Characterization and Anaerobic Pretreatment of the Effluent from a Wine Cooperative

By *Santino Di Berardino**, *Luisa Caetano*, and *Attilio Converti*

The wastewater from a modern Portuguese wine producing cooperative has been characterized by an automatic sampler which allowed for the collection of daily and hourly averaged samples in two distinct representative situations: the vintage and non-vintage periods of the year. Continuous data of room and wastewater temperatures, pH and flow rate were stored in a data logging system. The winery sells most of the husk and settled sour vine to distilleries, which reduces the quantity of waste and the wastewater pollution load as well as providing an additional source of income. However, the concentration values were higher than the limits allowed by the local authority for discharge into the municipal sewage system; therefore, lab-scale tests were carried out using an anaerobic hybrid filter, to get comparative data on the feasibility of such an anaerobic process to pre-treat this wastewater. The main results, obtained during 7 months of experimentation, indicate that satisfactory COD removals (0.65–0.90) can be ensured by this reactor configuration at relatively low hydraulic retention times (2–3 d), which makes this solution simple and favorable for application in this case study.

1 Introduction

The Portuguese Institute of Wine and Vineyards has reported that the national wine industry consists of approximately 124 wine cooperatives spread throughout the country. In 1995/1996, Portugal was the fifth largest wine producer in the European Union and the fourth in terms of consumption, with total (continental plus insular) wine production of $7.13 \cdot 10^6$ m^3, not including thousands of private producers, and total wastewater generation of $1.07 \cdot 10^6$ m^3. However, most of the wine cooperatives still do not have adequate wastewater treatment systems, which stimulates great interest in developing low-cost treatment technologies.

The present work deals with a laboratory-scale attempt to pre-treat the wastewater from a large wine cooperative, before discharging it into a municipal sewage treatment plant. The aim is to assess an efficient and economic system capable of reducing the concentration of pollutants below the limits imposed by municipal regulations (COD = 1000 mg L^{-1}, BOD_5 = 500 mg L^{-1}, TSS = 300 g L^{-1})[1)]. These concentrations would be consistent with the use of anaerobic methanogenic processes, which have a certain number of advantages with respect to the conventional aerobic processes: low energy consumption, less production of stabilized sludge, low nutrient requirement, and production of biogas which can be used in the winery as a fuel. In this way, in the short and medium term, the cooperative can achieve two different aims at the same time: acceptable effluent concentrations and reduction of both treatment and disposal costs.

Anaerobic processes can favorably compete with the traditional aerobic processes for the treatment of food industry wastewater, provided that the effluent is sufficiently concentrated, available at a relatively high temperature, and characterized by high biodegradability. In those cases where the effluent has CODs from 2 up to 4 times higher than those usually present in domestic wastewater, aerobic processes can be too expensive, therefore anaerobic digestion could be an interesting solution.

Among the possible alternatives to the use of a Continuous Stirred Tank Reactor (CSTR), which tolerates relatively low organic loads, one of the most attractive would be the adoption of the fluidized-bed reactor. Excellent results were obtained both at bench and pilot scales for the anaerobic digestion of dilute [1] and concentrated [2] domestic sewage, effluents from the washing operations of industrial wine production [3], whey [4], synthetic and sugar beet wastewaters, and effluents from yeast and soft drink production [1]. Methane contents of biogas exceeding 85% of the maximum theoretical value were achieved in most cases.

Since the industrial application of this technology could be hindered in the present case study by the presence of excess solids, which would make the control of the bed expansion difficult, a much simpler solution appeared to be the anaerobic hybrid filter (AHF). In this reactor configuration, which incorporates the principles of the UASB unit and the fixed bed anaerobic filter [5,6], anaerobic bacteria are retained by the inner support, which grow abundantly and form aggregates in the shape of flocs, thus allowing a biomass retention time longer than the hydraulic residence time.

The successful application of UASB technology hinges on the generation of sludge aggregating into bio-conglomerates, to facilitate biomass retention in the reactor [7,8]. It was used with good yield in the treatment of domestic sewage [9], cane vinasse [10], and wastewaters from food/beverage industries [9,11,12].

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1) List of symbols at the end of the paper.

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In the AHF, some of the bacterial population is fixed to the support, which partially contributes to the treatment efficiency. The convective motion which originated in the biogas production ensures the agitation of the digesting mass. Both fixed bed filters and AHFs were already utilized with success, in the presence of different supports, for the anaerobic digestion of pig slurry [13,14], food industry wastewaters [15–18], olive oil mill effluent [19], landfill leachate [20], and activated sludge [21].

