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Unraveling the influence of the COD/sulfate ratio on organic matter removal and methane production from the biodigestion of sugarcane vinasse

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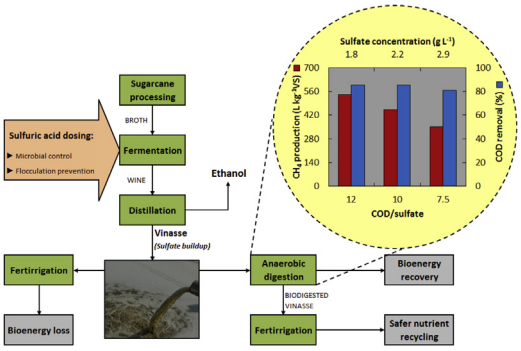
HIGHLIGHTS

- The influence of sulfate reduction on sugarcane vinasse biodigestion was assessed.
- Electron diversion to sulfidogenesis was negligible at COD/sulfate ratios above 25.
- Organic matter degradation was not greatly affected by sulfidogenesis.
- Higher sulfate concentrations led to decreased methane production from vinasse.
- Acetate buildup increased both methane production and COD removal rates.

GRAPHICAL ABSTRACT



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ABSTRACT

Throughout the sugarcane harvest, it is common for sulfate to accumulate in the vinasse of sugar and ethanol plants. However, little is known regarding the influence of sulfate on the anaerobic digestion (AD) of vinasse, which may lead to severe performance losses. This study assessed the influence of various COD/sulfate ratios (12.0, 10.0 and 7.5) on both COD removal and methane (CH_4) production from sugarcane vinasse AD. Batch assays were conducted in thermophilic conditions. At a COD/sulfate ratio of 7.5, CH_4 production was 35% lower compared with a ratio of 12.0, considering a diversion of approximately 13.6% of the electron flow to sulfidogenesis. The diversion of electrons to sulfidogenesis was negligible at COD/sulfate ratios higher than 25, considering the exponential increase in CH_4 production. Organic matter degradation was not greatly affected by sulfidogenesis, with COD removal levels higher than 80%, regardless of the initial COD/sulfate ratio.

Abbreviations: AcH, acetic acid; AD, anaerobic digestion; A-MA, aceticlastic methanogenic archaea; A-SRB, aceticlastic sulfate-reducing bacteria; BOD, biochemical oxygen demand; BuH, butyric acid; COD, chemical oxygen demand; FID, flame ionization detector; H-MA, hydrogenotrophic methanogenic archaea; H-SRB, hydrogenotrophic sulfate-reducing bacteria; MA, methanogenic archaea; PA, partial alkalinity; PrH, propionic acid; SCOD, soluble chemical oxygen demand; SRB, sulfate-reducing bacteria; TCD, thermal conductivity detector; TCOD, total chemical oxygen demand; TDS, total dissolved sulfide; TKN, total Kjeldahl nitrogen; TS, total solids; VFA, volatile fatty acid; VS, volatile solids; VSS, volatile suspended solids.

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Nomenclature

Symbols

C^{t}_{CH4}	concentration of methane in biogas at time "t"
C^{SCOD}	organic matter concentration (as SCOD – model)
C^{SO4}	sulfate concentration (model)
C^{SCOD}_{O}	initial organic matter concentration (as SCOD – model)
C^{SO4}_{O}	initial sulfate concentration (model)
C^{SCOD}_{R}	residual organic matter concentration (as SCOD – model)
e	Euler's number
ER_{SCOD}	total SCOD removal
ER^{CH4}_{SCOD}	SCOD removal via methanogenesis
ER^{SO4}_{SCOD}	SCOD removal via sulfidogenesis
k_1^{SCOD}	first-order kinetic coefficient for SCOD
$k_1^{SCOD,}$	specific first-order kinetic coefficient for SCOD
k_1^{SO4}	first-order kinetic coefficient for sulfate
$k_1^{SO4,}$	specific first-order kinetic coefficient for sulfate
K_S	saturation constant
P	pressure
P_M	methane production potential
P'_M	specific methane production potential
R	ideal gas constant
R_M	methane production rate
R'_M	specific methane production rate
$SCOD_O$	initial organic matter concentration (as SCOD)
$SCOD_R$	residual organic matter concentration (as SCOD)
$SO4_O$	initial sulfate concentration
$SO4_R$	residual sulfate concentration
T	temperature
V^{t}_{CH4}	cumulative methane production at time "t"
V^{t-1}_{CH4}	cumulative methane production at time "t−1"
$V_{headspace}$	volume of the headspace
V_M	cumulative methane production (model)
λ	lag phase

