



ANAEROBIC DIGESTION OF WINE DISTILLERY WASTEWATER IN DOWN-FLOW FLUIDIZED BED

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Abstract—In down-flow fluidization, particles with a specific density smaller than the liquid are fluidized downward by a concurrent flow of liquid. This paper describes the application of the down-flow (or inverse) fluidization technology for the anaerobic digestion of red wine distillery wastewater. The carrier employed was ground perlite, an expanded volcanic rock. Before starting-up the reactor, physical and fluidization properties of the carrier material were determined. 0.968 mm perlite particles were found to have a specific density of 280 kg m⁻³ and a minimum fluidization velocity of 2.3 m h⁻¹. Once the down-flow anaerobic fluidized bed system reached the steady-state, organic load was increased stepwise by reducing HRT, from 3.3–1.3 days, while maintaining constant the feed TOC concentration. The system achieved 85% TOC removal, at an organic loading rate of 4.5 kg TOC m³ d⁻¹. It was found that the main advantages of this system are: low energy requirement, because of the low fluidization velocities required; there is no need of a settling device, because solids accumulate at the bottom of the reactor so they can be easily drawn out, and particles with high-biomass content, whose specific density have become larger than 1000 kg m⁻³ can be easily recovered. © 1998 Elsevier Science Ltd. All rights reserved

Key words: anaerobic digestion, carbon removal, distillery waste water, down-flow fluidization, carrier.

NOMENCLATURE

V_{exp}	expanded bed volume (m ³)
ε	bed porosity (dimensionless)
ε_{mf}	bed porosity at minimum fluidization (dimensionless)
W	mass of particles (kg)
ρ_s	solid specific density (kg m ⁻³)
A	sectional area (m ²)
b	maximum perpendicular dimension of the particle (m)
c	intermediate perpendicular dimension of the particle (m)
d	minimum perpendicular dimension of the particle (m)
U_l	liquid superficial velocity (m h ⁻¹)
U_{mf}	minimum fluidization velocity (m h ⁻¹)
U_g	gas superficial velocity (m h ⁻¹)
ΔP	pressure drop (Pa)
H	bed height (m)
H_{mf}	bed height at minimum fluidization (m)
HRT	hydraulic retention time (days)
OLR	organic loading rate (kg TOC m ⁻³ d ⁻¹)
Y	carbon removal yield (%)
Q_{in}	inlet flow rate (m ³ d ⁻¹)
C_{in}	TOC inlet (kg TOC m ⁻³)
C_{out}	TOC outlet (kg COT m ⁻³)
TOC	total organic carbon (kg m ⁻³)
VFA	volatile fatty acids (kg m ⁻³)
TSS	total suspended solids (kg m ⁻³)
VSS	volatile suspended solids (kg m ⁻³)

INTRODUCTION

Anaerobic digestion offers significant advantages over aerobic systems, like low energy consumption,

reduced solids formation, low nutrient requirement and potential energy recovery from the methane produced (Hall, 1992; Stewart *et al.*, 1995). This process is now widely used in many environmental applications, in different configurations and modes of operation.

The anaerobic fluidized bed reactor utilizes small, fluidized media particles to induce extensive cell immobilization thereby achieving a high reactor biomass hold-up and a long mean cell residence time (Shieh and Hsu, 1996). The fluidized bed technology presents a series of advantages compared to other kinds of anaerobic processes (Diez-Blanco *et al.*, 1995), like high organic loading rates and short hydraulic retention times. Therefore, a number of design modifications have been tested or adapted in order to improve the performance of the systems.

The down-flow (or inverse) fluidized bed utilizes as carrier floatable particles with a specific density lower than the liquid, thus particles are fluidized downward. Down-flow fluidization has received less attention than up-flow fluidization. Studies in inverse fluidization are mostly focused on hydrodynamic characteristics (Chern *et al.*, 1982; Fan *et al.*, 1982a,b; Legile *et al.*, 1988; Hihn, 1992; Ibrahim *et al.*, 1996). Shimodaira *et al.* (1981); Shimodaira and Yushina (1983) were the first in applying the down-flow fluidization technology to wastewater treatment. Since then, this configuration

