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ANAEROBIC THERMOPHILIC FLUIDIZED BED TREATMENT OF INDUSTRIAL WASTEWATER: EFFECT OF F:M RELATIONSHIP

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ABSTRACT

This paper describes the thermophilic (55°c) anaerobic biodegradation of wine distillery wastewater (vinasses) in a laboratory fluidized bed reactor (AFB) with a porous support media. The experimental protocol was defined to examine the effect of the increase of organic loading rate on the efficiency of AFB and to report on its steady-state performance.

The AFB reactor was subjected to a programme of steady-state operation over a range of hydraulic retention time, HRTs, of 2.55 - 0.37 days and organic loaging rate, OLRs, up to 5.88 kgCOD/m^3·d in order to evaluate its treatment capacity. Porous support media particles used in AFB were previously colonized in semicontinuous anaerobic fixed-bed reactors treating wine-vinasses. The AFB reactor was initially operated with organic loading rate of 5.88 kgCOD/m^3·d and HRT of 2.55 days. The COD removal efficiency was found to be 96.5% in the reactor while the volumetric methane produced in the digester reached 1.08 m^3/m^3·d. Over 94 days operating period, an OLR of 32 kgCOD/m^3·d at an F:M ratio of 0.55 kgCOD/kgVS_{att}·d was achieved with 81.5% COD removal efficiency in the experimental AFB reactor. At this moment, the methane content of biogas produced in the digester reached 9.0 m^3/m^3·d. Furthermore, the increase of OLR at 40.5 kgCOD/m^3·d, corresponding to 0.37 days HRT, provokes malfunction of the process with a sudden drop in COD removal efficiency and stopping the biogas production.

KEYWORDS: thermophilic anaerobic digestion, fluidized bed, F:M ratio, MCRT, wine vinasses.

SHORT TITTLE: Anaerobic thermophilic fluidized bed treatment of vinasses

INTRODUCTION

Anaerobic treatment of industrial wastewater has became a viable technology in recent years due to the rapid development of high-rate reactors, such as anaerobic filter and upflow anaerobic sludge blanket (UASB) (Fang, 1996; Dinsdale, 1997), both upflow and downflow stationary packed beds (Nebot, 1995; Pérez, 1995, 1996, 1997a), and fluidized or expanded beds (Chen, 1988; Breintenbucher, 1990; Hickey, 1991; Iza, 1991; Pérez, 1995, 1997b; Seckler, 1996). This development is due to the fact that the method combines a number of significant advantages, including low energy consumption, low excess sludge production, enclosure of odours and aerosols, ..., over conventional aerobic methods with different activated sludge types of wastewater treatment.

The treatment capacity of an anaerobic digestion system is primariry determined by the amount of active population retained within the system, which in turn is influenced by wastewater composition, system configuration and operation of anaerobic reactor. Unlike the conventional biofilm systems in which the growth support media are fixed in space either by gravity or by direct attachment to the reactor wall, the anaerobic fluidized bed system retains the growth support media in suspension by drag forces exerted by upflowing wastewater. Moreover, the distribution of biomass holdup (in form of biofilm) is relatively uniform, because of the completely mixed conditions maintained and the continuous biofilm sloughing process which counterbalances the accumulation of biomass due to growth. Therefore, the anaerobic fluidized-bed system can be considered as a continuous-flow, completely-mixed homogeneous microbial system. The presence of growth support media in the reactor has not effect on the interpretation of biomass holdup in the anaerobic fluidized bed system, because the biomass holdup can be directly measured in terms of attached volatile solids using the techniques developed by Shieh et al. (1985) and Mulcahy and Shieh (1987).

Interest in AFB (Anaerobic Fluidized Bed) technology has grown as it couples the recovery of usable energy with good process efficiency and stability. Potential AFB applications for treatment of hazardous waste with inhibitory/recalcitrant compositions have also been reported (Tang, 1987; Fox, 1990; Suidan, 1996; Pérez, 1997b).