The lab-scale results obtained in this work using an AHF suggest that this technology could be used successfully in Portuguese wine processing cooperatives.

2 Experimental

2.1 Experimental Set-up

In this work a bench-scale anaerobic hybrid filter (AHF) was used for continuous digestion tests. The reactor, having an outer diameter of 110 mm, a height of 1.2 m, and a total volume of about 10 L, was made of transparent PVC pipes and was partially filled with a 20 cm high module of 4.5 cm long PVC pipes with 0.22 mm inner diameter, Fig. 1.

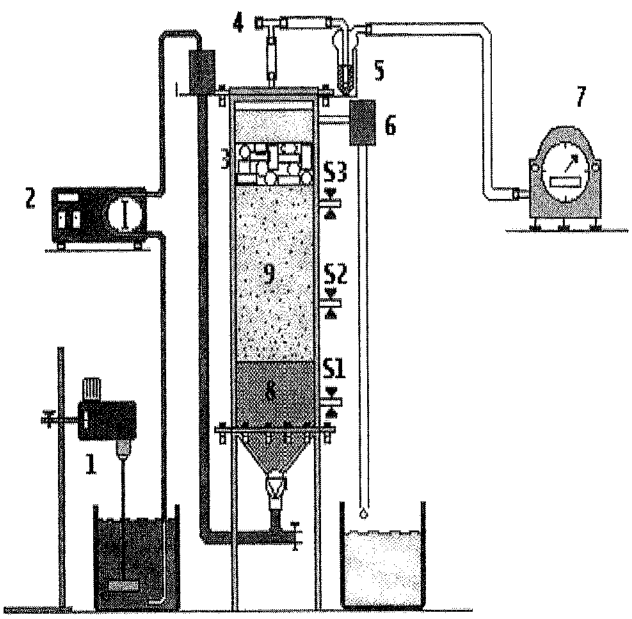

Figure 1. Experimental set-up of the anaerobic hybrid filter: 1 – stirrer, 2 – peristaltic pump, 3 – filter support, 4 – gas sampling point, 5 – trap, 6 – outlet, 7 – gas meter, 8 – sludge, 9 – sludge blanket, S1–S3 – lateral ports.

It had three equally spaced lateral ports to draw samples at different heights along the column.

The working temperature was controlled at the selected value (25 °C), which was close to that measured in the wastewater, by water re-circulation in external jackets. The reactor was fed by means of peristaltic pumps, regulated according to the selected hydraulic retention time (HRT).

2.2 Feeding Solution and Start-up

The wine cooperative under consideration receives about 7,000 tons of grapes per year, which corresponds to 5,000 m^3 of wine production. The available processing capacity consists of 2 lines for red wine fermentation, 1 line for white wine, 4 distillery vessels, and 1 bottling line. The effluents arise essentially from washing operations, except for water used to cool wine fermentation vats. In vintage, a small quantity of wine is distilled, producing small amounts of a concentrated effluent.

According to Mourgues and Maugenet [22], there is a seasonal variability in the effluent volume and composition, which depends on the grape material (kernel, grape skin, dust, sugar, acids, alcohol, polyphenols, yeast and bacteria cells), tartaric acid content, cleaning products, intermediate products of wine fermentation, and filtration media. The fermentation usually takes place from the middle of September until the middle of October; in this period the wastewater has the highest organic content, representing the biggest part of the yearly polluting power of this cooperative.

The reactor was inoculated with sludge from an Imhoff tank near Lisbon having a low methanogenic wintertime activity (0.15 g_{COD} g_{SSV}^{-1} day^{-1}) and the following characteristics: COD_t = 82 g L^{-1}; pH = 6.9; TS = 101 g L^{-1}; VS = 41.4 g L^{-1}. A quantity of anaerobic sludge corresponding to 20 % of the total volume was used. For the start-up operation, which was carried out according to the suggestions of Salkinoja-Salonen et al. [23], we used concentrated wastewater collected during the vintage and kept at 4 °C to reduce degradation during storage.

To get concentrations similar to those obtained during the vintage, continuous experiments following the start-up were performed using feeding solutions prepared by the combination of bottling and tank washing effluent and sour deposit, whose characteristics were: COD_t = 7.6–9.7 g L^{-1}, COD_s = 4.7–7.9 g L^{-1}, P_t = 30–43 mg L^{-1}; N_t (Kjeldahl) = 21–32 mg L^{-1}.

