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Review

Treatment of oil sands process-affected water using moving bed biofilm reactors: With and without ozone pretreatment

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HIGHLIGHTS

- OSPW treatment using MBBRs with and without ozone pretreatment were compared.
- The biodegradation of parent NAs was dependent on the n number and $-Z$ value.
- MiSeq sequencing and *q*-PCR analysis were applied to compare the microbial communities.
- Ozonation combined with MBBR may be a good choice for OSPW treatment.

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ABSTRACT

Two moving bed biofilm reactors (MBBRs) were operated to treat raw (untreated) and 30 mg/L ozone-treated oil sands process-affected water (OSPW). After 210 days, the MBBR process showed 18.3% of acid-extractable fraction (AEF) and 34.8% of naphthenic acids (NAs) removal, while the ozonation combined MBBR process showed higher removal of AEF (41.0%) and NAs (78.8%). Biodegradation of raw and ozone treated OSPW showed similar performance. UPLC/HRMS analysis showed a highest NAs removal efficiency with a carbon number of 14 and a $-Z$ number of 4. Confocal laser scanning microscopy (CLSM) showed thicker biofilms in the raw OSPW MBBR (97 ± 5 μm) than in the ozonated OSPW MBBR (71 ± 12 μm). Quantitative polymerase chain reaction (*q*-PCR) results showed higher abundance of gene copies of total bacteria and nitrogen removal relevant bacteria in the ozonated OSPW MBBR, but no significant difference was found. MiSeq sequencing showed *Proteobacteria*, *Nitrospirae*, and *Acidobacteria* were dominant.

1. Introduction

Oil sands process-affected water (OSPW) is generated during the caustic hot water extraction of bitumen from oil sands (Siddique et al., 2006). OSPW has become a critical environmental concern because of its huge quantity and acute toxicity (Lo et al., 2006). The slightly alkaline water is difficult to remediate mainly due to the persistent organic naphthenic acids (NAs) (Rogers et al., 2002). Classical NAs are a broad group of alkyl-substituted acyclic and cycloaliphatic carboxylic acids, having the general chemical formula $C_nH_{2n+Z}O_2$, where *n* indicates the number of carbon atoms and *Z* is zero or a negative even integer related to the hydrogen deficiency due to the ring or double bond equivalents, indicating the number of saturated rings (e.g., $Z = 0$, no rings; $Z = -2$, 1 ring, $Z = -4$, 2 rings, etc.) (Choi and Liu, 2014; Martin et al., 2010).

NAs are some of the most toxic components in OSPW, with concentrations of 20–120 mg/L (Pérez-Estrada et al., 2011; Toor et al., 2013). NAs can be toxic or inhibitory to plants, zooplankton, and bacteria (Clemente et al., 2004; Kamaluddin and Zwiazek, 2002). NAs concentrations higher than 2.5–5 mg/L were toxic to fish (Davis, 1998). The half-life for in situ biodegradation of NAs in OSPW has been reported to be 13 years (Han et al., 2009), therefore, NAs biodegradation by microorganisms in the field cannot meet the urgent need for OSPW treatment. NAs degradation in OSPW has mainly focused on the application of batch reactors (Dong et al., 2015). Bioreactors that employ microbial aggregates (i.e., biofilms or flocs) might provide a significantly higher NAs removal efficiency. Microbial biofilms or flocs consist of a consortium of microorganisms embedded in an extracellular polymeric substance (EPS). The EPS matrix forms a protective barrier against environmental stresses and dehydration, acts as a nutrient source,

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and allows exchange of genetic information. EPS contains electron donors and acceptors, and provides a sink for excess carbon. Members of the microbial community can therefore act synergistically within the context of the EPS matrix.

Among the six reported studies of engineered bioreactor treatments of OSPW, three studies provided important bioreactor operation options, which included bioreactor start up strategies (selection of mature fine tailings or municipal activated sludge as reactor seeds) (Choi and Liu, 2014), comparison of biofilm growth media selection (Hwang et al., 2013), and comparison of bioreactor operation modes (continuous or batch) (Choi et al., 2014). Headley et al. (2010) evaluated the potential of biofilm development in a rotating annular bioreactor using lake water. However, little impact on the degradation of OSPW NAs was achieved. Recently, granular activated carbon (GAC) was used as the biofilm support medium for OSPW treatment in fluidized bed biofilm reactors (FBBRs). Significantly improved acid-extractable fraction (AEF) and NAs removal was observed in these studies, which may be largely attributed to the synergetic effects of GAC adsorption and biofilm degradation (Islam et al., 2014a,b).

It should be noted that bioreactor configuration plays a significant role in controlling the nutrient removal efficiency in engineered reactors. Much research is needed to evaluate the potential application of industrially relevant bioreactors that are selected based on the OSPW characteristics for the OSPW treatment, in order to allow for full realization of the biological OSPW treatment capacity. The ideal bioreactor configuration for treatment of contaminants present in industrial wastewaters will not only operate efficiently (i.e. at a high removal rate), but also achieve the design performance objective (i.e. effluent quality requirement) (Sutton, 2006). OSPW contains contaminants that are resistant to biodegradation and toxic to microorganisms, thus, the key to successful bioreactor operation for OSPW treatment is to encourage and maintain the growth of NA removing microorganisms, to enhance the biomass concentration, and to improve the microbial resistance toward high OSPW toxicity.

