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Abstract

BACKGROUND. Olive mill wastewater (OMW) represents an environmental problem due to its high organic load and relevant concentration of phenolic compounds. OMW treatment and disposal represents a relevant challenge and cost for olive mills and multi-utilities in charge of waste management in Mediterranean countries. The goal of this study was to develop an anaerobic co-digestion (co-AD) process of OMW and sewage sludge (SwS) from municipal wastewater treatment.

RESULTS. Different volumetric OMW:SwS ratios up to 100% OMW were fed in continuous 1.7-L bioreactors. The reactors fed with raw OMW (rOMW) performed better than those fed with OMW dephenolized by adsorption (dOMW). At a 23-day hydraulic retention time the best performances were obtained in the reactor fed with 25% rOMW, with a 105% increase in methane yield in comparison to the 100% SwS test. At a 40-day hydraulic retention time, the reactor fed with 40% rOMW attained a 268 $NL_{CH4}/kg_{volatile\ solids}$ methane yield. The conversion of phenolic compounds reached 70% when the hydraulic retention time was increased from 23 to 40 days. A cost-benefit analysis indicated that both rOMW co-AD in existing digesters and PC recovery from OMW followed by co-AD of dOMW can lead to relevant additional revenues for the multi-utilities in charge of wastewater management.

CONCLUSION. This work proves that, using the existing network of SwS anaerobic digesters, it is feasible to co-digest the entire OMW production in regions characterized by intense olive oil production, attaining a relevant increase in methane production yield (144% increase in comparison to 100% SwS).

Keywords: olive mill wastewater, sewage sludge, anaerobic digestion, polyphenolic compounds, municipal wastewater, cost-benefit analysis.

Nomenclature

AD	anaerobic digestion
BOD_5	biological oxygen demand
CAPEX	capital expenditures
co-AD	anaerobic co-digestion
dCOD	dissolved chemical oxygen demand
dOMW	dephenolized olive mill wastewater
FRR	financial rate of return
GA	gallic acid
GC	gas chromatography
HPLC	high pressure liquid chromatography
HRT	hydraulic retention time
MWW	municipal wastewater
OLR	organic load ratio
OPEX	operational expenditures
PCs	polyphenolic compounds
rOMW	raw olive mill wastewater
SwS	sewage sludge
TS	total solids

VFAs volatile fatty acids
VS volatile solids
WACC weighted average cost of capital
WWTP wastewater treatment plant

INTRODUCTION

Olive cultivation is widespread across the entire Mediterranean region. Olive oil has excellent nutritional properties mostly due to the high concentrations of phenolic compounds (PCs). It is obtained from crushed olives, mainly by centrifugation methods such as the two-phase or the three-phase process. In the three-phase process the addition of warm water in the centrifugation step generates three by-products: olive oil, pomace and olive mill wastewater (OMW). 1-1.6 m^3 of OMW are generated for each ton of olives processed.[1] Almost 95% of the olive phenolic content moves from the oil phase to OMW during the oil extraction process.[2] OMWs are characterized by acidic pH (4 – 6), high organic content (COD up to 220 g/L, BOD_5 up to 100 g/L), high PCs concentration (0.1 – 18 g/L) and unpleasant odor. [1–3] This by-product represents a major environmental problem due the negative effects on soil and water microbial population when it is discharged directly in land or water bodies. Traditionally OMWs were used for olive trees irrigation, however several studies demonstrated that direct OMW application on crops inhibits seed germination and plant growth. Therefore, in several countries the legislator strongly limited the amount of OMW that can be released on soil. It is thus critically important to develop technologies for OMW treatment and for their efficient reuse in agriculture, above all in the Mediterranean region where the water crisis is becoming increasing relevant. [4] Numerous processes for OMW treatment have been proposed: reverse osmosis, flocculation, evaporation, chemical oxidation, lagooning and anaerobic digestion (AD).[5] The main challenge towards the development of a suitable process for OMW treatment is represented by the high cost, as a result also of the seasonality of OMW production and the small scale of several olive mills. Under this perspective, OMW AD is of high interest, thanks to the low operational cost and the production of biogas. However, the AD of only OMW is a challenging process because of the high concentration of inhibitory and recalcitrant compounds such as PCs, lack of ammonium nitrogen, low alkalinity and high seasonality.[1,6] The co-digestion of OMW with other wastes of urban or agricultural origin represents a potential solution to these challenges. Among the different wastes that can be co-digested, sewage sludge (SwS) is of high interest thanks to the widespread presence of digesters used for the stabilization of the sludge produced by wastewater treatment plants (WWTP).[7–9] Normally WWTP digesters are slightly oversized [10,11] and the AD process is typically conducted with very low organic loading rates (< 1 $kg_{VS}/m^3/d$; Nghiem et al.[12]). This spare capacity can be exploited for the anaerobic co-digestion (co-AD) process.[13,14] In particular the co-AD of SwS with the organic fraction of municipal solid waste is finding increasing applications.[15–18]

The co-AD of OMW with SwS has been reported in a limited number of studies, and only at laboratory / pilot scale. The batch co-AD process developed by Angelidaki et al.[19] required a 1:5 OMW dilution with water to avoid inhibition of biogas production. Athanasoulia et al.[20] found that OMW addition (30% v/v) to SwS in a cascade of two anaerobic continuous stirred tank reactors determined a 2.4-fold increase in biogas production rate. In continuous pilot-scale tests performed by Maragkaki et al.[21], the addition of 5% (v/v) of OMW to SwS led to a marked improvement of the biogas production rate (from 16 to 50 L/day).

Combining OMW co-AD with a pre-treatment aimed at recovering the OMW PCs represents an interesting opportunity to decrease the load of compounds that can potentially inhibit the AD process while, at the same time, recovering high-added value products. Indeed, in batch tests of OMW AD Vavouraki et al. [22] showed that an OMW pre-treatment of PC removal and recovery by adsorption led to an increase in methane production. At the same time, several studies demonstrated the strong antimicrobial, antioxidant and anti-inflammatory effects of OMW-derived PCs.[23,24] In the last few years polyphenols gained a key role in many industrial fields. PCs are used as antioxidants and antimicrobials in animal feeding, cosmetics and health care products.[25,26] Therefore, several researchers developed processes aimed at the recovery of PCs from OMW, such as solvent extraction, [27] membrane separation, [28] cloud-point extraction [29] and adsorption. [3,5,30,31] However, the vast majority of these studies did not include the development of a process aimed at completing the treatment of the dephenolized OMW, typically characterized by a very high organic load.

In this work, the co-AD of OMW with SwS was studied in continuous flow 1.7-L reactors, under different conditions in terms of OMW/SwS ratio and hydraulic retention time (HRT) using raw OMW and dephenolized OMW pretreated for PC recovery by adsorption. The aims of this work were: (i) to compare the performances obtained in co-AD reactors fed with raw and dephenolized OMW; (ii) to identify operational conditions that allow the attainment of a stable anaerobic co-digestion process of OMW and SwS, with a high OMW/SwS volumetric ratio; (iii) to develop strategies for the integration of the OMW/SwS co-AD process in the network of existing SwS digesters; and (iv) to perform a cost-benefit analysis (CBA) relative to the co-AD of OMW in an existing SwS digester, with and without a dephenolization pre-treatment.

This work presents three main novelties. Firstly, while a previous study compared the AD performances of raw and dephenolized OMW in batch tests fed with only OMW,[22] this work compares for the first time the performances of raw and dephenolized OMW in the more realistic condition of a continuous-flow process of OMW co-AD with SwS. In addition, this work innovatively presents strategies for the integration of the OMW/SwS co-AD process in the network of existing SwS digesters, based on the analysis of OMW and SwS production in 2 Italian regions characterized by intense olive oil production. Lastly, this is the first work in which experimental tests of OMW/SwS co-AD, with and without dephenolization pre-treatment, are integrated by a CBA aimed at quantifying the economic benefit for the companies in charge of WW and sludge treatment.

EXPERIMENTAL

Substrates: olive mill wastewater and sewage sludge

The OMW used in the present study was provided by a 3-phase olive mill located in Sant'Arcangelo di Romagna (Rimini, Italy) and obtained by olive oil extraction from olives harvested in Autumn 2018. OMW was fed into the AD reactors in two different forms: raw OMW (rOMW) and OMW with a reduced phenolic content (dOMW), produced by polyphenolic compounds (PCs) adsorption on a neutral adsorbent resin. These two OMWs were co-digested with sewage sludge (SwS), a thickened secondary sludge taken from the WWTP of Bologna (Italy). The chemical and physical characteristics of rOMW, dOMW and SwS, that were stored at +4°C for the entire experimental period, are reported in Table 1. OMW dephenolization led to a 50% reduction of the OMW volatile solids (VS) content, as a significant amount of organic matter is removed together with the PCs.

Olive mill wastewater microfiltration and polyphenolic compounds adsorption

Microfiltration of the OMW is required to prevent column clogging during PCs adsorption. The OMW given by the mill was tangentially microfiltered with a cross flow microfiltration plant supplied by Juclas Srl (Verona, Italy), equipped with a membrane pump with a 1–4 bar operating pressure and a ceramic circular filter (40 cm diameter, 0.2 μm average pore-size); more details are in Frascari et al.[31] The microfiltration pre-treatment determined a 6.1% loss of dissolved COD (dCOD) and a 14.3% loss of PCs. The dephenolized OMW was produced by means of a PCs adsorption plant consisting of 4 columns packed with the non-ionic styrene-divinylbenzene adsorbent resin Amberlite XAD16N (DOW Chemicals Europe GmbH, Horgen, Switzerland), with a total bed length of 2.00 m (Fig. S1, Supporting Information). The main characteristics of the resin and adsorption plant are reported in Table S1 in Supporting Information. More details on the adsorption plant are described by Frascari et al.[31]

Semi-continuous co-anaerobic digestion process

Experimental set-up

All continuous tests were made in laboratory-scale PVC bioreactors made by Tadeo Srl (Bologna, Italy), with a capacity of 1.7 L, an inner diameter of 0.1 m and a height of 0.23 m. All bioreactors were operated under mesophilic conditions at 34 ± 1°C with constant agitation at 130 rpm in an orbital shaker NB-205VL (N-BIOTEK, Korea). To evaluate the impact of PCs concentration on the co-AD process, twelve feedstock mixtures composed by different OMW/SwS ratios were tested for both rOMW and dOMW: 5:95, 12:88, 18:82, 25:75, 40:60 and 100:0% (v/v) OMW/SwS. An additional bioreactor was fed with 100% SwS and kept as benchmark for the AD process. Total solids (TS), VS, dCOD, VFAs, PCs and organic loading ratio (OLR) daily mass flow rates fed to the bioreactors are summarized in Table 2.

