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Conditioning of an anaerobic hybrid reactor for the treatment of effluents from the citrus industry

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Abstract

Southeastern Mexico is one of the country major citrus producing regions where a large volume of industrial effluents with high organic load are generated. In particular wastewater from the citrus industry can be treated by anaerobic digestion in bioreactors, as the Anaerobic Hybrid Reactor (AHR) which has the advantage of two reactor configurations in one device. The AHR was conditioned and operated for 30 days using an effluent of fruits and vegetables as substrate, while maintaining an OLR of 5 gCOD/L.d, pH = 6.6 to 7.7 and T = 35 °C ± 2. The monitored parameters were pH value, total and soluble COD, TSS, VSS, VS as biomass and biogas composition. The biofilm present in the support material of the inverse fluidized bed after the experiment was tripled, while the biomass in the anaerobic filter had a significant development, the pH was stable, removals of 60% were achieved in total COD, 86.90 and 90.80% for TSS and VSS respectively, a value of 0.3 LCH4/gCODrem for YCH4.

Keywords: *Anaerobic digestion, substrate characterization, citrus industry*

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1. Introduction

The wastewater generation in Mexico is a big problem mainly by discharges from industries, regardless of the line of business they have. The main problem is the high organic load of the effluents and the low treatment capacity. Southeastern Mexico is one of the major citrus producing regions of the country and as a consequence a large volume of liquid and solid wastes are generated. The effluents coming from the juice extraction are normally discharged into irrigated fields or water bodies, generating a serious pollution problem. A citrus plant which processes 100 tons/h of fruit, generates an estimated of 300,000 L/h of effluents from various stages of the process, being peel washing the responsible for most of the volume [2]. These effluents usually contain acids, alkalis and organic materials that are discharged at different times and sometimes at high temperatures so it is necessary to reduce them in order to prevent environmental pollution [15].

Currently, the best option to remove the high concentration of organic matter in the effluents is the use of bioreactors with anaerobic digestion [12]. The Fluidized bed technology exhibit better removal efficiencies in comparison with classic reactor configurations.

Cresson y col. [2009] y Parthiban R. [2011] showed the convenience of using support material with small size and irregular surfaces to increase the surface area and the adherence of bacteria, however even if both requirements are met, the anaerobic reactor start-up and stabilization time is a limiting factor for large scale application of biofilm reactors, because unlike the aerobic process with a biomass production of approximately 50% of the organic matter degraded, the anaerobic process only has a biomass yield between 5-10% of the degraded material [9].

In order to reduce the conditioning time, the reactor can be inoculated with a support which has methanogenic activity making possible to increase the influent concentration in the reactor start-up as was proposed by Martinez-Sosa *et al*., [2009]. Alvarado-Lassman *et al*., [2010] discuss a series of strategies for the start-up of an inverse fluidized bed reactor, pointing out that the use of precolonized support allows a reduction of the start-up period to 15 days. Other aspects to be considered are the operational conditions such as temperature a fluidization velocity as is mentioned by Kumar *et al*., [2008].

The purpose of this paper is to improve previous experience in the start-up and stabilization of a hybrid reactor using a prehydrolyzed substrate from the extraction of the soluble fraction of fruits and vegetables organic solid waste in order to subsequently treat an effluent from the citric industry.

2. Methodology

2.1Experimental device

The system used was an Anaerobic Hybrid Reactor (AHR) which consists of two sections, at the top an anaerobic filter (AF) and an inverse fluidized bed reactor (IFBR) at the bottom as shown in Figure 1. The anaerobic filter was used to eliminate part of the organic matter and solids present in the wastewater and to improve the liquid distribution in the IFBR section. The anaerobic filter consisted of an acrylic tube of 23 cm length and nominal diameter of 7.62 cm. The AF section was filled with 330 plastic tubes (2.76 cm length and cm diameter) previously covered with acrylic paint to improve biofilm adhesion. The inverse fluidized bed section was also constructed with an acrylic tube (length 80cm and 8.89cm diameter) and Extendosphere™ was used as support material. The density of support media was 0.69 g/mL mean particle diameter 170 μm, and the specific surface area of 20000 m^2/m^3. Biogas produced in the inverse fluidized bed section flows upward thru an acrylic tube which was placed concentrically to the anaerobic filter section, the biogas was accumulated in a collector recipient outside the reactor. At a suitable height in the effluent stream a container was adapted to control the liquid level in the reactor. Inlet and recirculation flows were supplied with peristaltic pumps (Masterflex®)

