

Anaerobic digestion treatment of olive mill wastewater for effluent re-use in irrigation

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Received 7 August 2000; accepted 21 August 2000

Abstract

Anaerobic digestion of olive mill wastewater (OMW) plus piggery effluent was carried out in an up-flow anaerobic filter type. The digester influent had up to 83% (v/v) of crude OMW with no need for chemical correction. The process converted 70–80% of the influent COD (20–60 kg COD m⁻³), produced 1–3 m³ m⁻³ d⁻¹ (65–75% CH₄) of gas and a more stabilised effluent with a neutral/basic pH was produced. Nevertheless, as some polymerised phenolic compounds are not readily biodegradable, no significant decrease in the OMW black colour was achieved. However, since those lignin residues are innocuous and oxidisable into humic matter, the produced effluent appears as environmentally safe and suitable for agricultural irrigation.

Keywords: Olive mill wastewater; Anaerobic co-treatment; Up-flow anaerobic filter; Soil irrigation

1. Introduction

Olive oil industries are of fundamental economic importance for many Mediterranean countries. However, olive oil extraction involves an intensive consumption of water and produces large amounts of olive mill wastewater (OMW), thus causing deleterious environmental effects [1]. OMW carries important amounts of organic matter (30–200 kg COD m⁻³), including aromatic

compounds that, in association to its high C/N ratio and low pH, compromise biological degradation processes [2]. Moreover, the strong dilution that is required for the attenuation of OMW pollution effects is not compatible with the water resources scarcity in most Mediterranean countries.

Anaerobic digestion can be regarded as a way to convert the greatest fraction of OMW organic

Presented at the conference on Desalination Strategies in South Mediterranean Countries, Cooperation between Mediterranean Countries of Europe and the Southern Rim of the Mediterranean, sponsored by the European Desalination Society and Ecole Nationale d'Ingenieurs de Tunis, September 11–13, 2000, Jerba, Tunisia.

content into biogas, a source of energy. However, current methods for the anaerobic treatment are only applicable to highly diluted OMW [3–5] and their economy is further compromised by the use of chemicals from alkalinity, pH and nitrogen contents setting [6,7]. Therefore, physico-chemical and biological pre-treatments have been suggested as means to reduce significantly the organic load and toxicity of OMW and, thus, to allow its biologic treatment [8–12].

This work aimed the improvement of the OMW anaerobic treatment, with no need for dilution or pre-treatments, and having in view to produce an effluent suitable for soil irrigation use. Amending OMW with a complementary substrate (piggery effluent) that could reduce the OMW toxicity and provide its limiting nutrients such as ammonia attained the objective. Two experimental lines were considered: one concerning digestion of OMW with piggery effluent (PE) and another with piggery effluent anaerobically digested (PD).

2. Materials and methods

2.1. Apparatus

Two identical up-flow anaerobic filters, the F1 and F2, had run at $35 \pm 1^\circ\text{C}$ to digest, respectively, the OMW with PE and OMW with PD. They were built in a PVC pipe (630 mm high and 66 mm diameter) and packed with folded polyethylene net (porosity of 92%) with a 0.31 settling chamber at the bottom and a total volume of 2.5 l. Reactor influent was kept at $4\text{--}5^\circ\text{C}$ by using a supply vessel cooled with an ethylene glycol mixture. Gas production was measured with a wet gas meter (Schlumberger).

2.2. Analytical methods

Chemical oxygen demand (COD) and ammonium nitrogen were determined according to Standard Methods [13] and total phenols (TP)

were evaluated by a modified Folin-Ciocalteu method [14]. Gases were separated in a $1/4" \times 3$ m Porapak column (80–100 mesh) and determined with a thermal conductivity detector in a Pye Unicam 304 chromatograph with column, injector and detector temperatures of 50, 60 and 100°C , respectively.

2.3. Substrates and reactor operation

The influent mixtures were prepared by gradual increases of the OMW proportions in the digester feed that varied from 8 to 83/91% v/v (Figs. 1a and 2a). The OMW came from a three-phase continuous olive oil extraction process and PE and PD were obtained, respectively, from a pig fattening installation and from a laboratory anaerobic digester. Following the start-up periods [15,16], each filter was fed every 4 h to give a hydraulic retention time (HRT) of around 6–7 days. Samples for analysis were taken two or three times a week, and gas production was measured daily and reported at standard conditions (0°C and 1 atm) and filter active volume. The experimental periods at each set of HRT and loading rate (L_a) were defined on the basis of similar gas production rate and effluent quality (COD).

