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Anaerobic thermophilic digestion of cutting oil wastewater: Effect of co-substrate

M. Perez [*], R. Rodriguez-Cano, L.I. Romero, D. Sales

Department of Chemical Engineering, Food Technology and Environmental Technologies, Faculty of Sea Sciences & Environmental Sciences,
University of Cadiz, Campus Rio San Pedro s/n, 11510 Puerto Real, Cadiz, Spain

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Abstract

This paper describes the thermophilic (55 °C) anaerobic biodegradation of a mixed feed composed of vinasses and cutting oil wastewater (COW) in a laboratory upflow anaerobic fixed-film reactor (UAFF) with a porous support medium. The experimental protocol was defined to examine the effect of increasing the percentage of cutting oil wastewater in the feed.

The UAFF reactor was initially started-up with vinasses as the only carbon source at an organic loading rate of 22.3 kg COD/m^3 day and HRT of 0.8 days using porous particles as the support (SIRAN). The percentage of organic matter composed of vinasses was subsequently reduced while increasing the amount of cutting oil until 100% of cutting oil wastewater was added in the feed. Four stages were considered in the study (0, 42.4, 66.6 and 100% COW). HRT was adjusted in order to maintain an approximately constant organic loading rate applied to the system. Under theses conditions, the UAFF reactor was subjected to a programme of steady-state operation with hydraulic retention times (HRT) in the range 0.8–0.15 days and organic loading rates (OLR) between 22.3 and 14.9 kg COD/m^3 day in order to evaluate the treatment capacity of the system.

The COD removal efficiency was found to be 87% COD and 94.6% TOC in the reactor when treating vinasses at 22.3 kg COD/m^3 day. The volumetric methane level produced in the digester reached 0.45 m^3/m^3 day. After an operating period of 120 days, the reactor was fed with cutting oil wastewater (COW) as the only source of carbon. An OLR of 16.7 kg COD/m^3 day was achieved with 85.8% COD removal efficiency (58.1%TOC) in the experimental UAFF reactor. Under these conditions the volumetric methane produced in the digester was negligible.

Hence, COW can be removed, if not degraded, by anaerobic treatment in the presence of a biodegradable co-substrate. Wine vinasses degradation creates conditions for non-biological removal of COW constituents. More studies are necessary in order to test the mechanisms of organic removal when biodegradation apparently had ceased. Also, toxicity assays of COW are necessary to evaluate the toxicity to the methanogenic community.

Keywords: Anaerobic digestion; Anaerobic fixed-film reactor; Thermophilic; Wine distillery wastewater; Cutting oil wastewater

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1. Introduction

Metal working fluids (MWF) are emulsionable fluids that are widely used in metalworking processes (for lubrication and refrigeration during the machining of metallic pieces and, to a lesser extent, glass) [1]. Cutting oil wastewaters normally consist of oil, water and additives (fatty acids, surfactants, heavy metals, biocides, etc.). It can be an extreme environment with a high alkalinity (pH ranging from 9 to 11) and high temperatures when the fluid is in-use. MWF derived from industrial processes are classified as Special Waste under Spanish legislation. This means that there are restrictions on the movement, treatment and disposal of waste oil.

Opportunities for the prevention of pollution mainly involve the reduction in the use of toxic materials, the prevention of the formation of large volumes of wastewater, hazardous waste or air emissions containing toxic pollutants and, finally, improvements in energy conservation. The breakthroughs outlined above should enable this manufacturing sector to improve environmental management and benefit from economies gained by speeding up the adoption of emerging technologies that will reduce waste

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Abbreviations: COD, chemical oxygen demand; COD$_r$, chemical oxygen demand removal; COW, cutting oil wastewater; HRT, hydraulic retention time; OF, organic fraction; OLR, initial organic load rate; OLR$_r$, organic load rate removed; OM, total organic matter; OM$_{COW}$, cutting oil wastewater organic matter; OM$_v$, vinasses organic matter; Q, total volumetric rate; Q_{COW}, volumetric cutting oil wastewater rate; Q_v, volumetric vinasses rate; TOC, total organic carbon; TSS, total suspended solids; UAFF, upflow anaerobic fixed-film reactor; VFA, volatile fatty acid; VS$_{att}$, volatile attached solids; VSS, volatile suspended solids

[*] Corresponding author. Fax: +34 956 016411.
E-mail address: montserrat.perez@uca.es (M. Perez).

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and costs in terms of environmental compliance and energy expenditure [2].

MWF have traditionally been treated using physical–chemical techniques such as ultrafiltration or evaporation [3]. Cracking stable emulsions and separating oil and water phase's results in an oily sludge and large volumes of strongly acidic water, both of which require further treatment before they can be safely disposed of. However, as legislation is amended and tightened the traditional routes of disposal are no longer economically or environmentally acceptable [4,5].