2.3 Analytical Methods

To measure the wastewater flow rate, a triangular PVC weir and a flow meter, consisting of an ultra sonic flow sensor, converter, and register (ISCO model-3210), were installed in an open square manhole. It was connected to an automatic sampler to proportionally obtain daily and/or hourly averaged samples of wastewater. Two temperature and pH sensors were installed in the same manhole and a logger apparatus acquired all the data.

The first monitoring campaign was conducted during the last week of vintage activity and the second one around the middle of March, i.e. during the normal yearly activities. In both campaigns, 7 daily averaged samples were collected. In addition, hourly averaged samples were collected during one additional day of the former campaign as representative of normal weekly activities, while hourly averaged samples collected in the course of two selected days of the latter campaign were considered as representative of the general daily equipment washing operation.

A wet gas meter measured biogas production, while its composition was controlled by gas chromatography, as described in detail in previous work [17].

Following the experience of previous studies, waiting for at least five days of relatively stable values of specific biogas production at a given average HRT was the criterion used to get an indication of the achievement of a pseudo steady-state.

The course of digestion was followed by the daily determination of the contents of total solids (TS), volatile solids (VS), total suspended solids (TSS), volatile suspended solids (VSS), chemical oxygen demand (COD), volatile fatty acids, and total nitrogen (N_t) and phosphorus (P_t), according to Standard Methods [24].

A qualitative analysis of the microbial population grown in the reactor was periodically made by a microscope examination of sludge samples drawn at different column heights.

3 Results and Discussion

3.1 Wine Wastewater Characterization

Fig. 2 shows the time behaviors of 4 hourly averaged values of sewage flow rate and temperature, collected by the continuous measurement system during the working activities of both campaigns.

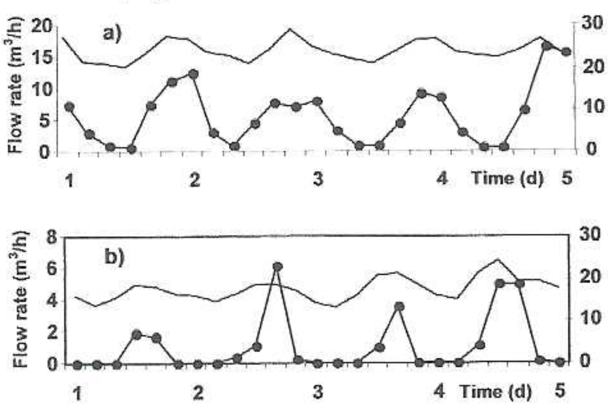

Figure 2. Variations of wastewater flow rate (●) and temperature (—) during: a) the vintage and b) the non-vintage periods.

These results demonstrate that the flow rate oscillated significantly due to batch washing operations, while temperature remained relatively constant during both periods.

Also the average COD during the week significantly varied (from 550 to 4400 mg_{COD} L^{-1}) according to the specific daily washing operations, while only small differences were observed between the vintage and the non-vintage periods, notwithstanding the production of the additional wastewater coming from wine distillation.

The hourly averaged COD values of one day samples collected during the vintage and of two selected days samples of the second campaign are illustrated in Fig. 3.

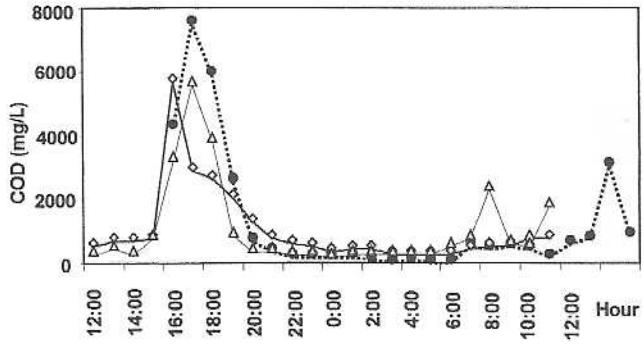

Figure 3. Hourly averaged COD values of one day-samples of wine wastewater collected during the vintage period (●), the 1[st] day (◇) and 2[nd] day (Δ) of the non-vintage period.

In both cases, the most concentrated effluents were discharged between 3.00 and 7.00 p.m., whereas significantly lower COD values were detected at other hours of the day, thus suggesting the possibility of applying a wastewater pretreatment stage during these peak values only. So, the deviation of the wastewater by means of adequate sensor and automatic valves will be recommended at full-scale plant, which can give rise to significant reductions in both capital costs (less homogenization and biological reactor volumes) and current costs (possible reduction in chemical and nutrient requirements).

