Performance of Fixed-Film reactors for Anaerobic Treatment of Wine-distillery Wastewaters: Effect of the Influent pH Conditions

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Anaerobic treatments are strongly influenced by the pH of the medium since this parameter affects the efficacy and operation of the process. Digester pH, or hydrogen ion activity, is a measure of the acidic or basic nature of the culture. The optimum pH for anaerobic digestion is normally in the range 7–8; pH levels that deviate significantly from this range can indicate potential toxicity and digester failure. Low pH levels, for example, can be a symptom of digester imbalance. As volatile acids concentration increases, the pH in the digester decreases. At pH levels below 6.0, the acidic conditions produced can become toxic to methane bacteria. Discrepancies remain regarding the effects of volatile acids and pH on digester stability. High volatile acids concentrations are reported to be a symptom rather than a cause of decreased digester stability. In fact, sudden increases in the concentrations of such volatile acids as acetic and butyric reportedly stimulate, rather than inhibit, anaerobic digestion.

The main purpose of this research was to compare the effect of the influent pH on the performance of a lab-scale anaerobic filter reactor treating distillery wastewater (vinasses) in thermophilic conditions. The results obtained showed that the pH influenced the performance of the biodegradation process: the depuration efficiency was higher for the operation with alkaline influent. The operation with acid influent allowed to operate at organic loading rates (OLR_0) around 5.6 kg · m^{-3} d^{-1} COD (hydraulic retention time: 1.5 days), while maintaining total Chemical Oxygen Demand removals (COD_r) of 77.2%; the operation with alkaline influent allowed total COD_r of 76.8% working at OLR around of 10.5 kg · m^{-3} d^{-1} COD.

The greatest efficiency of substrate removal was 87.5% for OLR 3.17 kg · m^{-3} · d^{-1} COD and hydraulic retention time (HRT) of 4.04 days when operating with alkaline influent. Therefore, the operation with alkaline influent implicates higher levels of purifying efficiency for similar organic load rate.

Key words:
Anaerobic digestion, anaerobic filter, thermophilic, pH influent, industrial wastewater.

Introduction

The anaerobic treatment of industrial wastewater has a number of potential benefits, including low energy consumption, low excess sludge production, and enclosure of odorous 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 twenty years have been reviewed by *Hickey* et al.[1], and are the upflow anaerobic sludge blanket (UASB), upflow and downflow stationary packed beds[2–3], and fluidized and expanded beds[4,5].

The pH of the medium influences the process rate and determines the type of micro-organisms which develop[6]. In anaerobic treatments, the pH conditions also affect the efficacy and the operation of the process. So, the stability relies on the equilibrium of degradation rate of the different bacterial groups implicated in the process, and each of them introduces a different process evolution depending on the pH selected[7].

In the mixed culture of an anaerobic reactor, several different degradation reactions take place. Complex kinetics, interactions and different steps have been reported by numerous authors[8]. Soluble substrates can be degraded by three major steps: acidogenesis, acetogenesis and methanogenesis. In the first combined step, compounds (e.g. carbohydrates) are hydrolysed by extracellular enzymes to organic monomers, e.g. glucose. Glucose is used by the acidogenic bacteria as a substrate and is converted to organic acids, mainly acetic, propionic and butyric. The first step is quickly compared with the subsequent reactions, where all the higher acids are converted to acetic acid. The final product, a biogas containing methane and carbon dioxide, is produced by methanogens along two different pathways; the acetoclastic path producing approximately 28% of methane. The H_2 pressure in the system is usually below 10^{-4} atm. Most of the H_2 is converted to methane very quickly. At overload, the H_2 pressure can exceed 10^{-4} atm. causing the thermodynamic inhibition of the acetogenic step. In addition, an inhibitory effect of high organic acids on their own degradation can be observed, even if the pH is controlled at 7. If organic overloading of an anaerobic digester occurs, the initial response in the effluent consists of an increase in total organic acid concentration, which results in poor effluent quality and a possible washout of the biomass. At the same time, the consumption of neutralising alkaline increases if the pH is controlled. If the pH is not held constant, the activity of the methanogens drops sharply and the effluent quality deteriorates furtheren[9,10].