The main solution to this disposal problem is on-site biological treatment using bioreactor systems. Biological treatment has been used to remove metal–working fluids (i.e., to trap oil and solids from cutting fluids) and has been investigated by several researchers [6–12]. Currently bioreactors are inoculated with undefined microbial communities from sewage treatment reactor, a notoriously heterogeneous and potentially dangerous source, because it is likely to harbour potential pathogens [13].

The anaerobic treatment of industrial wastewater has become a viable technology in recent years due to the rapid development of high-rate reactors, such as the anaerobic filter and upflow anaerobic sludge blanket (UASB) [14,15], both upflow and downflow stationary packed beds [16–18], and fluidized or expanded beds [20–22]. These developments are due to the fact that the methods combine a number of significant advantages – including low energy consumption, low excess sludge production, enclosure of odours and aerosols – over conventional aerobic methods with different activated sludge types for industrial wastewater treatment [23–25].

Interest in upflow anaerobic fixed-film reactor (UAFF) technology has grown as it combines the recovery of usable energy with good process efficiency and stability. Potential UAFF applications for the treatment of hazardous waste with inhibitory/recalcitrant compositions have also been reported [22,24–27,29–31].

The treatment capacity of an anaerobic digestion system is primarily determined by the amount of active population retained within the system, which in turn is influenced by wastewater composition, system configuration, and operation of the anaerobic reactor.

Previous investigations by the authors of this paper indicate that the wastewater composition influences the activity of the methanogenic microorganisms and, therefore, the volumetric biogas production rate [22]. The literature in this field contains several reports that describe how recalcitrant wastewater can be anaerobically digested and generate only low levels of biogas [28]. However, the volume of biogas can be further improved by the addition of a co-substrate [22,31] and, in addition, maintaining a sufficient time period for the adaptation of the biomass [32] or combining biological and physical processes for complete treatment of oily wastewater [33].

The experimental protocol described was designed to examine the effect of the percentage of organic matter from cutting oil wastewater (%$\mathrm{OM_{COW}}$) on the efficiency of COD and TOC removal of mixed industrial wastewater (wine-vinasses + cutting oil wastewater) at different bioreactor HRT conditions. Furthermore, the effect of %$\mathrm{OM_{COW}}$ on the volumetric methane generation rate and methane yield is described.

2. Materials and methods

2.1. Experimental system

A schematic diagram of the upflow anaerobic fixed-film reactor used in the laboratory study is shown in Fig. 1. The anaerobic reactor consisted of vertical cylindrical tanks with 3.45 L and useful volume of 3.00 L. The reactor was initially loaded with 300 $\mathrm{cm^3}$ of coated support medium (coated SIRAN), previously colonized in a semicontinuous anaerobic thermophilic fixed-bed reactor. The initial attached biomass concentration ($\mathrm{VS_{att}}$) was 0.063 kg $\mathrm{VS_{att}}$/kg SIRAN, equivalent to 29.80 kg $\mathrm{VS_{att}/m^3}$ SIRAN (on the basis of an apparent density of 470.9 kg SIRAN/$\mathrm{m^3}$ SIRAN). The HRT bed was defined in terms of the fixed bed volume occupied by bioparticles (300 mL).

Heated water was maintained at 55 ± 1 °C and was pumped from a recirculation water bath through the constant temperature jacket surrounding the reactor. The biogas generated was collected in a gas-meter.

Continuous feed was supplied by a peristaltic pump connected to programmable timer. Effluent recirculation (in the range 8–12 L/h) was used to mix and homogenise the liquid in the system. Under all conditions tested, the liquid phase in the reactor was completely mixed (tracer studies corroborate this affirmation).

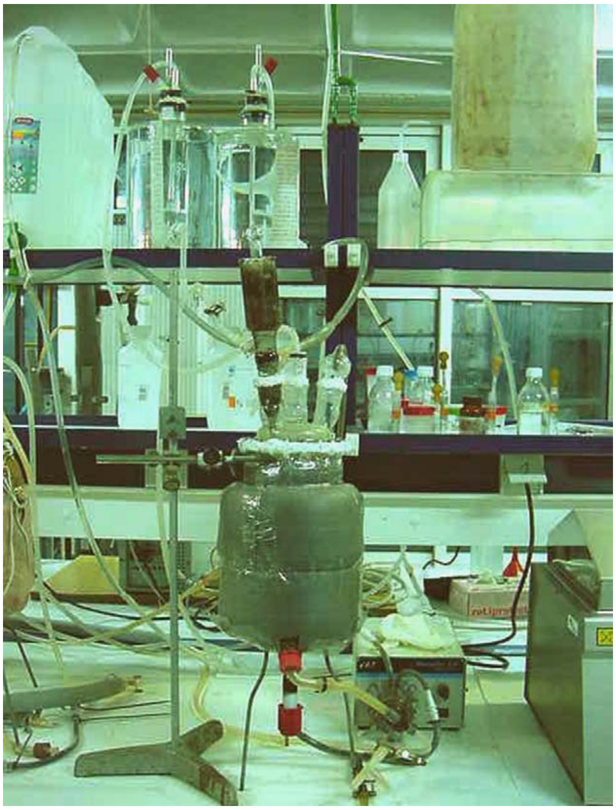

Fig. 1. Schematic upflow anaerobic fixed-film reactor (UAFF) used.