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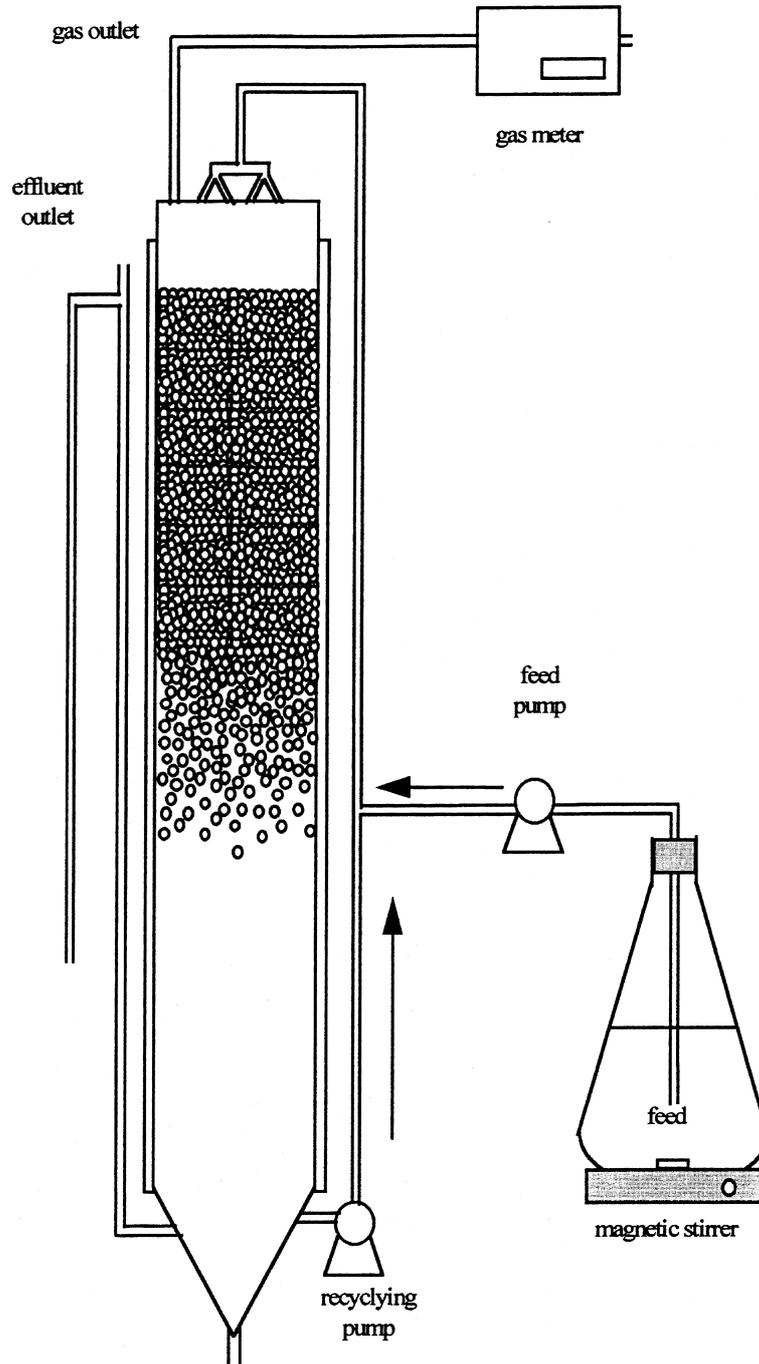


Fig. 1. Schematic diagram of the experimental set-up.

has been tested in laboratory and pilot scale for both aerobic (Boehler and Haldenwag, 1991; Chan Choi *et al.*, 1995; Nikolov and Karamanev, 1987, 1990) and anaerobic (Spiess *et al.*, 1991) treatment of wastewater. Synthetic materials are the most usual carriers in these studies, specially foamed polystyrene. Nevertheless, liquid superficial velocities required for fluidization are relatively high, when comparing to some up-flow anaerobic fluidized beds (Iza *et al.*, 1990; Setiadi, 1995; Diez-Blanco *et al.*, 1995; García-Calderón *et al.*, 1996).

The aim of this work was to determine the feasibility of a down-flow fluidized bed reactor for the anaerobic digestion of a wine distillery effluent, with a carrier material that allows low energy requirement for fluidization, providing also a good surface for biomass attachment and development.

