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Long-term operation of anaerobic immobilized biomass reactor treating organic wastewater containing sulfate

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ABSTRACT

This work evaluates the long-term performance (888 days) of a horizontal-flow anaerobic immobilized biomass (HAIB) reactor fed with synthetic wastewater containing organic matter and sulfate. The HAIB reactor achieved stable performance, exhibiting high sulfate and organic matter removal efficiencies subjected to organic matter concentration (expressed as chemical oxygen demand – COD) of 1500 mg/L and sulfate of 500 mg/L. Sulfate removal efficiency close to 100% was obtained for COD/sulfate ratios equal to or higher than 2.6, decreasing to ~80% for COD/sulfate ratio of 1.4. Sulfidogenesis was clearly dependent on the availability of electron donor; but not methanogenesis. The smaller COD removal efficiencies (~93%) were observed at the higher sulfate (1980 mg/L) and organic matter (COD of 7000 mg/L) concentrations, with COD/sulfate ratio of 3.5. Under these conditions, the presence of volatile fatty acids in the effluent indicates the occurrence of methanogenesis inhibition probably due to sulfide. The fixed-film HAIB reactor did not present bed clogging throughout the entire long-term operation period, thereby leading the way to new perspectives to use the efficient treatment of sulfate-rich wastewater.

1. Introduction

Anaerobic technology is competitive in wastewater treatment processes with more than 2200 high-rate reactors implemented worldwide, treating wastewater from alcohol distilleries, agro-food, beverage and pulp and paper production industries [1]. Despite the advantages of this technology, such as sustainable, cost effective and compact bioreactors, low sludge production, potential energy recovery from biogas, selective recovery of metals and nutrients [1], the implementation of anaerobic bioreactors for the treatment of sulfate-rich wastewaters is still problematic due to the uncertainties regarding the stability and performance of the reactors [2]. Sulfate-rich wastewaters are generated by several industrial processes that use sulfuric acid as raw material as well as by the processing of marine products, pulp and paper manufacture, mineral processing operations and petrochemical industries.

Sulfate reduction by sulfate-reducing bacteria (SRB) generates hydrogen sulfide, an important inhibitor of methanogenesis [2–4]. Additionally, SRB, methanogenic archaea (MA) and acetogenic bacteria compete for substrates, such as hydrogen, acetate, formate, butyrate [5]. In spite of this, recent researches have shown the possibility for a simultaneous removal of organic matter and sulfate using different anaerobic reactor configurations [6–11]. The COD/sulfate ratio and the organic matter and sulfate concentrations were the main parameters those studies focused on. Different results obtained by different authors may be related to how several factors influence the role of methanogenic archaea and sulfate reducing bacteria in the reactors. Growth kinetics, microorganism immobilization properties, substrate diffusion in the biofilm, operational time and environmental conditions such as sulfide concentration, temperature, pH and electron availability are among the main factors affecting the performance of reactors [2,5,10]. Short-term experiments have been carried out in order to clarify several of those influences on methanogenesis and sulfidogenesis processes [9,11–13]. However, there is a lack of data on long-term operation of reactors promoting the combined removal of COD and sulfate to establish design parameters for technological applications. With regard to this, our study evaluates the potential use of a horizontal anaerobic immobilized biomass (HAIB) reactor for long-term treat-

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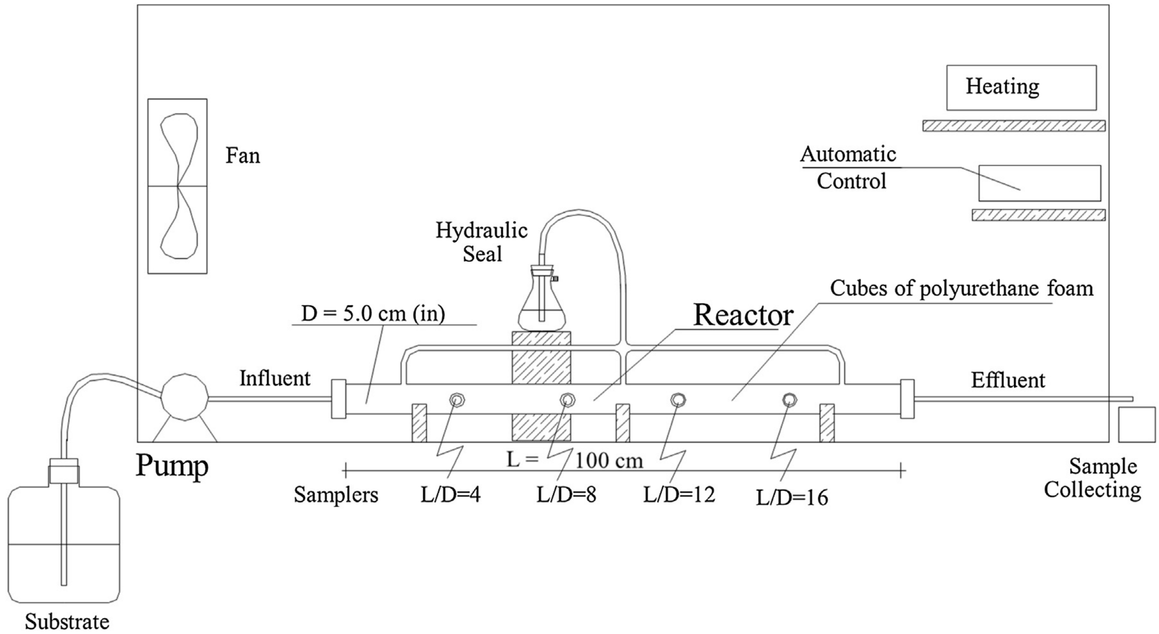