The feed was pumped directly from the refrigerator into the recycle lines. The reactor effluent passed through a sealed contact chamber connected to an inverted siphon in order to separate the gas formed in the effluent.

2.2. *Support media*

Open-pore sintered glass beads (SIRAN) were used as the medium for cell immobilization and retention. An essential advantage of sintered glass is the double-pore structure of the surface. The particles were sieved for uniformity and the resulting particles had an apparent diameter of approximately 1.5–2 mm. This material was chosen because of its uniformity and because it could be incinerated to measure dry organic matter concentrations. The main characteristics of SIRAN carriers are as follows: medium real density, 1832 g/L; bulk density, 570 g/L; pore volume, 50–60%; pore diameter, 60–300 μm, and high specific surface, 87,000 m^2/m^3, all of which make it suitable for use as a support medium in anaerobic fixed-film reactors [34].

SIRAN used in UAFF was previously colonized in a semi-continuous anaerobic fixed-bed reactor treating wine-vinasses at thermophilic conditions (55 °C). The open pore structure of the carrier offers high surface areas to be colonised by active biomass and the entire carrier can be populated. This characteristic favours a high biomass colonisation capacity in short periods of time: 20 kg VSS/m^3 SIRAN in a period of 70 days, operating at 2.0 kg COD/m^3 day with >95% COD reduction.

2.3. *Feed solutions*

Two different feeds were used in this experimental work: wine distillery wastewater and cutting oil wastewater.

2.4. *Wine distillery wastewater*

Wine distillery wastewater (vinasses) used in this study comes from an ethanol producing wine-distillery plant located in Tomelloso (Ciudad Real, Spain). In general, the vinasses showed an appropriate relationship between the different macro and micro-nutrients with a favourable COD/N/P ratio suitable for microbiological treatment. The vinasses had an acidic pH (approximately 3.7). A complete study of the characteristics and properties of this feed are shown in Table 1 [35].

Wine vinasses were transported and maintained at 4 °C prior to use. These feeds were diluted with tap water in order to attain the required feed chemical oxygen demand (COD) concentration to be used in this experiment (around 10 kg COD/m^3) and were supplemented with sodium hydroxide to maintain a neutral pH.

The main characteristics of the wine vinasses used in this experimental work are presented in Table 2.

Table 1
Main characteristics of the wine vinasses

Parameter	Main value
VSS (mg/L)	140–120
PO_4^{3-} (mg P_2O_5/L)	150–130
NH_4^+ (mg N/L)	16–17
Total Nitrogen (mg/L)	280–226
Total acidity (mg/L)	4000–3600
Sugars (mg glucose/L)	3300–3100
Polyphenols (mg galic acid/L)	500
K (mg/L)	2250–1700
Na (mg/L)	54–75
Cu (mg/L)	14–4
pH	3.4–4.0
COD (g O_2/L)	21.1–20.4
BOD_5 (g O_2/L)	14.6

2.5. *Cutting oil wastewater*

Cutting oil wastewater (COW) were supplied by Delphi Automotive Systems, S.A., which is located in Puerto Real (Cadiz) and is dedicated to the machining of metallic pieces for the automotive sector. In this installation, different types of oily waste are generated and the natures of these depend mainly on the working system used and the type of machine used in each process. The factory also has a conventional depurative treatment plant (physic-chemical one) for the effluent waste generated during the manufacturing process.

The feed used in this study was cutting oil wastewater arising from different production streams in the factory and prior to study it was not treated using the conventional treatment process. The main characteristics of the cutting oil wastewaters are shown in Table 3.

2.6. *Experimental procedure*

The experimental protocol was designed to examine the effect of a recalciltrant co-substrate (cutting oil wastewater) on the efficiency of the anaerobic filter reactors (UAFF) with SIRAN as the support medium in the thermophilic anaerobic treatment of wine vinasses.

Approximately 300 mL of coated medium was removed from a fixed-film thermophilic anaerobic reactor operated on the distillery wastewater used in this work. This substance was subsequently used as the seeding material for UAFF reactor start-up. The coated SIRAN contained 29.80 kg VS_{att}/m^3 SIRAN.

