



COMPARATIVE PERFORMANCE OF HIGH RATE ANAEROBIC THERMOPHILIC TECHNOLOGIES TREATING INDUSTRIAL WASTEWATER

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Abstract—The performance of two high rate technologies, anaerobic filter and fluidized bed at laboratory-scale, for treating distillery wastewater (wine vinasses) at anaerobic thermophilic conditions, have been compared in this study. Two kinds of media, corrugated plastic tubes and open-pore sintered glass pearls (SIRAN) were used as support on reactors. Experimentally, it was confirmed that the maximum organic load rate feed was 32 kg COD m⁻³ d⁻¹ for the fluidized bed reactor with the porous packing (SIRAN), 23 kg COD m⁻³ d⁻¹ for the stationary packed bed on SIRAN and 20 kg COD m⁻³ d⁻¹ for the anaerobic filter on corrugated plastic tubes. Under these conditions, the organic removal efficiency was 81.5, 75 and 50% respectively and the maximum organic removal efficiency was 97, 84 and 75%, respectively. The anaerobic fluidized bed technology is more effective than the anaerobic filter technology due, fundamentally, to this technology favouring the transport of microbial cells from the bulk to the surface and enhancing the contact between the microorganism and substrate phases. In this sense, the stationary packed bed technology is adequate for the treatment of easily biodegradable wastewater or for cases where elevated percentages of COD removal are not required, while the fluidized bed technology is especially suitable for treatment of hazardous wastes with recalcitrant compositions. © 1998 Elsevier Science Ltd. All rights reserved

Key words—thermophilic anaerobic digestion, anaerobic filter, fluidized bed, support media, wine vinasses

NOTATION

UAFF = upflow anaerobic fixed-film
 AFB = anaerobic fluidized bed
 COD = chemical oxygen demand
 HRT = hydraulic retention time
 OLR_r = organic load rate removed
 OLR₀ = initial organic load rate
 VS_{att} = volatile attached solids
 TSS = total suspended solids
 VSS = volatile suspended solids

INTRODUCTION

The anaerobic treatment of industrial wastewater has a number of potential benefits, including low energy consumption, low excess sludge production, enclosure of odours and aerosol. 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 over the last 20 years have been reviewed by Hickey *et al.* (1991), and are the upflow anaerobic sludge blanket (UASB), upflow and downflow stationary packed beds, and fluidized and expanded beds.

The media nature used for biofilm attachment has a significant effect on the reactor performance. A wide range of materials have been used as non-porous support media at laboratory- and pilot-scale, including glass beads (Salkinoja-Salonen *et al.*, 1983); red drain clay, sand and a number of different plastics (Nebot *et al.*, 1995), and as a porous materials, such as needle punched polyester (van den Berg and Kennedy, 1981), polyurethane foam (Fynn and Whitmore, 1982), sintered glass (Breitenbücher *et al.*, 1990; Perez, 1995).

The loading capacity and the subsequent biogas production rate and wastewater depollution yield are dictated by the amount of active biomass able to grow on the biodegradable fraction. Hence, the biomass retention capacity of a reactor, the specific sludge activity, the substrate biodegradability and concentration, and the daily availability of the wastewater will define the performance of the process. Furthermore, a suitable fluid flow pattern pro-

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vides adequate distribution of the feed to the microorganisms, enhances the contact between biomass and substrate and, therefore, reduces the limitations by substrate transfer.

The main objective of this paper is to compare the performance of two high rate technologies at laboratory scale, upflow anaerobic fixed-film reactor and anaerobic fluidized bed reactor, treating distillery wastewater (wine vinasses) at thermophilic conditions using two kinds of media support: corrugated plastic tubes and open pore sintered glass pearls (SIRAN).

MATERIALS AND METHODS

The experimental protocol was designed to examine the effect of organic loading rate on the efficiency of UAFF (up-flow anaerobic fixed-film reactor) and AFB (anaerobic fluidized bed reactor) in anaerobic thermophilic treatment of vinasses of wine. This study was conducted at laboratory scale.