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MATERIALS AND METHODS

Physical properties of the carrier material

Commercially-available perlite (an expanded volcanic rock) was ground in a Dietz Retsch Mühle grinder and sieved (mesh size 0.7–1 mm). It was calcinated (450°C, 24 h) to eliminate impurities and then washed. Settled fraction was eliminated. Shape and size of particles were determined by microscopic observations (Olympus CH-2 microscope, 2 mm Leitz–Wetzler slide with 0.01 mm intervals). Average particle diameter was calculated by Sauter's mean diameter method for a sample of 80 particles. Sphericity (Φ) was determined with the following expression (Zenz and Othmer, 1960):

$$\Phi = \frac{d}{\sqrt{bc}} \quad (1)$$

Apparent specific density was considered as the weight of 1 l of the material. Real specific density was calculated by taking the height of the bed at minimum fluidization:

$$\rho_s = \frac{W}{H_{mf}A(1 - \varepsilon_{mf})} \quad (2)$$

Bed porosity was calculated according to the following equation:

$$\varepsilon = 1 - \frac{H_{mf}(1 - \varepsilon_{mf})}{H} \quad (3)$$

with $\varepsilon_{mf} = 0.4$.

Minimum fluidization velocity was calculated by the correlation of pressure-drop experimental data at different fluidization velocities. Several materials were tested before choosing perlite: 3.85 mm polyethylene spheres, 3.6 mm polypropylene spheres and 0.92 mm ground cork particles. Minimum fluidization velocities were determined for these three materials using the same method described for perlite (results not shown).

Experimental set-up

The reactor consisted of a column with a conic bottom of a total volume of 5 l including conical bottom (0.08 m in diameter, 1 m in height). The flow distributor and the gas outlet were placed at the removable cap covering the top section. The gas outlet was connected to a gas meter. Effluent was discharged through a port on the low part of the column, connected to an outlet tube that kept the liquid level in the reactor (Fig. 1). Recycling was ensured by means of a peristaltic pump (Masterflex Cole Parmer). pH in the reactor was adjusted to 7 with NaOH during the start-up period, then it was naturally maintained between 7 and 7.5 without addition of NaOH, because of the alkalinity inside the reactor (between 0.9 and 1.3 g CaCO₃ l⁻¹). The reactor temperature was kept constant at 35°C by a water jacket. Figure 1 shows a schematic diagram of the experimental set-up.

Start-up

The reactor was inoculated with sludge from an anaerobic pond treating the same red wine distillery wastewater (average characteristics are given in Table 1). No nutrient complements were added. Wine distillery wastewater was kept in a refrigerator to avoid fermentation and it was constantly agitated by a magnetic stirrer to ensure homogenization. Anaerobic conditions in the reactor were obtained by bubbling with nitrogen gas.

The bed (1.2 l original volume) was expanded at 35%, at a superficial liquid velocity of 9 m h⁻¹.

The reactor was monitored for temperature, flow rate, pH and gas production and composition. Alkalinity, TSS, VSS, VFA and TOC were routinely analyzed. Retention time, based on expanded bed volume, was fixed at 3.3 days and it was reduced stepwise to 1.3 days when the steady state was reached, keeping the inlet feed COT (C_{in}) concentration constant.

The organic loading rate (OLR) was calculated as:

$$OLR = \frac{(Q_{in})(C_{in})}{(V_{exp})} \quad (4)$$

the carbon removal yield (Y) was calculated as:

$$Y = \frac{C_{in} - C_{out}}{C_{in}} \quad (5)$$

Biomass determination

Biomass development was monitored by taking biocovered particle samples and determining the attached VS (dry weight). Samples were dried at 110°C by 24 h and weighted. They were then calcinated at 450°C by 2 h and weighted. Difference between 2 weights was considered as the attached VS, that corresponded to the biomass weight.

Analytical methods

Liquid samples were centrifuged at 10000 rpm for 10 min before analysis to remove suspended solids. VFA analysis were done using a gas chromatograph with a flame ionization detector Chromapac CP 9000, nitrogen being the carrier gas (335 kPa). The column was a semi capillar Econocap FFAP (15 m. length and 0.53 mm diameter). Injector and detector temperatures were 250°C and 275°C respectively. The temperature of the oven was programmed to rise from 80°C to 120°C during the analysis with an elevation of 10°C per minute. The chromatograph was coupled with an integrator Shimadzu CR3A.

