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Review

Water treatment technologies for the remediation of naphthenic acids in oil sands process-affected water

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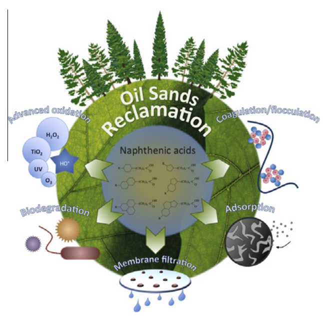
HIGHLIGHTS

- The hazards associated with naphthenic acids are discussed.
- The current status of naphthenic acid remediation technologies are described.
- An overview of the challenges facing oil sands producers is provided.

GRAPHICAL ABSTRACT



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ABSTRACT

For each barrel of bitumen produced in Canada's oil sands industry, approximately 0.5–2.5 barrels of freshwater must be withdrawn from local waterways to aid in the processing of the mined ore. This equates to approximately 2.9 million barrels of freshwater per day. Upon the mining and extraction of bitumen from oil sands ore, a number of contaminants are solubilized and concentrated in oil sands process-affected water (OSPW), prompting several environmental and process-related concerns. Among these contaminants is a very broad family of saturated aliphatic and alicyclic carboxylic acids known collectively as naphthenic acids (NAs), which have shown to be both corrosive toward process equipment and acutely toxic toward a number of aquatic organisms. In an effort to improve the recyclability and/or reduce the acute toxicity of OSPW, several methods have been investigated for the removal or degradation of NAs. These include, but are not limited to, advanced oxidation, biodegradation, coagulation/flocculation, membrane filtration, and adsorption. This review describes the recent developments in these technologies for use in OSPW remediation. Some of the major advances in the field involve the design and optimization of new technologies that reduce costs, operate more efficiently, and allow for greater throughput. Much of the current research is directed toward investigating combinatorial remediation techniques, such as advanced oxidation/biodegradation, biodegradation/adsorption and flocculation/membrane filtration, to achieve more comprehensive NA removal and/or improve the efficiency and sustainability of the process.

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Contents

1. Naphthenic acids

Naturally present in the oil sands of northern Alberta, Canada and other oil reserves throughout the world are a family of saturated aliphatic and alicyclic carboxylic acids known collectively as naphthenic acids (NAs) [1,2]. NAs are weak acids with a p*K*a in the range of 5–6 and have shown to possess surface-active properties [3,4]. Upon the mining and extraction of bitumen from oil sands ore, NAs are solubilized and concentrated in oil sands process-affected water (OSPW), where they present several environmental and process-related concerns. For example, a number of studies have shown that NAs present a significant health risk to aquatic and mammalian species upon exposure and may result in both acute and chronic toxicity [2,5–8]. Further, NAs have been identified as one of the primary causes of corrosion toward process equipment during bitumen extraction unit operations [1,2,9]. Their presence, however, is essential for the extraction of bitumen droplets from sand particles and the solubilization of these droplets in OSPW [10–12]. In fact, studies have shown that their concentration in process water directly correlates to extraction efficiency through a parabolic relationship, resulting in maximal process efficiency within a certain concentration range [10,13]. Therefore, if the concentration of NAs in OSPW is excessively low or high, bitumen extraction suffers. As a result, for oil sands producers to either remediate OSPW and reintroduce it into the local environment or recycle OSPW and reduce freshwater consumption, the concentration of NAs must be reduced to an acceptable level.

1.1. Molecular structure and physical properties

NAs originate in petroleum deposits and are believed to be a result of two natural phenomena: partial aerobic biodegradation [14] and incomplete catagenesis [15] of bituminous compounds. Natural geological events, such as earthquakes and erosion, expose bitumen to environments that are ideal for aerobic biodegradation and the high pressure and temperatures found in some petroleum deposits are probable triggers for the catagenesis of organic matter.

NAs are amphiphilic compounds, in which the hydrophobic segment is regularly composed of saturated 5- or 6-carbon rings in a variety of combinations, and the hydrophilic segment is constituted of a carboxyl group, separated from the ring structure by a carbon chain of at least two units in length [8]. Acyclic NAs also exist, but are more likely to contain aliphatic branching [16]. Some generalized monoacidic NA molecular structures are presented in Fig. 1.

NAs may be defined by the general chemical formula $C_nH_{2m+z}O_\alpha N_\beta S_\gamma$, where n is the carbon number, z is a negative even integer corresponding to hydrogen deficiency resulting from ring formation in the organic segment, and α, β, and γ, are the oxygen, nitrogen, and sulfur numbers [17], which for ‘classical’ NAs are

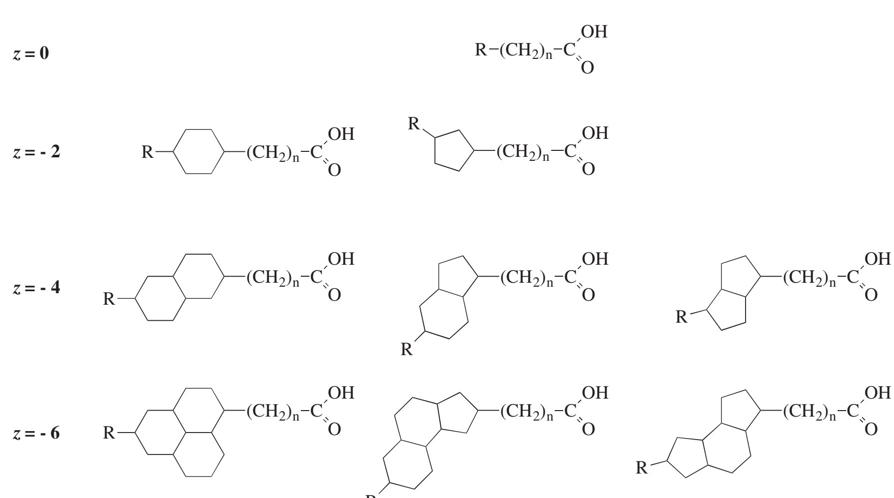

Fig. 1. Generalized molecular structure of some classical NAs. The *z* number represents hydrogen deficiency due to ring formation and *R* represents some aliphatic branching.