Thermophilic Anaerobic Degradation of Distillery Wastewater in Continuous-Flow Fluidized Bed Bioreactors

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This paper reports and discusses a laboratory experiment that tested the anaerobic fluidized bed (AFB) technology as a means for the treatment of concentrated industrial wastewater (wine distillery, vinasses) at thermophilic conditions. The purposes were to operate and characterize AFB under high organic loading conditions and to report on their steady-state performance. Experimentally, it was confirmed that AFB systems can achieve >82.5% chemical oxygen demand (COD) reduction at a COD loading of 32.3 kg of COD m^{-3} day^{-1} for treating vinasses of wine. At hydraulic retention time (HRT) of 0.46 day, the volumetric rate of methane generation was 5.8 m^3 of CH_4 m^{-3} day^{-1} with a methane yield of 0.33 m^3 of CH_4/kg of COD removal. The greatest efficiency of substrate removal was 97% for an organic loading rate of 5.9 kg of COD m^{-3} day^{-1} and HRT of 2.5 days. The food-to-microorganism (F:M) ratio can be used as a parameter for treatment performance evaluation of AFB. For vinasses, excellent COD reduction and methane production were achievable at the F:M ratio of 0.55 kg of COD kg^{-1} VS_{att} day^{-1} (more than 80% of feed COD was removed, and 9 m^3 m^{-3} day^{-1} of methane was produced).

Introduction

There is a wordwide and increasing interest in anaerobic wastewater treatment and in anaerobic digestion for energy-production purposes. This development is due to the fact that the method combines a number of significant advantages (including low energy consumption, low excess sludge production, and enclosure of odors and aerosols) over conventional biological aerobic methods (activated sludge variations, aerated lagoons, trickling filters, etc.) of wastewater treatment (Albagnac, 1990; Ramalho, 1991; Metcalf and Eddy, 1991).

Anaerobic treatment is a method especially suitable for the treatment of effluents containing high concentrations of organic carbon. High-rate anaerobic digesters which retain biomass also have a high treatment capacity and hence low site area requirements. The major process configurations developed for high-rate digesters are the upflow anaerobic sludge blanket (UASB reactor) (Lettinga et al. 1984; Lettinga and Hulshoff Pol, 1991), expanded granular sludge bed (EGSB reactor) (de Man et al., 1988) both upflow and downflow stationary packed beds (Romero et al., 1991; Nebot et al., 1995), and fluidized or expanded beds (Boening and Larsen, 1982; Jewell, 1982, 1985; Maestrojuan, 1987; Chen et al., 1988; Breintenbucher et al., 1990; Hickey et al., 1991; Iza, 1991; Balaguer et al., 1992, 1993).

Interest in AFB anaerobic fluidized bed (AFB) technology has grown as it couples the recovery of usable energy with good process efficiency and stability. The application of fluidized bed reactors as an anaerobic biological system for the treatment of industrial wastewaters containing organic end products has been studied by a variety of approaches in some detail on the laboratory scale (Denac et al., 1988; Gorris et al., 1989). Potential AFB applications for treatment of hazardous waste with inhibitory/recalcitrant compositions have also been reported (Wang et al., 1984; Tang and Fan, 1987; Fox et al., 1990).

The period of start-up and performance of anaerobic fluidized bed reactors is crucial but seldom investigated (Sreekrishnan et al., 1991; Zellner et al., 1991). Very little information exits on the treatment of wastes at thermophilic temperatures (55 °C). Several authors have reported that the start-up and performance are inextricably connected with biofilm growth and a gradual increase of organic loading rate (Balaguer et al., 1992). Additionally, the medium used for biofilm attachment has a significant effect on reactor performance (Fox et al., 1990; Yee et al., 1992).

This paper presents an analysis of the process variables that affect the performance of an anaerobic fluidized bed (AFB) reactor containing a porous medium (SIRAN) for treating distillery wastewaters (vinasses). This type of reactors could be useful to the treatment of high-strength organic wastewaters (i.e., wine vinasses) since extremely high "active biomass" concentrations can be maintained using porous medium support as a consequence of the biofilm thickness being limited by the liquid flow rate applied.