The reactor loaded with coated SIRAN was initially filled with 2 L of inoculum (the effluent produced in the aforementioned fixed-film thermophilic anaerobic reactor) and 1 L of fresh vinasses. An initial COD of 5 kg/m^3 was obtained. The

Table 2
Main characteristics of wine vinasses used

Feed	pH	COD (kgO_2/m^3)	TOC (ppm C)	TSS (kg/m^3)	VSS (kg/m^3)	Organic fraction (%SS)	Total acidity (g AcH/m^3)
Vinasse 1	7.3	10213.5	3640.0	0.817	0.757	92.7	45.26
Vinasse 2	7.6	9779.9	5162.5	0.303	0.280	92.3	77.52

Table 3
Main characteristics of the metal–working fluid used

Feed	pH	COD (kgO_2/m^3)	TOC (ppm C)	TSS (kg/m^3)	VSS (kg/m^3)	Organic fraction (%SS)	Total acidity ($g AcH/m^3$)
Cutting oil wastewater	7.1	2500.0	108.6	0.547	0.317	57.93	2.38

Table 4
Performance parameters of each operation stage

Stage	HRT[a]	Q	Q_v	Q_{COW}	COD	COD_v	COD_{COW}	OM	$\%OM_v$	$\%OM_{COW}$	OLR
S1a	0.80	375	375	0	9.8	9.8	0	5.6	100.0	0	12.2
S1b	0.80	375	375	0	17.9	17.9	0	5.6	100.0	0	22.3
S2	0.20	1500	200	1300	3.5	15	1.7	5.2	57.6	42.4	17.5
S3	0.21	1400	100	1300	3.2	15	2.3	4.5	33.4	66.6	14. 9
S4	0.15	2000	0	2000	2.5	0	2.5	5.0	0	100	16.7

HRT, as days; Q, Q_v, Q_{COW}, volumetric rate fed of mixed feeding, vinasses and cutting oil, respectively, as mL/day; COD, COD_v, COD_{COW}, chemical oxygen demand of mixed feed, vinasses and cutting oil, respectively, as kg O_2/m^3; OM, organic matter added, as g COD/day; %OM, percentage of organic matter of each substrate; OLR, organic loading rate fed, as kg/m^3 day.

[a] Referred to an active volume of 300 mL.

reactor was maintained until optimal microbial activity was detected (after 30 days, >90%COD removal was obtained with 0.29 m^3 CH_4/kg COD).

After this time, the amount of cutting oil wastewater added to the reactor was increased until the system was fed only with cutting oil wastewater. Four stages were considered in the study. HRT was modified in order to maintain an approximately constant organic loading rate applied to the system in the range 15–22 kg COD/m^3 day. The main operative parameters of each stage are presented in Table 4. The empty HRT was defined in terms of the bed volume occupied by bioparticles (300 mL).

Stage 1 was divided in two periods: S1a is an adaptation period in that vinasses with 9.8 kg COD/m^3 were fed with an organic loading rate of 12.2 kg/m^3 day and HRT of 0.8 days. This is an adaptation period for microorganims to substrate. After this adaptation process came the period denoted as S1b. At this point the reactor was fed with vinasses at a strength of 375 mL/day to give an organic loading rate of 22.3 kg COD/m^3 day, maintaining a HRT of 0.8 days.

Increasing amounts of COW were subsequently fed in and the OLR was maintained in the range 14.9–17.5 kg COD/m^3 day in stages S2, S3 and S4. The COD of the mixed feed decreased from 797.5 mg C/L to 108.5 mg C/L. In all stages the system was operated under total recycle conditions.

The hydraulic retention time was decreased and was kept constant during each stage until the steady-state conditions were reached. The attainment of the steady state was verified after an initial period (three times the HRT) by checking whether the constant effluent characteristic values (COD removal and methane generation) were the mean of the last measurements in each stage [22].

2.7. Sampling and analysis

Parameters measured in influent and effluent were as follows: soluble chemical oxygen demand (COD), total organic carbon (TOC), total suspended solids (TSS), volatile suspended solids (VSS), pH, alkalinity and total acidity. Gas production and gas composition (methane and dioxide carbon percentages) were periodically monitored.

Feed and effluent samples were taken in order to analyse filtered COD, TOC and both total suspended and volatile suspended solids in effluents (TSS, VSS). Such analyses were carried out on a daily basis. All analytical determinations were performed according to “Standard Methods” [36].

Gas produced was collected in a gas-meter filled with acidified saturated salt solution. A gas sampling valve was installed at the top of the collector to allow direct gas sampling with a syringe. The volume of gas produced in the reactor was directly measured in terms of the volume of salt solution displaced from the gas collector. Gas composition (methane and carbon dioxide) was assessed by gas chromatography with a stainless steel column packed with Carbosieve SII (diameter of 1/8 in. and 2 m length) and a thermal conductivity detector (TCD). The injected sample volume was 1 mL and operational conditions were as follows: 7 min at 55 °C; ramped at 27 °C/min to 150 °C; detector temperature: 255 °C; injector temperature: 100 °C. The carrier gas was helium and the flow rate used was 30 mL/min. A standard gas (from Carburos Metálicos, S.A.; composition: 4.65% H_2; 5.33% N_2; 69.92% CH_4 and 20.10% CO_2) was used for the calibration of the system.

Initially, the attached biomass concentration (VS_{att}) was determined determined by removing a representative sample from the reactor and then ashing the dried sample to measure the total volatile solids both attached to the particles and trapped between them. The determination was performed in accordance with the protocol described by Shieh [37].