Therefore, a neutral or alkaline influent, and/or a neutral pH control on line should favour the anaerobic biomass activity and, in this sense, the degradation process[11,12].

The main objective of this research was to compare the influence of the pH of the influent on the performance of an anaerobic filter reactor degrading distillery wastewater (vinasses) at thermophilic conditions.

Materials and methods

Experimental procedure. The experimental protocol was designed to examine the effect of organic loading rate on the efficiency of COD removal of anaerobic filter reactores (AFR) when treating vinasses at different pH conditions. This experimental study was divided into three stages:

Stage T1: AFR operation under acidic feeding (pH: 3.7)
Stage T2: AFR operation under alkaline feeding (pH: 7.5)
Stage T3: AFR operation with pH control on line.

HRT remained constant during each stage until reaching 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 were the mean of the last measurements. The steady state operating characteristics of all reactors were analyzed (organic removal efficiency, volumetric gas and methane rate production, pH, effluent suspended solids, effluent total and volatile suspended solids), studying the influence of the pH feed characteristics.

The methods and material used are briefly described in this section.

All assays were carried out in duplicate and all the shown results are the average values of the last data obtained.

Experimental systems. A schematic diagram of the upflow anaerobic fixed-film reactor used in the laboratory study is shown in Figure 1.

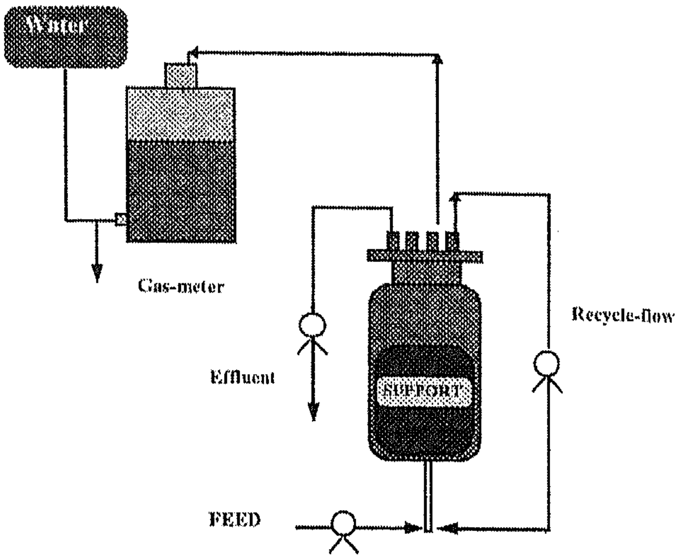

Fig. 1 — *Schematic diagram of the experimental anaerobic filter reactor (AFR).*

The anaerobic filter reactors consisted of vertical cylindrical tanks (25 cm at length and 10 cm in 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 at length). Reactor temperature was maintained at 55 °C and the biogas generated was collected in a gas-meter. Continuous feed was supplied by peristaltic pump connected to a programmable timer. Effluent recirculation was used to mix and homogenise the liquid in the system.

Feed solutions. Distillery wastewater proceeding of an ethanol producing wine-distillery plant placed in Tomelloso (Ciudad Real, Spain) was used. In general, the vinasses showed an adequate relationship between the different macro and micro-nutrients with a favourable COD:N:P ratio suitable for microbiological treatment, and acid pH (approximately 3.7). A complete study of the characteristics and properties of vinasses can be found in a previous paper by the authors[13].

Before their utilisation, vinasses were transported and maintained at 4 °C. The original substrate was diluted with tap water to attain the required Chemical Oxygen Demand (COD) concentration used in these experiments (around 15 $g \cdot L^{-1}$ COD). It was supplemented with sodium hydroxide to adjust to neutral pH, according to the case in point (stage T2 and T3).

After this study, vinasse biodegradation batch assays[14] under the completely mixed conditions 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 recalcitrant substrate fraction given the conditions of the experiment.

