

Treatment of winery wastewater by an anaerobic sequencing batch reactor

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Abstract Treatment of winery wastewater was investigated using an anaerobic sequencing batch reactor (ASBR). Biogas production rate was monitored and permitted the automation of the bioreactor by a simple control system. The reactor was operated at an organic loading rate (ORL) around 8.6 gCOD/L.d with soluble chemical oxygen demand (COD) removal efficiency greater than 98%, hydraulic retention time (HRT) of 2.2 d and a specific organic loading rate (SOLR) of 0.96 gCOD/gVSS.d. The kinetics of COD and VFA removal were investigated for winery wastewater and for simple compounds such as ethanol, which is a major component of winery effluent, and acetate, which is the main volatile fatty acid (VFA) produced. The comparison of the profiles obtained with the 3 substrates shows that, overall, the acidification of the organic matter and the methanisation of the VFA follow zero order reactions, in the operating conditions of our study. The effect on the gas production rate resulted in two level periods separated by a sharp break when the acidification stage was finished and only the breaking down of the VFA continued.

Keywords Anaerobic digestion ; anaerobic SBR; automation ; kinetics ; winery wastewater

Introduction

In wine production, considerable quantities of water are required, at intervals, mainly for cleaning purposes. This activity generates wastewater heavily polluted by organic matter which constitutes a major source of environmental pollution, particularly during the harvest period. In France, wineries must comply with the regulations governing installations classified under environmental protection legislation and they are subject to an anti-pollution tax to compensate for the damage caused to the quality of the water. The aim of the tax is to encourage the wineries to set up wastewater treatment facilities for which they are then allowed an abatement in the anti-pollution tax levied on them.

Of the possible solutions for dealing with winery wastewater, biological treatment processes are especially attractive in so far as the organic matter contained in winery effluent is mainly soluble and very readily biodegradable. This type of effluent can be efficiently treated either by: (i) activated sludge processes operated in a discontinuous manner (aerated storage (Rochard *et al.*, 1998), sequencing batch reactor (Torrijos and Moletta, 1997)), or in a continuous manner (Canler *et al.*, 1998 ; Racault *et al.*, 1998); (ii) or by anaerobic processes (Müller, 1998 ; Andreottola *et al.*, 1998).

An anaerobic process, the anaerobic sequencing batch (fill-and-draw) reactor (ASBR), has been used at laboratory-scale to treat winery wastewater. This process was developed at the beginning of the 90s (Kennedy *et al.*, 1991; Suthaker *et al.*, 1991; Dague *et al.*, 1992; Sung and Dague, 1992). Like the aerobic SBR, the ASBR involves repetition of a cycle including four discrete steps: fill, react, settle, and draw-off. The cycles should be as frequent as possible while allowing for completion of each of the four stages without any intervening idle time (Ruíz *et al.*, 2001).

The application of SBR technology to anaerobic treatment is of interest because of its

inherent operational flexibility (Kennedy *et al.*, 1991 ; Kennedy and Lentz, 2000), including a high degree of process flexibility in terms of cycle time and sequence and no separate clarifiers required. The SBR operation permits good effluent quality control since the reactor draw can be made when the soluble organic matter has been eliminated.

Due to the ease of instrumentation and control, these reactors can be employed in fundamental research in order to elucidate certain aspects of anaerobic digestion (Zaiat *et al.*, 2001). In this way, knowledge of the optimal conditions can be applied on an industrial scale without need of complex instrumentation and control.

In this paper, the results of the treatment of winery effluent with an ASBR process at 35°C are presented together with the description of the automation of the reactor and the detailed study of treatment cycles.

Materials and methods

Description of the reactor

The treatment of winery effluent by an anaerobic sequencing batch reactor at laboratory scale was carried out using a double-walled reactor of 5 L effective volume maintained at 35°C by a thermostatically regulated water bath. Peristaltic pumps were used to fill the reactor and draw off the effluent after settling. Mixing in the reactor was done by a system of magnetic stirring. The pH was regulated at 7 by addition of NaOH (25% v/v) in the reactor. The winery wastewater awaiting treatment was stored at 4°C and kept under magnetic agitation. The volume of biogas produced was measured by an Aalborg mass flow meter 0–50 mL/mn fitted with a 4–20 mA output. The software “Modular SPC”(c), developed at the INRA-Narbonne laboratory, was used for acquiring and treating the data (gas output, pH). This programme also managed the automated operation of the reactor.