Experimental system

The reactors used in this research are: upflow anaerobic fixed-film (UAFF) and the anaerobic fluidized bed (AFB). A schematic diagram of both the upflow anaerobic fixed-film reactor and the anaerobic fluidized bed reactor used in the laboratory study are shown in Fig. 1.

Anaerobic filter reactor. The anaerobic filter reactor consisted of a vertical cylindrical tank (25 cm length and 10 cm internal diameter). The active liquid volume was 2 l, and the empty volume was 2.4 l. The reactor was filled with 600 randomly distributed media support entities (16 mm length). Reactor temperature was maintained at 55°C and the biogas generated was collected in a gas-meter. Feed was supplied by a peristaltic pump connected to a programmable timer. Effluent recirculation was used to mix and homogenise the liquid in the system.

Fluidized bed reactor. A transparent Plexiglas column with a cross-section of 5.11 cm² and length of 170 cm was used. Its bottom was moulded into a conical shape to promote uniform fluidization of media and bioparticles (that is, biofilm coated media). Recycle flow was drawn using a centrifugal pump to provide upflow velocities for media and bioparticle fluidization. Such upflow velocities also ensured that completely mixed conditions were maintained in the liquid phase (Pérez, 1995). 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 the varying biomass in order to keep a constant fluidized bed level (incipient fluidization or 25% expansion, according the case). Feed was pumped directly from the refrigerator into the recycle lines. The reactor effluent passed throughout a sealed contact chamber connected to an inverted siphon to separate the gas form the liquid in the effluent. Reactor temperature was maintained at 55°C with external heating water jackets.

Gas produced in both reactors 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.

Feed solutions

Distillery wastewater from an ethanol producing wine-distillery plant in Tomelloso (Ciudad Real, Spain) was used. Such waste can be digested at thermophilic temperatures without the necessity for heating the feedstock. 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.

The selected vinasses were transported and maintained at 4°C before their utilisation. 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 COD l⁻¹) and was supplemented with sodium hydroxide to maintain a neutral pH (7).

Vinasses biodegradation batch experiments (Pérez, 1995) indicated that this was a complex medium formed by two substrates of different nature and biodegradability: S₁, easily biodegradable substrate fraction (80% of the total), and S₂, recalcitrant substrate fraction. Initial COD of vinasses was 30 g COD l⁻¹, and the concentration of total suspended solids was negligible.

Characteristic of the support media

Corrugated plastic tubes and open-pore sintered glass pearls (SIRAN) were used as the media for cell immobilisation and retention in this research. Both of these were chosen to compare the performance of porous and non-porous media in two different anaerobic technologies, i.e. as stationary packed bed and as fluidized bed. The main characteristics of both corrugated plastic tubes and SIRAN pearls (Breitenbücher *et al.*, 1990) are shown in Table 1.

Before operating each system, the initial quantities of immobilised biomass (as volatile solids attached, VS_{att}) were evaluated. Representative units of both supports were extracted from the reactors and the content of volatile solids and total solids were determined.

These analyses indicated a global biomass concentration of 65.0 kg VS_{att} m⁻³ plastic support media (Pérez *et al.*, 1996) and 89.3 kg VS_{att} m⁻³ SIRAN. The last determination was performed in accordance with the protocol described by Shieh *et al.* (1985).

Analytical methods

All analytical determinations were performed according to *Standard Methods* (A.P.H.A., A.W.W.A., W.P.C.F., 1989). For liquid samples, the parameters analysed in both the effluent and the influent were pH, soluble COD and both TSS and VSS. For gaseous samples the parameters analysed were the volume of biogas produced at STP and its composition (CH₄ and CO₂).

Soluble COD was determined by the dichromate reflux methods: 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 fibre filter method as described in *Standard Methods*. Gas production was measured continuously by water displacement. Gas composition (methane and carbon dioxide) was determined using a modified gas chromatography previously described by Nebot *et al.* (1995).