TOC was titrated by UV oxidation with a Dohrman DC 80 apparatus. Carbon compounds were oxidized in potassium persulfate at low temperature and the formed carbon dioxide was detected by infrared absorption. Samples were diluted twice with orthophosphoric acid at 10%. The carbon dioxide contained in the samples was previously eliminated by bubbling oxygen gas for 2 min.

Gas was analyzed by gas chromatography with a Shimadzu GC-8A apparatus with argon carrier (3 bars) using a catharometer detector. CO₂ was separated in a Hayesep column (80–100 mesh, 2 m × 1/8 inch); O₂, H₂, N₂ and CH₄ were separated in a molecular sieve 5 Å (80–100 mesh, 2 m × 1/8 inch). Oven temperature is 35°C; temperature of both injector and detector was 100°C. The chromatograph was coupled to a Shimadzu CR 3A integrator. Alkalinity, TSS and VSS were determined using Standard Methods (APHA-AWA-WPCF, 1985). pH was measured with a Mettler Toledo 1100 Calimatic pH meter.

RESULTS AND DISCUSSION

Fluidization and physical properties

Microscopic observations revealed that perlite particles present an irregular surface, with sharp

Table 1. Average wastewater composition

TOC	pH	TSS	VSS	VFA
5.5–6.5 kg m ⁻³	4.5–5	1.2–1.9 kg m ⁻³	0.9–1.6 kg m ⁻³	4–5.8 kg m ⁻³

Table 2. Physical properties of perlite particles

Real specific density (kg m^{-3})	Apparent specific density (kg m^{-3})	Mean diameter (mm)	Specific area ($\text{m}^2 \text{m}^{-3}$)	Shape
280	154	0.968	6980	Irregular, with angles and crevices. $\Phi = 0.78$

angles and crevices. These characteristics are suitable because biomass attachment and development are improved when particles present irregularities (Shieh and Keenan, 1986). Indeed, microorganisms preferably grow in the interstices provided by particle irregularities, protected from the shear forces of the bulk liquid (Fox *et al.*, 1990). Table 2 presents the observed physical properties of perlite particles.

Minimal fluidization velocity of the materials was calculated from the abscissa of the point from which the pressure drop remained constant. These observed values were: polyethylene, 13.2 m h^{-1} ; polypropylene, 8.6 m h^{-1} ; cork particles, 6.24 m h^{-1} ; perlite, 2.3 m h^{-1} . Perlite was chosen among the four materials because it presented the lowest minimum fluidization velocity. Effect of liquid superficial velocity on pressure drop and on bed expansion for perlite particles is plotted in Fig. 2.

It can be considered that perlite is an interesting carrier, when compared the others, like cork, polyethylene or polypropylene. Minimum fluidization velocities for these materials are higher because of surface phenomena (hydrophobic surfaces), their very low specific density (cork) and in the case of polyethylene and polypropylene, because of their size of particle. Table 3 shows the minimum fluidization velocity of different floatable carriers used in inverse fluidization.

Advantages could theoretically be achieved with down-flow fluidization of particles with density slightly lighter than that of water. However, a slight increase in particle density would result in considerable particle wash-out. Indeed, in down-flow fluidization, biomass accumulation makes particles heavier, increasing particle density and bed expansion. If there is an excess of biomass accumulation, density of the particles can attain 1000 kg m^{-3} , and particles can be washed out of the reactor.

Another important parameter is particle size, because it indicates the available surface for biofilm attachment and growth (Heijnen *et al.*, 1989). Particle size also affects hydrodynamics: shear, fluidization velocity, flow behavior of the gas bubbles and flow regime (Muroyama and Fan, 1985). In this case, 0.968 mm particles enabled a high biomass concentration at low liquid fluidization velocities. Nevertheless, perlite particles are irregular and non spherical, thus, comparisons with other studies become difficult, because most available correlations are made for spheres.

