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Selective inhibition of methanogenic archaea in leach bed systems by sodium 2-bromoethanesulfonate

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HIGHLIGHTS

- Enhancement of acidification during leaching of lignocellulosic biomass by selective suppression of methanogenic archaea using 2-bromoethansulfonate (BES).
- Derivation of an optimal BES inhibition concentration in eudiometer batch tests.
- Determination of volatile fatty acid and methane yields during inhibition in BMP tests.
- Validation of the inhibitory effect of BES in a semi-technical leach bed system continuously fed with urban lignocellulosic biomass.

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ABSTRACT

Lignocellulosic biomass is a feasible feedstock for biogas production through anaerobic digestion. Leaching, as part of a two-stage fermentation concept, is the most meaningful strategy to convert the substrate's organic carbon compounds into volatile fatty acids (VFA) during acidification. Various chemicals have been investigated so far to enhance the process of acidification by selective inhibition of methanogens. Hardly any of them were evaluated for technical leach bed systems. In order to enhance the process of acidification the inhibitory effect of sodium 2-bromoethanesulfonate (BES) on the activity of methanogens was evaluated. An optimal inhibition concentration of 40 mM BES was found in lab-experiments and was verified in a pilot scale leach bed system, which was fed with urban lignocellulosic biomass. Overall, 2200 g/m^3 of acetic acid were achieved during the leaching process by a one-time addition of BES. As VFA concentration levels were observed to be constant, BES approved suitable.

1. Introduction

Reflecting the increased sense of our society for sustainability, the generation of renewable energy through co-fermentation of urban lignocellulosic biomass and domestic wastewater is a promising and new concept that can be implemented either centralized or decentralized (Lübken et al., 2007a,b; Nettmann et al., 2008a,b; Kosse et al., 2015). Decentralized systems are known to be economically and ecologically reasonable approaches, especially for rural areas (Lübken et al., 2007a,b; Wichern et al., 2008). Due to the increasing volumes of lignocellulosic biomass from public green areas that are mostly left unused (Kosse et al., 2015), it is meaningful to implement such systems also in urban areas. Various types of decentralized systems exist, which also include leach bed concepts. Such engineered systems have been widely

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utilized in small scale for the fermentation of fibrous biomass in one-stage operation, as well as successfully in two-stage concepts, where the leach bed system has been coupled, for instance, to a UASB (Upflow Anaerobic Sludge Blanket) reactor (Han et al., 2005; Lehtomäki et al., 2008; Cysneiros et al., 2011, 2012; Nkemka et al., 2014; Gehring et al., 2015). In that way, the leach bed system has been used solely for hydrolysis and acidification purpose, which bears the advantage of maintaining the optimal hydrolytic and methanogenic conditions separately for involved microbial consortia (Han et al., 2005; Klocke et al., 2007; Cysneiros et al., 2012). Further advantages compared with one-stage approaches arise from higher methane yields, lower energy demands, application of higher organic loading rates (OLR), and the lesser sensitivity to toxic shocks and variations in the feedstock (Lehtomäki et al., 2008; Parawira et al., 2008; Nkemka et al., 2014). In practice, however, such two-stage concepts are still rarely implemented, since they suffer from high initial investment costs (Nkemka et al., 2014), while it still keeps challenging to isolate and maintain the individual processes like hydrolysis/acidification and acetogenesis/methanogenesis from each other. As the efficiency of the second-phase acetogenesis/methanogenesis is highly depending on the performance and intermediate products of hydrolysis/acidification (Yan et al., 2014), various strategies are driven in order to selectively suppress methanogenic activity such as pH modifications, product inhibition, or microaeration (Bouallagui et al., 2004; Han et al., 2005; Lim and Wang, 2013). However, the probably most performed approach for this purpose is the addition of a chemical inhibitor that is able to selectively suppress methanogens. Such inhibitory substances include, amongst others, 2-bromoethanesulfonate (BES), chlorethanesulfonate (CES), chloroform, trichloroacetic acid (TCA), fluoromethane, fluoroacetate, 2-nitroethanol, lumazine, 2-mercaptoethanesulfonate (MES) or propiolic acid (Liu et al., 2011). Among these inhibitors BES is currently the most potent and frequently used one, but its applied concentration varies from μM to mM range, according to its field of application. It is therefore required to investigate its optimal inhibition concentration beforehand and individually. At this, it is expected that pure cultures of methanogenic archaea can be inhibited at lower concentrations, while higher concentrations are expected to successfully suppress consortia of methanogens.

