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The impacts of ozonation on oil sands process-affected water biodegradability and biofilm formation characteristics in bioreactors

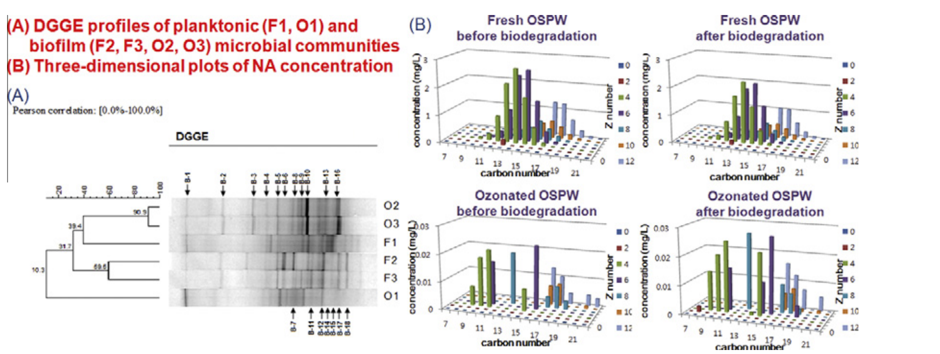
Geelsu Hwang, Tao Dong, Md. Sahinoor Islam, Zhiya Sheng, Leónidas A. Pérez-Estrada, Yang Liu *, Mohamed Gamal El-Din *

Department of Civil and Environmental Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2W2

HIGHLIGHTS

- ▶ Ozonation on biofilm formation and organic compounds removal in OSPW was tested.
- ▶ Two types of biofilm substrate materials and two types of wastewater were tested.
- ▶ The combined ozonation and biodegradation process effectively removed COD and TAO.
- ▶ UPLC/HRMS analysis showed that biodegradation of NA was dependent on the *Z* number.
- ▶ PVC supported a thicker biofilm and a greater microbial community diversity than PE.

GRAPHICAL ABSTRACT



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ABSTRACT

To examine the effects of the ozonation process (as an oxidation treatment for water and wastewater treatment applications) on microbial biofilm formation and biodegradability of organic compounds present in oil sands process-affected water (OSPW), biofilm reactors were operated continuously for 6 weeks. Two types of biofilm substrate materials: polyethylene (PE) and polyvinylchloride (PVC), and two types of OSPW—fresh and ozonated OSPWs—were tested. Endogenous microorganisms, in OSPW, quickly formed biofilms in the reactors. Without ozonation, the bioreactor (using endogenous microorganisms) removed 13.8% of the total acid-extractable organics (TAO) and 18.5% of the parent naphthenic acids (NAs) from fresh OSPW. The combined ozonation and biodegradation process removed 87.2% of the OSPW TAO and over 99% of the OSPW parent NAs. Further UPLC/HRMS analysis showed that NA biodegradability decreased as the NA cyclization number increased. Microbial biofilm formation was found to depend on the biofilm substrate type.

1. Introduction

In the Athabasca oil sands region in northeastern Alberta, the mined bitumen is separated from associated sands and clays using water-based extraction processes. Water management is becoming an enormous concern for the oil sands industry because, on average, three volume units of water are used to produce each volume unit of synthetic crude oil in a mining operation, accumulating in wet tailings, which contain a mixture of water, dissolved salts, organics, minerals, and residual bitumen in varying proportions (Allen, 2008). Recycling of tailings water has reduced the necessity for freshwater withdrawals. However, various inorganic (e.g., sodium, chloride and sulfate ions) and organic (e.g., naphthenic acids (NAs), benzene, toluene, and polycyclic aromatic hydrocarbons) pollutants become concentrated during recycling. The oil sands

* Corresponding authors. Tel.: +1 780 492 5115; fax: +1 780 492 0249 (Y. Liu), tel.: +1 780 492 5124; fax: +1 780 492 0249 (M. Gamal El-Din).

E-mail addresses: yang.liu@ualberta.ca (Y. Liu), mgamalel-din@ualberta.ca (M. Gamal El-Din).

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industry currently operates under a "zero discharge policy" because of the anticipated toxicity of the process-affected water (OSPW) to aquatic organisms (Clemente and Fedorak, 2005). Limitations on future tailings pond expansion and aggressive timelines for the reclamation (Ramos-Padrón et al., 2011) have been mandated by the Alberta government. Water treatment strategies are urgently needed to extend oil sands process-affected water (OSPW) recycling to reduce the need for additional withdrawal of fresh water from the Athabasca river and to permit the safe release of treated OSPW to the receiving environment.

The primary toxic constituents of OSPW are included in a group of low molecular weight organic acids, collectively known as the parent NAs (Scott et al., 2005). NAs are alicyclic or noncyclic alkyl-substituted carboxylic acids with the general chemical formula $C_nH_{2n+Z}O_2$, where n is the carbon number and Z is zero or a negative even number defining the hydrogen deficiency due to ring formation (e.g., 0, no rings; −2, 1 ring; −4, 2 rings, etc.) (Clemente and Fedorak, 2005; Afzal et al., 2012). Depending on the ore composition, extraction processes, the age of the tailings and NA detection methods, the reported NA concentration varied greatly and was in the range of 20–120 mg/L (Clemente and Fedorak, 2005; Allen, 2008; Han et al., 2008). It has been found that most of the physical water treatment processes are poorly efficient for aromatic compounds removal (Allen, 2008). Although ozonation process are capable of breaking highly branched and/or highly cyclic fractions of NAs (Martin et al., 2010; Gamal El-Din et al., 2011), it is not cost effective to completely remove (i.e., mineralize) organic pollutants using ozonation alone. Biodegradation is shown to be an effective, economical, and energy efficient approach for wastewater reclamation in various industries (Di Iaconi et al., 2003; Abd-Elsalam and EL-Hanafy, 2009; Gamal El-Din et al., 2011). However, previous biological treatment studies using planktonic cells have shown poor parent NAs treatability (Scott et al., 2005; Martin et al., 2010).

