

Resilience of methanogenesis in an anaerobic reactor subjected to increasing sulfate and sodium concentrations



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ABSTRACT

Various types of industrial activities produce saline and/or sulfate-rich effluents and could use the anaerobic treatment process as the core technology. However, both salinity and sulfate can interfere with the process. This study investigated the performance of a UASB reactor in the treatment of synthetic wastewater containing glucose, acetate, methanol and sodium sulfate. The reactor had a useful volume of 10.5 L and was operated for 266 days at the hydraulic detention time of 15.6 h. The influent chemical oxygen demand (COD) was kept at 2000 mg L⁻¹ whereas sodium sulfate concentrations increased along eighteen experimental phases, defined by the applied COD/[SO₄²⁻] ratio. Influent sulfate and sodium concentrations ranged from 25 to 10,000 mg L⁻¹ and from 750 to 5350 mg L⁻¹, respectively. The progressive increase of sodium and sulfate concentration and the consequent decrease of the COD/[SO₄²⁻] ratios affected the reactor's performance, but the average COD removal efficiency remained above 80%. The observed partial process inhibition can be attributed to the synergistic effect resulting from the sulfide generated and the presence of sodium cations.

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1. Introduction

Anaerobic systems have been employed in various industrial wastewater treatment processes, including those containing saline and sulfurous compounds – however, both cations and sulfates can interfere with the treatment process. Residues from food processing industries (salt refineries, fish processing and dairy), from petrochemical and chlorine chemical industries, tannery companies and pharmaceutical industries are some examples of residues with these characteristics.

Sulfate-reducing bacteria (SRB) promote competitive interactions with the consortium of methanogenic archaea (MA). The greater affinity for hydrogen causes the SRB to outcompete the hydrogenotrophic methanogens. The BRS can use acetate that also may compete with acetoclastic methanogenic [14,12]. Notwithstanding, Damianovic and Foresti [3], have shown that efficient treatment of sulfate-rich wastewater is feasible, since the association of methanogenesis and sulfidogenesis is possible depending on the electron donor availability.

According to O'Reilly and Colleran [15], the main parameter that controls the interactions between SRB and MA is the relationship between the amount of available organic substrates and sulfate. As organic matter is expressed as chemical oxygen demand (COD), the COD/[SO₄²⁻] ratio is usually considered the process control parameter. Theoretically, when the COD/[SO₄²⁻] ratio is equal to 0.67, there is enough sulfate to drive the electron flow to sulfidogenesis and not to methanogenesis. In situations where the COD/[SO₄²⁻] ratio is above 0.67, the sulfidogenesis and methanogenesis can occur simultaneously. Below this value, sulfidogenesis tends to be predominant, given that sulfide generation can partially inhibit methanogenesis, thus affecting the overall organic matter removal. However, there are contradictory results in the literature regarding the effects of sulfate reduction on the anaerobic process. While some authors have reported competition between SRB and MA by acetate and hydrogen, others have reported on a syntrophic relationship between these two bacterial groups.

SRB microorganisms are a very heterogeneous group that comprises representatives of the domains bacteria and Archaea, which use sulfate as the final electron acceptor. These microorganisms have been found in psychrophilic and hyperthermophilic environments, as well as in freshwater and hypersaline environments [8]. They have the ability to metabolize a variety of compounds,

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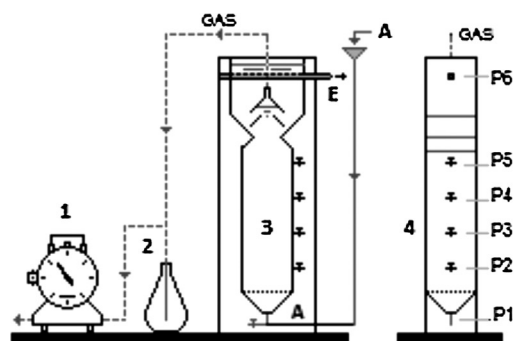


Fig. 1. Experimental setup.

such as hydrogen, carboxylic acids, alcohols, sugars and substituted aromatics. The oxidation of organic substrates by SRB can occur completely or incompletely, forming carbonic gas or acetate, respectively, as the main final products besides sulfide. The incomplete oxidation of organic substrates produces acetate, which is then available to other microorganisms [14].

Several researchers have also reported on methanogenic inhibition due to high salinity and toxicity of biogenically produced sulfide by SBR. Sulfide affect both SBR and MA thus reducing treatment efficiency of anaerobic process in mesophilic reactors [19,7,12].