Materials and Methods

The experimental protocol was designed to examine the effect of increasing organic loading rate (OLR) on the efficiency of an AFB reactor in the thermophilic anaerobic treatment of wine vinasses. This, in turn, would be useful for a rational design of the AFB process. The methods and material used are described briefly in this section.

Experimental Systems. A schematic diagram of the AFB reactor used in the laboratory study is shown in Figure 1. A transparent Plexiglas column with a cross section of 5.11 cm^2 and length of 170 cm was used. Its bottom was molded into a conical shape to promote

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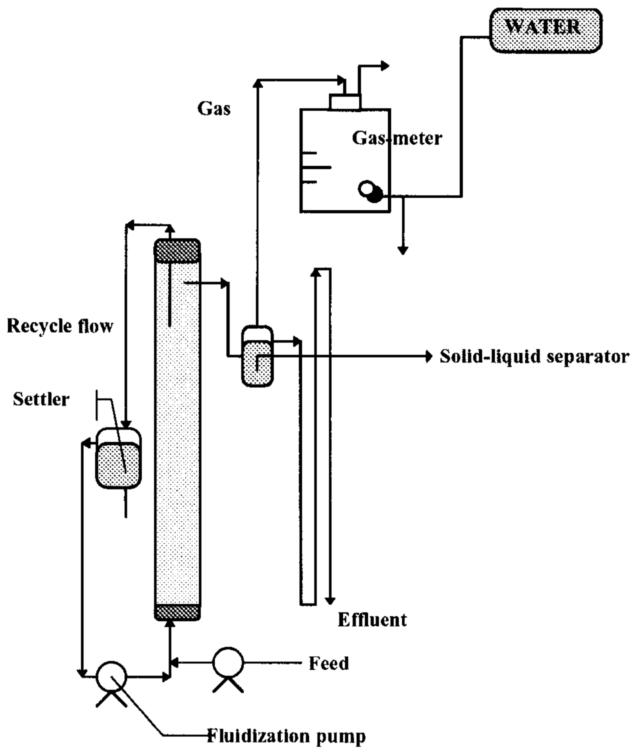

Figure 1. Schematic diagram of the experimental anaerobic fluidized bed (AFB) reactor.

uniform fluidization of media and bioparticles (that is, biofilm-coated media).

Open-pore sintered glass beads (SIRAN) were used as the support medium. Approximately 116.7 g of coated support medium was added to the column and occupied a total volume of 204 cm^3 in the unexpanded mode. In the expanded mode, the support occupied 255 cm^3.

Recycle flow was drawn using a centrifugal pump to provide upflow velocities for medium and bioparticle fluidization. Tracer studies (using stimulus response techniques) were conducted to characterize the hydraulic behavior of the AFB reactor used in this experimentation (Pérez, 1995). From that, it was demonstrated that the upflow velocities also ensured that completely mixed conditions (higher than 95%) were maintained in the liquid phase since the recycle ratios Q_r/Q (where Q_r is the recycle rate) maintained during the experimentation were higher than 1000. Recycle flow was drawn 7 cm below the free liquid surface in the enlarged section to avoid entrapment of gas accumulated in the headspace above and pumped into the bottom assembly. This stream was collected in a settler in order to separate the solid fraction from the liquid stream. The pumping rate was adjusted to account for varying biomass in order to keep a constant expanded bed level (25% expansion). However, in all cases, the required modification of the pumping rate lacked significance since flow rate variations were less than 1%.

Feed was pumped directly from the refrigerator into the recycle lines. The reactor effluent passed through a sealed contact chamber connected to an inverted siphon to separate the gas from the liquid in the effluent. Reactor temperature was maintained at 55 °C with external heating water jackets.