Bioreactors start-up and operation

The bioreactors were inoculated with 0.506 L of the anaerobic sludge sampled from the anaerobic digester of the Bologna WWTP, fed with the same thickened SwS used in this work. The inoculum characteristics are reported in Table 1. N_2 was fluxed in the reactor headspace to recreate anaerobic conditions. Effluent monitoring was done once a week measuring TS, VS, VFAs, dCOD and PCs concentrations. Biogas and CH_4 monitoring was done three times a week by means of quantifying the biogas volume produced and analyzing its composition. During the first 7 days of operations, all reactors were daily fed only with SwS (OLR 1.1 g_{VS}/L/day) to let the inoculum re-adapt to the experimental conditions. Considering the toxicity of PCs on microorganism growth, to acclimatize the microbial population to both rOMW and dOMW, the OMW volumetric percentage in each feeding was increased through the gradual stepwise programme reported in Fig. S3 in Supporting Information. The gradient slope was equal to 0.7%/day for the reactors fed with 5%, 12%, 18% and 25% (v/v) OMW, whereas it was four time steeper for the 100% OMW reactor, in order to reach a stationary feed at the latest on day 35 in all bioreactors. All co-AD processes were conducted for 63 days, except for the tests with 100% dOMW (100 days) and 25% OMWs (171 days). On day 120, in the two reactors initially fed with 25% rOMW and 25% dOMW, the OMW volumetric percentage was increased from 25% to 40%. The HRT was set at 23 days for the first 100 days, whereas it was increased to 40 days from day 101 to day 171 for the 2 bioreactors fed with 25% rOMW and 25% dOMW (increased to 40% rOMW and 40% dOMW on day 120).

Analytical methods

TS were measured weighting samples after an overnight drying process at 105°C and *VS* weighting the 105°C-dried samples after a calcination process of 1 h at 600°C. *dCOD* was measured spectrophotometrically using the Hach Lange LCI 400 (range: 0–1000 mg_{O2}/L) in the liquid fraction derived from sample centrifugation at 14000 rpm for 15 min. *Total BOD_5* has been analysed in accordance with Standard Method 5210 (APHA et al., 2017) using a Xylem Inc. (Rye Brook, New York, U.S.A.) OxiTop IS 6 - WTW system. *PCs* were analyzed with an HPLC method using an Agilent Infinity 1260 HPLC (Santa Clara, USA) and expressed as mg of gallic acid per liter (mg_{GA}/L); the instrument and method utilized are described in detail in Frascari et al.[31] *VFAs* were analysed with a Shimadzu Prominence HPLC (Kyoto, Japan) as reported in Longanesi et al.[32] VFAs concentration was determined as the sum of the single VFA concentrations. *Reducing sugars* were spectrophotometrically analysed following the dinitrosalicylic acid (DNS) assay (Miller [33]) as described in detail previously.[31] All analyses of the digestate, except TS and VS, were performed after centrifugation (14000 rpm, 15 min, 4°C) and filtration at 0.2 µm of the supernatant. The *volume of biogas* produced was measured via water displacement in a Mariotte flask. *Biogas composition* was analyzed with an Agilent Technologies 5890 SERIES II Plus gas-chromatograph (Santa Clara, USA), as described in Longanesi et al.[32] All biogas and methane values were corrected at normal temperature (273.15 K) and pressure (1 bar). *pH* was measured employing an XS Sensors electrode pH GEL HT PRO connected to an EUTECH Instruments PC2700 Series (Thermoscientific, Massachusetts, USA). *OMW density* was evaluated by means of a 100 mL ITI Tooling pycnometer. All chemicals used were provided by Sigma-Aldrich (Milano, Italy).

The relative average experimental errors, estimated by means of a statistical elaboration of repeated analyses of check standards, resulted equal to 5% for CH_4, 5% for biogas volume, 1% for PCs, VFAs and VS, 3% for dCOD.

The % conversion relative to each monitored parameter (VS, dCOD or PCs) was evaluated as:

$$P\ conversion\ \% = (P_{in} - P_{out})/P_{in} \cdot 100 \qquad (1)$$

where P_{in} and P_{out} indicate the concentrations of the generic parameter P in the feeding mixture and in the effluent.

Cost-benefit analysis of the OMW co-anaerobic digestion process

The CBA of the OMW co-anaerobic digestion process was performed according to the European Union guidelines for the appraisal of investment products.[34] The CBA was based on the full-scale scenario of a 500000 people equivalent (PE) WWTP, in which it was assumed to co-digest OMW in the existing digester during a 4-month period, with an OMW / (OMW + SwS) volumetric ratio equal to 0.25.

Two distinct CBA approaches were applied for the scenarios of rOMW co-AD and OMW dephenolization followed by dOMW co-AD. For the case of rOMW co-AD, since no additional infrastructure is required, the CBA did not include any capital expenditure, but only the additional revenues for the multi-utility company in charge of WW management. These additional revenues were assumed to result from the sum of two terms: the OMW disposal tariff paid by the olive mill, and the revenues associated to the additional electricity produced thanks to OMW co-AD, assuming that the biogas is entirely burnt for combined heat and power production (CHP) and taking into account the additional mixing energy required for OMW co-AD. On the basis of the OMW disposal costs in Italy, the OMW tariff was assumed to vary between 50 and 100 €/m^3. As for the additional electricity production, the total CH_4 production of the rOMW co-AD scenario was evaluated using the average CH_4/VS yield obtained in this work in the bioreactor with 25% OMW and the VS content of the SwS and rOMW used in this work. The corresponding electricity production during the reference 4-month period was compared to that of the benchmark scenario in which only SwS is digested. Both for rOMW co-AD and for the benchmark scenario, the possible cost associated to the purchase of additional CH_4 for maintaining 34 °C in the digester was considered, if the thermal energy produced by the CHP unit resulted not sufficient. Lastly, the additional revenues associated to rOMW co-AD were compared to the total cost for MWW treatment sustained by the WWTP manager, in order to assess the potential reduction of the cost of MWW treatment attainable thanks to rOMW co-AD. The CBA procedure relative to the rOMW co-AD scenario is described in detail in Table S2 in the Supporting Information.

For the scenario of OMW dephenolization followed by dOMW co-AD, the CBA was articulated in two steps characterized by different approaches. Indeed, OMW dephenolization by adsorption requires an initial investment (CAPEX) and an additional operational cost (OPEX) for the company in charge of MWW management, since the required infrastructure is not present in a typical WWTP. Therefore, PC recovery from OMW was seen in this work as an additional investment that the MWW company can choose to make only if – thanks to the revenues associated to the sale of the PC-rich antioxidant product – the Financial Rate of Return (FRR) is expected to be equal to a selected threshold value of the Weighted-Average Cost of Capital (WACC), the rate that a company is expected to pay to all its creditors and owners, to finance its assets. On the basis of previous studies of positive business cases for agricultural companies,[5] in this work the minimum WACC required to generate a positive business case for the MWW company was set to 6%. The CBA was referred to a 20-year period, assuming a financial discount rate equal to 4%. Conversely, for the dOMW co-AD process the CBA followed the approach described above for the rOMW co-AD process, taking into account the revenues from both OMW disposal and additional electricity production. The CBA procedure and assumptions relative to the scenario of OMW dephenolization + dOMW co-AD are described in detail in Table S3 in the Supporting Information.

RESULTS AND DISCUSSION

Dephenolized olive mill wastewater production through polyphenolic compounds adsorption

In order to produce the dOMW, the microfiltered OMW was dephenolized by adsorption according to the procedure described in section "Olive mill wastewater microfiltration and polyphenolic compounds adsorption". The trend of the normalized PCs concentration in the outlet fractions versus dimensionless time is shown in Fig. S2 in Supporting Information. The adsorption test was interrupted upon the attainment of a 0.22 normalized outlet PCs concentration. This led to the production of an average dOMW characterized by a PCs concentration equal to 65 mg_{GA} /L (6.4 % of the rOMW concentration). The adsorption process determined in addition the following removals: dCOD 32%, BOD_5 35%, VFAs 21%.

Continuous co-anaerobic digestion process

WWTP digesters typically work in the 20-40 days HRT range [8]. If one assumes to perform a co-digestion process in which a second waste (such as OMW) is added to a real SwS digester, the volumetric flow rate increases and, if the liquid volume is kept constant, the HRT decreases. Thus, to simulate the co-AD process performances with a decreased HRT, the first part of this study was focused on OMW/SwS co-AD with an HRT equal to 23 days, close to the lower HRT limit of the above-reported range.

Anaerobic digestion of pure sewage sludge

The reactor fed with 100% SwS was used as the internal benchmark of the AD process. The AD of SwS was performed with an HRT of 23 days, corresponding to an OLR of 1.1 g_{VS}/L/day. The biogas and methane yield trends over time are reported in Fig. S4 in Supporting Information. Both trends achieved a stable steady state after less than 7 days. The average yields relative to biogas (Y_{biogas}) and CH_4 (Y_{CH4}) were equal to 194 ± 13 NL/$kg_{VS\ fed}$ and 110 ± 11 NL/$kg_{VS\ fed}$, respectively. The CH_4 fraction in biogas fluctuated between 52% and 59%, whereas the average biogas and methane production rates were respectively 0.20 ± 0.02 NL_{biogas}/L/day and 0.12 ± 0.01 NL_{CH4}/L/day. In the last 2 HRTs the VS average conversion was 37% and the VS concentration was 16 ± 2 g/L. The absence of VFA in the digestate (<0.1 g/L) suggest that the methanogenesis was not inhibited by any metabolite. pH was stable at 7.2.
The Y_{biogas} obtained in this work (194 NL_{biogas}/$kg_{VS\ fed}$) is consistent with the typical yields achieved in full-scale SwS digesters, which vary in the 62 – 195 NL_{biogas}/$kg_{VS\ fed}$ range with HRTs of 20 – 40 days and OLRs of 0.8-1.0 kg_{TVS}/m^3/day. [8,16] However, the yields obtained in this study are lower than the corresponding values achieved in pilot-scale plants, which vary in the 290-390 NL_{biogas}/$kg_{VS\ fed}$ range for biogas and in the 183-250 NL_{CH4}/$kg_{VS\ fed}$ range for CH_4, with HRTs of 20-24 days and OLRs of 0.8-2.2 kg_{VS}/m^3/day. [9,35] The experimental VS conversion obtained in this study (37%) is slightly higher than the values obtained in full-scale digesters [8,35] and consistent with the optimal values recommended by Rittmann and McCarty (30-50%).[36]