Media support. Corrugated plastic tubes of 16 mm in diameter (non-porous media) of low density (1.161 kg L^{-1}), high porosity (93.71%), and high specific surface (450 m^2 m^{-3}) suitable for using as stationary packed media in filter reactors.

Analytical methods. All analytical determinations were performed according to "Standard Methods"[15]. For liquid samples, the parameters analysed in both effluent and influent were: pH, Chemical Oxygen Demand (COD) and both Total and Volatile Suspended Solids (TSS, VSS). For gaseous samples, the parameter analysed was the volume of biogas generated and its composition (CH_4 and CO_2).

COD was determined by the dichromate reflux methods. For soluble CODs, the sample was first filtered as in the TSS analysis and the filtrate was used for the COD analysis. Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS) were quantified by the glass fiber filter method. Gas production was measured continuously by water displacement. Determinations of methane and carbon dioxide were carried out using gas chromatography separation accomplished by using 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^{-1} until 150 °C; detector temperature: 255 °C; injector temperature: 100 °C. The carrier was Helium and the flow rate used was 30 mL min^{-1}. A standard gas (by Carburos Metalicos, S.A.) was used to calibrate the system. The composition was. 4.65% H_2; 5.33% N_2; 69.92% CH_4 and 20.10% CO_2.

Results and discussion

Performance and operation parameters for the evolution of the biodegradation experiments are shown in Table 1 (all the results shown are the average values of the last three data).

In STAGE T1, the volumetric organic loading rate (OLR_0) was gradually increased between 1.67 and 5.56 g · L^{-1} d^{-1} COD. The hydraulic retention time (HRT) ranged between 5.69 and 1.50 days (the empty HRT bed was defined in terms of the volume occupied by bioparticles: 2 liters). A concentration of 15 g · L^{-1} COD was maintained in all steady states studied.

Soluble COD remova (CODr) decreased from 85.9 to 77.2%. Firstly, at HRT of 4.22 days and organic load of 2.15 g · L^{-1} d^{-1} COD, the percentage of COD removal was 83.4%. Finally, at HRT of 1.50 days and organic load of 5.56 g · L^{-1} d^{-1} COD, the soluble percentage of COD removal decreased to 77.2%. These reactors showed instability in OLR_0 range above 5.56 g · L^{-1} d^{-1} COD.

Table 1 — *Performance and operation parameters for the evolution of anaerobic filter reactor in different stages: HRT (days); organic loading rate (OLR_0) as g · L^{-1} d^{-1} COD_0; organic removal efficiency (as percentage of initial COD); pH; TSS and VSS, as g · L^{-1}; volumetric CH_4 and CO_2 production, L · L^{-1} · d^{-1} digester; methane yield, as LCH_4 · g^{-1} COD_r.*

Stage	HRT	OLR_0	$\%COD_r$	pH	TSS
T1	5.69	1.67	85.91	8.92	0.37
	4.22	2.15	83.41	8.61	0.40
	1.83	5.22	76.04	8.30	0.49
	1.50	5.56	77.22	8.35	0.47
T2	4.04	3.17	87.53	8.69	0.35
	1.25	9.42	80.80	8.28	0.39
	1.15	10.41	76.83	8.28	0.61
T3	0.66	14.35	49.65	6.49	0.75

Stage	VSS	CH_4	CO_2	CH_4 yield
T1	0.24	0.46	0.34	0.32
	0.27	0.52	0.37	0.29
	0.23	1.04	0.75	0.26
	0.33	1.18	0.84	0.27
T2	0.19	0.83	0.28	0.30
	0.27	1.77	1.02	0.23
	0.42	2.07	2.68	0.26
T3	0.53	—	—	—

In these conditions, the VSS content of anaerobic filter reactors range between 0.24 and 0.33 gVSS L^{-1}, at HRT of 5.69 and 1.50 days respectively. The pH was maintained between 8.92 and 8.35 during the stable process phase. Methane production increased from 0.46 to 1.18 L L^{-1} d^{-1} when operating at HRT of 5.69 and 1.50 days respectively.