Experimental design

The experimental protocol was designed to examine the effect of initial organic loading rate (OLR₀) on the efficiency of COD removed in: a) fluidized bed reactor (operating on stationary SIRAN media, at incipient fluidization conditions), b) fluidized bed reactor (on SIRAN media) (Pérez *et al.*, 1997) and c) anaerobic filter (operating on corrugated plastic); all experiments performed at steady state conditions.

For UAFF, the HRT was defined in terms of the bed volume occupied by bioparticles. In AFB, the HRT was

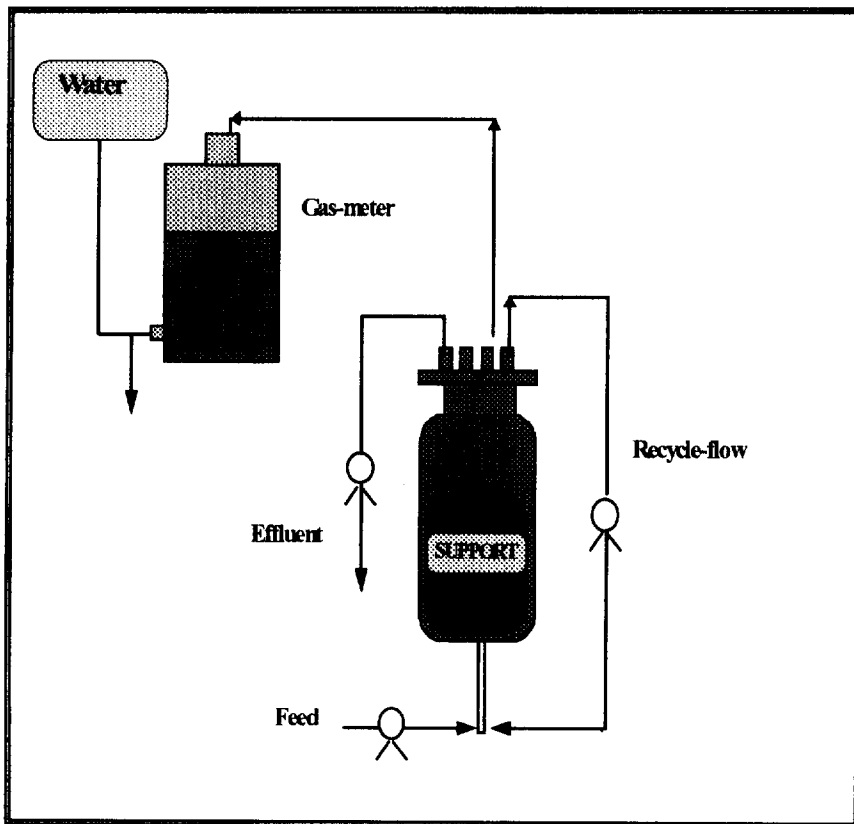
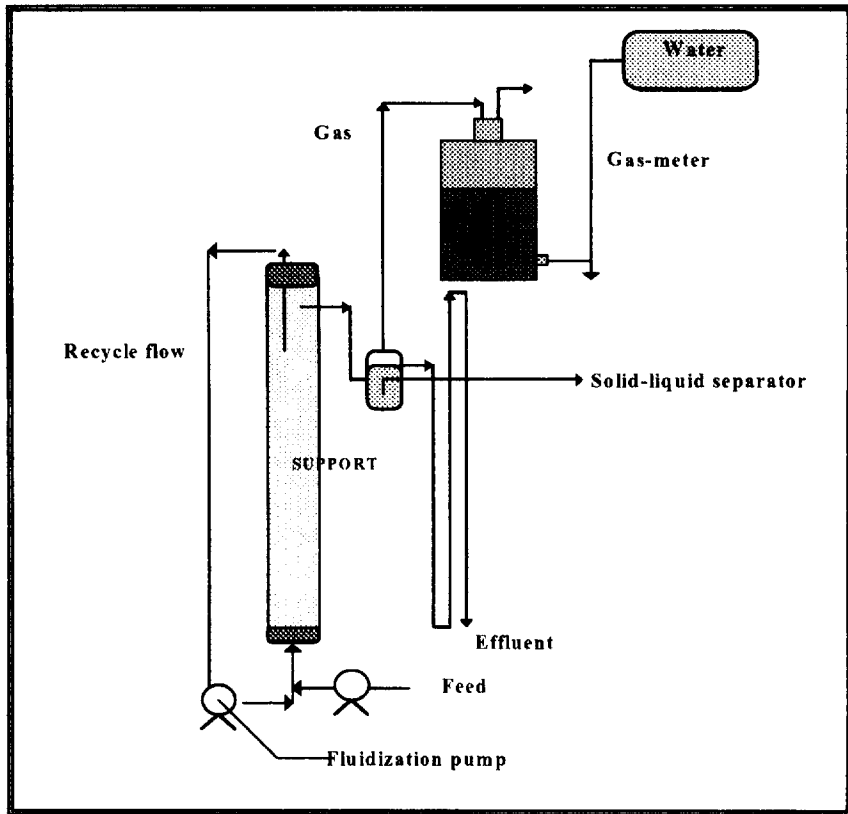