Anaerobic digestion of raw and dephenolized pure olive mill wastewater

The results obtained in the bioreactor fed with 100% rOMW are shown in Fig. 1A and 1C. The OLR increased from day 1 to day 35 as a result of the gradual increase of the OMW fraction in the feed, as the rOMW had a VS concentration higher than that of SwS (Table 1). After day 35, the reactor was fed with 100% rOMW and the OLR was maintained constant at 1.09 g_{VS}/L/day. Fig. 1A shows that both Y_{biogas} and Y_{CH4} increased during the first 35 days, with maximum values at the end of the incremental OMW gradient, equal to 790 NL_{biogas}/$kg_{VS\ fed}$ and 470 NL_{CH4}/$kg_{VS\ fed}$ respectively. These values are largely higher than those attained in the 100% SwS benchmark, showing the high biomethane potential of rOMW. It should be noted that these values cannot be taken as the yields obtainable from rOMW alone, as they are also the result of the biogas production from the residual SwS present in the reactor. Starting from the achievement of 100% rOMW in the feed (day 35), both the biogas and methane yields showed a rapid decrease, that led in 30 days to the complete halt of the methanogenic activity. In agreement with previous studies,[37,38] these results suggest that rOMW exerted an inhibiting action on the methanogenic activity.
The trends of VFAs concentration, PCs concentration (mg_{GA}/L) and dissolved COD conversion (%) over time of the 100% rOMW bioreactor are shown in Fig. 1C. dCOD conversion is an index of OMW VS conversion as SwS has no dCOD and, thus, dCOD comes only from OMW. dCOD conversion, and therefore OMW VS uptake, started to decrease on day 20, and was soon followed by the decrease in biogas yield. PCs increased over time, as the initial SwS inoculum did not contain PCs, reaching a value of about 600 mg_{GA}/L (60% of the inlet PC concentration). VFAs remained < 0.1 g/L until day 30 (about 1.5 HRTs), then they increased steadily up to a maximum value of 5.5 g/L. VFAs were mainly composed of acetic (2.73 g/L on day 63), propionic (0.66 g/L) and butyric (0.73 g/L) acids. In agreement with the increase in VFAs, the pH gradually decreased, reaching 6.1 on day 63 (data not shown). These results indicate that methanogenesis was progressively inhibited, with a consequent VFAs accumulation.
The results obtained in the bioreactor fed with 100% dOMW are shown in Fig. 1B and 1D. The daily OLR decreased from day 1 to 35 as a result of the gradual increase in OMW fraction, as the dOMW had less VS than SwS. Then, the daily OLR was kept constant at 0.6 g_{VS}/L/day. As in the case of rOMW, both Y_{biogas} and Y_{CH4} showed a rapid increase reaching particularly high maximum values on day 42 (1100 NL_{biogas}/$kg_{VS\ fed}$ and 750 NL_{CH4}/$kg_{VS\ fed}$). Then, both yields decreased, though with a lower slope than in the 100% rOMW-fed reactor (Fig. 1A). Finally, the methanogenic activity stopped on day 100. As reported in Fig. 1D, dCOD conversion was very high up to day 60 (about 3 HRTs), then, it showed a rapidly decreasing trend consistent with the decreases in biogas and methane yield. PCs concentration slowly increased during the whole test, until a maximum value of about 50 mg_{GA}/L. VFAs were very low up to day 69, then they started to accumulate reaching a final value of 5 g/L. The increase in VFAs was associated to a corresponding decrease in pH, that reached 5.7 on day 100.
The results obtained in the bioreactors fed with only rOMW or dOMW showed that the OMW volatile solids have a biomethane potential largely higher than that of the SwS. However, under the experimental

conditions of this work, the AD of both OMWs gradually led to the accumulation of toxic compounds that inhibited the methanogenic activity. Fig. 1 indicates that in the case of rOMW inhibition occurred earlier and could be tentatively ascribed to the corresponding increase in PCs concentration; however, this is not the case of dOMW as PCs were always very low (< 50 mg_{GA}/L).
To the best of the author's knowledge, only one previous study successfully demonstrated the continuous flow AD of pure OMW.[39] In that study the bioreactor was initially fed with pig manure for 14 days, then the OMW/pig manure ratio was gradually increased during a 232-day microbial acclimatization period. Starting from day 232, the digestion of pure OMW with a high OLR (8 $g_{COD}/L/day$) and a 6-day HRT led to a Y_{CH4} of 100 $NL_{CH4}/kg_{VS\ fed}$, an 80% COD conversion and a 46% PCs conversion. In that study, the key factors for the attainment of an effective OMW AD process seem to be the particularly long adaptation time (about 7-fold longer than the one of this work) during which the OMW fraction in the feed was gradually increased and the use of an initial inoculum derived from pig manure instead of SwS.

Co-digestion of olive mill wastewater and sewage sludge at different ratios up to a 25% OMW fraction
Moving on to the bioreactors in which rOMW and dOMW were co-digested with SwS at different ratios, the biogas and CH_4 yields are reported in Fig. S5 in Supporting Information. As reported in Table 3, for both rOMW and dOMW the partial replacement of SwS with OMW resulted in higher biogas and CH_4 production yields and rates. Furthermore, all the selected performance indicators (biogas and methane yield and production rate) increased with increasing OMW content in the feed. Excluding the reactors with 40% OMW, that will be discussed in section "Effect of the increase in hydraulic retention time and OMW/SwS ratio", for both rOMW and dOMW the best performances were achieved in the reactors with 25% OMW, with methane yields of 226 $NL_{CH4}/kg_{VS\ fed}$ for rOMW (+116 $NL_{CH4}/kg_{VS\ fed}$ in comparison with the 100% SwS reactor) and 179 $NL_{CH4}/kg_{VS\ fed}$ for dOMW (+69 $NL_{CH4}/kg_{VS\ fed}$).
As shown in Table 3, for all the OMW:SwS ratios tested the rOMW-fed bioreactors resulted in higher performances than the corresponding dOMW-fed bioreactors, indicating that OMW dephenolization did not lead to any beneficial effect in terms of methane production. The higher biogas and methane rates obtained in the rOMW-fed reactors can be explained by the slightly higher OLR load (Table 3, last line), which is due to the higher VS content of rOMW. Conversely, the higher VS content of rOMW cannot justify the 25-30% higher methane and CH_4 yields obtained in the rOMW-fed reactors in comparison with the dOMW-fed ones, since the yields refer to a normalized amount of VS in the feed.
Several studies report the continuous co-AD of OMW with animal manures,[40,41] municipal organic solid waste,[35] agro-industrial residues [42] and thickened SwS,[20,21] whereas no previous experiences of co-AD of dephenolized OMW are reported. These co-AD tests, conducted in a spectrum of operating conditions similar to those of this study (HRT = 19-30 days, OLR 0.6-4.4 $g_{VS}/L/day$, % of OMW in the feed 5-30%), led to comparable results in terms of CH_4 yield (100-300 $NL_{CH4}/kg_{VS\ added}$, versus 113-270 $NL_{CH4}/kg_{VS\ added}$ in this work) and CH_4 production rate (0.3-0.8 NL/L/day, versus 0.13-0.25 NL/L/day in this work).
The results of the first part of this study show that the use of OMW as a co-substrate for SwS co-AD leads to a significant boost of the process performances. The results also suggest that OMW dephenolization, tested in this work to investigate the potential inhibitory effect of PCs on OMW AD documented in previous works,[22] does not actually lead to any benefit in the OMW/SwS co-AD process, under the experimental conditions tested in this study. Therefore, this OMW pre-treatment is not economically justified, unless the produced PC mixture can be sold at a price high enough to make the investment in the adsorption/desorption plant economically attracting for investors. The financial aspects of the scenarios of rOMW co-AD and OMW dephenolization followed by dOMW co-AD are illustrated in section "Cost-benefit analysis of the OMW co-anaerobic digestion process with and without pre-dephenolization" in the last part of this work.

Effect of the increase in hydraulic retention time and OMW/SwS ratio
The second part of the work, that started on day 100, was aimed at assessing the maximum OMW/SwS ratio that can lead to a co-AD process with stable performances without the need of a long adaptation time, hardly compatible with the typical seasonality of OMW production. For this purpose, on day 100 the HRT of the reactors fed with 25% rOMW and 25% dOMW was raised from 23 to 40 days, in order to offset the possible inhibition effects which might have reduced the AD performances observed at a 23-day HRT. These reactors contained a methanogenic microbial consortium acclimatized to a PCs concentration of 260

mg_{GA}/L and 23 mg_{GA}/L, respectively. In addition, starting from day 120 the OMW volumetric percentage was increased from 25% to 40% in both reactors. The combined increase of HRT and OMW fraction determined a 42-55% decrease in OLR (Table 2). The trends of Y_{biogas}, Y_{CH4} and PCs concentration versus time obtained in these reactors are reported in Fig. 2.

The increase of both HRT and OMW content in the feed led to a rapid increase of the CH_4 yields, that reached 268 ± 3 $NL_{CH4}/kg_{VS\ fed}$ for rOMW and 235 ± 13 $NL_{CH4}/kg_{VS\ fed}$ for dOMW (average values during the last 10 days of test), with a 19% increase for $Y_{CH4,rOMW}$ and a 31% increase for $Y_{CH4,dOMW}$ in comparison with the yields obtained with a 23-day HRT and 25% OMW (Table 3). In both reactors there was no VFAs accumulation (concentration always <0.1 g/L) and pH remained stable at about 7 (data not shown). In the last 25 days of test both reactors showed a very high dCOD conversion (94% and 97% for rOMW and dOMW respectively). The 40% rOMW-fed reactor achieved a stable PCs concentration with a mean value of about 125 mg_{GA}/L during the last 25 days (70% PCs conversion), while the 40% dOMW-fed reactor reached an average PC concentration of 14 mg_{GA}/L (55% PCs conversion). These data suggest that the OMW phenolic content can be effectively degraded by a co-AD process. The PCs conversions obtained in these reactors are higher than those reported in the literature: Dareioti et al.[40] obtained a 27% PCs removal in the co-AD of OMW and liquid cow manure, whereas Sampaio et al.[39] achieved a 46% PCs conversion in the AD of pure OMW. Moreover, the residual phenolic compounds present in the digestate proved to be not significantly toxic to methanogenesis, as evidenced by the 144% increase in CH_4 yield obtained by the reactor fed with 40% rOMW in comparison with the value obtained by the 100% SwS-fed reactor.

Model-based evaluation of the biogas and CH_4 yields of pure olive mill wastewater

As shown in Fig. 1A and 1B, in the reactors fed with 100% rOMW or dOMW the inhibition of methanogenesis prevented the experimental determination of the biogas and methane production yields of rOMW and dOMW. In order to obtain estimates of these yields, the biogas and methane yields obtained in the digesters fed with different OMW/SwS ratios (Table 3) were correlated to the amount of OMW VS and SwS VS in the feed of each reactor:

$$\dot{V} = Y_{co-AD} \cdot \left(\dot{m}_{VS,OMW} + \dot{m}_{VS,SwS}\right) = Y_{OMW} \cdot \dot{m}_{VS,OMW} + Y_{SwS} \cdot \dot{m}_{VS,SwS} \quad (2)$$

where $\dot{V}$(NL/d) is the total volumetric flow rate of biogas or CH_4 produced, $Y_{co\text{-}AD}$ ($NL/kg_{VS\ fed}$) is the experimental biogas or CH_4 yield obtained for each OMW/SwS ratio (Table 3), $\dot{m}_{VS,OMW}$ and $\dot{m}_{VS,SwS}$ ($kg_{VS,fed}/d$) are the mass flow rates of VS from OMW and SwS fed to each bioreactor, Y_{OMW} and Y_{SwS} ($NL/kg_{VS\ fed}$) are the biogas or CH_4 yields obtained by the VS of only OMW and only SwS. This approach is based on three assumptions: a) that methane production in each co-AD reactor can be expressed as the sum of two parallel independent processes, relative to the AD of SwS and OMW, each characterized by a separate yield; b) that, for each of these two independent processes, Y_{OMW} and Y_{SwS} are constant values that do not depend on the load of OMW, and therefore of potentially inhibiting compounds; c) that the values of Y_{SwS} that applies in the co-AD process is equal to that experimentally obtained in the 100% SwS reactor, in the absence of inhibiting compounds.