The purposes of this study is to elucidate the treatment efficiency in a fluidized bed reactor which decomposes distillery wastewater.

MATERIALS AND METHODS

The study was conducted in the laboratory over a three-month period. Parameters measured were soluble chemical oxygen demand (COD), effluent suspended solids (TSS), effluent volatile suspended solids (VSS), pH, gas production, composition of gas (methane and dioxide carbone percentages) and attached microbial mass (VS_{att}). The methods and material used are described in this section.

Description of anaerobic fluidized bed scheme (AFB). The experimental system used in the lab-scale study consists of a transparent Plexiglas column with a cross-section of 5.11 cm^2 and 170 cm of length. Its bottom was molded into a conical shape to promote uniform fluidization of media and bioparticles (that is, biofilm coated media). Heated water was maintained at 55°C and was pumped from recirculating water bath through the constant temperature jacket surrounding the reactor.

The reactor was initially charged with 116.6 mg of coated support medium (coated SIRAN), previously colonized in semicontinuous anaerobic thermophilic fixed-bed reactor (Pérez, 1997). The support occupied a total volume of 204 cm^3 in an unexpanded mode. In expanded mode, the support occupied 255 cm^3.

The effluent from the fluidized bed reactor was recycled through a variable speed centrifugal pump in order to provide upflow velocities for media and to maintain 25% bioparticle expansion. Such upflow velocities also ensured that completely mixed conditions were maintained in the liquid phase (Pérez, 1995) and the active volume of the digester remained constant throughout the study. 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 periodically to account for varying biomass to keep a constant fluidized bed level. Plugging of the SIRAN bed was not observed at this level of expansion.

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 form the liquid in the effluent.

Open-pore sintered glass beds (SIRAN) were used as the media for cell immobilization and retention. An essential advantage of the sintered glass is the double-pore structure of the surface. The micropores in the range of 1-10 μm provide the initially submerged micro-organisms with a population area from which the entire carrier can be populated (Breintenbucher, 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. The main characteristics of SIRAN carriers are the follows: medium real density= 1832 g/L; bulk density= 570 g/L; pore volume = 50-60%; pore diameter= 60-300 μm, and high specific surface (87000 m^2/m^3) suitable for using as support media in anaerobic fluidized-bed reactors.

The feed used throughout the study was collected from an ethanol producing wine-distillery plant placed in Tomelloso (Ciudad Real, Spain). The selected vinasses were transported and maintained frozen and, afterwards, vinasses were maintained at 4°C to minimize microbial growth in the feed lines. 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 kgCOD/L) and was supplemented with sodium hydroxide to maintain a neutral pH.

The thermophilic condition was selected because this kind of waste can be digested at such temperature (55°C) without the necessity for heating the feedstock because vinasses come from distillation column at 90°C and, in this operational conditions, additional methane can be obtained and the volume of reactor can be significatively reduced. In general, vinasses show an adequate relationship between the different macro and micro-nutrients with a favourable COD/N/P ratio suitable for microbiological treatment.

Vinasses biodegradation batch experiments (Pérez, 1995) indicated that this was a complex medium formed by two substrates 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.

Samplig and analysis. During the operation of the fluidized bed reactor, temperature, pH, gas composition and gas production rate were monitored daily.

Gas produced was collected in a gas-meter filled with acidified saturated salt solution. 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 salt solution displaced from the gas collector while gas composition (methane and carbon dioxide) was carried out by gas chromatography separation with a stainless steel column packed with Carbosive SII (diameter of 1/8" and 2 m length) and 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 30mL/min. A standard gas (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.

Feed and effluent samples were taken for the analyses of filtered COD and both, total suspended and volatile suspended solids (TSS, VSS) analyses were carried out once per day. All analytical determinations were performed according to "Standard Methods" (A.P.H.A., A.W.W.A., W.P.C.F., 1989).