Fig. 1. Schematic diagram of the experimental reactors: anaerobic fluidized bed (AFB) and upflow anaerobic fixed-film (UAFF).

Table 1. Main characteristics of SIRAN and corrugated plastics carriers

Physical properties	Corrugated plastics	Siran
Bulk density (g l^{-1})	1161.4	1832
Apparent density (g l^{-1})	73	499.3
Porosity (%)	93	55–60
Surface area ($\text{m}^2 \text{m}^{-3}$)	450	87 000
Height (cm)	1.6	—
Diameter (cm)	1.6	0.15

defined in terms of the expanded bed volume occupied by bioparticles. In both cases, HRT remained constant during each stage until reaching the steady-state. 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. The steady state operating characteristics of all reactors were analysed (organic removal efficiency, volumetric gas and methane rate production, pH, effluent suspended solids, effluent volatile suspended solids and attached microbial mass), studying the influence of the nature of the support utilized as well as to the model of contact between the different phases implicated in the process. All the performance and operation results shown are the average values of the last three data of each stage.

RESULTS AND DISCUSSION

Performance of fluidized bed (incipient fluidization on SIRAN)

Hydraulic retention time was gradually decreased between 1.20 and 0.65 days. The empty bed HRT was defined in terms of the bed volume occupied by bioparticles (208.4 ml). The volumetric COD loadings were between $12.52 \text{ kg COD m}^{-3} \text{ d}^{-1}$ and $22.99 \text{ kg COD m}^{-3} \text{ d}^{-1}$.

COD removals were observed to vary from 83.56 to 74.7%. At HRT of 1.20 days, a COD removal of 83.56% was obtained at organic loads of $12.52 \text{ kg COD m}^{-3} \text{ d}^{-1}$, and at HRT of 0.65 days, COD removal decreased to 74.70% at organic load of $22.99 \text{ kg COD m}^{-3} \text{ d}^{-1}$. As expected, the highest overloading caused the most dramatic changes. A later applied organic overload (higher than $23 \text{ kg COD m}^{-3} \text{ d}^{-1}$) produced a fast decrease in pH, which resulted in poor effluent quality and possibly washout of the biomass. This meant that the methanogens activity dropped sharply and the effluent quality deteriorates further.

Methane gas production averaged 2.59, 3.63 and $4.35 \text{ m}^3 \text{ m}^{-3} \text{ d}^{-1}$ at HRT of 1.20, 0.75 and 0.65 days respectively. The methane yield, as liters of methane produced per grams of COD removal remained constant at $0.24 \text{ l CH}_4 \text{ g}^{-1}$ COD removal. This value is slightly inferior to the stoichiometric theoretical of $0.35 \text{ l CH}_4 \text{ g}^{-1}$ COD removal (1 g of COD is equivalent to 0.35 l of methane at STP conditions) due that the synthesis of new microorganisms and the initial attachment of the biomass processes on the support surface implies the initial production of polysaccharide to bind the material

and a high consumption of organic material for the synthesis route (anabolism).