Eq. (2) can be more easily used to assess Y_{OMW} if $Y_{co\text{-}AD}$ is expressed as a function of $\omega_{VS,OMW}$, the ratio (mass fraction) of OMW-derived VS to total (OMW + SwS) VS content in the feed: $\omega_{VS,OMW} = \dot{m}_{VS,OMW}/\left(\dot{m}_{VS,OMW} + \dot{m}_{VS,SwS}\right)$. Therefore, $\dot{m}_{VS,SwS}$ can be expressed as $\left(1 - \omega_{VS,OMW}\right) \cdot \left(\dot{m}_{VS,OMW} + \dot{m}_{VS,SwS}\right)$. Substituting these expressions in Eq. (2) and dividing by $\left(1 - \omega_{VS,OMW}\right) \cdot \left(\dot{m}_{VS,OMW} + \dot{m}_{VS,SwS}\right)$, one obtains:

$$Y_{co-AD}/\left(1 - \omega_{VS,OMW}\right) = Y_{OMW} \cdot \frac{\omega_{VS,OMW}}{1 - \omega_{VS,OMW}} + Y_{SwS} \quad (3)$$

Eq. (3), if plotted against $\omega_{VS,OMW}/\left(1 - \omega_{VS,OMW}\right)$, is a straight line with slope equal to Y_{OMW} and y-intercept equal to Y_{SwS}. Thus, Y_{OMW} can be assessed by linear regression of the experimental values of $Y_{co\text{-}AD}$ obtained at different values of $\omega_{VS,OMW}$, whereas Y_{SwS} is taken equal to the value experimentally determined in the 100% SwS reactor (Table 3). The experimental data and the best-fit lines are shown in Fig. 3, together with the coefficients of determination R^2. The high R^2 values obtained (0.978-0.995) indicate the validity of the three above-reported hypothesis, and in particular the absence of significant inhibition in the co-AD process up to the 40% v/v of OMW in the feed.

The biogas and CH_4 yields assessed by linear regression are reported in Table 3. These results indicate that, if the AD of 100% rOMW and dOMW had been stable, the process would theoretically have reached a Y_{CH4} of 520 $NL_{CH4}/kg_{VS\ fed}$ for rOMW, and 587 $NL_{CH4}/kg_{VS\ fed}$ for dOMW, 5 times higher than that of SwS alone. Indeed, a similar Y_{CH4} was obtained in the 100% dOMW bioreactor after 50-60 days (600-620 $NL_{CH4}/kg_{VS\ fed}$; Fig. 1B), but the process was not stable due to inhibition phenomena. The theoretical CH_4 yields assessed in this work are significantly higher than that reported in the only study in which the continuous AD of pure OMW was successfully demonstrated, even though at a very low HRT (about 100 NL_{CH4}/kg_{VS}; Sampaio et al.[39]). The above-reported CH_4 yields are higher than the theoretical one relative to the AD of glucose, to which the OMW carbohydrates can be compared (373 NL_{CH4}/kg_{VS}; Wiesmann et al.[43]), but lower than those typical of substrates with a C/O ratio similar to that of PCs, such as fats, oil and greases (700 – 1100 NL_{CH4}/kg_{VS}; Mata-Alvarez et al.[14]). Even though it is unlikely to perform an AD of pure OMW in real applications, due to the strong seasonality of this waste, the results of this section show that OMW presents a very high biomethane potential, and that therefore its co-AD with other wastes such as SwS is a very promising process from the energetic point of view.

Strategies for the integration of the studied OMW co-AD process in the network of sewage sludge digesters

The goal of the last part of the work was to assess the large-scale applicability of the OMW/SwS co-AD process in the context of Italy, one of the largest producers of olive oil and consequently OMW. In particular, the analysis focused on Apulia and Tuscany, the Italian regions with the highest production of olives for oil (5,421,000 and 1,211,380 tons in 2018, respectively [44]). Assuming an OMW/olive oil yield of 6.2 $m^3_{OMW}/ton_{\ olive\ oil}$,[1] the OMW produced in Apulia and Tuscany in 2018 is equal to $0.71 \cdot 10^6$ m^3 and $0.16 \cdot 10^6$ m^3, respectively.

The volumetric production of SwS was estimated equal to $22 \cdot 10^6$ m^3/y for Apulia and $20 \cdot 10^6$ m^3/y for Tuscany on the basis of the following elements: a) the production of sewage sludge solids in Italy is equal to 1,102,000 ton/y;[45] b) since the volumetric sludge production depends on the extent of SwS thickening before the AD process, a specific sewage sludge volumetric production of 5.5 m^3/inhabitant/y was estimated in Italy by applying the average concentration of solids in the SwS fed to the AD process in several WWTPs examined (0.034 ton/m^3).

In the unlikely hypothesis that the OMW produced by different mills dispersed across a given region is uniformly distributed among *all* the SwS digesters present in that region, if the OMW co-AD process is distributed over a 4-month period (about equal to the period of OMW production), the above-reported data of OMW and SwS production result in a volumetric OMW fraction in the feed of the OMW/SwS co-AD process equal to 8.5% for Apulia and 2.3% for Tuscany. In the more reasonable hypothesis that the OMW produced in a given region is concentrated in just a fraction of the total AD capacity of that region (for example 1/4 to 1/3 of the total capacity), the volumetric OMW fraction in the feed would vary in the 25-35% range for Apulia and 6.8-9.1% range for Tuscany. Thus, this analysis indicates that the range of OMW fraction in the feed of the co-AD process tested in this work (5-40%) allows the co-AD of the total OMW production in regions characterized by a high olive oil production, under the assumption that OMW co-AD is concentrated during the 4 months of OMW production and in 1/4-1/3 of the total AD capacity of the region.

In the perspective of a large-scale application of the proposed OMW/SwS co-AD process, a crucial issue to be tackled is represented by the impact of the resulting increase in the flow rate fed to the digesters on the process HRT. According to Montusiewicz and Lebiocka[11], most SwS digesters have a spare capacity that can reach 30%, and that can be exploited to increase the inlet flow rate while maintaining the same HRT. Assuming for example that a SwS digester operates with a 30-day HRT with a 10% spare capacity, an OMW amount corresponding to a 25% volumetric fraction of the total OMW+SwS flow rate (a reasonable value for a strong olive oil producer such as Apulia) can be co-digested by exploiting the spare capacity and reducing the HRT from 30 to 25 days. The results of this work show that a 25% OMW fraction can be effectively co-digested with SwS at a 23-day HRT, and that therefore the above-described scenario is applicable at a large scale in regions characterized by a strong olive oil production, with a significant increase of the amount of methane produced by the AD process. In particular, the application of an incremental CH_4 yield equal to 116 $Nm^3_{CH4}/t_{VS\ fed}$ (Table 3; difference between the Y_{CH4} of the 25% rOMW

reactor and that of the 100% SwS reactor) to the total OMW production and to 1/4 of the SwS production of Apulia results in an additional CH_4 production equal to $1.4 \cdot 10^7$ Nm^3/y.

Cost-benefit analysis of the OMW co-digestion process with and without pre-dephenolization

The CBA was based on the scenario of a 500,000 PE WWTP, that receives 0.2 $m^3/d/PE$,[46] and therefore treats 100,000 m^3/d of municipal wastewater (MWW). If the flowrate of thickened sludge fed to the AD process is equal to 0.6% of the MWW flowrate treated (average ratio of several WWTPs examined in Northern Italy), the digester was assumed to treat 600 m^3/d of SwS. Assuming to feed to the digester an OMW / (OMW + SwS) volumetric ratio equal to 0.25 for a 4-month period, the flowrate of treated OMW is equal to 200 m^3/d. The total OMW treated in 4 months (24,000 m^3) is equal to about 3% of the yearly OMW production of the Apulia region in Italy. Under the above-described assumption of a 10% spare capacity in the digester, OMW co-AD determines an HRT reduction from 30 to 25 days.

In the benchmark scenario of only SwS AD, assuming the VS content of the thickened SwS used in this work (24.5 kg/m^3) and the Y_{CH4} reported in Table 3 for 100% SwS, CH_4 production results equal to 1617 Nm^3/d. Considering an electrical consumption of 311 MWh for mixing during the 4-month period taken into consideration, the net electricity production of the CHP unit results 503 MWh, and the thermal energy production 1028 MWh. As the heating of the digester to 34°C requires 1345 MWh, it is necessary to purchase additional CH_4 for an equivalent of 317 MWh, at a cost of 22,800 €.

In the scenario of only SwS + rOMW co-AD, assuming the VS content of the thickened SwS and rOMW used in this work and the Y_{CH4} reported in Table 3 for 25% rOMW, CH_4 production results equal to 4565 Nm^3/d. Taking into account the electricity required for mixing, rOMW co-AD allows the attainment of an additional net electricity production of about 1450 MWh in comparison to the benchmark scenario. Assuming that this additional energy is used internally in the WWTP, it corresponds to a net saving equal to the purchase cost of the same amount of energy, equal to about 217,500 € at a cost of industrial electricity of 0.15 €/kWh. Furthermore, the OMW tariff paid by the olive mills for the disposal of 200 m^3_{OMW} /d (24000 m^3_{OMW} during the 4-month period considered) ranges between 1,200,000 € (at 50 €/m^3_{OMW}) and 2,400,000 € (at 100 €/m^3_{OMW}). Considering that the thermal energy produced by the CHP unit (2903 MWh) is 60% higher than the amount required to heat the digester, in this scenario there is no need to purchase additional CH_4, which determines an additional saving of 22,800 €. The further potential revenue associated to the excess of thermal energy was not considered, in order to make a prudential assessment of the benefits deriving from rOMW co-AD. Thus, the total additional revenues associated to rOMW co-AD in the existing digester vary in the 1,440,000-2,640,000 € range. Assuming a total cost of MWW treatment equal to 0.65 €/m^3 (average value declared by several WWTP managers in Northern Italy), these additional revenues correspond to an 18-34% reduction of the cost of MWW treatment, during the 4-month OMW season taken into consideration.

In the scenario of only OMW dephenolization followed by SwS + dOMW co-AD, the first part of the CBA was aimed at calculating the market price at which the PC-rich antioxidant product obtained from OMW dephenolization should be sold in order to attain a 6% FRR. To this goal, the first step consisted in the preliminary sizing of the full-scale plant for OMW filtration, PC adsorption / desorption and desorption solvent recovery. On the basis of the results of previous works of PC recovery from OMW by adsorption,[3,5] XAD16N was selected as sorbent resin and ethanol acidified with HCl as desorption solvent. The plant includes the following equipment: a microfiltration unit; a column packed with XAD16N, in which adsorption and desorption cycles are alternated; a rotary dryer, to evaporate ethanol from the PC-rich desorbed product; a condenser, to recover and recycle the ethanol vapor; a cooling tower, to cool down the water exiting from the ethanol condenser; an OMW tank and an ethanol tank; 3 centrifugal pumps. The items that contribute to the plant's operational expenditures (OPEX) are the labor cost (2 hours per day), the period re-integration of ethanol, HCl and water, the periodic replacement and disposal of the sorbent resin (assumed to take place every 3 OMW treatment seasons), the electricity consumption for pumping and the CH_4 consumption for evaporating ethanol in the rotary drier. With regard to the latter, it was assumed to buy additional CH_4 instead of using a fraction of the CH_4 produced by the co-AD process, in order to develop an independent CBA for the PC recovery step. In order to treat 200 m^3/d of OMW, the process was organized in adsorption / desorption cycles of the duration of about 42 h, with each cycle treating 353 m^3_{OMW} and 30 $m^3_{acidified\ ethanol}$. Assuming the average PC concentration of the OMW used in

this study (Table 1), a 95% adsorption yield and an 87 desorption yield,[3,5] the process was estimated to produce during the 4-month OMW treatment period an antioxidant product containing 19730 kg of PCs. The preliminary sizing of the components of the PC recovery plant and the evaluation of the items that contribute to the plant's operational expenditures are reported in Table S4 in Supporting Information, whereas the resulting CAPEX and OPEX values referred to a 20-year operational period are shown in Table S5 in Supporting Information. The resulting price at which the PC-rich final product should be sold in order to attain a 6% FRR, and therefore to generate an attractive investment for the multiutility company in charge of WW management, resulted equal to 8.17 €/kg_{PC}. Considering that the market price of PC-rich antioxidants varies between 250 and 2500 €/kg_{PC},[47] even if the antioxidant product obtained from the above-described plant needs a further refining before being placed in the market, the resulting price for the generation of an attractive business case is considered a realistic one. The net revenues deriving from the sale of the antioxidant product at 8.17 €/kg_{PC}, calculated as (yearly revenues) – (yearly OPEX) – (yearly fraction of the CAPEX) are equal to about 52,000 € for each OMW treatment season.

