



## Structure-reactivity relationship of naphthenic acids in the photocatalytic degradation process

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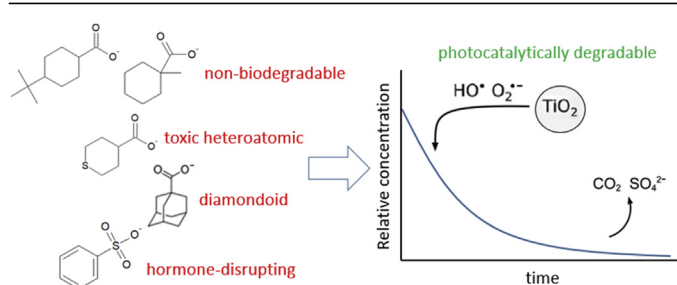
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### HIGHLIGHTS

- Rate of photocatalysis varied significantly with molecular structure.
- Aromatic, heteroatomic, and diamondoid NAs showed preferential degradation.
- Quaternary carbons minimally affected treatment rates.
- Photocatalysis shown to degrade estrogenic disrupting intermediates.
- Superoxide-mediated pathway explains observed trend and offers potential advantages.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Bitumen extraction in Canada's oil sands generates oil sands process-affected water (OSPW) as a toxic by-product. Naphthenic acids (NAs) contribute to the water's toxicity, and treatment methods may need to be implemented to enable safe discharge. Heterogeneous photocatalysis is a promising advanced oxidation process (AOP) for OSPW remediation, however, its successful implementation requires understanding of the complicated relationship between structure and reactivity of NAs. This work aimed to study the effect of various structural properties of model compounds on the photocatalytic degradation kinetics via high resolution mass spectrometry (HRMS), including diamondoid structures, heteroatomic species, and degree of unsaturation. The rate of photocatalytic treatment increased significantly with greater structural complexity, namely with carbon number, aromaticity and degree of cyclicity, properties that render particular NAs recalcitrant to biodegradation. It is hypothesized that a superoxide radical-mediated pathway explains these observations and offers additional benefits over traditional hydroxyl radical-based AOPs. Detailed structure-reactivity investigations of NAs in photocatalysis have not previously been undertaken, and the results described herein illustrate the potential benefit of combining photocatalysis and biodegradation as a complete OSPW remediation technology.

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## 1. Introduction

Oil sands process-affected water is a by-product of surface-mined bitumen extraction in Canada's oil sands and is stored in tailings ponds for reuse due to a zero discharge policy (Masliyah

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et al., 2004). Although water recycling efforts have been instituted, fresh water consumption by the oil sands industry was approximately 180 million m<sup>3</sup> (Rogers et al., 2002) in 2015 (Oil Sands Mining Operators, 2015). Naphthenic acids are among the constituents of OSPW chiefly responsible for its chronic and acute toxicity to aquatic and mammalian organisms (Rogers et al., 2002; Mohseni et al., 2015; Kamaluddin and Zwiazek, 2002; Lacaze et al., 2014; Kavanagh et al., 2011; Morandi et al., 2015), and consist of a complex mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids (Clemente and Fedorak, 2005; Kannel and Gan, 2012). Classic NAs have the formula C<sub>n</sub>H<sub>2n+2</sub>O<sub>2</sub>, but heteroatomic and aromatic acids that do not conform to this conventional structure have recently been identified in OSPW (Headley et al., 2011, 2013; Barrow et al., 2010; Barrow et al., 2015; Pereira et al., 2013). Novel water treatment technologies are required to address these organic fractions and reclaim tailings ponds (Martin, 2015), as NAs have been shown to be recalcitrant to biodegradation (Quagraine et al., 2005; Han et al., 2009), as well as direct ultraviolet or solar photolysis owing to poor absorption (Headley et al., 2009; Leshuk et al., 2016a; McMartin et al., 2004), their toxicity often persisting after decades of environmental exposure (Marentette et al., 2015).

