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Mechanistic investigation of industrial wastewater naphthenic acids removal using granular activated carbon (GAC) biofilm based processes

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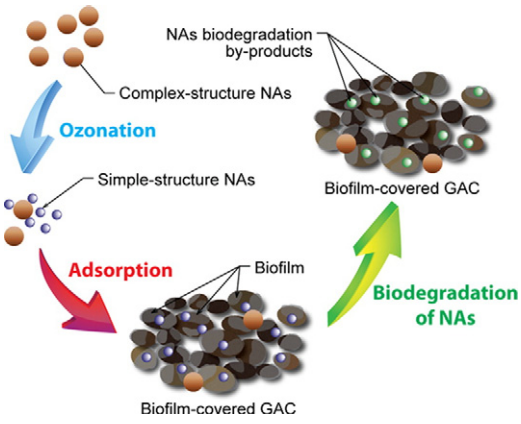
HIGHLIGHTS

- Contributions of biodegradation and adsorption identified in GAC biofilm process.
- Synergistic effects found for biodegradation and bioregeneration in GAC biofilms.
- 454-pyrosequencing showed various bacterial assemblages in each treatment.
- Naphthenic acids removals highest for ozonated OSPW and combined treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

Naphthenic acids (NAs) found in oil sands process-affected waters (OSPW) have known environmental toxicity and are resistant to conventional wastewater treatments. The granular activated carbon (GAC) biofilm treatment process has been shown to effectively treat OSPW NAs via combined adsorption/biodegradation processes despite the lack of research investigating their individual contributions. Presently, the NAs removals due to the individual processes of adsorption and biodegradation in OSPW bioreactors were determined using sodium azide to inhibit biodegradation. For raw OSPW, after 28 days biodegradation and adsorption contributed 14% and 63% of NA removal, respectively. For ozonated OSPW, biodegradation removed 18% of NAs while adsorption reduced NAs by 73%. Microbial community 454-pyrosequencing of bioreactor matrices indicated the importance of biodegradation given the diverse carbon degrading families including *Acidobacteriaceae*, *Ectothiorhodospiraceae*, and *Comamonadaceae*. Overall, results highlight the ability to determine specific processes of NAs removals in the combined treatment process in the presence of diverse bacteria metabolic groups found in GAC bioreactors.

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1. Introduction

The extraction of bitumen from oil sands mining in northern Alberta, Canada has generated the huge amount of oil sands process-affected water (OSPW) containing a complex mixture of toxic organics that are acutely and chronically toxic to a range of organisms such as fish, amphibians and mammals (Anderson et al., 2012; Garcia-Garcia et al., 2011; Hagen et al., 2014). Among the organics in OSPW, naphthenic acids which are naturally occurring, aliphatic or alicyclic carboxylic acids, are considered to be the major contributors to the acute toxicity of OSPW (Clemente and Fedorak, 2005). Given this toxicity, vast quantities (over 1 million cubic meters) of OSPW are currently being stored in large tailings ponds adjacent to environmentally sensitive areas of the Athabasca River and its tributaries (Pereira et al., 2013). Despite the recent concerted efforts to develop efficient treatment technologies for OSPW, no OSPW is currently being released into the environment by any of the oil sands developers.

Previous research has demonstrated the recalcitrance of oil sands' NAs to biological treatment processes because of their extensive cyclical molecular structures (Han et al., 2008). Thus, there is a need for physical/chemical processes that are capable of degrading (e.g., ozonation) or adsorbing (e.g, granular activated carbon) these cyclical molecules that could then be coupled with biological treatment to create cost-effective and efficient treatment technologies. Ozonation can successfully degrade recalcitrant compounds at high doses but this high usage is not economically viable for industry. GAC treatment is an interesting alternative because of the high adsorption capacity for organics given its high surface area containing interconnected micropores, mesopores, and macropores (Sulaymon et al., 2013). However, a prolonged contact of GAC with wastewaters diminishes the available sites for adsorption of organic pollutants, eventually leading to the need for the adsorbent to be either replaced or regenerated (Nath and Bhakhar, 2011). Fortunately, the irregularity, roughness, and porosity of the GAC surface provides an excellent environment for the development and growth of bacterial biofilms (Yapsakli and Cecen, 2010). Thus, this bacterial growth can help to regenerate the GAC surface by preferentially biodegrading adsorbed organics that the bacteria become acclimated to (Aktas and Cecen, 2007). This in situ regenerative capacity, as compared to costly GAC replacement or ex situ regeneration, makes the GAC biofilm combined adsorption and biodegradation a promising treatment methodology for industrial wastewaters (Baban et al., 2010) and oil field process waters (Zhao et al., 2006) that contain a large variety of recalcitrant organic compounds. Our previous studies using GAC-fluidized bed biofilm reactors showed high OSPW NAs removals of 86% from raw OSPW (Islam et al., 2014b) and over 99% from ozonated OSPW (Islam et al., 2014a) with hydraulic retention times (HRT) of 2 h over 4-month operation. In addition, biofilm reactors using non-adsorptive supportive media resulted in OSPW NAs removals of 38% indicating that the biofilm bacteria were actively degrading NAs (McKenzie et al., 2014). Thus, the combination of adsorption and biodegradation processes in GAC biofilm treatment is a promising process for advanced OSPW treatment. However, previous research has reported only the combined removal of adsorption/biodegradation but not the individual contributions of these processes. Most importantly, the impact of biodegradation is of significance as this process becomes of a greater interest once the GAC adsorption capacity is exhausted and its regeneration is needed for improved removals.