This work reports the main results obtained in F1 and F2 digesters by comparing its behaviours under identical L_a ranges. L_a 's increased from 1 to $8 \text{ kg COD m}^{-3} \text{ d}^{-1}$ and $1\text{--}10 \text{ kg COD m}^{-3} \text{ d}^{-1}$ and were performed during 103–439 and 105–473 experimental days, respectively (Figs. 1b and 2b).

3. Results and discussion

3.1. COD conversion

During the periods corresponding to L_a 's lower than around $6 \text{ kg COD m}^{-3} \text{ d}^{-1}$, the influent COD concentration of one filter did not vary significantly. Ranges of $7\text{--}45 \text{ kg m}^{-3}$ (F1) and

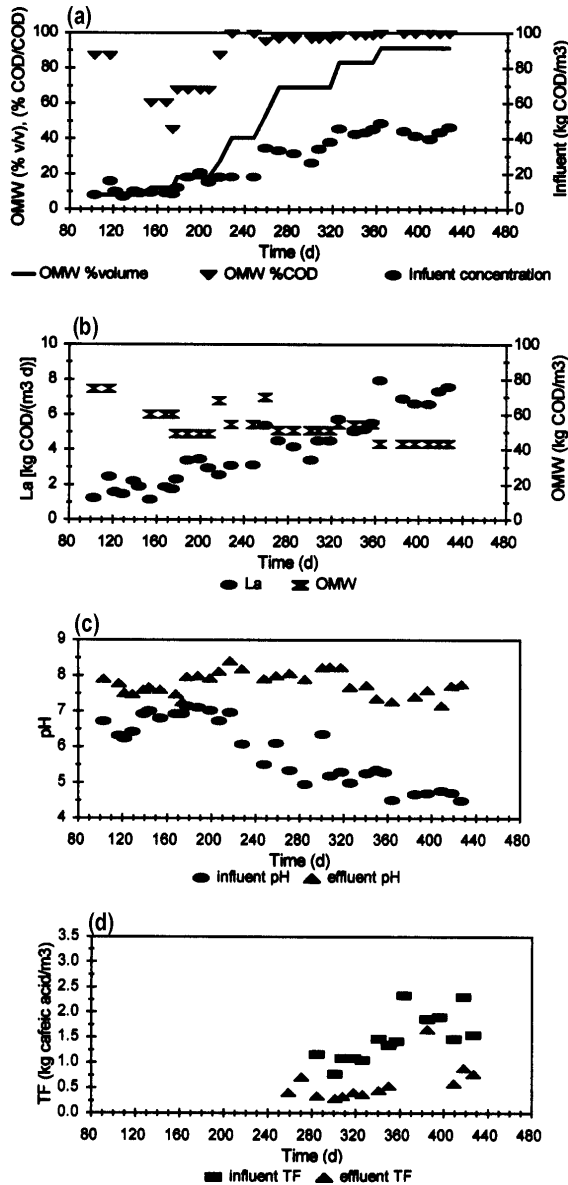


Fig. 1. F1 digester. (a) influent composition; (b) La and OMW concentration; (c) pH; (d) total phenols. OMW, olive mill wastewater; COD, chemical oxygen demand; La, loading rate; HRT, hydraulic retention time; TF, total phenols.

6–42 kg m⁻³ (F2) were obtained (Figs. 1a and 2a). Nevertheless, regarding the performed lower loads till values of 4.3 Kg COD m⁻³ d⁻¹, the F1

