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Thermophilic anaerobic co-digestion of olive mill wastewater with olive mill solid wastes in a tubular digester

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Abstract

This study investigates for the first time the thermophilic (55 °C) anaerobic co-digestion of olive mill wastewater (OMW) with olive mill solid wastes (OMSW) in laboratory scale semi-continuous tubular digesters. Each digester was fed with an influent composed of OMW and OMSW over a range of hydraulic retention times (HRTs) of 12, 24 and 36 days and at organic loading rates (OLRs) between 1.19 and 10.84 g COD/(l day). The TCOD concentration of OMW were 43, 67 and 130 g COD/l and the amount of the dry OMSW co-digested with OMW was 56 g TS/l. The results indicated that the best methane productivity and SCOD removal efficiency of 46 l/((l OMW) day) and 69%, respectively, were achieved at an OLR of 3.62 g COD/(l day) corresponding to an OMW of 130 g COD/l digested at an HRT of 36 days. Furthermore, the best net energy production from digesters operated at thermophilic temperature was 427 kJ/day higher than from those operated at mesophilic temperature for the same conditions of feed concentration and HRT. In contrast, an HRT of 12 days caused a sharp increase of both total volatile fatty acids (TVFA) and chemical oxygen demand (COD) contents in the effluents and a cessation in methane production for the three influents substrate concentrations studied.

Keywords: Olive mill wastewater; Olive mill solid wastes; Tubular digester; Anaerobic co-digestion; Biogas; Thermophilic temperature

1. Introduction

The disposal of olive mill wastewater (OMW) is a serious environmental problem in the olive oil producing areas and many processes have been proposed to treat OMW over the last 20 years such as concentration by evaporation, chemical and electrochemical treatments, aerobic biological treatments and anaerobic digestion process [1]. In general, anaerobic digestion process is a widely applied process for treating organic wastes because it combines production of energy, in the form of biogas and decreasing of pollution with high efficiency. This process can be carried out at two different temperature ranges, namely mesophilic (35–40 °C) and thermophilic (55–60 °C). Thermophilic digestion has become in recent decade an important alternative to mesophilic digestion because it offers several potential advantages compared to mesophilic temperature. First, hydrolysis and biochemical reactions are faster than those at low temperatures [2]. Second, the maximum specific growth rates of microorganisms increase with temperature [3,4]. Third, the destruction of pathogens organisms and weed seeds are more efficient at higher temperature [5]. Moreover, specific biogas production rates are higher under thermophilic conditions than under mesophilic conditions which may lead to an improvement in the energy balance [6]. Applying anaerobic digestion either at mesophilic or thermophilic temperature to treat OMW without previous treatment was failed [7,8]. The main reason is that OMW is an acid influent possesses low alkalinity and contains low amount of ammonium nitrogen and high levels of phenol and TCOD concentration (pH 5.4 ± 0.07, TK-N = 750 ± 24 mg N/l, total phenol = 10.2 ± 0.14 g C_6H_6O/l and TCOD = 105.37 ± 13.8 g/l) [9]. Several proposals have been suggested to overcome the difficulties of treating OMW by anaerobic digestion such as high dilution of OMW (1:10) and addition of ammonium chloride or urea [10–12], aerobic biological pre-treatments [9,13] and co-digestion with substrates rich in ammonium nitrogen [14].

The co-digestion of OMW with others organic wastes containing high level of ammonium nitrogen to compensate the lack in OMW has becoming the most interesting because it does not require any addition of chemical substances which are not

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Nomenclature

OMW	olive mill wastewater
OMSW	olive mill solid wastes
TS	total solid (g/l)
VS	volatile solids (g/l)
TSS	total suspended solids (g/l)
VSS	volatile suspended solids (g/l)
TVFA	total volatile fatty acids (g/l)
TCOD	total chemical oxygen demand (g COD/l)
SCOD	soluble chemical oxygen demand (g COD/l)
$TPO_4{}^-$-P	total mineral ortho-phosphorus (g/l) or (g/kg TS)
TK-N	total Kjeldhal nitrogen (g/l) or (g/kg TS)
$TNH_4{}^+$-N	total ammonium nitrogen (mg/l) or (mg/kg TS)
NH_3-N	free ammonia nitrogen (ppm)
H_2S	dihydrogen sulphur (ppm)
CH_4	methane (%)
CO_2	carbon dioxide (%)
HRT	hydraulic retention time (days)
OLR	organic loading rate (g COD/(l day))
CST	continuous stirred tank
USAB	up flow anaerobic sludge blanket