1. Introduction

The application of anaerobic digestion (AD) to vinasse, which is the primary wastewater from ethanol production (Fuess and Garcia, 2014), has been widely studied, in light of the suitability of this wastewater for methane (CH_4) production and bioenergy recovery (Fuess and Garcia, 2015; Moraes et al., 2014). Previous studies have reported various operational conditions and reactor configurations (upflow sludge blanket and fixed-film reactors, sequencing batch reactors, and fluidized-bed reactors, among others) for processing vinasses from different feedstocks, such as sugarcane, beet, corn, cassava and cellulosic materials (Wilkie et al., 2000). Organic matter removal efficiencies and CH_4 yields as high as 80% and 0.31 $Nm^3CH_4\,kg^{-1}$ chemical oxygen demand (COD) (Kumar et al., 2007), respectively, have been achieved.

Despite the successful results of previous reports, the presence of specific compounds in vinasse, such as recalcitrant (melanoidins and phenols) and interfering (primarily sulfate) compounds (Ferreira et al., 2011; Fuess and Garcia, 2014, 2015), must be carefully considered based on the potential inhibition of the anaerobic microbial populations, especially methanogenic archaea (MA). Among such compounds, the presence of average-to-high levels of sulfate in vinasses from sugarcane is highlighted in this study. Sugarcane-based distilleries widely employ sulfuric acid to prevent microbial contamination and yeast flocculation in fermentation vessels (Barth et al., 2014), leading to sulfate concentrations as high as 9 $g\,L^{-1}$ in vinasse (Table 1). The use of molasses, a residual carbohydrate-rich solution from sugar plants, in the production of ethanol tends to enhance the levels of sulfate in vinasse, because sulfuric acid is also employed in the sugar clarification step (Fuess and Garcia, 2015).

The application of sulfate-rich wastewaters to AD systems stimulates the sulfidogenesis process, in which the sulfate is reduced primarily to sulfide by a specific group of microorganisms known as sulfate-reducing bacteria (SRB) (Lens et al., 1998; Vilela et al., 2014). SRB compete with MA for common substrates, such as acetate and hydrogen (H_2) (Chen et al., 2008; Vilela et al., 2014), limiting the extraction of energy through CH_4. The toxicity of sulfide may also suppress methanogenic activity in AD systems, either by directly permeating the cell membrane as the non-ionized form (H_2S) and denaturing specific proteins or by indirectly enhancing the precipitation of essential metals as the ionized forms (HS^- and S^{2-}) (Camiloti et al., 2014; Chen et al., 2008; Vela et al., 2002). However, during sulfate shortage, populations of established SRB may act as acetogenic bacteria (Damianovic and Foresti, 2009; Vilela et al., 2014), partially oxidizing organic acids to acetate and consequently enhancing the activity of MA in a syntrophic association (Vela et al., 2002).

Table 1
COD, sulfate concentration and COD/sulfate ratio of raw sugarcane vinasse according to the type of ethanol fermentation feedstock.

Feedstock	COD ($g\,L^{-1}$)	Sulfate ($g\,L^{-1}$)	COD/sulfate	Reference
Juice	33.0	0.76	43.4	Costa et al. (1986)
	42.0	1.3	32.3	Ferreira et al. (2011)
	13.4	0.71	18.9	Christofoletti et al. (2013)
Molasses	65.0	6.4	10.1	Costa et al. (1986)
	51.2	3.5	14.6	Bories et al. (1988)
	40.9	4.65	8.8	Reis et al. (1988)
	31.0	4.3	7.2	Jain et al. (2005)
	110.0–190.0	7.5–9.0	12.2–25.3	Mohana et al. (2009)
Juice + molasses	45.0	3.73	12.1	Costa et al. (1986)
	36.0–49.0	2.3–2.9	14.4–16.7	Siqueira et al. (2013)
	22.9[a]	1.7	13.5	Fuess et al. (2017a)
	24.6	3.7	6.6	Fuess et al. (Unpublished results)
	32.1	3.8	8.4	Fuess et al. (Unpublished results)
	22.9	2.3	9.9	Fuess et al. (Unpublished results)

Note: [a]Soluble COD.