The CBA relative to the 2nd step of the scenario of OMW dephenolization + dOMW co-AD was based on the approach illustrated above for the rOMW co-AD scenario. The
VS content of dOMW was taken equal to 16.3 kg/m^3, instead of 13.3 kg/m^3 as reported in Table 1, assuming that the 3 kg/m^3 of volatile suspended solids removed in the microfiltration step are sent to the co-AD process. Applying the Y_{CH4} reported in Table 3 for 25% dOMW, CH_4 production resulted equal to 2628 Nm^3/d. Considering the electricity required for mixing, dOMW co-AD determines the attainment of an additional net electricity production of 474 MWh in comparison to the benchmark scenario. The net saving corresponding to the purchase cost of the same amount of energy is equal to about 71,100 €. As in the first scenario, the OMW tariff paid by olive mills for disposing 24000 m^3_{OMW} during the 4-month period ranges between 1,200,000 € (at 50 €/m^3_{OMW}) and 2,400,000 € (at 100 €/m^3_{OMW}). As the thermal energy produced by the CHP unit (1671 MWh) is slightly lower than the amount required to heat the digester (1794 MWh), it is necessary to purchase a small amount of additional CH_4 (123 $MWh_{thermal}$), with a saving of about 13,000 € in comparison to the additional CH_4 required in the benchmark scenario of only SwS AD. Thus, the total additional revenues associated to dOMW co-AD in the existing digester vary in the 1,284,000-2,484,000 € range, corresponding to a 16-32% reduction of the cost of MWW treatment during the 4-month OMW season taken into consideration.

The comparison between the CBA of the two scenarios (rOMW co-AD, or PC recovery + dOMW co-AD) indicates that the benefit for the company in charge of WW management is relevant in both cases. As in both situations the largest fraction of the additional revenue is associated to the OMW disposal tariff paid by the olive mills, the difference between the two scenarios is not considered significant, in relation to the uncertainties that affect this analysis. On the other hand, the scenario of OMW dephenolization requires the construction of an additional plant and the availability of technicians with skills not typical among the WWTP personnel, and it is inherently characterized by an economic uncertainty associated to the actual feasibility of selling at a reasonable price the entire PC-rich antioxidant mixture produced in each season. Furthermore, this scenario does not lead to a relevant improvement of the quality of the digested sludge, as the results of this work show that rOMW / SwS co-AD leads to a significant degradation of the OMW PCs. Therefore, the scenario of rOMW co-AD is considered the best choice for the companies in charge of WW management in Mediterranean countries.

CONCLUSIONS

This study demonstrates that the co-digestion of olive mill wastewater with sewage sludge in a mesophilic single-stage anaerobic process is feasible and leads to a marked increase in the amount of methane obtained from each ton of sewage sludge. The bioreactor fed with 40% raw OMW with a 40-day HRT attained a methane yield of 270 $NL_{CH4}/kg_{VS\ fed}$, 1.5-fold higher than the yield obtained with pure SwS. The co-AD of dephenolized OMW resulted in lower biogas and CH_4 yields, in comparison with raw OMW. The total PC conversion reached 70% when the HRT was increased from 23 to 40 days, indicating that the proposed AD process has a high potential to degrade most of the PCs contained in OMW. An analysis referred to the two Italian regions featuring the highest production of olives for oil showed that the complete co-AD of the produced OMW is applicable at large scale, using the network of existing SwS digesters. The CBA of the scenarios of (i) co-AD of raw OMW and (ii) PC recovery from OMW followed by co-AD of dephenolized

OMW indicated that both scenarios lead to relevant additional revenues for the companies in charge of WW management, corresponding to potential reductions of the cost of municipal WW treatment in the 16-34% range.

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Data availability
Research data underlying this manuscript have been published in the AMS Acta Institutional Research Repository (doi: 10.6092/unibo/amsacta/6407).

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Table 1
Physico-chemical characteristics of the different substrates used in the study, with standard deviations: raw olive mill wastewater (rOMW), dephenolised olive mill wastewater (dOMW), sewage sludge (SwS) and inoculum.
* Data not available.

Parameter	rOMW	dOMW	SwS	Inoculum
TS (*g/L*)	34.7 ± 0.3	21.9 ± 0.1	37.4 ± 0.1	26.1 ± 0.1
VS (*g/L*)	25.5 ± 0.5	13.3 ± 0.3	24.5 ± 0.1	16.6 ± 0.1
VFAs (*g/L*)	8.7 ± 0.1	6.9 ± 0.2	0.4 ± 0.001	*
dCOD (g_{O2}/L)	47.9 ± 0.6	32.5 ± 0.7	0.6 ± 0.01	0.4 ± 0.002
Total BOD_5 (g_{O2}/L)	13 ± 1	8.5 ± 0.9	5.5 ± 0.5	1.1 ± 0.1
PCs (mg_{GA}/L)	1010 ± 40	65 ± 5	7 ± 0.3	*
Reducing sugars ($g_{C6H12O6}/L$)	*	1.7 ± 0.2	*	*
pH	4.3 ± 1	4.5 ± 0.1	6.3 ± 0.01	7.2 ± 0.1
Density (*g/mL*)	1.01 ± 0.01	1.01 ± 0.01	1.01 ± 0.01	*

Table 2

Daily mass flow rate of TS, VS, VFAs, dCOD, PCs and organic loading ratio (OLR) of all reactor feedstocks.

[*] On day 101, the HRT of this reactor was increased to 40 days. On day 120, while maintaining a 40-day HRT, the relative content of OMW in this reactor was increased to 40%. The values in parenthesis are relative to this last period, from day 120 to day 172, with 40% OMW and 40-day HRT.

Daily mass flow rate or OLR	5% rOMW	12% rOMW	18% rOMW	25% (40%) rOMW*	100% rOMW	5% dOMW	12% dOMW	18% dOMW	25% (40%) dOMW*	100% dOMW	100% SwS
TS (*g/day*)	0.82	0.81	0.81	0.92 (0.46)	0.76	0.81	0.78	0.76	0.74 (0.40)	0.49	0.82
VS (*g/day*)	0.54	0.54	0.54	0.60 (0.31)	0.55	0.53	0.51	0.50	0.48 (0.26)	0.30	0.54
VFAs (*g/day*)	0.02	0.03	0.04	0.05 (0.05)	0.19	0.02	0.03	0.03	0.04 (0.04)	0.15	0.01
dCOD (g_{O2}/day)	0.07	0.14	0.21	0.29 (0.26)	1.11	0.05	0.10	0.14	0.19 (0.17)	0.72	0.01
PCs (mg_{GA}/day)	1.30	2.84	4.16	5.70 (5.18)	22.22	0.26	0.35	0.42	0.51 (0.40)	1.43	0.20
OLR ($g_{VS}/L/day$)	1.07	1.07	1.07	1.07 (0.62)	1.09	1.04	1.01	0.98	0.95 (0.55)	0.6	1.07

Table 3
Average biogas and CH_4 yields and production rates obtained in all reactors during the last 10 days of operation, with standard deviations. All data are referred to a 23-day HRT, except for the 40% rOMW and 40% dOMW bioreactors that refer to a 40-day HRT. 100% OMWs biogas and CH_4 yields reported theoretical values are obtained by the linear best fit reported in Fig. 3.
[*] Data referred to the period of operation with a 40-day HRT.
[†] Theoretical yields estimated by means of the linear best fit reported in Fig. 3.

	Biogas and CH_4 yield		Biogas and CH_4 production rate	
	Biogas	CH_4	Biogas	CH_4
	NL/kg$_{VS\ fed}$	*NL/kg$_{VS\ fed}$*	*NL/L/day*	*NL/L/day*
100% SwS	194 ± 13	110 ± 11	0.22 ± 0.01	0.12 ± 0.01
5% rOMW	203 ± 3	120 ± 12	0.25 ± 0.01	0.14 ± 0.02
12% rOMW	239 ± 4	139 ± 14	0.30 ± 0.02	0.17 ± 0.02
18% rOMW	282 ± 3	168 ± 58	0.34 ± 0.01	0.20 ± 0.01
25% rOMW	359 ± 27	226 ± 24	0.41 ± 0.03	0.25 ± 0.03
40% rOMW	457 ± 5 [*]	268 ± 3 [*]	0.31 ± 0.01 [*]	0.17 ± 0.02 [*]
100% rOMW	874 ± 36 [†]	522 ± 30 [†]		
5% dOMW	190 ± 3	113 ± 16	0.24 ± 0.01	0.13 ± 0.02
12% dOMW	219 ± 4	129 ± 12	0.26 ± 0.01	0.15 ± 0.01
18% dOMW	239 ± 4	151 ± 15	0.27 ± 0.01	0.16 ± 0.01
25% dOMW	282 ± 3	179 ± 16	0.31 ± 0.01	0.18 ± 0.02
40% dOMW	413 ± 5 [*]	235 ± 13 [*]	0.15 ± 0.01 [*]	0.08 ± 0.03 [*]
100% dOMW	1027 ± 78 [†]	587 ± 21 [†]		

