Bioresource Technology **38** (1991) 23–29

Comparison Between Anaerobic Filter and Anaerobic Contact Process for Fermented Olive Mill Wastewaters

M. Hamdi* & J. L. Garcia‡

Laboratoire de Microbiologie ORSTOM, Université de Provence, 3 Place Victor-Hugo, F-13331 Marseille Cédex 3, France

(Received 24 July 1990, revised version received 7 December 1990; accepted 12 December 1990)

Abstract

During the anaerobic digestion of olive mill wastewaters (OMW) prefermented by aerobic growth with Aspergillus niger, *a stationary state was reached more quickly with the anaerobic contact process than with an anaerobic filter, but was more stable with the anaerobic filter. The daily methane production and COD removal recorded with the anaerobic filter were greater than those obtained in the anaerobic contact reactor. The anaerobic filter yielded a biogas with a higher percentage of methane, and effluent with a lower volatile fatty acid and volatile solid content than the anaerobic contact. The immobilizing of VS in an anaerobic filter fermenter is a means of reducing the inhibition of methanogenic bacteria by the residual phenolic compounds present in prefermented OMW. A yield of 0·15 and 0·33 litres methane/g COD removed was obtained with the anaerobic contact and anaerobic filter reactors, respectively. Additional advantages of fixed film over contact fermenters include the elimination of mechanical mixing and sludge settling and return.*

Key words: Methanization, anaerobic filter, anaerobic contact, olive mill wastewaters, phenolic compounds,

INTRODUCTION

In the olive growing countries of the Mediterranean area, olive mill wastewater (OMW) production is estimated to reach more than 30 million m^3 every year (Fiestas Ros de Ursinos, 1981). The maximum BOD_5 and COD concentrations are as high as 100 and 220 kg/m^3, respectively (Balice *et al.*, 1982).

In previous experiments on the anaerobic digestion of unmodified OMW, many problems such as the high toxicity and low biodegradability of this effluent and the acidification of reactors have been studied (Aveni & D'Erasmo, 1982; Boari *et al.*, 1984; Fiestas Ros de Ursinos *et al.*, 1982). Acidifying micro-organisms grow easily on carbohydrates dissolved in the wastewater during methanogenesis; these compounds are the limiting factor in the anaerobic digestion. The process is severely hindered by the combined inhibition caused by high concentrations of aromatic compounds and the buildup of volatile acids (Boari *et al.*, 1984). These problems were partly solved by diluting the waste; the results obtained in this way are not very satisfactory, however (Boari *et al.*, 1984).

Preliminary results have shown that pretreatment of OMW with *Aspergillus niger* decreased the toxicity for methanogenic bacteria and increased the methane production and COD removal in anaerobic batch culture (Hamdi, 1991).

The purpose of the present experiments was to make comparisons between anaerobic contact and anaerobic filter processes for the digestion of *A. niger*-prefermented OMW. These two processes differ as regards the means of retaining micro-organisms in the fermenter: in the contact process, this depends on settling and sludge return, while in the fixed film reactor it depends on attachment and growth of micro-organisms on surfaces.

*Present address: Centre de Biotechnologie, BP-W, 3038 Sfax, Tunisia.
‡To whom correspondence should be addressed.

METHODS

Reactors

The anaerobic filter reactor was a 50-cm glass column, with an internal diameter of 12 cm. The volume of this reactor was 3·5 litres. The inner tube was enclosed in a non-reactive jacket through which hot water was circulated to maintain the temperature of the filter at 35°C. The anaerobic filter was packed with 750 g of PVC rings with a volume of 600 ml. This packing medium had a porosity of 83%.

The anaerobic contact reactor contained 7·5 litres medium in a 10-litre fermenter (Biolaffite, Rueil Malmaison, France). The agitation speed was 75 rpm. This reactor was coupled with a 1-litre settler (Fig. 1).

The two reactors were fed sequentially using a programmer.

