BIOMETHANIZATION OF OLIVE MILL SOLID WASTE AFTER PHENOLS RECOVERY THROUGH LOW-TEMPERATURE THERMAL PRE- TREATMENT

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Abstract

Due to the high polluting potential of Olive Mill Solid Waste (OMSW), it is necessary to develop an economical and environmental-friendly sustainable management method. OMSW anaerobic digestion has been shown to be an interesting management alternative, although it should be optimized to improve its economic viability. In the present study, low-temperature thermal pre-treatment of OMSW is proposed to allow the extraction of high added-value compounds, such as phenols, and to enhance the subsequent biomethanization of the substrate. OMSW low-temperature thermal pre-treatment facilitated the separation of a solid phase, where most of organic compounds remained, and a liquid phase, where most of phenolic compounds were concentrated. Hydroxytyrosol presented the highest concentration of the measured individual phenols in the liquid phase, i.e. 1034 ± 22 mg/L. Anaerobic digestion of OMSW and the

different pre-treated phases and mixtures operated under stable conditions, except the biomethanization of the liquid phase, which was mainly inhibited by the high phenols content. Low-temperature thermal pre-treatment allows obtaining an improvement on biodegradability and methane production up to 37% and 34%, respectively. The proposed economic assessment showed that the combination of low-temperature pre-treatment, phenols recovery and the subsequent biomethanization of the substrates was the most attractive treatment option. This management option could reach economic benefit of €0.845/kg OMSW, i.e. twenty times higher than only energy recovery.

Keywords:

Phenols recovery; Methane production rate; Improved anaerobic digestion; Olive Mill Solid Waste; Economic assessment; Thermal Pre-treatment

1. Introduction

The two-phases olive oil extraction process is the most important technology for olive oil production. In this technology, the olive paste is separated into two-phases: olive oil and wet pomace or olive mill solid waste (OMSW). The OMSW is a semi-solid by-product composed by olive husk, olive pulp and olive vegetation water, which is usually reprocessed to further extract the residual oil increasing oil yields (Demerche et al., 2013). OMSW has a high organic matter concentration, which results in an elevated polluting load (Hanandeh, 2015). The large volumes of OMSW generated, around 2-4 millions of tons per year only in Spain, pose important environmental problems such as aquifer contamination, eutrophication, undesirable smells, etc. (Tortosa et al., 2012 and 2015). The management of OMSW presents several challenges caused by its high organic content and the presence of lignocellulosic and phenolic compounds. Use of bioprocesses for OMSW treatment is limited because of the presence of forehand mentioned lignocellulosic

and phenolic compounds (Rodríguez-Gutierrez et al., 2012). Most of these phenolic compounds are very interesting for industrial application due to its high bioactive properties as e.g. antioxidants (García et al., 2016). During olive oil processing most of these phenols remain in the OMSW (García et al., 2016). The extraction and recovery of phenolic compounds from OMSW has a double benefit: In one hand, the detoxification of the OMSW and, on the other hand, the potential utilization of these compounds as functional ingredients in foods or cosmetics or for pharmacological applications given their excellent antioxidant properties.

Anaerobic digestion of solid waste is an interesting alternative for their treatment due to the excellent waste stabilization and high energy recovery. Hydrolysis of organic waste is often the rate-limiting step in anaerobic processes (Wang et al., 2006). Furthermore, the presence of important concentrations of phenolic, lignocellulosic and other aromatic compounds difficult and impair anaerobic degradation (Borja et al., 2006).

In order to improve solid waste digestibility thermal pre-treatments are often used.

Thermal pre-treatments are those where biomass or complex substrate are solubilized by applying heat. Their performance may be influenced by both temperature and exposure time. However, temperature seems to be the most influencing factor on biomass disintegration and anaerobic biodegradability (Jain et al., 2015). Temperatures ranging from 60 °C to 180 °C are generally used for thermal pre-treatments. The optimal temperature range depends on the substrate characteristics, although high temperature pre-treatments are the most commonly proposed (Carrere et al., 2010). High-temperature pre-treatment entails huge energy consumption and high safety and control procedures, which incurs high costs and largely offset the overall benefit of this pre-treatment (Liao et al., 2016). In order to overcome these drawbacks, low-temperature thermal pre-treatment (50-90 °C) could be an interesting alternative. Low-temperature thermal pre-treatments have

