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Characterization of the sulfate reduction process in the anaerobic digestion of a very high strength and sulfate rich vinasse

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HIGHLIGHTS

- Sulfate reduction of a very high strength and sulfate rich vinasse was characterized.
- Close mass balances indicated that the data were suitable for dynamic modeling.
- Variations in biogas quality (by H_2S_{gas}) were highest at a SO_4^{2-}/COD ratio of 0.05.
- H_2S_{aq} and $[H_2S]_{free}$ inhibited methanogens and SRBs at SO_4^{2-}/COD ratios $\geqslant$0.10.
- Propionate uptake at SO_4^{2-}/COD ratios $\leqslant$0.10 suggested strong contribution of pSRB.

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ABSTRACT

This article characterizes the sulfate reduction process in the anaerobic digestion of a very high strength and sulfate rich vinasse, where chemical oxygen demand (COD) and sulfate (SO_4^{2-}) pulses were applied at different SO_4^{2-}/COD ratios to obtain dynamical responses. The results showed an increase in H_2S_{gas} of up to 33%, when influent COD (inf_COD) and influent SO_4^{2-} (inf_SO_4^{2-}) increased at a SO_4^{2-}/COD ratio of 0.05. A decrease of inf_COD together with an increase of inf_SO_4^{2-} caused propionic acid degradation (up to 90%), suggesting strong contribution of propionate degrading sulfate reducing bacteria at SO_4^{2-}/COD ratios $\leqslant$0.10, in contrast to literature results. The inf_COD and inf_SO_4^{2-} fluctuations at a SO_4^{2-}/COD ratio of 0.10 caused inhibition by H_2S_{aq}, $[H_2S]_{free}$ and propionic acid to sulfate reducing bacteria (SRBs), methanogens or both. At a SO_4^{2-}/COD ratio of 0.20 this inhibition became severe for methanogens and SRBs, leading to reactor failure. Mass balance calculations showed COD and sulfur recoveries from 90% to 98% in most cases. Increments of inf_COD within a constant SO_4^{2-}/COD ratio (0.05 or 0.10) accumulated as effluent COD rather than as COD_CH_{4gas}, showing deterioration of the anaerobic digestion, while the sulfur was displaced to the gas phase at a SO_4^{2-}/COD ratio of 0.05 or to the liquid phase at SO_4^{2-}/COD ratios $\geqslant$0.10. Based on the closed mass balances results, the data presented here are considered reliable for calibrating mathematical models, when sulfate reduction in the anaerobic digestion of a very high strength and sulfate rich vinasse is of primary interest.

1. Introduction

Many industrial processes, especially in the food and fermentation industries, generate wastewaters with high levels of organic matter and sulfate [1]. Vinasse obtained from ethanol distillation in the sugar cane industry is a typical example of a sulfate rich liquid substrate [2]. The anaerobic digestion of vinasse promotes the activity of sulfate reducing bacteria (SRB) producing H_2S, which is distributed among H_2S_{aq} ($[H_2S]_{free}$, HS^- and S^{2-}), insoluble metallic sulfides and H_2S_{gas}.

Sulfate reduction processes have been studied by many authors [3–12] by using synthetic wastewaters to feed upflow anaerobic sludge bed reactors (UASB). An overview of previous works is given in Table 1. These studies have mainly focused on the inhibitory

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Nomenclature

COD	chemical oxygen demand concentration g COD L^{-1}
COD_ΔSO_4^{2-}	COD of reduced SO_4^{2-} used for COD mass balances g COD d^{-1}
COD_CH_{4gas}	COD of gas CH_4 used for COD mass balances g COD d^{-1}
eff_COD	effluent COD used for COD mass balances g COD d^{-1}
eff_SO_4^{2-}	effluent SO_4^{2-} used for sulfur mass balances mg S d^{-1}
VFAs	volatile fatty acids mg L^{-1}
HRT	hydraulic retention time d
H_2S_{aq}	concentration of total aqueous H_2S mg S L^{-1}
HS^-	concentration of ionized H_2S mg S L^{-1}
$[H_2S]_{free}$	concentration of free H_2S mg S L^{-1}
H_2S_{gas}	concentration of H_2S in biogas mg S L^{-1}
inf_COD	influent COD (as g COD d^{-1} for COD mass balance consistency) g COD L^{-1}
inf_SO_4^{2-}	influent SO_4^{2-} (as mg S d^{-1} for sulfur mass balance consistency) g SO_4^{2-} L^{-1}
OLR	organic loading rate g COD L_R^{-1} d^{-1}
SLR	sulfate loading rate g SO_4^{2-} L_R^{-1} d^{-1}
S_H_2S_{gas}	H_2S in biogas used for sulfur mass balances mg S d^{-1}
S_HS^-	ionized H_2S in the effluent used for sulfur mass balances mg S d^{-1}
S_$[H_2S]_{free}$	free H_2S in the effluent used for sulfur mass balances mg S d^{-1}
TOC	total organic carbon concentration mol C L^{-1}
TKN	total kjeldahl nitrogen concentration mol N L^{-1}
TP	total phosphorous concentration mol P L^{-1}
Vup	liquid upflow velocity m h^{-1}

Table 1
Values of COD, SO_4^{2-} and SO_4^{2-}/COD ratios in synthetic wastewaters used to study sulfate reduction in UASB reactors.