Olive-mill wastewater and operation

The anaerobic treatment was carried out on *A. niger*-prefermented OMW (Hamdi, 1991; Hamdi *et al.*, 1991). The chemical characteristics of this wastewater are given in Table 1. Only during the acclimatation and start-up of the reactors, was the prefermented OMW supplemented with trace element (without nitriloacetic acid) and vitamin solutions (Balch *et al.*, 1979). During the comparative testing of the two processes, the COD concentration of the inlet wastewater was maintained at about 30 g/litre. In all cases, the prefermented OMW was adjusted to pH 7·5 by adding $Ca(OH)_2$ and supplemented with urea (COD:N, 50). This was pumped from a tank into the anaerobic filter and anaerobic contact reactors at flow rates of 0·21 and 4·16 ml/min, respectively. The pumps were operated for 20 min every 4 h to give a hydraulic retention time of 15 days in the two reactors with a loading rate of around to 2 g COD/litre per day.

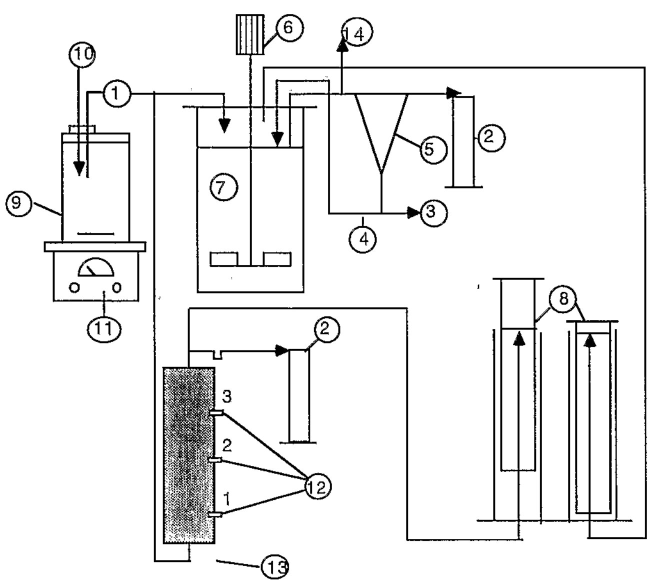

Fig. 1. Schematic diagram of the anaerobic contact and anaerobic filter reactors: (1) influent, (2) effluent, (3) drain sludge, (4) returned sludge, (5) settler, (6) stirrer motor, (7) 10 litre reactor, (8) gas reservoir, (9) feed reservoir, (10) oxygen-free nitrogen, (11) magnetic stirrer motor, (12) sampling levels, (13) anaerobic filter.

Acclimatation and start-up

In order to acclimatize sludge for degradation of *A. niger*-prefermented OMW, and to load the anaerobic filter and anaerobic contact reactors with the same sludge, two different sludges (filtered cow manure, VS = 12·7 g/litre; urban digester sludge, VS = 14·6g/litre) were mixed under O_2-free nitrogen, and then mixed with treated OMW. Two 2-litre completely mixed reactors were filled under O_2-free nitrogen with 0·5 litres of filtered cow manure, 0·5 litres of urban digester sludge, and 0·5 litres of *A. niger*-prefermented OMW (3 g COD/litre); these reactors were incubated for 15 days. The biogas produced was collected. These reactors were then fed daily with 100 ml of the same prefermented OMW (7·5 g COD/litre) for 15 days. The effluents were collected in another 10-litre fermenter. At the end of this stage, the contents of the two reactors were transferred to the 10-litre fermenter. The liquid in this reactor was adjusted to 7·5 litres by sludge transferred from other anaerobic batch cultures of OMW carried out in 120-ml serum bottles. This 10-litre digester, the future anaerobic contact reactor, was fed daily with 500 ml of the same prefermented OMW (15 g COD/litre) for 10

Table 1. Composition of OMW before and after prefermentation by *Aspergillus niger* (g/litre)

Compounds	*Unmodified OMW*	*Prefermented OMW*
COD	157	63·7
Reducing sugars	16·7	2·1
Glucose	7	0·7
Fats	3·6	t
Proteins	2·15	5·7
Condensed tannins	2·3	1·7
Hydrolysed tannins	7	1·35
Monomeric flavoids	1·5	1·86
Simple phenolics	6·4	2·8
Methanol	t	0·52

t: Traces.

days. The effluent was collected in a packed filter column.