Assays in STAGE 2 were performed by adding alkaline influent (pH: 7.5). Hydraulic retention times were gradually decreased from 4.04 to 1.15 days. The volumetric COD loading was between 3.17 g · L^{-1} d^{-1} COD and 10.41 g · L^{-1} d^{-1} COD.

Soluble COD removal was observed to decrease from 87.53 to 76.83%. COD removal of 87.53% was obtained at HRT of 1.15 days and organic load of 3.17 g · L^{-1} d^{-1} COD. This value decreased to 76.83% at organic load of 10.41 g · L^{-1} d^{-1} COD. A later organic overload applied produced a fast decrease in pH (increase in total organic acid concentration), which resulted in poor effluent quality and possible washout of the biomass. Then, the medium was suplemented with sodium hydroxide (NaOH 7 mol L^{-1}) in order to maintain a neutral pH the reactor (on line pH control, STAGE 3). Nevertheless, the adjustment of neutrality of the medium did not allow to operate at organic load rate higher than 10.41 g · L^{-1} d^{-1} COD. This caused sharp drops of methanogenic activity and, subsequently, the deterioration of effluent quality (49.65% COD removal).

Methane gas production averaged 0.83 and 2.07 $L \cdot L^{-1}\ d^{-1}$ when operating at HRT of 4.04 and 1.15 days respectively. The pH ranged from 8.57 to 7.65 during the stable process phase. In the last stage, the generation of biogas ceased and the suspended volatile solids increased from 0.42 $g \cdot L^{-1}$ VSS to 0.53 $g \cdot L^{-1}$ VSS.

Figure 2 shows the relationship between the organic load rate (OLR_0 expressed as a $g \cdot L^{-1}\ d^{-1}$ COD) and the organic consumed rate in the process (OLR_r, $g \cdot L^{-1}\ d^{-1}$ COD), for all experiments tested. Figure 3 shows purifying efficiency expressed as the percentage of COD removed versus the hydraulic retention time (HRT). As can be expected, the efficiency of substrate removal is a function of the hydraulic retention time, HRT, and concomitant organic loading rate, OLR. However, as can be seen in Figures 2 and 3, the operation with neutral influent allows to operate at higher OLR maintaining upper removal efficacy values than the operation with acid influent. Figure 4 shows the volumetric methane evolution rate as a function of the OLR removal. The methane yield, as liters of methane produced per grams of COD removal, keeps constant values between 0.30 and 0.26 $L_{CH_4} \cdot g^{-1}\ COD_r$ during the stable process. Consequently, methane production yield is independent of the pH influent value for a fixed OLRr. Nevertheless, this value is slightly inferior to the stechiometric theoretical of 0.35 $L_{CH_4} \cdot g^{-1}\ COD_r$ (1 g of COD is equivalent to 0.35 L of methane at STP conditions). In this way, the synthesis of new micro-organisms and the initial attachment biomass processes on support surface implicate the initial production of polysaccharide for the biofilm production. This phase supposes a great consumption of organic substances for the synthesis route (anabolism), diminishing, therefore, the quantity of substrate it transforms in methane.

Therefore, the volumetric methane production activity (expressed as $L \cdot L^{-1} \cdot d^{-1}$) could be expressed as a linear function of organic loading rate removal (OLR_r, expressed as $g \cdot L^{-1}\ d^{-1}$ COD). The linear regression obtained can be expressed as follows:

$$\gamma\left(L_{CH_4} L_{digester}^{-1} d^{-1}\right) = 0.26\left(L_{CH_4} g_{COD_r}^{-1}\right) \cdot OLR_r\left(g_{COD_r} L_{digester}^{-1} d^{-1}\right) - 0.09 \qquad (1)$$

It is verified that the operation under alkaline feeding increases the purifying efficiency for similar organic load rate, but the methane production yield stays approximately constant in both conditions. According to the equation (1), the suitable threshold level appears to be 0.35 $g \cdot L^{-1}\ d^{-1}$ COD.