Clearly, the understanding of the contributions of the individual adsorption and biodegradation removal processes in GAC biofilm systems is necessary for optimization of bioreactor performance efficiencies. However, bioreactor performance is substantially dependent on the abundance and metabolism of microrganisms in the reactors in both planktonic and biofilm matrices. Thus, there is a clear need to further investigate these bacterial assemblages for better understanding, and potential optimization, of the bioreactor biodegradation. Previously, we used conventional microbial community characterization methods including denatured gradient gel electrophoresis (DGGE) to analyze the microbial community structure in GAC biofilm reactors (Islam et al., 2014a,b). However, this conventional molecular biological method does not provide comprehensive and systematic information on the various microbial communities. A more precise and complete characterization of the microbial communities can be assessed using next-generation high throughput pyrosequencing (Luo et al., 2013). Previously, this next-generation technique has been used to characterize biofilms developed on Athabasca river sediments and soils using ion torrent pyrosequencing (McKenzie et al., 2014; Yergeau et al., 2013), and raw water distribution using 454-pyrosequencing analysis (Luo et al., 2013). However, no relevant study has previously been conducted to investigate the biofilm community structure on GAC during OSPW treatment using high throughput pyrosequencing techniques.

Based on this defined knowledge gap in GAC treatment process understanding, the major objective from this study was to assess the individual roles of adsorption and biodegradation in bioreactors containing various GAC treatments using both raw and ozonated OSPW. The role of using a low dose of ozonation was to allow the degradation of recalcitrant NAs for the improved degradation in the biological processes while limiting the need for higher, more cost-prohibitive ozone doses. The NAs are a complex mixture of noncyclic, monocyclic, and polycyclic alkanes containing a carboxylic group with the general empirical formula $C_nH_{2n+Z}O_2$ for classical NAs, where n is the number of carbon atoms and Z is either zero or a negative even integer representing the number of hydrogen atoms lost because of ring formation ($Z = 0$ to -12) (Grewer et al., 2010). Moreover, the microbial communities developed in the individual treatment processes were identified using 454-pyrosequencing. The knowledge of the bacterial assemblages may be useful in future work to pre-dose GAC with known bacteria strains to more efficiently treat OSPW and may also be considered for applications in other industrial wastewaters containing recalcitrant compounds.

2. Materials and methods

2.1. Materials

In October 2012 raw OSPW was collected in 200 L barrels at Fort McMurray, AB, shipped to the University of Alberta and preserved at 4 °C in a cold storage room prior to use in experiments. The steam-activated granular activated carbon (GAC) was purchased from Calgon Carbon Corporation (Pittsburgh, PA, USA). The GAC was sterilized at 121 °C for 30 min (Model 733LS vacuum/gravity system sterilizer, NY, USA), dried at 104 °C for ~72 h and allowed to cool in a desiccator before being used in GAC experiments.

2.2. Ozonation of OSPW

The ozonation procedure and calculation of the utilized ozone dose have been reported previously by Wang et al. (2013a). Briefly, an ozone generator (PCI-WEDECO, GSO-40, Herford, Germany) generated ozone from extra pure dried air which was passed through a ceramic fine bubble gas diffuser located at the bottom of a 200 L plastic barrel filled with raw OSPW. Two ozone monitors (model HC-500, PCI-WEDECO) were used to monitor the ozone concentrations in the feed and off-gas lines during the ozonation process and the residual ozone was purged using pure nitrogen. More detailed information about ozonation is included in supplementary data.

2.3. Experimental methods

Prior to adsorption and biodegradation experiments, suitable and consistent biofilms had to be developed on the GAC for use in the various experimental treatments. The GAC biofilms for all raw and ozonated experiments were cultured in 1 L amber coloured bottles reactors containing 2 g GAC in 500 mL raw/ozonated OSPW at room temperature