The two reactors were then fed under the same conditions to compare their behaviour during anaerobic digestion of *A. niger*-prefermented OMW alone. During this comparative study, the loading rate was maintained at a low level (nominally 2 g COD/litre per day) to prevent the anaerobic filter changing from plug flow to mixed conditions.

Analytical methods

Gas samples were taken with a syringe from the headspace of each gasometer and analysed with a Delsi chromatograph (Delsi-Nermag, Argenteuil, France) equipped with a flame ionization detector, and fitted with a 80 cm × 1/8″ stainless steel column packed with 4% H_3PO_4 on Porapack Q (80–100 mesh). N_2 was used as carrier gas (28 ml/min) with H_2 and air flows of 25 and 30 ml/min, respectively. The oven injector and detector temperature was 200°C. The methane concentration was calculated with an ENICA 10 integrator (Delsi-Nermag). The same apparatus was used for volatile fatty acid (VFA) analysis. The samples were centrifuged at 4000 rpm for 10 min and acidified with 1% of H_3PO_4 (50%). Hydrogen was measured with an H_2-analyser (Trace Analytical Stanford, California, USA) based on the HgO-Hg conversion technique (Seiler *et al.*, 1980). The total solids were determined after drying the sludge overnight at 105°C. The ash content was determined after calcination of the dry sludge at 600°C for 1 h. The difference between total solids and ash content was taken as the Volatile Solids (VS). The chemical oxygen demand (COD) was estimated according to *Standard Methods* (APHA, 1975).

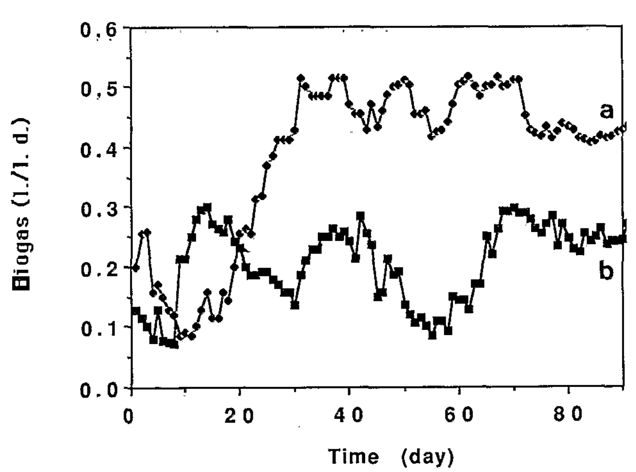

Fig. 2. Daily biogas production in anaerobic filter (a) and anaerobic contact (b) reactors, after acclimatation (see Methods).

RESULTS AND DISCUSSION

Day-by-day examination of the biogas production levels showed that during this experiment, the two reactors functioned differently (Fig. 2). During the first 10 days, the biogas and methane production decreased, while the VFA concentration remained or slightly decreased in both reactors, with the loading rate changing from an average of

