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Biodegradation and detoxification of naphthenic acids in oil sands process affected waters

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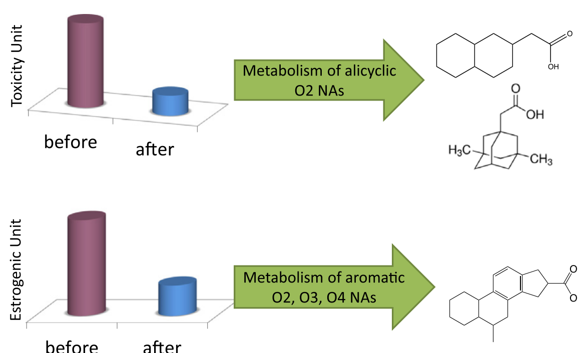
HIGHLIGHTS

- Toxicity/estrogenicity of SPE/HPLC fractions of biologically treated OSPW using EDA
- Relate compositional change of key fractions with biodegradation and detoxification
- C12–14 bicyclic, tricyclic O2 NAs linked to toxicity decrease
- O3, O4, C16 DBE = 5–6, C16–17 DBE = 7, C19 DBE O2 NAs linked to estrogenicity decrease

GRAPHICAL ABSTRACT



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ABSTRACT

After oil sands process affected water (OSPW) was treated in a continuous flow biofilm reactor, about 40% of the organic compounds in the acid extractable fraction (AEF) including naphthenic acids (NAs) were degraded resulting in a reduction of 73% in the Microtox acute toxicity and of 22% in the yeast estrogenic assay. Using effect directed analysis, treated and untreated OSPW were fractionated by solid phase extraction and the fractions with the largest decrease in toxicity and estrogenicity were selected for analysis by electrospray ionization combined with linear ion trap and a high-resolution Orbitrap mass spectrometer (negative ion mode). The aim of this study was to determine whether compositional changes between the untreated and treated fractions provide insight related to biodegradation and detoxification of NAs. The O2S, O3S and O4S compounds were either not major contributors of toxicity or estrogenicity or the more toxic or estrogenic ones were biodegraded. The O3- and O4-NAs seem to be more readily metabolized than O2NAs and their degradation would contribute to detoxification. The decrease in acute toxicity may be associated with the degradation of C12 and C13 bicyclic and C12–C14 tricyclic NAs while the decrease in estrogenicity may be linked to the degradation of C16 O2-NAs with double bond equivalents (DBE) = 5 and 6, C16 and 17 O2-NAs with DBE = 7, and C19-O2-NAs with DBE = 8. The residual acute toxicity may be caused by recalcitrant components and/or degradation products such as the O2 bicyclic and tricyclic NAs, particularly the C14 and C15 bicyclic and C14–C16 tricyclic NAs as well as the polycyclic aromatic NAs (DBE ≥ 5 compounds). The decrease in estrogenicity may be linked to the degradation of the O3 and O4 oxidized NAs while much of the residual estrogenicity may be due to the recalcitrant polycyclic aromatic O2-NAs. Hence, treatment to further detoxify OSPW should target these compounds.

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1. Introduction

Canada's oils sands in northern Alberta are the world's third largest petroleum reserve after Venezuela and Saudi Arabia (Government of Alberta, 2014a) containing 167 billion barrels of recoverable bitumen (Alberta Energy Regulator, 2014). In 2013, 2.1 million barrels per day of crude bitumen was produced and production is expected to increase to 4.1 million barrels per day by 2023 (Alberta Energy Regulator, 2014). The Clarke hot water extraction process to recover bitumen from surface mined ore produces large quantities of wastewater, known as oil sands process affected water (OSPW). OSPW has demonstrated acute and/or chronic toxicity to a number of aquatic and mammalian species (MacKinnon and Boerger, 1986; Holowenko et al., 2002; Gagne et al., 2012; Kavanagh et al., 2011; Rogers et al., 2002; He et al., 2011) and cannot be discharged to ground or surface waters under Alberta's Environmental Protection and Enhancement Act. These waters are held in tailing and settling ponds, the total volume of which exceeded 720 million m^3 in 2011 (ERCB, 2011) and covers 220 km^2 (Government of Alberta, 2014b). Furthermore, it has been reported that OSPW from tailing ponds have seeped to adjacent groundwater, and ultimately, to nearby rivers (Oiffer et al., 2009; Ross et al., 2012; Frank et al., 2014).

Although OSPW contain many classes of toxic compounds, the acid extractable fraction (AEF) containing naphthenic acids (NAs) has been shown to contain the majority of the toxicity (Madill et al., 2001, MacKinnon and Boerger, 1986; Lo et al., 2006). NAs have the formula $C_nH_{2n+z}O_x$ (Grewer et al., 2010) which includes classical NAs (c-NAs, $x = 2$) and oxidized NAs (oxy-NAs, $x = 3–10$), where "n" is the number of carbons, and "z" is zero or a negative, even integer that specifies a family of homologous compounds and is related to the hydrogen deficiency or double bond equivalents (DBE) that includes ringed structures and double bonds containing carbon. Some of these compounds may also have N and/or S atoms.