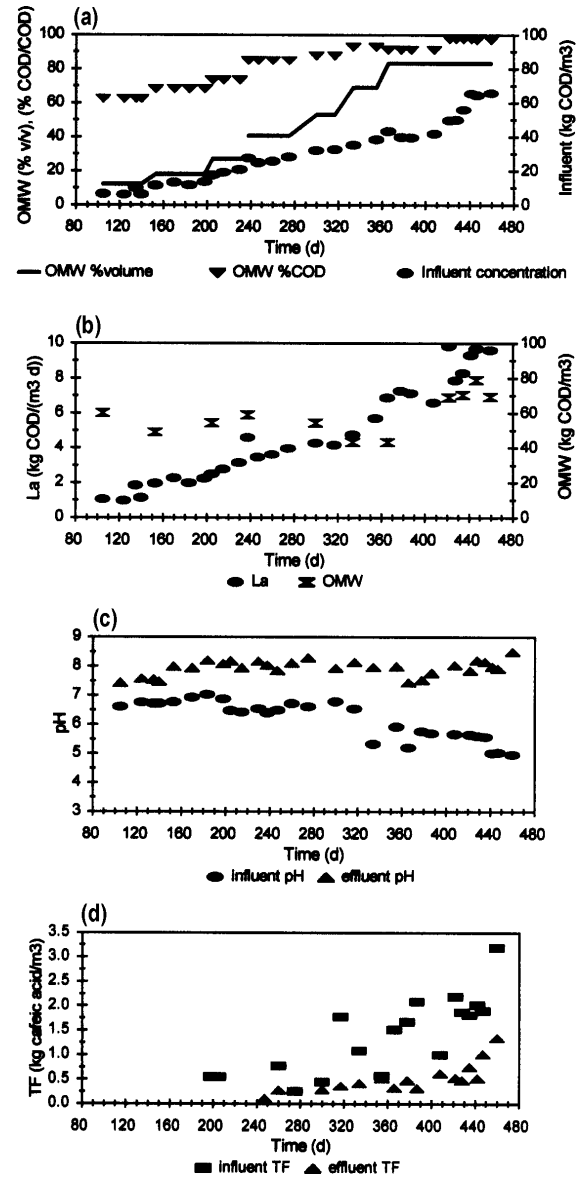


Fig. 2. F2 digester. (a)–(d) and abbreviations as in Fig. 1.

digester showed an higher removal capacity converting a greater COD amount into methane (Table 1). For the 4.5–5.7 kg COD m⁻³ d⁻¹ load period, F1 had run with a more concentrated substrate than F2 but identical gas yields resulted in both cases. The higher COD removal

Table 1
Influent COD and biogas production of F1 and F2 digesters

	F1 digester				
	<3 [8–18/27]	3.1–4.2 [18/41–69]	4.5–5.7 [53/69–83]	6.6–8.0 [91]	
La, kg COD m ⁻³ d ⁻¹ [OMW (% v/v)]	<3 [8–18/27]	3.1–4.2 [18/41–69]	4.5–5.7 [53/69–83]	6.6–8.0 [91]	
Influent COD, kg m ⁻³	$\bar{X} = 11.0$ ($\sigma_{n-1} = 3.54$; n = 12)	$\bar{X} = 22.1$ ($\sigma_{n-1} = 5.581$; n = 6)	$\bar{X} = 39.5$ ($\sigma_{n-1} = 5.190$; n = 8)	$\bar{X} = 43.9$ ($\sigma_{n-1} = 3.267$; n = 6)	
COD removal, %	$\bar{X} = 73.6$ ($\sigma_{n-1} = 8.622$ n = 12)	$\bar{X} = 76.6$ ($\sigma_{n-1} = 4.921$; n = 6)	$\bar{X} = 76.4$ ($\sigma_{n-1} = 2.976$; n = 7)	$\bar{X} = 63.2$ ($\sigma_{n-1} = 4.448$; n = 6)	
Biogas, m ³ m ⁻³ d ⁻¹	$\bar{X} = 0.63$ ($\sigma_{n-1} = 0.253$; n = 12)	$\bar{X} = 1.3$ ($\sigma_{n-1} = 0.253$; n = 6)	$\bar{X} = 1.95$ ($\sigma_{n-1} = 0.193$; n = 8)	$\bar{X} = 2.08$ ($\sigma_{n-1} = 0.148$; n = 5)	
Methane, %	$\bar{X} = 75.1$ ($\sigma_{n-1} = 1.914$; n = 12)	$\bar{X} = 68.9$ ($\sigma_{n-1} = 5.049$; n = 6)	$\bar{X} = 67.4$ ($\sigma_{n-1} = 1.629$; n = 8)	$\bar{X} = 63.4$ ($\sigma_{n-1} = 3.029$; n = 5)	
Y ^a , m ³ kg ⁻¹ COD removal	$\bar{X} = 0.331$ ($\sigma_{n-1} = 0.111$; n = 12)	$\bar{X} = 0.342$ ($\sigma_{n-1} = 0.017$; n = 6)	$\bar{X} = 0.341$ ($\sigma_{n-1} = 0.026$; n = 7)	$\bar{X} = 0.310$ ($\sigma_{n-1} = 0.029$; n = 5)	
	F2 digester				
	<3 [12–27]	3.1–4.3 [27/41–53]	4.6–5.7 [41–69]	6.9–8.0 [83]	8.3–10 [83]
La, kg COD, m ⁻³ d ⁻¹ , [OMW (% v/v)]	<3 [12–27]	3.1–4.3 [27/41–53]	4.6–5.7 [41–69]	6.9–8.0 [83]	8.3–10 [83]
Influent COD, kg m ⁻³	$\bar{X} = 11.4$ ($\sigma_{n-1} = 4.514$; n = 10)	$\bar{X} = 27.1$ ($\sigma_{n-1} = 4.554$; n = 6)	$\bar{X} = 33.6$ ($\sigma_{n-1} = 5.589$; n = 3)	$\bar{X} = 42.7$ ($\sigma_{n-1} = 4.245$; n = 5)	$\bar{X} = 60.1$ ($\sigma_{n-1} = 7.151$; n = 5)
COD removal, %	$\bar{X} = 62$ ($\sigma_{n-1} = 11.723$; n = 10)	$\bar{X} = 77.1$ ($\sigma_{n-1} = 5.668$; n = 6)	$\bar{X} = 71.4$ ($\sigma_{n-1} = 7.143$; n = 4)	$\bar{X} = 70.1$ ($\sigma_{n-1} = 2.481$; n = 4)	$\bar{X} = 73.6$ ($\sigma_{n-1} = 4.196$; n = 5)
Biogas m ³ m ⁻³ d ⁻¹	$\bar{X} = 0.44$ ($\sigma_{n-1} = 0.299$; n = 10)	$\bar{X} = 1.29$ ($\sigma_{n-1} = 0.139$; n = 6)	$\bar{X} = 1.71$ ($\sigma_{n-1} = 0.193$; n = 3)	$\bar{X} = 2.64$ ($\sigma_{n-1} = 0.242$; n = 4)	$\bar{X} = 3.42$ ($\sigma_{n-1} = 0.488$; n = 5)
Methane, %	$\bar{X} = 73.6$ ($\sigma_{n-1} = 2.605$; n = 10)	$\bar{X} = 74.7$ ($\sigma_{n-1} = 1.267$; n = 6)	$\bar{X} = 74.1$ ($\sigma_{n-1} = 2.117$; n = 3)	$\bar{X} = 67.3$ ($\sigma_{n-1} = 1.491$; n = 4)	$\bar{X} = 64.5$ ($\sigma_{n-1} = 1.324$; n = 5)
Y ^a , m ³ CH ₄ kg ⁻¹ COD removal	$\bar{X} = 0.249$ ($\sigma_{n-1} = 0.86$; n = 10)	$\bar{X} = 0.335$ ($\sigma_{n-1} = 0.021$; n = 6)	$\bar{X} = 0.344$ ($\sigma_{n-1} = 0.008$; n = 3)	$\bar{X} = 0.348$ ($\sigma_{n-1} = 0.009$; n = 4)	$\bar{X} = 0.323$ ($\sigma_{n-1} = 0.048$; n = 5)

