Effect of the pH influent conditions in fixed-film reactors for anaerobic thermophilic treatment of wine-distillery wastewater

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Abstract In anaerobic treatments, the pH conditions affect the efficacy and operation of the process. The main purpose of this research is to compare the effect of the pH influent on the performance of a high rate technology at laboratory scale, upflow anaerobic fixed-film reactor, treating distillery wastewater (wine vinasses) in thermophilic conditions. The results obtained shown that the pH influent influences the performance of the biodegradation process: the depurative efficiency is higher for the operation with alkaline influent. The operation with acid influent allows us to operate at organic loading rates (OLR) around 5.6 kgCOD/m^3/d (hydraulic retention time: 1.5 days), maintaining total Chemical Oxygen Demand removals (COD$_r$) of 77.2%; the operation with alkaline influent allows total COD$_r$ of 76.8% working at OLR around 10.5 kgCOD/m^3/d. The greatest efficiency of substrate removal was 87.5% for OLR 3.2 kgCOD/m^3/d and hydraulic retention time of 4.0 days operating with alkaline influent. Therefore, the operation with alkaline influent implicates senior levels of purifying efficiency for similar organic load rate.

Keywords Anaerobic digestion; fixed-bed reactor; industrial wastewater; pH influent; thermophilic conditions

Water Science and Technology **Vol 51 No 1 pp 183–189** © IWA Publishing 2005

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 aerosols. 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.* (1991), and are the upflow anaerobic sludge blanket (UASB), upflow and downflow stationary packed beds (Nebot, 1992; Nebot *et al.*, 1995; Pérez, 1995; Pérez *et al.*, 2001), and fluidized and expanded beds (Ratledge, 1991; Pérez, 1995; Pérez *et al.*, 1999).

The biodegradation processes are strongly influenced by the pH of the reaction medium. The pH medium influences the process rate and determines the type of micro-organisms which develop (Gray, 1989). In anaerobic treatments, the pH conditions, also affect the efficacy and 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 one of them introduces a very different evolution depending on the pH selected (Atkinson, 1987).

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 (McCarty and Smith, 1986). Soluble substrates can be divided into three major stages: 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. This first step is fast compared with the subsequent reactions, where the higher acids are all 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 28.0% of methane. The H_2 concentration 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 level 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 further (Hobson and Wallace, 1982; Tiagy, 1990).

Therefore, a neutral or alkaline influent, and/or a neutral pH control online should favour the anaerobic biomass activity and, in this sense, the degradation process (Koster and Kooman, 1988; Kennedy *et al.*, 1985).

The main objective of this research is to compare the influence of the pH influent on the performance of a high rate technology at laboratory scale, anaerobic fixed-film reactor, treating distillery wastewater (wine vinasses) at thermophilic conditions.

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 reactors (UAFF) treating vinasses of wine at different pH conditions. The experimental study was divided in three stages, as follows:

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

Hydraulic retention time (HRT) remained constant during each stage until steady-state was achieved. The attainment of steady state was verified after an initial stage of three times the HRT by checking that the constant values of the characteristics of effluent 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 and effluent volatile suspended solids. The methods and material used are briefly described in this section.

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

Experimental reactor

A schematic diagram of the upflow anaerobic fixed-film reactor (UAFF) used in the laboratory study is shown in Figure 1. The UAFF reactors consist of vertical cylindrical tanks (25 cm length and 10 cm internal diameter). The active liquid volume was 2.0 L, and the empty volume was 2.4 L. 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. Continuous feed was supplied by peristaltic pump connected to programmable timer. Effluent recirculation was used to mix and homogenise the liquid in the system.

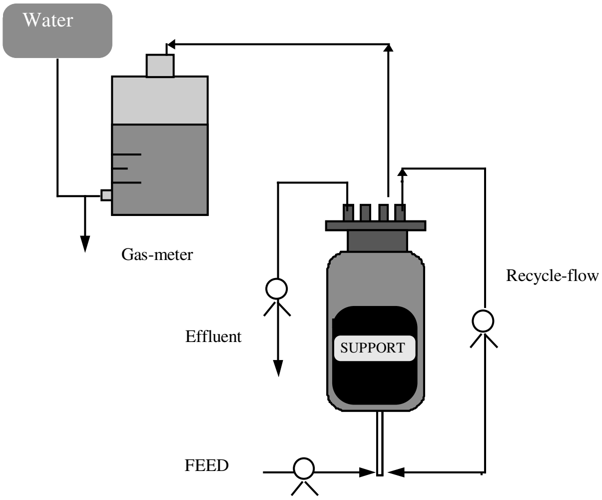

Figure 1 Experimental upflow anaerobic fixed-film reactor (UAFF)

Feed solutions

Distillery wastewater proceeding from an ethanol producing wine-distillery plant situated 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 (Pérez, 1995).

