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Influence of up-flow velocity on the performance of an anaerobic filter under oleic acid overloads

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Abstract

An upflow velocity of 0.21 m h^{-1} was optimal to minimize the effect of organic shocks (from 6 to 30 kg COD m^{-3} d^{-1}) when operating an upflow anaerobic filter for the treatment of an oleic acid-based effluent (50% w/v COD). This value represented the transition between a mass transfer controlled regime and a kinetic regime. Under hydraulic shock loads, an increase in upflow velocity from 0.3 to 0.4 m h^{-1} decreased the removal efficiency from 68 to 51%.

Introduction

The recent development of a new generation of anaerobic digesters has proved that anaerobic technology can compete advantageously with aerobic processes for treating industrial wastewaters. However, as the growth rate of anaerobic bacteria is slower than that of aerobes, cell retention times should be about 4- to 10-fold higher in anaerobic than in aerobic treatment systems. As a result of these slow dynamics, every disturbance to the normal biomass growth will be more harmful and the recovery from a shock will be longer in anaerobic processes, giving rise to malfunctioning and even process collapse. Therefore, the parameters that may affect process stability need to be studied. Some research studies have focused on the impact of operational disturbances on the performance of a number of anaerobic digester configurations treating a wide range of wastewaters (Grobicki & Stuckey 1991, Pullammanapallil *et al.* 1998, Chua *et al.* 1997). The microbial response of an anaerobic filter under organic and hydraulic shocks of an oleic acid-based effluent has been previously evaluated (Cavaleiro *et al*. 2001).

Oleic acid, produced by the hydrolysis of lipids, is toxic to the acetogenic, acetoclastic and hydrogenotrophic bacteria (Hanaki *et al*. 1981, Alves *et al*. 2001). Furthermore it adsorbs onto the sludge causing biomass flotation and washout (Hwu *et al*. 1998). A shock load of long chain fatty acids (LCFA) can make a reactor inactive for long periods (Angelidaki & Ahring 1992).

The use of recycling induces a protective effect when dealing with toxic wastewaters, improving the stability by decreasing the toxic concentration (Young 1991). Furthermore, for LCFA-based wastewaters, Hwu *et al.* (1997) reported the benefit of using biomass recycling on digester performance. These authors reported that the washed-out biomass exhibited a higher oleate degradation capacity than the biomass remaining inside the reactor.

To study to what extent the increase in recycle rate could improve stability, in the present work, organic and hydraulic shocks were applied to an upflow anaerobic filter fed with an oleic acid-based synthetic effluent, under different upflow velocities. Oleic acid was used as a model for LCFA because it is in general the most abundant of all LCFA present in wastewater, has a good solubility and it is recognized as one of the more toxic LCFA (Komatsu *et al*. 1991).

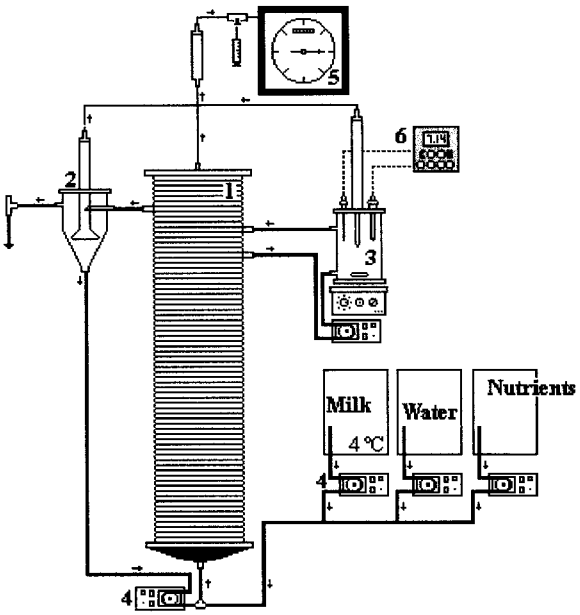

Fig. 1. Experimental set-up. 1. Anaerobic filter, 2. settler, 3. probes tank, 4. pumps, Watson–Marlow 101U/R (Falmouth, UK), 5. gas meter, Sinagawa Seiki DC-1C dry gas meter (Tokyo, Japan), 6. pH and temperature meter, WTW quadroline pH 296 (Weilheim, Germany). Liquid (=), gas (—) and data (- - - -) flow.