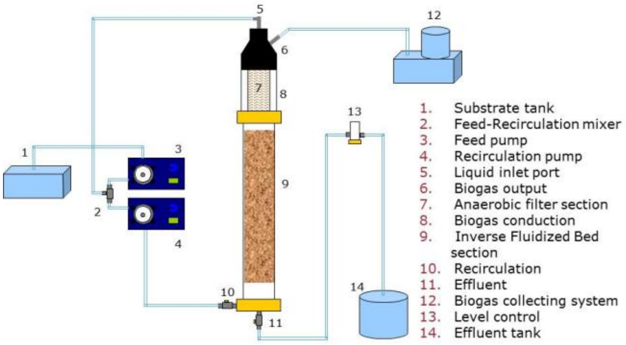

Fig. 1 Components of the Anaerobic Hybrid Reactor

2.2 Inoculation, AHR start-up and operating conditions

The inoculum source was 300 mL of pre-colonized Extendosphere™ which was taken from a different reactor that used apple juice as substrate. The biofilm attached to the support measured as volatile solids was 13.98 gVS/L. Before the reactor start-up 1200 mL of biomass free Extendosphere™ were added to complete the fluidized bed volume.

The substrate used was the effluent of a pilot scale hydrolysis reactor which treats the soluble fraction of organic solid waste (mainly fruits and vegetables), adjusting the pH value near neutrality. The soluble fraction of organic solid waste were prepared using a commercial waste disposal unit to ground the material, and then the shredded waste was filtered using a fabric with a pore size of 0.2 mm. The liquid portion corresponded to the soluble fraction.

Reactor start-up was conducted using an Organic Loading Rate (OLR) of 5 gCOD/L.d, pH value inside the reactor between 6.6 and 7.7 and a temperature of 35 ± 2 °C.

During the experiment the following parameters were determined at the feed an effluent streams: pH, total and soluble COD, TSS, VSS. Biofilm formation was measured as volatile solids.

2.3 *Analytical methods*

The pH values of the feed and effluent streams and inside the reactor were measured using an Orion 250A potentiometer.

The chemical oxygen demand (COD) was determined by the colorimetric method [3] using a solution of sulfuric acid with potassium dichromate as oxidizing agent in the presence of silver and mercuric sulfates in a digester plate (Hach®) at 250 °C for 2 hours.

Total and soluble COD were determined to evaluate the percentages of organic matter removal associated with colonization of the support and reactor stabilization. To measure the soluble COD, 10 mL of sample was centrifuged in a centrifuge (Hermle™ Z 383) using 3500 rpm for 5 minutes, the supernatant was taken for the soluble COD. Samples of total and soluble COD were read on a HACH spectrophotometer at 620 nm.

Total Suspended Solids (TSS), and Volatile Suspended Solids (VSS) were measured by the gravimetric method [3] 0.5 mL of sample were taken and placed in a constant weight crucible, then placed in an oven at 105 °C for 24 hours and then calcinated in a muffle furnace at 550 °C for 2 hours. Samples were taken at the inlet and outlet of the reactor and the crucibles were weighed on a digital balance. The Volatile Solids (VS) attached to the support media of the FA an IFBR sections were determined as volatile solids.

Biogas composition was determined on a gas chromatograph Buck 310 with capillary column All Tech CTR-I (length 6 in, diameter ¼ in), which detects CH_4, CO_2, O_2 and N_2. The chromatographic sample was 2 mL and the operating conditions were: helium as carrier gas at 70 psi, column and detector temperatures 36 °C and 121 °C respectively.

Results and discussion

The reactor parameters, COD, TSS, VSS and pH were used as monitoring parameters to indicate the behavior of the reactor with respect to organic matter removal.

Characterization of substrates

The substrate used in the reactor start-up stage was the soluble fraction of fruits and vegetables residues. The substrate was pretreated in a pilot scale anaerobic hydrolysis reactor which has been operating for a period of 180 days adjusting the influent pH to 5.5 to maintain acidogenic conditions in the reactor, with a Hydraulic Retention Time (HRT) of 10 days. From the day on which the substrate extraction began to feed the hybrid reactor, the hydrolysis reactor reached average COD removals of approximately 22% with an average production of 1.2 g/L of Volatile Fatty Acid (VFA) as can be seen in Figure 2.

The pretreatment offers several advantages including the following: the reduction of solids, reduction of complex substrates from macromolecules hydrolysis and volatile fatty acids production which are intermediates in the anaerobic digestion process for methane formation.

