Chemosphere 90 (2013) 449–458

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Degradation and aquatic toxicity of naphthenic acids in oil sands process-affected waters using simulated wetlands

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HIGHLIGHTS

- Toxicity of oil sands process-affected waters associated with naphthenic acids (NAs).
- Examined NAs degradation and aquatic toxicity using simulated wetland microcosms.
- Microcosms successfully reduced total NAs concentrations, but process was incomplete.
- Persistent Microtox® toxicity is likely associated with the residual NAs components.
- Acute toxicity of oil sands process-affected waters to rainbow trout was completely removed.

ARTICLE INFO

Article history:
Received 13 January 2012
Received in revised form 25 July 2012
Accepted 27 July 2012
Available online 20 September 2012

Keywords:
Oil sands process water
Naphthenic acids
Microcosms
Microtox®

ABSTRACT

Oil sands process-affected waters (OSPWs) produced during the extraction of bitumen at the Athabasca Oil Sands (AOS) located in northeastern Alberta, Canada, are toxic to many aquatic organisms. Much of this toxicity is related to a group of dissolved organic acids known as naphthenic acids (NAs). Naphthenic acids are a natural component of bitumen and are released into process water during the separation of bitumen from the oil sand ore by a caustic hot water extraction process. Using laboratory microcosms as an analogue of a proposed constructed wetland reclamation strategy for OSPW, we evaluated the effectiveness of these microcosms in degrading NAs and reducing the aquatic toxicity of OSPW over a 52-week test period. Experimental manipulations included two sources of OSPW (one from Syncrude Canada Ltd. and one from Suncor Energy Inc.), two different hydraulic retention times (HRTs; 40 and 400 d), and increased nutrient availability (added nitrate and phosphate). Microcosms with a longer HRT (for both OSPWs) showed higher reductions in total NAs concentrations (64–74% NAs reduction, $p < 0.05$) over the test period, while nutrient enrichment appeared to have little effect. A 96 h static acute rainbow trout (*Oncorhynchus mykiss*) bioassay showed that the initial acute toxicity of Syncrude OSPW (LC50 = 67% v/v) was reduced (LC50 > 100% v/v) independent of HRT. However, EC20s from separate Microtox® bioassays were relatively unchanged when comparing the input and microcosm waters at both HRTs over the 52-week study period ($p > 0.05$), indicating that some sub-lethal toxicity persisted under these experimental conditions. The present study demonstrated that given sufficiently long HRTs, simulated wetland microcosms containing OSPW significantly reduced total NAs concentrations and acute toxicity, but left behind a persistent component of the NAs mixture that appeared to be associated with residual chronic toxicity.

1. Introduction

At the Athabasca Oil Sands (AOS) in northeastern Alberta, Canada, the caustic hot water extraction process described by Clark in 1932 is still used by some companies with surface mining operations to separate bitumen from oil sand ore (Clark and Pasternack, 1932). In current integrated surface mining operations at the AOS, approximately 2–2.5 m^3 of fresh water is required to produce 1 m^3 of synthetic crude oil (W. Zubot, Syncrude Canada Ltd., Edmonton, AB, Canada, personal communication). At production rates that are approaching one million barrels of oil per day, this results in the build-up of large inventories of liquid tailings, of which oil sands process-affected waters (OSPWs) is a major component and a significant stakeholder concern (MacKinnon, 1989; Holroyd and Simieritsch, 2009). Previous toxicological investigations have shown that freshly produced OSPW, and OSPW contained within the active tailings system, are toxic to various aquatic organisms

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0045-6535/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.chemosphere.2012.07.059

(MacKinnon and Boerger, 1986; Leung et al., 2001; Nero et al., 2006b). The aquatic toxicity of OSPW has largely been linked to elevated concentrations of a relatively persistent group of dissolved organic acids known as naphthenic acids (NAs) (MacKinnon, 1989; Verbeek, 1994; Holowenko et al., 2002; Headley and McMartin, 2004). Currently, waters containing OSPW are not released from the oil sands mining lease sites into the natural water bodies of the region (Quagraine et al., 2005b). As a result, tailings and their OSPW are retained within large holding ponds and settling basins, but with the understanding that eventual reclamation of both of these materials must be undertaken. Successful reclamation of OSPW will require a reduction in NAs concentrations in the OSPW and the removal of the water's toxic character. Natural or enhanced bioremediation in lakes and wetlands within the lease closure landscapes will likely play a critical role in meeting these requirements.

Field observations at the AOS suggest that NAs in OSPW tailings ponds degrade very slowly (low oxygen environments), but even under aerobic conditions isolated from active tailings, the observed degradation of NAs is slow and incomplete (Holowenko et al., 2002). Complete microbial mineralization under natural conditions does not appear to be occurring and a portion of the NAs mixture, particularly the higher molecular weight NAs, appears to be resistant to further degradation (Quagraine et al., 2005a). Even after a period of 7–11 years, with no subsequent input of tailings material, the total concentration of NAs in experimental ponds containing fresh OSPW ($\sim$50 mg L^{-1} NAs) did not decrease below 20 mg L^{-1} (Leung et al., 2001; Holowenko et al., 2002). However, Herman et al. (1994) demonstrated that mineralization of oil sands NAs, via microbial activity, was possible and that it corresponded to a reduction in Microtox® toxicity. Some residual (i.e. chronic) toxicity persisted, suggesting that this toxicity could be related to the more persistent NAs. A clear relationship between the persistent fraction of NAs and the associated persistent aquatic toxicity of OSPW has not been established in wetland environments and requires further investigation.