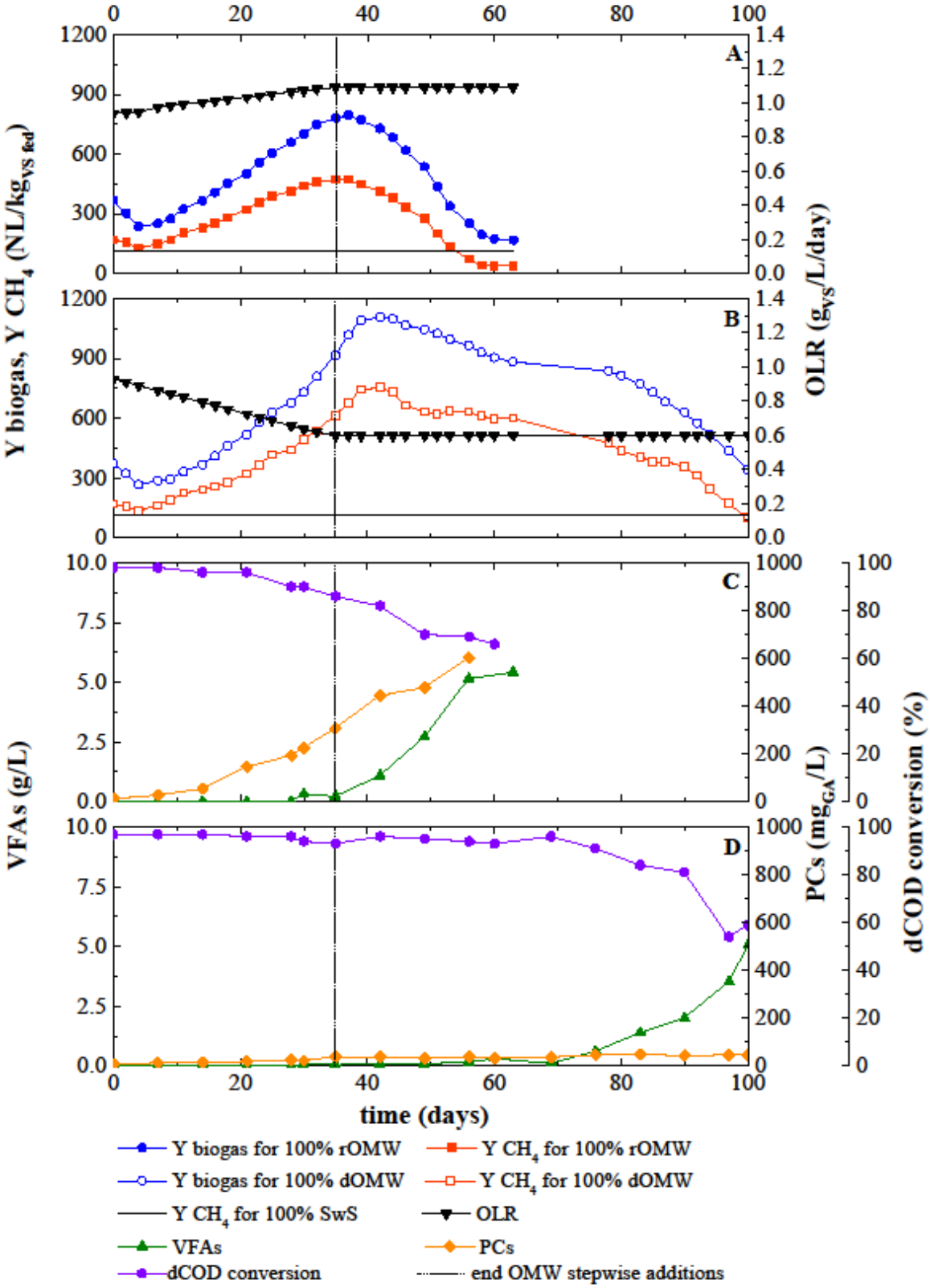

Figure 1. Comparison between the performances of 100% raw OMW (rOMW) and 100% dephenolized OMW (dOMW) reactors. (A): 100% rOMW biogas yield, CH_4 yield and OLR trend over time, (B): 100% dOMW biogas yield, CH_4 yield and OLR trend over time, (C): 100% rOMW VFAs, PCs concentration and dissolved COD conversion versus time time, (D): 100% dOMW VFAs, PCs concentration and dissolved COD conversion versus time.

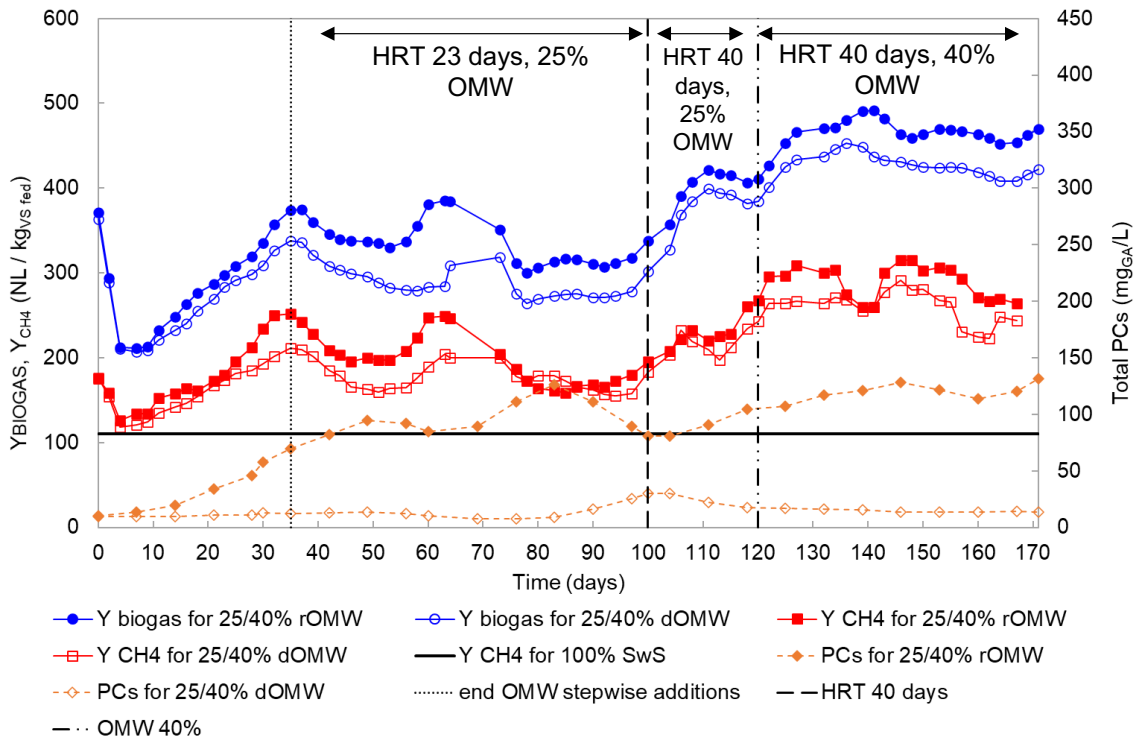

Figure 2. Comparison between the performances achieved by 25/40% raw OMW (rOMW) and 25/40% dephenolized OMW (dOMW) reactors. Biogas and CH_4 yield and PCs concentration versus time.

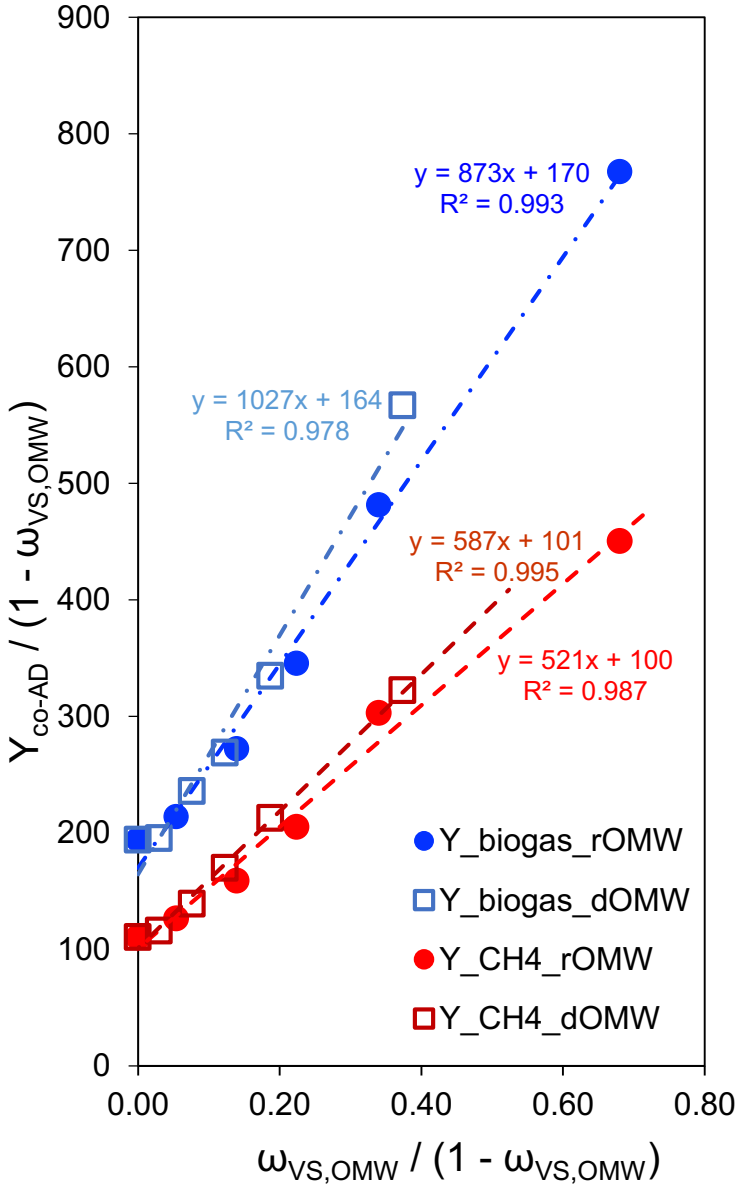

Figure 3. Co-AD biogas and CH_4 yields obtained in the bioreactors fed with different OMW/SwS ratios: experimental data and best-fitting linear regression performed according to Eq. (3). The slope of each linear regression represents the estimate of the biogas or CH_4 yield of pure rOMW or dOMW. $\omega_{VS,OMW}$ indicates the ratio of OMW-derived VS to total (OMW + SwS) VS content in the bioreactor feed.

Development of a continuous-flow anaerobic co-digestion process of olive mill wastewater and municipal sewage sludge

Sara Bovina, Dario Frascari, Alessandro Ragini, Francesco Avolio, GianNicola Scarcella, Davide Pinelli

SUPPORTING INFORMATION

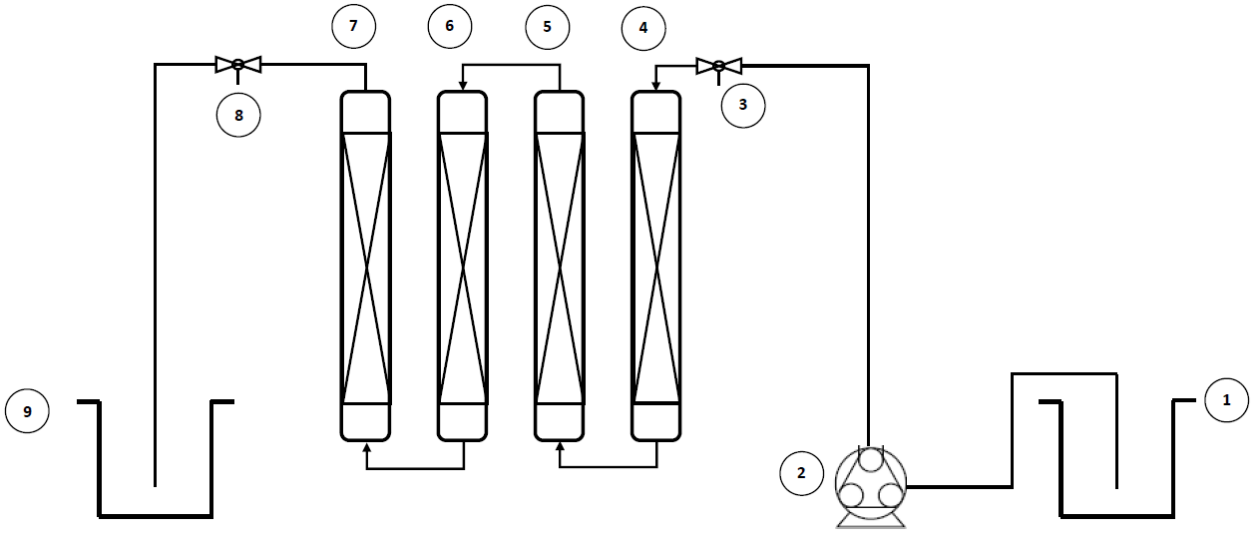

Fig. S1. Flow sheet of the adsorption plant used to produce the dephenolized OMW. 1, raw OMW tank; 2, peristaltic pump; 3, sampling valve for raw OMW; 4, first column; 5, second column; 6, third column; 7, fourth column; 8, sampling valve for dephenolized OMW; 9, tank for dephenolized OMW.