Advanced oxidation processes (AOPs) have been shown to be especially effective at degrading NAs and reducing toxicity of OSPW (Leshuk et al., 2016a; Afzal et al., 2012; Wang et al., 2013; Drzewicz et al., 2012; Liang et al., 2011), but the chemical and physical properties of NAs have been shown to be strongly correlated with molecular structure (Afzal et al., 2012; Pérez-Estrada et al., 2011; Martin et al., 2008). It has been demonstrated that NAs more complex in structure were preferentially degraded in the UV/H<sub>2</sub>O<sub>2</sub> and ozonation processes (Afzal et al., 2012; Pérez-Estrada et al., 2011), but this structure-reactivity relationship has not been elucidated in the photocatalytic degradation of naphthenic acids. Many AOPs, such as ozonation, cannot oxidize all NA fractions to completion and the treated water is left with high residual total organic carbon (TOC) and degradation byproducts, a limitation not shared by photocatalysis (Leshuk et al., 2016a; Scott et al., 2008; Klammer et al., 2015; He et al., 2011). Heterogeneous photocatalysis offers several additional advantages, such as its demonstrated use of sunlight as a renewable, free energy source, lack of need to modify existing infrastructure to introduce costly chemicals and rectification units, and the potential to recycle stable photocatalytic materials (Headley et al., 2009; Leshuk et al., 2016a; Mishra et al., 2010; McQueen et al., 2016, 2017; Liu et al., 2016). Its efficacy against real OSPW samples from different locations has been previously demonstrated (Leshuk et al., 2016b), making solar photocatalysis a promising treatment technology. Furthermore, biodegradability of model NAs has also been shown to vary drastically with molecular structure. The location and extent of side branching can slow the biotransformation and render molecules completely recalcitrant (Smith et al., 2008; Misiti et al., 2014; Han et al., 2008). Geometric isomers can also differ in their biodegradability, owing to the different intramolecular hydrogen bonding (Headley et al., 2002). Consequently, it is necessary to understand the structure-reactivity of technologies proposed to treat OSPW.

The primary objective of this work was to examine the relative degradation of model NAs toward photocatalytic degradation over titanium dioxide. Based on previous investigations utilizing hydroxyl radical-based AOPs, we hypothesized that an increase in complexity in structure, caused by the presence of alkyl branching and rings, would lead to increased reactivity. Photocatalytic degradation of carboxylic acids, like many AOPs, is generally accepted to begin with the formation of a carbon-centered radical, derived from the abstraction of H atoms by reactive oxygen species (Gebel et al., 2010). It is important to note, however, that photocatalysis generates superoxide radicals in addition to •OH radicals,

which enables oxidation to proceed via auxiliary mechanisms. Relative kinetics was used to compare selected model NAs to evaluate the effect of molecular structure on photocatalytic oxidation rates. Given the biologically recalcitrant nature of complex NAs and the aforementioned advantages offered by photocatalysis, this study aimed to demonstrate the potential of photocatalysis to address pollutants not amenable to biodegradation, and consequently increase their overall bioavailability. Implementing biodegradation in conjunction with photocatalysis could be used as a more efficient and thorough OSPW treatment process, particularly if both technologies work synergistically.