Carbon removal

During the start-up period, organic load was maintained at approximately $1.5 \text{ kg TOC m}^{-3} \text{ d}^{-1}$. When the system reached the steady-state, organic load was increased by reducing HRT. Figure 3 shows the carbon removal yield reached by the sys-

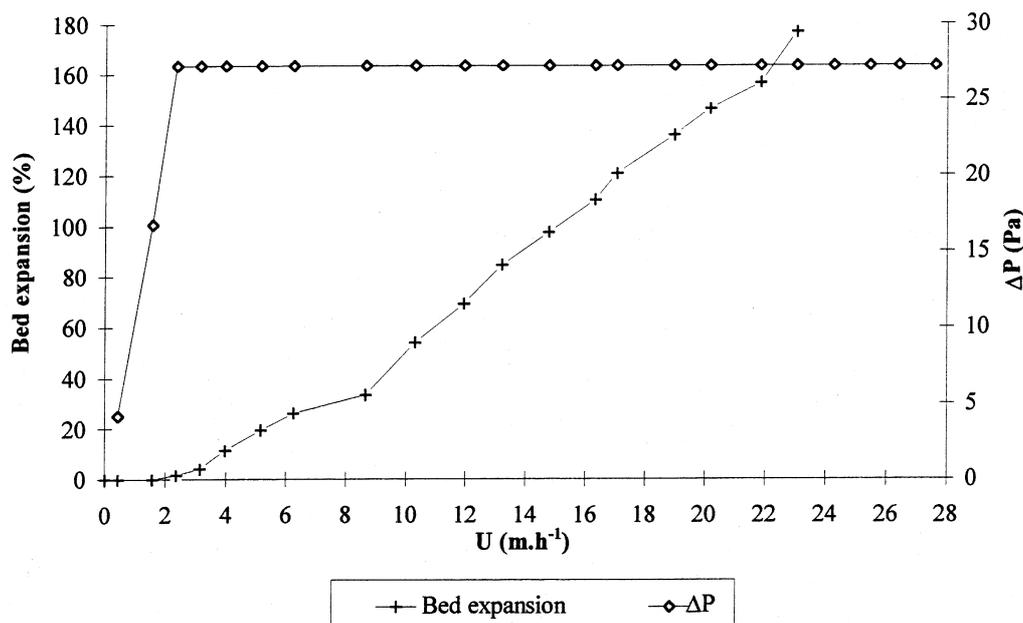


Fig. 2. Effect of liquid superficial velocity on pressure drop and bed expansion for perlite particles.

Table 3. Minimum fluidization velocity of different floatable carriers in inverse fluidization

Carrier	U_{mf} (m h ⁻¹)	Application	Authors
0.98 mm perlite particles	2.3	anaerobic digestion of wine distillery wastewater	this study
3.6 mm foamed polypropylene spheres	39	aerobic treatment of oil refinery wastewater	Shimodaira and Yushina, 1983
0.8–1 mm foamed polystyrene spheres	—	—	aerobic treatment Nikolov and Karamanev, 1987
2–3 mm polyethylene granules	—	Fe ²⁺ oxidation	kinetic and diffusional studies of biofilm Nikolov and Karamanev, 1990
1.8–2.2 mm styrofoam particles	—	—	this study
3.85 mm foamed polypropylene spheres (low density)	8.6	hydrodynamic study	Hihn, 1992
4 × 3 mm polyethylene cylinders	18–28	hydrodynamic study	Hihn, 1992
3 × 2 mm syntactic foam cylinders	20–30	hydrodynamic study	Hihn, 1992
2–6 cm foamed polystyrene particles	45–60	nitrate removal	Boehler and Haldenwag, 1991
0.92 mm cork particles	6.2	hydrodynamic study	this study

tem at the different HRTs and respective OLRs, after the start-up period. Carbon removal varied between 88% and 98%, showing no dramatic change with HRTs longer than 1.3 d (OLR of 4.6 kg TOC m⁻³ d⁻¹).

Carbon removal attained by the system can be compared with those obtained from some up-flow anaerobic fluidized bed reactors in similar conditions; and even better than the performance of other anaerobic reactor configurations (Rozi, 1988). It attained 85% of carbon removal with 4.5 kg TOC m⁻³ day⁻¹ (approximately 11.3 kg COD m⁻³ day⁻¹), without pH regulation. Gas production was also found to be affected by changes in OLR (Fig. 4). Every increase in OLR brought about an increase in gas production rate. At 4 kg TOC m⁻³ d⁻¹, gas production diminished and rose again as did carbon removal, while OLR continued to increase.