The vinasses were transported and maintained at 20°C before their utilisation. This feed was diluted with tap water to attain the required Chemical Oxygen Demand (COD) concentration used in these experiments (around 15.5 kgCOD/m^3). It was supplemented with sodium hydroxide to adjust the neutral pH, according to the case in point (stages T2 and T3).

Vinasse biodegradation bath experiments (Perez, 1995) indicated that this feed was a complex medium formed by two substrates of different nature and biodegradability: S1, a fraction of substrate easily biodegradable (80% of the total) and S2, that represents recalcitrant substrate fraction in the conditions under which the assays were carried out.

Media support

Corrugated plastic tubes of 16 mm diameter (non-porous media) present low density (1.161 kg/L), high porosity (93.71%) and high specific surface (450 m^2/m^3) suitable for using like stationary packed media in fixed-film reactors.

Analytical methods

All analytical determinations were performed according to *Standard Methods* (Clesceri and Greenberg, 1989). For liquid samples, the parameters analysed in both effluent and influent were: pH, COD and both Total and Volatile Suspended Solids (TSS, VSS). For gaseous samples, the parameter analysed was the volume of biogas produced at STP and its composition (percentage of 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. TSS and VSS were determined by the glass fibre filter method as described in *Standard Methods*. Gas production was measured continuously by water displacement. Determinations of methane and carbon dioxide were carried out using gas chromatography separation accomplished using a stainless steel column packed with Carbosive SII (diameter of 1/8$''$ and

Table 1 Performance and operation parameters of upflow anaerobic fixed-film reactor in different stages: HRT (days); organic loading rate (OLR_0) as $kgCOD_0/m^3/d$; organic removal efficiency (as percentage of initial COD); pH; TSS and VSS, as kg/m^3; volumetric CH_4 and CO_2 production, m^3/m^3digester/d; methane yield, as $m^3CH_4/kgCOD_r$. Feed: dilute vinasses of 15.0kgCOD/ m^3

Stage	HRT	OLR_0	$\%COD_r$	pH	TSS	VSS	CH_4	CO_2	CH_4 yield
T1	5.69	1.67	85.91	8.92	0.37	0.24	0.46	0.34	0.32
	4.22	2.15	83.41	8.61	0.40	0.27	0.52	0.37	0.29
	1.83	5.22	76.04	8.30	0.49	0.23	1.04	0.75	0.26
	1.50	5.56	77.22	8.35	0.47	0.33	1.18	0.84	0.27
T2	4.04	3.17	87.53	8.69	0.35	0.19	0.83	0.28	0.30
	1.25	9.42	80.80	8.28	0.39	0.27	1.77	1.02	0.23
	1.15	10.41	76.83	8.28	0.61	0.42	2.07	2.68	0.26
T3	0.66	14.35	49.65	6.49	0.75	0.53	–	–	–

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; rammed 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 30 mL/min. A standard gas (by Carburos Metalicos, S.A.) was used to calibrate the system (composition: 4.65% H_2; 5.33% N_2; 69.92% CH_4 and 20.10% CO_2).

Results and discussion

The performance and operation parameters in the three stages of this study are shown in Table 1 (all the results presented are the average values of last three dates).

In Stage T1, the volumetric organic loading rate (OLR_0) was gradually increased between 1.67 and 5.56 $kgCOD/m^3/d$. 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 L). A concentration of 15.0 $kgCOD/m^3$ was maintained in all steady states studied.

Soluble COD removal (COD_r) decreased from 85.9 to 77.2%. Firstly, at HRT of 4.22 days and organic load of 2.15 $kgCOD/m^3/d$, the percentage of COD removal was 83.4%. Finally, at HRT of 1.50 days and organic load of 5.56 $kgCOD/m^3/d$, the soluble percentage of COD removal decreased to 77.2%. These reactors showed instability above OLR_0 higher to 5.56 $kgCOD/m^3/d$.