Gas produced in the reactor was collected in a gas meter filled with an acidified saturated salt solution in order to prevent carbon dioxide absorption. A gas sampling valve was installed at the top of the collector to allow direct gas sampling with a syringe. The volume of gas produced in the reactor was directly measured in terms of the volume of the salt solution displaced from the gas collector.

Table 1. Main Characteristics of SIRAN Carriers

sphere diameter (mm)	1.5
bulk density (g/L)	570.0
pore diameter (μm)	60−300
pore volume (%)	55−60
surface area (m^2/L)	87

Feed Solutions. Distillery wastewater from an ethanol-producing wine distillery plant in Tomelloso (Ciudad Real, Spain) was used. The vinasses were frozen and then transported and maintained at −20 °C before their utilization. This feed was diluted with tap water to attain the required feed chemical oxygen demand (COD) concentration to be used in this experiment (around 15 g of COD/L) and was supplemented with sodium hydroxide (NaOH, 7 N) to maintain a neutral pH. The hydraulic retention time (HRT) inside the storage feed tank was 0.5 day.

After this study, batch experiments under the completely mixed conditions (Pérez, 1995) were conducted in order to investigate the decomposition characteristics of the vinasses by the anaerobic biomass. The obtained results indicated that this was a complex substrate consisting of two fractions of different nature and biodegradability: S_1, the easily biodegradable substrate fraction (80% of the total), and S_2, the non-easily biodegradable substrate fraction (recalcitrant substrate) given the conditions of the experiment.

Characteristics of the Support Media. Open-pore sintered glass beads (SIRAN) were used as the medium for cell immobilization and retention. This carrier has been developed and marketed by Schott Glaswerke, and it is produced by sintering a mixture of glass and salt powder, followed by a washing process which elutes the nonsinterable salt. The resulting glass sponge has a well-defined pore size distribution. An essential advantage of the sintered glass is the double-pore structure of the surface, which is determined by micropores and macropores. The micropores in the range of 1−10 μm provide the initially submerged microorganisms with a population area from which the entire carrier can be populated (Breitenbucher et al., 1990).

The particles were sieved for uniformity, and the resulting particles had an apparent diameter of approximately 1.5−2 mm. This material was chosen because of its uniformity and because it could be incinerated to measure dry organic matter concentrations. Also, data obtained from the operation with this type of support material can be used for comparison with those of other technologies or from nonporous carriers. The main characteristics of SIRAN carriers are shown in Table 1.

Analytical Methods. For liquid samples, the parameters analyzed in both the effluent and the influent were pH, chemical oxygen demand (COD), both total and volatile suspended solids (TSS, VSS), and attached microbial mass (VS_{att}). COD was determined by the dichromate reflux methods. For soluble COD, the sample was first filtered as in the TSS analysis, and the filtrate was used for the COD analysis. TSS and VSS were determined by the glass fibber filter method as described in *Standard Methods* (APHA, 1989). For gaseous samples, the parameters analyzed were the volume of biogas produced at STP and the composition of the biogas (methane, CH_4, and carbon dioxide, CO_2). Gas production was measured continuously by water displacement. Determinations of methane and carbon dioxide were carried out by gas chromatography separation with a stainless steel column packed with Carbosive SII (diameter of 1/8 in. and 2 m length) and a thermal conductivity detector (TCD). The injected sample volume was 1 cm^3, and operational conditions were as follows: 7 min at 55 °C; ramped at 27 °C/min until 150 °C; detector temperature, 255 °C; injector temperature, 100 °C. The carrier was helium, and the flow rate used was 30 mL/min. A standard gas (supplied by Carburos Metálicos, S.A; composition: 4.65% H_2, 5.33% N_2, 69.92% CH_4, and 20.10% CO_2) was used for the calibration of the system.

From each stage of the colonization process, a small fraction of colonized particles was utilized for the evaluation of the attached biomass concentration evolution in the reactor and for their morphological characterization, using optic microscopy and epifluorescence microscopy (wavelength excitation (λ_{exc}) at 400−440 nm with barrier filter (λ_{barr}) at 460 nm).