Biomass hold-up and bed expansion

Corrections were made because of the bed expansion due to biomass accumulation (Fig. 5). Indeed, changes in bed expansion can be explained by the biomass accumulation, that enlarges particle volume, and modifies particle density (Myška and Švek, 1994; Setiadi, 1995).

In this case, density of perlite particles increased with biomass accumulation (density of wet biomass was considered as 1000 kg m⁻³ (Myška and Švek, 1994).

Biomass accumulation is not the only parameter affecting bed expansion; gas production should be also considered, because gas flow can also contribute to bed expansion. Some authors (Legile *et al.*, 1988; Hihn, 1992) have observed that in three-phase inverse fluidization, bed expansion increases when increasing gas flow rate and that particles can be even fluidized only by gas. This phenomenon is called pseudofluidization (Legile *et al.*, 1988). This can explain why biomass accumulation is not proportional to bed expansion increase. Figure 5 shows that in the last period of study, biomass accumulation remained almost constant, while bed expansion increased about 30% and U_g increased more than 60%. Biogas up-flow velocity (U_g) can be calculated as biogas production rate (m³ h⁻¹) divided by reactor cross sectional area (m²). Thus, it is possible that both particle density increase and gas production had an effect on bed expansion. In up-flow anaerobic fluidized bed bioreactors, several authors (Diez-Blanco *et al.*, 1995; Setiadi, 1995) have observed that biogas production (at gas up-flow velocities higher than those reached in this study) had no influence on the hydrodynamic behavior. A study should be done in order to determine if whether or not gas production has an effect on bed expansion.

Figure 6 shows the evolution of the TSS in the influent and in the exit. TSS in the exit were about

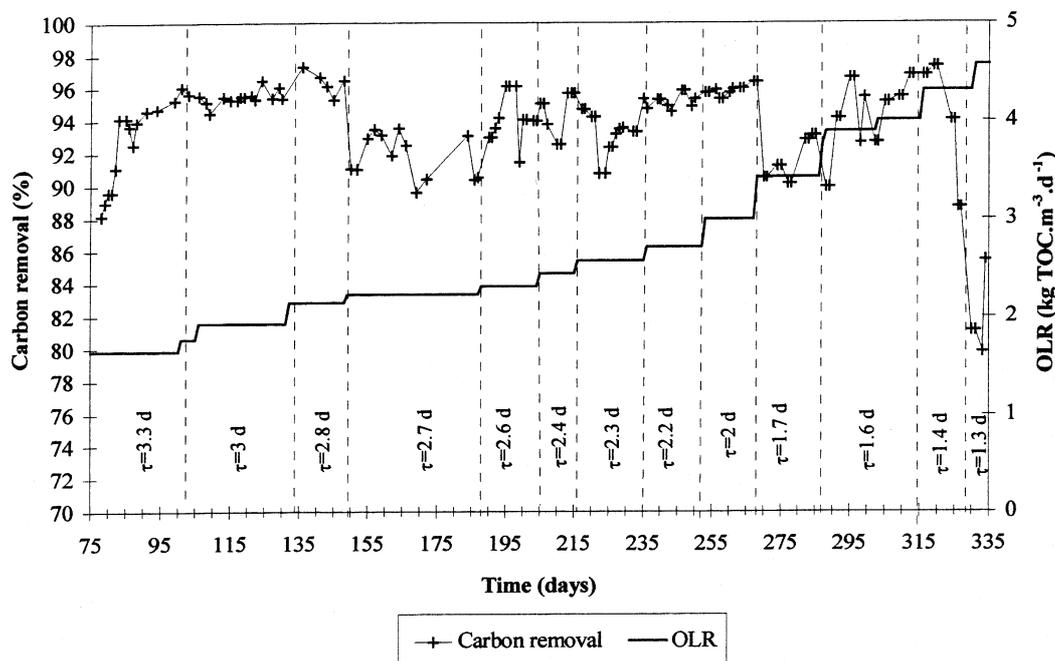


Fig. 3. Carbon removal performed by the system as a function of the different HRT and respective OLR.

50% less than in the influent. This difference can be due to the fact that suspended solids precipitate inside the reactor, because during operation it was noticed that some solids accumulated at the conical bottom. Nevertheless, it is also possible that some of these solids are degraded inside the reactor.