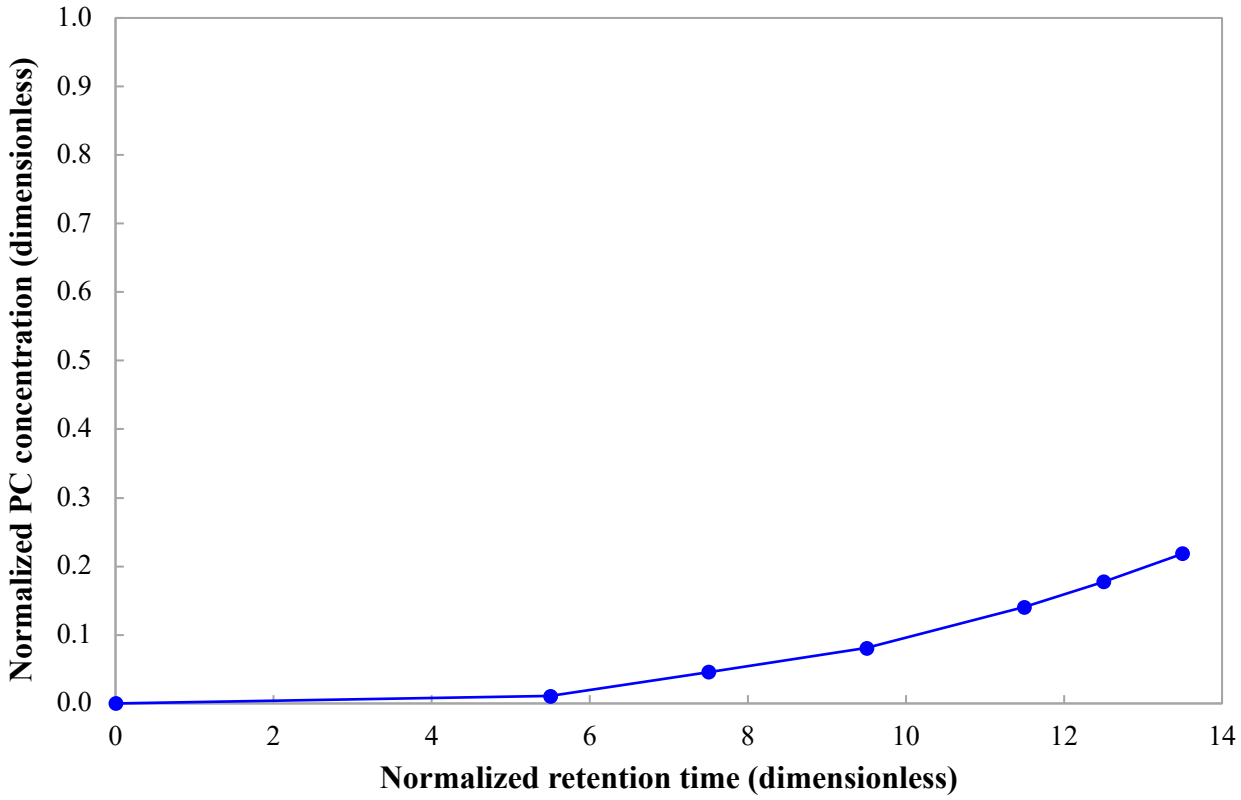

Fig. S2. Normalized phenolic compounds (PC) concentration at the column outlet (PC outlet concentration / PC inlet concentration) versus normalized retention time (actual time/column HRT), during the OMW dephenolization test performed with Amberlite XAD16N.

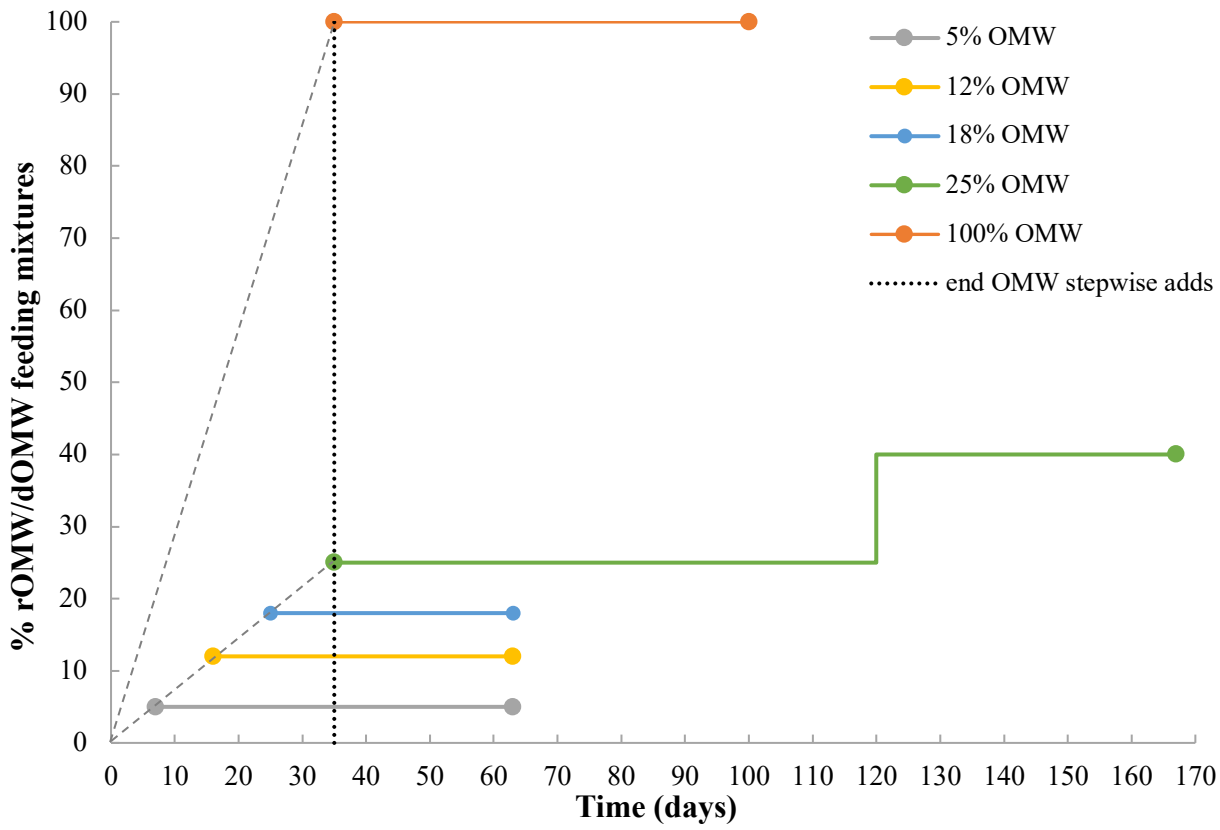

Fig. S3. OMW stepwise volume additions in reactors fed with raw OMW or dephenolized OMW at different OMW/SwS ratios (0.71 % a day) and 100% OMW (2.84 % a day). For all reactors, the incremental gradient lasted 35 days.

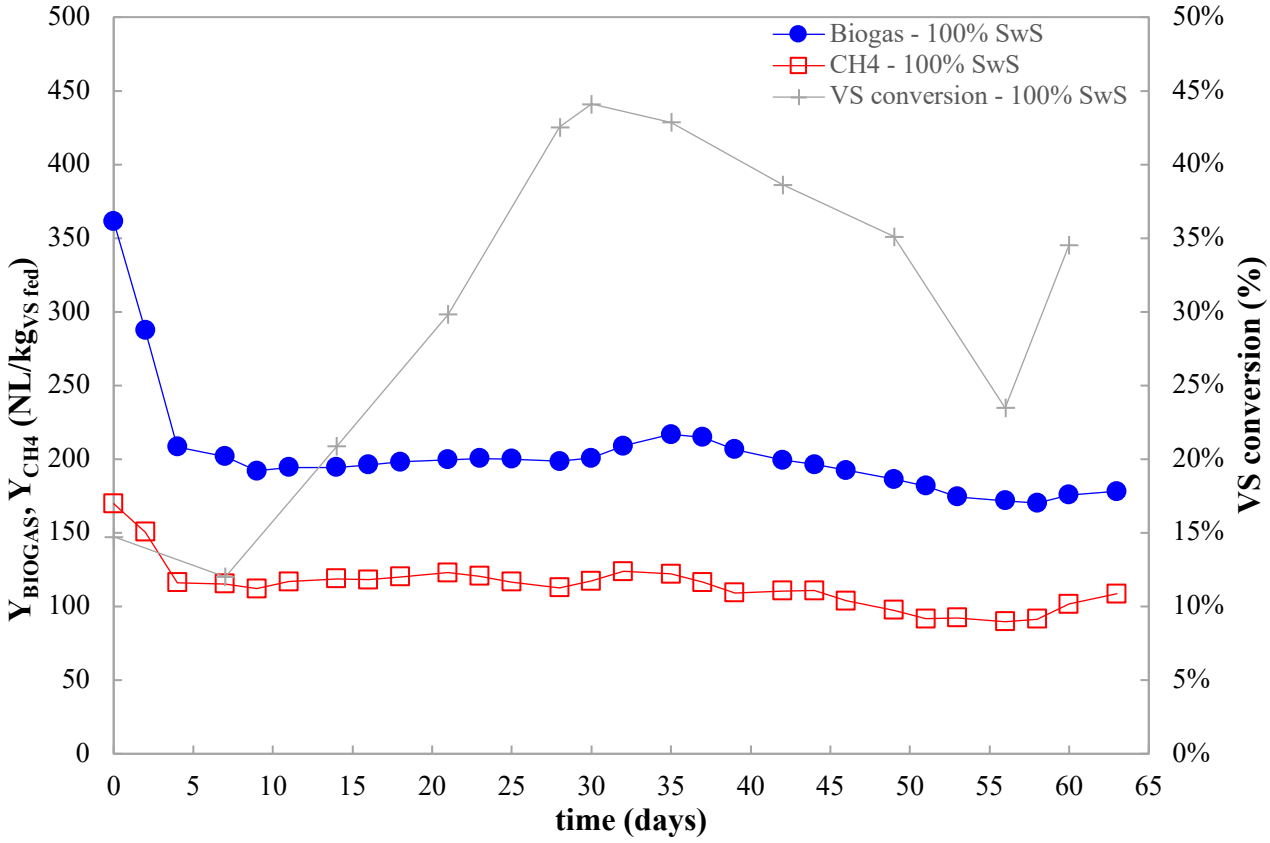

Fig. S4. Bioreactor fed with 100% SwS: biogas yield, methane yield and % volatile solids (VS) conversion trend over time (HRT = 23 d, OLR = 1.1 g_{VS}/L/day).