Because the SIRAN used would not volatilize at 550 °C, the procedure recommended by Shieh et al. (1981) was applicable. The immobilized cell mass was measured as follows. The expanded bed material was collected through a sampling port (5−10 mL) and dried at 103 °C for 24 h in a ceramic evaporating dish. The dried sample was then muffled at 550 °C for 1 h. The difference between two dried weights would yield the mass of total volatile solids (TVS) in the sample. The difference between the mass of TVS and mass of free cells in the mixed liquor would yield the mass of immobilized calls as attached volatile solids (VS_{att}).

Experimental Design. The experimental protocol was designed to examine the effect of the organic loading rate on the efficiency of the fluidized bed reactor (with SIRAN media) process and to test the attached biomass concentration evolution in the reactor. The study was conducted in the laboratory over a 3-month period. The hydraulic retention time (HRT) bed was defined in terms of the expanded bed volume occupied by bioparticles.

Reactor Start-Up. Approximately 116 g of coated media removed from a fixed-film thermophilic anaerobic reactor operated on the distillery wastewater used in this investigation was used as the seeding material for AFB reactor start-up. The coated SIRAN contained 89.26 kg of VS_{att}/m^3 of SIRAN (Pérez, 1995). Reactor loaded with coated SIRAN was initially filled with the feed solution with a COD of 15 000 mg/L. Then it was operated under the total recycle conditions. The reactor was operated at organic loading rates (OLR_0) of 5.9 and 8.58 kg of COD m^{-3} day^{-1} at HRTs of 2.5 and 1.7 days, respectively.

During the experimental research, HRT was gradually decreased between 1.34 days and 0.37 day. The volumetric COD loading was between 11.16 and 40.51 kg of COD m^{-3} day^{-1}. A concentration of 15 mg/L was maintained in all the stages studied.

HRT remained constant during each stage until reaching the steady state (except during the last stage at HRT of 0.37 day). The attainment of the steady state was verified after an initial period (3 times the HRT) by checking whether the constant effluent characteristic values were the mean of the last measurements in each stage.

Results and Discussion

The organic removal efficiency of the AFB compared to the applied hydraulic retention time is shown in Figure 2 (including initial start-up period). Removal efficiencies were quite high. COD soluble removals (COD_r) were observed to vary from 95.5 to 81.4%. At HRT of 0.59 day, a COD_r of 92.5% was obtained at an ORL of 25.3 kg of COD m^{-3} day^{-1}, and at HRT of 0.46 day, COD_r decreased to 81.5% at an ORL of 32.31 kg of COD m^{-3} day^{-1}. Clearly, the efficiency of substrate removal is a function of the hydraulic retention time and concomitant with the organic loading rate. The last organic overload applied (HRT of 0.37 day) produced a fast decrease in pH, probably due to an increase in total organic acid concentration, which resulted in poor effluent quality. This meant that the methanogen's activity dropped sharply and the effluent quality deteriorated further. As expected, the highest overloading caused the most dramatic changes, as reported by Denac et al. (1988).

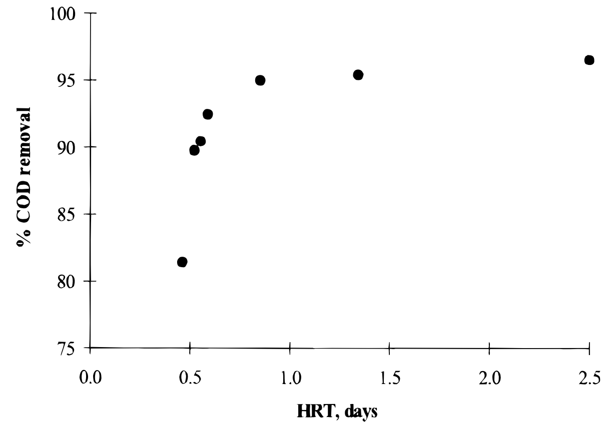

Figure 2. Organic removal efficiency (as percentage of chemical organic demand, %COD removal) as influenced by hydraulic retention time (HRT).

