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Improvement of anaerobic digestion performance by continuous nitrogen removal with a membrane contactor treating a substrate rich in ammonia and sulfide

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HIGHLIGHTS

- Membrane contactor for nitrogen removal in ammonia and particle rich substrates.
- Technology decreases ammonia inhibition and leads to better reactor performance.
- Microbial consortium at high nitrogen and elevated sulfur levels.
- Mono-digestion of slaughterhouse wastewater.

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ABSTRACT

The effect of reduced ammonia levels on anaerobic digestion was investigated. Two reactors were fed with slaughterhouse waste, one with a hollow fiber membrane contractor for ammonia removal and one without. Different organic loading rates (OLR) and free ammonia and sulfide concentrations were investigated. In the reactor with the membrane contactor, the NH_4–N concentration was reduced three-fold. At a moderate OLR (3.1 kg chemical oxygen demand – COD/m^3/d), this reactor performed significantly better than the reference reactor. At high OLR (4.2 kg COD/m^3/d), the reference reactor almost stopped producing methane (0.01 Nl/g COD). The membrane reactor also showed a stable process with a methane yield of 0.23 Nl/g COD was achieved. Both reactors had predominantly a hydrogenotrophic microbial consortium, however in the membrane reactor the genus *Methanosaeta* (acetoclastic) was also detected. In general, all relevant parameters and the methanogenic consortium indicated improved anaerobic digestion of the reactor with the membrane.

1. Introduction

In anaerobic digestion (AD) the essential nutrients sulfur and nitrogen are present in reduced oxidation state. While a well-balanced nutrient supply is indispensable for AD, several substrates like swine and poultry manure or certain industrial residues contain a surplus of these elements. This element surplus can lead to several difficulties. Ammonia released into the aqueous environment is toxic for fish, decreases dissolved oxygen in water bodies and causes corrosion. Sulfide is also toxic and corrosive. Furthermore, it has an unpleasant smell. Beside these environmental and technical related problems, the un-ionized forms H_2S and NH_3 are considered as inhibitory for microbial conversion processes (Chen et al., 2008). NH_3 diffuses into cells where it causes potassium depletion and a change of the intercellular pH (Sprott et al., 1984) and as a result it affects methanogenic microorganisms (Sprott and Patel, 1986). The concentration of nitrogen that causes a 50% reduction in methane yield has been reported as being between 1.7 and 14 g/l total ammonium nitrogen (Chen et al., 2008). The inhibitory concentrations for H_2S causing the same decrease in methane yield range from 50 to 1000 mg/l (Isa et al., 1986). Hansen et al. (1999) showed that inhibition occurs at lower concentrations in the combined presence of NH_3 and H_2S.

In general, the methanogens are less tolerant of inhibitors than microorganisms from the other trophic groups of the AD process and thus they are more likely to cease methane production in

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the case of inhibition (Kayhanian, 1994). According to Hansen et al. (1998), the acetoclastic species are the rate limiting step. However, many recent studies showed that stable processes can also be achieved by predominant hydrogenotrophic methanogenesis. *Methanosarcina barkeri* and *Methanosaeta concilii* are especially sensitive to free ammonia concentrations (Sprott and Patel, 1986). Generally, methane is produced via the acetoclastic pathway or via the hydrogenotrophic pathway (reduction of CO_2 with hydrogen). Moreover, the growth rate of acetoclastic methanogens is affected at lower ammonia concentrations than that of hydrogenotrophic microorganism (Angelidaki and Ahring, 1993). Thus, it can be expected that in reactors with high ammonia concentrations, hydrogenotrophic pathways are predominant.

Several concepts have been scientifically discussed to counteract the inhibition effects of NH_3 and H_2S. Approaches for ammonia removal include ammonia stripping (Zhang and Jahng, 2010), ion exchange (Wirthensohn et al., 2009), and membrane contactor processes (Lauterböck et al., 2012). Adaptation of microorganisms (Calli et al., 2005) and co-digestion (Callaghan et al., 1999) are additional possibilities. In order to control H_2S inhibition, measures like dilution, co-digestion or adaptation are also possible. Moreover, there are other measures suggested in literature such as addition of iron salts (for example iron (III) chloride) (Deublein and Steinhauser, 2008) or moderate oxygen supply (van der Zee et al., 2007). The technical thresholds for H_2S, 0.1–200 mg/Nm^3 (Deublein and Steinhauser, 2008), are lower than the inhibitory concentrations thus a common approach is to remove H_2S from the biogas stream and not from the digestion process.