Tab. 1 lists the average physico-chemical parameters of wastewaters collected during both campaigns, from which it can be seen that the effluents were slightly alkaline and had moderate organic contents, low suspended solids levels, and low nutrient concentrations.

Table 1. Average physico-chemical composition of wastewaters collected during the vintage and non-vintage periods.

	Vintage period (1[st] campaign)	Non-vintage period (2[nd] campaign)
Flow rate (m^3 h^{-1})	11.0	0.9
Temperature (°C)	22.4	17.7
pH	7.9	7.7
COD (mg L^{-1})	2,070	1,900
BOD5 (mg L^{-1})	700	700
TS (mg L^{-1})	1,140	1,538
VS (mg L^{-1})	680	727
TSS (mg L^{-1})	190	367
VSS (mg L^{-1})	130	193
P_t (mg L^{-1})	10.6	5.6
N_t (Kjeldahl) (mg L^{-1})	12.7	18.8
N (ammonia) (mg L^{-1})	0.0	0.0
Acetic acid (mg L^{-1})	100	190
Propionic acid (mg L^{-1})	30	118
Butyric acid (mg L^{-1})	<10	33
Other acids (mg L^{-1})	<10	3

Although the feed pH occasionally ranged between 5.6 and 11.0, due to sodium hydroxide addition during washing operations, it did not diverge too much from the average values during both campaigns (7.9 and 7.7, respectively).

3.2 Anaerobic Digestion Tests

After the monitoring campaign, the industrial effluent from the vintage period was submitted to preliminary batch digestion tests, in order to assess the feasibility of methanogenic processes to reduce their organic content. These tests indicated that they could remove up to 90 % of COD and produce a biogas with more than 65 % methane content, thus encouraging continuous laboratory-scale digestion tests in a reactor configuration which could provide useful data for a future full-scale system. To this purpose, an AHF reactor was used, which allows, notoriously, the growth and the immobilization of specific methanogenic micro flora, thus standing short HRTs. Moreover, such a reactor configuration does not need specialized sludge as seed for start-up, which can be very useful for dissemination in small cooperatives. On the other hand, granular sludge, which is generally unavailable in Portugal, is an essential requirement in UASB technology [25]. For this reason, start-up under difficult operating conditions was simulated in the present case study, and only 10 % of the reactor volume was seeded with sludge from a cold sludge-full scale reactor. The selected start-up procedure proved quite reliable with this small quantity of sludge, lasting only 30 days.

The biogas production (BP) and the organic load (OL) applied during the continuous anaerobic digestion tests carried out at 25 °C are shown in Fig. 4.

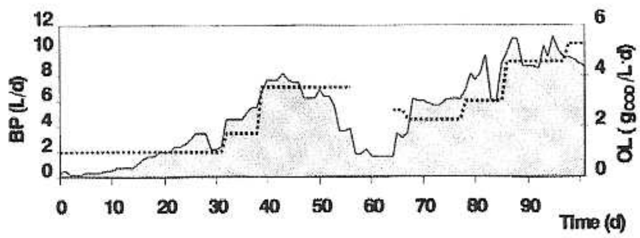

Figure 4. Time behaviors of (—) biogas production (BP) and (...) organic load (OL) during the digestion of wine wastewater with the anaerobic hybrid filter.

After a starting phase in the course of which the AHF was fed at very long HRT (240 h) and relatively low OL (2.0 g_{COD} L^{-1} d^{-1}), necessary to spare the anaerobic biomass a shock due to excess substrate, the HRT was progressively lowered up to 40 h and the OL increased up to 5.25 g_{COD} L^{-1} d^{-1}. The anaerobic population adapted itself well to this feed within 48 d and produced increasing quantities of biogas. After about 40 d of continuous feeding, the reactor achieved pseudo-stationary conditions and showed excellent performance, demonstrated by alkaline pH values (7.6–8.2), low organic acid level (50–120 mg L^{-1}), high COD removal yield (0.72–0.76), low COD of the effluent (1800–2000 mg L^{-1}), and a very high methane content of biogas (about 77–81 %), at HRT = 2.5 h and OL = 3.6 g_{COD} L^{-1} d^{-1}. Effluent concentrations from the AHF varied from about 300 to 3800 mg_{COD} L^{-1}, according to the organic load applied, with average values ranging between 2000 and 3000 mg_{COD} L^{-1}, Fig. 5.

