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Abiotic and bioaugmented granular activated carbon for the treatment of 1,4-dioxane-contaminated water☆

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ABSTRACT

1,4-Dioxane is a probable human carcinogen and an emerging contaminant that has been detected in surface water and groundwater resources. Many conventional water treatment technologies are not effective for the removal of 1,4-dioxane due to its high water solubility and chemical stability. Biological degradation is a potentially low-cost, energy-efficient approach to treat 1,4-dioxane-contaminated waters. Two bacterial strains, *Pseudonocardia dioxanivorans* CB1190 (CB1190) and *Mycobacterium austroafricanum* JOB5 (JOB5), have been previously demonstrated to break down 1,4-dioxane through metabolic and co-metabolic pathways, respectively. However, both CB1190 and JOB5 have been primarily studied in laboratory planktonic cultures, while most environmental microbes grow in biofilms on surfaces. Another treatment technology, adsorption, has not historically been considered an effective means of removing 1,4-dioxane due to the contaminant's low K_{oc} and K_{ow} values. We report that the granular activated carbon (GAC), Norit 1240, is an adsorbent with high affinity for 1,4-dioxane as well as physical dimensions conducive to attached bacterial growth. In abiotic batch reactor studies, 1,4-dioxane adsorption was reversible to a large extent. By bioaugmenting GAC with 1,4-dioxane-degrading microbes, the adsorption reversibility was minimized while achieving greater 1,4-dioxane removal when compared with abiotic GAC (95–98% reduction of initial 1,4-dioxane as compared to an 85–89% reduction of initial 1,4-dioxane, respectively). Bacterial attachment and viability was visualized using fluorescence microscopy and confirmed by amplification of taxonomic genes by quantitative polymerase chain reaction (qPCR) and an ATP assay. Filtered samples of industrial wastewater and contaminated groundwater were also tested in the bioaugmented GAC reactors. Both CB1190 and JOB5 demonstrated 1,4-dioxane removal greater than that of the abiotic adsorbent controls. This study suggests that bioaugmented adsorbents could be an effective technology for 1,4-dioxane removal from contaminated water resources.

1. Introduction

1,4-Dioxane, a heterocyclic ether, is an emerging contaminant that has been detected in surface and groundwater. The compound is harmful to human health and is possibly carcinogenic to human (class 2B) based on the classification by the International Agency for Research on Cancer (International Agency for Research on Cancer, 1999). It is also a known toxicant, which causes adverse effects to kidney, liver, and nervous system at chronic, low doses (DeRosa et al., 1996), and can lead to death at high doses (Mohr et al., 2010). The contamination of 1,4-dioxane in water is usually due to the historical use as a stabilizer for the chlorinated solvent 1,1,1-

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trichloroethane (TCA), and direct use as a solvent in many industries (Mohr et al., 2010). Moreover, it has been detected as a by-product during the esterification reactions between ethylene glycol and dimethyl terephthalate during the manufacturing of surfactants used in detergent and personal care products (Popoola, 1991). Because 1,4-dioxane is capable of establishing hydrogen bonds with water, the compound is highly miscible and mobile in water. The results of a recent national survey of public drinking water supplies deposited in the USEPA UCMR3 Occurrence Database revealed that 11.9% and 3.9% of 7171 water samples taken during the first year of the program contained 1,4-dioxane exceeding 0.07 μg/L detection limit and the reference concentration of 0.35 μg/L, respectively. The reference concentration represents the 1×10^{-6} cancer risk for 1,4-dioxane for the average consumer (United States Environmental Protection Agency, 2014; Water Research Foundation, 2014). To prevent the adverse effects to human health, it is very important to eliminate 1,4-dioxane in contaminated drinking water, as well as sources of 1,4-dioxane contamination.

Many abiotic technologies used in conventional water treatment are largely ineffective for remediation of 1,4-dioxane due to its miscibility in water and poor adsorption properties. Neither gas stripping nor photolytic technologies are effective to remove or degrade 1,4-dioxane in water. Similarly, chemical oxidation, which uses oxidants such as permanganate or chlorine to chemically transform contaminants, was previously reported as ineffective to remove 1,4-dioxane (McGuire et al., 1978). Although 1,4-dioxane can be partially degraded by using some oxidants, byproducts from the degradation process, especially by chlorinated oxidants, are of public and ecological health concern since they are often more toxic than the parent compound (Woo et al., 1980). Effective chemical oxidation also requires adjustment of pH and temperature, which is not economically feasible in full scale plants (Klecka and Gonsior, 1986). Alternatively, advanced oxidation processes such as UV photooxidation and sonolysis were proven as effective means for the removal of 1,4-dioxane (Beckett and Hua, 2000, 2003; Kim et al., 2006; Son et al., 2006). However *in situ* and *ex situ* applications can be limited by subsurface oxidant distribution capabilities and requirements of expensive and energy-intensive pump and treat systems, respectively (Simpkin et al., 2011; United States Environmental Protection Agency, 2001).