^aMethane yield.

efficiency of the first filter was in some way compensated by its lower methane percentage. Comparing a higher La range of 6.6–8.0 kg COD

m⁻³ d⁻¹, the situation turned upside-down. The F1 showed a performance decrease but the capacity of F2 was relatively maintained. While the F1

Table 2
Operation at 83% v/v OMW in influent of F1 and F2 digesters

	F1 digester	F2 digester		
OMW, kg COD m ⁻³	54	43	70	75–76
Percent OMW COD in influent	98	91	97	97
COD influent, kg m ⁻³	42–46	39–43	50–56	64–66
La, kg COD m ⁻³ d ⁻¹	5–6	7	8–10	10
Biogas, m ³ m ⁻³ d ⁻¹	1.7–2.1	2.1–2.8	2.9–3.6	3.6–4.0
Methane, m ³ m ⁻³ d ⁻¹	1.1–1.4	1.5–1.9	1.9–2.3	2.3–2.6
Y, m ³ CH ₄ kg ⁻¹ COD removal	0.311–0.340	0.345–0.357	0.336–0.349	0.341–0.345

influent change to 91% v/v OMW originated a decrease in COD removal level of 17%, the decrease in F2 was lower than 2% (Table 1).

The results obtained indicated that for the same La intervals the operation at 91% v/v OMW could compromise the process efficiency. On the other hand, the use of 83% v/v of OMW in influent allows the application of more concentrated substrates (Table 1, F2 unity). Although both filters had worked with organic matter concentrations proceeding from OWM higher than 90% influent CQO, the F1 carried substrates much more diluted than F2. OMW concentrations of around 40 kg COD m⁻³ and 40–80 kg COD m⁻³ were performed (Fig. 1b and 2b), respectively. In addition, working at 83% v/v OMW and identical OMW proportions into feed (97–98% COD/influent COD), the operation with more concentrated oil mill effluents (54 kg COD m⁻³, F1; ≥70 kg COD m⁻³, F2) had displayed a higher methane conversion (Table 2).