Attached biomass concentrations (VS_{att}) were determined by removing a representative sample from the reactor and then ashing the dried sample to measure the total volatile solids both attached to the particles and entrapped between them. The determination was performed in accordance with protocol described by Shieh (1985).

Reactor operation. 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) and to evaluate the attached biomass concentration evolution in the reactor. The empty HRT bed was defined in terms of the expanded bed volume occupied by bioparticles. The AFB reactor was subjected to a programme of steady-state operation over a range of hydraulic retention time of 2.55 and 0.47 days. The volumetric COD loadings were between 5.88 and 32.31 kgCOD/m^3·d.

Initially, the reactor was fed with distillery wastewater at strength of 15 kg/m^3 to give an organic loading rate of 5.88 kgCOD/m^3·d with a HRT of 2.55 days. After this, hydraulic retention time was gradually decreased, remaining constant during each stage until reaching the steady-state conditions. The attainment of the steady state was verified after an initial period (3 times the HRT) by checking whether the constant effluent characteristic values (COD removal and methane generation) were the mean of the last measurements in each stage (Pérez, 1997).

RESULTS AND DISCUSSION

Performance and operation parameters during all stages of the experiment are shown in Fig. 1 In this, the organic loading and removing rate, OLR_0 and OLR_r, organic removal efficiency (as percentage of initial COD), volatile and total suspended solids, and volumetric CH_4 and biogas rate production versus time are presented.