Materials and methods

Experimental set-up

The anaerobic filter was constructed in Plexiglas and is schematically presented in Figure 1. The initial liquid volume was of 15 l and the support matrix consisted of PVC Raschig rings 21 mm in size, with a specific surface area of 230 $m^2\ g^{-1}$ and a porosity of 92.5%. The settler, 1.8 l, was also constructed in Plexiglas. The substrate was stored at 4 °C in order to minimize acidification. An external tank receiving a recirculation loop from the reactor was used to install the pH and temperature probes. The reactor was kept at 35 ± 1 °C using a water jacket. The biogas was collected from the digester, probes tank and settler.

The digester's performance was monitored by determining every three or four days the soluble COD (chemical oxygen demand) removal, the VFA (volatile fatty acids) and the VSS (volatile suspended solids) in the effluent. Methane production, pH and temperature were measured every day. Under shock conditions analyses were performed 0, 4, 8, 12, 16, 24, 32, 44, 60, 78 and 96 h after starting each shock.

Substrate and seed sludge

The substrate was based on oleic acid (50% COD) with skim milk as co-substrate (50% COD), supplemented with macro and micronutrients which had the following composition: Macronutrients – $MgSO_4 \cdot 7H_2O$, 30.2 g l^{-1}; KH_2PO_4, 28.3 g l^{-1}; KCl, 45 g l^{-1}. 0.6 $cm^3\ l^{-1}$ of this solution was added per gram of COD fed. Micronutrients (Zehnder *et al.* 1980) – $FeCl_2 \cdot 6H_2O$, 2 g l^{-1}; H_3BO_3, 0.05 g l^{-1}; $ZnCl_2$, 0.05 g l^{-1}; $CuCl_2 \cdot 2H_2O$, 0.038 g l^{-1}; $MnCl_2 \cdot 4H_2O$, 0.5 g l^{-1}; $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 0.05 g l^{-1}; $AlCl_3 \cdot 6H_2O$, 0.09 g l^{-1}; $CoCl_2 \cdot 6H_2O$, 2 g l^{-1}; $NiCl_2 \cdot 6H_2O$, 0.092 g l^{-1}; $Na_2SeO_3 \cdot 5H_2O$, 0.164 g l^{-1}; EDTA, 1 g l^{-1}, Resazurine, 0.2 g l^{-1}; HCl 37%, 1 $cm^3\ l^{-1}$. One $cm^3\ l^{-1}$ of this solution was added to the influent feed. To give suitable alkalinity 5 g $NaHCO_3\ l^{-1}$ were added.

The inoculum was taken from a local municipal sludge anaerobic digester. A volume of 5 l of anaerobic sludge containing 15 g VSS l^{-1} was inoculated.

Analytical methods

COD and VSS were determined by Standard Methods (APHA, AWWA, WPCF 1989). VFA were determined by HPLC using a Chrompack column (6.5 × 30 mm); the mobile phase was 5 mM sulphuric acid at 0.7 ml min^{-1}. The column temperature was set at 60 °C and the detection was made at 210 nm. Methane content of biogas was measured by gas chromatography using a Chrompack column Haysep Q (80–100 mesh). N_2 was used as carrier gas (30 ml min^{-1}) and the temperatures of the injection port, column and flame ionisation detector were 120, 40 and 130 °C, respectively. Biogas production was measured by Sinagawa Seiki dry gas meter and the values were converted to Standard Temperature and Pressure (STP) conditions.

Shock-loading experiments

When the operation of the digester was stable at 16 h of Hydraulic Retention Time (HRT) and 4 g COD l^{-1}, the applied organic load was increased from 6 to 30 kg COD $m^{-3}\ day^{-1}$ over 4 days, either by increasing the COD in the feed to 20 g COD l^{-1} (organic shocks) or by decreasing the HRT to 3.2 h (hydraulic shocks). A total of 6 shocks were performed at different recycle rates (r = recycle flow rate/influent flow rate) of 1.2, 1.7, 2.8 and 6.2 for the organic shocks and 0.2 and 0.6 for hydraulic shocks (Table 1).

