



## Review

# Oil sands naphthenic acids: A review of properties, measurement, and treatment



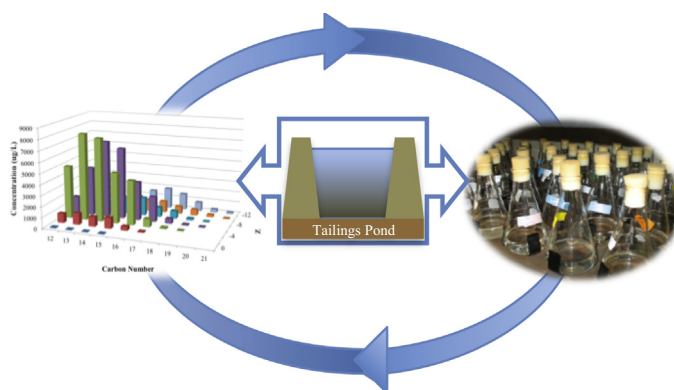
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## HIGHLIGHTS

- Toxicity and ubiquity of NAs in OSPW continues to drive concerted research efforts.
- Research, monitoring plagued by lack of universal adoption of single analytical method.
- NA recalcitrance to biodegradation by indigenous microorganisms firmly established.
- Treatment strategy has evolved to advanced oxidation, attached growth bioreactors.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The Alberta oil sands contain one of the world's largest reserves of oil – over 169 billion barrels of bitumen are economically recoverable with current extraction technologies. Surface mining and subsequent hot water extraction of bitumen from the ore generates about nine cubic meters of raw tailings per cubic meter of oil. Oil sands facilities are required to operate under a policy of zero water discharge, resulting in ponds containing more than one billion cubic meters of tailings, a mixture of sand, fines and process-affected water. Process-affected water contains numerous organic compounds, including naphthenic acids (NAs), which have been identified as the primary source of acute toxicity of process-affected water. Developments in analytical techniques, aerobic biodegradability, and treatment via chemical oxidation (ozone) of NAs are reviewed. The field continues to be challenged by the lack of a cost-effective, accurate analytical technique for NAs or an understanding of all the organic constituents in process-affected water that may be contributing to observed toxicity and thus requiring treatment.

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## 1. Introduction

One of the world's largest oil reserves, containing over 169 billion remaining barrels ( $27 \times 10^9 \text{ m}^3$ ) of recoverable bitumen, is located in northern Alberta, Canada (ERCB, 2012). Bitumen is extracted from the surface mined Athabasca oil sands deposit using a caustic hot water extraction process, resulting in nine cubic meters of raw tailings per cubic meter of oil (Alberta Chamber of Resources, 2004). Fine tailings, consisting of oil sands process-affected water (OSPW), clay and residual sand particles, are currently stored in tailings ponds, in part due to a “zero discharge policy” maintained by the regulatory framework (Allen, 2008a). Use of tailings ponds as process-affected water retention basins enables water recycling for use in the extraction process, as well as allows for the settling of solids and, as originally hoped, partial mineralization of residual organics (Allen, 2008b; Scott et al., 2008b). Due to water recycling efforts, actively utilized tailings ponds continue to exhibit increasing concentrations of dissolved salts, minerals, trace metals, residual bitumen and organics, including naphthenic acids (NAs) (Allen, 2008a). The development of appropriate treatment technologies for OSPW is one of the most formidable challenges facing the oil sands industry (Allen, 2008a). This review is focused on the treatment of naphthenic acids (NAs), which have been linked to the acute toxic responses aquatic life exhibit when exposed to OSPW (MacKinnon and Boerger, 1986; Clemente and Fedorak, 2005).

The term “naphthenic acids” is used to describe the polar organic carboxylic acids that occur naturally in petroleum (Brient et al., 2000). Those occurring in the Athabasca oil sands likely resulted from the biodegradation of mature petroleum (Clemente and Fedorak, 2005). Although NAs are found in many crude oil deposits (Tissot and Welte, 1984), development in the Athabasca oil sands presents unique challenges due to the concentration of NAs in tailings ponds, intensified with water recycling efforts. MacKinnon and Boerger (1986) identified NAs as the primary source of acute toxicity when aquatic life is exposed to oil sands process affected water, driving the increase in research focused on NAs in OSPW (Grewer et al., 2010).

