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Prediction of naphthenic acid species degradation by kinetic and surrogate models during the ozonation of oil sands process-affected water

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HIGHLIGHTS

- A kinetic model was developed to predict the removal of NAs during ozonation.
- Surrogate parameters were used to determine the degradation of NAs during ozonation.
- Speciation and distribution of classical and oxidized NAs were examined.
- The structure–reactivity of individual NA species was obtained.
- High correlations between the AEF and COD of OSPW and NA species were found.

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ABSTRACT

Oil sands process-affected water (OSPW) is a complex mixture of organic and inorganic contaminants, and suspended solids, generated by the oil sands industry during the bitumen extraction process. OSPW contains a large number of structurally diverse organic compounds, and due to variability of the water quality of different OSPW matrices, there is a need to select a group of easily measured surrogate parameters for monitoring and treatment process control. In this study, kinetic and surrogate correlation models were developed to predict the degradation of naphthenic acids (NAs) species during the ozonation of OSPW. Additionally, the speciation and distribution of classical and oxidized NA species in raw and ozonated OSPW were also examined. The structure–reactivity of NA species indicated that the reactivity of individual NA species increased as the carbon and hydrogen deficiency numbers increased. The kinetic parameters obtained in this study allowed calculating the evolution of the concentrations of the acid-extractable fraction (AEF), chemical oxygen demand (COD), and NA distributions for a given ozonation process. High correlations between the AEF and COD and NA species were found, suggesting that AEF and COD can be used as surrogate parameters to predict the degradation of NAs during the ozonation of OSPW.

1. Introduction

The bitumen extraction process of the oil sands in Northern Alberta, Canada, leads to the generation of oil sands process-affected water (OSPW), which is a complex mixture of organic compounds, inorganic compounds, and suspended solids (Fedorak et al., 2002; Holowenko et al., 2002). OSPW has been shown to be toxic toward aquatic organisms (Anderson et al., 2012; Gagné et al., 2012; He et al., 2012; Kavanagh et al., 2011), therefore, it needs to be extensively treated before being released into the receiving environments (Schramm et al., 2000). Of particular environmental concerns are the complex mixture of naphthenic acids (NAs) found in OSPW since they are both highly recalcitrant and toxic to fish (He et al., 2012), bacteria (Gamal El-Din et al., 2011), and benthic invertebrates (Anderson et al., 2012).

The NAs are described as a mixture of alicyclic and alkyl-substituted aliphatic carboxylic acids with the general formula of $C_nH_{2n+Z}O_x$, where n is the carbon number, Z is the hydrogen deficiency due to ring or double bond formation, and x represents the number of oxygen atoms. When $x = 2$, these acids are referred as classical NAs, while they are referred as oxidized NAs (oxy-NAs) when $x \geq 3$. In this study, the oxy-NAs with $x = 3$, $x = 4$, $x = 5$, and $x = 6$ are designated as O-NAs, O_2-NAs, O_3-NAs, and O_4-NAs, respectively. Advanced Oxidation Processes (AOPs), particularly ozonation of OSPW at a laboratory scale, have been considered previously as OSPW remediation treatment processes (Gamal El-Din et al., 2011; Scott et al., 2008; Wang et al., 2013) and the impact of ozonation on the speciation of classical NAs has been demonstrated (Hwang et al., 2013; Wang et al., 2013). However, reports on the structure–reactivity of classical NAs in OSPW have been limited (Han et al., 2008; Perez-Estrada et al., 2011). To our knowledge,

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the distribution of the oxy-NAs after ozone treatment considered in the present study has not been previously examined.

The use of kinetic modeling of structure–reactivity relationships may be useful in broadening the understanding of organic compound degradation (or lack thereof) following the ozonation of OSPW. Kinetic modeling of this relationship for binary mixtures of model NA compounds has been considered previously by Perez-Estrada et al. (2011), where OSPW and commercial NAs were assumed to be of first- and second-order reactions, respectively. Additionally, it was found that model NA compounds with multiple rings and alkyl branching were preferably degraded during the ozonation process (Perez-Estrada et al., 2011). It has been reported that classical NAs in OSPW are more recalcitrant than commercial NAs during biodegradation (Han et al., 2008). Moreover, it has been reported that *n* had little effect on the biodegradation rate, whereas a general structure–persistence relationship was observed with the *Z* number, which indicates that an increase in cyclization (i.e., increase in *Z*) resulted in a decrease in the biodegradation rate of both commercial and OSPW classical NAs.

The OSPW contains thousands of unidentified organic compounds (in addition to NAs) in a highly complex OSPW mixture; many of these compounds do not have established analytical methods for their identification and quantification (Grewer et al., 2010; Rowland et al., 2011). Given this inability to directly identify/quantify these organic compounds, the use of simply measured 'surrogate' parameters (such as chemical oxygen demand) may be considered to determine the degradation of these compounds in OSPW, following a treatment process without the need for their direct measurement. Although surrogate parameters have been investigated extensively for municipal wastewaters, the use of surrogates for OSPW has not been extensively considered. Mohamed et al. (2008) used UV absorption and fluorescent emission spectroscopy as surrogate parameters to determine chromophoric surrogate compounds that serve as an internal standard for the indirect analysis of NAs in OSPW.