Table 1. Experimental conditions applied during reactor operation.

Period	Time (d)	HRT (d)	Influent COD (g l^{-1})	Influent oleate COD (g l^{-1})	Applied organic load (g COD l^{-1} d^{-1})	Recycle flow (l d^{-1})	Upflow velocity (m h^{-1})
Startup	[0–15]	4	2	0	0.5	4.1	0.02
	[15–34]	2	2	0	1	8.2	0.04
	[34–53]	2	4	0	2	8.2	0.04
	[53–83]	1	4	0	4	16.5	0.08
Oleate introduction →	[83–102]	1	4	2	4	16.5	0.08
	[102–133]	0.67	4	2	6	24.6	0.12
Organic shock 1	[133–137]	0.67	20	10	30	24.6	0.12
Normal operation	[137–149]	0.67	4	2	6	24.6	0.12
Organic shock 2	[149–153]	0.67	20	10	30	39.4	0.15
Normal operation	[153–168]	0.67	4	2	6	24.6	0.12
Organic shock 3	[168–172]	0.67	20	10	30	62.7	0.21
Normal operation	[172–181]	0.67	4	2	6	24.6	0.12
Organic shock 4	[181–185]	0.67	20	10	30	138.8	0.40
Normal operation	[185–208]	0.67	4	2	6	24.6	0.12
Hydraulic shock 1	[208–212]	0.13	4	2	30	24.6	0.32
Normal operation	[212–231]	0.67	4	2	6	24.6	0.12
Hydraulic shock 2	[231–235]	0.13	4	2	30	69.2	0.41
Normal operation	[235–244]	0.67	4	2	6	24.6	0.12

Results and discussion

During the start-up, the HRT was decreased from 4 to 0.67 days, the influent COD increased from 2 to 4 g l^{-1} and, on day 83, sodium oleate was introduced in the feed as 50% COD. At the end of the start-up period, COD removal efficiency averaged 94.9 ± 0.8%, the biogas production was 1.81 ± 0.09 $l l^{-1}$ day^{-1}, the pH was maintained between 7 and 7.3 and the temperature remained between 34 and 36 °C. The total VFA and VSS averaged 101 ± 18 mg COD l^{-1} and 610 ± 18 mg VSS l^{-1}, respectively (Figure 2 and Table 2).

Under shock loading conditions, there was a decrease of the removal efficiency (Figure 2a), an increase in the effluent VSS and VFA concentrations (Figures 2b and 2c, respectively) and an increase in the biogas production (Figure 2d). The increase in VSS, VFA and biogas production was much more evident during the organic than during the hydraulic shocks. The removal efficiency decreased more in the hydraulic than in the organic shocks but the maximum effluent COD was higher in the organic than in the hydraulic shocks (Table 2). Oleic acid is toxic to the anaerobic populations involved in the consortia. At the highest organic shock load, the concentration of oleic acid was 10 g COD l^{-1}. At this concentration, acetoclastic, hydrogenophilic and acetogenic bacteria involved in the β-oxidation process suffer from inhibition unless sufficient calcium or magnesium salts are present (Roy *et al*. 1985). During the organic shock the molar ratio oleate/(Ca^{2+}+Mg^{2+}) was 2.3, exceeding the stoichiometric ratio 2. However, during the hydraulic shock and during the steady-state periods, the molar ratio oleate/(Ca^{2+}+Mg^{2+}) was only 1.5. This means that it would be theoretically possible to precipitate all the oleate with the divalent cations during the hydraulic, but not during the organic shock, and possibly explains the more acute toxic effect in the organic than in the hydraulic shock. The time course of the individual volatile fatty acids indicated that formate and lactate accumulated to lower concentrations than acetate, which was the main accumulating acid (Figure 3). *n*-Butyric acid was detected in concentrations higher than iso-butyric acid. Accumulation of volatile fatty acids led to pH oscillation, but always inside the range between 6.6 and 7.6, optimal for the development of the anaerobic consortia (Zehnder *et al.* 1980).