been shown to promote protein solubilization and to increase particulate carbohydrates removal, inducing the deflocculating of macromolecules (Jain et al., 2015). Nges and Liu (2009) reported an improvement of methane production by 11% after 48 h pre-treatment of sludge at 50 °C. Ferrer et al. (2008) reported an improvement of methane production by 30-50% after 9 h thermal pre-treatment of sludge at 70 °C. Low-temperature (75-95 °C) thermal pre-treatment was demonstrated to be effective at enhancing microalgae anaerobic biodegradability, increasing the methane yield by 70% with respect to non-pretreated biomass (Passos and Ferrer, 2014).

The aim of this research was to evaluate the effect of low-temperature thermal pre-treatment on OMSW. A phenols recovery process and the effects on the subsequent anaerobic digestion process were evaluated. Additionally, an economical assessment was developed to compare the viability of the different treatment options described in the present research.

2. Material and Methods

2.1 Olive Mill Solid Waste and anaerobic inoculum

Olive mill solid waste (OMSW) was obtained from the centralized management plant “Oleícola El Tejar” located in Marchena (Seville), Spain. Previously to its characterization and use, OMSW was preserved under freeze conditions (-18° C) to avoid undesirable fermentation processes.

The anaerobic inoculum was obtained from a full-scale anaerobic reactor treating sewage sludge from “COPERO” wastewater treatment plant (Seville, Spain). The main characteristics of the anaerobic inoculum where: pH= 7.9 ± 0.2 ; VS= $20,765 \pm 310$ mg/kg; ammoniacal nitrogen= 1950 ± 70 mg/kg.

2.2 *Low-temperature thermal pre-treatment and phenol recovery system*

Low-temperature thermal pre-treatment was carried out in a 100-L reactor, which can operate at temperatures of between 50 and 190 °C by direct or indirect heating, and at a maximum pressure of 1.2 MPa. OMSW was loaded into the reactor and treated for 90 min at a fixed temperature of 65 °C by indirect heating at atmosphere pressure. Then, pre-treated material was centrifuged at 4700 g (Comteifa, S.L., Barcelona, Spain). The centrifugation allowed the separation of pre-treated OMSW into a solid phase (SP) and a liquid phase (LP), in a ratio of 63:37, in VS, respectively. Samples were stored at 4°C before characterization.

Phenols were removed using an industrial chromatographic system under patent (WO 2013/007850A1) in order to reproduce the real effluent without the major part of these compounds. The obtaining of a dephenolized liquid phase (DLP) by extraction of phenols from LP did not entail a decrease in the sample volume during the process.

2.3 *Anaerobic digestion experimental procedure*

The anaerobic digestibility of untreated OMSW and the different pre-treated phases was evaluated by biochemical methane potential (BMP) tests. Additionally, the mixtures SP:LP and SP:DLP, in a ratio 63:37, in VS, were also assayed. BMP tests were performed in 250 mL Erlenmeyer flasks at 35 °C, i.e. mesophilic conditions, using a working volume of 220 mL. Mechanical stirring was provided, at 300 rpm, to facilitate an adequate mass transfer between inoculum and substrate. In all cases, the BMP reactors were loaded with an inoculum to substrate ratio of 2, based on volatile solids. All these assays were carried out in triplicate. BMP reactors were sealed and the headspace of each flask was flushed with nitrogen at the beginning of the assay. The produced biogas was passed through a 2 N NaOH solution to capture CO₂, the

remaining gas was assumed to be methane. The BMP tests were carried out the time interval required to exhaust gas production and VS removal (24-day period). Methane production was monitored daily throughout the process.

2.4 Data fitting

The Transference Function (TF) model was applied to fit the experimental data of methane production during BMP tests (eq. 1). TF model was successfully applied by several authors for biomethanization of OWSM and other organic wastes (Donoso-Bravo et al. 2010; Li et al. 2012; Pinto-Ibieta et al., 2016) using the following expression:

$$G = G_{max} * \left(1 - \exp \left[-\frac{R_{max}(t-\gamma)}{G_{max}} \right] \right) \quad (1)$$

where G (mL CH₄/g VS_{added}) is the cumulative specific methane production, G_{max} (mL CH₄/g VS_{added}) is the ultimate methane production, R_{max} is the maximum methane production rate (mL CH₄/(g VS_{added}*d)), t (d) is the time and γ (d) is the lag time.