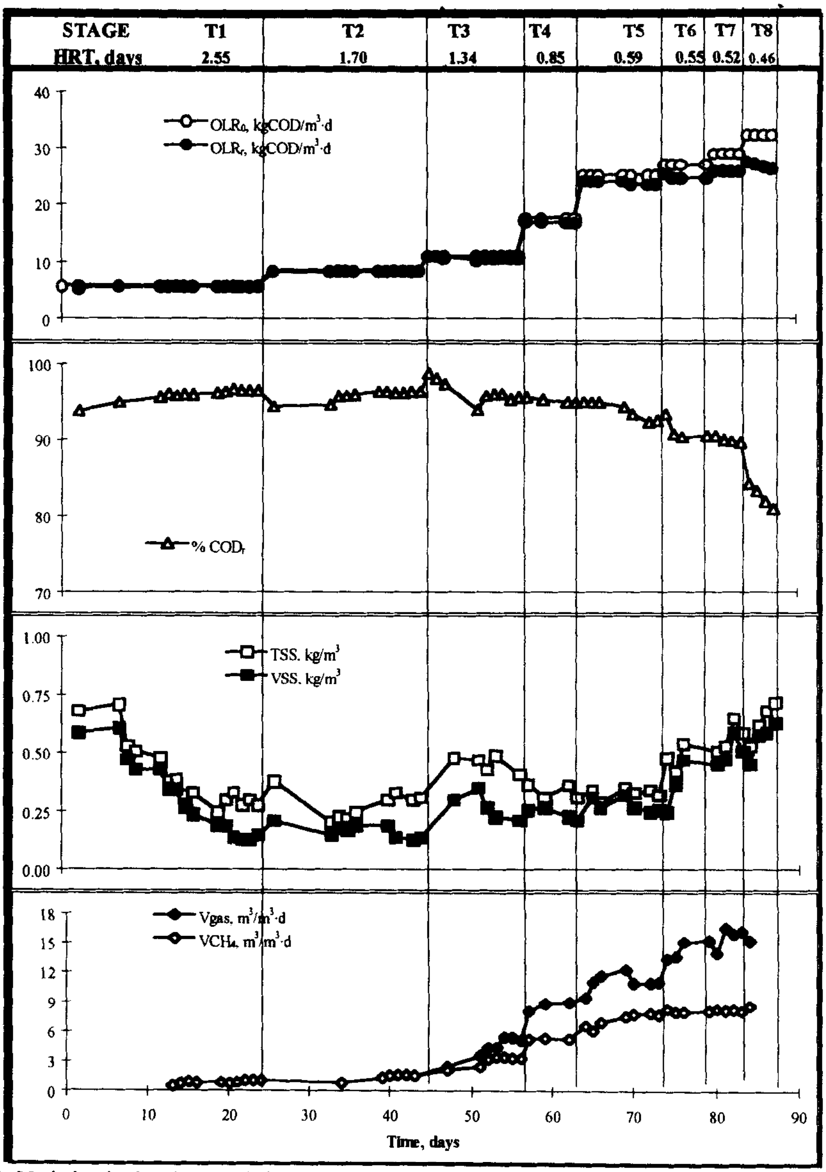

Fig. 1. Variation in the characteristic parameters of the anaerobic process with time: **a)** organic loading and removing rate, OLR_0 and OLR_r, as $kgCOD/m^3 \cdot d$; **b)** organic removal efficiency (as percentage of initial COD); **c)** VSS and TSS, as kg/m^3; **d)** volumetric CH_4 and biogas rate production, m^3/m^3digester·d. Feed: dilute vinasses 15 $kgCOD/m^3$.

Experiments in this investigation were performed with the expanded bed height in the reactor controlled at 50 cm, yielding a working reactor volume of 0.25 L. Under all conditions tested, the liquid phase in the reactor was completely mixed. Last date (period of HRT: 0.37 days) corresponding to the instability stage, has no been represented in Fig. 1.

Fig. 1a shows the changes of OLR_0 and OLR_r at different HRTs. During the initial period of operation, including HRTs between 2.55 to 1.34 days, both parameters have almost identical values, indicating that, in this conditions, experimental reactor provides good chemical oxygen demand (COD) reduction. Subsequently, for HRT lower than 1.34 days, the differences between the OLR_0 and OLR_r values are higher, due to the COD removal efficiency decreased gradually with the increase of HRT, as can be observed in Fig. 1b.

However, the value obtained for the last HRT presented show an important decrease of COD removal efficiency. This phenomena indicates that OLR added (32.31 $kgCOD/m^3 \cdot d$) is close to the maxima treatment capacity of the system. Thus, increase of OLR to 40.5 $kgCOD/m^3 \cdot d$ lead to instability stage with a sudden drop in efficacy and stopping biogas production.

An important variable for effluent quality is the volatile suspended solids concentration, VSS (Fig. 1c). As can be seen, during the first stage (HRT:2.55 days), a detachment of immobilized biomass is produced until reaching constant values of 0.14 gVSS/L. This detatchment is due that SIRAN beads had been previously colonized in a fixed bed reactor and, consequently, the initial biofilm thickness was very high. The necessary increase of superficial velocity through a bed media at a velocity sufficient to maintain fluidized state (and the consequently large drag forces exerted by upflowing wastewater) provokes an elevated biomass detatchment which is noted in the initial evolution of VSS in effluent (Fig. 1c). Subsequently, the effluent VSS concentration increases only slightly for large increases in the hydraulic loading rate (period between 1.34 to 0.46 days). The fluidized bed reactor contained an average of between 0.21 and 0.61 gVSS/L, at HRT 1.34 and 0.46 days 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.

Fig. 1d shows the effect of HRT on volumetric methane and biogas rate production. At HRT of 2.55 and 1.70 days, the values of both parameters are the same as a consequence of CO_2 is used for the formation of $CO_3^{=}/CO_3H^{-}$ media tampon. Subsequently, methane production rate increased and the pourcentage of CH_4 in the gas produced decreased with time (with decreasing HRT).

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 until 0.37 days, the pH dropped dramatically until 5.5. The generation of biogas ceased. and the effluent's suspended volatile solids increased from 0.61 gVSS/L to 0.64 gVSS/L in the last stage.

