Use of activated carbon and natural zeolite as support materials, in an anaerobic fluidised bed reactor, for vinasse treatment

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Abstract In Cuba, the alcohol distillation process from cane sugar molasses, produces a final waste (vinasse), with an enormous polluting potential and a high sulfate content. Applying the anaerobic technology, most of the biodegradable organic matter can turn into biogas, rich in methane but with concentrations of sulfide above 1%. The present work develops two experiences with anaerobic fluidized bed reactors (AFBR) using both Cuban raw material**,** activated carbon and natural zeolite, as support media, with the purpose of obtaining high organic matter removal rates and keeping sulfide and ammonium concentrations in the permissible ranges. The reactors were operated during 120 days, achieving an organic loading rate of 10 kg COD/m^3 day, with COD removal above 70%, and a methane production of 2 L/d. The activated carbon and natural zeolite used support materials in anaerobic fluidized bed reactors, and showed good results of distillery waste removal.

Keywords Anaerobic; activated carbon; fluidized bed reactor; natural zeolite; vinasse

Introduction

In Cuba, one of those byproducts of the sugar cane industry is the alcohol, which is produced from the cane sugar molasses. The alcohol distillation process produces a final waste, vinasse, with an enormous polluting potential.

In Latin America, some of the most polluting industrial wastewaters are malting-brewery and distillery wastes. It is known that, for example, 450,000 kg of COD of distillery wastes are treated daily.

In Cuba there are 15 distilleries, with an alcohol production of the order of 50,000 litres/day per distillery, that implies the necessity to evacuate some 1,500 m^3 of vinasse a day. Taking into account that the average of organic matter concentration of distillery waste can be higher than 70,000 mg COD/L and considering that the equivalent contamination per person is of 80 g COD/day, it can be stated that the population equivalent from the vinasses is equal to 1,300,000 inhabitants. This figure indicates that the environmental impact of vinasse, is similar to that of 10% of the Cuban population.

The vinasse also has a high sulfate content and that provokes an environmental impact and the need to restrict biogas use due to the appearance in the biogas of sulfide concentrations above 1% [Noyola, 1996].

Anaerobic intensive processes such as the anaerobic fluidized bed, have been used for purification of wastewater with high organic matter content, as distillery waste, but in this case care must be taken with the conversion of sulfates to sulfide which is a natural

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consequence of sulfates anaerobiosis [Conde *et al*., 1993]. It was found that this conversion can be reduced by using activated carbon [Montalvo and Almeida, 1994].

It is good to highlight that, in fact, the type of support material used in AFBR is the physical factor that has more influence on this kind of reactor. The support material constitute one of the aspects of more economic influence on the reactor initial investment and operational costs [Speece, 1996]. For that reason it is very convenient to look for media from national production that, in general, are cheaper.

The objective of this paper is to study the behaviour of AFBR, in the vinasse treatment, using both activated carbon and natural zeolite as the support materials. The conversion of sulfates to sulfide and also the quality of produced biogas were determined.

Materials and methods

Laboratory-scale reactor system

Two different lab-scale AFBRs, were used.

A schematic diagram of both reactors is shown in Figure 1.

a) AFBR with activated carbon as support material.

The reactor consisted of a cylindrical acrylic tube 6.5 cm internal diameter with 750 mL of effective volume.

The support used for the immobilization of the biomass was the activated carbon produced from coconut shell, with the following characteristics: size of particles around 0.5–0.8 mm, density 1,600 kg/m^3, porosity 0.63.

b) AFBR with natural zeolite as support material.

The reactor consisted of a cylindrical acrylic tube 6.5 cm internal diameter with 1 L of effective volume. The used support was the natural zeolite in a range of particle size, 0.5–0.8 mm, density of 2,128 kg/m^3 and porosity of 0.58.

