



Adsorption characteristics of siloxanes in landfill gas by the adsorption equilibrium test

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ABSTRACT

Due to the increase in energy cost by constantly high oil prices and the obligation to reduce greenhouse effect gases, landfill gas is frequently used as an alternative energy source for producing heat and electricity. Most of landfill gas utility facilities, however, are experiencing problems controlling siloxanes from landfill gas as their catalytic oxidizers are becoming fouled by silicon dioxide dust. To evaluate adsorption characteristics of siloxanes, an adsorption equilibrium test was conducted and parameters in the Freundlich and Langmuir isotherms were analyzed. Coconut activated carbon (CA1), coal activated carbon (CA2), impregnated activated carbon (CA3), silicagel (NCA1), and activated alumina (NCA2) were used for the adsorption of the mixed siloxane which contained hexamethyldisiloxane (L2), octamethylcyclotetrasiloxane (D4), and decamethylcyclopentasiloxane (D5). L2 had higher removal efficiency in noncarbon adsorbents compared to carbon adsorbents. The application of Langmuir and Freundlich adsorption isotherm demonstrated that coconut based CA1 and CA3 provided higher adsorption capacity on L2. And CA2 and NCA1 provided higher adsorption capacity on D4 and D5. Based on the experimental results, L2, D4, and D5 were converted by adsorption and desorption in noncarbon adsorbents. Adsorption affinity of siloxane is considered to be affected by the pore size distribution of the adsorbents and by the molecular size of each siloxane.

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1. Introduction

Landfill gas generated from solid waste landfills consists of methane (40–60%) and carbon dioxide (40–50%), and has a high caloric value (35–40 MJ/Nm³). Landfill gas is being used as an alternative resource for natural gas and fossil fuels (Schweigkofler and Niessner, 1999; Rasi et al., 2010; Appels et al., 2008). Carbon dioxide is an indicator of the global warming potential, and methane is known to have a global warming effect 25 times larger than carbon dioxide (Starr et al., 2012; Rasi et al., 2008). Converting landfill gas to heat or electricity is expected not only to reduce the levels of greenhouse gas emissions increase availability of alternative sources of new renewable energy (Rasi et al., 2007). Due to these reasons the landfill gas recycling market has been rapidly expanding.

Landfill gas contains trace compounds that decrease the efficiency of recycling, such as hydrogen sulfide and siloxane (Schweigkofler and Niessner, 1999; Rasi et al., 2010; Abatzoglou and Boivin, 2009; Chiriac et al., 2011). Siloxanes are used as a raw material in various products such as detergents, shampoos, and cosmetic items (Dewil et al., 2006). Siloxanes generated by

the decomposition of these products are contained in landfill gas because of their high vapor pressure and low water solubility (Kochetokov et al., 2001; McBean, 2008). When the landfill gas containing such compounds is combusted to generate energy, siloxanes are converted to silicon dioxide, which can have negative effects, such as abrasion of the main facilities and reduction of the heat transfer (Appels et al., 2008; Matsui and Imamura, 2010). In the late 1990s, lean burn engines were introduced to replace old diesel engines, but it was more easily damaged by silicon dioxide (Appels et al., 2008; Martin et al., 1996; Ajhar et al., 2010a). Therefore, the pretreatment of siloxane must be seriously considered in terms of the cost and management of landfill gas utility facilities (Wheless and Pierce, 2004; Schweigkofler and Niessner, 2001; Dewil et al., 2006; Nam et al., 2011).

Various methods for removing siloxane through adsorption, absorption, cooling, biological methods, and catalysts are being investigated and some of them have been commercialized (Ajhar et al., 2010a; Schweigkofler and Niessner, 2001; Acsettola et al., 2008; Boulinguez and Le Cloirec, 2009; Finocchio et al., 2009; Matsui and Imamura, 2010). Among those pretreatment methods, adsorption is simple and easy to use in comparison with the other techniques, so it is popular in the market (Arnold, 2009). Various studies about siloxane adsorption have been conducted, and carbon adsorbents have been widely used due to their excellent

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adsorptive capacities (Doczyck, 2003; Rossol et al., 2003; Matsui and Imamura, 2010; Wheless and Pierce, 2004; Hagmann et al., 2002; Dewil et al., 2006; Finocchio et al., 2009; Schweigkofler and Niessner, 2001). In these studies, manufactured model gas or actual landfill gas have been employed to evaluate adsorption characteristics of adsorbents (Ajhar et al., 2010a).

It is necessary to have a test with landfill gas, before adopting the adsorbent to the landfill gas utility facilities. However, it is difficult to compare the adsorption characteristics of siloxane using landfill gas produced from landfill sites. The initial concentration of landfill gas is not constant, and it also contains hundreds of substances as well as siloxane (Rasi et al., 2008). The adsorption characteristics of adsorbents are more related to the total contaminant load than the siloxane concentration. Some studies conducted with model gases, were usually focused on a removal for each siloxane substance (Matsui and Imamura, 2010; Boulinguez and Le Cloirec, 2009; Lee et al., 2001). Due to the diverse siloxanes, the adsorption tests for multi adsorbates are primarily required for adsorption processes. When multi adsorbates coexist, the adsorption capacity based on adsorption affinities between adsorbates and adsorbents are various. Furthermore, identical adsorbent can have a range of adsorption capacity under different physical controls (Weber, 1972). Thus, the adsorption results of multi adsorbates to diverse adsorbents can provide various information on removal of siloxane.