Fig. 2a shows the relationship between COD removal efficiency and the hydraulic retention time in the reactor. Initially, removal efficiencies were quite high. COD soluble removals were observed to decrease from 96.6 to 81.5 % at HRTs of 2.55 and 0.46 days, respectively, and organic loads of 5.88 and 32.31 kgCOD/m^3·d. Clearly, the efficiency of substrate removal is a function of the hydraulic retention time and concomitant with the organic loading rate (Fig. 2b): the COD removal efficiency declined with decreased HRT (increased load) and was comparatively ineffective at HRT < 0.46 days (loading rates > 32.31 kgCOD/m^3·d). A subsequent organic overload applied (HRT: 0.37 days) produced a fast decrease in pH (5.5), which resulted in poor effluent quality (low efficiency of substrate removal). This drop in efficiency was illustred further by the decrease in volumetric CH_4 production rate which became nill at this HRT.

Other wine distillery waste studies have been reported using other anaerobic processes such as the anaerobic filter (Pérez, 1996) and the UASB reactor (Craveiro, 1986) with 80% and 83% COD removal at organic loads of 12.0 and 13.2 kg/m^3/d and HRT of 1.4 and 2.4 days, respectively.

Table 1 summarizes data on F:M ratio (as $kgCOD/kgVS_{att}·d$), reactor immobilized biomass (as $kgVS_{att}$ per m^3 of SIRAN) and reactor suspended biomass (as $kgVSS/m^3$ and gVSS/d) from each operation reactor stage, and the mean cells retention time, MCRT, as days (Thirumurthi, 1988).

HRT days	F:M $kgCOD/kgVS_{att}·d$	Immobilized cells $kgVS_{att}/m^3SIRAN$	VSS kg/m^3	Suspended Cells gVSS/d	MCRT days
2.55	0.0429	137.00	0.14	0.01	2446.3
1.70	0.0908	97.00	0.14	0.02	1221.4
1.34	0.1419	78.66	0.21	0.04	501.9
0.85	0.2441	73.21	0.22	0.07	282.8
0.59	0.3270	77.26	0.26	0.11	178.8
0.55	0.3446	78.42	0.47	0.22	91.8
0.52	0.4199	71.54	0.55	0.27	67.6
0.46	0.5508	68.66	0.61	0.34	51.8
0.37	0.7634	53.10	0.64	0.44	30.9

Table 1. Biomass distribution in AFB reactor. Summary of data on reactor biomass (immobilized biomass, suspended biomass and MCTR in different stages of the process.

The F:M ratio could be used as a parameter for treatment performance evaluation of AFB (Boening, 1982; Frostell, 1982; Chen, 1988). This parameter implies that the observed COD removal 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 1, which show that, under all the tested conditions more than 95% of the total biomass was immobilized on SIRAN (depending on the prevailing F:M ratio, between 20.09 to 17.53 gVS_{att} could be immobilized in the active volume reactor, that is, 0.0429 and 0.0375 $kgSV_{att}/kgSIRAN$, respectively). Therefore, no COD removal was caused by suspended growth. F:M ratios observed in this investigation were between 0.0429 and 0.7634 $gCOD/gVS_{att}·d$. Fig. 2c shows 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 0.04 and 0.55 $gCOD/gVS_{att}·d$, respectively. This observation is in agreement with those reported elsewhere on AFB (Frostell, 1982; Boening, 1982; Chen, 1988).

As can be seen in Fig. 2c, evolution of COD removal efficiency versus F:M ratios shows two different trends. For F:M ratios between 0.04 and 0.22 gCOD/gVS_{att}·d, a linear relationship can be observed but between 0.22 to 0.55 gCOD/gVS_{att}·d F:M values range, the slope in the linear relation between both variables is different. This aspects can be observed in Fig. 2a and 2b, also. The reason of this system behaviour could be related with the organic overloading due to the increase in the detatchment of biomass adhered onto the media support particles (Fig. 2c). This observation is in agreement with those reported by Chen (1988) operating on corn starch wastewater (4.1-9.1 gCOD/L) in anaerobic fluidized bed reactors.