3.2. pH

Influent pHs higher than 6 resulted from La's below 3.5 (F1) and 4.5 kg COD m⁻³ d⁻¹ (F2) (Figs. 1c and 2c). The pH decrease to 5–6 was more pronounced in the F1 case and was observed when the unities received loads of 4.2–5.7 kg COD m⁻³ d⁻¹ (F1) and 4.7–9.8 kg COD

m⁻³ d⁻¹ (F2). These conditions resulted from mixtures with 69% v/v and 83% v/v of OMW where the concentrations of this substrate corresponded to 96–98% (F1) and 91–98% COD/influent COD (F2), respectively.

Influent with a pH similar to the original OMW (<4.8) were only tested in F1 during the La's of 6.6–8.0 kg COD m⁻³ d⁻¹. In this case the substrates bore 91% v/v of OMW and 98–99% of the influent COD originated from this substrate.

With respect to effluent pHs, the F1 digester showed a more heterogeneous behaviour than F2, but values higher than 7.3 were recorded in both unities. Lowest pH values (between 7.2 and 7.8) were also only obtained in F1 and during the 91% OMW experimental phase.

3.3. Phenol compounds

The comparison of total phenol concentration related to La's between 3.5 and 6.6 kg COD m⁻³ d⁻¹ suggested that the administration of higher concentrations to F1 [\bar{x} = 1.26 kg m⁻³, σ_{n-1} = 0.184; n = 8 (F1), and \bar{x} = 0.84 kg m⁻³, σ_{n-1} = 0.507; n = 7 (F2)] had a reflex action on the more concentrated effluents. Average values of 0.469 kg m⁻³ (σ_{n-1} = 0.128, n = 9) and 0.397 kg m⁻³ (σ_{n-1} = 0.135, n = 7) were obtained in the F1 and F2 unities, respectively. However, the mean removal values of influent and effluent

concentrations indicated that the F1 capacity to convert these kinds of compounds was higher than F2 (63% vs. 53%).

At higher La 's, the F1 digester has been operated with 91% OMW and effluent values compromised the results comparison (Fig. 1d). Nevertheless, it can be pointed out that the supply of higher concentrations to the F2 digester (1.5–2.1 kg TP m^{-3} ; \bar{x} = 1.83 kg m^{-3} at La 's of 7–9 kg COD $m^{-3} d^{-1}$) resulted in effluents of 0.3 and 0.8 kg TP m^{-3} (\bar{x} = 0.486 kg m^{-3}) and a mean removal capacity of about 73% (Fig. 2d). These levels had never been recorded in F1, and it can be related to a worse adaptation degree of this process. Anaerobic biomass could be acclimated to degrade phenol-like substances, even hydrolyz-able and condensed tannins, at appreciable concentrations of 2 kg m^{-3} [5,17]. On the other side, nitrogen compounds, as proteins and amino acids, act as a protector of cellular viability by promoting the decrease of phenols that can bind to bacterial cell walls [18]. Thus, as PD cosub-strate (F1) had a lower amount of these kinds of compounds than PE, it is possible also to attribute a positive influence of these substances during higher La operation of F2.

With respect to effluent colour, no significant clarification was noticed in either of the filters, as has been previously reported [19,20]. The OMW black colour results from polymerization of aromatic molecules into polymers of greater molecular-mass that are not readily biodegradable [21–23].

4. Conclusions

OMW could be digested successfully by combining it with a complementary effluent, as original or degraded piggery effluents, with no need for chemical correction or dilution with water. Volumes of around 80% of OMW in the influent can be considered a limit in terms of filter efficiency. At this inlet composition, the

digestion of OMW with PD (F2 unity) allowed olive oil mill effluents more concentrated than OMW with PE (F1 unity). Around 70–80% of the influent COD, ranging from 20 to 60 kg COD m^{-3} could be converted into biogas. Volumes of 1–3 $m^3 m^{-3} d^{-1}$ containing approximately 65–75% of methane were obtained.

The process provided the neutralization of influent, as well as the conversion of 50–70% of its phenol contents. The remaining substrate colour is mainly due to the presence of highly polymerized phenolic compounds that are not readily biodegradable. However, since these residues are not toxic and oxidable into humic matter, the produced effluent appears as environmentally safe and suitable for agricultural irrigation, provided that potassium accumulation in soil is avoided.

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