These values agree with the results reported by *Bories*[16] and *Nebot*[3] refering to similar conditions with pilog-scale and lab-scale anaerobic filter reactors respectively.

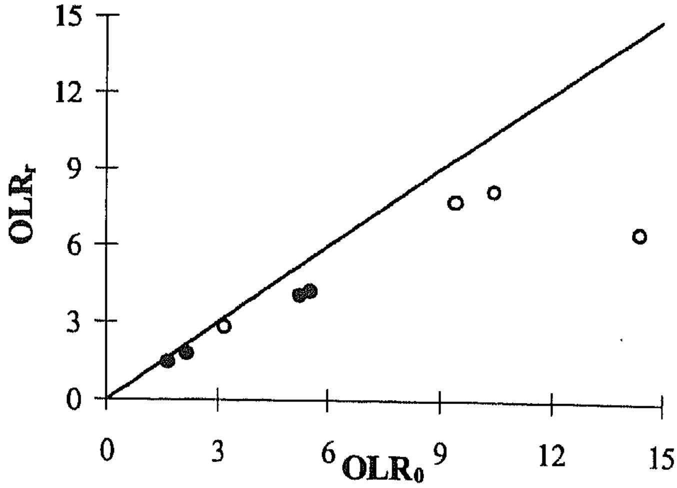

Fig. 2 — *Organic load rate removal (OLR_r, as $g \cdot L^{-1}\ d^{-1}\ COD_r$ as influenced by organic load rate applied (OLR_0, as $g \cdot L^{-1}\ d^{-1}\ COD_0$; Legend: ● acid influent, O alkaline influent.*

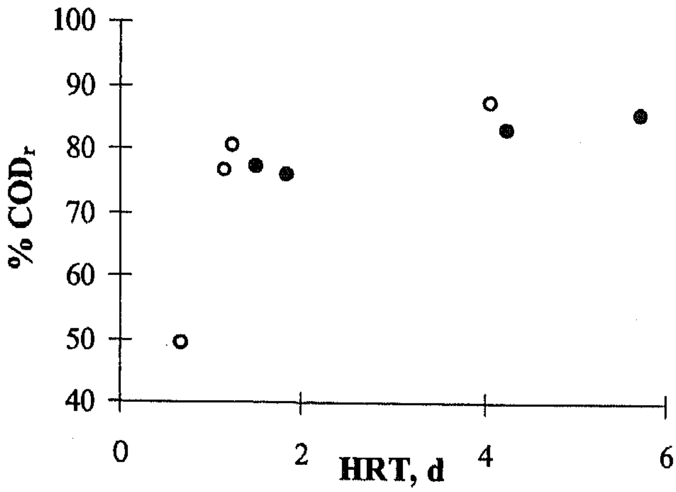

Fig. 3 — *Effect of hydraulic retention time (days) on the organic removal efficiency (percentage of COD removal). Legend: ● acid influent, O alkaline influent.*

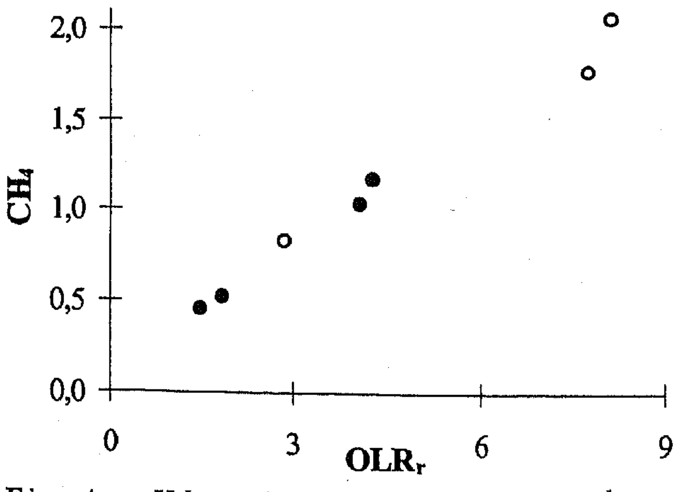

Fig. 4 — *Volumetric methane retge ($L_{CH_4} \cdot L_{digester}^{-1} \cdot d^{-1}$) as a function of the OLR removal ($g \cdot L^{-1}\ d^{-1}\ COD_r$). Legend: ● acid influent, O alkaline influent.*