This results indicate that SIRAN is an adequate media 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, and therefore, the energy requirements for fluidization of bioparticles are not excessive.

The applied HRT influences the cell residence times (MCRT). Reactor MCRTs decreased from 502 to 30.9 days as the HRT decreased from 1.34 to 0.37 days, corresponding to F:M 0.14 and 0.76 gCOD/gVS_{att}·d, respectively. Thus, except for HRT: 0.37 days, all the rest of the hydraulic retention times present values of immobilized cells higher 68.6 kgSV_{att}/m^3SIRAN, and MCTRs of more than 50 days.

The MCRT (as days) during the OLRs applied is illustrated in Fig. 3a. As can be observed, organic loading applied to an AFB had a profound effect on its MCRT at lower F:M ratios (Fig.3b). Reactor MCTRs decreased from 501.9 to 282.8 days as the F:M ratio increased from 0.142 to 0.244 gCOD/gVS_{att}·d. Chen (1988) concluded that 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 are an intrinsic property of AFBs.

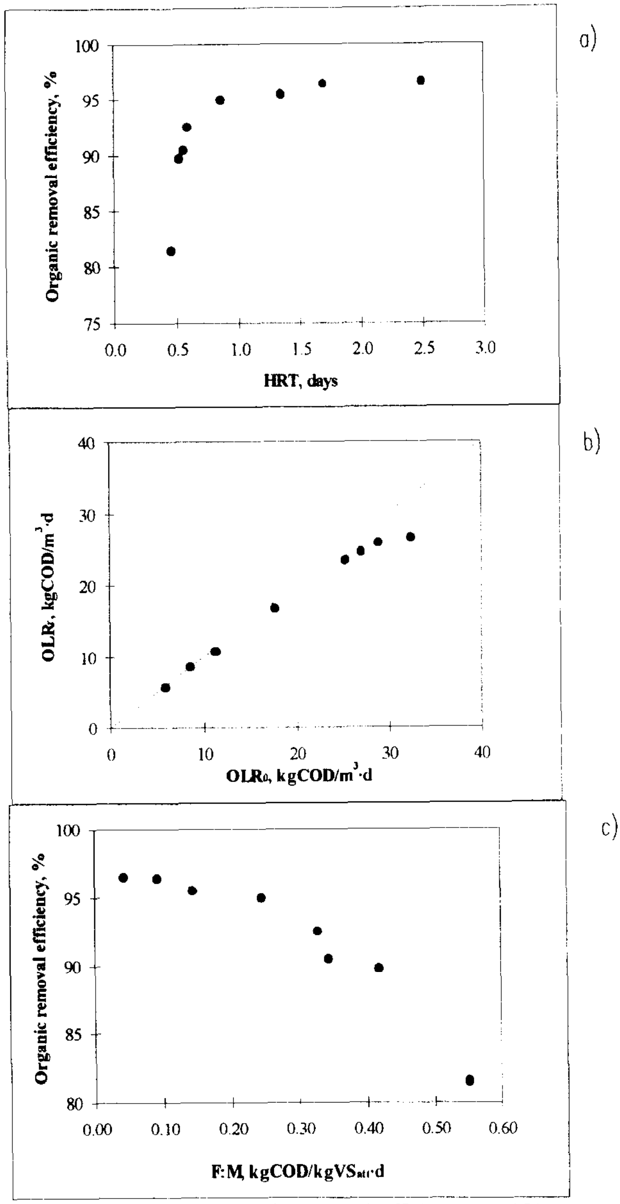

Fig. 2. a) Effect of HRT (days) on the organic removal efficiency (%COD removal); **b)** organic loading rate applied versus organic loading rate removal (as kgCOD/m^3·d); **c)** organic removal efficiency (as percentage of initial COD) as a function of F:M ratio (kgCOD/kgVS$_{att}$·d).

