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Optimization of ozonation combined with integrated fixed-film activated sludge (IFAS) in the treatment of oil sands process-affected water (OSPW)

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ABSTRACT

Effects of hydraulic retention time (HRT) and the chemical oxygen demand/nitrogen (COD/N) ratio on the microbial community composition of integrated fixed-film activated sludge (IFAS) and its ability to treat raw and ozonated oil sands process-affected water (OSPW) were evaluated. After 11 months of HRT and ammonium optimization, 54.56% of the COD and 30.20% of the acid extractable fraction (AEF) were removed in raw OSPW IFAS, and 56.83% of the COD and 51.51% of the AEF were removed in ozonated OSPW IFAS. Extension of the HRT in the IFAS had no significant effect on the removal of COD and nitrogen, whereas a lower COD/N ratio increased the removal of organics and total nitrogen. The quantitative polymerase chain reaction (*q*-PCR) indicated that the abundance of nitrifier and denitrifier genes decreased during HRT optimization, and increased significantly after ammonium optimization. *Proteobacteria*, *Nitrospirae*, *Acidobacteria*, and *Bacteroidetes* were the dominant phyla in IFAS flocs and biofilms according to 454 sequencing. *Proteobacteria* showed significant decreases in flocs and biofilms after HRT and ammonium IFAS optimization. *Nitrospirae* and *Acidobacteria* showed significant upward trends in all biomass forms in optimized IFAS systems compared to unoptimized IFAS systems.

1. Introduction

Water associated with bitumen extraction in the Athabasca oil sands region of northern Alberta contains a mixture of suspended solids, residual bitumen, heavy metals, inorganic compounds, and naphthenic acids (NAs) (Sun et al., 2014) and is acutely and chronically toxic to aquatic organisms, invertebrates, and mammals (Gamal El-Din et al., 2011; He et al., 2012; Anderson et al., 2012; Garcia-Garcia et al., 2011). Due to its toxicity, this oil sands process-affected water (OSPW) is currently being stored in tailings ponds following Alberta's zero discharge policy (Speight, 2000). A conservative estimate suggests that the accumulated volume of OSPW will reach 1 billion m^3 in the next 15–20 years (Lo et al., 2003; Del Rio et al., 2006). The concentration of classical naphthenic acids (NAs) in OSPW ranges from 7.1 to 47 mg L^{-1} (Grewer et al., 2010; Gamal El-Din et al., 2011; Wang et al., 2013) and presents a major threat to aquatic organisms (Anderson et al., 2012). Adequate OSPW treatment technologies will reduce the accumulation of OSPW in the tailings ponds and enable OSPW recycling to reduce the demand for fresh water intake from the Athabasca River (Islam et al., 2015a).

Bioreactor technology exploits the degradation of organic compounds through reactions mediated by microbial aggregates (i.e., flocs and biofilms) formed in activated sludge, and has been used effectively for OSPW reclamation (Hwang et al., 2013; Choi and Liu, 2014; Shi et al., 2015; Huang et al., 2015). Hwang et al. (2013), using attached biofilms, observed that 41.0% of chemical oxygen demand (COD), 18.5% NAs, and 13.8% of the AEF were removed from OSPW in a 1 L continuous flow biofilm reactor operated in batch mode for 24 h Islam et al. (2014a) observed 62% of COD, 88% of AEF and 99.9% of classical NAs removal with HRT of 8.5 h using a 0.3 L fluidized bed biofilm reactor (FBBR) with granular activated carbon (GAC) as support media. However, FBBR requires high upflow velocity and thus has high energy requirements. Choi and Liu (2014) demonstrated that 12% of COD and 8.7% of the AEF were removed in an activated sludge-sequencing batch reactor (AS-SBR), and 20% of COD and 16.6% of the AEF were removed in a

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mature fine tailings-sequencing batch reactor (MFT-SBR). Using 8.5 L moving bed biofilm reactors (MBBRs) with polyethylene carriers as support media, Shi et al. (2015) observed the removal of 18.3% of the AEF and 34.8% of the NAs without OSPW ozonation and removal of 41% of the AEF and 78.8% of the NAs with OSPW ozonation.

An IFAS reactor comprising combined suspended and attached growth in a single reactor can achieve significant microbial population diversity and the degradation of a wide range of contaminants. Our recent study (Huang et al., 2015) demonstrated that 12.1% of the acid extractable fraction (AEF) and 43.1% of parent NAs were removed in IFAS treatment of raw OSPW, while 42.0% of the AEF and 80.2% of parent NAs were removed in IFAS treatment of ozonated OSPW. Most published work on OSPW remediation using engineering bioreactors focus on the potential feasibility and start-up treatment performance. To date, no bioreactor optimization study has been conducted for OSPW treatment using IFAS.

To develop an efficient OSPW bioremediation system, the hydraulic retention time (HRT) and influent COD/N ratio must be optimized. The HRT contributes to the biomass characteristics and the microbial community composition (Huang et al., 2011). A high HRT benefits the removal of recalcitrant organics but an increase in reactor volume is required to achieve higher removal performance. Low HRT values result in higher organic loading rates (OLR) (Fallah et al., 2010), which can lead to more active biomass and faster degradation rates. However, a high OLR might also lead to incomplete organics removal. The chemical oxygen demand (COD) measures the amount of organic compounds in water, which can significantly influence microbial community structures (Feng et al., 2012). As microbial growth requires nitrogen (N), an optimal COD/N ratio can facilitate the growth of degraders leading to a higher OSPW treatment efficiency. Nitrifiers such as *Nitrosomonas europaea* catalyze the oxidation of ammonia to nitrite. Ammonia is first converted to hydroxylamine by the enzyme ammonia monooxgenase (AMO), followed by the oxidation of hydroxylamine to nitrite by hydroxylamine oxidoreductase. Previous studies showed that AMO may catalyze the oxidation of various organics, including hydrocarbons and halogenated hydrocarbons (Rasche et al., 1990). The investigation of the effects of HRT and COD/N ratio on treatment performance and microbial community structure are necessary for OSPW bioremediation strategy development. Studies are needed to evaluate these parameters for OSPW treatment using ozonation combined with IFAS.