Surrogate parameters used for municipal wastewaters have included total organic carbon (TOC), chemical oxygen demand (COD), UV absorbance at 254 nm (UV_{254}), and UV fluorescence (Chang et al., 1998; Gerrity et al., 2012; Lee and Ahn, 2004; Lee et al., 2013). The selection of specific surrogate parameters depends on the water treatment step being monitored. As illustration, COD has been commonly used in kinetic studies during the ozonation of wastewater because it provides insight of the magnitude of the oxidation process (Beltrán, 2004). TOC has been used as "true" parameter for the determination of organic pollution (Bourgeois et al., 2001). UV_{254} has been found to be an accurate precursor surrogate parameter to predict the trihalomethane formation in raw and alum-coagulated waters (Pifer and Fairey, 2014). In contrast to the typical surrogate parameters used for municipal wastewater, a more suitable surrogate typically measured during OSPW remediation is the acid-extractable fraction (AEF) which is commonly employed to monitor treatment effectiveness (Gamal El-Din et al., 2011; Zubot et al., 2012). The benefit of using the AEF measurements is that they determine the total organic acid fraction concentrations, which includes all NAs species. Currently, surrogate parameter(s) used to predict the oxidation of the organic fraction in OSPW have not been fully developed despite the usefulness of these easily measured parameters for onsite assessment of treatment efficiency via non-specialized, user-friendly instrumentation.

The main objective of this study was to develop, for the first time, kinetic and surrogate correlation models to predict the degradation of NA species during the ozonation of OSPW. The surrogate parameters investigated in the present study included COD, TOC, UV_{254}, and fluorescence, in addition to a typical OSPW remediation AEF parameter. Correlation analysis was evaluated using the Pearson product–moment correlation coefficient with statistically significant correlations determined based on the *p*-value and Student's *t*-test on slope and intercept during the linear regression. In addition to the main objective, this study also examined, for the first time, the effects of ozonation on the speciation of oxy-NAs, while the structure–reactivity of both classical and oxy-NAs species were estimated using a pseudo-first-order reaction model.

2. Materials and methods

2.1. Chemicals and reagents

The following chemicals were used, as received, without any further treatment: Fluka NA mixture (Sigma-Aldrich, ON, Canada); lucine enkaphenlin and sodium formate standard solutions (Waters Corporation, Milford, MA, USA) used as standards for NA analysis; as well as potassium hydrogen phthalate (Fisher scientific, Fair Lawn, New Jersey, USA) as a COD standard. Phenol bioextra (>99.5% Sigma, Aldrich, CA) was used in Microtox analysis. The OSPW was provided by Syncrude Canada Ltd., and collected from West In-pit pond, Fort McMurray, Alberta, Canada, on September 27th 2010. OSPW samples were stored at 4 °C in sealed polyethylene containers and used without additional pre-treatment prior to the ozonation experiments.

2.2. Ozonation experiments

The OSPW was ozonated following the procedure described elsewhere (Wang et al., 2013). Ozone gas (O_3) was produced by an ozone generator (AGSO 30 Effizon, WEDECO AG Water Technology, Herford) from extra dry high purity oxygen. Ozonation experiments were performed in a 4-L vacuum flask reactor equipped with a cylindrical shape rock fine bubble gas diffuser. Throughout the experiment, the ozone concentrations in feed and off-gas lines were continuously monitored by two identical ozone monitors (HC-500, PCI-WEDECO). The experiments were performed at natural OSPW pH (8.4 ± 0.1) and at room temperature (20 ± 1 °C). For sample analysis, triplicate samples ($n = 3$) were taken periodically over the 20 min experiment duration.

2.3. Sample analyses

The AEF was measured using Fourier Transform Infrared Spectroscopy (FT-IR) as described elsewhere (Gamal El-Din et al., 2011). A calibration curve for the quantification of AEF was done using a Fluka NA mixture. The concentrations of classical and oxy-NAs were measured using a high performance liquid chromatography-high resolution mass spectrometry (UPLC-HRMS) Waters Acquity UPLC® System, Milford, MA, USA equipment, according to a method described elsewhere (Wang et al., 2013) and included in the Supplementary data. Ion-mobility spectrometry (IMS) was conducted in a Tri-Wave® ion-mobility cell of 15 cm long, using nitrogen (purity >99%) as the drift gas. The IMS consisted of a transfer cell that collected a certain amount of ions and a helium gate that released the ions into the ion-mobility cell. The COD was measured according to standard methods (American Public Health Association, 2005). An Apollo 9000 TOC Combustion Analyzer (FOLIO Instruments Inc.) was used to measure the TOC levels. A Varian Cary Eclipse fluorescence spectrophotometer (Ontario, Canada) was used to measure the fluorescence using a 1-cm cuvette with excitation–emission spectra collected over a range of excitation wavelengths from 220 nm to 400 nm and emission wavelengths from 260 nm to 500 nm. The excitation and emission slits were maintained at 10 and 5 nm, respectively, with a scanning speed of 600 nm min^{-1}. A medium photomultiplier voltage (600 mV) was applied for the fluorescence signal. Both raw and ozonated OSPW samples were filtered through a 0.45 micron nylon filter (Whatman) before performing the fluorescence spectroscopy measurements.

A Microtox analyzer (AZUR Environmental, Carlsbad, USA) was used to determine the toxicity of the untreated and ozonated OSPW samples (Chelme-Ayala et al., 2011). The results are reported for an incubation time of 5 min by using the 81.95% screening test protocol. The percentage of inhibition caused by the untreated and ozonated samples after