economically and environmentally desirable [14–17]. Also, the co-digestion process has no negative effects on the potential of biogas production rate from OMW compared to the others pre-treatment [18]. Fewer researchers have investigated the anaerobic co-digestion of OMW with other substrates either at mesophilic or thermophilic temperature. At mesophilic temperature we have investigated in our previous work the anaerobic co-digestion of OMW with olive mill solid wastes (OMSW: TK-N = 12 ± 5 g N/l) in semi-continuous tubular digester [18]. The results indicated that OMSW–OMW co-digestion was successful with a TCOD reduction up to 90% compared to 70% from the separate treatment of diluted OMW [11,12]. On the other hand, at thermophilic temperature only Angelidaki et al. [16] were the first who have studied the anaerobic co-digestion of OMW with other substrates (manure and sewage sludge) in both continuous stirred tank and batch reactors and showed that OMW could be treated successfully without high dilution if it was co-digested with manure or swage sludge. For the co-digestion of OMW with manure (50:50 and 75:25 OMW:manure) the TCOD removal efficiency was 75% compared to 55% for the sewage sludge–OMW co-digestions (50:50 and 75:25 OMW:sewage sludge). The best performance observed for manure–OMW co-digestions were due to the fact that manure contains high content of ammonium nitrogen and possesses high buffering capacity ($TNH_4{}^+$-N = 2.5 g N/l and alkalinity = 14.5 g $CaCO_3$/l). Whereas sewage sludge contains low level of ammonium nitrogen ($TNH_4{}^+$-N = 470 mg N/l and TK-N = 1.2 g N/l) and OMW should be diluted with water (1:5) to be co-digested with sewage sludge [15].

Continuing the research of the anaerobic co-digestion of OMW with others substrates rich in nitrogen amounts and taking into account the potentials advantages of thermophilic temperature the objective this work was to study for the first time the feasibility of the anaerobic co-digestion of OMW with OMSW at thermophilic conditions in a semi-continuous tubular digester. This report discusses a laboratory scale investigation with emphasis placed on the evaluation of optimal values of biogas production, methane percentage, TCOD removal efficiency and the qualities of effluents under different HRT and influent substrate concentrations at thermophilic temperature.

2. Materials and methods

2.1. Equipments

Five tubular digesters of 18 l useful volume were used. Each digester consisted of two coaxial cylinders. The Plexiglas outside cylinder had an internal diameter of 30 cm, a thickness of 0.5 cm and a length of 70 cm. The glass internal cylinder had an internal diameter of 20 cm, a thickness of 1 cm, a length of 70 cm and a volume of 22 l. The latter was equipped with three ports, two of them for daily manual feeding and effluent discharge and the other port for collecting gas into a plastic bag. These digesters were warmed with a water heating system equipped with thermostat and pump. Agitation (seven times per hour) was performed using a motor agitator equipped with a time switch. Fig. 1 shows in detail the tubular digester used in this study.

2.2. Substrates composition

2.2.1. Olive mill wastes

OMSW and OMW used in this study were collected from Ben Yeder three-phase olive mill located in El-Mornaguia at Tunis capital. The chemical composition of these wastes, in main values, at the beginning of experiments are summarised in Tables 1 and 2.

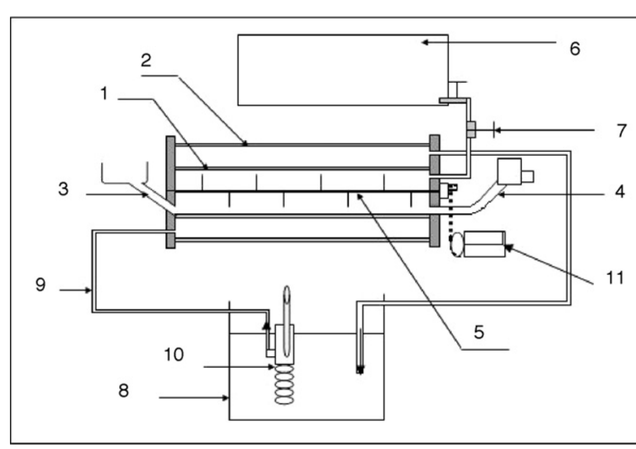

Fig. 1. Semi-continuous feeding tubular digester: (1) inside cylinder of 20 cm diameter; (2) outside cylinder of 30 cm diameter; (3) inlet port; (4) outlet port; (5) agitator; (6) plastic bag; (7) plastic tap; (8) metal container filled with water; (9) plastic pipe; (10) water heater with thermostat and pump; (11) agitator motor.

