially with naphthenic acids (NAs) of higher cyclicity and MW.
- Ozone reactivity with acyclic/ monocyclic model NAs depended on molecular structure.
- NA branching, tertiary and quaternary carbons reduced ozone reactivity.
- Semibatch ozonation of commercial NAs mixture followed pseudo first-order kinetics.
- Ozonation-biodegradation removed NAs by 89% and decreased toxicity by 15-fold.

GRAPHICAL ABSTRACT
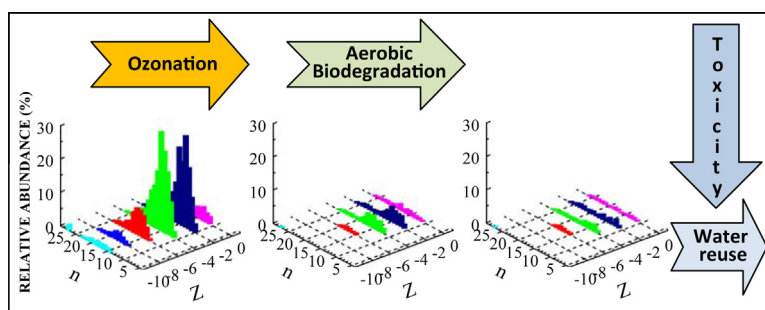
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ABSTRACT

A commercial naphthenic acids (NAs) mixture (TCI Chemicals) and five model NA compounds were ozonated in a semibatch mode. Ozonation of 25 and 35 mg/L NA mixture followed pseudo first-order kinetics (k_{obs} = 0.11 ± 0.008 min^{-1}; r^2 = 0.989) with a residual NAs concentration of about 5 mg/L. Ozone reacted preferentially with NAs of higher cyclicity and molecular weight and decreased both cyclicity and the acute Microtox® toxicity by 3.3-fold. The ozone reactivity with acyclic and monocyclic model NAs varied and depended on other structural features, such as branching and the presence of tertiary or quaternary carbons. Batch aerobic degradation of unozonated NA mixture using a NA-enriched culture resulted in 83% NA removal and a 6.7-fold decrease in toxicity, whereas a combination of ozonation-biodegradation resulted in 89% NA removal and a 15-fold decrease in toxicity. Thus, ozonation of NA-bearing waste streams coupled with biodegradation are effective treatment processes.

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1. Introduction

Naphthenic acids (NAs) are a complex group of alkyl-substituted acyclic, monocyclic and polycyclic carboxylic acids. Classical NAs have a general formula of $C_nH_{2n+Z}O_2$, where n is the carbon number and Z is the number of hydrogen atoms lost due to ring formation, also known as hydrogen deficiency. Z is zero or a negative, even integer, and reflects the degree of cyclicity. NAs are anionic surfactants, have pK_a values in the range of 5–6, and their molecular weight (MW) typically varies between 140 and 500 Da (Whitby, 2010). Recently, use of advanced mass spectrometric techniques has shown that oil sands process-affected water (OSPW), as well as oil field and refinery wastewaters contain oxidized NAs ($C_nH_{2n+Z}O_x$, where x is three or more oxygen atoms) in addition to classical NAs which contain 2 oxygen atoms (Headley

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et al., 2013; Pereira et al., 2013a; Sun et al., 2014; Wang et al., 2013a). The range of NA structures has recently been expanded to include other polar and N–S-containing heteroatomic species and aromatic species found in the oil sands acid extractable fraction (Headley et al., 2011a,b, 2013; Sun et al., 2014).

NAs are found in OSPW, crude oil and petroleum products, as well as in refinery process water and wastewater. Typical NA concentrations are 40–120 mg/L in OSPW (Kannel and Gan, 2012), 0.9–3.6 mg/g in heavy crude oil, 4.2–40.4 mg/L in refinery desalter brine, and 4.5–16.6 mg/L in the influent of refinery wastewater treatment systems (Misiti et al., 2013b). NAs are corrosive and among the most toxic components of OSPW, refinery process water and wastewater, acutely toxic to both aquatic and terrestrial species (Whitby, 2010). To mitigate NA toxicity and treat OSPW, various removal and degradation technologies have been tested. The most well documented and cost effective method investigated is biodegradation. Model NAs, commercial NA mixtures and NAs in refinery process water can be aerobically degraded by indigenous or enriched bacterial cultures, although some types of NAs are recalcitrant (Choi et al., 2014; Hwang et al., 2013; Misiti et al., 2013c; Scott et al., 2005). However, previous reports have shown that complete NA biodegradation may not be feasible (Misiti et al., 2013a,b). Thus, combination of advanced oxidation and biodegradation processes may be more effective resulting in very low NA concentrations, thus achieving a higher quality effluent. The toxicity and biodegradability of NAs depend strongly on their structure. Complex NAs, i.e., those with higher cyclicity, branching and high MW, higher degree of alkyl-substituted aliphatic chains, tertiary substituents at positions other than the β-position relative to the carboxylic group of the main carbon chain, methyl substitution on the cycloalkane rings, are the most recalcitrant and thus persistent NAs (Han et al., 2008; Kannel and Gan, 2012; Misiti et al., 2013c, 2014; Scott et al., 2005; Smith et al., 2008; Whitby, 2010).

