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ANAEROBIC TREATMENT OF OLIVE MILL EFFLUENTS

G. Ubay* and I. Öztürk**

** Istanbul University, Department of Environmental Engineering, Avcilar, 34850, Istanbul, Turkey*
*** Istanbul Technical University, Department of Environmental Engineering, Maslak, 80626, Istanbul, Turkey*

ABSTRACT

The anaerobic treatability of olive mill effluent was investigated using a laboratory scale upflow anaerobic sludge blanket reactor (UASBR) operated for about six months. The effects of various operating conditions including pH, feed strength and hydraulic retention time on the performance of the anaerobic treatment process were determined. In the first part of this study, the reactor was operated with feed COD concentrations from 5000 to 19,000 mg/l and a retention time of 1 day, giving organic loading rates from 5 to 18 kg COD/m^{3}d. Soluble COD removal was around 75% under these conditions. In the second part of the study, feed CODs were varied from 15,000 to 22,600 mg/l while retention times ranged from 0.83 to 2 days; soluble COD removal was around 70% . A methane conversion rate of 0.35 m^3 per kg COD removed was achieved during the study. The average volatile solids (VS) concentration in the reactor had increased from 12.75 g l^{-1} to 60 g l^{-1} by the end of the study. Sludge volume index (SVI) determinations performed to evaluate the settling characteristics of the anaerobic sludge in the reactor indicated excellent settleability with SVI values of generally less than 20 ml g^{-1}. Sludge granules ranging from 3 to 8 mm in diameter were produced in the reactor. The second order substrate removal kinetics was applied by assuming that hydraulic conditions in the UASBR are approximately completely mixed and the model fitted well to the steady state operating results. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Anaerobic treatment; bioenergy recovery; high strength wastes; olive mill effluent; second order kinetic.

INTRODUCTION

The olive oil extraction industry is principally located around the Mediterranean, Aegean and Marmara seas. Olive oil extraction is mainly carried out by means of the traditional discontinuous press or by the more recent continuous solid/liquid centrifuge system. Both processes produce two waste streams : the residual solids (prina), which contain oil to be recovered by means of solvent extraction, and olive mill wastewaters (black water). In general, the organic pollution load in wastewater from olive oil extraction processes is practically independent of the processing method and amounts to 45-55 kg BOD_5 per ton of olives. The corresponding volume of black water from the traditional press process is 0.4-0.5 m^3 per ton of olives (Öztürk *et al.*, 1990).

Olive oil processing is a seasonal operation which starts in September and ends in February at the latest. Individual olive crops are brought to the plant which processes the crop of each customer separately and gives back the processed oil and soap stock to the customer. In Turkey, olive oil processing is generally carried out by many small plants rather than by large edible oil refineries. An appropriate treatment technology has not been developed to solve the environmental pollution problem from olive oil extraction plants. The traditional production capacity of an olive oil plant is about 100 tons per day. Most of the treatment processes used for high strength industrial wastewaters have been applied to olive mill effluents. Aerobic biological processes are not appropriate due to various factors, including high energy and nutrient consumption, production of large amounts of secondary biological sludges and high capital cost. Incineration and concentration by distillation are reliable but very expensive and energy consuming. Evaporation in shallow lagoons is also not practical due to ground water pollution, bad odour and flies. Anaerobic biological treatment processes, however, have distinct advantages including energy and chemical saving and low biological sludge yield. Seasonal operation of olive oil mills is not a disadvantage for anaerobic treatment systems since anaerobic digesters can be easily restarted after several months of shut-down (Craveiro and Rocha, 1986).

MATERIALS AND METHODS

The upflow anaerobic sludge blanket reactor (UASBR) used in this study was made of Plexiglas and had an active volume of 10.35 litres. The internal diameter of the reactor was 12 cm, while total height was 130 cm. Temperature was controlled by circulating hot water from an electrically controlled heat exchanger through polyethylene pipe wrapped around the reactor column.

The black water collected from a traditional olive oil extraction plant in Gemlik village was used as the feed. The black water was diluted with tap water to obtain the desired COD concentration. Feed characteristics are given in Table 1, together with consent limits for olive mill effluents discharged to receiving waters.