Other wine distillery waste studies have been reported using other thermophilic anaerobic processes such as the anaerobic filter (Pérez, 1995) and the UASB reactor (Craveiro et al., 1986) with 80 and 83% COD removal at organic loads of 12 and 13.2 kg of COD m^{-3} day^{-1} and HRT of 1.6 and 2.4 days, respectively. Balaguer et al. (1992) reported that the efficiency of substrate removal was 70.5% at an ORL of 36 kg of COD m^{-3} day^{-1} (HRT of 0.5 day), treating distillery wastewater at mesophilic conditions (35 °C) and using sepiolite as support medium.

Methane gas production averaged 3.27, 7.82, and 9.00 L L^{-1} day^{-1} at HRT of 1.34, 0.59, and 0.46 day, respectively. Therefore, the volumetric methane production activity (expressed as m^3 m^{-3} day^{-1}) could be expressed as a linear function of organic loading rate removal (OLR_r, expressed as kg of COD m^{-3} day^{-1}). The linear regression obtained can be expressed as:

$$CH_4\ (m^3\ m^{-3}\ day^{-1}):\ -1.10 + 0.33 OLR_r\quad (\text{kg of COD } m^{-3}\ day^{-1})\qquad (1)$$

Figure 3 shows the volumetric methane rate as a function of the OLR_r. The methane yield, as liters of methane produced per gram of COD removal, keep constant at 0.33 $LCH_4/gCOD_r$. This represents 90% of the theoretical methane yield (1 g of COD is equivalent to 0.35 L of methane at STP conditions) when the carbon requirements for cells synthesis are excluded (Metcalf & Eddy, 1991). According to eq 1, the suitable threshold level is 3.33 kg of COD m^{-3} day^{-1}.

An important variable for effluent quality is the volatile suspended solids concentration (VSS). Data of both reactor-immobilized biomass (as kg of VS_{att} per m^3 and per kg of SIRAN) and reactor-suspended biomass (as g of VSS/day) from each operation reactor stage are shown in Table 2. Initially, a detachment of immobilized biomass is produced. Subsequently, during the period of stable operation given in Table 2, the effluent VSS concentration increases only slightly for large increases

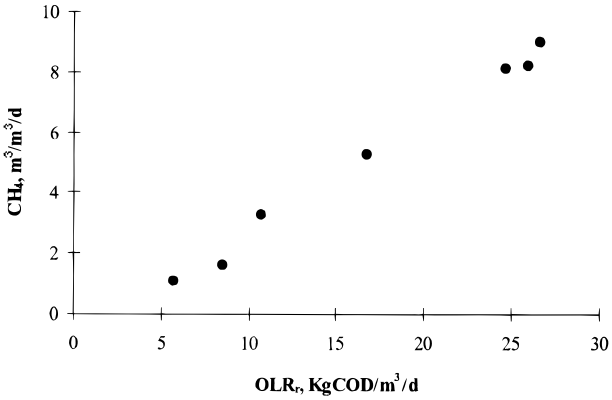

Figure 3. Volumetric methane rate as a function of the organic load rate (OLR) removal.

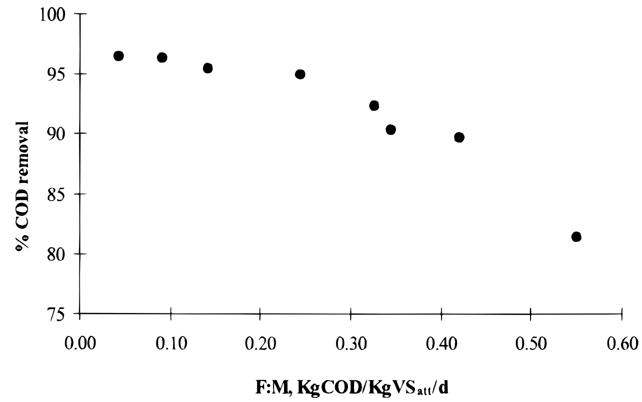

Figure 4. Organic removal efficiency (as percentage of initial COD) as a function of food-to-microorganism (F:M) ratio.