Fig. 1. Scheme of the bench-scale HAIB reactor.

ment of wastewater containing high sulfate and organic matter concentrations.

2. Material and methods

2.1. Reactor

An anaerobic fixed-bed horizontal reactor (HAIB) (Fig. 1), total volume of 2000 mL and working volume of 720 mL, diameter (D) of 5 cm and 4 equally spaced sampling ports along its length (L of 1.0 m), was fed with synthetic wastewater containing sulfate. The reactor was filled with 20.8 g of polyurethane foam cubes (side width of 0.5 cm), impregnated with 500 mL of sludge, (volatile solids of 36 g/L) from an UASB reactor treating poultry slaughterhouse effluent. The hydraulic retention time (HRT) was maintained at 12 (±1) hours and the temperature was controlled at 30 (±1) °C.

2.2. Synthetic wastewater

The synthetic wastewater was composed of ethanol and supplemented with macro-nutrients according to Visser et al. [14], metal and vitamin solutions according to Zhender et al. [15] and Widdel and Bak [16], respectively. Ethanol was chosen as the electron source for sulfidogenesis due to its easy manipulation and low cost in Brazil. Sulfate was added as Na_2SO_4. The wastewater pH was maintained close to 8.0 by adding NaOH solution, to minimize the toxic effects of hydrogen sulfide [17,18].

2.3. Experimental set up

Sulfidogenesis was previously established in the HAIB reactor (data not shown). Next, the reactor was kept in operation for 888 days. This period was divided in phases (Table 1). From day 0–530 (phases 1, 2 and 3a), the reactor was subjected to variable COD/sulfate ratio of 3.5–1.4 and sulfate was added at concentrations ranging from 2000 to 520 mg/L. From day 530–730 the reactor remained at ambient temperature without receiving wastewater. In the final period, from day 730–888 (phase 3b), the operating conditions were similar to those of 3a (COD ~1500 mg/L; sulfate ~500 mg/L). Table 1 resumes the operating conditions applied to the reactor.

2.4. Reactor performance monitoring

The reactor performance was evaluated by COD determinations and sulfate concentrations in influent and effluent samples. During the operation at steady-state conditions (identified by variations lower than 10% in the effluent COD and sulfate concentrations) COD, sulfate, sulfide and volatile acids spatial profiles were obtained, in independent replicate assays. The analytical determinations were carried out according to APHA [19].

Volatile acids were determined by gas chromatography according to Moraes et al. [20]. As sulfide contributes to COD, zinc sulfate ($ZnSO_4$) was added to the samples prior to the COD analysis to remove the dissolved sulfide. The eventual sulfide re-oxidation observed in the system output due to the contact of the effluent

Table 1
Developed phases and operating conditions.

Operating conditions	1	2	3a	3b
COD/Sulfate Ratio	3.70 ± 0.30	1.45 ± 0.30	3.30 ± 0.40	3.02 ± 0.15
COD (mg/L)	7160 ± 395	1545 ± 270	1540 ± 100	1,52 ± 75
Sulfate (mg/L)	1990 ± 10	1160 ± 95	500 ± 50	500 ± 15
Organic Load Rate[a] (g COD/day[a]L)	5.78 ± 0.31	1.23 ± 0.22	1.24 ± 0.10	1.22 ± 0.10
Sulfate Load Rate[a] (g SO_4^{2-}/day[a]L)	1.57 ± 0.10	0.86 ± 0.10	0.38 ± 0.04	0.34 ± 0.15
Time (days)	30	99	399	157

[a] Considering total volume of 2 L.