The reactor was seeded with activated sludge taken from a stirred anaerobic reactor used to treat distillery vinasse and from an anaerobic pond treating winery wastewater. Before this study, the reactor was used to treat different types of agri-food industry wastewater. The sludges were not changed for this experiment and, to acclimatise the sludge, the reactor was fed over 87 days with a low concentration winery effluent (8.5 g of total COD/L). Thereafter, it was fed over 2 months with the winery wastewater studied here.

Characteristics of the wastewater

The winery effluent was withdrawn from the wastewater storage tank of the cooperative winery at Narbonne (southern France). The organic matter concentration of the wastewater was an average of 19.7 g total COD/L and 17.5 g soluble COD/L. The suspended solids (TSS) concentration was 1.4 g/L and the pH was 5.5.

Winery effluents have low concentrations of nitrogen and phosphorus so, during this experiment, the wastewater was supplemented with nitrogen (1.6 g/L of NH_4Cl), phosphorus (0.35 g/L of $\text{NH}_4\text{H}_2\text{PO}_4$) and 90 mg/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; 36 mg/L yeast extract; 36 mg/L peptone and 9.6 mL/L of a mineral solution containing: 500 mg/L $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; 50 mg/L H_3BO_3 ; 100 mg/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; 10 mg/L NaI; 40 mg/L $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$; 20 mg/L $\text{Na}_2\text{MoO}_4 \cdot 5\text{H}_2\text{O}$; 40 mg/L $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$; 50 mg/L $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. The feed stock was stored at 4°C and renewed twice a week.

Sampling and analysis

Samples were taken regularly at feed, in the reactor and at ASBR outflow. When necessary, samples were centrifuged at 6,000 g for 10 minutes before analysis to remove suspended solids. Volatile fatty acids (VFA) were analysed using a gas chromatograph fitted with a flame ionization detector (Chrompac CP 9000) and coupled with an integrator (Shimadzu CR 3A). COD concentration in samples withdrawn during cycles was measured using a

colorimetric method (Jirka and Carter, 1975). Other parameters were measured following *Standard Methods* (APHA, 1992).

Results

Working conditions of the reactor

The ASBR was operated with cycles including the following four discrete steps: (i) **fill** (14 min): 900 ml of effluent were added to the reactor at the beginning of the react phase; (ii) **react**: during this phase, the reactor was stirred and the organic matter eliminated. The length of this phase was variable and automatically adjusted according to the biogas production rate (see next paragraph); (iii) **settle** (1 hour): settling started when the react phase was finished; (iv) **draw-off** (14 min): at the end of the settling period, the volume of wastewater added at the beginning of the cycle was drawn off from the reactor. Under these operating conditions, the S_0/X_0 ratio was 0.38 gCODt/gVSS.

The reactor was run by an automatic control programme which adjusted the length of the react phase to the behaviour of the reactor. This system is based on the measurement of the rate of biogas production during the reaction stage following additional feeding (Ruíz *et al.*, 2000). The rate of biogas production was greatest at the start of the cycle, just after the feed period, and then decreased with time, reaching very low levels at the end of the reaction stage, indicating very weak metabolic activity. At this stage, the concentration of VFA was nil and COD concentration at its lowest. Thus, the reaction stage is interrupted automatically when the biogas production rate drops below a minimum limit, which indicates that the added organic matter has been eliminated, provided the pH is at 7 or more and there has been a minimum reaction time per cycle. An example of the evolution of the biogas production rate and of the pH during several cycles is presented in Figure 1.

Performance of the ASBR

The functioning of the reactor fed with winery wastewater was monitored over 2 months. On average, the automated digester worked at an hydraulic retention time of 2.2 d, with a volumetric loading rate of 8.6 gCOD/L.d and a mass loading rate of 0.96 gCOD/gVSS.d.

The average residual soluble COD concentration in the treated effluent was 204 mg/L which corresponds to a purification level of 98.8% for soluble COD. This result shows that the organic matter of winery wastewater is highly biodegradable using anaerobic digestion, with the refractory soluble COD representing less than 1.2% of initial soluble COD. Furthermore, it is interesting to note that the residual concentrations measured for soluble COD are very similar to results obtained with aerobic treatments such as continuous or discontinuous activated sludges (Torrijos and Moletta, 1997; Canler *et al.*, 1998). The biodegradability of the organic matter in winery effluent is thus almost the same, whether