Table 1
Average chemical composition of OMW used as main substrate

Parameter	Units	OMW[a]
pH	–	4.90 ± 0.1
Density	kg/l	1.1 ± 0.1
TS	g/l	80 ± 0.5
VS	g/l	55 ± 1.5
TSS	g/l	36 ± 0.5
VSS	g/l	24 ± 0.5
TCOD	g/l	130 ± 3.5
SCOD	g/l	80 ± 2.5
TOC	g/l	65 ± 1.5
TNH_4^+-N	mg N/l	750 ± 55
TK-N	g N/l	1.65 ± 0.05
TPO_4^--P	mg/l	980 ± 20
Total phenols	g C_6H_6O/l	13 ± 0.7
TVFA	g/l	9.65 ± 0.3
Alkalinity	g $CaCO_3$/l	3.8 ± 0.3
Potassium	g/l	3.75 ± 0.5
Calcium	mg/l	950 ± 50
Sodium	mg/l	450 ± 20
Magnesium	mg/l	575 ± 40

[a] Each value is an average of three replicates. "±" shows standards errors among replicates.

2.2.2. Inoculum

The digesters were inoculated with a sludge collected from an aerobic wastewater treatment plant located in Beja (northern Tunisia). The composition of the sludge, in average values, is given in Table 3.

2.3. Experimental procedure

The thermophilic anaerobic co-digestion experiments of OMW with OMSW were carried out in four runs using three different influents concentration composed of OMW (43, 67 and 130 g COD/l) and OMSW. The amount of the dry OMSW was 56 g TS/l of OMW. Alkalinity in the form of $Ca(OH)_2$ was added to all influents (5–25 g/l of OMW) to ensure a neutral medium (pH 7.0–8.0) for the methanogenic bacteria growth. At the beginning, all the digesters were inoculated with 18 l of sludge and set in batch mode with gradual increase of temperature from 37 to 55 °C (2 °C/day) [6] during 15 days until the start-up of biogas production from the sludge. Then, in the first run the digesters were fed with an influent substrate concentration of 130 g COD/l at flow rates of 0.5, 0.75 and 1.5 l/day which corresponded to 36, 24 and 12 days of HRT, respectively. In the second run the digesters were fed with an influent substrate concentration of 67 g COD/l at flow rates of 0.5, 0.75 and 1.5 l/day which corresponded to 36, 24 and 12 days of HRT, respectively. In the third run the digesters were fed with an influent substrate concentration of 43 g COD/l at flow rates of 0.5, 0.75 and 1.5 l/day which corresponded to 36, 24 and 12 days of HRT, respectively. In the fourth run two digesters were fed with only OMW (TCOD = 67 g COD/l) at flow rates of 0.75 which corresponded to an HRT of 24 days. Each run had a duration of two to three times the corresponding HRT. The volume of biogas and its composition were determined daily and samples were collected from effluents and analysed for at least five times per week.

Table 4 summarises, in detail, the operation conditions and the feed composition used in these runs.

Table 2
Average chemical composition of OMSW used as co-substrate

Parameter	Units	Average value	Standard deviation
Water	%	3	2
TS	%	97	2
VS	g/kg TS	970	0.5
TCOD	g/kg TS	1180	2
TOC	g/kg TS	560	5
TNH_4^+-N	g N/kg TS	1.1	0.3
TK-N	g N/kg TS	20	1.5
TPO_4^--P	g/kg TS	1.57	0.05
Potassium	g/kg TS	12.74	0.5
Calcium	g/kg TS	10.2	0.5
Sodium	g/kg TS	1.32	0.5
Magnesium	g/kg TS	2.7	0.5

Table 3
Average chemical composition of the sludge

Parameter	Units	Average value	Standard deviation
pH	–	7.5	0.2
TS	g/l	36	1.2
VS	g/l	24	0.8
TSS	g/l	26	1.2
VSS	g/l	19	0.7
TCOD	g/l	37.5	0.5
SCOD	mg/l	40	5
TNH_4^+-N	g N/l	1.3	0.2
TK-N	g N/l	2.2	0.1
TPO_4^--P	mg/l	1050	5
Alkalinity	g $CaCO_3$/l	3.2	0.35

2.4. Chemical analyses

The followings parameters were determined: pH, total and soluble COD, TS, VS, TSS, VSS, TOC, TKN, ammonium nitrogen, phosphorus, calcium, potassium, TVFA, alkalinity and total phenolic compounds (reported as phenylic acid equivalent). All analyses were carried out according to the recommendations of the standard methods of APHA [19]. The volume of biogas was measured using a gas-meter. The methane percentage was measured using a chemical method that consist in dissolving the CO_2 gas of 100 ml biogas into NaOH solution (270 g/l). Whereas H_2S and NH_3 percentages were measured using Dräger tubes (Dräger, Germany).

2.5. Statistical analyses

The statistical analyses of the data and the results in this study (analysis of average values, variance and standards deviation) were performed using Excel 2003.