Although NAs are a major component of the OSPW toxic fraction (Frank et al., 2008; Garcia-Garcia et al., 2011b; Jones et al., 2011; Scarlett et al., 2012), a majority of the organic compounds in OSPW do not fit the strict formula for NAs (Headley et al., 2009a; Grewer et al., 2010; Headley et al., 2011) and NAs are not the only organic compounds in OSPW which could contribute to chronic toxicity of OSPW (Garcia-Garcia et al., 2011a,b). Identifying all organic compounds present in OSPW, and determining their potential contribution to toxicity, continues to be an area of research in the oil sands industry. Utilization of both synthesized representative organic compounds, especially NAs, and the entire OSPW matrix in the investigation of appropriate treatment technologies is essential while analytical challenges prevail.

Remediation options for OSPW are an imminent requirement as industry-wide expansion increases demand on local water

resources and the public and government mount pressure to decommission tailings ponds. Decades-long retention times have allowed acclimated microbial communities to develop in tailings ponds and utilize NAs and other organic compounds as substrates, but a fraction of oil sands NAs has proven to be recalcitrant (Scott et al., 2005; Quagraine et al., 2005b) such that natural attenuation is not a feasible treatment option for OSPW.

Ozone treatment has been proposed for pretreatment to break down NAs in OSPW to render these compounds amenable to biodegradation (Scott et al., 2008b; Martin et al., 2010; Wang et al., 2013). Advanced oxidation processes are often used to oxidize complex organic compounds in wastewaters, enabling or enhancing their biodegradability (Metcalf and Eddy, 2003).

Bioremediation of organic compounds in OSPW remains an attractive treatment option due to low cost and minimal waste generation (Allen, 2008b). Exploration of candidate microorganisms capable of significantly biodegrading NAs and other organics (Johnson et al., 2011) may enable bioaugmentation of tailings ponds or reclamation environments as well as provide appropriate microbial seeds for *ex situ* biological treatment technologies (Quagraine et al., 2005b).

This review will provide a brief summary of the properties of naphthenic acids. A discussion of analytical techniques for NAs will be conducted, as the method greatly impacts what compounds are being measured. An extensive review of the biodegradation of NAs is presented, focussing on those occurring in the Athabasca oil sands region. In addition, two treatment options for oil sands process-affected water, chemical oxidation by ozone and wet landscape reclamation, will be discussed.

## 2. Properties of NAs

Naphthenic acids (NAs) are classically defined as a complex mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids with the general chemical formula  $\text{C}_n\text{H}_{2n+z}\text{O}_2$ , where  $n$  indicates the carbon number and  $Z$  specifies a homologous series, or the degree of cyclization (Brient et al., 2000). The  $Z$  variable is an even negative integer between 0 and  $-12$ , which indicates the loss of covalently bonded hydrogen due to the presence of ring structures (Marsh, 2006). The saturated ring structures predominantly contain five or six carbon atoms, and each multiple of  $-2$  indicates the presence of another ring. Thus, NAs contain three components: one or more five- or six-carbon cycloalkane rings, an aliphatic side chain of various lengths, and a carboxylic group (Herman et al., 1994). The carboxyl functional group is usually bonded to the side chain versus directly to the ring structure (Headley and McMartin, 2004). Values of  $n$  range from 5 to 33, resulting in molecular weights between approximately  $100\text{--}500 \text{ g mol}^{-1}$  (Clemente et al., 2003). Some typical NA structures are shown in Fig. 1.

Fatty acids also satisfy the general chemical formula for NAs, but are differentiated based on the biomolecules' absence of highly branched alkyl groups (Scott, 2007). In addition to NAs, aromatic,

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