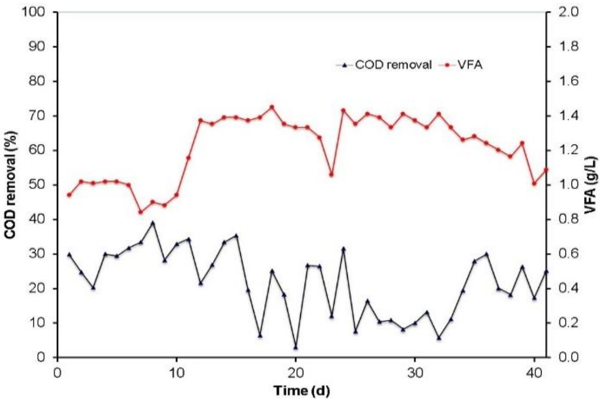

Fig. 2 COD removal and VFA production in the anaerobic pilot scale Hydrolysis Reactor

The results of the substrate characterization are showed in Table 1. As can be observed the citric effluent contains a higher amount of organic matter than the pretreated effluent of the fruits and vegetables residues with a good ratio of volatile to total solids of 83.5% but a lower pH value that has to be taken in account to avoid the acidification of the reactor.

As mentioned before, the utilization of the hydrolysis stage to conditioning the fruits and vegetables substrate offers the advantage that the remaining organic matter is more biodegradable than the crude substrate and the pH value tends to neutrality which benefits the overall anaerobic digestion process.

Table 1 Characterization and comparison of substrates according to their origin

Parameter	Origin	
	Pretreated fruits and vegetables residues	Citric effluent
CDO total (mg/L)	13,765	38,780.00
CDO soluble (mg/L)	11,335	35,420.00
TSS (mg/L)	7,160	21,662.00
VSS (mg/L)	4,360	18,084.00
pH	5.7	3.76

Development of biomass

The volatile solids analysis in the pre-colonized support used as inoculum for the IFBR section resulted in a value of 13.98 gVS/L.

After 30 days of operation, the support material in both the anaerobic filter and the inverse fluidized bed sections showed a significant colonization. The inverse fluidized bed section was stratified and three distinct zones can be observed, this is because as the support is colonized, the particle density increases and they tend to accommodate in the bottom of the bed. The three zones are, the upper zone (23.75 % of the bed), the middle zone (47.5 %) and the lower zone (28.75 %) with a biomass concentration of 18.75, 20.05 and 47.87 g VS/L respectively. Then the total amount of biomass accumulated in the reactor is 46.49 g VS.

With respect to the Anaerobic Filter, the plastic tubes used as support material, had not adhered biomass at the reactor start-up. At the end of the experiment each of the 330 plastic tubes was covered with 0.0072 g VS, therefore the total biomass in the AF section was 2.376 g VS.

The rapid colonization of the reactor in both sections is related to two strategies that improve previous experiences. First, the use of a prehydrolyzed mixed substrate, to enhance their biodegradability and the reactor start-up using a colonized support as inoculum applying a high organic loading rate of 5 gCOD/L.d, equivalent to the reactor OLR where the inoculum was obtained allowing the bacteria to degrade a considerable amount of organic matter without medium acidification and favoring biomass formation and adhesion (anabolism), and also without apparent methane conversion, as evidenced by Michaud *et al*., (2002) who demonstrated that at the beginning of the start-up period, bacteria seem to use carbon principally to build the initial biopolymer matrix, reducing the methane yield, then at steady state conditions, organic carbon is mainly converted to biogas and the methane yield is close to the theoretical value.

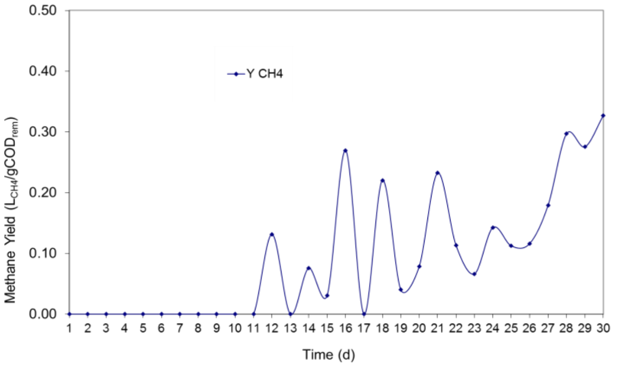

Fig. 3 Methane yield based on the removed COD

As can be seen in Figure 3, the first 11 days of reactor operation the methane yield was zero although the COD removal was considerable. Material balances showed that if degraded organic matter was used in biomass formation, the start-up of the reactor can be reduced to 15 days.

Evaluation of parameters

The reactor pH values at the feed were between 6.6 and 7.7. There was no necessity to adjust the pH value with any type of buffer solution. Inside the reactor, the pH values reached a range between 6.73 and 8.01, while at the effluent the values oscillated between 7.2 and 8.4, this proves that the biofilm has buffer ability which helps the adequate development of the anaerobic digestion process because most bacteria have good performance at pH values between 6.8-7.2. A lower pH value may cause bacterial inhibition associated with volatile fatty acids accumulation (Figure 4).