Table 4
Influents composition used under different OLR in a semi-continuous feeding tubular digester

Run	Influent TCOD (g COD/l)	HRT (day)	OLR (g COD/(l day))	Operational time (day)	Flow rate (l/day)	Influent pH	Influent composition	
1	130	36	3.62	70	0.5	7.5 ± 0.1	OMW (ml)	500 ± 0.1
							Water (ml)	0.0
							OMSW (g)	28 ± 0.1
		24	5.42	70	0.75	7.5 ± 0.1	OMW (ml)	750 ± 0.1
							Water (ml)	0.0
							OMSW (g)	56 ± 0.1
		12	10.834	40	1.5	7.5 ± 0.1	OMW (ml)	1500 ± 0.1
							Water (ml)	0.0
							OMSW (g)	112 ± 0.1
2	67	36	1.862	70	0.5	7.5 ± 0.1	OMW (ml)	375 ± 0.1
							Water (ml)	125 ± 0.1
							OMSW (g)	28 ± 0.1
		24	2.792	70	0.75	7.5 ± 0.1	OMW (ml)	500 ± 0.1
							Water (ml)	250 ± 0.1
							OMSW (g)	56 ± 0.1
		12	5.584	50	1.5	7.5 ± 0.1	OMW (ml)	1000 ± 0.1
							Water (ml)	500 ± 0.1
							OMSW (g)	112 ± 0.1
3	43	36	1.194	70	0.5	7.5 ± 0.1	OMW (ml)	125 ± 0.1
							Water (ml)	375 ± 0.1
							OMSW (g)	28 ± 0.1
		24	1.792	70	0.75	7.5 ± 0.1	OMW (ml)	250 ± 0.1
							Water (ml)	500 ± 0.1
							OMSW (g)	56 ± 0.1
		12	3.584	50	1.5	7.5 ± 0.1	OMW (ml)	500 ± 0.1
							Water (ml)	1000 ± 0.1
							OMSW (g)	112 ± 0.1
4	67	24	2.792	60	0.75	7.5 ± 0.1	OMW (ml)	500 ± 0.1
							Water (ml)	250 ± 0.1

Each value is an average of three replicates. "±" shows standards errors among replicates.

3. Results and discussion

3.1. Biogas production

3.1.1. Effect of the HRT on biogas production

The daily biogas production observed at different HRT for the three influents substrate concentrations are illustrated in Fig. 2. As can be seen at an HRT of 12 days and for the three influent substrate concentration studied we observe an intense production of biogas followed by sharp drop of biogas production. Whereas, for the others two influent substrate concentrations studied at an HRT of 24 and 36 days we observe a fluctuated production of biogas followed by a steady state of biogas production. Table 5 summarises the steady state operation result including HRT, biogas productivity, pH and TVFA of effluents.

The best biogas productivity (66 l/((l OMW) day)) with methane content of 70% was obtained at an HRT of 36 days with an influent substrate concentration of 130 g COD/l. We notice also that the pH of effluents remained within the optimal working range (7.2–7.7) and the TVFA level in effluents were below 1500 mg/l for the three influents studied at an HRT of 24 and 36 days. However, for all the influent studied at an HRT of 12 days the pH of effluents dropped below 6.3 and TVFA rose over 6.5 g/l. This accumulation of volatiles fatty acids in effluents at short HRT was due to the fact that acedogenic bacteria may produce volatile fatty acids (VFA) faster than methanogenic bacteria can consume it and the excess of VFA can build up in the digester causing consequently a drop in the effluent pH and an inhibition of the methanogenesis process. Besides, methanogenic bacteria were washed out from the digester, operated at a short HRT, before growing enough to achieve the process of biogas production. Comparing the results of biogas productivity with those obtained at mesophilic temperature for the same conditions of feed concentration and HRT we notice that best methane productivity was increased from 23 l/((l OMW) day) at mesophilic conditions to 46 l/((l OMW) day) at thermophilic conditions [18]. This increase of methane productivity was due to the increase of hydrolysis rate of OMSW that contribute with much more amount of ammonium nitrogen, also to the increase of both methanogenic bacteria growth and biological reactions rates inside the digester operated at thermophilic conditions compared to mesophilic conditions.

3.1.2. Effect of the OMSW on biogas production

Fig. 3 shows biogas productions, effluent ammonium nitrogen and effluent TVFA for an OMW of 67 g COD/l co-digested with OMSW compared to those obtained for the same influent

Table 5
Steady-state results of the anaerobic co-digestion of OMW with OMSW under different experimental conditions