Biodegradation of 1,4-dioxane via aerobic, monooxygenase-catalyzed metabolic or propane monooxygenase-catalyzed co-metabolic pathways is well documented in several laboratory studies (Huang et al., 2014; Mahendra and Alvarez-Cohen, 2005, 2006; Vainberg et al., 2006; Zhang et al., 2017). The metabolic transformation of the primary substrate (1,4-dioxane in this context) produces energy and/or carbon for the microbe while the co-metabolic transformation of the target compound (1,4-dioxane) might result in energy depletion or product toxicity in the microbe. Remediation systems that utilize co-metabolism rely on continuous low concentration feeds of the primary substrate or periodic pulses of the primary substrate in order to sustain the microbial growth and enzyme induction.

Biodegradation can be used as a sole remediation strategy or 1,4-dioxane-degrading bacteria can be used to bioaugment other treatment systems, such as plants or electrochemical processes (Jasmann et al., 2017; Kelley et al., 2001; Suh and Mohseni, 2004). However, providing the nutrient requirements of the bacteria in many systems is difficult, and research into incorporating biodegradation into other treatment processes is on-going (Isaka et al., 2016; Lee et al., 2014).

Processes using bioaugmented adsorbents, including granular activated carbon (GAC), have been successfully established for the treatment of other hydrophilic organic compounds with similar water solubility and partition coefficients to 1,4-dioxane, such as methyl *tert*-butyl ether (MtBE) and *tert*-butyl alcohol (TBA) (Aslett et al., 2011; Deeb et al., 2000; Lee, 2015; Mohr et al., 2010). Furthermore, attached growth reactors have been used to remove other compounds, especially with the selection of a granular activated carbon to support microbial growth (Caldeira et al., 1999; Frascari et al., 2014; Hai et al., 2013; Khanitchaidecha and Kazama, 2012).

The objective of this study was to evaluate removal or destruction of 1,4-dioxane from synthetic waters and environmental samples using abiotic GAC as well as GAC augmented with 1,4-dioxane-metabolizing or co-metabolizing bacteria.

2. Materials & methods

2.1. Adsorbent specifications and preparation

The activated carbon Norit 1240™ (Norit Americas Inc., hereafter referred to as GAC) which was produced by steam activation of coal was used in this study (Norit Americas, 2003). The activated carbon, which possesses the iodine number of 1020 mg/g, has a negative surface charge at pH greater than 4. At the pH range used in this study (pH 6.8–7.3), the GAC has a zeta potential between −26 and −32 mV (Anielak and Grzegorczuk-Nowacka, 2011).

2.2. Culture conditions

Axenic cultures of *Pseudonocardia dioxanivorans* CB1190 (CB1190) were grown in sterile 2 L conical baffled flasks containing 400 mL ammonium mineral salts (AMS) medium (Parales et al., 1994), with 100 mg/L 1,4-dioxane (Sigma-Aldrich, St. Louis, MO, USA) as the sole carbon and energy source. The bacterial cultures were grown aerobically at 30 °C in a rotating incubator with shaking speed of 150 rpm. Concentrations of 1,4-dioxane in bacterial cultures were monitored over time using a Hewlett-Packard 6890 gas chromatograph equipped with a flame ionization detector (GC-FID) (Agilent Technologies, Santa Clara, CA, USA). Pure cultures of *Mycobacterium austroafricanum* JOB5 (JOB5) were grown in sterile 500 mL serum bottles with septa and crimp seals. Nitrate mineral salts (NMS) medium (Chu et al., 2004) (100 mL) was added into the bottles, with a supplement of 12.5% (vol/vol) headspace propane that served as a sole carbon and energy source for the growth of JOB5. The bacterial cultures were grown at 30 °C in a rotating incubator with 150 rpm agitation. Concentrations of propane in headspace were analyzed by injecting gaseous samples directly into a GC-FID. The purity and viability of bacterial cultures were maintained by supplementing the specific carbon sources and transferring to fresh media prior to their use in subsequent studies.

2.3. Abiotic adsorption and desorption of 1,4-dioxane in batch reactors

Abiotic adsorption of 1,4-dioxane was performed in 100 mL sterile media bottles with screw caps. The bottles were filled with 20 mL AMS medium with different 1,4-dioxane concentrations (12.5–800 mg/L). To investigate the effectiveness of the activated carbon, sterile GAC (0.4 mg dry weight) was then added into each bottle. The bottles were then placed at 30 °C in an incubator. Samples (100 μL) were collected at different time periods until reaching equilibrium, filtered through 0.2 μm-pore Fisherbrand nylon syringe filters, and stored at −20 °C prior to further analysis. The concentrations of 1,4-dioxane in filtrates were determined by GC-FID.

The amounts of 1,4-dioxane adsorbed by the GAC (q_e) were estimated from concentration data and dry weight of the GAC using