## 2. Experimental

### 2.1. Chemicals and reagents

Hexanoic acid (HA, C<sub>6</sub>H<sub>12</sub>O<sub>2</sub>), nonanoic acid (NOA, C<sub>9</sub>H<sub>18</sub>O<sub>2</sub>), undecanoic acid (UA, C<sub>11</sub>H<sub>22</sub>O<sub>2</sub>), dodecanoic acid (DA, C<sub>12</sub>H<sub>24</sub>O<sub>2</sub>), benzoic acid (BA, C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>), cyclohexanoic acid (CHA, C<sub>7</sub>H<sub>12</sub>O<sub>2</sub>), cyclohex-3-ene-1-carboxylic acid (CHE, C<sub>7</sub>H<sub>10</sub>O<sub>2</sub>), 1-methyl-1-cyclohexanoic acid (1meCHA, C<sub>8</sub>H<sub>14</sub>O<sub>2</sub>), 2-methyl-1-cyclohexanoic acid (2meCHA, C<sub>8</sub>H<sub>14</sub>O<sub>2</sub>), 4-methyl-1-cyclohexanoic acid (4meCHA, C<sub>8</sub>H<sub>14</sub>O<sub>2</sub>), tetralin-2-carboxylic acid (TRA, C<sub>11</sub>H<sub>12</sub>O<sub>2</sub>, DBE = 6), 1,4-cyclohexanedicarboxylic acid (CHDA, C<sub>8</sub>H<sub>12</sub>O<sub>4</sub>), isonipecotic acid (NCHA, C<sub>6</sub>H<sub>11</sub>NO<sub>2</sub>), 4-*tert*-butyl-1-cyclohexanoic acid (4tbuCHA, C<sub>11</sub>H<sub>20</sub>O<sub>2</sub>), 1-adamantanecarboxylic acid (AA, C<sub>8</sub>H<sub>14</sub>O<sub>2</sub>), sodium benzenesulfonate (BS, C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>Na), sodium cyclohexanesulfonate (CHS, C<sub>6</sub>H<sub>11</sub>SO<sub>3</sub>Na), and ammonium hydroxide solution (28 wt%, ACS Reagent) were purchased from Sigma-Aldrich. The compounds tetrahydropyran-4-carboxylic acid (OCHA, C<sub>6</sub>H<sub>10</sub>O<sub>3</sub>), 4-propyl-1-cyclohexanoic acid (4prCHA, C<sub>10</sub>H<sub>18</sub>O<sub>2</sub>), 4-hydroxycyclohexanoic acid (OHCHA, C<sub>7</sub>H<sub>11</sub>O<sub>2</sub>), 4-*n*-butyl-1-cyclohexanoic acid (4nbuCHA, C<sub>11</sub>H<sub>20</sub>O<sub>2</sub>), 4-*iso*-butyl-1-cyclohexanoic acid (4ibuCHA, C<sub>11</sub>H<sub>20</sub>O<sub>2</sub>), and 4-pentyl-1-cyclohexanoic acid (4pnCHA, C<sub>12</sub>H<sub>22</sub>O<sub>2</sub>) were purchased from TCI America Chemicals. Tetrahydrothiopyran-4-carboxylic acid (SCHA, C<sub>6</sub>H<sub>10</sub>SO<sub>2</sub>) was purchased from Maybridge Chemicals. The 24 surrogate organic acids used in this investigation were chosen to study specific structural properties of interest, namely, location and type of side branching, degree of cyclicity and unsaturation, molecular weight, the presence of heteroatoms, and non-classical structures, without confounding factors. Given the many species encompassed in the definition of classical and heteroatom-containing NAs, the chosen compounds are good analogues for OSPW-sourced NAs, and several have, in fact, been shown to be present in the Athabasca region and in commercial mixtures of NAs (Lengger et al., 2015; Rowland et al., 2011a, 2011b, 2012). Furthermore, many of these compounds have been studied previously as model compounds (Afzal et al., 2012; Pérez-Estrada et al., 2011; Misiti et al., 2014), thus enabling comparisons to the literature, and their structures were shown in Table 1. In Table 1, c represents the carbon number for each molecule, while Z represents the degree of cyclicity and resulting loss of H atoms due to ring formation, and DBE (double bond equivalents) represents the degree of unsaturation, calculated according to Equations (1) and (2) for a NA of the formula C<sub>c</sub>H<sub>h</sub>N<sub>n</sub>O<sub>s</sub>S<sub>s</sub>, respectively (Kannel and Gan, 2012; Headley et al., 2013).

$$Z = -2\text{DBE} + n + 2 \quad (1)$$

$$\text{DBE} = c - \frac{h}{2} + \frac{n}{2} + 1 \quad (2)$$

Titanium dioxide nanoparticles, often used as a standard, (P25 Aeroxide, 55 m<sup>2</sup>g<sup>-1</sup> surface area, 10–50 nm particle diameter) were purchased from Acros and used as received for all photocatalytic

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