Advanced oxidation processes (AOPs) have been suggested as the best alternative method for the degradation of recalcitrant NAs (Kannel and Gan, 2012). AOPs, such as ozonation, UV radiation, and other catalytic processes create oxidizing conditions by the generation of highly reactive oxidizing species, mainly hydroxyl radicals (.OH). Photolysis using natural UV radiation is very limited in degrading NAs; however, photocatalysts, such as TiO_2, microwaves and H_2O_2 combined with UV radiation are effective in oxidizing NAs (Afzal et al., 2012; Headley et al., 2010; Mishra et al., 2010). Ozonation of NAs is considered the most promising AOP with a great potential for OSPW remediation, and has been suggested as a pre-treatment step to biodegradation (Brown et al., 2013; Choi et al., 2014; Gamal El-Din et al., 2011; Hwang et al., 2013; Kannel and Gan, 2012; Martin et al., 2010; Pereira et al., 2013b; Perez-Estrada et al., 2011; Scott et al., 2008; Sun et al., 2014; Wang et al., 2013b). This suggestion is based on the ability of ozone to degrade recalcitrant NAs with relatively high MW and cyclicity, leading to a reduction of their toxicity and an increase of their biodegradability. However, NAs are not expected to be completely degraded by ozone due to their complex nature, whereas formation of potentially more toxic and/or hazardous by-products cannot be excluded. NA structure, MW and the rate of generation of hydroxyl radicals strongly affect the effectiveness of NA degradation by ozone (Hwang et al., 2013; Kannel and Gan, 2012; Pereira et al., 2013b; Perez-Estrada et al., 2011; Wang et al., 2013b).

In spite the fact that NAs are found in refinery waste streams where are proven difficult to treat and create operational problems, such as corrosion and toxicity (Dorn, 1998; Misiti et al., 2013b; Whitby, 2010), relatively less is known about the fate and degradation of NAs in such streams compared to OSPW and other waste streams related to oil sands processes. The impetus of the work reported here was the observation that aerobic biodegradation processes, typically employed for the treatment of refinery wastewater, were not able to completely remove NAs resulting in low, residual NA concentrations (Misiti et al., 2013a,b). Ozonation coupled with biodegradation may result in a more effective treatment of NA-bearing waste streams, potentially leading to water reclamation and reuse.

The objectives of this study were to assess: (a) the degradation of a commercial NA mixture and select model compounds by ozonation; (b) the effectiveness of ozonation relative to NA molecular structure; and (c) the toxicity and biodegradability of the ozonated NA mixture.

2. Methods

2.1. Chemicals

A commercial mixture of NA sodium salt, purchased from TCI Chemicals (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), was used in this study. The mixture consists of mostly 0, 1 and 2 ring NA structures (i.e., $Z = 0$, -2, -4) with carbon numbers (n) ranging between 10 and 25 (Misiti et al., 2013a). The fraction of 0, 1, and 2 ring NA structures in the TCI NA mixture was 10.5%, 34.6%, and 35.4%, respectively. The TCI NA mixture is representative of the types of NAs found in refinery wastewater streams, having a similar NA congener distribution to refinery desalter brine, which was identified as the main source of NAs in refinery wastewater (Misiti et al., 2013b). A stock solution of 8 g NA/L in deionized water (DI) was prepared and used in all assays. NA concentrations mentioned in this work refer to NAs and not the NA salt. The NA concentrations used in this study are of the same order of magnitude to those found in refinery desalter brine and wastewater influent streams (Misiti et al., 2013b).

To investigate the significance of NAs structure relative to the ozone reactivity, five model NA compounds were used in this study: octanoic acid (OCT; $n = 8$ acyclic, unbranched), 2-ethylhexanoic acid (EHA; $n = 8$ acyclic, branched), 1-methyl-1-cyclo-hexane carboxylic acid (1MCH; $n = 8$ monocyclic with a quaternary carbon), 4-methyl-1-cyclo-hexane carboxylic acid (4MCH; $n = 8$ monocyclic with two tertiary carbons), and 2,2-dicyclo-hexylacetic acid (DCH; $n = 14$ dicyclic with a tertiary carbon) (Table 1). All model compounds were of >99% purity, purchased from Sigma–Aldrich (St. Louis, MO). Stock solutions of 10 g/L of each model compound were prepared in 1 N NaOH and used for the preparation of working solutions, which were then adjusted to pH 7 with 1 N HCl.

2.2. Ozonation

An ozone generator (model CD 06-A; Aqua-Flo Inc., Baltimore, MD) was used to produce ozone gas from extra dry, high purity oxygen. The electrical discharge of the ozonator was set at maximum output (120 V, 60 Hz, 30 W) and the oxygen flow rate fed to the ozonator was kept constant at 100 L/h during all experiments. Ozonation was performed at room temperature (22–24 °C) in a modified 1-L Pyrex graduated cylinder reactor (5.6 cm inner diameter × 20.3 cm water column height). Ozone gas was fed to the bottom of the glass reactor through a fine pore size glass sparger. Excess ozone was constantly provided for the whole duration of each ozonation test. The steady-state gas-phase O_3 concentration was 9.3 ± 0.2 mg/L at 23 °C and 1 atm, regardless if the reactor was empty, filled with DI water or NAs solution.

Ozonation was conducted in a semibatch mode (liquid batch, ozone continuous) as follows. The reactor was filled up to 500 mL with either a TCI NA mixture or a model NA working solution and