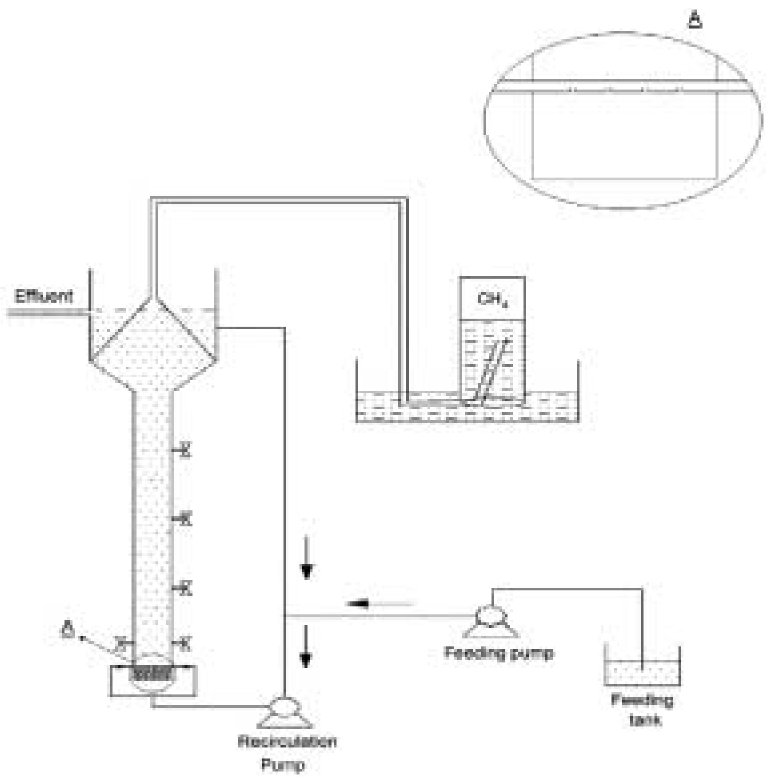

Figure 1 Schematic diagram of reactor

In both experiments wastewater was fed to the reactor by means of a peristaltic pump.

The control and monitoring of reactors were carried out daily, by controlling the fluidization level, the influent and effluent pH and the temperature.

The biogas produced was collected in a gas collector system placed in the upper part of the reactor and its flow was measured by liquid displacement.

Wastewater

The characteristics of the wastewater used in the experiment are summarized in Table 1.

As can be observed in the experience with natural zeolite, two different vinasse sample were used.

The relationship COD/N/P values of wastewater for all experiences were within the adequate range recommended for the good development of anaerobic processes [Chernicharo, 1997].

Inoculum sludge source

The AFBR with activated carbon as support material was inoculated with 250 mL anaerobic sludge obtained from an industrial-scale UASB reactor treating vinasse from beet sugar molasses that had a specific methanogenic activity of 0.3 g COD/g VSS d.

The AFBR with natural zeolite as support material was inoculated with 350 mL anaerobic sludge from a lab-scale reactor treating piggery wastes with a specific methanogenic activity of 0.25 g COD/g VSS d.

Analytical method

Influent and effluent liquid samples were analyzed two days per week. Chemical Oxygen Demand (COD), Total Kjeldahl Nitrogen (TKN) were determined according to Standard Methods, ammonium ($N\text{-}NH_4^+$) and sulfide in the liquid (S^{2-}) using selective electrodes [Standard Methods, 1995].

The methane produced was measured by displacement of 0.1 N sodium hydroxide solution. The hydrogen sulfide in the gas was analyzed in a Tutweiler burette (Fernández, 2000).

Results and discussion

Reactor start-up

Both reactors were filled with the amount of inoculum described above and dilute vinasse was added to reach the reactor total volumes. A concentration of 1 g COD/L was kept in the reactors for 30-day batch processes. Total and continuous recirculation was carried out. After this procedure both reactors were continuously fed with an organic load of 1 g DQO/L d, at a hydraulic retention time (HRT) of around 8 h for the reactor with activated carbon and at a HRT of 11 h for the reactor with natural zeolite.

The reactors were operated in continuous regime at OLRs from 1 to 10 g COD/L day over a 120-day period. The OLR was increased step by step as will be explained later.

Table 1 Average influent composition

	AFBR (activated carbon)	AFBR (natural zeolite)	
		Vinasse 1	Vinasse 2
pH	4.1	3.9	4.2
COD (mg O_2/L)	79,220	56,170	83,000
TKN (mg N/L)	6,020	556	1,333
$S\text{-}SO_4^{-2}$ (mg S/L)	2,935	1,150	1,228
$P\text{-}PO_4^{3-}$ (mg P/L)	737	114	175.7

a) Behaviour of reactor with activated carbon as support material

Initially the OLR was increasing in a progressive way by increasing feeding COD at constant HRT, but there were some problems that did not allow the flow to be kept constant and for that reason it was decided to vary the flow, keeping a constant influent COD.

During the 120 days of continuous operation several parameters were analysed, see Figures 2, 3, 4 and 5.

In Figure 2 can be observed that in spite of the COD influent increase, the values of COD in the effluent stay stable, at around 8 g/L. The trend for COD removal efficiency was to stabilise at values between 75 and 78% (Figure 1). The increasing of methane flow in correspondence with the organic load increase (Figure 3).