COD (g COD L^{-1})	SO_4^{2-} (g SO_4^{2-} L^{-1})	SO_4^{2-}/COD ratios (w/w)	References
5	0.3–30	0.06–6	[3]
2.5	5	2	[4]
0.5	0.03–0.6	0.06–1.2	[5]
1.5–4	0.75–8.3	0.1–2	[6]
0.53–2.54	1.2–4.55	1.78–2.5	[7]
0.1–3	0.45–1.8	0.6–4.5	[8,9]
5.14–6.8	0.28–1.36	0.05–0.2	[10]
1.87–2.63	1.5–1.8	0.57–0.8	[11,12]

effect of H_2S_{aq} and $[H_2S]_{free}$, the influence of operational parameters and the assessment of competition between SRBs and methanogens, whereas the gas phase hydrogen sulfide produced from the sulfate reduction process has received less emphasis.

Typically, the ratio SO_4^{2-} to chemical oxygen demand (COD) in sugar cane vinasse (as g SO_4^{2-} g COD^{-1}) ranges from 0.05 to 0.10 [13] while maximum values of 0.22 have been reported [14]. Sulfate reduction at those SO_4^{2-}/COD ratios has been studied [3,5,6,10] (Table 1). However, knowledge about sulfate reduction of substrates at very high COD concentration of vinasses (between 30 and 130 g COD L^{-1}, [13]) is needed. The dilution of wastewater streams may reduce the high COD content of vinasse, but in general this approach is considered undesirable because of the increase in the total volume of wastewater that must be treated [15]. Successful treatment during the anaerobic digestion of very high strength and sulfate rich vinasse has been reported [16–18]. COD removal efficiencies up to 71% at COD concentrations between 36 and 100 g COD L^{-1} and organic loading rates between 5 and 24 g COD L^{-1} d^{-1} have been achieved [16–18].

The production and characteristics of vinasse are variable and dependent on the feed stocks and the ethanol production process. Wash water used to clean the fermenters, cooling water blow down, and boiler water blow down may all be combined with the vinasse and contribute to its concentration variability [13]. The variations in the COD and SO_4^{2-} concentrations of vinasse may cause dynamical responses in the sulfate reduction process during the anaerobic treatment, influencing the reactor performance as well as the biogas quality and the performance of the gas treatment processes. Although, modeling and simulation are useful tools to predict these variations, dynamical data of the anaerobic digestion of very high strength and sulfate rich vinasse was not found in literature [2]. A low time consuming and appealing alternative to obtain this data is to evaluate the dynamical response of a continuous reactor after specific substrate pulses [19].

Therefore, the research described in this article characterizes the sulfate reduction process in the anaerobic digestion of a very high strength and sulfate rich vinasse by means of giving COD and SO_4^{2-} pulses at different SO_4^{2-}/COD ratios to obtain dynamical responses.

2. Materials and methods

2.1. Experimental setup

The 3.5 L working volume UASB reactor (as the sum of the sludge bed, the sludge blanket and the settler volumes) consisted of an acrylic transparent column with an internal diameter of 8 cm and a height of 70 cm. The sludge level in the reactor was set to 40% of the reactor working volume. Hot water was circulated through a jacket to ensure a temperature of 35 ± 1 °C during the UASB reactor operation. Sludge temperature and effluent pH were measured online and data stored with a data acquisition system. The influent vinasse supply tank was constantly stirred at 50 rpm. A schematic representation of the experimental setup used during the experiments is shown in Fig. 1.

2.2. Seed sludge

Sludge was obtained from a 3600 m^3 UASB reactor treating vinasse (Heriberto Duquesne, Santa Clara, Cuba). After a 55 days startup and acclimatization period, granular sludge with the following characteristics was obtained: sludge volume index (16.7 ml g TSS^{-1}), average granular size (4 mm), settling velocity (47.2 m h^{-1}), volatile suspended solids (47.4 g VSS L^{-1}), and sulfidogenic (0.25 g COD_ΔSO_4 g VSS^{-1} d^{-1}) and methanogenic (0.33 g COD-CH_4 g VSS^{-1} d^{-1}) activities (to vinasse).

2.3. Substrate feed

A sample of 60 liter of sugar cane vinasse was obtained from a distillery plant in Sancti Spiritus, Cuba and immediately stored at −20 °C to avoid excessive biodegradation. The COD concentration of vinasse was adjusted by adding tap water as required by the experiments. To increase the sulfate concentration of vinasse, Na_2SO_4 was used ensuring that sodium concentration (<3.3 g L^{-1}) remained below the inhibition limit of 8 g L^{-1} [15]. The characteristics of the raw vinasse are shown in Table 2.