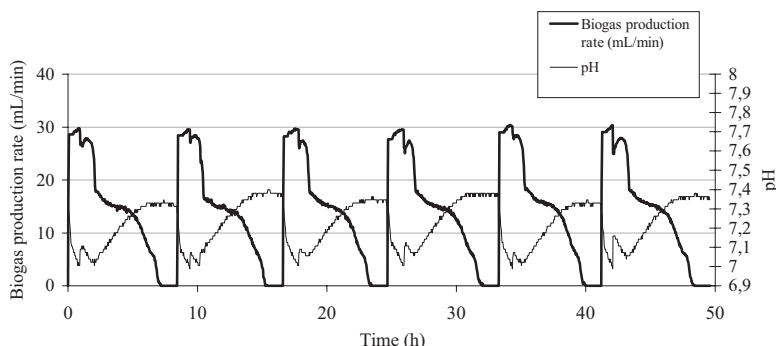


Figure 1 Evolution of the biogas production rate and of the pH during several cycles. Anaerobic SBR treatment of winery wastewater

treated aerobically or anaerobically. Occasional discharge of suspended matter in the treated effluent was observed. The organic loading rates used during this study have shown that a free-cell ASBR, by its ability to achieve very thorough elimination of soluble organic matter even when dealing with relatively high loading rates, is an effective process for treating winery wastewater.

Detailed study of treatment cycles

For each cycle, the rate of biogas production as well as the pH were monitored continuously. For some cycles, samplings were regularly withdrawn from the reactor and measured for concentrations of COD and VFA to study the evolution of these parameters during a cycle. The profiles obtained for a typical cycle with winery wastewater are presented in Figures 2 and 3.

In the conditions prevailing in this study, the biogas production rate with winery wastewater displays a specific profile, with two level periods showing this parameter as fairly constant and a sharp drop in this rate around two hours after the beginning of the feed period. A treatment cycle can then be divided into two parts. In the first part, corresponding to the 1.93 hours following feed input, biogas production was at a maximum (around 27 mL/mn) and an increase in the concentration of VFA was observed. At the start of the second part, there was a sharp drop in the rate of biogas production prior to a stable period lasting several hours with a rate of biogas production around 14.5 mL/mn. Concentrations of VFA peak at the end of the first phase, decreasing regularly thereafter during the second phase at a constant rate of 279 mgVFA/L.h until disappearing completely at the end of the cycle. COD concentration decreased at a lower rate in the second part compared to the first.

To better understand these observations, the cycles for the winery wastewater were compared to those where the carbon substrate was composed of a single product only: ethanol or acetate. Ethanol was chosen because it is the main organic substance found in winery wastewater (Bories *et al.*, 1998) and acetate because it is the major VFA produced from winery wastewater (Figure 3).

When ethanol alone is added to the reactor (2 gCOD/L), the cycle obtained (Figures 4 and 5) appears to be very similar to that for winery wastewater, both for biogas production (with two level periods) and concentrations in VFA and COD.

A cycle with acetate alone (2 gCOD/L) is presented in Figures 6 and 7. With this substrate, there is no acidification step and it is thus possible to study the profiles obtained for the degradation of the main VFA produced from the acidification of winery wastewater. In this case, biogas production rate, COD and VFA consumption rates appear to remain more