Error (%), r^2 and standard error of estimate (σ_{est}) were calculated to evaluate the goodness-of-fit and the accuracy of the results. Error was defined as the percentage difference between the experimental and the predicted methane yield coefficient. Additionally, t_{80} (d) was defined as the time required to producing the 80% of the final accumulated methane for each BMP. The kinetic parameters for each experiment and mathematical adjustment were determined numerically from the experimental data obtained by non-linear regression using the software Sigma-Plot (version 10.0).

2.5 Chemical analyses

The following chemical analyses were used for the characterization of the inoculum and OMSW as well as for the effluents from each BMP test at the end of the process. The concentration of total solids (TS; g/kg), total volatile solids (VS; g/kg), alkalinity (mg CaCO₃/L); conductivity (mS/cm) and pH were carried out according to the recommendations of the Standard Methods of APHA (2005). Specifically, TS and VS were determined according to the Standard methods 2540B and 2540E, respectively. Alkalinity as determined by pH titration to 4.3. Chemical Oxygen Demand (COD; g/kg) was determined using the method described by Raposo et al. (2008), while soluble COD was determined by the closed digestion and the colorimetric standard method 5220D. Total phenols were quantified by spectrophotometry with a calibration curve of gallic acid through the Folin-Ciocalteu method, after an extraction with a methanol/water solution (80:20) (García et al. 2016). Soluble phenols (mg/L) were quantified by the same procedure after filtration through a Millipore 0.45 µm filter (Albet GF 47mm, Dassel, Germany). Ammoniacal nitrogen (mg/L) was also determined from filtered samples by spectrophotometry at 635 nm. pH was analyzed using a pH-meter model Crison 20 Basic. Total carbohydrates (mg/L) were determined according to the colorimetric method described by Bellou and Aggelis (2013) by using UV/Vis spectrophotometer (DU 730, Beckman Coulter, USA) at 632 nm.

2.6 Analysis of individual phenols

Phenols were quantified using Hewlett-Packard 1100 liquid chromatography system with a C-18 column (Mediterranea SEA 18, Teknokroma, 250 mm x 4.6 mm, i.d. 5 µm) and diode array detector (DAD, the wavelengths used for quantification were 254, 280, and 340 nm) with Rheodyne injection valves (20 µL loop). The mobile phase was Milli-Q water acidified with 0.01 % trichloroacetic acid and acetonitrile (A) utilizing the following gradient over a total run time of 55 min: 95 % A initially, 75 % A in 30 min,

50 % A in 45 min, 0 % A in 47 min, 75 % A in 95 min, and 95 % A in 52 min until completion of the run. Quantification was carried out by integration of the peaks at different wavelengths in function of the compounds, with reference to calibrations made using external standards.

Hydroxymethylfurfural (HMF), furfural and trichloroacetic acid were obtained from Sigma-Aldrich (Deisenhofer, Germany). Hydroxytyrosol was obtained from Extrasynthese (Lyon Nord, Geney, France). Tyrosol was obtained from Fluka (Buchs, Switzerland). HPLC-grade acetonitrile was purchased from Merck (Darmstadt, Germany) and ultrapure water was obtained using a Milli-Q water system (Millipore, Milford, MA, USA).

3. Results and discussion

3.1 Effect of low-temperature thermal pre-treatment on the substrate

A low-temperature pre-treatment, carried out at 65°C during 90 min, could allow separation of SP and LP, as well as to concentrate the phenolic compounds concentration in the LP. Table 1 shows the physicochemical characterization of untreated OMSW and the different phases after carrying out the low-temperature thermal pre-treatment. Most of organic compounds remained in the SP, i.e. around 88% of VS and 88% of COD from OMSW. Soluble compounds were mainly displaced to the LP, where the sCOD/COD ratio increased from 0.17 g sCOD/COD for OMSW to 0.39 and 0.61 g sCOD/COD for LP and DLP, respectively. The increase of sCOD/COD ratio cannot be related to COD solubilization as the sum of sCOD of SP and LP was only 4% higher than the sCOD for OMSW. According to Table 1, extraction by industrial chromatographic system resulted in a decrease of COD concentration in the DLP, i.e. around 39% of VS compared to LP (Table 1). The slight decrease of sCOD could

correspond to the retention of phenolic compounds, which varied from 3.56 ± 0.14 g gallic acid/L to 2.40 ± 0.17 g gallic acid/L.

