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Removal of sulfur compounds and siloxanes by physical and chemical sorption

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ABSTRACT

The removal of sulfur compounds and siloxanes, which are major impurities in the biogas produced from the anaerobic digestion of sewage sludge, was studied using a bench-scale adsorptive gas purification experimental setup. The main impurities are hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS2), octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5). The commercially available adsorbents iron oxide (IO), iron oxide hydroxides (IH, IHS), activated carbon (AC), impregnated activated carbon (IAC), silica gels (A2 and NS10) and molecular sieves (5A and 13X) were first extensively characterized using scanning electron microscopy (SEM), X-ray fluorescence (XRF), and BET surface area measurements. IHS, comprising mainly 42% iron oxide hydroxide, 11% silica gel, and 10% activated carbon, exhibited the best adsorption capacities for H2S (539 mg/g) and COS (32 mg/g) among the adsorbents studied, as well as relatively good adsorption capacities for siloxanes D4 and D5. AC and IAC showed the greatest CS2 removal efficiency. A2 demonstrated extremely high adsorption capacities for siloxanes D4 and D5, namely 1055 and 1968 mg/g, respectively.

1. Introduction

Biogas is a renewable energy source that can be produced by means of anaerobic digestion by anaerobic organisms of sewage, municipal waste, agriculture waste, manure, food waste, etc. Biogas comprises mainly methane (60–70%) and carbon dioxide (30–40%), and contains smaller amounts of nitrogen (< 1%), oxygen, and hydrogen; volatile organic compounds including sulfur compounds, halogenated compounds, and organic silicon compounds may also exist [1–4]. Methane, the primary component, can be utilized as fuel in many industrial applications such as heating, combined heat and power, and fuel cells. However, any sulfur compounds present in biogas can induce fatal damage to industrial facilities, especially corrosion damage [5,6]. Silicon compounds also have a poisoning effect on the anode side of the solid oxide fuel cell, and can form scale on the surface of devices such as turbines, thereby reducing their working efficiency [7]. Thus, to use the methane in biogas industrially, purification is required to avoid corrosion and scaling problems [8].

Adsorption, absorption, and membrane-based gas separation processes have been widely used to remove impurities from biogas. Among these purification methods, the adsorption process tends to be the most efficient owing to its simplicity of design, ease of operation, and insensitivity to toxic substances [9]. Moreover, it may be suitable for small-scale applications such as fuel cells [6]. To supply biogas as a fuel to these devices, a hybrid purification process has been proposed to combine a physicochemical adsorption process for removing sulfur compounds and siloxanes and a membrane separation process for concentrating methane by means of carbon dioxide separation [5,7,8].

Most recent works on membrane-based gas purification have focused on the removal of hydrogen sulfide or siloxanes (D4, D5) by using activated carbon and impregnated activated carbon [10–14], but very few studies have suggested metal oxides or other inorganic materials as potential adsorbents for hydrogen sulfide removal [15–22]. Thus, most studies have considered adsorption characteristics on a specific adsorbent of a specific impurity among the impurities generated from actual biogas. According to Xiao et al. [15], who studied some carbon-based absorbents, the adsorption capacity of impregnated activated carbon for hydrogen sulfide is about 420 mg/g, higher than that of activated carbon. Activated carbon, which has good performance in removing hydrogen sulfide, was evaluated by Bandosz [16]. Activated

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carbon impregnated with metal catalyst, as well as natural activated carbon, are also very effective in removing hydrogen sulfide. In addition, the binders used to bind additional materials onto the surface of activated carbon are also known to be important. Nguyen-Thanh and Bandosz [17] studied the catalytic hydrogen sulfide removal effects of metallic catalysts (Fe, Zn, Cu) supported on activated carbon using bentonite binders. Yamamoto et al. [18] found that an iron oxide–-hydroxide adsorbent has exceptional adsorption performance at room temperature. A commercially available adsorbent (Sulfatreat 410-HP), which is a combination of iron oxides (Fe_2O_3 and Fe_3O_4), has been tested under various conditions by Truong and Abatzoglou [19], who showed that the absorbent exhibits good efficiency under dry conditions, whereas the discharge concentration of H_2S increases by about 10 times under wet conditions. To develop a method to predict early breakthrough profiles of H_2S via theoretical analysis, Felice and Pagliai [20] performed pseudo-steady-state testing of Sulfatreat with a small adsorption column and then a long-run breakthrough test using a laboratory-scale setup at ambient temperature. Sigot et al. [21] conducted an experimental study on the H_2S removal performance of zeolite 13X and impregnated AC using real biogas. Based on their results, the adsorption performance of zeolite 13X was better than that of impregnated AC in dry conditions; the opposite result was observed in wet conditions. Steuten et al. [23] analyzed the effect of CO_2 and water on the adsorption of sulfur compounds on methane purification using zeolite and silica gel adsorbents. It was found that water and CO_2 inhibited the adsorption of hydrogen sulfide in binary and ternary system tests, and that water, H_2S and CO_2 were strongly bound to the adsorbents in this order. Chowanietz et al. [24] conducted the experiments on the effect of temperature ranging from 25 to 300 °C on the adsorption of sulfur compounds, water and carbon dioxide using a commercial silica-alumina gel. It was found that the capacity of all adsorbents decreased at high temperatures. Also, water was most affected by temperature, while H_2S and CO_2 had not only a very low temperature effect but also a small amount of adsorption. Hussain et al. [22] tested various synthesized mesoporous silica materials as support materials for ZnO adsorbents; these showed better adsorption capacities than commercial titania or activated carbon-based adsorbents.

