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Case Study

Using mechanisms of hydrolysis and sorption to reduce siloxanes occurrence in biogas of anaerobic sludge digesters

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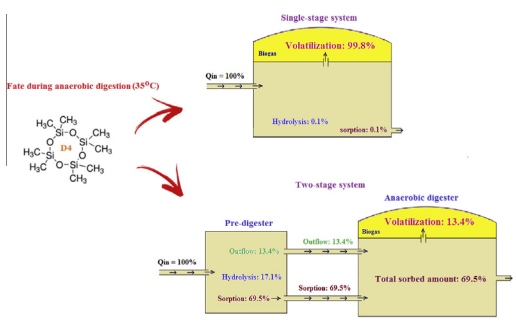
HIGHLIGHTS

- Hydrolysis and sorption constants for sludge (K_d) determined for cyclic siloxanes.
- Hydrolysis increased with temperature and decreased with size of cyclic siloxanes.
- Sorption increased with molecule size with $LogK_d$ values from 1.46 to 3.84.
- During single-stage anaerobic digestion, >91% of siloxanes end up in biogas.
- Cyclic siloxanes volatilization predicted to be mitigated using a pre-digester.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrolysis of hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), dodecamethylcyclohexasiloxane (D6) and dodecamethylcyclohexasilane (D6_silane) and their sorption to digested sludge was studied in batch experiments. Hydrolysis was affected by the type of the compound and the applied temperature, while the relevant half-life values ranged between 0.07 ± 0.01 d (D3, 55 °C) and 48.4 ± 17.1 d (D6_silane, 4 °C). D5 showed the greatest affinity for sorption to digested sludge ($logK_d$: 3.84 ± 3.42), the lowest $LogK_d$ value was found for D3 (1.46 ± 0.95). Prediction of investigated compounds' fate in a single-stage anaerobic digestion system indicated that volatilization seems to be the major fate in both mesophilic and thermophilic conditions. The addition of a pre-digester with 3 d retention time would significantly decrease the expected concentrations of all siloxanes in biogas, enhancing their removal through hydrolysis and sorption to sludge.

1. Introduction

Siloxanes consist of a backbone of silicon and oxygen atoms which are alternated with organic side-chains attached to each silicon atom. These compounds can be found in linear, cyclic or tetrahedral formation with organic groups (Allen et al., 1997). Their physicochemical properties are noteworthy since they are hydrophobic and volatile at the same time depending on their molecular weight. The longer the chain length the lower the water solubility. Furthermore, these compounds are characterized by high stability, biocompatibility, surface activity and lubricating properties (Allen et al., 1997). Siloxanes can undergo hydrolysis in the environment. According to Durham (2005, 2006) this

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process is relatively slow in freshwaters under environmentally realistic conditions. Half-lives of octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) have been estimated to be equal to 16.7 d and 315 d in freshwater at pH 7 and 12 °C, while the rate of hydrolysis was dependent on the pH and temperature. Among different siloxanes, D4 is toxic to sensitive aquatic organisms presenting long-term NOEC lower than 10 μg L^{-1}. D5 does not exhibit adverse effects on fish and water flea at concentrations as high as 17 μg L^{-1} (Wang et al., 2013a) but shows considerable persistence and bioaccumulation (Sparham et al., 2008). Cyclic siloxanes have been also incriminated as potential endocrine disruptors, while they have been implicated in connective tissue disorders, adverse immunologic responses, and liver and lung damage in animal studies (Bletsou et al., 2013).

Due to their rather unusual properties, siloxanes are widely used in many applications such as antifoaming agents, coatings, shampoos, cosmetics (de Arespacochaga et al., 2015) and as a result they end up in sewage treatment plants (STPs). Occurrence of siloxanes at ppb and ppm levels in wastewater and sludge, respectively, has been reported worldwide (Wang et al., 2013b; Bletsou et al., 2013; Van Egmond et al., 2013; Liu et al., 2014) and their fate during activated sludge process has been described (Xu et al., 2013; Wang et al., 2015a,b). Among the different processes that determine the removal of compounds in STPs, volatilization in the aeration tank and adsorption to sludge are the most important pathways for the elimination of siloxanes (Wang et al., 2015a).

Certain semi-volatile siloxanes have also been detected in biogas produced by anaerobically digested sludge in concentrations high enough to damage the gas motors used to convert biogas to electricity (Dewil et al., 2006; Rasi et al., 2010; Raich-Montiu et al., 2014). Despite the frequent detection of siloxanes in sludge and produced biogas, so far, their fate during sludge anaerobic digestion has not been investigated. Additionally, no information is available for the hydrolysis of these compounds at different temperatures used during anaerobic digestion (35, 55 °C), as well as for their sorption potential in anaerobically digested sludge.

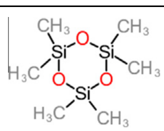
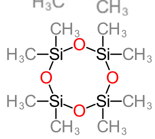
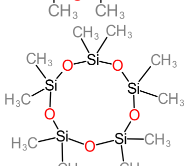
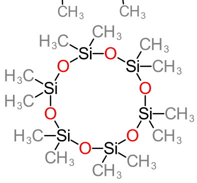
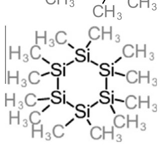
Based on the above, the main objectives of the present study were to investigate hydrolysis of selected cyclic siloxanes (hexamethylcyclotrisiloxane, D3; D4; D5; dodecamethylcyclohexasiloxane, D6; dodecamethylcyclohexasilane, D6_silane) (Table 1) under different temperatures including those typically used in mesophilic and thermophilic digestion (4 °C, 20 °C, 35 °C and 55 °C), and to determine sorption distribution coefficient (K_d) of these compounds in anaerobically digested sludge. Determination of investigated compounds in dissolved and solid phase was accomplished by applying a modified and fully validated previously developed (Bletsou et al., 2013) liquid-liquid extraction – gas chromatography–mass spectrometry method (LLE – GC–MS). A model was developed to predict the fate of investigated compounds during single-stage mesophilic and thermophilic anaerobic sludge digestion and to investigate the contribution of hydrolysis, sorption and volatilization to their elimination. Finally, a two-stage system was proposed to reduce the concentrations of investigated siloxanes in biogas.

2. Materials and methods

2.1. Analytical standards and reagents

High purity analytical standards of D3, D4, D5, D6, D6_silane and tetrakis (trimethylsiloxy)-silane (M4Q) (all >95% purity) were purchased from Sigma-Aldich (Seelze, Germany). M4Q was used as surrogate standard for the analysis. All organic solvents including ethyl acetate, methanol, pentane, dichloromethane and isooctane

Table 1
Abbreviations, structures, molecular weights and physico-chemical properties of target cyclic siloxanes.

Compound	Structure	Molecular weight (g mol^{-1})	[a]Vapour pressure at 25 °C (Pa)	[a]Water solubility at 25 °C (mg/L)	[a]Log K_{OW}	[b]Log K_{AW}	[c]Log K_{OC}
D3		222	1146.6	1.56	3.85	–	3.55
D4		297	131.99	0.056	4.45	2.69[b]	4.17
D5		371	23.198	0.017	5.2	3.13[b]	4.60
D6		445	3.999	0.005	5.86	3.01[b]	5.08
D6_silane		349	–	–	–	–	–

[a] Palczewska-Tulińska and Oracz (2005)
[b] Xu and Kropscott (2012)
[c] Allen et al. (1997)