Table 1. Wastewater characteristics and consent standards for olive mill effluents discharged to receiving waters in Turkey

Parameter	Discharge Standards (24 hours average)	Concentrated Black Water
pH	6-9	4.7
COD(gl^{-1})	0.230	115-120
SS (gl^{-1})		8.5-9.0
Oil and Grease (gl^{-1})	0.040	7.7
Total N (gl^{-1})		0.18
Total P (gl^{-1})		1.2

Active anaerobic sludge retained in the UASBR after a previous study was used as the seed. The average volatile solids (VS) concentration of the UASBR was determined as 12 750 mg l^{-1} at the beginning of this study. The reactor was started by feeding the diluted black water with a COD of 10,000 mg l^{-1} at a flow rate of 5 l per day at mesophilic operating conditions. The corresponding organic loading rate (OLR) was about 5.4 kg COD per m^3 per day during the first start-up period. During the start-up, pH was maintained in the range of 6.8 to 8.0 and the average temperature was kept at 34°C in the reactor. NaOH solution was added to the reactor directly to maintain the required pH levels when it was necessary. Urea was added to the feed to provide a COD:N:P ratio of 350:5:1 in the system due to N deficiency of the feed. The COD removal efficiency of the UASBR had increased to about 74% after 10 days of operation. This mode of operation was continued for 34 days and then, in view of the stability of the anaerobic digester system, the OLR was gradually increased.

The experimental procedure involved in this study is summarized in Table 2. In the first part of the study (Run I), the feed strengths in terms of COD were varied in the range of 5000 to 19,000 mg l^{-1} at one day hydraulic retention time (HRT). In the second part of the study (Run II) the initial COD of the feed was varied in the range of 15,000 to 22,600 mg l^{-1} and HRTs were varied from 0.83 to 2 days. Major operating parameters, including pH, COD, suspended solids (SS), alkalinity, nitrogen, phosphorus and volatile solids concentration were analysed according to Standard Methods (Standard Methods, 1989). Biogas flowrates were measured by a Wet Test-meter. The CO_2 content of the digester gas was determined by Orsat apparatus. Some parameters, including pH, alkalinity, gas flowrate and temperature were measured on a daily basis, but others, including COD, SS, and CO_2 were analysed three times in a week. The VS content of the sludge was measured once in two weeks.

Table 2. Experimental procedure

Parameter	Run I 0-128th days	Run II 129-175th days
Hydraulic retention time, HRT(day)	1.0	0.83 - 2.0
Feed COD(mgl^{-1})	5250 - 18650	15000 - 22600
Organic loading rate, OLR, (kgCODm^{-3}d^{-1})	5.02 - 18.65	9.80 - 21.90

RESULTS AND DISCUSSION

Substrate utilization

The UASBR was operated for a total of 175 days, including the 34 days start-up period. Table 3 summarizes influent and effluent characteristics, including pH, alkalinity, COD, SS together with parameters such as influent flow rates, organic loading rate (OLR), biogas production rates (Q_g), COD removal efficiencies (E), sludge retention times (θ_x), and specific methane production rate (Y_{CH4}).

The results were obtained at two different operating conditions (Table 3). In the first part of the study (Run I), soluble COD removals around 75% were achieved. The corresponding OLRs were in the range of 5 to 18 kg COD $m^{-3}d^{-1}$. OLRs were gradually increased starting from the 75th day at a rate of 2.5 kg COD $m^{-3}d^{-1}$ for each operating mode and at the end of this run the OLR reached 18.65 kg COD $m^{-3}d^{-1}$. In general, steady state operating conditions were achieved following 2 weeks of operation for each new loading trial.

In the second run (Run II), starting from the 129th day, the average soluble COD removal was about 70%. HRTs were varied from 0.83 to 2 days, corresponding to OLRs of 9.8 to 21.9 kg COD m^{-3} d^{-1}. Table 3 summarizes steady state averages of the UASBR treatment study results for olive mill effluents. Volumetric loading rate affected the COD removal rates and consequently the effluent COD (Fig. 1). COD removal efficiencies in the range of 70 to 75% were achieved for organic loading rates as high as 18.65 kg COD $m^{-3}d^{-1}$ (Fig. 2). An increase in the UASBR effluent suspended solids concentration was observed at high OLRs, although it generally remained below 400 mg l^{-1}. This increase was attributed to increased gas production rates. The COD removal efficiency of the reactor was decreased to less than 70% at OLRs greater than 19 kg COD $m^{-3}d^{-1}$, possibly because of inhibition by polyphenols and high influent suspended solids . This result confirms the findings reported by some authors in the literature (Boari *et al.*, 1984; Rozzi *et al.*, 1986; Boari and Mancini, 1990). In this study, the relatively poor COD removal observed from day 129 was mainly attributed to the high influent SS to the reactor (Table 3).