3. Results and discussions

During the experimental procedures, HRT was decreased from 0.8 to 0.15 days. The volumetric COD loading was maintained in the range 22.3–14.9 kg COD/m^3 day. Performance and operational parameters during the evolution of the biodegradation experiments (all the results shown are the average values of the last three data) are shown in Table 5.

Table 5
Main parameters of the stable process

Stage	OLR	pH	%COD	%TOC	TSS	VSS	Biogas	CH_4	Y_{CH_4}
S1a	12.2	7.70	88.6	92.1	0.64	0.52	0.462	0.439	0.340
S1b	22.3	7.56	87.0	94.6	1.43	1.08	0.555	0.450	0.290
S2	17.5	7.47	86.1	82.1	0.59	0.39	0.121	0.050	0.034
S3	14.9	7.53	88.6	69.0	0.94	0.69	0.006	0.004	0.003
S4	16.7	7.80	85.8	58.1	0.99	0.46	0.002	0.002	0.001

Organic loading rate applied, OLR, as kg COD/m^3 day; organic removal efficiency as percentages of COD_r and TOC_r removal; total and volatile suspension solids, TSS and VSS, as kg/m^3; methane and biogas production rate, as m^3/m^3 digester day; methane yield, Y_{CH_4}, as m^3 CH_4/kg COD_r.

The start-up phase (S1a) was satisfactory: the efficiency of COD removal increased until it reached 88.6% COD_r after 13 days. At this moment, the pH was maintained at about 7.70 and the biogas production was 0.462 m^3/m^3 day (with a yield of methane, Y_{CH_4}, near to 0.34 m^3/kg COD_r). Later, an increase in applied OLR caused an increase in organic matter removal, which reached values of 93–94% COD_r and 95% TOC_r. The volumetric biogas production rate also increased markedly in this period.

The organic removal rate (ORR) as influenced by organic load rate applied, OLR, is shown in Fig. 2. The maximum organic load rate fed into the system was 22.3 kg COD/m^3 day for the anaerobic fixed-film reactor treating vinasses. The ORR removal was found to be 20.7 kg COD/m^3 day. Hence, the efficiency of COD removal was 87.0% COD after 38 days (S1b stage). When the system operated with only COW as substrate, the OLR and ORR were 16.7 kg COD_0/m^3 day and 14.29 kg COD_r/m^3 day, respectively. Under these conditions the organic removal efficiency was 85.8% COD_r.

The temporal evolution of COD and TOC removal are represented in Fig. 3. Initially, during the start-up period, COD removal is very high when vinasses are added to the reactor at OLR of 12.2 and 22.3 kg COD/m^3 day. In the later stage, the percentage of COD removal is maintained approximately constant in the range 85.8–88.6% COD_r. Hence, the removal efficiency of COD is very high during all the stages, with values greater than 86% regardless of the nature of the feed and the applied load (Fig. 3a).

The TOC removals are shown in Fig. 3b. Initially, the removal efficiency (TOC_r soluble removal) was quite high (greater than 94%) in the stage operating with vinassses, which is higher than the COD removal percentage.

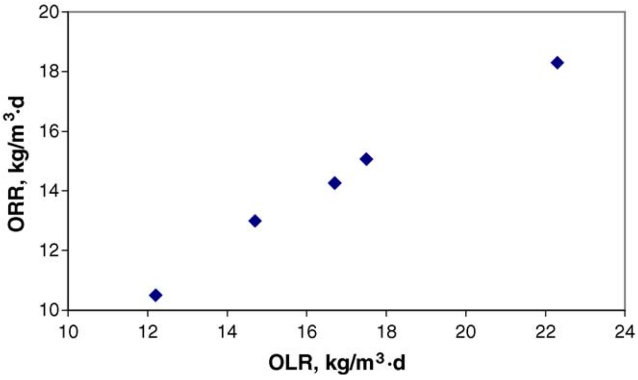

Fig. 2. Organic removal rate (ORR) as influenced by organic loading rate (OLR).

The addition of COW causes a significant decrease in the removal efficiency from 94.6 to 58.1 at HRTs of 0.8 and 0.15, respectively, while the percentage of COD removal is maintained approximately constant in the range 85.8–88.6%. Clearly, the efficiency of substrate removal (expressed as TOC) is a function of the HRT and is concomitant with the organic loading rate, which in turn is dependent on the nature of the feed added.

As can be observed, the TOC removal percentages are lower than the COD removals. This is due to the fact that the COD analysis includes the determination of several compounds as metallic cations, inorganic compounds, etc., that are chemically oxidisable but are not included in the TOC determinations. Initially, the vinasses are easily biodegraded but the COW contains recalcitrant compounds (HC or FA with long chains). Some of these compounds can be absorbed in biofilms.