HPLC was used to determine the variations in the concentration of individual phenolic compounds. According to Table 2, most of individual phenolic compounds were mainly displaced to LP after low-temperature thermal pre-treatment. Among the different measured phenolic compounds, hydroxytyrosol is considered the main active ingredient of OMSW due to its powerful antioxidant activity and therapeutic benefits (Ciriminna et al., 2016; Visioli et al., 1998). However, Luteolin and Luteolin-7-O-glucuronide were retained in SP, probably due to their high molecular mass, which difficult their solubilization. In the subsequent industrial chromatographic process, hydrotyrosol was removed from DLP in a high percentage, around 96.3%. The other measured individual phenolic compounds were extracted in percentages higher than 70%, with the exception of 3,4-Dihydroxyphenylglycol (DHPG) and hydroxytyrosol 4- β -D-Glucoside, which only were retained 59.7% and 13.2%, respectively. Decrease of the sum of measured individual phenols from LP to DLP was in the same order of magnitude than the decrease of total phenols from LP to DLP (Table 2). Therefore, analysed individual phenolic compounds were the main species obtained in the extraction process.

3.2 Stability of the anaerobic process, biodegradability and inhibitory compounds

Anaerobic digestion has been proposed to obtain a close-loop process, given that it allows suppling energy for the phenols extraction as well as to stabilize the organic matter to avoid environmental risks. BMP tests were employed to evaluate the behavior of the biomethanization process, biodegradability of the substrates and their potential as energy sources. The stability of the process was evaluated by monitoring the pH and alkalinity at the end of each BMP test. The mean values of these variables are graphed

in Figure 1. Most of pH values remained within the recommended limits for the methanogenic activity, i.e. 7.3-7.8 (Wheatley, 1990), although mean pH values for LP were in the limit of this range. Alkalinity presented a mean value of 7562 ± 431 mg CaCO_3/L for the different BMP tests. Acetic acid was not detected at the end of the BMP tests for the different substrates and mixtures (Table 3). Therefore, it could be ensured that the acidification of the different BMP tests was not occurred. The concentrations of ammonia nitrogen, which was mainly provided by the inoculum, clearly remained under the limits described as inhibitory for the different BMP tests at the working pH (Rajagopal et al., 2013). In the LP, the high concentration of sCOD at the end of the experimental time was in line with the low biodegradation of the substrate, whereas the other phases and mixtures presented final concentrations of sCOD 50% lower at least (Table 3). Total carbohydrates were largely degraded, reaching removal efficiencies higher than 85% in the most cases. In the SP, total carbohydrate final concentration was 36 ± 6 mg/L, which was in the same range than the total carbohydrates concentration at the end of the other BMP tests (Table 3).

Table 3 also shows the mean values of biodegradability, which were calculated from methane production. As can be seen, biomethanization of LP entailed a marked decrease in the biodegradability with respect to the untreated OMSW, i.e. around 57% lower. The decrease could be related to the presence of some phenolic compounds in the LP given that, after the chromatographic extraction, DLP showed a biodegradability value slightly higher than that for OMSW. The main difference between LP and DLP is the much higher concentration of phenols in LP compared to DLP. Therefore, anaerobic digestion inhibition in LP can be attributed to phenols concentration. Co-digestion of pre-treated phases resulted in an improvement of the biodegradability up to 37%. This enhancement could be a consequence of deflocculating of macromolecules, as well as

degradation of complex molecules (Jain et al., 2015; Prorot et al., 2011). Co-digestion SP:LP allowed the dilution of the possible inhibitory compounds in LP, avoiding the negative effects determined in the individual biomethanization of LP (Chen et al., 2008).