Table 2. Biomass Distribution in Anaerobic Fluidized Bed (AFB) Reactor (Immobilized Biomass, Suspended Biomass, and Mean Cells Retention Time (MCRT) at Different Stages of the Process

F:M (g of COD g^{-1} of VS_{att} day^{-1})	HRT (days)	immobilized cells (kg of VS_{att}/m^3 SIRAN)	immobilized cells (kg of VS_{att}/kg of SIRAN)	suspended cells (g of VSS/day)[a]	MCRT (days)
0.14	1.34	78.66	0.0429	0.04	501.9
0.24	0.85	73.21	0.0400	0.07	282.8
0.33	0.59	77.26	0.0422	0.11	178.8
0.34	0.55	78.42	0.0428	0.22	91.8
0.42	0.52	71.54	0.0391	0.27	67.6
0.55	0.46	68.66	0.0375	0.34	51.8
0.76	0.37	53.10	0.0290	0.44	30.9

[a] Volatile solids in effluent.

in the hydraulic loading rate (period between 1.34 and 0.46 day). The fluidized bed reactor contained an average of between 0.21 and 0.61 g of VSS/L at HRT of 1.34 and 0.46 day, respectively. This is one of the major advantages of the AFB system over a suspended microbial system, in that even at very high loading (hydraulic and organic) conditions, washout is not a problem. On the other hand, the pH maintained a range of between 8.57 and 7.65 during all the stable processes.

When the HRT decreased to 0.37 day, the pH dropped dramatically to 5.5. The generation of biogas ceased, and the effluent's suspended volatile solids increased from 0.58 to 0.75 g of VSS/L in the last stage.

A term commonly used in practice as a design and control parameter and closely related to both the specific utilization rate, U, and the process efficiency is known as the food-to-microorganism (F:M) ratio. The F:M ratio for an AFB is defined as follows:

$$\text{F:M} = Q\frac{S_0}{XV} \tag{2}$$

where Q is the volumetric rate feed (L/day), S_0 is the feed concentration (g of COD/L), X is the attached biomass (Shieh et al., 1981) in terms of g of VS_{att}/L of SIRAN, and V (L of SIRAN) is the active volume reactor.

The F:M ratio could be used as a parameter for treatment performance evaluation of AFB (Boening and Larsen, 1982; Frostell, 1982; Chen et al., 1988). This equation implies that the observed COD_r in the reactor is attributable to immobilized cells and that suspended growth in the reactor is irrelevant. This assumption is validated by the biomass distribution data (summarized in Table 2), which show that, under all the tested conditions, more than 95% of the total biomass was immobilized on SIRAN. Therefore, no COD_r removal was caused by suspended growth. F:M ratios observed in this investigation were between 0.14 and 0.76 g of COD g^{-1} of VS_{att} day^{-1}.

Figure 4 presents observed COD removal data as a function of F:M ratio. The percentage of COD removal decreased linearly with increasing F:M ratio, from 96.6 to 81.5% for 0.0429 and 0.5508 g of COD g^{-1} VS_{att} of L^{-1}, respectively. This observation is in agreement with those reported elsewhere on AFB (Frostell, 1982; Boening and Larsen, 1982; Chen et al., 1988).

Methane production performance, percentage of methane in the gas produced, and the methane production activity as a function of F:M ratio are shown in Figure 5. As would be expected, the volumetric production rate of methane increased with the F:M ratio. Approximately 8.12 L of CH_4 L^{-1} of support day^{-1} could be produced per expanded bed volume at the F:M ratio of 0.42 g of COD g^{-1} of VS_{att} day^{-1}. From the vinasses tested, 95.5% of feed COD can be removed and 3.27 L of CH_4 can be produced per expanded bed volume at the F:M ratio of 0.14 g of COD g^{-1} of VS_{att} day^{-1}. Chen et al. (1988) reported that approximately 90% of feed COD can be removed and 5 L of CH_4 L^{-1} of digester day^{-1} can be produced at the F:M ratio of 0.14 g of COD g^{-1} of VS_{att} day^{-1} treating corn starch wastewater at mesophilic conditions.