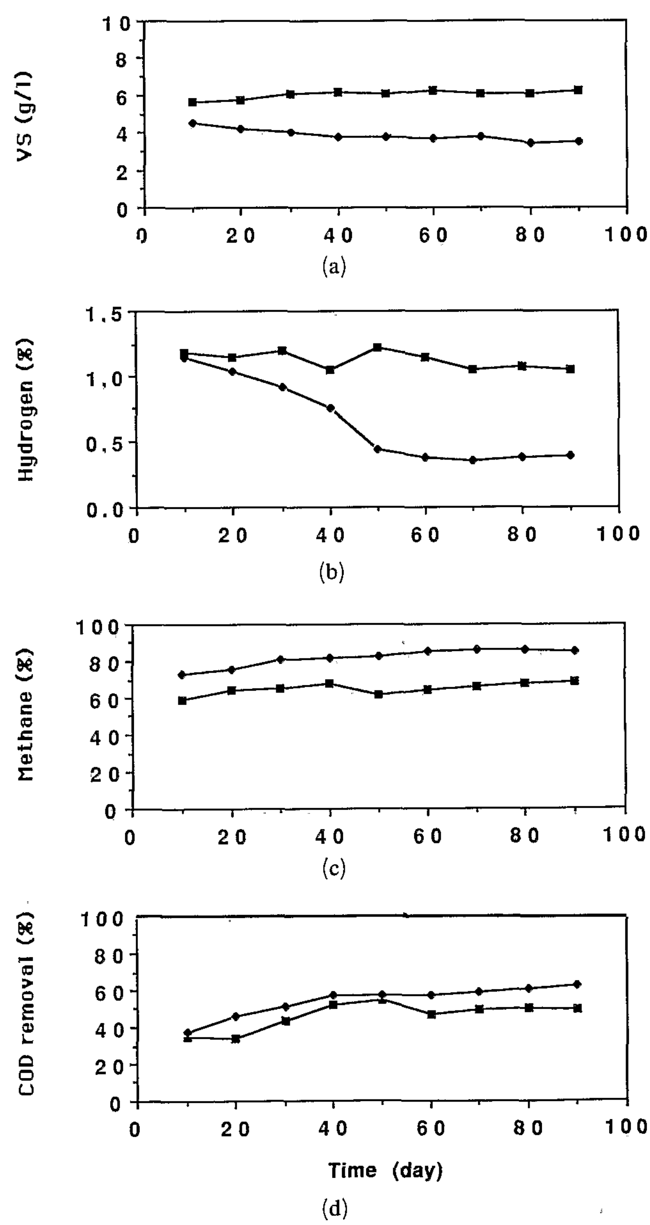

Fig. 3. Time course of COD removal (d) and VS (a) concentrations in effluent, and CH_4 (c) and H_2 (b) contents of biogas obtained from anaerobic filter (◆) and anaerobic contact reactors (■).

1 g COD/litre per day (during acclimatation) to 2 g COD/litre per day. After the 30th day, when the anaerobic filter reached the stationary state, the biogas and methane productivity became greater than that of the anaerobic contact reactor. The stationary state was more quickly reached in the case of anaerobic contact than in that of anaerobic filter, where the growth of bacteria was slower