Performance under organic shock loads improved with increasing upflow velocity up to 0.2 m h^{-1}. This positive effect was possibly due to the dilution of the

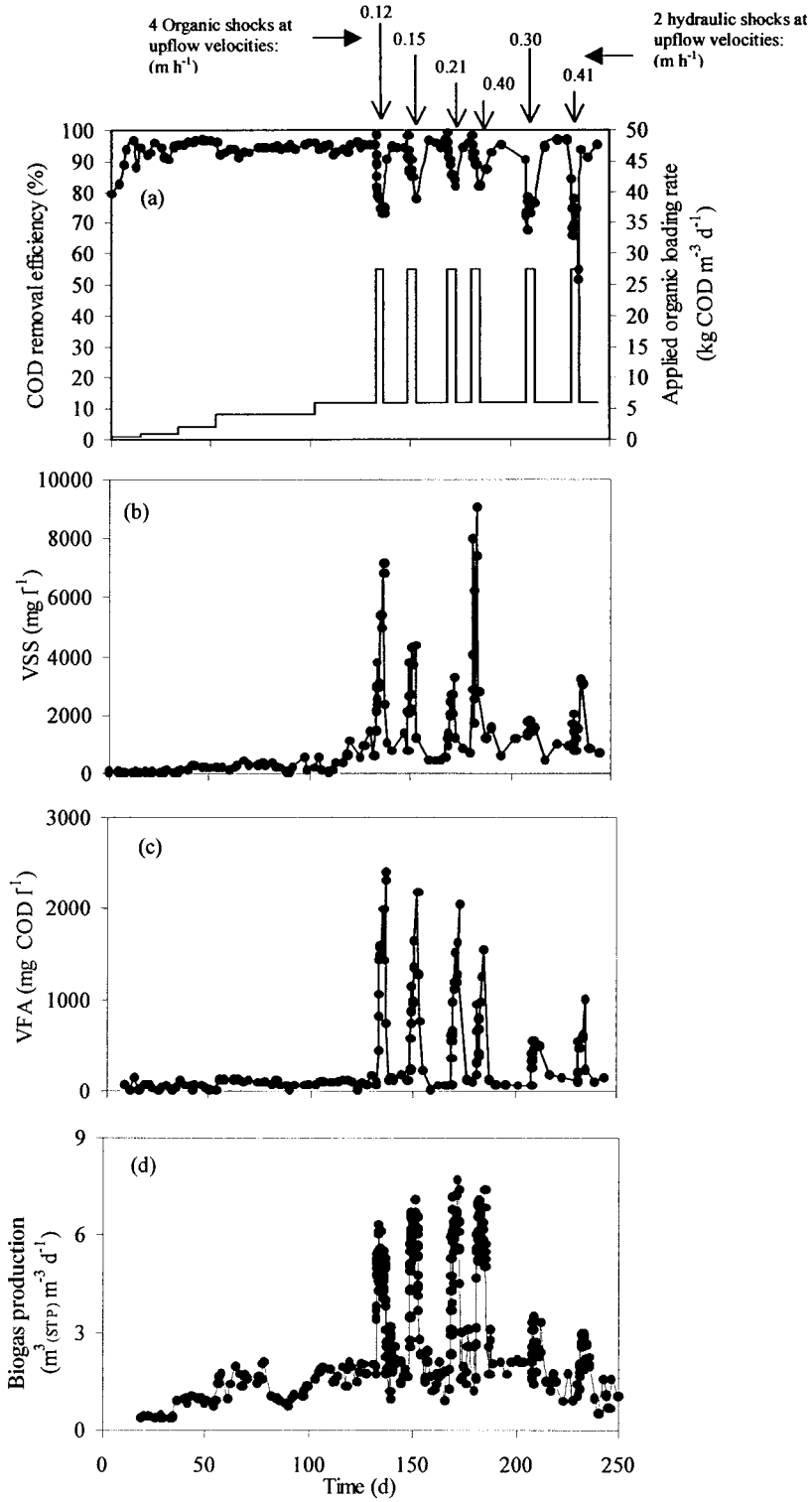

Fig. 2. Time course of (a) applied organic loading rate and COD removal efficiency. (b) Volatile suspended solids (VSS). (c) Volatile fatty acids (VFA). (d) Biogas production.

