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Adsorption and transport of methane in biochars derived from waste wood

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ABSTRACT

Mitigation of landfill gas (LFG) is among the critical aspects considered in the design of a landfill cover in order to prevent atmospheric pollution and control global warming. In general, landfill cover soils can partially remove methane (CH_4) through microbial oxidation carried out by methanotrophic bacteria present within them. The oxidizing capacity of these landfill cover soils may be improved by adding organic materials, such as biochar, which increase adsorption and promote subsequent or simultaneous oxidation of CH_4. In this study, seven wood-derived biochars and granular activated carbon (GAC) were characterized for their CH_4 adsorption capacity by conducting batch and small-scale column studies. The effects of influential factors, such as exposed CH_4 concentration, moisture content and temperature on CH_4 adsorption onto biochars, were determined. The CH_4 transport was modeled using a 1-D advection–dispersion equation that accounted for sorption. The effects of LFG inflow rates and moisture content on the combined adsorption and transport properties of biochars were determined. The maximum CH_4 adsorption capacity of GAC (3.21 mol/kg) was significantly higher than that of the biochars (0.05–0.9 mol/kg). The CH_4 gas dispersion coefficients for all of the biochars ranged from 1×10^{-3} to 3×10^{-3} m^2 s^{-1}. The presence of moisture significantly suppressed the extent of methane adsorption onto the biochars and caused the methane to break through within shorter periods of time. Overall, certain biochar types have a high potential to enhance CH_4 adsorption and transport properties when used as a cover material in landfills. However, field-scale studies need to be conducted in order to evaluate the performance of biochar-based cover system under a more dynamic field condition that captures the effect of seasonal and temporal changes.

1. Introduction

One of the major environmental problems associated with landfills is the generation of landfill gas (LFG), which is produced by the anaerobic decomposition of the organic waste fraction (Scheutz et al., 2009a,b). The main components of LFG are CH_4 (50% v/v) and CO_2 (50% v/v), both of which are powerful, long-lived greenhouse gases with a high potential to cause adverse effects on global climate change. The molar absorption coefficient of CH_4 for infrared (IR) radiation is much stronger than CO_2, which results in CH_4 being a more powerful greenhouse gas (GHG) with a Global Warming Potential (GWP) of 28 over a period of 100 years (IPCC, 2013). According to a report released by the USEPA on the U.S. inventory of GHG emissions in 2010, landfills are the third largest source of anthropogenic CH_4 emissions in the U.S. Thus, the mitigation of LFG by incorporating efficient LFG management systems has gained the utmost importance over the past few decades.

Methane mitigation can be achieved by a combination of adsorption and biochemical oxidation in landfill cover systems. To date, extensive research conducted in this field highlights the importance of employing organic rich biocover materials to improve the microbial methane oxidation capacity of landfill cover systems (Park et al., 2004; Stern et al., 2007; Huber-Humer et al., 2008, 2009; Scheutz et al., 2011; Roncato and Cabral, 2011). However, researchers have not yet explored the process of methane adsorption within landfill cover systems that can also contribute to methane mitigation. The combined effects of both adsorption and microbial oxidation of methane need to be quantified upon employing a suitable biocover material that can facilitate both of these processes (Sadasivam and Reddy, 2014).

Although the addition of organic rich compost amendments to landfill cover soils can enhance the microbial methane oxidation

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capacity of the cover, exo-polymeric substances can form within the cover system over time that clog the pores and hinder the diffusion of gases (Powelson et al., 2006). Thus, using a biocover material with a relatively higher porosity and enhanced gas transport properties can minimize the consequences of EPS formation within the cover system. In order to design an efficient biocover system for methane mitigation, a stable biocover material also needs to be selected such that the material has a high porosity with the capability to enhance methane adsorption capacity as well as favor the growth of methanotrophs to promote microbial methane oxidation.

Biochar is an organic rich material derived from wood, manure or plant biomass through pyrolysis under limited oxygen environments (Lehmann and Joseph, 2009). The choice of waste biomass conversion process and treatment conditions is dependent upon the desired end-product, which includes biofuel for energy (Lehmann, 2007) and biochar for the purpose of environmental management (Lehmann and Joseph, 2009). The physical and chemical characteristics of biochars are dictated by the pyrolysis conditions, such as temperature and residence time (Lua et al., 2004; Xie et al., 2015). The porosity and specific surface area of biochars are dependent upon the highest treatment temperature (Brown et al., 2006) and post-treatment processes, such as activation (Zhang et al., 2004). Generally, the biochar surface area increases with a rise in treatment temperatures and the process of chemical activation tends to increase the microporosity of biochars. Some chemical activation methods used for enhancing the surface area of biochars include steam activation using KOH (Ippolito et al., 2012) and phosphoric acid impregnation (Lin et al., 2012). The presence of micropores in the biochars makes it highly preferable for gas adsorption (Billemont et al., 2013). When used as a soil amendment, biochars have a high potential to increase the sorption ability of soils, mainly due to their pyrogenic production process (Sadasivam and Reddy, 2014). Several studies have compared the sorption properties of pyrogenic and non-pyrogenic or fresh biomass and found that the sorption ability of pyrogenic substances, such as biochars, is a couple of orders of magnitude higher than that of fresh biomass (Baring et al., 2002; Huang et al., 2003; Nguyen et al., 2004). The highly porous structure of biochars can facilitate the effective colonization of methanotrophic communities, which are major drivers for methane oxidation to occur in landfills. Moreover, biochars have a high organic content and are stable in the soils for a long period of time, which increases its suitability for use as a soil amendment in environmental management.