Table 4 shows the soluble phenols and individual phenolic compounds concentrations at the end of the BMP tests. The removal phenol efficiency on LP was significantly lower than that determined for untreated OMSW and the other phases and mixtures (Table 4). The main difference between LP and the other phases and mixtures resided in the markedly higher concentrations of hydroxytyrosol, tyrosol and DHPG (Table 2). Therefore, these compounds, and their interactions, could be the main responsible of the inhibition of the biomethanization of LP. The other measured individual phenols were not considered as potential inhibitors due to their minority relevance in the characterization of the substrates and their concentrations at the end of the BMP tests (Table 2 and Table 4). Anaerobic digestion inhibition caused by these minority relevant phenols has been described at much higher concentrations that the reached at the present study (Borja et al., 1996 and 1997).

It is remarkable the higher concentration of DHPG at the end of the BMP tests of DLP compared to its value after the BMP of the LP (Table 4). The pre-treatment enhances the hydrolysis of part of the cell wall, in which phenols are linked, releasing soluble fiber with phenols from OMSW, like phenolic glucosides, making them more bioavailable for the microorganisms (Rubio-Senent et al. 2013). The effect of the low-temperature thermal pre-treatment on the cell walls was the same for both LP and DLP phases. Therefore, the higher solubilization of DHPG on DLP respect LP could correspond to a higher bacterial degradation in the biomethanization of DLP that helps to release this alcoholic phenol. DHPG presents a high economic potential due to its

anti-oxidant activity, which could be even higher than for hydroxytyroxol (Rodriguez et al., 2007). Further studies are highly recommended to determine the suitability of solubilization and recovery of DHPG through anaerobic digestion.

3.3 Kinetic study and methane production rate

Figures 2A and 2B show the mean values of the accumulated methane productions during the experimental time for the different substrates and mixtures. For most cases, the methane production increased after a short lag phase up to achieve a maximum value. LP presented a low and unusual methane production, which clearly corresponds to an inhibition process, in line with the results described previously.

Table 5 summarized the parameters obtained from the application of TF to the experimental data showed in Figures 2A and 2B, as well as the values of r^2 , Error (%) and standard error of estimate (σ_{est}) to evaluate the goodness-of-fit. r^2 values were higher than 0.98 in all cases, except for LP, which was 0.86 (Table 5). Likewise, Error and σ_{est} , with similar low values, also indicated a good fit of the experimental data to the proposed model, even for LP.

Untreated OMSW reached a G_{max} value of 264 ± 1 mL CH₄/g VS (Table 5). This value is lower than the value described by Pinto-Ibieta et al. (2016), which reported a G_{max} value of 352 ± 31 mL CH₄/g VS for OMSW at similar conditions. The difference could be explained because the high presence of olive stones in the substrate used in the present study, which is mainly composed by hard to degrade compounds such as lignin (Borja et al., 2006). SP showed a very similar G_{max} with respect to OMSW, whereas the biomethanization of LP resulted in a marked decrease of G_{max} , i.e. around 42% lower (Table 5). Extraction of phenols allowed the improvement of G_{max} 24% and 114% comparing to OMSW and LP, respectively (Table 5). Both co-digestion processes

markedly improved G_{max} with respect to OMSW, reaching improvements of around 34% and 22% for SP:LP and SP:DLP mixtures, respectively (Table 5). Ferrer et al. (2008) described a similar enhancement on biogas production in the anaerobic digestion of sludge by thermal sludge pre-treatment, at 70°C and 9 h. Phenols could be considered as the main inhibitory compounds given that the reduction of its concentration from LP by extraction or co-digestion allowed significant improvements. By contrast, no increase in methane yields were observed in BMP tests of a mixture of olive husks, olive mill wastewater and dairy wastewater previously pre-treated at 134 °C during 20 minutes compared to the untreated mixture (Gianico et al. 2013).

According to Table 5, the highest R_{max} was determined for OMSW, which reached a value of 107 ± 2 mL CH₄/(g VS·d). Low-temperature thermal pre-treatment resulted in a decrease of R_{max} in all cases. LP showed the lowest R_{max} , which only reached a value of 9 ± 1 mL CH₄/(g VS·d). This fall was in line with the poor biomethanization of LP and could be a consequence of the high concentration of phenols presented in this fraction, as was previously described by Borja et al. (1997). The decrease in R_{max} in the different pre-treated phases is a good indication that compounds in sCOD after low-temperature thermal pre-treatment might have a lower initial availability for its biodegradation, although the total biodegradability was higher as shown by the G_{max} values (Table 5). According to t_{80} values, OMSW is the most interesting option for energy recovery given that the time required to produce the 80% of methane was clearly lower than that after carried out the low-temperature thermal pre-treatment. Nevertheless, the proposed soft thermal pre-treatment could be interesting if the process focus on recovery of phenols and the stabilization of organic wastes, given the associated enhancement on biodegradability, rather than energy production.