An important variable for effluent quality is the volatile suspended solids concentration (VSS). The bed reactor contained an average of between 1.63 and $2.01 \text{ g VSS l}^{-1}$, at HRT 1.20 and 0.65 days respectively. The pH maintained a range of between 8.83 and 7.84 during all the stable processes.

Performance of fluidized bed (25% expansion on SIRAN)

The assays 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 the tested conditions, the liquid phase in the reactor was completely mixed.

Hydraulic retention time, defined in terms of the expanded bed volume occupied by the bioparticles, was gradually decreased between 2.50 and 0.46 days. The volumetric COD loadings were between $5.9 \text{ kg COD m}^{-3} \text{ d}^{-1}$ and $32.31 \text{ kg COD m}^{-3} \text{ d}^{-1}$. Removal efficiencies were quite high. At HRT of 0.59 days, a COD removal of 92.5% was obtained at organic loads of $25.3 \text{ kg COD m}^{-3} \text{ d}^{-1}$, and at HRT of 0.46 days, COD removal decreased to 81.5% at organic load of $32.31 \text{ kg COD m}^{-3} \text{ d}^{-1}$. A posterior applied organic overload produced the instability of the process (Pérez *et al.*, 1997).

Methane gas production averaged 3.27, 7.82 and $9.00 \text{ l CH}_4 \text{ l}^{-1} \text{ d}^{-1}$ at HRT of 1.34, 0.59 and 0.46 days respectively. The methane yield, as liters of methane produced per grams of COD removal remained constant at $0.33 \text{ l CH}_4 \text{ g}^{-1}$ COD removal (Pérez *et al.*, 1997).

Initially, a detachment of immobilized biomass was produced. Subsequently, the effluent SSV concentration increases only slightly for large increases in the hydraulic loading rate (period between 1.34 and 0.46 days). The fluidized bed reactor contained an average of between 0.21 and $0.61 \text{ g VSS l}^{-1}$, at HRT of 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, washout is not a problem (Pérez *et al.*, 1997).

The pH maintained a range of between 8.57 and 7.65 during all the stable processes. When the HRT decreased to 0.37 days, the pH dropped dramatically down to 5.5. The generation of biogas ceased and the effluent's suspended volatile solids increased from $0.58 \text{ g VSS l}^{-1}$ to $0.75 \text{ g VSS l}^{-1}$ in the last stage (Pérez *et al.*, 1997).

Anaerobic filter reactor on corrugated plastic tubes

Volumetric organic loading was gradually increased between 6.29 and $19.56 \text{ kg COD m}^{-3} \text{ d}^{-1}$. The hydraulic retention time, defined in terms of the volume occupied by bioparticles (2 l), was between 2.50 and 0.82 days.

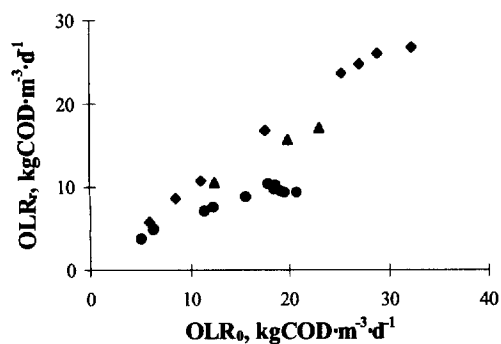


Fig. 2. Organic load rate removal (OLR_r) as influenced by organic load rate applied (OLR_0). (▲) Fluidized bed on SIRAN (incipient fluidization); (◆) fluidized bed on SIRAN; (●) anaerobic filter on corrugated plastic tubes.

COD removals were observed to vary from 75.5 to 47.89%. This reactor with non-porous packing showed instability above an OLR removal higher than $20 \text{ kg COD m}^{-3} \text{ d}^{-1}$.

Methane gas production averaged 1.45 and $3.55 \text{ l CH}_4 \text{ l}^{-1} \text{ d}^{-1}$ at HRT of 2.50 and 0.82 days respectively. The methane yield remained constant at $0.31 \text{ l CH}_4 \text{ g}^{-1} \text{ COD removal}$.