Table 2. Summary of operating data under steady-state and shock loading conditions (±95% confidence intervals).

Period	Time (d)	COD removal efficiency (%)	Effluent COD (mg l^{-1})	Effluent VSS (mg l^{-1})	Biogas production (1 l^{-1} day^{-1})	Methane yield 1 $CH_4 kg_{CODrem}^{-1}$
Startup	[0–15]	92.6±2.8	152±58	73±16	–	–
	[15–34]	93.8±1.6	111±16	75±18	0.41±0.02	311±38
	[34–53]	96.3±0.4	136±20	209±44	0.94±0.05	302±19
	[53–83]	93.8±0.7	258±33	294±45	1.6 ±0.14	240±23
Oleate introduction	[83–102]	95 ±0.5	161±29	268±50	1.24±0.14	204±24
	[102–133]	94.9±0.8	212±21	568±218	1.81±0.09	209±14
Organic shock 1	[133–137]	73.1[a]	4889[b]	7200[b]	6.33[b]	158[b]
Normal operation	[137–149]	94 ±2	268±52	1015±247	2.15±0.15	263±25
Organic shock 2	[149–153]	77.8[a]	3476[b]	4360[b]	7.1[b]	166[b]
Normal operation	[153–168]	96.8±1.1	145±27	733±278	1.76±0.22	210±29
Organic shock 3	[168–172]	82[a]	3238[b]	3300[b]	7.74[b]	187[b]
Normal operation	[172–181]	96.1±1.7	246±76	787±59	2.22±0.37	237±47
Organic shock 4	[181–185]	82[a]	3225[b]	9080[b]	7.41[b]	181[b]
Normal operation	[185–208]	93 ±2.3	247±36	1206±280	2.15±0.2	248±24
Hydraulic shock 1	[208–212]	68.1[a]	1297[b]	1860[b]	3.53[b]	109[b]
Normal operation	[212–231]	93.5±5.3	153±49	1012±312	1.36±0.19	148±13
Hydraulic shock 2	[231–235]	51.9[a]	1894[b]	3240[b]	4.07[b]	137[b]
Normal operation	[235–244]	93.5±1.8	244±55	800±83	1.38±0.13	184±22

[a]Minimum values.
[b] Maximum values.

toxic shock and to the reintroduction into the reactor of sludge with high capacity of oleate degradation as reported by Hwu *et al.* (1997). However, a further increase in the upflow velocity up to 0.4 m h^{-1} provoked a strong washout effect during the organic shock, detected by the increase in the effluent VSS values, which attained values as high as 9080 mg l^{-1} for the organic shock performed with a recycle flow rate of 139 l d^{-1} (superficial velocity, of 0.4 m h^{-1}). It should be noted that the type of substrate used is adsorbable and VSS values account for all organic matter that can be ignited at 550 °C. The methane yields obtained under shock conditions were far below the theoretical maximum value of 350 l $CH_{4(STP)}$ kg COD^{-1} removed (Table 2). Furthermore, lower values were obtained in the hydraulic than in the organic shocks. As explained above, this could be due to the higher degree of oleate precipitation during the hydraulic shock, reducing the available substrate for methanization. Although higher inhibition of populations involved in the anaerobic degradation during the organic shock should be expected (Cavaleiro *et al.* 2001), the higher methane yields measured indicate that more substrate was in fact converted into methane in that situation. On the other hand, the hydraulic shocks induced a decrease of internal temperature to 28 °C. This decrease of temperature would have resulted in a reduction in the metabolic rate, which may also explain the lower yields in this case.