Conclusions

The results of this work suggest that the pH of the influent determines the performance of the biodegradation process as follows:

a) Acid influent allows to operate at organic loading rates (OLR_0) around 5.6 kg · m^{-3} · d^{-1} COD with HRT of 1.5 days and maintaining soluble COD removals of 70.2% using acid influent.

b) Alkaline influent allows soluble COD removals of 76.8% if working at OLRo around 10.5 kg · m^{-3} · d^{-1} COD and HRT of 0.7 days.

c) pH control on line does not allow to operate with higher organic loading rates.

Therefore, the operation with alkaline influent implicates higher levels of purifying efficiency for similar organic load rate (OLR_0).

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List of symbols

AFR — Anaerobic Filter Reactor
COD — Chemical Oxygen Demand
COD_0 — Initial Chemical Oxygen Demand
COD_r — Chemical Oxygen Demand removal
HRT — Hydraulic Retention Time
OLR_r — Organic Load Rate removed
OLR_0 — Initial Organic Load Rate
TSS — Total Suspended Solids
VSS — Volatile Suspended Solids

References

1. *Hickey R.F., Wu W.M., Veiga M.C., Jones R.l*, Wat. Sci. Technol. **24** (1991) 207–255
2. *Nebot E.*, Caracterización de los principales parámetros de operación de sistemas tipo filtro anaerobio: Aplicación al diseño. PhD Thesis. Serv. Pub. Univ. Cádiz. University of Cádiz, 1992, Cádiz, Spain.
3. *Nebot E., Romero L.I., Quiroga J.M., Sales D.l*, Anaerobe **1** (1995) 113–120.
4. *Ratledge C.*, Bioquímica del crecimiento y metabolismo. In Bu'lock, J.; Kristiansen, B. (eds) Biotecnología básica, Acribia, S.A., Zaragoza, Spain (1991), pp. 11–55
5. *Iza J.*, Wat. Sci. Technol. **24** (1991) 109–132
6. *Gray N.F.*, Biology of wastewater treatment. Oxford University (1989) New York
7. *Atkinson B.*, Reactores Bioquímicos. Ed. Revertá, S.A. (1987) Barcelona, Spain
8. *McCarty P.L., Smith D.P.*, Env. Sci. Tech. **20** (1986) 1200–1206
9. *Hobson P.N., Wallace R.J.*, CRC Crit. Rev. Microbiol. **9** (1982) 162–225, 253–320
10. *Tyagi R.D.*, Wastewater treatment by immobilised cells. Tyagi R.D. y Vembu K. (eds), CRC Press, Boca Ratón, Florida 1990
11. *Kennedy K.J., Muzar M., Copp J.H.*, Biotech. Bioeng. **27** (1985) 86–93
12. *Koster I.W., Koomen E.*, Appl. Microbiol. Biotechnol. **28** (1988) 500–505
13. *Sales D., Valcárcel M.J., Párez L., Martínez de la Ossa* E. Química e Industria **28**, 10 (1982) 701–706
14. *Pérez, M.*, Utilización de bio-reactores avanzados en la degradación anaerobia de vertidos de alta carga orgánica. PhD Thesis. Serv. Pub. Univ. Cádiz. ISBN: 84–7786–293–1 (1995), Cádiz, Spain
15. A.P.H.A., A.W.W.A., W.P.C.F. In Standard Methods for the examination of water and wastewater; Rhodes Trussell, Eds. 17th Edition Washington 1989
16. *Bories A., Raynal J., Jover J.P.*, Proc. 2nd Conference Energy from Biomass, Commission of the European Communities, Berlin (1982), pp. 20–23