Performance of sulfur and of nitrogen species was also studied (Figures 4 and 5). Sulfate conversion was always higher than 95% and hydrogen sulfide was not detected in the gas. The sulfide production in the liquid was also very small.

Figure 5 shows TKN values of influent and effluent from AFBR, as well as the ammonium concentration in the effluent, during the whole period. In this representation a certain anomaly is observed, because TKN in the influent is not similar to TKN in the effluent.

b) Behaviour of reactor with natural zeolite as support material

Figure 6 shows the COD values in the influent and in the effluent and the COD removal efficiencies. On the other hand Figure 7 shows the reported values of methane production during the operational period, as well as OLR.

In order to increase OLR values, the COD values were increased progressively without varying HRT.

The main results are shown in Figures 6 and 7.

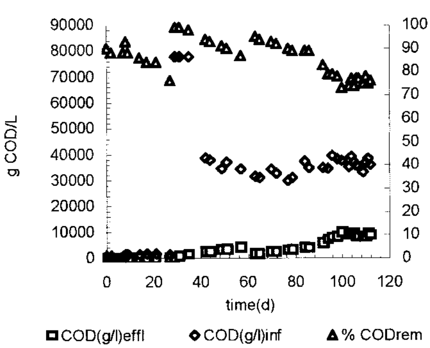

Figure 2 Performance of organic matter

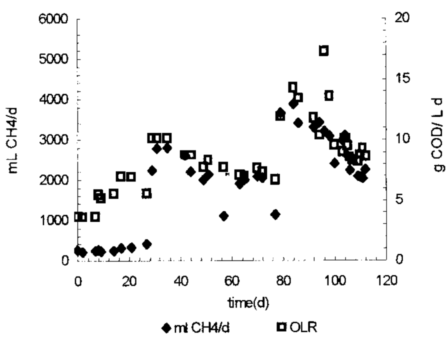

Figure 3 Performance of methane production and OLR

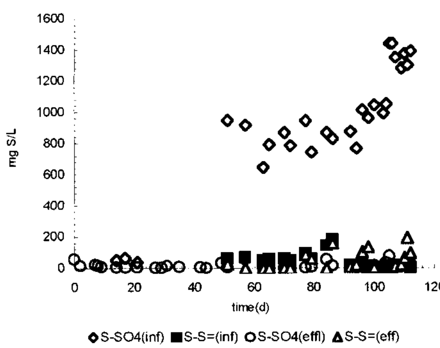

Figure 4 Sulfur species in liquid phase

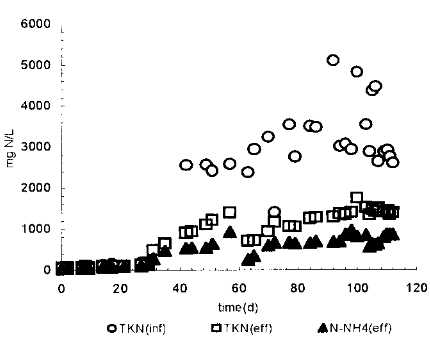

Figure 5 Nitrogen species in liquid phase

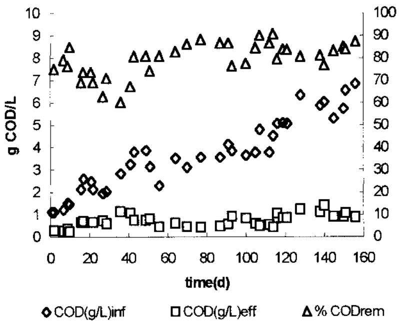

Figure 6 Performance of organic matter

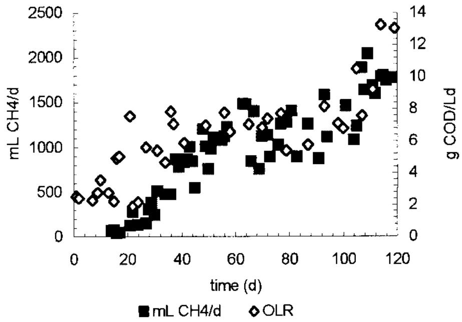

Figure 7 Performance of methane production and OLR

It can be observed that in spite of the COD increase in the feeding (increase of OLR), the COD effluent values stay around 1 g COD/L. At the beginning COD efficiency removal stays in the range of 50–70%, and from day 50 these values were increasing until they reached stability around 70–90%, with a prevalence of removal values higher than 80%. Figure 7 shows that the reported values of methane flow were increased, corresponding with the increments of organic load rates.