The stationary-packed reactor contained an average between 1.09 and $1.52 \text{ g VSS l}^{-1}$, at HRT 2.50 and 0.83 days respectively. The pH maintained a range of between 8.24 and 7.31 during all the stable processes.

The degradation efficiency is the most important parameter to be considered. In all the OLR_0 ranges studied, the COD removal efficiency of the fluidized technology was greater than the stationary packed bed reactors (on SIRAN or corrugated plastic). Figure 2 shows organic load rate removal (OLR_r) as influenced by organic load rate applied (OLR_0).

Maximum organic load rate feed was $32 \text{ kg COD m}^{-3} \text{ d}^{-1}$ for the fluidized bed reactor, $23 \text{ kg COD m}^{-3} \text{ d}^{-1}$ for the stationary packed bed on SIRAN and $20 \text{ kg COD m}^{-3} \text{ d}^{-1}$ for the anaerobic filter on corrugated plastic tubes. Under these conditions, the organic removal efficiency was 81.5,

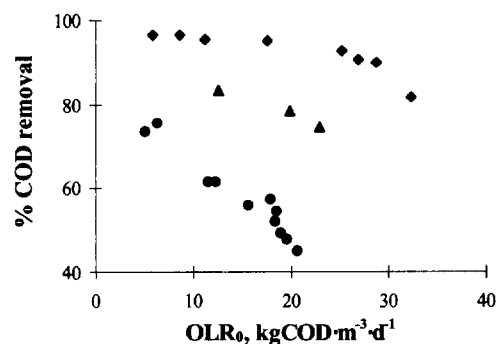


Fig. 3. Effect of organic load rate feed on the organic removal efficiency (% COD removal). (▲) Fluidized bed on SIRAN (incipient fluidization); (◆) fluidized bed on SIRAN; (●) anaerobic filter on corrugated plastic tubes.

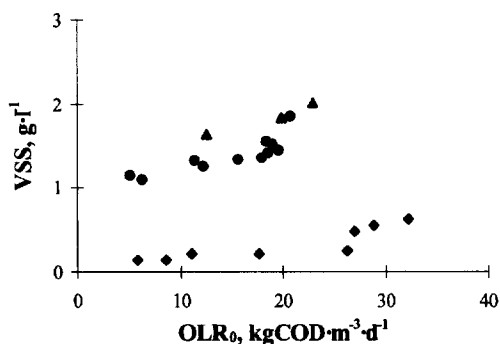


Fig. 4. Effect of OLR_0 on the VSS. (▲) Fluidized bed on SIRAN (incipient fluidization); (◆) fluidized bed on SIRAN; (●) anaerobic filter on corrugated plastic tubes.

75 and 50% respectively. The organic removal efficiency of the reactors compared to the organic load rate is shown in Fig. 3. The maximum organic removal efficiency was 97, 84 and 75%. So, the fluidized bed technology can degrade the substrate S_2 (recalcitrant substrate) in all stage operations. Other wine distillery waste studies have been reported using other anaerobic processes such as the anaerobic filter (Pérez, 1995, 1996) and the UASB reactor (Craveiro *et al.*, 1986) with 80% and 83% COD removal at organic loads of 12 and $13.2 \text{ kg m}^{-3} \text{ d}^{-1}$ and HRT of 1.4 and 2.4 days, respectively. Thus, fluidized technology enhances the high rate organic operation with high efficiency of COD removal.

Figure 4 shows the changes in VSS concentration in the reactors at different OLR_0 , with a higher VSS concentration profile in the effluent from the stationary packed reactors (irrespective of the carrier used: sintered glass or corrugated plastic) than the fluidized process. In all the cases, the biomass concentration increased with the applied OLR_0 . Thus, the technology used determines the extent of the detachment. The porous glass medium had a rapid biomass accumulation and were not susceptible to shear stresses, and the fluidized technology enhances a suitable fluid flow pattern that provides adequate distribution of the feed to the microorganisms, favours the contact between biomass and substrate and, therefore, reduces the limitations by substrate transfer.