Wang et al. [25] conducted a breakthrough test under various operating conditions (i.e., temperature, carbonyl sulfide (COS) concentration, relative humidity, gas composition). They reported that modified activated carbon with $Cu(NO_3)_2$-CoPcS-KOH impregnation achieved significantly improved COS adsorption ability (43.34 mg COS/g adsorbent). Li et al. [26] developed a theoretical model for predicting COS adsorption characteristics at low temperature. Their model was in good agreement with experimental breakthrough curves and described well the performance of COS removal. Sakanishi et al. [27] presented adsorption profiles of H_2S and COS on activated carbon over the temperature range from 200 to 400 °C, and demonstrated that the adsorption capacities of H_2S are much higher than those of COS because H_2S has a more acidic and polar character.

To date, only a few studies have reported the removal of siloxanes from biogas. Notably among these studies, Nam et al. [28] investigated and compared the adsorption characteristics of cyclic and linear siloxanes (D4, D5, and L2) with those of three commercial carbon adsorbents and two inorganic adsorbents (i.e., silica gel, alumina oxide), reporting that all these adsorbents showed good performance for removing siloxanes, and that silica gel and two carbon adsorbents with relatively higher BET surface areas showed the highest adsorption capacities. Sigot et al. [29] studied the adsorption of siloxane D4 on silica gel for biogas purification; as the temperature increased from 27 to 45 °C, the adsorption capacity of silica gel was reduced by 15% and its performance at 70% relative humidity decreased by 90% compared to dry conditions. Cabrera-Codony et al. [30] investigated the adsorption capacity and recovery efficiency of siloxane D4 using six synthetic zeolites and a natural zeolite (clinoptilolite); the recovery rate was found to be up to 80% in at least three cycles. However, the accumulation of siloxane D4 and/or byproducts during continued cycling led to continuous deterioration in the catalytic activity of the zeolite, and the conversion of D4 to linear silanediols inhibited both the catalytic activity and the adsorption capacity.

Table 1
Typical composition of biogas from the anaerobic digestion of the Seunggi sewage treatment plant in Incheon, Korea.

Constituent		Concentration	Unit	Method
Methane		67.7	%	KS I ISO 6974-6
Carbon dioxide		27.8	%	KS I ISO 6974-6
Oxygen		0.163	%	KS I ISO 6974-6
Nitrogen		3.774	%	KS I ISO 6974-6
Hydrogen		14.955	ppm	KS I ISO 6974-6
Hydrogen sulfide		4027.8	ppm	KS I ISO 19739
Carbon disulfide		None	ppm	KS I ISO 19739
Ethane		None	ppm	KS I ISO 6974-6
Propane		1.77	ppm	KS I ISO 6974-6
Halogens		0.57	ppm	KS I ISO 16017-1
Siloxanes	L2	0.57	ppm	Methanol impingement GC/MS
	L3	0.09	ppm	
	L4	None	ppm	
	L5	None	ppm	
	D3	None	ppm	
	D4	1.13	ppm	
	D5	6.6	ppm	
	D6	0.52	ppm	

As such, information on the adsorption behaviors of various adsorbents for various other impurities that may exist in actual biogas is extremely limited. However, there are many different types of sulfur compounds and siloxanes in biogas, and each will have a different reaction rate and adsorption capacity depending on the adsorbent.

Accordingly, in the present work several commercially available adsorbents were selected to analyze their removal characteristics for the major impurities in biogas. The main impurities considered in the present work were hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS_2), octamethylcyclotetrasiloxane (D4), and decamethylcyclopentasiloxane (D5), based on measurements from the anaerobic digestion of the Seunggi sewage treatment plant in Incheon, Republic of Korea. Table 1 lists the typical composition of the biogas from this plant. The ultimate objective of this study was to develop a hybrid biogas purification process able to provide high-purity methane to a solid oxide fuel cell, and integrating two purification processes, namely physicochemical adsorption and membrane separation. As a part of this study, we first carried out basic experiments on the adsorption process. The main focus of the present paper therefore is to examine the physical properties and adsorption characteristics of adsorbents used to remove the sulfur compounds and siloxanes that are the major impurities of biogas. In bench-scale adsorption experiments, iron oxide, iron oxide hydroxide, activated carbon, impregnated activated carbon, and inorganic adsorbents including zeolites and silica gels were tested as candidate adsorbents for the removal of impurities from synthetic biogas, and their physical properties were analyzed by means of XRF, SEM, and BET. Additionally, we identified the most promising adsorbent for removal of high-concentration H_2S from biogas, and performed further experimental investigations on this adsorbent to ascertain its H_2S adsorption features under various operating conditions of reactor temperature, feed concentration, and space velocity.

2. Experimental section

2.1. Adsorbents

Some commercially available adsorbents have been reported to remove typical impurities (e.g., H_2S, COS, CS_2, Siloxanes D4 and D5) from biogas [10–22]. Contrastingly, in the present work we evaluated nine