A moving bed biofilm reactor (MBBR) with the addition of freely moving carrier media has advantages of greater solids residence time (SRT), higher biomass concentrations and higher resistance to toxicity, compared to conventional activated sludge systems (Sombatsompop et al., 2006). It may be an ideal bioreactor option for the treatment of OSPW, which has low biodegradability (BOD/COD ratio <0.1), relatively low COD (200–300 mg/L) and high toxicity mainly due to NAs, the primary toxic constituents in OSPW (He et al., 2012). MBBRs are operated similarly to activated sludge, except that biofilm grows on small carriers suspended in constant motion throughout the volume of the reactor. MBBRs are easy to operate and have been applied widely for industrial wastewater treatment (BrochDue et al., 1997; Hosseini and Borghei, 2005).

MBBR remediation of OSPW with and without ozone pretreatment was evaluated in this study. Ozonation was found to increase the biodegradability of organic components, including NAs, in OSPW and reduce the toxicity of OSPW toward *Vibrio fischeri* (El-Din et al., 2011). Both raw OSPW and ozone-treated OSPW were treated by MBBRs under the same bioreactor operational conditions to compare the degradation of organic compounds and microbial community changes in the reactors. A toxicity assessment was carried out to evaluate the overall performance of the MBBRs.

2. Methods

2.1. OSPW source and ozonation

Raw and ozone-treated OSPW were used in this study. Raw OSPW (OSPW with no pretreatment) was collected from the West In-Pit water pumping station (Syncrude Canada Ltd., Fort McMurray, Canada) in September 2013. OSPW was stored in 200 L polyvinyl chloride barrels in a step-in cold room (4 °C) prior to use. A ozone dose of 30 mg/L was applied based on our previous research (Dong et al., 2015). Ozone pretreated OSPW (i.e., ozonated OSPW) was obtained using an AGSO 30 Effizon ozone generator (WEDECO AG Water Technology, Herford, Germany), as described in the study of Wang et al. (2013). Briefly, the ozone generator was first stabilized for 10 min to obtain a stable ozone concentration, then the produced ozone gas was introduced into the liquid phase (raw OSPW) through a ceramic fine bubble gas diffuser placed at the bottom of the 200 L container. Two identical ozone monitors (HC-500, PCI-WEDECO, USA) were used to control the ozone concentrations in feed-gas and off-gas and the ozone residual in the reactor was measured using the Indigo method (APHA, 2005). Ozone treated OSPW was then purged with nitrogen for 10 min to remove residual ozone. The utilized ozone dose (amount of ozone reacted with the contaminants in the water phase, per unit water volume) was calculated using the equation expressed in the study of Wang et al. (2013), which is presented in detail in SI. Characteristics of raw and ozone treated OSPW are listed in Table S1.

2.2. Reactor set-up and operation

Two rectangular shaped moving bed biofilm reactors (MBBRs), kindly provided by Napier-Reid Ltd. (Markham, Canada), were used in this study, one for raw OSPW treatment and the other for ozonated OSPW treatment. Bioreactors had a working volume of 8.5 L (15 cm × 35 cm base, 30 cm height). Air diffusers were installed for aeration and to continue the movement of biofilm support carriers. High-density polyethylene carriers (Bioflow 9, Rauschert, Steinwiessen, Germany) with specific biofilm growth areas of 800 m^2/m^3 were applied in the MBBRs. Effluent water quality and solid content were evaluated with a clarifier placed after each reactor. The reactors were operated continuously at room temperature (~23 °C). A peristaltic pump (Masterflex L/S, Gelsenkirchen, Germany) was used for continuous feeding, with a flow rate of 2.95 mL/min to maintain a hydraulic retention time (HRT) of 48 h. DO (dissolved oxygen) was maintained between 6 and 8 mg/L.

To start the bioreactors, activated sludge collected from Gold Bar Wastewater Treatment Plant (Edmonton, Canada) was used for inoculation, with an initial sludge concentration of 2.1 g/L in the reactor. A volume fraction of 60% carriers were introduced to the MBBR reactors. The volume ratio of OSPW was initially 10%, increasing step-wise to 100% (Table 1). Extra carbon (sodium acetate, 200 mg/L COD) as well as nitrogen (ammonium chloride, 30 mg N/L), phosphorus (monopotassium phosphate, 3 mg P/L) and other necessary nutrients (Shi et al., 2011) were provided to maintain the growth of bacteria in the systems. All chemicals and supplies were obtained from Thermo Fisher Scientific.

Table 1
The start-up strategies of MBBR systems.

Stages	Operation days	The volume ratio of OSPW (%)	Influent COD (mg/L)		
			COD from OSPW	COD from sodium acetate	Total COD
I	1–9	10	20	200	220
II	10–37	20	40	200	240
III	38–99	40	80	200	280
IV	100–128	60	120	200	320
V	129–173	80	160	200	360
VI	174–208	100	200	200	400