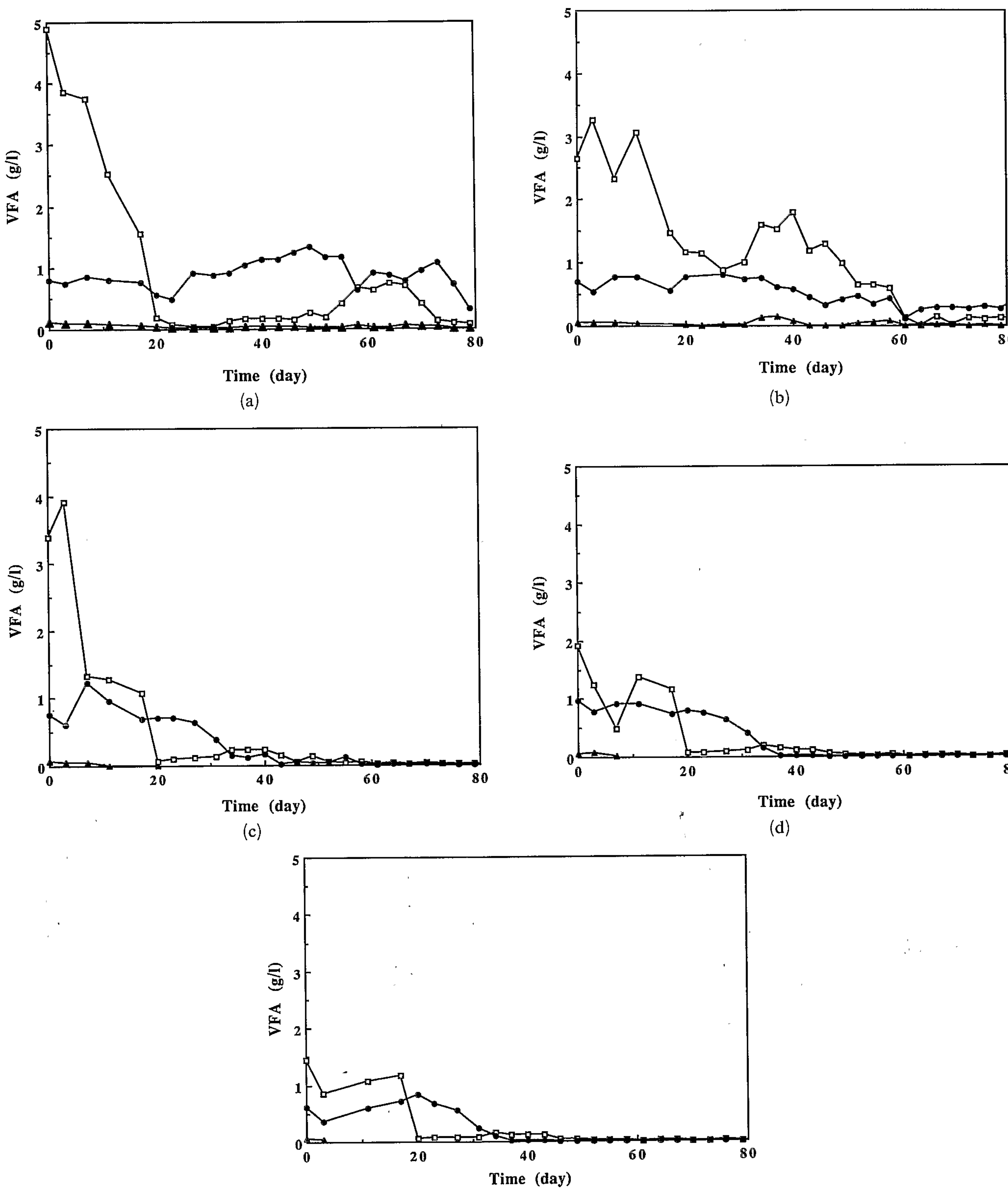

Fig. 4. VFA concentrations in anaerobic contact effluent (a), in anaerobic filter effluent (e) and in samples from levels 1, 2 and 3 (b, c, d) of anaerobic filter reactor. Symbols: acetate (□), propionate (●), butyrate (▲).

(Colvin *et al.*, 1979; Van Den Berg *et al.*, 1980), but the stationary state was more stable in the latter than the former case.

On the 40th and 50th days, each reactor received 0·3 litres air/litre during 40 min because the feed tank was empty. The anaerobic filter reactor remained more stable than the anaerobic contact. This was due to the fact that more oxygen transfer occurs in the anaerobic contact (completely mixed) reactor than in the anaerobic filter reactor. The greater stability of the anaerobic filter facilitates its start-up when variations in the loading rate take place. The start-up time of the anaerobic filter fed with OMW was much shorter than those reported for suspended growth reactors such as anaerobic contact and UASB (Rozzi *et al.*, 1989) processes.