pH, alkalinity and volatile acids

pH, alkalinity and volatile acids (VA) in the reactor were precisely monitored during the study. The alkalinity in the reactor was gradually increased from 1600 mg $CaCO_3$/l at the beginning to 5000 mg $CaCO_3$/l after 128 days from the start-up (Table 3). No problem with low pH was encountered during the study, and it was found controlling the effluent pH between 6 to 6.5 was sufficient to maintain a stable pH of more than 7 in the reactor. The pH levels in the lab-scale UASBR were generally in the range of 7.5 to 8.0 due to the high buffering capacity. Considering this, volatile acid measurements in the anaerobic reactor effluent were performed once for each specific operating condition at steady state. Total volatile acids measurements have indicated that the effluent VA concentrations were in the range of 85 to 145 mg l^{-1} as acetic acid and the VA to alkalinity ratios were below the safety factor of 0.1 for anaerobic treatment of olive mill effluents (Öztürk, 1987).

Table 3. Summary of waste and operating parameters

Time	Flowrate	HRT	pH	Alkalinity	COD		SS		Q_g	θ_x	E	OLR	Y_{CH4}	Average Biomass
					Influent	Effluent	Influent	Effluent						
(d)	($l\ d^{-1}$)	(d)		($mgCaCO_3/l$)	($mg\ l^{-1}$)	($mg\ l^{-1}$)	($mg\ l^{-1}$)	($mg\ l^{-1}$)	($l\ d^{-1}$)	(d)	(%)	($kgCOD\ m^{-3}\ d^{-1}$)	($l\ CH_4(gVS.d)^{-1}$)	($mg\ VS\ l^{-1}$)
0-34	5	2	7.5	1600	10840	2830	210	120	10.44	139	74	5.42	0.068	12750
35-70	7.5	1.38	8.0	1850	6930	1965	210	137	13.70	94	72	5.02	0.107	11525
71-97	10.35	1	7.8	2300	7590	2130	1000	93	20.00	268	72	7.60	0.081	22490
98-104	10.35	1	8.0	2950	10880	2765	500	110	35.40	229	75	10.90	0.1434	22490
105-117	10.35	1	7.9	3600	13380	3800	495	190	40.00	130	72	13.40	0.165	22490
118-128	10.35	1	8.0	4100	18650	4975	1760	270	68.00	125	73	18.65	0.180	30660
129-138	12	0.83	8.1	5175	18180	6020	1370	380	74.80	77	67	21.90	0.191	30660
139-155	5	2	6.9	4500	19600	7250	1215	800	28.40	126	63	9.80	0.0575	43900
156-175	8	1.25	6.3	3510	22600	9750	1630	660	46.00	130	59	18.10	0.0699	60000

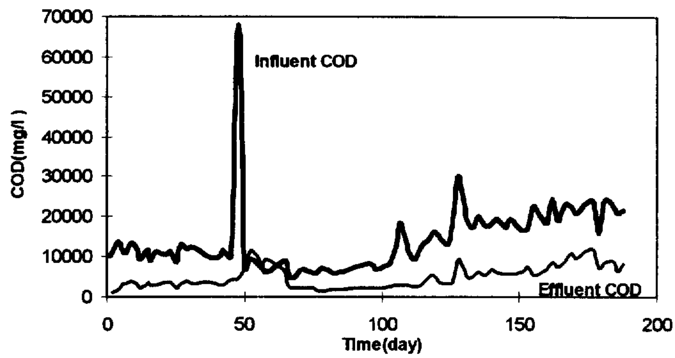

Figure 1. Influent and effluent CODs versus time.