Solids, as well as high-biomass content settled particles could easily be drawn-out of the bottom by purging. This fact can be considered as an ad-

vantage, because a settler is not necessary like in up-flow biological reactors. This is especially interesting in the case of effluents like wine distillery wastewater, in which solids content is high. Gas outlet was placed at the top of the reactor. It was found that a space or "release zone" between the level of the liquid in the reactor and the top section was necessary. This way, gas can freely go through the outlet.

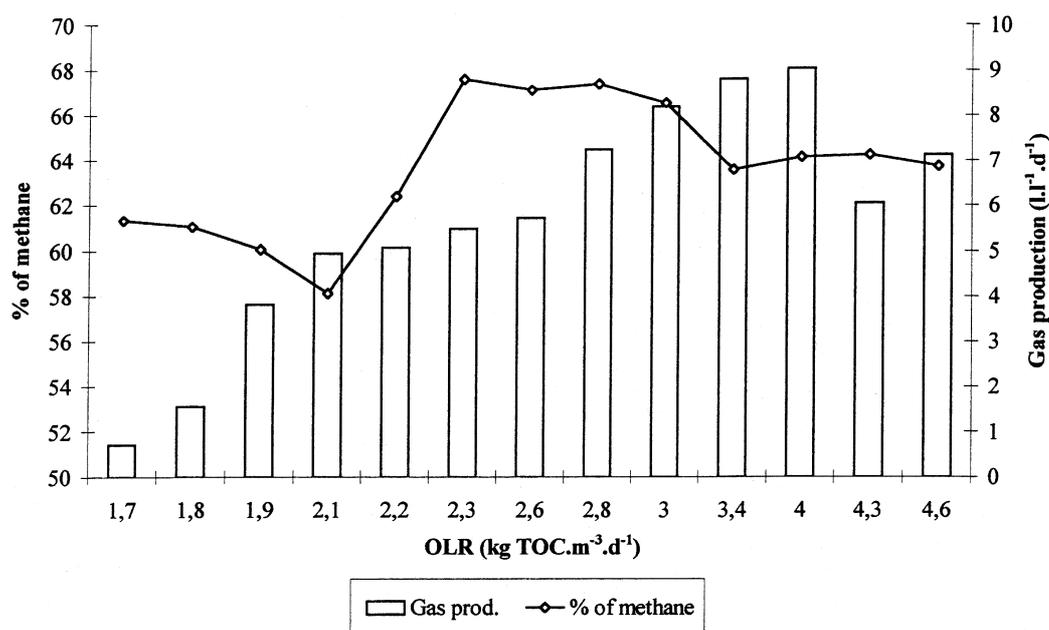


Fig. 4. Influence of OLR on gas production and gas composition.