Figure 5 shows the methane yield and the methane volumetric rate in the off-gas system having greater stability in the fluidized system at higher OLR_0 . An examination of OLR_0 between 6 and $20 \text{ kg COD m}^{-3} \text{ d}^{-1}$ shows that the fluidized bed on SIRAN produced a much higher methane rate than those stationary systems. The methane yield is similar in all reactors, except the fluidized process on SIRAN.

These experimental results confirm that the fluidized technology, irrespective of the nature of the carrier used, may give better performance than an anaerobic filter reactor. Breitenbücher *et al.* (1990) confirmed the ability of the porous media (SIRAN)

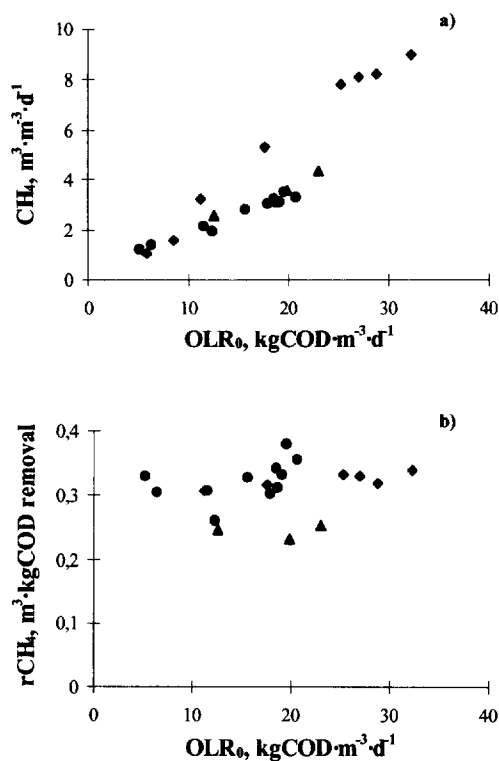


Fig. 5. (a) Methane yield and (b) volumetric methane rate, as a function of the OLR_0 . (▲) Fluidized bed on SIRAN (incipient fluidization); (◆) fluidized bed on SIRAN; (●) filter on corrugated plastic tubes.

to retain a high quantity of biomass and demonstrated that using porous sintered glass media increases reactor performance compared to other media. This study shows, furthermore, that this support is more effective when a fluidized system is used. Corrugated plastic is an adequate carrier for stationary filters to avoid the main problems of these systems: the obstruction of the filter when excessive growth is reached.

CONCLUSIONS

The results obtained in this research show that the stationary packed bed, with a corrugated plastic support, operated under stable conditions at organic loading rates (OLR_0) around $20 \text{ kg COD m}^{-3} \text{ d}^{-1}$, gives maximal total COD removal of 76% at OLR_0 of $6.29 \text{ kg COD m}^{-3} \text{ d}^{-1}$; the anaerobic filter, with an open pore sintered-glass support gives total COD removal of 84% with an OLR_0 around $12.5 \text{ kg COD m}^{-3} \text{ d}^{-1}$; the fluidized bed reactor, operated on open pore sintered-glass media, gives total COD removal of 96% at OLR_0 of $5.88 \text{ kg COD m}^{-3} \text{ d}^{-1}$.

Thus, the media nature used for biofilm attachment has a significant effect on the reactor performance. The open pore structure of the SIRAN carrier offers higher surface areas to be colonized by active biomass (entire carrier can be populated) than

corrugated plastic tubes. Nevertheless, important differences have been observed when SIRAN operates as stationary packed beds or as fluidized/expanded bed support. As a result, and irrespective of the support media utilized, anaerobic fluidized bed technology is more effective than anaerobic filters, fundamentally, due to this technology favoring the transport of microbial cells from the bulk to the surface and enhancing the contact between the microorganism and substrate phases. At the end of the investigation, attachment studies were carried out and the results showed a heavy biomass attachment in porous media, whereas mainly unattached biomass was retained in the voids of the non-porous media. However, their application considerably increases the costs of operation and maintenance and, also, demands a strict control process.

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