3.4 Economic assessment

The following economic assessment was proposed to compare the viability of the different treatment options described in the present study. The net benefit of the OMSW management was defined as the balance between benefits, i.e. energy improvement and phenols sale value, and costs, i.e. pre-treatment and anaerobic digestion energy requirement and phenols extraction costs. This balance was made by adopting the following assumptions:

- 0.10 kg of diesel was consumed per kg of pre-treated OMSW under the experimental conditions tested, with a diesel calorific power of 10,276 kcal/kg.
- Energy self-supply for anaerobic digestion reached 50% of energy generated by the system (Angelidaki et al., 2006; Serrano et al., 2014).
- Methane production of each substrate or mixture was estimated from G_{max} values, whereas calorific power of methane was considered as 8.555 kcal/L (Wheatley, 1990).
- The price of electricity was fixed in €0.12/kWh (Goerten, 2013).
- Hydroxytyrosol was considered as the phenol which could be valorized according to its higher concentration and economic interest.
- Extraction cost for phenols were fixed in €50/kg of extract, including the price of centrifugation of pre-treated OMSW as well as the chromatographic extraction (Ciriminna et al., 2016).
- Sale price for hydroxytyrosol was considered €520/kg of extract (Ciriminna et al., 2016).

The estimated economic assessments of the different management alternatives are summarized in Table 6. The proposed economic assessment is considered as an approach to compare the different management options in the defined scenario.

As can be seen in Table 6, anaerobic digestion of OMSW without pre-treatment could be the most interesting option if phenols recovery was not carried out, with a net benefit of €0.040/kg OMSW. Pre-treatment without phenols recovery entailed a marked decrease on benefits, reaching only a negative benefit of €-0.023/kg OMSW for the co-digestion of SP:LP. Treatment of OMSW without pre-treatment for only energy valorization would be the most recommended option due to the high net benefits and the high R_{max} value. However, the high value of the extracted hydroxytyrosol made much more interesting the phenols recovery strategy than only energy valorization. Concretely, extraction of phenols, followed of the co-digestion of SP:DLP mixture reached a net benefit of €0.845/kg OMSW, i.e. more than twenty times higher than that only for energy production. For further industrial implementation, some other aspects should be also considered in order to evaluate the real economic feasibility. Industrial scale application should entail carrying out the low-temperature thermal pre-treatment in continuous mode to reduce the energy consumption. Transport cost may limit the economic viability of the process and also should be considered, although centralized management plants are widely implemented and, therefore, this cost could be avoided. Variations on phenols price directly affect to the economic viability of the process. Nevertheless, the commercialization of other phenolic compounds and added value compounds from OMSW are currently being developed and may incur in even higher benefits. Biomethanization of OMSW after phenols recovery through low-temperature thermal pre-treatment should be consider an interesting management option, which allows obtaining an important economic benefit as well as the correct treatment of this organic waste to avoid environmental pollution.

4. Conclusions

- OMSW low-temperature thermal pre-treatment facilitated the separation of a solid phase, where most of organic compounds remained, and a liquid phase, where most of soluble compounds were concentrated.
- Phenols were mainly displaced to the liquid phase. Hydroxytyrosol presented the highest concentration of the measured individual phenols.
- Anaerobic digestion of OMSW and the different pre-treated phases and mixtures operated under stable conditions, except the biomethanization of the liquid phase, which was mainly inhibited by the high phenols content.
- Low-temperature thermal pre-treatment allows obtaining an improvement on biodegradability and methane production up to 37% and 34%, respectively. By contrast, the highest methane production rate was determined from untreated OMSW.
- The proposed economic assessment showed that the combination of low-temperature pre-treatment, phenols recovery and the subsequent biomethanization of the substrates was the most interesting treatment option. This management option could reach economic benefit twenty times higher than only energy recovery.