HRT (days)	Influent TCOD (g COD/l)	Effluent pH	Effluent TVFA (g/l)	Effluent total phenol (g C_6H_6O/l)	Biogas productivity (l/((l OMW fed) day)	CH_4 (%)	H_2S (ppm)	NH_3 (ppm)	Phenol removal efficiency (%)
36	130	7.5 ± 0.1	0.5 ± 0.1	3.6 ± 0.2	66.024 ± 0.059	70 ± 0.016	280 ± 30	10 ± 3	72.30 ± 0.2
24		7.5 ± 0.1	1.4 ± 0.1	4.75 ± 0.2	45.336 ± 0.036	68 ± 0.02	320 ± 30	1 ± 0.5	63.46 ± 0.2
12		6.1 ± 0.2	10.4 ± 0.5	11.50 ± 0.2	2.5 ± 0.016	20 ± 0.032	45 ± 20	0	11.5 ± 0.2
36	67	7.7 ± 0.1	0.5 ± 0.5	2.55 ± 0.2	42.01 ± 0.023	76 ± 0.025	250 ± 10	20 ± 5	70.55 ± 0.2
24		7.7 ± 0.1	0.6 ± 0.05	3.30 ± 0.2	53.35 ± 0.024	72 ± 0.032	280 ± 25	5 ± 2	61.89 ± 0.2
12		6.2 ± 0.2	12.5 ± 0.5	6.20 ± 0.2	1.5 ± 0.037	24 ± 0.022	50 ± 40	0	28.4 ± 0.2
36	43	7.5 ± 0.1	0.4 ± 0.1	2.15 ± 0.2	23 ± 0.020	75 ± 0.025	210 ± 10	12 ± 5	50.4 ± 0.2
24		7.6 ± 0.1	0.5 ± 0.1	2.35 ± 0.2	40 ± 0.031	74 ± 0.025	220 ± 35	7 ± 3	45.76 ± 0.2
12		6.3 ± 0.2	6.5 ± 0.5	3.50 ± 0.2	1.5 ± 0.031	25 ± 0.025	45 ± 20	0	19.22 ± 0.2

Each value is an average of three replicates taken after the steady-sate conditions were reached; "±" shows standards errors among replicates.

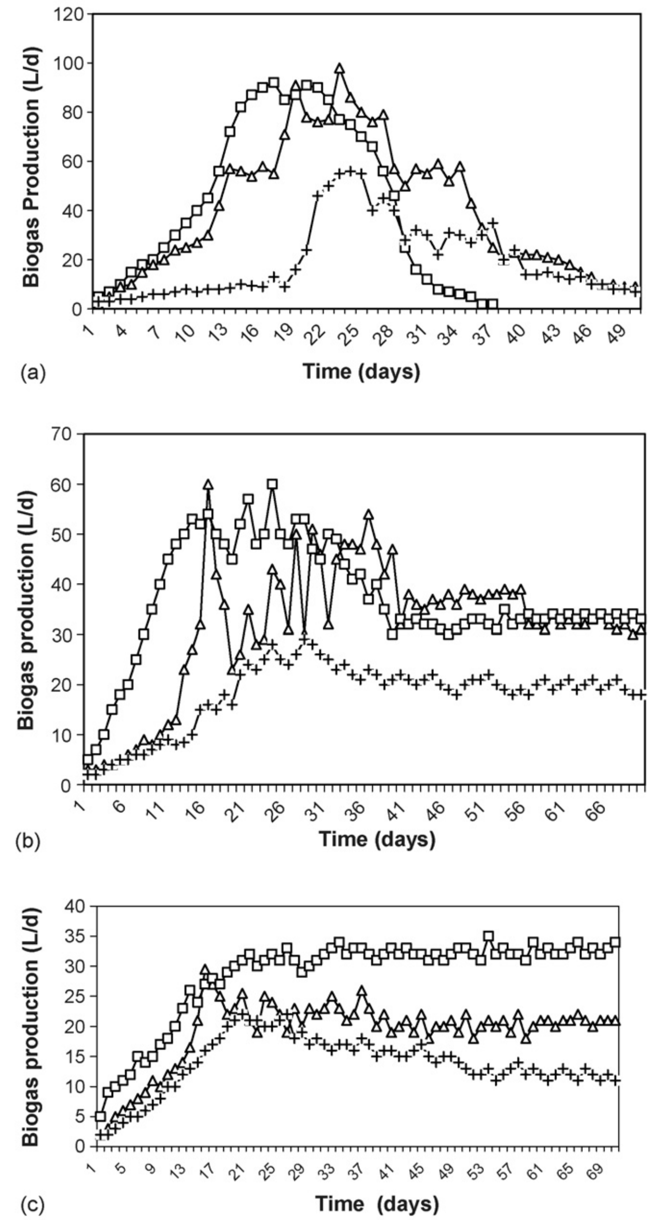

Fig. 2. Biogas production at different HRTs: 12 days (a), 24 days (b) and 36 days (c) and different OMW substrate concentrations: 130 g COD/l (□), 67 g COD/l (Δ) and 43 g COD/l (+).

digested alone under thermophilic conditions at an HRT of 24 days.