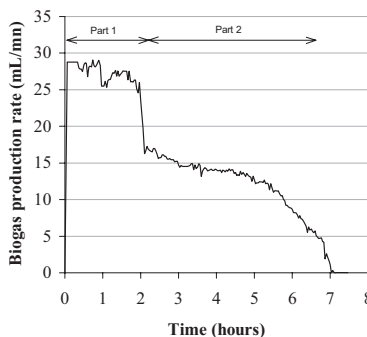


Figure 2 Biogas production rate during a cycle. ASBR treating winery effluent

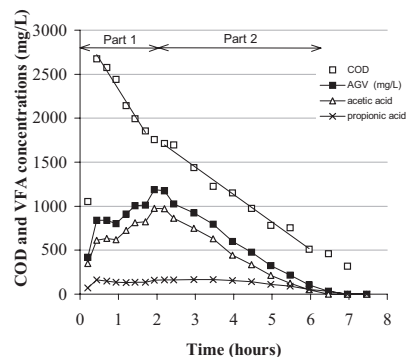


Figure 3 COD and VFA profiles during a cycle. ASBR treating winery effluent

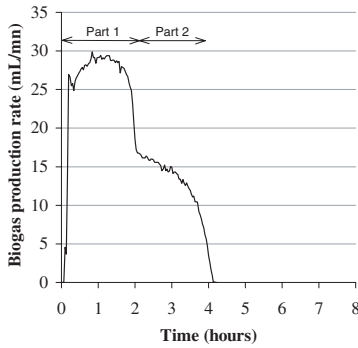


Figure 4 Biogas production rate during a cycle. ASBR treating ethanol

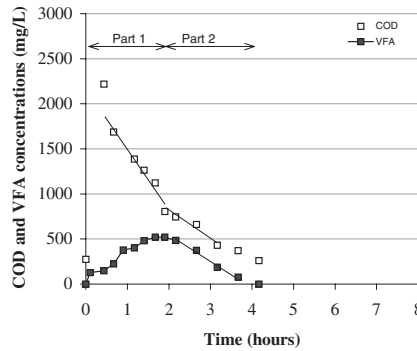


Figure 5 COD and VFA profiles during a cycle. ASBR treating ethanol

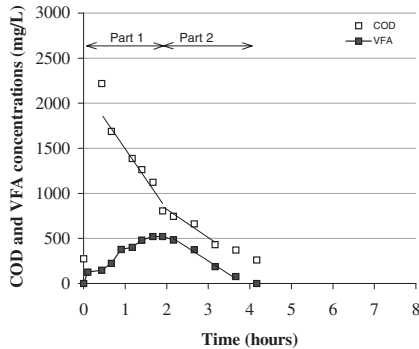


Figure 6 Biogas production rate during a cycle. ASBR treating acetate

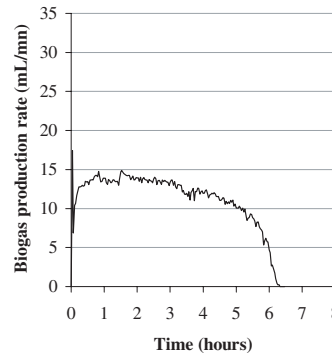


Figure 7 COD and VFA profiles during a cycle. ASBR treating acetate

or less constant throughout the cycle. This result shows that, in the operating conditions of this study, the degradation of acetate follows a zero order reaction.

The comparison between the results with winery effluent or ethanol and the results with acetate suggests that the gas output during the first phase of a cycle using winery wastewater or ethanol reflects the cumulative production of gas deriving from the acidification of the organic matter and from the methanisation of the VFA that arise. An accumulation of VFA appears during this first phase showing that they are produced faster than they can be eliminated. Around two hours after the beginning of the cycle, the reaction of acidification of the added organic matter is finished, with a resulting sudden drop in the rate of gas production. From this point on, gas production becomes a function only of the degrading of the VFA. Level rates of biogas output, along with the clear break observed two hours after the beginning of the cycle, suggest that the rates of the two reactions remain fairly constant and the acetate conversion into biogas is the limiting step of the overall degradation process. The biogas production rates remains quite constant during the first phase of a cycle, which suggests that the acidification of the main compounds of winery wastewater is also a zero order reaction.

The average reaction rates for COD degradation (r_{COD}) and VFA degradation (r_{VFA}) during a cycle for the 3 substrates are presented in Table 1. This table shows that the degradation rate for COD in the first part of a cycle is very close for winery wastewater and ethanol, with an average value of 0.688 gCOD/L.h. The rates of degradation of VFA are very close for the 3 substrates, averaging 0.282 g/L.h or 0.310 g/L.h expressed in COD. From the values measured during the two phases of a cycle, it is possible to estimate the rate of acidification for winery wastewater and for ethanol: 0.375 gCOD/L.h.

Table 1 Average COD and VFA degradation rates for winery wastewater, ethanol and acetate

	Winery wastewater	Ethanol	Acetate
Phase 1 $r_{\text{COD}1}$	0.699 gCOD/L.h	0.677 gCOD/L.h	No acidification phase
Phase 2 $r_{\text{COD}2}$	0.312 gCOD/L.h	0.314 gCOD/L.h	0.303 gCOD/L.h
Phase 2 r_{VFA}	0.279 gVFA/L.h	0.276 gVFA/L.h	0.291 gVFA/L.h

Conclusions

A free-cell anaerobic SBR working at mesophilic temperatures offers qualities of performance that are very attractive for treating winery wastewater. Indeed, in this study, it was possible to use an average loading rate of 8.6 gCOD/L.d while maintaining yields of more than 98% for soluble COD. The monitoring of the biogas production rate throughout each cycle made it possible to design an automation programme that was simple yet reliable.

The kinetics of COD and VFA removal were investigated for winery wastewater and for simple compounds such as ethanol, which is a major component of winery effluent; and acetate, which is the main volatile fatty acid (VFA) produced. The comparison of the profiles obtained with the 3 substrates shows that overall, the acidification of the organic matter and the methanisation of the VFA follow zero order reactions, in the operating conditions of our study. The effect on the gas production rate resulted in two level periods separated by a sharp break when the acidification stage was finished and only the breaking down of the VFA continued.

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