Methane production activity remained relatively constant at approximately 0.33 L produced methane per gram of the COD removed over the range of F:M imposed ratios. This represents 94% of theoretical methane yield when the carbon requirements for cell synthesis are excluded (Metcalf and Eddy, 1991). For comparison, other authors (Chen et al., 1988) have reported that approximately 0.32 L of methane could be produced per gram of COD removed with glucose as the sole substrate. The reported values were also constant. Chen et al. (1988) reported that the methane production activity, in terms of liters of methane produced per gram of COD removed, could be considered an intrinsic property of an anaerobic system.

Depending on the prevailing F:M ratio, between 20.09 and 17.53 g of VS_{att} could be immobilized in the active volume reactor (255.35 cm^3), 0.0429 and 0.0375 kg of SV_{att}/kg of SIRAN, respectively.

The mean cell residence time (MCRT) can be defined as follows (Thirumurthi, 1988):

$$\text{MCRT (days)} = (XV + X_eV_t)/QX_e \tag{3}$$

where X is the immobilized cell concentration in g of VS_{att}/L, V is the expanded media bed volume in L, X_e is the effluent VSS concentration in g/L, V_t is the reactor liquid volume in L, and Q is the feed rate in L/day.

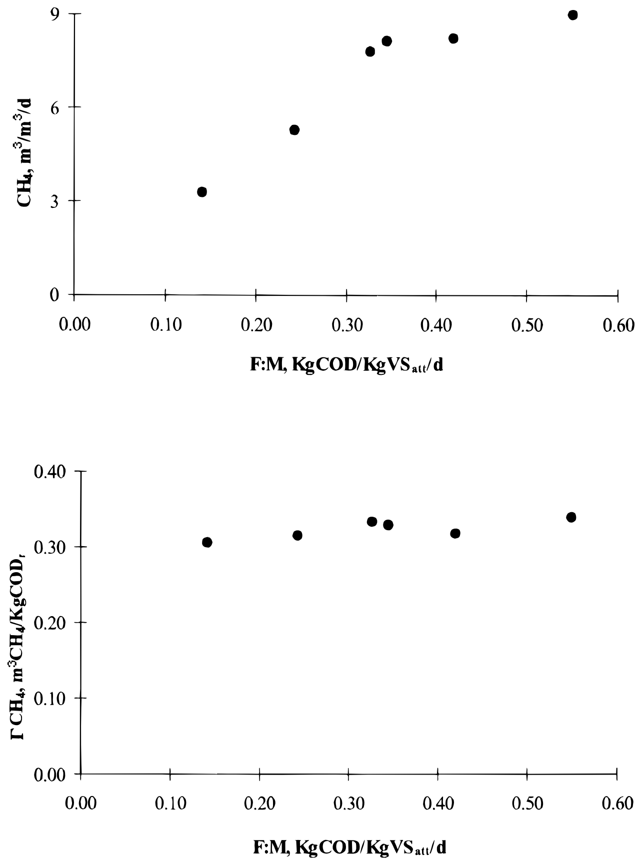

Figure 5. (a) Methane production performance. (b) Methane production activity (Γ) as a function of food-to-microorganism (F:M) ratio.

Equation 3 assumes that (i) effluent VSS originated from the detachment of immobilized cells, since the feed used was free of suspended matter, and (ii) completely mixed conditions were prevalent in reactors, since the recycle ratio maintained during the pseudo-steady-state experimentation was greater than 1000.