For the reasons outlined above, the anaerobic thermophilic reactor provides good chemical oxygen demand (COD) reduction at high OLR in the treatment of COW (period S4). In any case, a fixed-film reactor can eliminate COW and maintain a high treatment capacity. Several authors have reported that the biological treatment of COW in an anaerobic fixed-film reactor was higher than 90% during the whole process when the applied OLR was increased from 1.5 to 10 kg COD/m^3 day [7,8]. The authors also reported that the adaptation period is shorter in a fixed-film system than in a suspended one (4 days as opposed to 30 days) due the significant advantages of immobilized technologies.

The temporal evolutions of TSS and VSS in effluents of the reactor are shown in Fig. 4. Total suspended solids were maintained in the range 0.59–0.99 kg TSS/m^3 throughout the

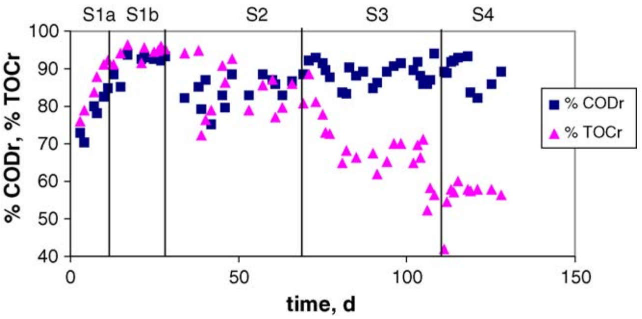

Fig. 3. Temporal evolution of COD removal (%COD_r) and TOC removal (%TOC_r).

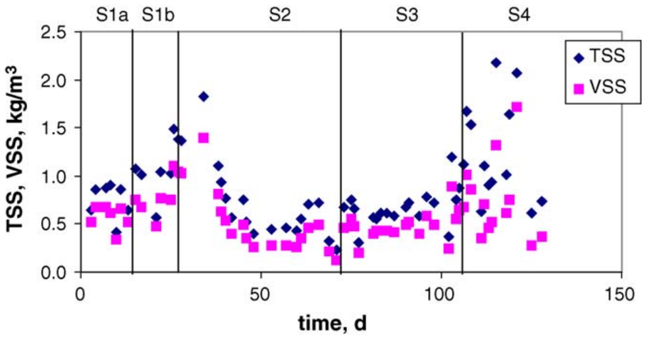

Fig. 4. Evolution of TSS and VSS (g/L) with time.

process. At the beginning of the assay (S1a stage) values of 0.64 kg TSS/m^3 and 0.52 kg VSS/m^3 were determined whereas at the end of period S1b, the average values found were 1.43 kg TSS/m^3 and 1.08 kg VSS/m^3. These values are higher than those in all of the other stages. In the last period, an increase in TSS is observed.

During the start-up stage (S1) a noticeable suspended organic solids is registered in the effluent and this reaches 75.7% OF, which is a typical value in anaerobic fixed-film reactors treating wine vinasses [19]. The organic nature of SS in effluent decreased when increasing the COW amount in the feed. The stabilized value of SS at the end of the process was 47.0%.

The temporal evolution of pH, total acidity and alkalinity are shown in Fig. 5. As can be seen, the pH is maintained in the range 7.5–7.8, which is an optimum value in the thermophilic range.

At the beginning of the biodegradation process, the total acidity is higher (100 ppm) due to the instability of the start-up period. After 10 days of operation, however, the total acidity had decreased to reach 10–30 mg C/L. The organic nature of the feed and the higher value of the volatile fatty acids in the vinasses (stage S1) implicate the higher values of acidity. In addition, each change in the operating conditions led to an increase in the total acidity. However, the VFA concentrations in effluents are low during the whole process.

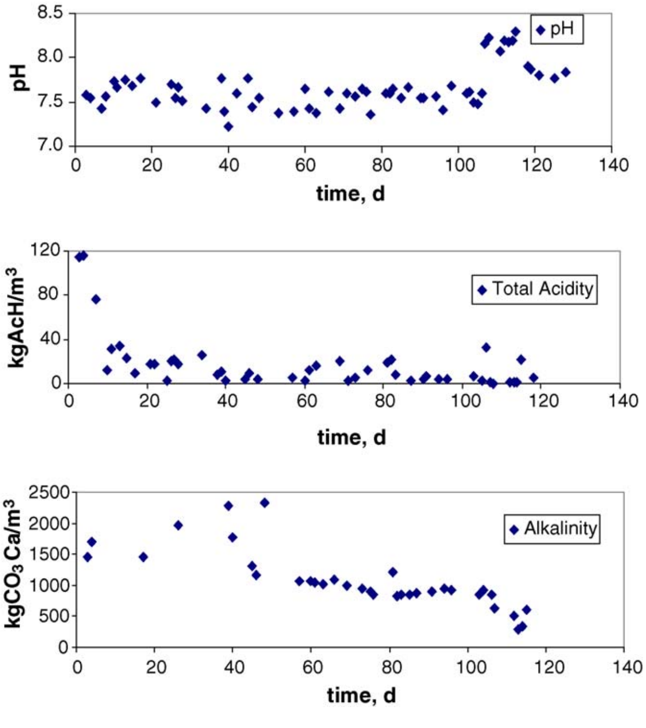

Fig. 5. Temporal evolution of: (a) pH and (b) total acidity (kg AcH/m^3) and alkalinity (kg CO$_3$Ca/m^3).