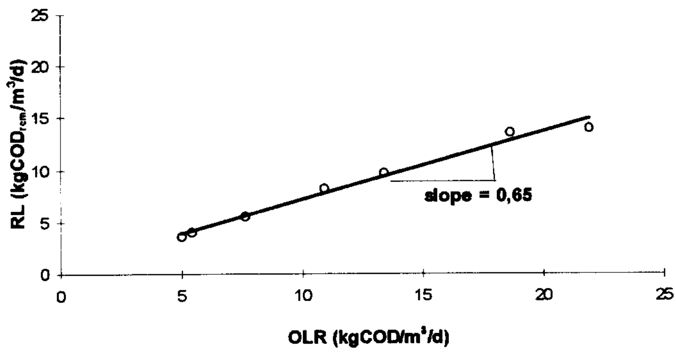

Figure 2. COD removal rates versus organic loading rate.

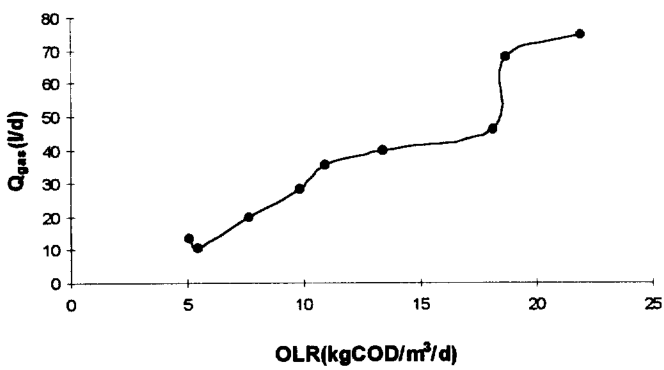

Figure 3. Variation of the gas flowrate versus organic loading rates.

Biogas production

Because the COD removal rate (R_L) in the UASBR increased with an increasing OLR, a similar relationship may be observed between the daily gas production rate and the COD loading as illustrated in Fig. 3. It is generally expected that the methane content of the digester gases decreases as the COD loadings are increased. The specific methanogenic activity of the anaerobic biomass was as high as 0.19 l CH_4 per g VS per day and the maximum biological loading rate was about 0.7 g COD per g VS per day. The observed methane yields for this study were about 0.35 m^3 CH_4 per kg COD removed at 35°C.

Biomass accumulation and characteristics

Biomass concentration measurements carried out on samples withdrawn from different heights in the UASBR revealed that the distribution of the biomass along the height of the reactor was not uniform. The concentration of volatile solids in the sludge bed at the bottom part of the reactor reached values of 80 g l^{-1}. However, the VS concentrations in the upper part of the sludge blanket ranged from 16 to 0.7 g l^{-1}. The ability of the UASBR to retain a very high biomass is shown in Fig. 4. The average VS concentration in the reactor increased from 12.75 g l^{-1} to 60 gl^{-1} at the end of the study. Sludge Volume Index (SVI) determinations performed to evaluate the settling characteristics of the anaerobic sludge in the reactor indicated that the sludge has excellent settleability with SVI values of generally less than 20 ml g^{-1}. Sludge granules ranging from 3 to 8 mm in diameter were produced. Sludge retention time (θ_x) remained always greater than 77 days despite the fact that it had a tendency of decreasing as the OLRs increased.

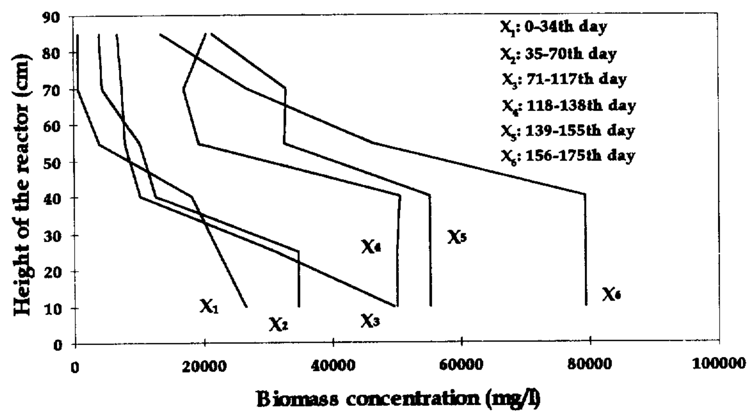

Figure 4. Variation of biomass concentration along the height of the reactor.