Data on the mean cells retention time (MCRT), as days, are shown in Table 2. These results indicate that SIRAN is an adequate medium in AFB applications. Its cell retention capacity was not affected by significant gas production activities observed at high F:M ratios. Furthermore, SIRAN is light; therefore, the energy requirements for fluidization of bioparticles are not excessive. As can be deduced from Table 2, the applied HRT influences the MCRT. Reactor MCRTs decreased from 502 to 30.9 days as the HRT decreased from 1.34 to 0.37 day, corresponding to F:M 0.14 and 0.76 g of COD g^{-1} of VS_{att} day^{-1}, respectively. Thus, except for HRT of 0.37 day, all the rest of the hydraulic retention times present values of immobilized cells higher than 68.6 kg of SV_{att}/m^3 of SIRAN and MCRTs of more than 50 days. The long MCRTs indicated that pore characteristics of SIRAN carriers were highly conducive for better immobilization and retention of immobilized cells, in agreement with those reported by Yee et al. (1992).

Organic loading applied to an AFB had a profound effect on its MCRT at lower F:M ratios. Reactor MCRTs decreased from 501.9 to 282.8 days as the F:M ratio increased from 0.142 to 0.244 g of COD g^{-1} of VS_{att} day^{-1}. Chen et al. (1988) concluded that the MCRT of AFBs operated at high F:M ratios becomes an operating parameter which is, to some extent, directly controllable. MCRT of AFBs operated at low F:M ratios is an intrinsic property of AFBs.

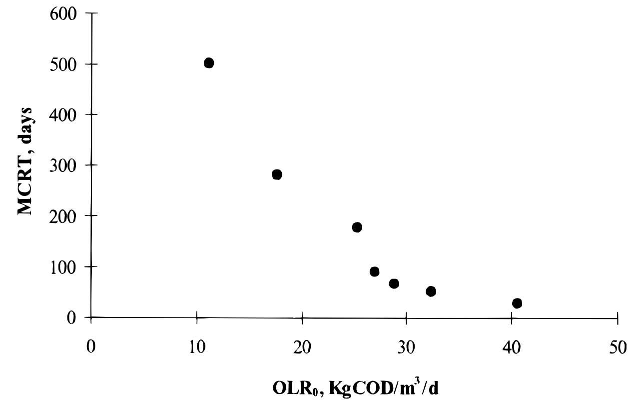

Figure 6. Effect of organic load rate (OLR) on mean cell retention time (MCRT).

The MCRT of the reactors remained unchanged at high F:M ratios. This observation suggests that, through proper medium selection, the impact of reduced MCRT on an AFB can be minimized, and a desirable MCRT can be maintained to ensure adequate COD_r removal and methane production performance.

Conclusions

AFB technology was tested as a means for pretreatment of concentrated industrial wastewater, such as wine distillery wastewater (vinasses). Laboratory results confirm that AFB technology provides good chemical oxygen demand (COD) reduction and methane production at high organic loading conditions.

Experimentally, it was confirmed that anaerobic fluidized bed systems can achieve >82.5% COD reduction at a COD loading of 32.3 kg of COD m^{-3} day^{-1} treating vinasses of wine in continuous-flow conditions. At HRT of 0.46 day, the volumetric rate of methane generation was 5.8 m^3 of CH_4 m^{-3} day^{-1} with a methane yield of 0.33 m^3 CH_4/kg of COD removal. The greatest efficiency of substrate removal was 97% for OLR 5.9 kg of COD m^{-3} day^{-1} and hydraulic retention time of 2.5 days.

The F:M ratio can be used as a parameter for treatment performance evaluation of AFB. For vinasses, excellent COD reduction and methane production were achievable at F:M ratio of 0.55 g of COD g^{-1} of VS_{att} day^{-1} (more than 80% of feed COD was removed and 9 m^3 m^{-3} day^{-1} of methane was produced).

Acknowledgment

This work was funded by a grant of the Comisión Interministerial de Ciencia y Tecnología (C.I.C.Y.T.) of the Spanish Government (No. BIO 92-0859, Madrid, Spain).

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Accepted September 24, 1996.⊗

BP9600795

⊗ Abstract published in *Advance ACS Abstracts,* November 1, 1996.