Biodegradation of model NAs (Del Rio et al., 2006; Johnson et al., 2011, 2012; reviewed by Whitby, 2010) and commercial mixtures of NAs (Clemente et al., 2004; Videla et al., 2009) is well established with OSPW NAs being much more difficult to biodegrade (Scott et al., 2005). Biodegradation of commercial mixtures of NAs (Clemente et al., 2004; Herman et al., 1994) and OSPW NAs (Scott et al., 2008) reduces toxicity. Lower molecular weight NAs are considered to be more biodegradable (Clemente et al., 2004; Holowenko et al., 2002; Scott et al., 2005) resulting in an accumulation of recalcitrant NAs and metabolites (Biryukova et al., 2007; Clemente et al., 2004; Scott et al., 2005) where biodegradation is sterically hindered by the presence of alkyl substitutions that prevent β-oxidation in aliphatic structures or prevent ring opening in cyclic or aromatic structures.

McKenzie et al. (2014) showed that about 40% of the NAs in OSPW were biologically degraded in a continuous flow biofilm reactor but had not determined the effect on toxicity. Since OSPW contains so many different compounds, it is difficult to determine which ones are most responsible for toxicity. The complexity of OSPW can be reduced using effect directed analysis in which OPSW is fractionated and individual fractions evaluated using toxicity assays such as the Microtox® or yeast estrogenic screening (YES) (Yue et al., 2015a). Chemical composition of treated and untreated OSPW fractions of interest can then be analyzed by linear ion trap Quadropole (LTQ)-OrbitrapVelos Pro hybrid mass spectrometer which combines a linear ion trap with an Orbitrap analyzer that has high resolution (>100,000 at *m/z* 400) and high mass accuracy (<5 ppm). In addition to the molecular formula, the structure of the NAs which affect toxicity and biodegradation is also very important and may be elucidated by tandem MS that fragments the molecular mass peaks to produce distinctive daughter ions.

The aim of this study is to evaluate whether biological treatment as described by McKenzie et al. (2014) resulted in detoxification and, if so, whether compositional changes may provide insight related to detoxification of NAs. This study will provide useful information to improve treatment performance.

2. Methods and materials

2.1. Untreated and treated OSPW

Untreated OSPW was obtained from the active settling basin (WIP) of Syncrude Canada located north of Fort McMurray, Alberta. OSPW was treated by two ISBRs connected in series as described by McKenzie et al. (2014) in which about 40% NAs was degraded under aerobic conditions by microorganisms immobilized in the ISBR, and the effluent was collected as treated OSPW for analysis.

2.2. Fractionation strategy

Fractionation of untreated and treated OSPW was performed using solid phase extraction (SPE) columns which separated components based on their hydrophobicity. Based on toxicity results, fractions were selected for further fractionation by semi-preparative reverse phase HPLC to achieve fractions that have less complex compositions.

2.2.1. Solid phase extraction (SPE)

The pH of treated or untreated OPSW was adjusted to 10 and filtered through a 0.45 μm nylon filter (Millipore Corporation, Billerica, MA, USA). Every 1 L of sample was extracted by two C18 (octadecylsilane) and a polystyrene-divinylbenzene (PSDVB) column (J.T.Baker, Phillipsburg, NJ, USA) connected in series for a total of 5 L of treated or 5 L of untreated OSPW containing 49.0 ± 2.1 and 30.2 ± 1.4 mg of NAs per Liter respectively. Each column contained 1 g of sorbent. Columns were pre-conditioned by passing 25 mL methanol followed by 25 mL high-purity water before passing the water samples as described by Yue et al. (2015a). Fractions from each Liter were eluted with an increasing amount of methanol (20, 60, 80, and 100%), pooled, methanol evaporated then resuspended to achieve a 50-fold concentration compared to the original sample.

2.2.2. Semi-preparative reverse-phase HPLC

The SPE fractions with the highest estrogenic activity and the greatest decrease in estrogenicity upon biological treatment (F2) were further fractionated by semi-preparative reverse-phase, high-performance liquid chromatography (RP-HPLC; Hewlett-Packard 1050, Agilent Technologies, Bracknell, UK). A 1 mL sample was injected four times (total equivalent of 1 L of original OSPW) onto a silica guard column (5 cm × 10 mm × 5 μm) connected to a ZORBAX Eclipse XDB-C8 semipreparative HPLC column (25 cm × 10 mm × 5 μm; Agilent) equipped with a UV detector (230 nm). The mobile phase consisted of HPLC-grade methanol (Fisher Scientific Inc., CA) (eluant A) and water containing 5% formic acid and 20 mM NH_4Ac at pH = 7 (eluent B) pumped at a total flow rate of 1.5 mL min^{-1} using a gradient: 60% A for 10 min, then to 80% A in 10 min and maintained for 15 min, then to 100% A in 10 min and maintained for 15 min for a total run-time of 60 min. Fractions were collected at 1 min intervals using a fraction collector (Dynamax model FC-4, Varian) obtaining a total of 60 1.5 mL samples. Separation and collection were controlled by a Varian Star Chromatography Workstation. Fractions were evaporated to dryness under nitrogen gas and redissolved in methanol to achieve a 200-fold concentration compared to the original sample.

2.3. Microtox® assay

The toxicity of the fractions was measured by the Microtox® assay (Azur Environmental, Fairfax, CA, USA) adapted to 96 well plates (Fiehn et al., 1997). Triplicates samples were analyzed, 1 g L^{-1} glucose was used as a negative control and $ZnSO_4$ as a positive control and found to be within the parameters set by Microtox® such that the

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