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Treatment of oil sands process-affected water using membrane bioreactor coupled with ozonation: A comparative study

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HIGHLIGHTS

- Ozonation reduced the toxicity to *V. fischeri* and enhanced subsequent biodegradation.
- *Thauera* was the most dominant bacterial genus in the MBR.
- MBR combined with ozonation achieved naphthenic acids removal of 70%.
- Ozone pretreatment delayed the occurrence of membrane fouling.
- TMP of ceramic membrane never exceeded −12 kPa throughout 450-day operation.

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ABSTRACT

The huge amount of toxic oil sands process-affected water (OSPW) stored in northern Alberta is of great concern to the public health and aquatic life. Therefore, cost-effective and more efficient approaches for OSPW treatment are urgently needed. In this study, mild ozonation followed by a modified Luzack–Ettinger membrane bioreactor (MLE-MBR) were employed for the treatment of OSPW. It was shown that with a utilized ozone dose of 30 mg/L, 42.5–47.4% of classical naphthenic acids (NAs) were removed with toxicity reduction towards *Vibrio fischeri*. While ozonation targeted the heteroatomic NAs and classical NAs with high cyclicity and carbon number, MBR showed its advantages in removing oxidized NAs and classical NAs with less hydrogen deficiency. With excellent nitrification and denitrification performance, MBR achieved the removal of 46% for classical NAs, indicating the success of sludge acclimation in the MBR. *Thauera* became the most dominating bacterial genus in MBR, revealing its potentials in OSPW treatment. Compared with MBR treating raw OSPW, ozone pretreatment contributed to improved denitrification and NA removal in MBR. Moreover, it altered microbial community structure, thus delaying the occurrence of membrane fouling. During 426 days of continuous operation, no severe membrane fouling was observed as the transmembrane pressure (TMP) of the MLE-MBR never exceeded −12 kPa. With a reduction of classical NAs by around 70%, our results indicated that the MLE-MBR coupled with ozonation, is a promising approach for removing recalcitrant organics in OSPW.

1. Introduction

The bitumen extraction process used by the petroleum industry produces large volumes of oil sands process-affected water (OSPW), which has become a critical issue for the surrounding environment. OSPW is a complex mixture of toxic organic and inorganic compounds with a pH of 8.0–8.4. Presently, it is stored in settling ponds around the mining sites due to the lack of suitable, cost-effective, treatment technologies. In OSPW, the dissolved organic matter concentration is 50–100 mg/L which is mainly comprised of organic acids, including naphthenic acids (NAs) [1]. The NAs have been considered to be the primary toxic constituents to aquatic organisms [2], bacteria [3], benthic invertebrates [4] and mammalian species [5]. Most research has been focused on the classical NAs which have a general chemical formula $C_nH_{2n+Z}O_2$, where n is the number of carbon atoms, and Z is zero or a negative even integer related to a hydrogen deficiency due to ring formation. Recently, significant amount of oxidized NAs (O_x-NAs) ($C_nH_{2n+Z}O_x$, where $x > 2$; O_3, O_4, O_5 and O_6 class) found in OSPW has aroused attention due to their potential toxicity [6–8].

Biological treatments have been shown to be effective, economical, and energy efficient approaches for wastewater reclamation in

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various industries, which can lead to actual degradation, instead of only a phase separation, as compared to other processes such as adsorption and membrane filtration. Recently, various engineered biological treatments that employ microbial aggregations in reactors have been used for the treatment of OSPW. Although engineered bioreactors were shown to remove model NAs and a commercial NA mixture effectively [9–11], their performances were unsatisfactory for OSPW NAs because of their extensive cyclical molecular structures. Headley et al. [12] used a rotating annular bioreactor to study the biofilm treatment of extracted Athabasca oil sands NAs and commercial NAs spiked into lake water having high nitrate and orthophosphate levels. The researchers found no dissipation of the oil sands NAs, although there was 65% of dissipation for commercial NAs. More recently, Hwang et al. [13] observed about 18.5% NAs removal using continuous biofilm reactors seeded with endogenous microorganisms, indicating that biofilm reactors have the potential to be used for OSPW biological treatment. However, the efficiency of biodegradation is not satisfying due to the recalcitrance of OSPW NAs. Choi et al. [14] reported that batch and continuous biofilm reactors removed NAs in OSPW by only 10.5% and 20.1%, respectively. Membrane bioreactors were expected to enhance the biodegradation rates of NAs in OSPW given that the retention of slow-growing microorganisms inside might improve the degradation of refractory organics. In our recent study, a membrane bioreactor with modified Luzack–Ettinger (MLE) configuration has shown its effectiveness in the treatment of OSPW with NA removal of 24.7% [15].