More recent studies have better demonstrated the pathways of degradation of OSPW NAs and the limitations of natural processes (Han et al., 2009). With improvements in analytical capabilities, better information on the refractory fractions of NAs has become available suggesting that these refractory constituents are more associated with the presence of hydroxylated metabolites of degradation than with molecular weight and ring structures alone. In fact, the presence of additional components within oil sands NAs mixtures that are not consistent with the "classical" definition of NAs can make up a significant proportion of the total acid-extractable organic (AEO) fraction isolated from OSPW (Grewer et al., 2010). These components include heteroatomic species, polycyclic aliphatic carboxylates, and other heterocyclic aromatic fractions that may or may not be more persistent than the "classical" NAs within a given oil sands NAs mixture (Barrow et al., 2010; Grewer et al., 2010). However, in this research, the authors have decided to retain the use of the term "naphthenic acids (NAs)" to represent the broader definition of the AEO fraction, or oil sands naphthenic acids. The pathway(s) of natural NAs degradation, including the persistent components present within oil sands NAs mixtures, still needs to be fully understood as options for reclamation are actively being developed and deployed.

Reclamation landscapes using both lakes and wetlands offer a strategy for the reclamation of OSPW at the AOS. Using small simulated wetlands (laboratory microcosms), we evaluated the potential for NAs degradation, the influence of hydraulic retention time (HRT) and nutrient enrichment on NAs degradation, and the associated reduction in aquatic toxicity of OSPW generated by Syncrude Canada Ltd. (Syncrude) and Suncor Energy Inc. (Suncor). Laboratory microcosms, under flow-through conditions, were used to mimic wetland environments in order to better understand their role in aquatic reclamation landscapes as opposed to the traditional detention ponds (without an inlet and outlet) used in previous field studies. A greater understanding of possible design and management criteria to optimize such aquatic environments for NAs remediation, and the associated rates of OSPW detoxification (e.g. thresholds for naphthenic acids toxicity to aquatic biota), will increase stakeholder confidence in performance goals within reclamation plans.

2. Materials and methods

2.1. Experimental design

Two sources of OSPW (Syncrude and Suncor) were used to charge and recharge flow-through, simulated wetland microcosms in the laboratory. Two exposure times were used to create wetland systems with a short (40 d) and long (400 d) hydraulic retention time (HRT). Nutrient levels were also modified by the addition of mineral forms of nitrogen ($NaNO_3$) and phosphorus (Na_2HPO_4) to provide a low (no added nutrients) and high ($\sim$1 mg L^{-1} N and $\sim$150 μg L^{-1} P) nutrient loading. The resulting matrix of test conditions allowed for the evaluation of basic factors possibly linked to enhanced biodegradation of NAs and associated reduction in aquatic toxicity. Laboratory microcosms were constructed to simulate a simplistic wetland habitat similar to those that could be used in the reclamation of OSPW at the AOS. An array of indigenous microbial communities present in the input OSPW and in the sediments from a local wetland (both added to the microcosms) were the main sources of microbial activity in each system. Overall there were 12 different treatment scenarios, tested in triplicate, resulting in a total of 36 microcosms (Appendix A).

Microcosms were evenly spaced on shelves in a controlled-environment chamber at the Toxicology Centre, University of Saskatchewan (Saskatoon, SK, Canada). Input waters for the 12 treatments were placed in 10 L (long HRT) and 20 L (short HRT) high density polyethylene plastic containers located above the experimental microcosms. A Masterflex® multi-channel peristaltic pump (Cole–Parmer Canada Inc., Montreal, QC, Canada) was used to continually pump the 12 treatment waters to their respective triplicate microcosms at two different rates to achieve the arbitrarily selected 40 d (short) and 400 d (long) HRTs. The 10-fold difference in flow rates were achieved using two different sizes (3.1 and 0.8 mm I.D.) of Masterflex® high performance precision pump Tygon® tubing. Microcosms with a short HRT were recharged at a rate of 18 mL h^{-1} and microcosms with a long HRT were recharged at a rate of 1.8 mL h^{-1}, resulting in a residence time of about 40 and 400 d, respectively. Nitrogen and phosphorus, in the form of sodium salts (5 mg L^{-1} $NaNO_3$ and 0.64 mg L^{-1} Na_2HPO_4), were added to the input water containers of the six treatments with nutrient enrichment. All input water containers were covered with black plastic, and the tubes conducting the water to the microcosms were wrapped with duct tape to minimize light exposure and biological activity until the input water reached the test microcosms.

Environmental variables such as dissolved oxygen (DO) concentration, pH, temperature, and photoperiod were maintained at levels intended to promote microbial activity. The DO concentration in each microcosm was maintained between 2 and 8 mg L^{-1} by low and constant aeration. Microcosm pH was monitored regularly and on average was stable between 8.7 to 8.9, and 7.7 to 8.0, for those containing OSPW and control waters, respectively (Appendix B; Table B.1). The temperature of the test chamber was maintained at 25 ± 1 °C. Additional fluorescent light bulbs, with a spectral range of 350–750 nm, were attached to the shelves directly above