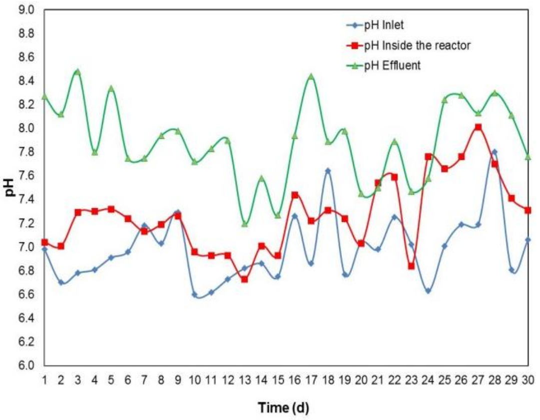

Fig. 4 pH values in the AHR

Since this is a reactor which can handle effluents with high organic load the inlet concentrations were used without dilution with average inlet concentrations of 11207.10 and 8233.00 mg COD/L corresponding to the total and soluble COD respectively.

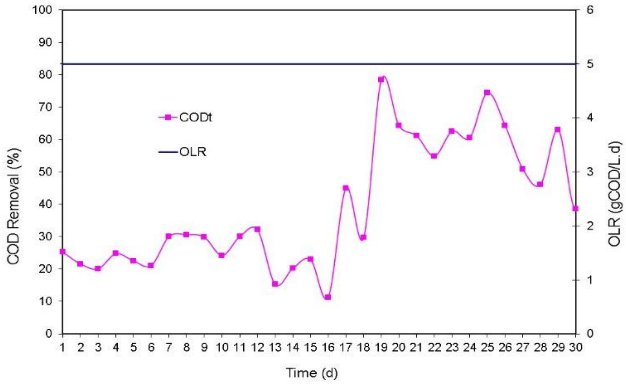

Fig. 5 COD removal in the AHR

The COD removal is presented in Figure 5, and as can be seen during the first 16 days the values ranged from 10 to 30% and then a significantly increase to reach values between 50 and 70 % during the last 15 days of operation maintaining constant OLR of 5 gCOD/L.d in all the experiment. Ying *et al*. [2014] reported COD removal efficiencies with an acclimated anaerobic sludge from a UASB reactor was operated 120 days of 85% at an OLR of 8.64 gCOD/L.d, this suggests that for the AHR we can expect equivalent COD removal efficiencies in a shorter time, as Alvarado-Lassman *et al*., [2008] observed in a IFBR treating brewery wastewater with a COD removal of 90% after the reactor conditioning time.

The anaerobic reactors are characterized as devices that have low removal efficiencies of Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS), but when the anaerobic filter section of the AHR was colonized, the filter retain solids. Thus in the first seven operation days the reactor showed no removal efficiency in these two forms of solids (Figure 6).

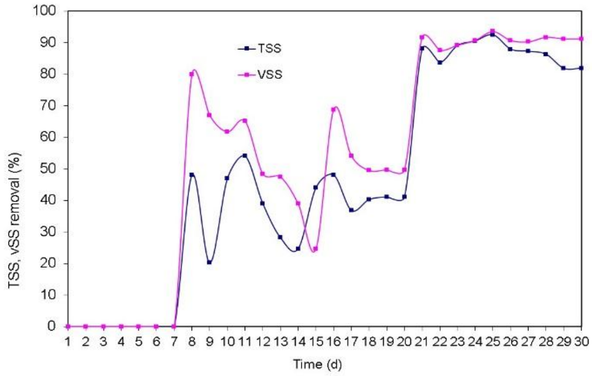

Fig. 6 Removal efficiencies of TSS and VSS

From days 8 to 20 there was a marked increase with values between 20 and 50% for TSS and 20 to 70% for SSV but with significant differences between the two curves. From day 21 to 30, the TSS and VSS removal was improved reaching values between 80 and over 90% with closer curves. This demonstrated that the anaerobic filter is capable of retaining solid resulting in a better performance of the IFB section.

Conclusions

The reactor start-up and stabilization time was shorten with respect to previous experiences mainly for the use of a prehydrolyzed mixed substrate and the use of colonized support as inoculum applying a high organic loading rate since the beginning of the experiment.

Only 15 days was necessary to stabilize the reactor with presence of biofilm both in the anaerobic filter and the fluidized bed sections.

The use of a mixed substrate that already contains citric residues will make it simpler to change to a substrate from the citric industry.

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