As for salinity, the major problems encountered in the biological treatment of these effluents are due to several possible reasons: the need to adapt to saline environments of conventional cultures (non-halophilic); sensitivity to ionic strength changes caused by excess of cations; reduced substrate degradation rates and; increased suspended solids content in the final effluent [19]. There can also be loss of cell activity, plasmolysis, and water loss from the cell into the medium [4].

Several types of reactors have been used in studies of methanogenic and sulfidogenic processes, as for example horizontal-flow anaerobic fixed bed reactors [17,3]; anaerobic sequencing batch reactors [6]; and also upflow anaerobic sludge blanket reactors – UASB [12] used in different wastewater treatments.

This study was meant to evaluate the performance of the anaerobic process in a UASB reactor treating a synthetic wastewater subjected to increasing concentrations of sodium and sulfate. The COD/[SO₄²⁻] ratio ranged from 75.6 to 0.2 and Na⁺ cation concentration between 0.76 gL⁻¹ and 5.5 gL⁻¹.

2. Material and methods

2.1. Reactor

An acrylic-built reactor with a useful volume of 10.5 L was used. The bench-scale up-flow anaerobic sludge blanket (UASB) reactor consisted of two parallel 38 cm × 78 cm Plexiglass plates, 12 cm

Table 1
Composition of the mineral and metal solution.

Formula	Compound	Concentration
FeSO ₄ ·7H ₂ O	Ferrous sulfate	5.0 mgL ⁻¹
MgSO ₄ ·7H ₂ O	Magnesium sulfate	22.5 mgL ⁻¹
NiSO ₄ ·7H ₂ O	Nickel sulfate	0.5 mgL ⁻¹
CaCl ₂	Calcium chloride	44.5 mgL ⁻¹
CoCl ₂	Cobalt chloride	0.08 mgL ⁻¹
FeCl ₃ ·6H ₂ O	Ferric chloride	0.5 mgL ⁻¹
Na ₂ HPO ₄ ·7H ₂ O	Dibasic sodium phosphate	33.4 mgL ⁻¹
K ₂ HPO ₄	Dibasic potassium phosphate	21.75 mgL ⁻¹
KH ₂ PO ₄	Monobasic potassium phosphate	8.5 mgL ⁻¹

Legend:

1: Gas Meter

2: Water seal

3: UASB Reactor – front view

4: UASB Reactor – side view

A: Affluent

E: Effluent

⊕ Sampling sections (longitudinal profile)

apart, tightened together by bolts against a variable stainless steel contour. On the top part there was a sedimentation chamber with the gas–liquid–solid separation device. Six ports allowed to collect samples from influent, effluent and four intermediate points along the reactor height. The output of the gas separation device was connected, with a rubber hose, to the water seal, followed by a gas meter (Wet Gas Meter Alexander Wright – DM 39), as illustrated in Fig. 1.

2.2. Inoculum

Sludge granules from an upflow a UASB taken from a domestic wastewater treatment plant were used as inoculum.

2.3. Synthetic wastewater

The synthetic wastewater was prepared daily with glucose (1.75 gL⁻¹), ammonium acetate (0.40 gL⁻¹) and methanol (0.50 mL L⁻¹) as organic carbon sources. In addition to these components, the wastewater was enriched with mineral and metal solutions (Table 1). Sodium bicarbonate was added to ensure the amount of alkalinity enough to keep the pH within the range of 7.0–8.0 (to limit the H₂S concentration in the gas phase).

2.4. Reactor operation

The reactor was operated for 266 days, with a flow rate of 8 L day⁻¹ of sodium sulfate solution and 8 L day⁻¹ of synthetic substrate, totaling 16 L day⁻¹, resulting in a hydraulic detention time of 15.6 h. The operation temperature was between 19.8 and 27 °C. The sodium sulfate solution (Na₂SO₄) was the sulfate source, which together with sodium bicarbonate (NaHCO₃) added as a buffer, was also a sodium source in the system. The sodium sulfate solution concentration was gradually increased, while the synthetic substrate concentration remained constant at around 2000 mg L⁻¹. Consequently, the COD/[SO₄²⁻] ratio was gradually reduced, resulting in 18 operational phases (Fig. 2). Each phase lasted 14 days.

In phase 1, Na₂SO₄ was not added. Therefore, the concentrations of SO₄²⁻ and Na⁺ resulted from the amounts of sulfate and sodium contained in the synthetic substrate.

2.5. Analytical determinations

Analyses of influent and effluent, sulfate, pH, COD, total solids (TS) and volatile solids (VS), fixed solids (FS) were performed according to the Standard Methods for the Examination of Water and Wastewater (2005). Samples for determination of effluent COD were previously centrifuged to obtain the dissolved organic matter thus eliminating the dissolved sulfide COD fraction. To evaluate the effect of progressive addition of sodium sulfate on the biomass into

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