The alkalinity of the medium decreased on decreasing the vinasses/COW ratio in the feed. The acidity/alkalinity ratio was maintained near to 0.1, which indicates that the system has a high buffer capacity.

The volumetric methane generation rate is presented in Fig. 6 for each individual stage. The methane yield is also presented in this figure. As can be observed, the volumetric methane generation rate decreased on increasing the amount of COW in the feed. The methane yield (as m^3 CH$_4$/kg COD$_r$) also decreased continuously due the low volumetric methane generation and the high organic matter removal during the last period.

During the start-up period, the volumetric methane value is approximately 0.5 m^3/m^3 day, with a methane yield of 0.27 m^3 CH$_4$/kg COD$_r$. This value is near to the theoretical stoichiometric value of 0.35 m^3 CH$_4$/kg COD$_r$ and is consistent with those reported by several authors operating with wine vinasses in similar reactors [19]. The change of feed in period S2 causes a significant decrease in the yield. Thus, after one day operating under the new conditions, a sudden reduction in the yield is observed (from 0.24 to 0.10 m^3 CH$_4$/kg COD$_r$) and this value steadily decreases to a final value in this period of 0.034 m^3 CH$_4$/kg COD$_r$, with a volumetric rate of 0.05 m^3/m^3 day. In this stage (S2) nitrogen is detected in the biogas in considerable amounts.

In the third period, in which the contribution of the organic vinasses is reduced to 33.4%, the volumetric biogas rate decreased to give a value of 0.006 m^3/m^3 day and the methane yield was reduced to 0.003 m^3 CH$_4$/kg COD$_r$.

The use of 100% COW gave rise to a very small volumetric biogas production rate (0.002 m^3/m^3 day) and the methane yield was reduced to 0.001 m^3 CH$_4$/kg COD$_r$. These observations corroborated the results obtained in an anaerobic thermophilic fluidized bed reactor treating COW under different OLR conditions [22]. In any case, laboratory results confirm that both anaerobic fluidized bed and anaerobic fixed-film technologies provide good chemical oxygen demand (COD) reduction when operated at low HRT and high organic loading rates. However, negligible amounts of biogas are produced. In the fluidized-bed reactor, the greatest efficiency in terms of substrate removal was found to be 95% for an OLR of 13 kg COD/m^3 day and a hydraulic retention time of 5 h.

The methane yields obtained were significantly lower than the stochiometric theoretical value of 0.35 m^3 CH$_4$/kg COD$_r$. Thus, the synthesis of new microorganisms and the initial biomass attachment processes on the support surface involved the initial production of polysaccharides to bind the material. This phase involves a high consumption of organic material through the synthesis route (anabolism), thereby diminishing the quantity of substrate that it transforms into methane. For this reason,