Acknowledgements

The authors are very grateful to the Spanish Ministry of Economy and Competitiveness for funding this research through Project CTM2014-55095-R.

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476 **Figure captions**

477 **Figure 1.** Mean values of pH and alkalinity at the end of the BMP test for untreated
478 olive mill solid waste and pre-treated phases and mixtures.

479 **Figure 2.** Accumulated methane production with time for untreated olive mill solid
480 waste and pre-treated phases and mixtures.

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Highlights

- OMSW low-temperature thermal pretreatment facilitated the separation of two phases
- Hydroxytyrosol showed the highest concentration of the measured individual phenols
- Biomethanization of liquid phase was mainly inhibited by the high phenols content
- Low-temperature thermal pretreatment improved biodegradability up to 37%
- Pretreatment, phenol recovery plus biomethanization was the most interesting option
- This option could reach a net benefit twenty times higher than only energy recovery

Figure 1

Figure 1.

Figure 2

Figure 2.

A)

B)

Table 1

Table 1. Physicochemical characterization of untreated OMSW and of the different pre-treated fractions.

		Untreated OMSW	Solid phase (SP)	Liquid phase (LP)	Dephenolized liquid phase (DLP)
pH		4.79 ± 0.01	4.93 ± 0.01	4.76 ± 0.01	4.57 ± 0.01
Alkalinity	mg CaCO ₃ /L	6559 ± 5	8880 ± 5	3636 ± 5	303 ± 5
Conductivity	mS/cm	13.16	12.80	13.08	19.15
TS	g/L	266 ± 4	370 ± 2	82 ± 2	56 ± 1
VS	g/L	250 ± 4	354 ± 4	66 ± 2	42 ± 1
COD	g/L	322 ± 11	438 ± 22	103 ± 1	62 ± 3
sCOD	g/L	57 ± 11	71 ± 3	40 ± 2	38 ± 1
Total Phenols	g/kg VS (g/L)	24 ± 2 (5.90 ± 0.38)	15 ± 2 (5.47 ± 0.70)	54 ± 2 (3.56 ± 0.14)	57 ± 4 (2.40 ± 0.17)
Total Carbohydrates	g/kg VS (g/L)	45 ± 1 (11.14 ± 0.28)	3 ± 0 (1.04 ± 0.11)	152 ± 15 (10.01 ± 0.99)	253 ± 16 (10.49 ± 0.67)
Acetic Acid	mg/L	nd	Traces	Traces	Traces

nd, non detected; Traces, <0.01 mg/L

Table 2

Table 2. Individual phenolic compounds concentration of untreated OMSW and of the different pre-treated fractions.

		Untreated	Solid phase	Liquid phase (LP)	Dephenolized
		OMSW	(SP)		liquid phase (DLP)
3,4-Dihydroxyphenylglycol	mg/L	157 ± 5	96 ± 2	182 ± 4	73 ± 2
Hydroxytyrosol 4-β-D-Glucoside	mg/L	88 ± 5	638 ± 3	134 ± 8	116 ± 7
Hydroxytyrosol	mg/L	540 ± 13	62 ± 2	1034 ± 22	38 ± 2
Tyrosol	mg/L	122 ± 9	87 ± 3	187 ± 8	22 ± 2
Homovanillic acid	mg/L	nd	Traces	Traces	nd
Vanillic acid	mg/L	15 ± 2	15 ± 2	16 ± 1	4.22 ± 0.02
Caffeic acid	mg/L	16.19 ± 0.08	6.3 ± 0.4	19 ± 1	Traces
p-Coumaric acid	mg/L	32 ± 2	33 ± 2	18 ± 1	2.54 ± 0.06
Luteolin-7-O-Glucoside	mg/L	10.4 ± 0.8	13 ± 1	1.80 ± 0.02	< D.L.
Luteolin	mg/L	11 ± 1	18 ± 1	Traces	Traces
Sum of individual phenols	mg Gallic Acid/L	1153	428	1832	273
Total phenols (Folin-Ciocalteu method)	mg Gallic Acid/L	5902 ± 379	5467 ± 701	3559 ± 136	2397 ± 169

nd, non detected; Traces, <0.01 mg/L