As can be seen, for OMW digested alone we observe an intense biogas production of about 75 l/day during the first 15 days followed by a sharp decrease in biogas production which stopped at the 41 days. We notice also a sharp increase of TVFA level and a sharp decrease of ammonium nitrogen below 200 mg/l in the effluent. Whereas, for OMW co-digested with OMSW we observe a sharp rise of biogas production to approximately 60 l/day followed by a gradual decrease until reaching a steady state of biogas production about 32 l/day. In the case of OMW digested alone the cessation of biogas production and the high level of TVFA level in effluents were due to the

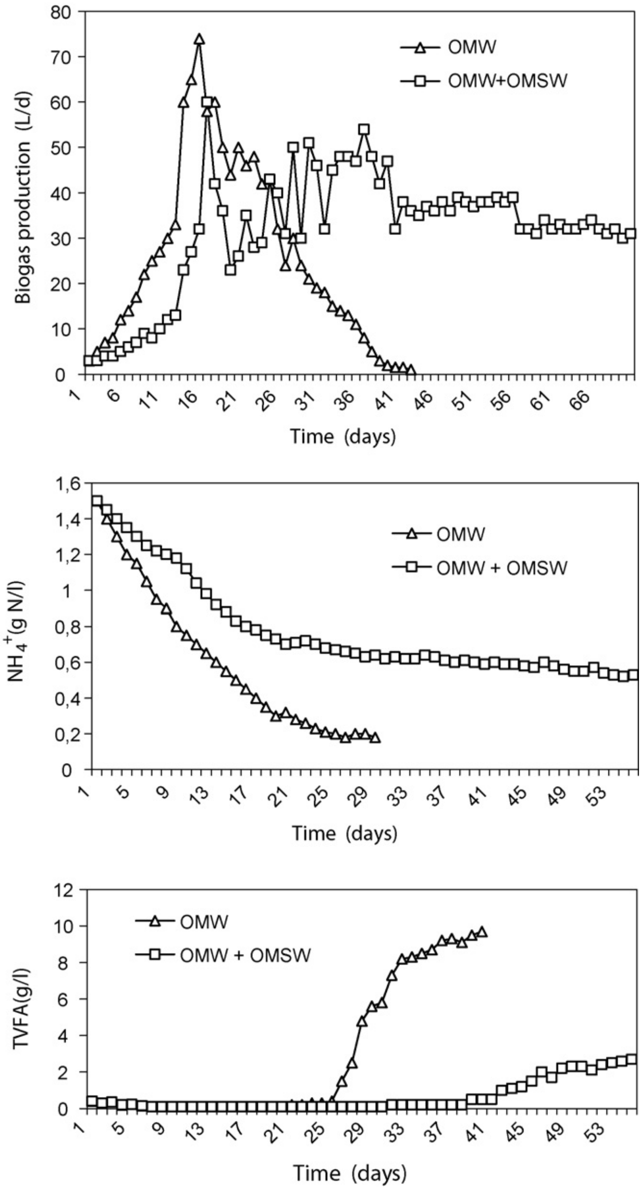

Fig. 3. Effect of OMSW on biogas production, effluent ammonium nitrogen and TVFA at an HRT of 24 days and OMW substrate concentration of 67 g COD/l.

rapid decrease of ammonium nitrogen inside the reactor below 200 mg N/l. Whereas for OMW co-digested with OMSW, a gradual decrease of ammonium nitrogen and a low level of TVFA in effluents were observed. In fact, OMSW contains a high level of particulate nitrogen which after hydrolysis under thermophilic conditions contributes with a significant amount of ammonium nitrogen to compensate the low level of NH_4^+ in OMW that decreases rapidly by methanogenic bacteria needs. This continual supply in ammonium nitrogen by OMSW will ovoid the risk of shortage in NH_4^+ and maintains methanogenic bacteria growth to achieve the process of biogas production at steady state. Table 8 confirms our deductions and gives the amounts of ammonium nitrogen of the two effluents (OMW and OMW + OMSW) at steady state. As can be seen for OMW digested alone the amount of ammonium nitrogen in the effluent was decreased to 200 ± 30 mg N/l compared to 600 ± 30 mg N/l in the effluent of OMW co-digested with OMSW. These results would support the earlier work by Angelidaki and coworkers [15–17] who studied the anaerobic co-digestion of OMW with manure under thermophilic conditions and their results showed that OMW could successfully treated without previous dilution due to the high content of ammonium offered by manure to compensate for the deficiency in OMW.

Also, she showed in other work that TVFA level in effluents increased rapidly at NH_4^+-concentrations lower than 250 mg N/l [16].

3.2. Composition of biogas

Table 5 shows the average composition of the produced biogas during the steady state period of the three influents of OMW (43, 67 and 130 g COD/l) co-digested with OMSW at the following HRT: 12, 24 and 36 days. As can be seen, the methane percentage was increased with the increase of HRT. The best methane percentage (76%) was obtained with an influent substrate concentration of 67 g COD/l digested at an HRT of 36 days. Indeed, at long HRT there were increase of contact between bacteria and substrates. Besides, OMW influents which have low concentration of COD have also low concentration of inhibiting compounds such as phenol and TVFA, reason why the methanogenic process was improved.