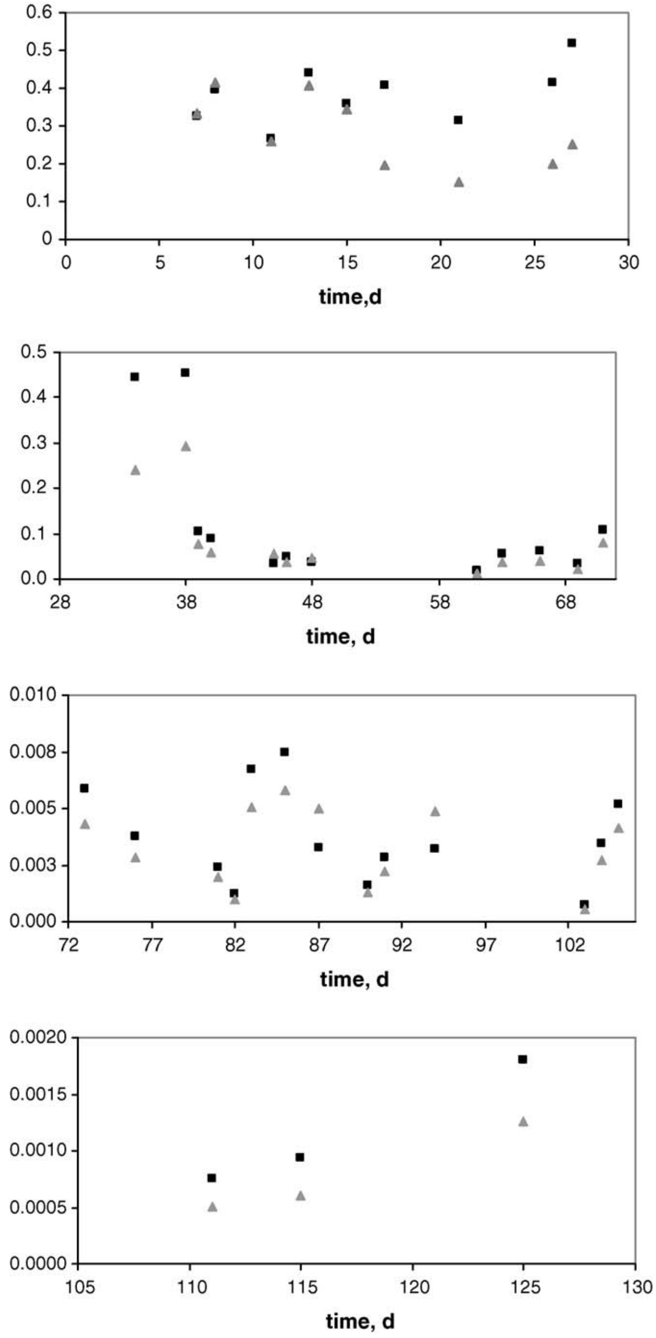

Fig. 6. Temporal evolution of volumetric methane generation rate (■) as m^3/m^3 day and methane yield (▲) as m^3 CH_4/kg COD_r: (a) stage S1, (b) stage S2, (c) stage S3 and (d) stage S4.

the theoretical value of 0.35 m^3 CH_4/kg COD_r is higher than the calculated experimental values.

Previous investigations by the authors indicate that the nature of the feed influences the activity of the methanogenic microorganisms and, therefore, the generation of biogas. The literature in this field contains several reports that recalcitrant wastewater can be anaerobically digested and generate small amounts of biogas [28]. This was not observed in this study: there was an absence of signs of biological activity, as can be observed by methane production and VFA generation.

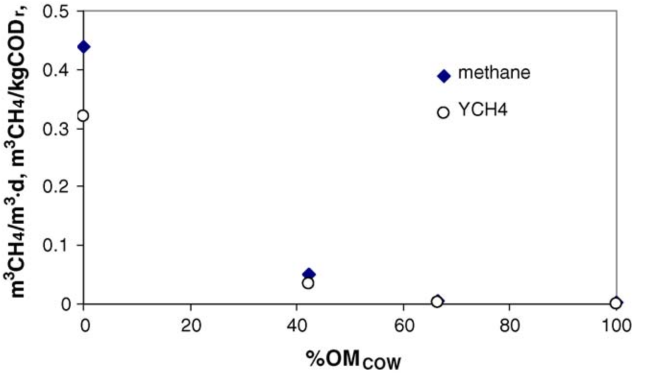

Fig. 7. Relationship between volumetric biogas and methane generation rate (m^3/m^3 day) and on the yield coefficient (m^3 CH_4/g COD_r) with the percentage of organic matter added by the oily wastewater in the feeding (%OM_{COW}).

Several researches indicate that the volume of biogas can be improved by the addition of a co-substrate [22,31] and also by maintaining sufficient time for the adaptation of the biomass [32]. In this study, wine vinasses degradation created conditions for non-biological removal of COW constituents.

The effect of the percentage of organic matter coming from the COW on the volumetric methane generation rate and methane yield is presented in Fig. 7.

As can be observed, the volumetric methane generation rate decreases sharply with the percentage of COW and this is an exponential relationship. Therefore, the percentage of OM_{COW} has a remarkable effect on the gas production rate and composition as well as on the methane yield.

4. Conclusions

An upflow anaerobic fixed-film reactor (UAFF) was tested as a way to treat increasing amounts of cutting oil wastewaters (COW) in the initial feed composed by wine vinasses.

Experimentally, it was confirmed that anaerobic fixed-film system can achieve >87% COD reduction and 94.6%TOC removal at loading of 22.3 kg COD/m^3 day treating wine vinasses at steady-state conditions. Methane yield reached 0.29 m^3 CH_4/kg COD_r.

Biological activity, as indicated by methane production, decreased dramatically as soon as COW was added, although considerable COD removal continued throughout the testing. TOC removal also was observed with COW but in decreasing amounts.

COW was toxic and actually reduced biodegradation of the vinasse. It was confirmed experimentally that UAFF technology can achieve >85.8% COD reduction and 58.1% TOC at a COD loading of 16.7 kg COD/m^3 day and HRT of 0.15 days in the treatment of COW under thermophilic conditions. In these conditions, there is an absence of signs of biological activity, as can be observed by methane production and VFA generation.

Hence, COW can be removed, if not degraded, by anaerobic treatment in the presence of a biodegradable co-substrate. Wine vinasses degradation creates conditions for non-biological removal of COW constituents. More studies are necessary in order to test the mechanisms of organic removal when biodegradation apparently had ceased. Also, toxicity assays of COW are necessary to evaluate the toxicity to the methanogenic community.

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