The VS concentration measured at the outlet of the reactors was greater in the anaerobic contact than in the anaerobic filter fermenter (Fig. 3(a)). The variations in the biogas of hydrogen and methane contents produced by anaerobic contact and anaerobic filter reactors are given in Figs 3(b) and (c), respectively. The growth and accumulation of methanogenic bacteria in the digesters decreased the partial pressure of hydrogen. This decrease was greater in the anaerobic filter than in the anaerobic contact reactor. Increasing the pH_2 did not favour the syntrophic degradation of alcohols (Bryant *et al.*, 1967), fatty acids (McInerney *et al.*, 1979; Boone & Bryant, 1980) or aromatic compounds (Mountfort & Bryant, 1982). In fact, the COD removal was more efficient in the anaerobic filter than in the anaerobic contact reactors, as shown in Fig. 3(d).

VFA were analysed in effluents of the two reactors, at three levels of the anaerobic filter corresponding to three different sample points (Fig.1). This analysis showed that, contrary to the anaerobic contact (Fig.4(a)), the acetate in the anaerobic filter at level 1 gradually increased near 40 days (Fig.4(b)). No VFA accumulation occurred in the anaerobic filter at levels 2 and 3 (Fig. 4(c)–(e)).

The agitation in the case of anaerobic contact was more favorable to the growth of acidogenic bacteria than to that of methanogenic bacteria. Moreover, agitation increased the toxicity of aromatic compounds and lipids of OMW towards the methanogenic bacteria (Hamdi, 1991). Due to the agitation the acetate accumulation was higher in the anaerobic contact than in the anaerobic filter reactor. In fact, the performances of anaerobic contact digesters tested in previous studies were not satisfactory because too much mechanical mixing occurred (Boari *et al.*, 1984). The accumulation of propionate associated with the anaerobic contact (Fig.4(a)) might also be a factor which decreased the methane production (Hanaki & Nagase, 1981).

The weak concentration of VFA in the effluent of the anaerobic filter and the low hydrogen content in the biogas improved the yield (litres methane/g COD removed) with the anaerobic filter as compared with the anaerobic contact (Fig. 5), and this could be due to the immobilization of methanogenic bacteria which decreases the toxicity of phenolic compounds (Dwyer *et al.*, 1986). Indeed, the use of anaerobic fixed-film reactors has been shown to be a means of limiting the toxicity of inhibitory compounds (Parkin & Speece, 1983; Khan *et al.*, 1981).

The gradual concentrations of VFA shows that the anaerobic filter was similar to a plug-flow process at an average loading rate of 2 g COD/litre per day (Fig. 4). The anaerobic filter is indeed basically a plug-flow reactor in which waste enters at the bottom and flows up through the media matrix (Young, 1983); the anaerobic contact reactor is a completely mixed reactor. However, as biological solids accumulate and the evolving gases cause a mixing of the fermenting liquor, the hydraulic regime of a fixed bed reactor more closely approaches completely mixed conditions (Hall, 1982).

The difference between the performances of the two reactors is due especially to the concentration, the specific activities and structure of the sludge. According to results in the literature,

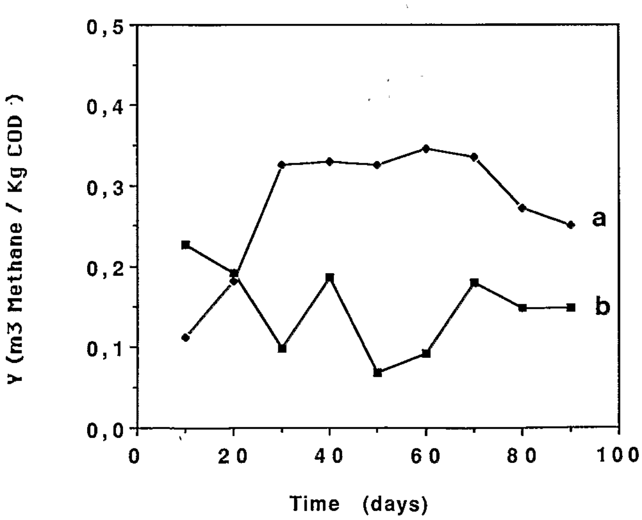

Fig. 5. Yield (litres methane/g COD removed) calculated from the experimental data obtained with anaerobic filter (a) and anaerobic contact (b) reactors.