Biofilms could be a better option than planktonic microorganisms for OSPW reclamation. Biofilms consist of a consortium of microorganisms in an extracellular polymeric substance (EPS) matrix (Flemming and Wingender, 2010). The EPS matrix promotes microbial adhesion, aggregation, and cohesion and it forms a protective barrier against any environmental stresses and dehydration. The EPS matrix is also a nutrient source; it allows exchange of genetic information, contains electron donors and acceptors, and provides a sink for excess carbon (Flemming and Wingender, 2010). Members of the microbial community act synergistically within the context of the EPS matrix. As a result, growth and degradation of substances are possible in biofilms that might not occur with planktonic microorganisms (Sillankorva et al., 2004). Biofilms are extensively used in environmental biotechnology because biofilm reactors can be operated at high biomass concentrations to treat industrial and municipal wastewaters without the need for settlers for biomass retention and recirculation, and can support multi-species microbial systems that are capable of degrading recalcitrant organic compounds (Di Iaconi et al., 2003).

Previous studies suggest that there is a wealth of microbial diversity in oil sands tailings from which to draw members for a biofilm consortium. For instance, the microbial community compositions at increasing depths (e.g., 6 m, 10 m, 20 m) of the Syncrude's West In-Pit pond were analyzed by Penner and Foght (2010). They found that acetoclastic *Methanosaeta* spp. were dominant among *Archaea* in mature fine tailings. The most common bacterial class found was *β-Proteobacteria*. Ramos-Padrón et al. (2011) also reported that microbial community structures varied depending on the depth in an active tailings pond. Recently, Golby et al. (2012) established biofilms from oil sands tailings samples grown under aerobic, microaerophilic and anaerobic conditions. Mixed biofilm communities were recovered under each incubation condition. However, the potential organic compounds degradation capability of these biofilms was not investigated.

The potential of biofilm treatment of OSPW has only recently been addressed. A biofilm was developed in a rotating annular bioreactor using lake water having high nitrate and orthophosphate levels, and commercial NAs and NAs extracted from OSPW were spiked into the reactor (Headley et al., 2010). This biofilm-based bioremediation had no impact on the degradation of Athabasca oil sands NAs (i.e., OSPW parent NAs) although there was some degradation of commercial NAs. To our knowledge, no research has been done on OSPW parent NAs degradation and removal using biofilms formed by oil sands endogenous microorganisms, although natural bioremediation of OSPW occurs (albeit very slowly) (Gamal El-Din et al., 2011).

The present study evaluates parent NAs degradation and removal using combined ozonation and biofilm reactor processes (Martin et al., 2010; Gamal El-Din et al., 2011). Biofilms formed by oil sands endogenous microorganisms were applied to degrade and remove NAs from both ozonated and fresh OSPW. The initial formation of biofilm is known to be affected by biofilm substrate material characteristics and the initial stage of biofilm formation can play a significant role in later stages of the biofilm efficacy of degrading organic pollutants. Therefore, two different biofilm substrate materials composed of polyethylene (PE) and polyvinylchloride (PVC), were employed in bioreactors to examine and compare their roles in supporting OSPW endogenous biofilm formation. Biodegradation of OSPW parent NAs and the total acid-extractable organics (including NAs, also known as extractable organic fraction or EOF) in a biofilm reactor was evaluated. Dynamic changes in the biofilm microbial community, density, and thickness in the bioreactor were also investigated.

2. Methods

2.1. Source water information

The fresh OSPW was collected from the West In-Pit water pumping station at the Syncrude Canada Ltd. site in Fort McMurray, AB, Canada. OSPW samples were preserved in 200 L polyvinyl chloride containers in a cold room (4 °C) prior to use.

2.2. Biofilm reactor operation

Six continuous flow biofilm reactors (CDC reactors, Biosurface Technologies, Bozeman, MT, USA) were used to develop biofilms and to degrade and remove parent NAs from OSPW. Among the six reactors, two reactors, one containing sterilized (heat-killed)

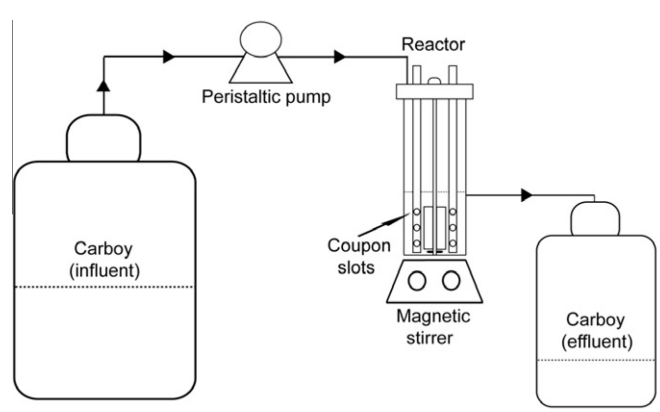

Fig. 1. Schematic diagram of continuous flow biofilm reactor.