Kinetic model development

Considering an n-th order substrate removal kinetics, the general differential equation of anaerobic treatment can be given by the following expression (Grau *et al.*, 1975).

$$-\frac{dS}{dt} = k_{n(S)} \cdot X \cdot (S/S_O)^n \tag{1}$$

where, $k_{n(S)}$: n-th order substrate removal kinetic constant (1/d)

X : average biomass concentration in the reactor (mg/l)

So and S : influent and effluent substrate concentrations (mg/l)

Integrating equation (1) for n = 2 yields the second order substrate removal kinetic expression as :

$$S = \frac{S_o^2}{S_o + k_{2(S)} \cdot X \cdot \theta} \tag{2}$$

where θ is the hydraulic retention time (d). Rearranging Equation (2) yields

$$\frac{S_o \cdot \theta}{S_o - S} = \theta + \frac{S_o}{k_{2(S)} \cdot X} \tag{3}$$

In general this Equation is linearized in the following form:

$$\frac{S_o \cdot \theta}{S_o - S} = a + b \cdot \theta \qquad (4)$$

The model was tested using the results of experimental data obtained from a lab-scale UASBR with a volume of 10.35 l, fed with olive mill effluent. The data which were used for verification of this study are given in Table 3 and the model equation is plotted in Fig. 5. The graph clearly illustrates that the steady state treatment performance data fit quite well to the model, although the hydraulic flow conditions are not completely mixed in UASBRs with a correlation coefficient of 99%. A comparison of values predicted by using the model equation with experimental results is given in Fig. 6.

$$S = S_o \cdot \left[1 - (\theta / (1.31\theta + 0.087)\right] \qquad (5)$$

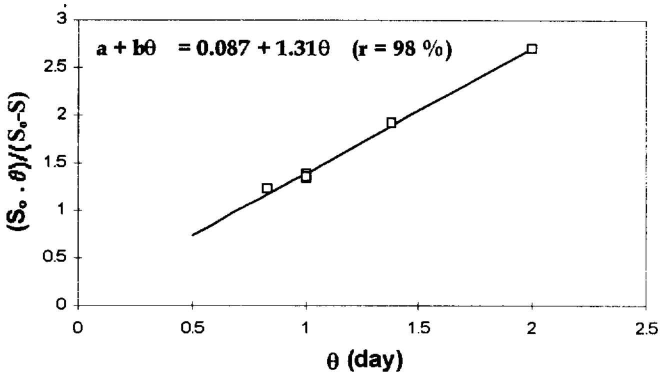

Figure 5. Application of second order kinetics on steady state results.

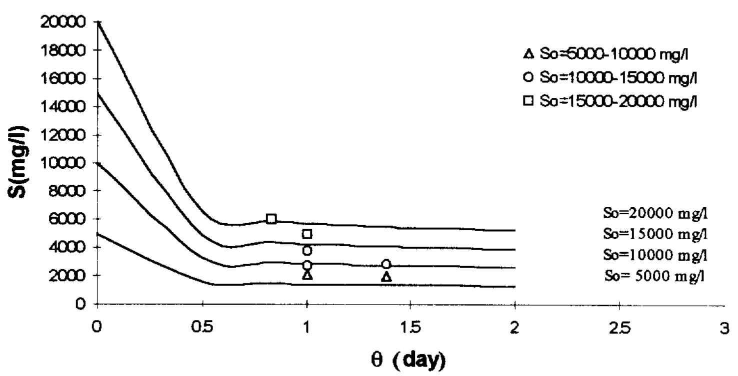

Figure 6. Comparison of values predicted by using model equation with experimental results.

CONCLUSIONS

The results of this treatability study demonstrate that the UASBR is highly effective for methane generation from olive mill effluents. A COD removal efficiency of about 75% can be achieved by an UASBR at an OLR of 18 kg COD m^{-3} d^{-1} with a HRT of one day. Because of this, anaerobic treatment may be a very feasible alternative for olive mill effluents, but additional post treatment would be needed to satisfy discharge standards to receiving waters. Active granules ranging from 3 to 8 mm in diameter can be cultivated. The alkalinity in the anaerobic reactor may be as high as 5000 mg $CaCO_3$ per litre and this provides a very stable buffer against pH decrease due to volatile acid accumulation or low pH feed. The second order substrate removal kinetics can be applied by assuming that hydraulic conditions in the UASBR are approximately completely mixed. The model fitted well to the steady state operating results with the correlation coefficient of 99%.

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