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Removal of siloxanes in sewage sludge by thermal treatment with gas stripping

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ABSTRACT

In this study, thermal treatment with gas stripping of sewage sludge before anaerobic digestion to reduce siloxanes in the sludge and accelerate the anaerobic digestion was studied experimentally.

Regarding siloxanes in the sludge, D5 concentrations were the highest. Siloxane concentrations in the digested sludge were decreased, versus those in thickened sludge, because siloxanes in the sludge are moved to the biogas during the anaerobic digestion.

Thermal treatment and gas stripping experiments were conducted. The optimum conditions for siloxane removal from sludge were found to be thermal treatment with gas stripping at 80 °C with 0.5 L/min of air flow for 48 h. Under these conditions, approximately 90% of all siloxanes in the sludge were removed.

Next, anaerobic digestion experiments were conducted with the optimally treated sludge and untreated sludge. The biogas volume of the optimally treated sludge was 1.6-fold larger than that of the untreated sludge. Furthermore, D5 contents in biogas from the optimally treated sludge were 95% lower than in biogas from untreated sludge.

Thus, thermal treatment with gas stripping of sludge before anaerobic digestion was effective in increasing biogas amounts, decreasing siloxane concentrations in the biogas, and reducing the need for a siloxane removal process from the biogas.

1. Introduction

Biogas produced from sewage sludge is a mixture of CH_4, CO_2, and other minor constituents, such as oxygen, nitrogen, and hydrogen sulphide. Various trace constituents are also contained in biogas, some of which can potentially cause problems during energy recovery operations that involve generating equipment, such as gas engines, micro-gas turbines, and fuel cells. Thus, attention must be paid to the make-up and concentrations of these trace components when using biogas.

"Siloxane" is a generic term referring to a subgroup of silicones that contain silanol bonds (Si–O) with methyl and ethyl groups bonded to the silicon atom. Common siloxanes are shown in Fig. 1 and Table 1, where 'L' and 'D' are the abbreviations for linear and cyclic siloxanes, respectively, and the number after the L or D denotes the number of silicon atoms. Because of the unique properties of siloxanes, they are used in various industrial processes, such replacing organic solvents, and in consumer products, such as deodorants, hair and skin care products, lubricants, and water repellents. These products are disposed of in wastewater and eventually produce volatile siloxane compounds in biogas [1].

During combustion in a gas engine, siloxanes are converted to silicates and microcrystalline silicon dioxide, which abrade the inner walls of engines and form deposits within combustion chambers, increasing the costs of engine maintenance [2–4].

Removing siloxanes from biogas upstream of generating equipment is thus necessary, and an adsorptive method using activated carbon is the currently favoured technique [5–7]. However, moisture and middle-boiling hydrocarbons in biogas can inhibit the removal of siloxanes by activated carbon, and activated carbon that has adsorbed siloxanes can be difficult to thermally regenerate completely. These factors increase the costs associated with using biogas. Additionally, the potential toxicity of D4 has been reported from animal experiments [8]. Therefore, it is desirable to remove siloxanes not only from biogas but also from sewage sludge and generally to prevent siloxanes from circulating in the environment.

Because the volume reduction rate of sludge, in terms of organic matter, is only 30–50% by conventional anaerobic digestion [9], various pre-treatment methods have been developed that can decompose organic content in sludge before anaerobic digestion, such as sonication, ozonation, microwave, thermal treatments,

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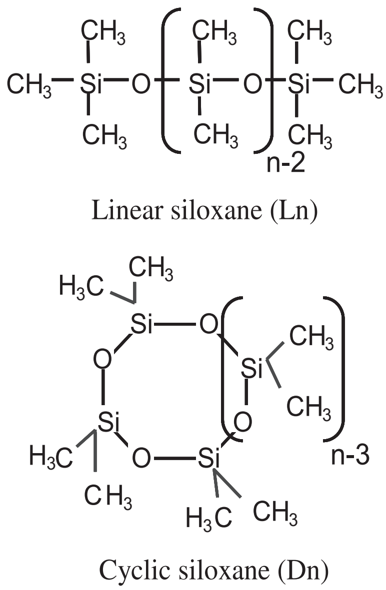

Fig. 1. Siloxane structures.

and the addition of alkalis [10–14]. Although the volume and organic reduction rate of sludge and the volume of digestion gas are increased by these techniques, there are few data about the behaviour of siloxanes in these processes. Considering that siloxanes have low water solubility and can be conjugated and adsorbed with organic particles in sludge, siloxanes have a relatively high vapour pressure at room temperature (Table 1).