In these conditions, the UAFFs contained an average among 0.24 and 0.33 $kgVSS/m^3$, at HRT of 5.69 and 1.50 days, respectively. The pH was maintained ranged between 8.92 and 8.35 during all the stable process. Methane gas production increased from 0.46 to 1.18 $m^3/m^3/d$ operating at HRT of 5.69 and 1.50 days respectively.

Assays in Stage 2 were performed adding alkaline influent (pH: 7.5). HRT values were gradually decreased among 4.04 and 1.15 days. The volumetric COD loading was between 3.17 $kgCOD/m^3/d$ and 10.41 $kgCOD/m^3/d$.

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 $kgCOD/m^3/d$. This value decreased to 76.83% at organic load of 10.41 $kgCOD/m^3/d$. A posterior 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. In this moment, the medium was supplemented with sodium hydroxide (NaOH 7N) in order to maintain a neutral pH into the reactor (pH control online, Stage 3). Nevertheless, the adjustment of neutrality of the medium did not allow us to operate at an organic load rate higher than 10.41 $kgCOD/m^3/d$. This supposed a sharply drops of methanogen activity and, further, the deterioration of effluent quality (49.65% COD removal).

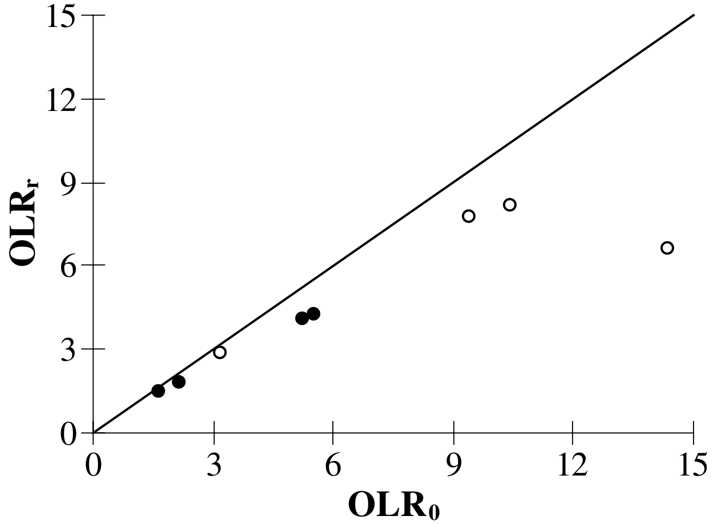

Figure 2 Organic load rate removal (OLR_r, as $kgCOD_r/m^3/d$) as influenced by organic load rate applied (OLR_0, as $kgCOD_0/m^3/d$). (● acid influent, o alkaline influent)

Methane gas production averaged 0.83 and 2.07 $m^3/m^3/d$ operating at HRT of 4.04 and 1.15 days respectively. The pH ranged among 8.57 and 7.65 during all the stable process. In the last stage, the generated biogas ceased and the effluent volatile solids suspended increased from 0.42 $kgVSS/m^3$ to 0.53 $kgVSS/m^3$.

Figure 2 shows the relationship between the organic load rate (OLR_0 expressed as a $kgCOD/m^3/d$) and the organic consumed rate in the process (OLR_r, $kgCOD/m^3/d$), for all experiments tested. Figure 3 shows purifying efficiency expressed as percentage of COD removed versus the HRT. As can be expected, the efficiency of substrate removal is a function of the HRT, and concomitant OLR. However, as can be seen in Figures 2 and 3, the