OSPW has low biodegradability, a relatively low COD (250–350 mg L^{-1}), and a biological oxygen demand (BOD)/COD ratio < 0.1. The high toxicity of OSPW leads to a high resistance to biodegradation of NAs. As ozonation breaks down highly branched, highly cyclic NA fractions (Martin et al., 2010; Gamal El-Din et al., 2011), pretreatment of OSPW with ozone has been tested to break down recalcitrant NAs and enhance OSPW biodegradability (Dong et al., 2015; Islam et al., 2014b). In this study, the ability of microbial community structures in IFAS to detoxify raw and ozonated OSPW was tested, and the impacts of HRT and the COD/N ratio on microbial community dynamics in the IFAS systems were evaluated.

2. Materials and methods

2.1. Source water information

Raw (untreated) OSPW was obtained from oil sands tailings ponds in Fort McMurray, AB, Canada, in September 2013. OSPW samples were stored in 200 L polyvinyl chloride containers in a step-in cold room (4 °C) prior to use.

A 0.1% (v/v) trace nutrient solution was prepared containing: $MgCl_2 \bullet 6H_2O$, 3 g L^{-1}; $CaCl_2$, 1.5 g L^{-1}; $FeSO_4 \bullet 7\ H_2O$, 0.28 g L^{-1}; $MnCl_2 \bullet 4\ H_2O$, 0.13 g L^{-1}; $ZnSO_4 \bullet 7\ H_2O$, 0.12 g L^{-1}, $CuSO_4 \bullet 5\ H_2O$, 0.0074 g L^{-1}. The pH was 7.3 ± 0.3. All chemicals and supplies were obtained from Thermo Fisher Scientific.

2.2. Reactor operation

Two identical bench-scale IFAS reactors provided by Napier-Reid Ltd (Markham, Canada) were operated in parallel, one to treat raw OSPW and the other to treat ozonated (30 mg L^{-1}, utilized ozone dose) OSPW under the same conditions. The IFAS reactors had a working volume of 8.5 L (15 cm × 35 cm base, 30 cm height) and a clarifier (Fig. S1). Air diffusers were installed for aeration and to circulate the support carriers. The dissolved oxygen (DO) concentration was maintained at 6–7 mg L^{-1} during operation. A 60% volume fraction of polyethylene (PE) carriers (Bioflow 9, Rauschert, Steinwiessen, Germany) with specific biofilm growth areas of 800 m^2 m^{-3} were applied in the IFAS reactors. The reactors were operated continuously at room temperature (20 ± 1 °C).

Both reactors were inoculated with seed sludge taken from the Gold Bar Wastewater Treatment Plant (Edmonton, Canada). The bioreactor start-up strategies and reactor performance results (from 0 to 280 days) have been published previously (Huang et al., 2015). After reactor reached stable operation, reactor optimization started (from day 280). During the optimization stage, the carbon sources in the influents of the IFAS systems were raw or ozonated OSPW and sodium acetate, the HRT was increased from 48 to 72–96 h. To maintain a stable HRT, a peristaltic pump (Masterflex L/S, Gelsenkirchen, Germany) was used to control the flow rate of the influent. Ammonium chloride was added to increase the ammonium concentration of the influent from 30 to 45–60 mg L^{-1} in three phases resulting in COD/N ratios of 10.8, 7.2, and 5.4 in raw OSPW IFAS and 10.3, 6.9, and 5.2 in ozonated OSPW IFAS (Table 1). During the entire optimization stage, extra carbon (sodium acetate, 130 mg COD L^{-1}), nitrogen (ammonium chloride, 30, 45, and 60 mg N L^{-1}), phosphorus (KH_2PO_4, 3.0 ± 0.2 mg P L^{-1}), and other necessary nutrients (see section 2.1) were provided to maintain the growth of biomass in the IFAS systems. The average activated sludge solid retention time (SRT) was 43 days, which was maintained by manually wasting sludge from the clarifier. The detailed optimization strategies are listed in Table 1.

2.3. Ozonation of OSPW

A sufficient experimental volume of OSPW was ozonated before the experiment. An utilized ozone dose of 30 mg L^{-1} was applied according to our previous research (Dong et al., 2015). Ozone pretreatment of raw OSPW was performed using an AGSO 30 Effizon ozone generator (WEDECO AG Water Technology, Herford, Germany), which can produce ozone gas using extra dry, high purity oxygen. A detailed description of the ozonation procedure is reported in Wang et al. (2013). Briefly, ozone was introduced into the liquid phase by a ceramic fine bubble gas diffuser installed at the bottom of the 200 L polyvinyl chloride container. Ozone concentrations in the feed-gas (110–120 mg L^{-1}) and off-gas (varied from 0 to 80 mg L^{-1}) were continuously monitored during the process by two identical ozone monitors (HC-500, PCI-WEDECO, USA), With the ozone contact time of 15–17 min gas flowrate of 10 L min^{-1}, the cumulative consumption of ozone was approximate 6000 mg for 200 L OSPW. The Indigo method was used to estimate the residual ozone (American Public Health Association (APHA, 2005). The ozonated OSPW was purged with nitrogen for 10 min to strip oxygen and excess ozone.