The amendment of biochars to cover soil increases the shear strength of the cover soil and, consequently, results in higher safety factors for the slope stability of landfill covers (Sadasivam and Reddy, 2015a). Preliminary results indicate that methane adsorption by biochars enhances the methane oxidation efficiency of biochar-amended soils in long-term column experiments (Reddy et al., 2014). Since sorption of methane onto biochars was found to significantly affect the methane transport through biochar-amended cover systems (Xie et al., 2013), it is important to quantify the extent of methane mitigation contributed solely by adsorption and evaluate the effects of varying environmental conditions on the CH_4 sorption capacities. The primary focus of this paper is to quantify and analyze the effects of varying levels of exposed CH_4 concentrations, moisture content and temperature on the methane adsorption and transport characteristics of different biochars derived from waste wood and compare those results with that of a more conventional adsorbent, such as GAC. The results from this study can help researchers identify the potential use of biochar-based biocover amendments to landfill soil with the view of achieving cost-effective, sustained methane mitigation.

2. Materials and methods

2.1. Biochars and GAC

Seven types of hardwood biochars were obtained from commercial vendors in 5-gallon buckets and stored in air-tight containers prior to use. The biochars were produced through varying treatment processes and production conditions (Sadasivam and Reddy, 2015b). GAC was obtained from Fisher Scientific for use in the methane adsorption studies. Detailed physical and chemical characteristics of these biochars and GAC are presented by Yargicoglu et al. (2015). Prior to use, the biochars were autoclaved in a Napco® model 8000-DSE autoclave at 121 °C for 30 min for two consecutive days (Benett et al., 2003) to minimize the microbial interference on adsorption. Biochars were sealed in sterilized glass containers at 22 °C for 24 h between autoclave treatments (Carter et al., 2007).

2.2. Batch adsorption testing

Batch adsorption tests were conducted to determine the methane adsorption capacity of the biochars and GAC under different levels of moisture content, temperature and exposed methane concentrations. The materials were used as obtained from the vendors (As-is) without being subjected to physical–chemical pretreatment except for sterilization. Five grams of biochar samples were placed inside 250 g amber glass bottles and sealed with long sleeved rubber stoppers. Then, predetermined amounts of air in the headspace were replaced with synthetic landfill gas (50% CH_4 and 50% CO_2) to achieve headspace CH_4 concentrations of 2, 5, 8, 10, 15, and 20% (v/v). The control test units were also set up similar to the sample test units, but without adding the biochar to determine the initial CH_4 headspace concentration (v/v) achieved for each experimental set.

In order to determine the effects of moisture content on methane adsorption, test units were set up following the aforementioned procedure, but with the addition of measured volumes of de-ionized water using a calibrated pipette to achieve moisture levels of 25%, and 75% with respect to the corresponding water holding capacity (WHC) based on dry weight basis (Yargicoglu et al., 2015). To study the effects of moisture content on the adsorption of CH_4 onto the biochars and GAC, the temperature in all the test units was maintained at 295 K and the CH_4 gas pressure within the test units ranged from 0.15 to 1 kPa. To simulate the effects of increasing temperature on methane adsorption, as expected to occur under field conditions, a hydrometer water bath (Model H-4239A, Humboldt Co., Arlington Heights, IL) was used to maintain preselected constant temperature conditions (25 °C, 35 °C and 45 °C) within the test units. All the test units (including the controls) were placed in a water bath and allowed to acclimate to those preset temperature levels. A thermometer was used to ensure that appropriate temperature conditions existed prior to the start of the tests. The concentrations of CH_4 in the headspace of all the adsorption test units were increased until the material's maximum adsorption capacity was achieved. Gas samples were collected and analyzed as described in Section 2.4 at different intervals until the equilibrium headspace CH_4 concentrations were achieved.

2.3. Column adsorption testing

The column adsorption tests were conducted to assess the combined transport and adsorption characteristics of CH_4 through biochars and GAC. These tests were conducted using a Kontes brand Chromaflex® glass chromatography column (420870) measuring

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