Huppmann et al. [15] removed 95% of D4 from digested sludge by helium gas stripping at a flow rate of 0.4–0.6 L/min at 50 °C. Ajhar et al. [16] reviewed papers about technologies for siloxane removal from landfill and digester gas, and referred to Klingel et al. [17] regarding the possibility of L2 removal from sludge by gas stripping. Siloxanes in sludge can be removed by adding some amount of energy to the sludge in the form of a pretreatment before anaerobic digestion and gas stripping.

In this study, a new system involving thermal treatment and gas stripping to remove siloxanes from sludge before anaerobic digestion were examined experimentally. Fig. 2 shows a conceptual diagram of the new system. The thermal treatment is expected to decrease the amount of digested sludge and increase the biogas volume. Furthermore, removing siloxane from the sludge before anaerobic digestion could reduce the need for a siloxane removal process from biogas.

First, the amount of siloxane in sludge was estimated. Next, thermal treatment and gas stripping experiments using raw sludge to determine the optimal conditions for siloxane removal were conducted. Then the siloxane concentrations in biogas derived from the anaerobic digestion experiments using optimally treated sludge were investigated.

2. Materials and methods

2.1. Materials

As shown in Table 1, eight types of siloxane were used: L2 (99%), L3 (98%), L4 (97%), L5 (97%), D3 (99%), D4 (99%), D5 (99%), and D6 (99%). L2–L4 and D3–D6 were obtained from Shin-Etsu Chemical Co., Ltd. (Tokyo, Japan) and L5 from Acros Organics (Geel, Belgium) as reference materials.

2.2. Sampling sewage sludge

Sewage sludge samples were taken from a single site, wastewater treatment plant A (WWTP A; 280,000 m^3 of wastewater/day). The influent wastewater flows into a primary sedimentation tank, is treated in the biological treatment tank in a standard activated sludge process, settles into the final sedimentation tank, and is then released into a river after disinfection with chlorine. Primary sludge and excess activated sludge generated from the primary and final sedimentation are thickened by gravity and centrifugation, respectively, and are then mixed and digested anaerobically in a digestion tank. The digested sludge is then dewatered with a belt-press dewatering machine and incinerated in a fluidised-bed incinerator. Biogas from the anaerobic digestion without siloxane removal is used as fuel for the incineration of the sludge.

Two kinds of sewage sludge were sampled at the WWTP A: thickened sludge, a mixture of primary sludge thickened by gravity, and excess activated sludge, thickened by centrifugation. The sludge samples were obtained before the anaerobic digestion process at the WWTP, and digested sludge was sampled after the anaerobic digestion process. They were slurries and contained more than 95% moisture. The samples were stored in a cold room at 4 °C until the experiment. Thickened sludge was used for the

Table 1
Properties of siloxanes [7].

Category	Nomenclature	Abbreviation	Molecular weight	Appearance	Melting point (°C)	Boiling point (°C)	Density (g/cm^3) at 20 °C	Refractive index at 20 °C	Viscosity (cSt) at 25 °C	Solubility (μg/L) at 25 °C	Vapour pressure (Pa) at 25 °C	Water-octanol partition coefficient LogKow (–)	Henry's constant (–)
Linear	Hexamethyl disiloxane	L2	162.38	Colorless liquid	−68	100	0.7619	1.38	0.63	933	5613	4.2	397
	Octamethyl trisiloxane	L3	236.53	Colorless liquid	−86	153	0.8200	1.38	1.04	34.5	445	–	–
	Decamethyl tetrasiloxane	L4	310.77	Colorless liquid	−76	194	0.8536	1.39	1.53	6.76	50	–	–
Cyclic	Hexamethyl cyclotrisiloxane	D3	222.46	Colorless crystalline solid	64.5	134	–	–	–	1563	471	3.85	–
	Octamethyl cyclotetrasiloxane	D4	296.62	Colorless liquid	17.5	172	0.9558	1.40	2.30	56.3	140	4.45	259
	Decamethyl cyclopentasiloxane	D5	370.77	Colorless liquid	−38	210	0.9593	1.40	3.87	17.2	27	5.2	185
	Dodecamethyl cyclohexasiloxane	D6	444.93	Colorless liquid	−3	245	0.9672	1.40	6.62	5.14	3	5.86	104