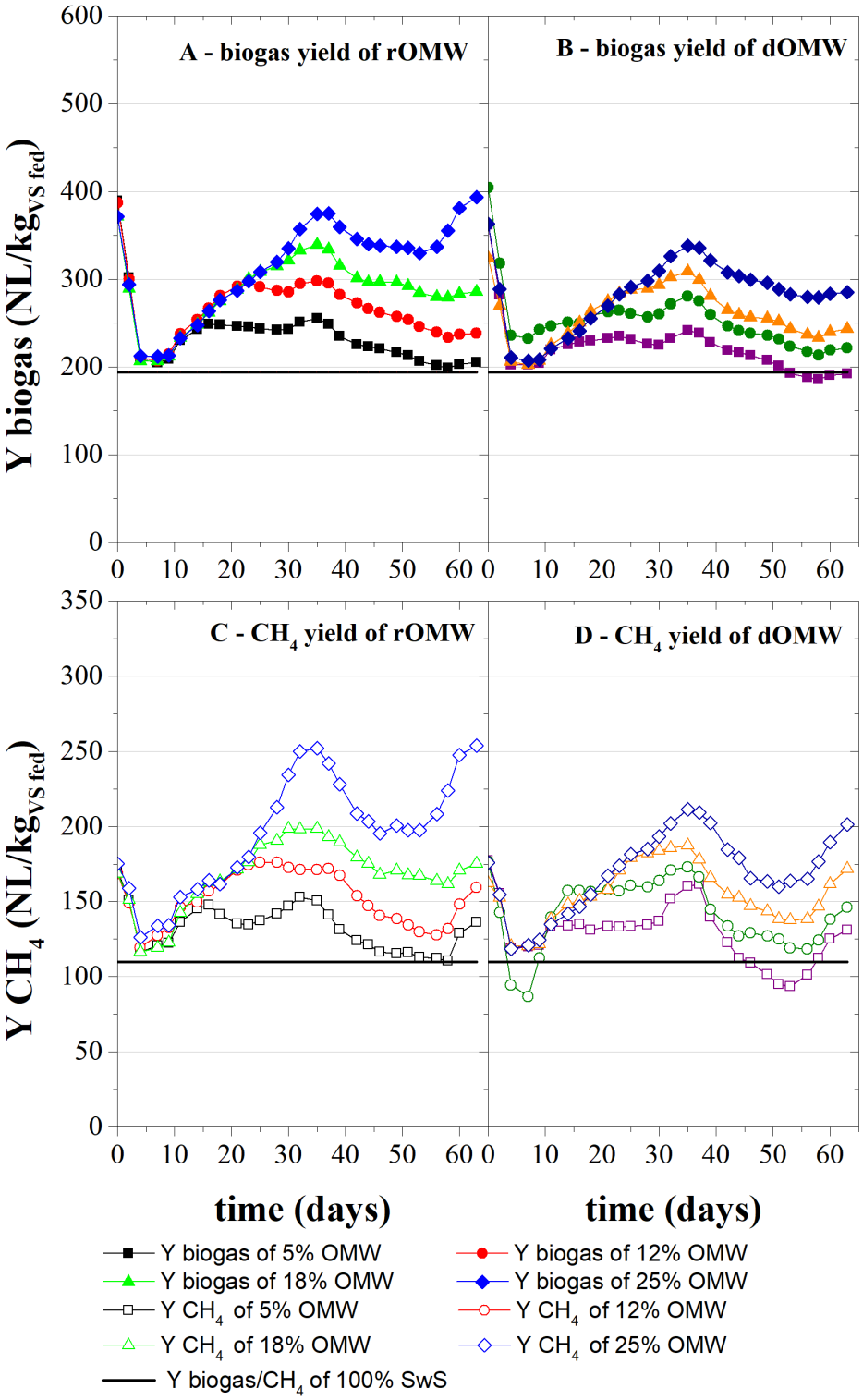

Fig. S5. Comparison between the performances obtained in the bioreactors operated with different OMW/SwS ratios and in the 100% SwS-fed reactor, with a 23-day HRT. (A) and (B): biogas yields; (C) and (D): CH_4 yields. Left graphs: raw OMW (rOMW); right graphs: dephenolized OMW (dOMW).

Table S1: Characteristics of the adsorption/desorption plant and resin used for the continuous breakthrough test for the production of dephenolized OMW.

Parameters	Value	Units
Resin name	Amberlite XAD16N	
Resin type	Macroporous styrene-divinylbenzene copolymer	
Resin beads diameter	0.56 - 0.71	mm
Surface area	800	m^2/g
Pore size	150	Å
Approximate industrial cost	31	€ / L
Bed length single column	50	cm
Total resin bed length	200	cm
Resin bed section	5.8	cm^2
Resin bed volume	1162	mL
Flow rate	30.8	mL/min
Superficial velocity (v_s)	5.31	cm/min
Empy Bed Contact Time	37.7	min
HRT	32.1	min
Pressure	0.1	bar
Temperature OMW fed	14	°C

Table S2. Procedure and assumptions applied in the cost benefit analysis of the OMW co-AD process.

For both the benchmark scenario (AD of only SwS) and the scenarios of rOMW and dOMW co-AD, the daily methane production was calculated by multiplying the inlet flowrate (600 m^3/d of SwS, 200 additional m^3/d of OMW in the co-AD scenarios) by the VS content of each matrix fed to the process and by the CH_4/VS yield estimating in this work for the corresponding scenario, at a 0.25 OMW/(SwS + OMW) ratio.

The total energy theoretically obtainable from the produced methane was calculated on the basis of the methane enthalpy of combustion (891 MJ/kmol). The corresponding amounts of electricity and thermal energy produced by the combined heat and power (CHP) unit were calculated on the basis of the following yields: electrical yield = 0.38, thermal yield = 0.48 (Persson T, Murphy JD, Jannasch AM, Ahern E, Liebetrau J, Trommler M, Toy-Ama J, A perspective on the potential role of biogas in smart energy grids. International Energy Agency Task 37, ISBN 978-1-910154-13-7 (2014); Kaparaju P, Rintala J, Generation of heat and power from biogas for stationary applications: boilers, gas engines and turbines, combined heat and power (CHP) plants and fuel cells. In Wellinger A, Murphy J, Baxter D, editors, The biogas handbook: science, pro-duction and applications. Woodhead Publishing series in energy, number 52, ISBN 978-0-85709-498-8 (2013)).

The amount of thermal energy required to heat the digester at 34°C was approximately taken equal to the amount of energy required to heat the digester feed (assumed equal to water in terms of thermal properties) from 18°C to 34°C.

In the scenarios that require to purchase additional methane to heat the digester, the cost of natural gas was taken equal to 0.072 €/kWh (https://ec.europa.eu/eurostat/statistics-explained/index.php/Natural_gas_price_statistics; accessed on September 1, 2020; average value in the European Union).

Table S3. Procedure and assumptions applied in the cost benefit analysis of the process of OMW dephenolization followed by dOMW co-AD with SwS.

The adsorption / desorption process for PC removal from OMW was designed on the basis of the following elements, partly based on previous works of PC adsorption from OMW (Frascari D, Bacca AEM, Zama F, Bertin L, Fava F, Pinelli D, Olive mill wastewater valorisation through phenolic compounds adsorption in a continuous flow column. Chem Eng J 283:293–303 (2016); Frascari D, Molina Bacca AE, Wardenaar T, Oertlé E, Pinelli D, Continuous flow adsorption of phenolic compounds from olive mill wastewater with resin XAD16N: life cycle assessment, cost–benefit analysis and process optimization. J Chem Technol Biotechnol 94:1968–81 (2019); Frascari D, Rubertelli G, Arous F, Ragini A, Bresciani L, Arzu A, Pinelli D, Valorisation of olive mill wastewater by phenolic compounds adsorption: Development and application of a procedure for adsorbent selection. Chem Eng J 360:124–38 (2019)):

- OMW flow rate to be treated: 200 m^3/d
- Hydraulic retention time during the adsorption step: 0.56 h
- OMW superficial velocity during the adsorption step: 2.5 m/h
- PC adsorption yield: 0.93
- PC desorption yield: 0.87
- Resin utilization efficiency: 0.45
- Solvent (ethanol acidified with HCl 0.0005 M) superficial velocity during the desorption step: 1.1 m/h

The dry mass of resin XAD16N to be loaded in the plant was calculated as (volume of resin bed) · (bulk density of the packed resin).

The duration of a single adsorption/desorption cycle was calculated as the sum of the duration of the following three steps: i) adsorption, ii) desorption and iii) rinsing with water.

The desorption process was articulated in two steps: the 1st one was conducted with 100% acidified ethanol, and required a total volume equal to 2 bed volumes of resin; the 2nd one was conducted with 50% acidified ethanol and 50% water, and required a total volume equal to 3 bed volumes of resin.

The resulting preliminary sizing of the components of the PC recovery plant and the evaluation of the items that contribute to the plant's operational expenditures are reported in Table S4 in Supporting Information.

The procedure and assumptions applied in the cost benefit analysis of the process of dOMW co-AD with SwS are equal to those illustrated in Table S2 for the rOMW co-AD process.

Table S4. Preliminary sizing of the components of the PC recovery plant and evaluation of the items that contribute to the plant's operational expenditures.

	Amount	**Unit**
Infrastructure		
Microfiltration unit (flow rate 200 m^3/d)	1	unit
Adsorption / desorption column (diameter 2.35 m, resin bed height 2.00 m)	1	unit
Desorption solvent evaporation / recovery unit (rotary dryer; 25 m^3/d of solvent to be evaporated)	1	unit
Desorption solvent and OMW storage tanks	2	units
Gas Boiler (340 kW)	1	unit
Ethanol recovery condenser (9.4 m^2; 29.3 m^3/h of cooling water flowing in the condenser)	1	unit
Cooling tower (0.5 m^3/h of water to be evaporated)	1	unit
Centrifugal pumps (7-12 m^3/h)	2	pumps
Operation		
Ethanol periodic re-integration[a]	22.2	m^3/season
HCl periodic re-integration	38	kg/season
Resin XAD16N periodic disposal and re-integration[b]	712	kg/season
Water periodic re-integration	1857	m^3/season
Electricity for pumping[c]	6,200	kWh/season
Heat for ethanol evaporation	980 100	kWh/season
PC mass produced	19,700	kg_{PC}/season

[a] The total ethanol volume to be re-integrated resulted from the sum of two contributions: ethanol lost with the solid PC-rich product (assuming a residual 0.5% ethanol mass fraction in the solid product) and ethanol lost in the inert purge in the condenser.

[b] Assuming that the resin load is removed and re-loaded every 3 OMW treatment seasons.

[c] Evaluated on the basis of a 0.40 bar pressure loss in the adsorption step, 0.65 bar pressure loss in the desorption step, 1.15 kWh/m^3_{OMW} consumption for microfiltration.

Table S5. Absolute value and relative contribution of the single CAPEX and OPEX elements to the total cost of the PC adsorption / desorption process, relatively to the 20-year period taken in consideration

Type	**Cost item**	**Total cost over reference period (NPV @ 4% discount rate):**	**% of total cost**
CAPEX	Rotary dryer with gas boiler for desorption solvent evaporation	€ 201 823	10.0%
	Adsorption / desorption column, storage tanks, pumps	€ 194 742	9.6%
	Condenser for ethanol recovery , with cooling tower	€ 144 463	7.1%
	Microfiltration unit	€ 57 360	2.8%
OPEX	Heat for ethanol evaporation	€ 901 080	44.5%
	Resin XAD16N periodic disposal and re-integration	€ 289 890	14.3%
	Desorption solvent periodic re-integration (ethanol + HCl)	€ 102 051	5.0%
	Labor costs (plant control + periodic maintenance)	€ 85 108	4.2%
	Water periodic re-integration	€ 37 421	1.8%
	Electricity for pumping	€ 12 217	0.6%