Mass transfer considerations

The effect of the upflow velocity was evaluated in both shocks and related to the external mass transfer resistance (Figure 4). A correlation between Sherwood number (Sh), Reynolds number (Re) and Schmidt number (Sc) was applied (Van Krevelen & Krekels 1948):

$$\mathrm{Sh} = 0.45\mathrm{Re}^{0.5}\mathrm{Sc}^{0.4}$$

where

$$\mathrm{Sh} = \frac{k_c d_p}{D_{ab}}, \quad \mathrm{Re} = \frac{v_{\mathrm{sup}} \rho d_p}{\mu}, \quad \mathrm{Sc} = \frac{\mu}{\rho D_{ab}},$$

K_c, external mass transfer coefficient (m s^{-1}); d_p, characteristic size of the support media (diameter of the sphere with the same surface area = 0.028 m); D_{ab}, diffusion coefficient = 0.47E-9 m^2 s^{-1} for lactose on acidogenic biofilms (Yu & Pinder 1993); v_{sup},

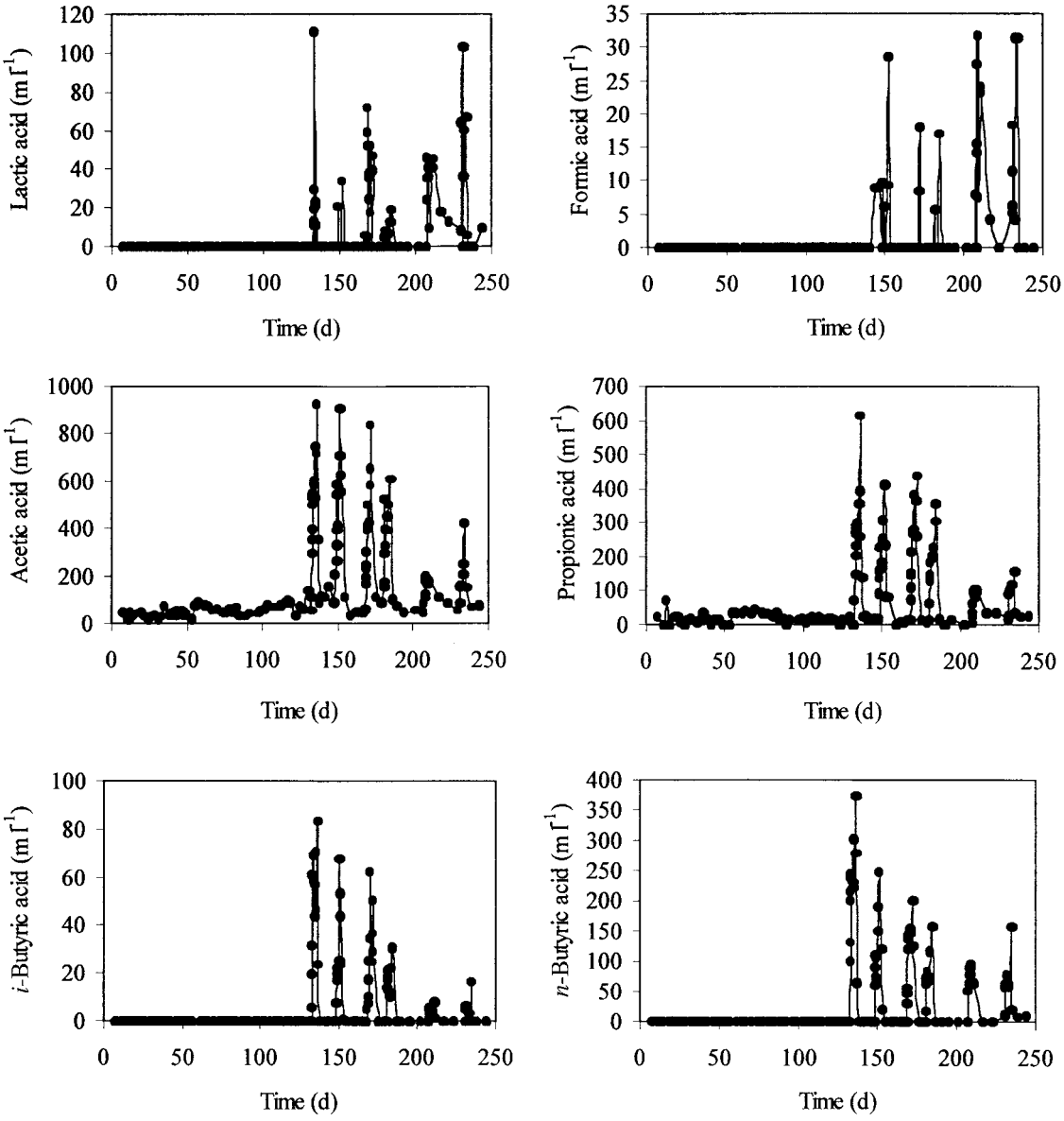

Fig. 3. Time course of VFA production during the trial period.

upflow superficial velocity (m s^{-1}); ρ, Fluid density = 994 kg m^{-3} at 35 °C; μ, fluid viscosity = 7.9E-4 kg m^{-1} s^{-1} at 35 °C.

This correlation was developed for fixed bed reactors and applied under the range of Re between 0.5 and 10 and Sh > 6. Bulk upflow fluid velocity has an effect on the transport of substrate from the bulk liquid to the film surface. According to the magnitude of the external mass transfer resistance, two extreme situations can be created: a mass transfer controlled regime and a kinetic regime. Reactor performance under mass transfer regime is less efficient and it is possible to increase it by decreasing mass transfer resistance. From the present results during the organic shocks diffusion regime controlled the performance for upflow velocities up to 0.21 m h^{-1}. Higher upflow velocities did not increase the COD removal efficiency, though the external mass transfer coefficient was still increasing (Figure 4). This indicates that kinetic regime was controlling the process afterwards. The same was observed for the hydraulic shocks, where similar COD removal efficiencies were