In this experience the performance of sulfur and nitrogen species was also studied (Figures 8 and 9).

Figure 8 shows the behaviour of sulfur species, it being observed that the sulfur increases in the form of sulfate in the feeding, however, the sulfur values in the effluent stay stable and very near to 0 ppm. In the case of the sulfur in the gas, although there is a certain trend to increase, the percentage of H_2S that was achieved are extremely small.

Figure 9 shows the nitrogen species values. It can be observed that the behaviour of TKN in the reactor is similar to the behaviour observed in AFBR with activated carbon. However, when TKN increases with feeding, the TKN and ammonium values in the effluent decrease. This phenomenon did not correspond with the values of fed nitrogen and that means that there was a nitrogen amount that could not be detected.

This could be due mainly to two phenomenon: first, that the biota or biomass are incorporating nitrogen for their growth [Speece, 1996], secondly, elementary nitrogen may be forming and some nitrogen may be leaving the AFBR with the biogas.

In this representation it is important to highlight the evolution of the ammonium in the reactor, it can be observed that the trend of the ammonium is to decrease gradually at the beginning of the experimentation, registering values, from day 100, close to 0. This behaviour is contradictory with the ammonium formation process that should usually happen in

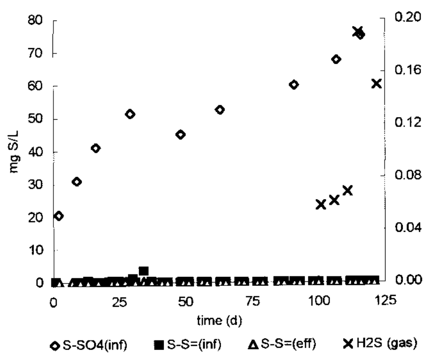

Figure 8 Sulfur species in liquid and gas phase

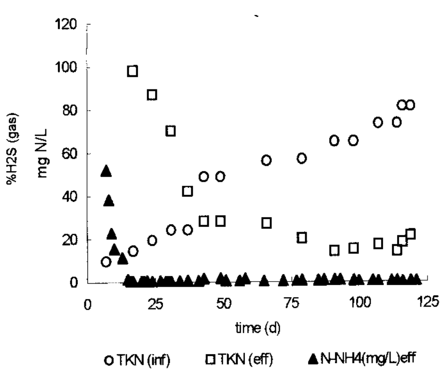

Figure 9 Nitrogen species in liquid phase

the anaerobic digestion. Although it is certain that the support can be influencing this behaviour (ionic exchange and/or absorption), the effluent ammonium concentration must increase with an OLR increase.

As can be observed, in the system with activated carbon, as well as in the system with natural zeolite, there is an uncommon evolution of nitrogen and sulphur species in the reactors, which could be justified by two facts:

a) That in the reactors ammonia and sulfate removal seems to follow a biological mechanism that it is possible from the thermodynamic point of view [Fdz-Polanco *et al.*, 2000]:

$$SO_4^{2-} + 2\,NH_4^+ \rightarrow S + N_2 + 4\,H_2O\ (\Delta G° = -47.8\ kJ/mol)$$

b) The sulphur and nitrogen species have been retained in the support (in both reactors) and were assimilated for biomass growth.

This analysis has served as a basis for new experiments that are being carried out at present, with the objective of studying the possible evolution paths of these species in greater depth and arriving at more conclusive results.

Conclusions

The following conclusions can be drawn from the results in this study:

The use of the activated carbon and the natural zeolite, both Cuban raw material, as media in AFBR, allowed us to obtain good results in the purification of highly polluting organic wastes.

In both systems, operating with OLR of 10 kg/m^3.day, removal of organic matter above 70%, as COD, and a methane production of 2 L/d were reached.

In the system with activated carbon, effluent ammonium concentration around 800 mg/L was obtained. The sulfide levels, as much in the liquid as in the gas, are worthless.

In the system with natural zeolite, effluent ammonium concentration smaller than 1 mg/L was obtained. The sulfide levels in the effluent are worthless and in the gas are smaller than 0.1%.

The uncommon evolution observed in the nitrogen and sulfur species, in both systems, could be justified by two facts: the occurrence of the biological mechanism:

$$SO_4^{2-} + 2\,NH_4^+ \rightarrow S + N_2 + 4\,H_2O\ (\Delta G° = -47.8\ kJ/mol)$$

or that the biomass is incorporating this species for its growth.

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