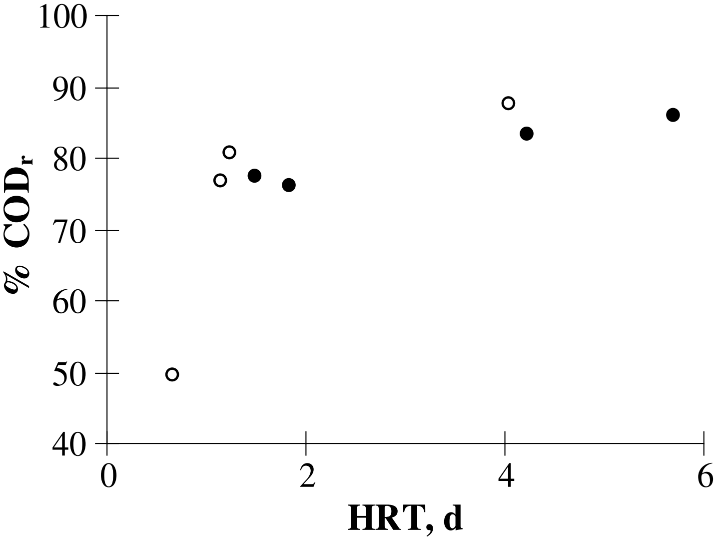

Figure 3 Effect of HRT (days) applied on the organic removal efficiency (percentage of COD removal). (● acid influent, o alkaline influent)

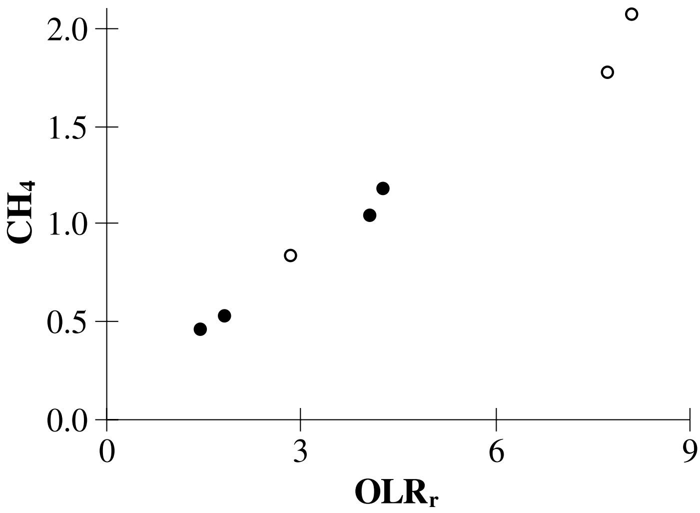

Figure 4 Volumetric methane rate (m^3CH_4/m^3digester/d) as a function of the OLR removal ($kgCOD_r/m^3$/d). (● acid influent, o alkaline influent)

operation with neutral influent allows operate at higher OLR maintaining upper removal efficacy values than the operation with acid influent.

Figure 4 shows the volumetric methane rate as a function of the OLR removal. The methane yield, as litres of methane produced per grams of COD removal, keeps constant values between 0.30 and 0.26 $m^3CH_4/kgCOD_r$ throughout the stable process. Consequently, methane production yield is independent of the pH influent value for a fixed OLR_r. Nevertheless, this value is slightly inferior to the stechiometric theoretical value of 0.35 $m^3CH_4/kgCOD_r$ (1 kg of COD is equivalent to 0.35 m^3 of methane at STP conditions). In this way, the synthesis of new micro-organisms and the initial attachment biomass processes on the support surface implicate the initial production of polysaccharide for binding to material. This phase supposes a great consumption of organic material for the synthesis route (anabolism), diminishing, therefore, the quantity of substrate that it transforms in methane.

The volumetric methane production activity (expressed as m^3/m^3/d) could be expressed as a linear function of OLR ($kgCOD/m^3$/d). The linear regression obtained, using all values, can be expressed as:

$$\gamma(m^3CH_4/m^3\text{digester}/d) = 0.26(m^3CH_4/kgDQO_r)\; OLR_r(kgDQO_r/m^3\text{digester}/d) - 0.09 \quad (1)$$

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 above-mentioned equation (1), the suitable threshold level is 0.35 $kgCOD/m^3$/d.

These values are agreed with the results reported by Bories *et al.* (1982) and Nebot *et al.* (1995) working at similar conditions with pilot-scale and lab-scale anaerobic fixed-film reactors respectively.

Conclusions

The results of this research show that the pH of the influent determines the performance of the biodegradation process: (a) acid influent allows operate at organic loading rates (OLR_0)

around 5.6 kgCOD/m^3/d, 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% working at OLR$_0$ around 10.5 kgCOD/m^3/d 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 senior levels of purifying efficiency for similar organic load rate (OLR$_0$).

Acknowledgements

The authors wish to thank the Comisión Interministerial de Ciencia y Tecnologia for providing support (CICYT: BIO 92-0859, Madrid, Spain).

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