Table 2. Performance data of anaerobic filters and contact process digesters fed with unmodified OMW

Process	Volume (litres)	Load (g COD/litre per day)	Efficiency[h]	References
Contact	2 600	1·55	70	Antonacci *et al.* (1981)
	70 000	2·55	80	Fiestas Ros de Ursinos *et al.* (1982)
Fixed bed	21[a]	2·80	83	Rigoni-Stern *et al.* (1988)
	300[a]	8·00	87	Rigoni-Stern *et al.* (1988)
	10[b]	2·50	60	Rozzi *et al.* (1989)
	10[c]	2·50	55	Rozzi *et al.* (1989)
	11[d]	3·00	65	Rozzi *et al.* (1989)
	11[e]	3·00	60	Rozzi *et al.* (1989)
	2[f]	2·70	65	Hamdi (1987)
	2[g]	4·40	75	Hamdi (1987)

Package used: [a]polyurethane; [b]prisms; [c]cubes; [d]cylindrical plugs T30; [e]cylindrical plugs TR30; [f]plastic; [g]clay; [h]% COD removal.

anaerobic digestion of unmodified OMW shows that the maximum loading rate and the COD removal obtained with the anaerobic filter could be better than that obtained with the anaerobic contact (Table 2). The great stability and short start-up time of an anaerobic filter fed with unmodified OMW (Rozzi *et al.*, 1989) or with *A. niger*-prefermented OMW (this study) show that this process seems to be the most suitable for OMW treatment.

ACKNOWLEDGEMENTS

Many thanks to Dr R. Moletta for critically reviewing this manuscript and to J. Blanc for revising the English.

REFERENCES

American Public Health Association (APHA) (1975). *Standard methods for the examination of water and wastewater*, 14th ed, pp. 550–4.

Antonacci, R., Brunetti, A., Rozzi, A, & Santori, M. (1981) Trattemento anaerobico de acque di vegetazione di frantoio. I. Risultati preliminari. *Ingegneria sanitaria*, **6**, 257–62.

Balch, W. E., Fox G. E., Magrum, L. J., Woese, L. R. & Wolfe, R. S. (1979). Methanogens: reevaluation of a unique biological group. *Microbiol. Rev.*, **43**, 260–96.

Balice, V., Boari, G., Cera, O. & Abbaticchio, P. (1982). Indagine analitica sulle acque di vetetazione. Nota 1. *Inguinamento*, **7–8**, 49–53.

Boari, G., Brunetti, A., Passino, R. & Rozzi A. (1984). Anaerobic digestion of olive oil mill wastewaters. *Agric. Wastes.*, **10**, 161–75.

Boone, D. R. & Bryant, M. P. (1980). Propionate-degrading bacterium, *Syntrophotobacter wolinii* gen. nov., sp. nov., from methanogenic ecosystem. *Appl. Environ. Microbiol.*, **40**, 626–32.

Bryant, M. P., Wolin, E. A., Wolin, M. J. & Wolfe, R. S. (1967). *Methanobacillus omelianski*, a syntrophic association of two species of bacteria. *Arch. Microbiol.*, **59**, 20–31.

Colvin, J. R., Sowden, L. C. & Van Den Berg, L. (1979). The ultrastructure of the major species of an enriched methanogenic culture utilizing acetic acid. *Can. J. Microbiol.*, **25**, 826–32.

Dwyer, D. F., Krumme, M. L., Boyd, S. A. & Tiedje, J. M. (1986). Kinetics of phenol biodegradation by an immobilized methanogenic consortium. *Appl. Environ. Microbiol.*, **47**, 850–7.