In order to enhance the treatment efficiency by the biodegradation process alone, a pretreatment technology is clearly required to improve the biodegradability of OSPW prior to biological treatments. Gamal El-Din et al. [3] demonstrated that ozonation can decrease the total NAs concentrations in OSPW while also increasing their overall biodegradability. Martin et al. [16] found that ozonation, followed by biological degradation using a native microbial inoculation, significantly accelerated the detoxification and the biodegradation of NAs in batch reactors. Recently, Wang et al. [17] found a complete removal of toxicity toward *V. fischeri* after ozonation followed by a 28-day biodegradation treatment in a batch study. Thus, ozonation combined with biological treatment might be an excellent solution for the treatment of OSPW. Furthermore, it was reported that indigenous microbes can survive at ozone dose of 50 mg/L and that ozone-treated indigenous microbial communities had the same ability to degrade organic matter in OSPW as the microbial community not exposed to ozone [18].

In addition to batch bioreactors, ozonation was also coupled with engineered bioreactors for the treatment of OSPW. Hwang et al. [13] observed the removal of over 99.9% of classical NAs after the treatment of ozonation followed by continuous biofilm reactors. Islam et al. [19] employed a fluidized bed biofilm reactor (FBBR) with granular activated carbon (GAC) as support media to treat ozonated OSPW. It was found that the combined ozonation, GAC adsorption, and biodegradation process removed 62% of chemical oxygen demand (COD) and 99.9% of classical NAs under optimized operational conditions. However, in both studies the majority of the NAs removals were attributed to a 'high' ozone dose (80 mg/L). Such an intensive ozonation is not economically feasible for large-scale industrial applications due to a high energy and chemical needs. A 'mild' ozone dose of 50 mg/L that removed 56% of NAs was identified as the most suitable ozone treatment dose for OSPW prior to biodegradation treatments [20]. Mild ozonation could increase the biodegradability of OSPW by targeting NAs with high cyclicity and branches [21], thus, energy-efficient bioreactors could play a more extensive role in NAs removals and toxicity mitigation. Although the combination of ozonation and biological processes has been studied for the treatment of OSPW [20], bioreactors with different configurations might have different response to ozone pretreatment. Previous study has demonstrated the bioreactor configuration has an influence on the efficiency of integrated systems [22]. MBR as an emerging technique has a good potential in the wastewater treatment. Therefore, it is essential to investigate whether ozone pretreatment could further enhance the treatment of OSPW. Furthermore, to the best of our knowledge, this is the first time the degradation of oxidized NA in engineered bioreactor was studied. Previous study only focused on the degradation of classical NAs, nevertheless, oxidized NAs also contribute to the toxicity of OSPW substantially.

Our previous study has demonstrated NAs showed a sharp decrease after ozonation up to about 50 mg/L and ozone dose of 30 mg/L led to the maximal toxicity reduction [23]. Therefore, in this study, an ozone dose of 30 mg/L was applied for the pretreatment of OSPW prior to the biological treatment using a membrane bioreactor with a modified Luzack–Ettinger (MLE) configuration in order to further reduce the cost of ozonation and tap the potential of MBR reactor. MLE-MBR was expected to help reduce the aeration cost and improve the removal of recalcitrant organic compounds by using different electron accepting conditions (nitrification and denitrification) [24,25]. The objective of this study was to investigate the feasibility of MBR coupled with ozonation in treating OSPW. The fates of classical, heteroatomic and oxidized NAs were studied after ozonation and during the MBR operation. Moreover, the microbial community structure in the system was also characterized by real-time PCR and pyrosequencing in order to explore their role in the OSPW treatment. Furthermore, the impact of ozonation on MBR performance and membrane pressure was also evaluated by comparing with MBR treating raw OSPW.

2. Materials and methods

2.1. Source of OSPW

OSPW was received in 200 L polyvinyl chloride barrels in two shipments from OSPW recycle ponds in Fort McMurray, Alberta, Canada. OSPW from the first shipment (OSPW I) was used for the system start-up and acclimatization stage. After acclimatization stage, both OSPW I and OSPW II (OSPW with a higher concentration of NAs from the second shipment) were tested in this study to demonstrate the feasibility of this combined process for the treatment of OSPW from different sources. The OSPWs were stored at 4 °C before subjected to any treatment.

2.2. Ozonation of OSPW

The detailed description of the ozonation procedure and calculation of utilized ozone dose have been previously reported by Wang et al. [17]. Briefly, ozonation of raw OSPW was performed by generating ozone from extra-dry and high-purity oxygen using an ozone generator (WEDECO GSO-40, Herford, Germany). A 200 L polyvinyl chloride reactor was equipped with gas diffusers in its bottom, enabling the feed gas to be sparged into the liquid phase with a flow rate of 10 L/min. The utilized ozone dose of 30 mg/L was used as calculated by the difference between the feed and off-gas lines ozone concentrations which were continuously monitored by two identical ozone monitors (WEDECO HC-500, Herford, Germany).

2.3. Configuration and operation of MBR

The experiment setup in this study was shown in Fig. 1. The MLE-MBR system included an anoxic tank followed by an aerobic