The current study investigates an option to reduce inhibition and improve the overall process performance by continuous NH_3 removal with a membrane contactor. This technology allows a gaseous transfer between two liquid phases. To accomplish this mass transfer, a microporous hydrophobic membrane separates an NH_3 rich feed and an acidic absorption solution. The gas filled pores of the membrane are the actual transfer area. The difference in NH_3 partial pressure between the two liquid phases is the driving force for the mass transfer.

As shown in Waeger and Fuchs (2012), hollow fiber membrane contactors can remove NH_3 from anaerobic digestate and as shown in Lauterböck et al. (2012), also directly from an operating AD reactor. The advantage of the latter is that it counteracts ammonia inhibition during AD, as a consequence this leads to a better degradation and a higher gas yield. Furthermore, the study by Lauterböck et al. (2013) identified the great potential of improving the NH_3 removal by designing a customized membrane.

In the current study, the nitrogen removal with hollow fiber membrane contactors was used to evaluate the impact of lower NH_3 levels on the process perfomance of an AD process under synergistic inhibition of H_2S and NH_3 and medium and high organic loading rates (OLR). For 425 days, laboratory-scale reactors were operated with slaughterhouse waste and thoroughly monitored under various H_2S concentrations, high organic loading rates and short hydraulic retention times (HRT).

2. Methods

2.1. Batch degradation test

The effect of various H_2S and NH_3 concentrations on AD was tested in advance to the continuous experiment. Seven degradation tests to determine the total biogas production were carried out at 37 °C, one reference test and six tests supplemented with 1, 5, 10, 18, 28 and 37 mg/l un-ionized H_2S (Section 2.7). The H_2S concentrations in the degradation tests were set with a sodium sulfide hydrate solution (20 g/l S^{2-}) after the determination of the H_2S concentration in the reference test. The prevailing condition in the reference test was 5.7 g/l NH_4–N, 57.1 g COD/kg, 3.1% dry matter (DM), 1.1% organic dry matter (oDM), 0.1 mg/L un-ionized H_2S and a pH of 8.3.

The batch degradation tests were carried out in triplicate and according to the guideline VDI 4630. The anaerobic seed culture was obtained from a mesophilic anaerobic digester treating pig slurry, maize silage and other agricultural residual wastes. The fermenter was running at 40 days HRT and an OLR of 2–3 kg chemical oxygen demand (COD)/m^3/d. The applied substrate was the same as used in the continuous experiment from period 1 to period 3 (substrate 1, see Table 3 and Section 2.2).

2.2. Set-up of continuous experiments

Two laboratory scale reactors (1 L laboratory glass bottles with a working volume of 800 ml) were operated in semi-batch mode continuously for 425 days. Reactor A was the membrane reactor with a hollow fiber membrane contactor module that was directly submerged into the fermentation broth. A peristaltic pump circulated sulfuric acid (120 mM, 38.0 ± 0.5 °C) through the lumen of the fiber tubes. Reactor B was the reference reactor with the same setup, except without the ammonia removal system. To maintain an appropriate temperature, the acid bottle and the reactors were placed in a water bath at 38.0 ± 0.5 °C. Further details on the experimental set-up are described in Lauterböck et al. (2012). Daily feeding and sample taking was performed by means of a fully automated programmable syringe pump. This allowed more stable process conditions because of constant and accurate dosage of the feed and sample volume. The biogas production was determined with a measuring device connected to a computer via a programmable controller. For weekly analyses of the gas composition, gas samples were taken out of the headspace of the reactor with a 20 ml syringe. Continuous stirring (300 rpm) was applied in both reactors.

Prior to the actual experiments, a start-up of the two reactors was conducted for 75 days to test and optimize the functionality of the system. During this time, the fermenters were operated at the same conditions as in the subsequent test period 1. The hydraulic retention time (HRT) was constant throughout the test period. The organic loading rate (OLR) was increased once to apply an extra stress for the two reactors and to provoke inhibition. The H_2S concentrations in the reactors were set with sodium sulfide

Table 1
Prevailing conditions of both reactors.

	Day	Duration [days]	HRT [days]	OLR		H_2S in liquid [mg/l]
				[kg COD/m^3*d]	[kg oDM/m^3*d]	
Period 1	1–86	86	21.1	3.1	1.1	0.4
Period 2	87–160	74	21.1	3.1	1.1	1.3
Period 3	161–246	86	21.1	3.1	1.1	3.3
Period 4	247–363	117	21.1	4.2	1.5	3.3
Period 5	354–425	62	21.1	4.2	1.5	Decreasing to 0.8