Fiestas Ros de Ursinos, J. A. (1981). Différentes utilisations des margines. In: *Proc. Séminaire International sur la Valorisation des Sous-Produits de l'Olivier.* Organisation des Nations Unies pour l'Alimentation et l'Agriculture, Tunisie, pp. 93–110.

Fiestas Ros de Ursinos, J. A., Navarro Gamero, R., Leon Gabello, R., Garcia Buendia, A. J. & Mastrojuan Saez de Jauragui, G. M. (1982). Depuracion anaerobia del apechin como fuente de energia. *Grasas y Aceites.*, **33**, 265–70.

Hall, E. R. (1982). Biomass retention and mixing characteristics in fixed-film and suspended growth anaerobic reactors. In: *IAWPR-Specialised Seminar on Anaerobic Treatment*, Copenhagen, Denmark.

Hamdi, M. (1987). Digestion anaérobie des margines par filtres anaérobies. Diplôme d'ingénieur, Université de Provence, Marseille.

Hamdi, M. (1991) Effects of agitation and pretreatment on the batch anaerobic digestion of olive mill wastewater. *Biores. Technol.*, **36**, 173–8.

Hamdi, M., Khadir, A. & Garcia, J. L. (1991). The use of *Aspergillus niger* for the bioconversion of olive mill wastewaters. *Appl. Microbiol. Biotechnol.*, **34**, 828–31.

Hanaki, K. & Nagase, M. (1981). Mechanism of inhibition caused by long-chain fatty acids in anerobic digestion process. *Biotechnol. Bioeng.*, **23**, 1591–610.

Khan, K. A., Suidan, M. T. & Cross, W. H. (1981). Anaerobic activated carbon filter for the treatment of phenol bearing wastewaters. *Journal WPCF.*, **53**, 1519–32.

McInerney, M. J., Bryant, M. P. & Pfenning, N. (1979). Anaerobic bacterium that degrades fatty acids in syntrophic association with methanogens. *Arch. Microbiol.*, **41**, 129–35.

Mountfort, D. O & Bryant, M. P. (1982). Isolation and characterization of an anaerobic syntrophic benzoate-degrading bacterium from sewage sludge. *Arch. Microbiol.*, **133**, 149–56.

Parkin, G. F. & Speece, R. E. (1983). Attached versus suspended growth anaerobic reactors: response to toxic substances. *Water Sci. Tech.*, **15**, 305–8.

Rigoni-Stern, S., Rismondo, R., Szpyrkowicz, L. & Zilio Grandi, F. (1988). Anaerobic digestion of vegetation water from olive mills on a fixed biological bed with a biogas production. In: *Proc. Fifth Int. Symp. on Anaerobic Digestion*, Bologna, Italy, ed. A. Tilche & A. Rozzi. Monduzzi Editore, S.p.A. Bologna, pp. 561–6,

Rozzi, A., Passino, R. & Limoni, M. (1989). Anaerobic treatment of olive mill effluents in polyurethane foam bed reactors. *Process Biochemistry*, **4**, 68–74.

Seiler, W., Giehl, H. & Roggendorf, P. (1980). Detection of carbon monoxide and hydrogen by conversion of mercury oxide to mercury vapor. *Atmos. Technol.*, **12**, 20–45.

Van Den Berg, L., Lentz, C. P. & Armstrong, D. W. (1980). Methane production rates of anaerobic fixed film fermentors as compared to those of anaerobic contact and fully mixed continuous fermentors. In: *Proc. Sixth International Fermentation Symposium*, London, Canada, 20–25 July (*Advances in Biotechnology*). Pergamon Press, Oxford.

Young, J. C. (1983). The anaerobic filter-past, present and future. In: *Third Int. Symp. on Anaerobic Digestion*, Boston, USA.