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

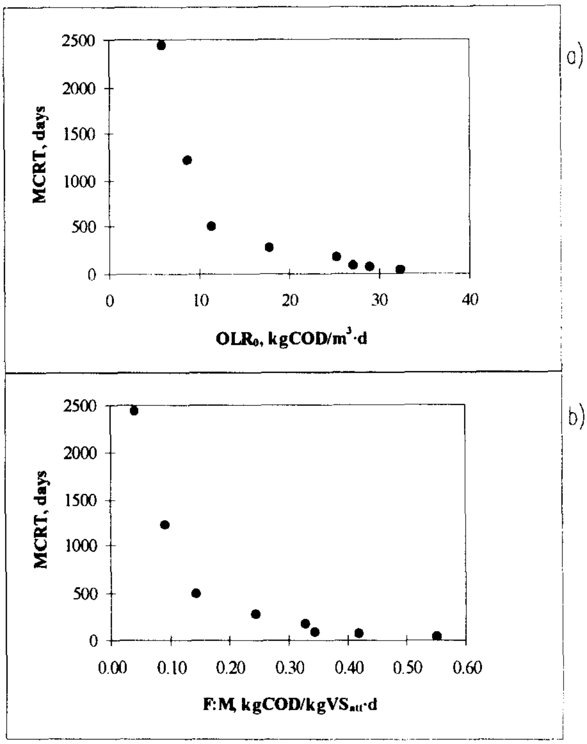

Fig. 3. Change in mean cell retention time (MCTR, days) with: **a)** OLR_0 applied ($kgCOD/m^3 \cdot d$); **b)** F:M ratio ($kgCOD/kgVS_{att} \cdot d$)

Fig. 4 shows methane production performance as a function of HRT (days), OLR_r ($kgCOD/m^3 \cdot d$) and F:M ($kgCOD/kgVS_{att} \cdot d$). As would be expected, the volumetric methane increased with decreasing

HRT (Fig. 4a). Methane gas production averaged 1.1 and 9.0 $m^3/m^3 \cdot d$ at HRT of 2.55 and 0.46 days respectively. The volumetric methane production activity (expressed as $m^3/m^3/d$) could be expressed as a linear function of OLR_r ($kgCOD/m^3 \cdot d$). Over the range of OLR imposed, the methane yield (methane production activity) as liters of methane produced per gram of COD removal remained relatively constant at approximately 0.37 $m^3CH_4/kgCOD_r$. This represents 97% of the theoretical methane yield when the carbon requeriments for cell synthesis are excluded. The value obtained in the linear function of OLR_r is lightly inferior to the stoichiometric theoretical of 0.382 $m^3CH_4/kgCOD_r$ (at 25°C) due the synthesis of new micro-organisms and the initial attachment biomass processes on support surface. For comparison, other authors have reported that approximately 0.32 L of methane could be produced per gram COD removed with glucose as the sole substrate. The reported values were also constant. Chen (1988) reported that the methane production activity, in terms of liters of methane produced per gram, could be considered an intrinsic property of an AFB.

Methane production performance and the methane production activity as a function of F:M ratio, are shown in Fig. 4c. As would be expected, the volumetric production rate of methane increased with the F:M ratio. Approximately 8.12 LCH_4/Lsupport·d could be produced per expanded bed volume at the F:M ratio of 0.42 $gCOD/gVS_{att} \cdot d$. From the vinasses tested, 95.5% of feed COD can be removed and 3.27 LCH_4 can be produced per expanded bed volume at F:M ratio of 0.14 $gCOD/gVS_{att} \cdot d$. Methane production activity remained relatively constant over the range of F:M imposed ratios.