When applied, 2-bromoethanesulfonate will lead to an irreversible inhibition of methanogenic activity, as well as to an accumulation of acetate and H_2 (Chidthaisong and Conrad, 2000). The decisive factor for the inhibitory effect of BES lies in its structural analogy towards methyl-coenzyme M (2-mercaptoethanesulfonate), which is only found in methanogenic archaea. Under strictly anaerobic conditions methyl-coenzyme M (CH3-S-CoM) reacts with the electron donor coenzyme B (HS-CoB) to form the heterodisulfide CoM-S-S-CoB and methane (CH_4) (Nettmann et al., 2008a,b). This reaction is catalyzed through methyl-coenzyme M reductase (MCR) and its prosthetic group F430 containing Ni(I) (Nettmann et al., 2008a,b). Both coenzymes M and B are regenerated through a heterodisulfide reductase reaction. When applying BES in solution it oxidizes Ni(I)F430–Ni(II)F430, bromide, ethane and sulfite thus leading to an inhibitory effect as Ni(I)F430 is no longer available to participate in the reaction mechanism.

Nowadays it has become apparent that leach bed systems are a preferred technology to treat lignocellulosic biomass in the context of anaerobic digestion. Up to date various studies have been performed on enhancing the methane yield from anaerobic digestion processes also in connection with phase separation. However, there is hardly information available on the effect of an inhibitory substance during the operation of a leach bed system under practical operational conditions. As results from laboratory experiments have neither been transferred to technical scale, it remains unclear whether previous investigated concentrations will have the desired inhibitory effect on a technical scale. The objective of this study was to fill this gap by investigating the optimal inhibition concentration of 2-bromoethanesulfonate for fermentation of urban lignocellulosic biomass in batch experiments and to transform the obtained results to a semi-technical leach bed system that is operated with the same substrate in monofermentation and in a continuous feeding/withdrawing mode. In that way the inhibitory effect of BES is verified under practical operational conditions for enhancement of hydrolysis and acidification in two-stage biogas systems.

2. Materials and methods

2.1. Lignocellulosic biomass and sewage sludge

The substrate used within the experiment was grass, which was frozen after harvesting at 253.15 K before its use in the leach bed system. The substrate had a total solids (TS) content of 231 g/kg and a COD of 1380 g/kg. Digested sludge from the wastewater treatment plant "Ölbachtal" (Ruhrverband) in Bochum, Germany was used as inoculum. The sludge had a TS of 21.5 g/kg, COD of 6300 g/kg, total nitrogen (TN) of 1.863 mg/kg and total phosphorus (TP) of 0.057 mg/kg.

2.2. Eudiometer

Determination of the optimal inhibition concentration was conducted using 12 eudiometer batch digesters. Each eudiometer consisted of a batch digester with a capacity of 750 cm^3, which was connected to a eudiometer tube through a connecting tube of 6 mm diameter. The eudiometer was a long shape tube with a total volume of 400 cm^3 and a diameter of 30–35 mm. It was graduated from the top down (division unit 5 cm^3). The upper end of the eudiometer tube had a fixed glass valve to take gas samples and to set the scale to zero. On the lower edge of eudiometer there was a glass olive from which a pipe link went to an external leveling vessel that contained a sealing liquid for the eudiometer tube. The sealing liquid was made from 30 cm^3 of sulfuric acid (H_2SO_4) ($\rho = 1.84$ g/cm^3), added to 1 dm^3 of distilled water. 200 g of sodium sulfate