Table 6
Steady-state results of COD removal efficiency of OMW co-digested with OMSW at different HRT and influent substrate concentration

HRT (day)	Influent COD (g/l)		Effluent COD (g/l)		COD removal efficiency (%)	
	TCOD	SCOD	TCOD	SCOD	Δ(g)	Δ(SCOD)
12	130 ± 0.5	80 ± 0.5	95 ± 0.5	65 ± 0.5	26.92 ± 0.5	18.75 ± 0.5
	67 ± 0.5	56 ± 0.5	55 ± 0.5	46 ± 0.5	17.91 ± 0.5	17.85 ± 0.5
	43 ± 0.5	36 ± 0.5	37 ± 0.5	28 ± 0.5	13.95 ± 0.5	22.22 ± 0.5
24	130 ± 0.5	80 ± 0.5	46 ± 0.5	28 ± 0.5	64.61 ± 0.5	65 ± 0.5
	67 ± 0.5	56 ± 0.5	41 ± 0.5	24 ± 0.5	38.8 ± 0.5	57.14 ± 0.5
	43 ± 0.5	36 ± 0.5	30 ± 0.5	19 ± 0.5	30.23 ± 0.5	47.22. ± 0.5
36	130 ± 0.5	80 ± 0.5	37 ± 0.5	25 ± 0.5	71.54 ± 0.5	68.75 ± 0.5
	67 ± 0.5	56 ± 0.5	34 ± 0.5	20 ± 0.5	49.25 ± 0.5	64.28 ± 0.5
	43 ± 0.5	36 ± 0.5	25 ± 0.5	17 ± 0.5	41.86 ± 0.5	52.78 ± 0.5

Each value is an average of three replicates. "±" shows standards errors among replicates.

We notice also for non-failed reactors, that H_2S percentages into biogas were decreased with the increase of HRT, whereas NH_3 percentages were increased with the increase of HRT. This increase of free ammonia with HRT was due to the increase in ammonium nitrogen concentration offered by the hydrolysis of organic nitrogen compounds contained in OMSW and which passes into the biogas in the form of free ammonia. Furthermore, the presence of these gases in thermophilic reactors in great amounts compared to mesophilic reactors were due to the solubility of NH_3, H_2S and H_2 gases that decreased with increasing temperature causing high transfer of these gases into the biogas and producing consequently an odorous effluent.

3.3. COD removal efficiency

Effluents COD removal efficiency and their qualities are summarised in Table 6. As can be seen an OMW of 130 g COD/l co-digested with OMSW at an HRT of 36 days gave the best performances with a SCOD removal efficiency of 68.75%. Whereas, the best quality of effluents (SCOD = 17 g COD/l) was obtained with the lowest influent TCOD concentration and the highest HRT studied. These results of COD destruction were lower than those obtained from the anaerobic co-digestion of OMW with manure in CST reactor that gave a SCOD removal efficiency of 75% [15]. Whereas they were higher than those obtained from the anaerobic co-digestion of OMW with manure in USAB reactors that gave a SCOD removal efficiency of 65% [17]. Moreover, comparing these results with those given by the previous work that studied the co-digestion of OMW with OMSW in tubular digester at mesophilic temperature we found that COD removal efficiencies of influents treated under thermophilic conditions were decreased [18]. For instance, an OMW of 67 g COD/l co-digested with OMSW at an HRT of 36 days, the SCOD removal efficiency was 64% under thermophilic conditions compared to 77% under mesophilic conditions. Besides, the colour of all effluents, rejected from digesters operated at thermophilic temperature, were dark red purple due to the fact that they still contain polyphenolic compounds of high molecular weight such tannins and anthocyanes [20] that increase after the hydrolysis of OMSW. This means that these polyphenolic compounds were not degradable by thermophilic bacteria. Table 5 confirms our deductions and shows both total phenol levels in effluents and phenol removal efficiency under thermophilic conditions. As can be seen, phenol removal efficiency were below 75% and the total phenol levels in all effluents were above 2 g C_6H_6O /l for the three influents studied under different thermophilic conditions.

3.4. Mineral contents of digested effluents

Total Kjeldhal nitrogen, phosphorus, potassium and calcium of different effluents at different HRT are presented in Table 7. As can be seen the concentration of mineral elements in effluents were much higher than those in influents. These results were due to the degradation of organic compounds into methane and liberation of mineral elements that accumulate in effluents.

The richness of effluents in mineral substances made them very important for agricultural grounds to increase their fertility.

3.5. Net energy production

The net energy production E_p (kJ/day) is the difference between the produced energy and the energy consumed by the process and expressed as follows:

$$E_p = EA - (EB + EC + ED) \quad (1)$$

where EA is the daily energy production by an anaerobic digester (kJ/day), EB the daily energy required to heat influent substrate (kJ/day), EC the energy loss through the digester walls (kJ/day), and ED is the electrical energy required by the digester (kJ/day).