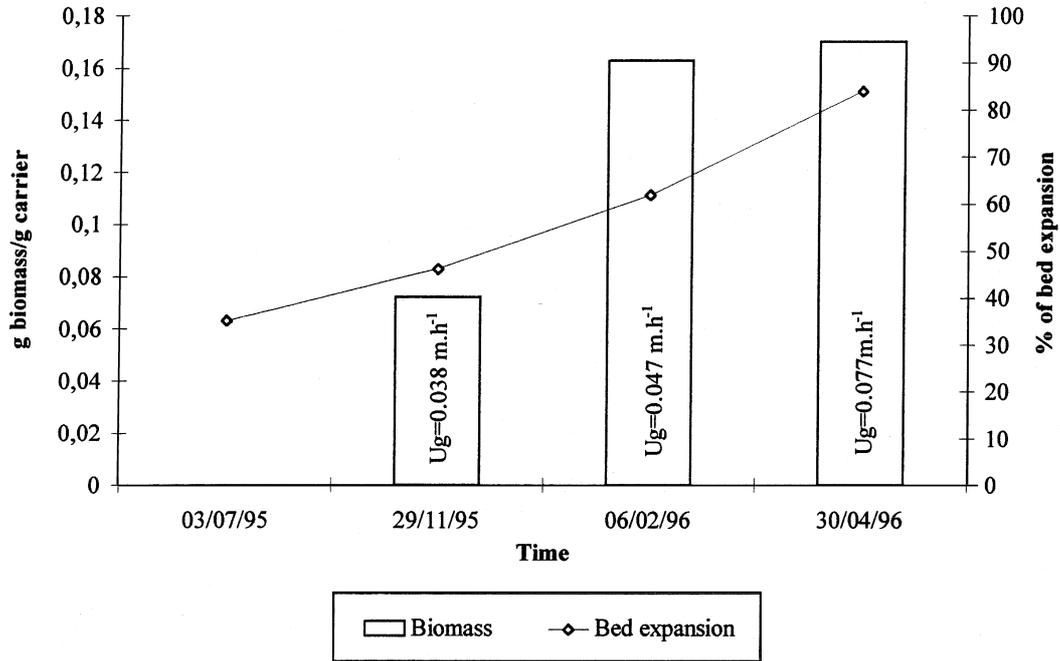


Fig. 5. Bed expansion and biomass accumulation vs time. $U_1 = 9 \text{ m h}^{-1}$.

SUMMARY AND CONCLUSIONS

This study showed that down-flow fluidization technology can be considered as an option for the anaerobic wastewater treatment. Carbon removal performances attained by the system were similar to those attained by up-flow anaerobic fluidized beds

in similar conditions and better than other anaerobic configurations.

The carrier material was found to be a very important parameter, because biomass accumulation brings about changes in particle volume and density, affecting the whole system. Perlite was found to be a good carrier for the anaerobic digestion of

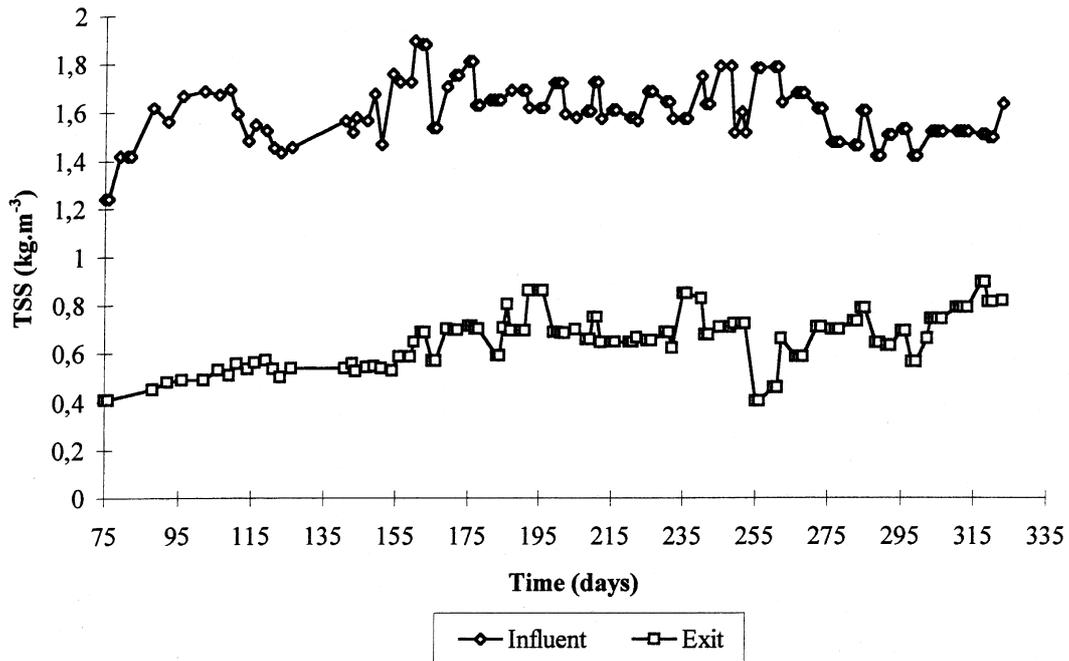


Fig. 6. Evolution of TSS with time.

wine distillery wastewater in down-flow fluidized bed. It allowed a high biomass hold-up, with minimum particle wash out, because of its density.

The main advantages of the down-flow fluidization configuration are that a settler is not necessary because solids accumulate at the conical bottom of the reactor; no clogging and the low energy requirement, because of the low fluidization velocities required.

A more complete study about the influence of biomass accumulation on bed expansion would be suitable, in order to know if whether or not there is an effect of biogas production.

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