To investigate and compare the adsorption characteristics of siloxanes: L2; D4 and D5. Five adsorbents tested, three commercial activated carbons, one commercial silicagel, and one activated alumina.

2. Materials and methods

2.1. Materials

2.1.1. Adsorbents

Several studies reported that the use of different adsorbents strongly affects the siloxane adsorption by its source, BET surface, impregnation and porous volume (Ajhar et al., 2010a). Five adsorbents (Table 1) applied in this study can be classified into two categories, carbon or noncarbon adsorbents. CA1, CA2, and CA3 were the carbon adsorbents, and NCA1 and NCA2 were the noncarbon adsorbents, which are the most widely used adsorbents. CA3 was generated from CA1 using 2.5% KOH impregnation. NCA1 has been

known to desorb siloxane (regeneration) in the high temperature (Schweigkofler and Niessner, 2001), and NCA2 has inverse characteristics of NCA1 because the adsorption capacity of NCA1 increases as the temperature goes up (Ajhar et al., 2010a).

The adsorbents were homogenized using a 40–80 mesh sieve before use. The specific surface area of sieved adsorbents was analyzed by SEM (scanning electron microscope, JSM-6380, Japan). The rational surface area and pore diameter of samples were examined using ASAP2020 (Micromeritics, USA).

2.1.2. Mixed siloxane gas

Siloxane is an organosilicon compound with silicon, oxygen, and another function group combined. According to the molecular structure, siloxane is classified into linear siloxane and cyclic siloxane, which are represented as “L” and “D” in this manuscript, respectively. L2, octamethyltrisiloxane (L3), decamethyltetrasiloxane (L4), dodecamethylpentasiloxane (L5), hexamethylcyclotrisiloxane (D3), D4, D5 and dodecamethylcyclohexasiloxane (D6) are usually occur in landfill gas, and among these, D4, D5, and L2 shows the highest concentration and frequency (Tower, 2004; Arnold, 2009).

In this study, the mixed siloxane was used as a stock solution, prepared using D4, D5, and L2, with a volume ratio of 1:1:1. Table 2 shows the types and properties of the siloxanes used in the experiment. Fig. 1 describes the molecular structures of D4, D5, and L2.

2.2. Methods

2.2.1. Analysis

Siloxane was analyzed using GC-MSD (Shimadzu QP-2010 ultra, Japan), and the Restek-5MS column (30 m, 0.25 mm) was used. For GC conditions, the temperature was 250 °C at the injector, the gas injection volume was 0.2 mL, the split ratio was 5:1, and the gas flow rate was 1.5 mL/min. The oven temperature was held constant at 40 °C for 5 min, and then gradually increased by 15 °C per minute until reaching 250 °C.

2.2.2. Conditions of adsorption equilibrium test

Each 250 mL serum bottle was used as a reactor and it sealed with Teflon septum to prevent gas leakage, contained 0.01–0.1 g of dried (at 100 °C) adsorbents. After then there actor headspace was flushed with nitrogen gas for 20 min and the reactors were incubated at 30 °C.

Table 1
Classifications and properties of the adsorbents used in this study.

Category	Sample name	Product name	Manufacturer	Origin	Bulk density (g/mL)	Porosity (%)	pH
Carbon adsorbent	CA1	ENsorb C	E&Chem solution (Korea)	Coconut based	0.55	56	10.1
	CA2	Coal AC	Duksan (Korea)	Coal based	0.43	60	7.5
	CA3	ENsorb CI	E&Chem solution (Korea)	Coconut based	0.47	70	9.6
Noncarbon adsorbent	NCA1	Silicagel	Daejung (Korea)	SiO ₂	0.90	40	3.7
	NCA2	Alumina oxide	Daejung (Korea)	Al ₂ O ₃	0.80	56	9.2

Table 2
Siloxane standards used in this study.

Substances	Formula	Abbr. ^a	MW ^b	VP ^c	Manufacturer	Assay (%)
Octamethylcyclotetrasiloxane	C ₈ H ₂₄ O ₄ Si ₄	D4	296.6	0.13	Aldrich	98
Decamethylcyclopentasiloxane	C ₁₀ H ₃₀ O ₅ Si ₅	D5	370.8	0.05	Aldrich	97
Hexamethyldisiloxane	C ₆ H ₁₈ O ₂ Si ₂	L2	162.4	4.12	Aldrich	99.5

^a Abbreviations.

^b Molecular weight (Arnold and Kajolina, 2010).

^c Vapor pressure (Oshita et al., 2010; kPa, 25 °C).

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