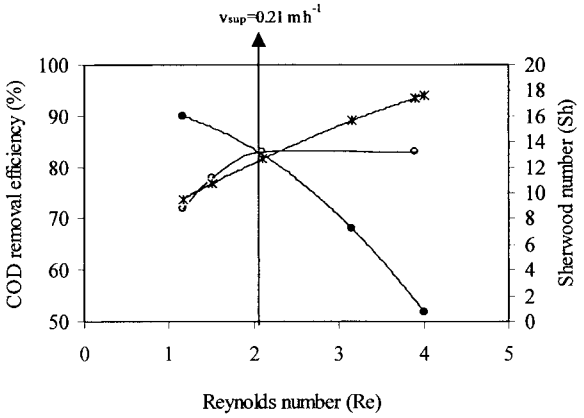

Fig. 4. Influence of the Reynolds number on COD removal efficiency obtained in: o, the organic shocks; •, the hydraulic shocks; ∗, Sherwood number according to the correlation of Van Krevelan & Krekels (1948).

obtained for the critical velocity of 0.21 m h^{-1}, but a sharp decrease was observed for higher velocities, indicating a kinetic regime. On the other hand, bulk fluid velocity can influence internal mass transfer. Convective flow through a macro-porous biofilm due to pressure fluctuations was reported (Van den Heuvel *et al.* 1992). Brito & Melo (1999) reported that, although no effect on internal mass transfer coefficients was detected when a biofilm was formed at constant velocity, transient increases in the upflow velocity to a value 8.8 times higher led to an increase of 20% in the internal mass transfer coefficient.

Conclusions

An upflow velocity of 0.21 m h^{-1} was optimal to minimize the effect of organic shocks (from 6 to 30 kg COD m^{-3} d^{-1}) when operating an upflow anaerobic filter for the treatment of an oleic acid-based effluent (as 50% COD). A further increase in the upflow velocity to 0.4 m h^{-1}, led to an increase in volatile suspended solids from 3 to 9 g l^{-1}. The value of 0.21 m h^{-1} represented the transition between a mass transfer controlled regime and a kinetic regime. Under hydraulic shock loads the increase in upflow velocity from 0.3 to 0.4 m h^{-1} decreased the removal efficiency from 68 to 51%. Methane yield was higher in the organic than in the hydraulic shocks, which was attributed to the possible total precipitation of oleic acid with divalent cations under the conditions of hydraulic shocks, reducing the total substrate available for methanisation.

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