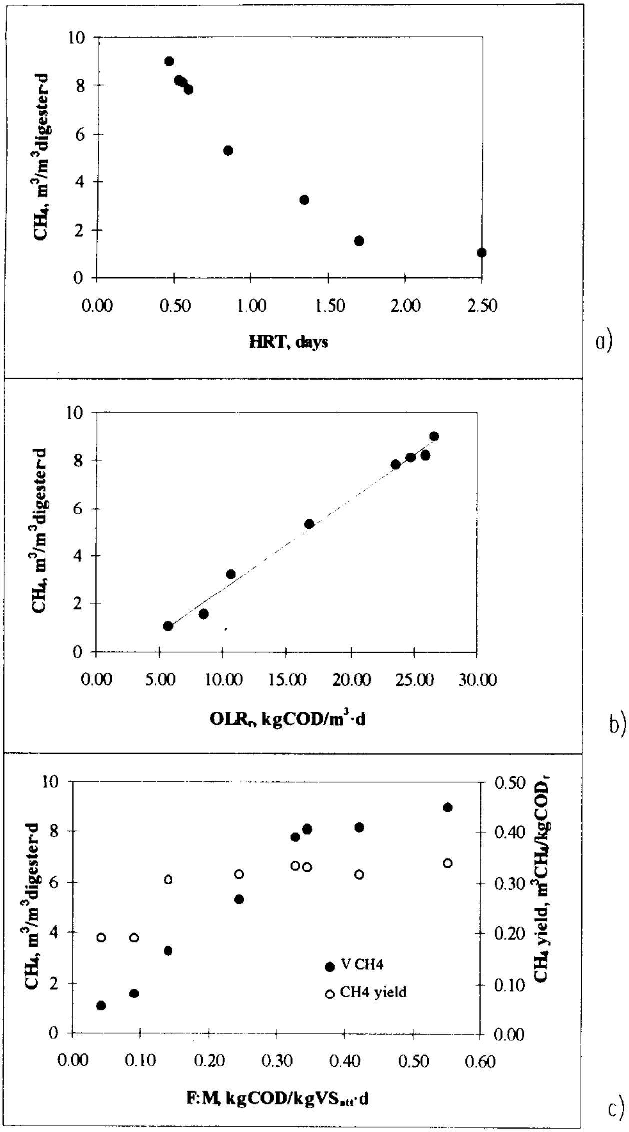

Fig. 4. a) Volumetric methane rate ($m^3/m^3 \cdot d$) as a function of HRT (days); **b)** methane production activity ($m^3/kgCOD_r$) as a function of OLR_r ($kgCOD/m^3 \cdot d$); **c)** Effect of F:M ratio on methane production performance and the methane production activity.

CONCLUSIONS

Laboratory results confirm that AFB technology provides good chemical oxygen demand (COD) reduction and methane production at proper food:microorganism (F:M) ratios. Experimentally, it was confirmed that anaerobic fluidized bed systems can achieve > 82.5% COD reduction at a COD loading of 32.31 $kgCOD/m^3 \cdot d$ treating vinasses of wine in steady-state conditions. The greatest efficiency of substrate removal was 97% for OLR 5.90 $kgCOD/m^3 \cdot d$ and hydraulic retention time of 2.55 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 the F:M ratio of 0.55 $kgCOD/kgVS_{att} \cdot d$ (more than 80% of feed COD was removed and $9.0 m^3/m^3 \cdot d$ of methane was produced).

ABBREVIATIONS AND SYMBOLS

AFB = Anaerobic Fluidized Bed

COD = Chemical Oxygen Demand

COD_r = Chemical Oxygen Demand removal

VS_{att} = Volatile Attached Solids

TSS = Total Suspended Solids

VSS = Volatile Suspended Solids

F:M = Food:Microorganisms ratio

HRT = Hydraulic Retention Time

MCRT = Mean Cell Retention Time

OLR_r: Organic Load Rate removed

OLR_0: Initial Organic Load Rate

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