The expressions of EA, EB, EC and ED were described in detail by Bouallagui et al. [6] who studied the thermophilic anaerobic digestion of fruits and vegetables wastes in the same digesters. The results of the net energy production from the anaerobic co-digestion of OMW with OMSW under different operation conditions were summarised in Table 9. As can be seen, the net energy under thermophilic temperature were higher compared to those under mesophilic temperature. For instance the net energy production obtained from the digestion of an influent substrate concentration of 67 g COD/l at an HRT of 24 days in thermophilic temperature was 427 kJ/day higher than that obtained from the same influent operated at mesophilic digesters.

Table 7
The amount of TKN, phosphorus, potassium, calcium, sodium and magnesium in the effluents at different HRT and influents TCOD concentrations

HRT (day)	Influent TCOD (g/l)	TK-N (mg/l)	TPO_4^--P	K (mg/l)	Ca (mg/l)	Na (mg/l)	Mg (mg/l)
12	130	1950 ± 20	1282 ± 15	3520 ± 10	2010 ± 20	314 ± 15	570 ± 15
	67	1350 ± 20	1050 ± 15	3490 ± 10	3630 ± 20	546 ± 15	1390 ± 15
	43	850 ± 20	520 ± 15	2650 ± 10	2800 ± 20	225 ± 15	430 ± 15
24	130	2350 ± 20	1170 ± 15	5200 ± 10	4750 ± 20	670 ± 15	2700 ± 15
	67	1560 ± 20	780 ± 15	3860 ± 10	2450 ± 20	510 ± 15	670 ± 15
	43	950 ± 20	490 ± 15	2800 ± 10	3250 ± 20	425 ± 15	750 ± 15
36	130	2450 ± 20	1220 ± 15	5650 ± 10	5200 ± 20	750 ± 15	950 ± 15
	67	1870 ± 20	860 ± 15	4300 ± 10	4350 ± 20	655 ± 15	1250 ± 15
	43	1050 ± 20	540 ± 15	3000 ± 10	3600 ± 20	550 ± 15	850 ± 20

Each value is an average of three replicates. "±" shows standards errors among replicates.

Table 8
The amount of ammonium nitrogen, phosphorus and potassium in the effluents of OMW digested alone compared to those in OMW co-digested with OMSW

HRT (day)	Influent TCOD (g/l)	TNH_4^+-N (mg N/l)		TPO_4^--P (mg/l)		K (mg/l)	
		OMW	OMW + OMSW	OMW	OMW + OMSW	OMW	OMW + OMSW
24	67	200 ± 30	600 ± 30	530 ± 15	780 ± 15	1380 ± 10	3860 ± 10

Each value is an average of three replicates. "±" shows standards errors among replicates.

Table 9
Effect of influent TCOD concentrations and temperature on net energy production at an HRT of 24 days

Influent TCOD (g COD/l)	*T* (°C)	Energy production in the digester (kJ/day)	Energy consumed for load heating (kJ/day)	Energy loss through the digester walls (kJ/day)	Net energy production (kJ/day)	Reference
130	55	828.18	111.91	86.28	629.99	This study
	35	360.86	47.97	38.34	274.55	[18]
67	55	1034.70	111.91	86.28	836.51	This study
	35	496.20	47.97	38.34	409.89	[18]
43	55	536.46	111.91	86.28	338.27	This study
	35	329.30	47.97	38.34	242.99	[18]

4. Conclusion

We conclude from this study that OMW could be degraded successfully in co-digestion with OMSW under thermophilic conditions without previous dilution and without addition of chemical nitrogen substances. The best performance in methane productivity and SCOD removal efficiency were 46 l CH_4/((L OMW fed) day) and 68.97%, respectively. They were obtained with an OMW of 130 g COD/l co-digested with OMSW at an HRT of 36 days. Besides, the best net energy production from digesters operated at thermophilic temperature was 427 kJ/day higher than from those operated at mesophilic temperature for the same conditions of feed concentration and HRT. Nevertheless and despite the above mentioned benefits, thermophilic anaerobic co-digestion of OMW with OMSW is not entirely successful in reaching the treatment efficiencies required by the national regulations of all the Mediterranean area countries and the COD removal efficiency was lower than that obtained using mesophilic conditions. Besides, effluents rejected from the thermophilic digesters contained higher level of polyphenolic compounds responsible of the dark purple colour (tannins and anthocyanes) compared to those rejected from digesters operated under mesophilic conditions because thermophilic bacteria could not degrade these kinds of polyphenolic compounds. Furthermore, an inhibition of the methanogenic process was observed with all influents studied at an HRT ≤ 12 days.

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