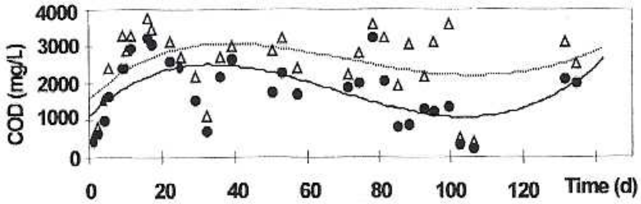

Figure 5. Total (Δ) and soluble (●) COD concentrations of the effluents discharged from the anaerobic hybrid filter.

In addition, the total COD concentration was significantly influenced by losses of suspended solids. Predominantly flocs of *Methanosarcina sp.* grew in the reactor, constituting a layer of not very dense flocculent sludge. These results suggest that mixing the reactor effluent with that part of the industrial wastewater which deviated from the income of the full-scale plant, an average value of about 900 mg_{COD} L^{-1} could be obtained, which would agree with the environmental regulations imposed by the local authorities.

The time behavior of total COD removal yield, depicted in Fig. 6, demonstrates that, within the ranges of HRT and OL investigated in this study, the performance of the reactor was not significantly influenced by the HRT.

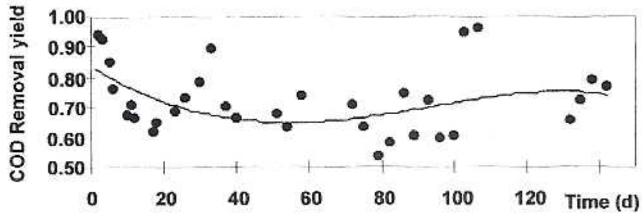

Figure 6. Total COD removal efficiency of the anaerobic hybrid filter.

The COD removal efficiency varied between 0.58 and 0.96, depending essentially on the applied load.

Biogas production revealed a good process response to load variations. The biogas yield varied, according to the organic load, from 0.20 to 0.45 L g_{COD}^{-1} d^{-1}, with the highest value being detected at an organic load of 3.5 g_{COD} L^{-1} d^{-1}.

The volatile fatty acids (namely acetic acid) detected in the effluents were usually well below 200 mg L^{-1} under pseudo steady-state conditions, whereas higher levels of acidity were detected in other situations. Determinations of ethyl alcohol concentration along the column demonstrated that, under the operating conditions investigated in this study, it was nearly completely consumed in the first three-quarters of the AHF height (outlet concentration of 220 mg L^{-1}).

Finally, although the highest COD removals obtained with this reactor configuration (0.60–0.90) are comparable with those of a fluidized bed reactor, the latter showed faster biogas production (2–10 L per liter of reactor per day) working at higher OL (5–40 g_{COD} L^{-1} d^{-1}) [3]. Thus, the advantages of the AHF are recognized in better operational stability, capacity to handle with middle concentration of suspended solids, lower maintenance costs, easier start-up and operation, better ability to make up its performances after interruptions, and capability to face wastewater variations in terms of composition and flow rate. These aspects make the process quite attractive for adaptation to the characteristics of a wine cooperative.

4 Conclusions

Two continuous monitoring campaigns carried out in a Portuguese wine cooperative revealed that the winery effluents have low pollutant concentrations and similar composition all year round, apart from vintage, during which larger volumes are produced, with the effluent discharged between 3.00 and 7.00 p.m. being by far the most concentrated. With the objective of discharging the industrial effluent into the local sewage system, it is necessary to pre-treat only this part of effluent, while the remainder could be discharged directly into the sewage system, thus greatly reducing the cost of the treatment.

The pre-treatment of these effluents by anaerobic digestion indicates that, with the seed sludge currently available, the microbial growth stimulates the aggregation of flocs more than the development of active granular biomass. The results of this work demonstrate that the anaerobic hybrid filter would be an appropriate system for wine waste water digestion because of its easy start-up and operation, besides its ability to tolerate high organic loads.

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Symbols used

BOD_5	[mg L^{-1}]	biological oxygen demand
BP	[L d^{-1}]	biogas production
COD	[mg L^{-1}]	chemical oxygen demand
HRT	[d]	hydraulic retention time
N	[mg L^{-1}]	nitrogen concentration
OL	[g_{COD} L^{-1} h^{-1}]	organic load
P	[mg L^{-1}]	phosphorus concentration
TS	[mg L^{-1}]	total solids concentration
TSS	[mg L^{-1}]	total suspended solids concentration
VS	[mg L^{-1}]	volatile solids concentration
VSS	[mg L^{-1}]	volatile suspended solids concentration

Subscripts

s	soluble
t	total

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