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Effects of Ultrasound and Green Synthesis ZnO Nanoparticles on Biogas Production from Olive Pomace

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Abstract

Agro-biomass residues can play a crucial role in promoting the fossil-fuel replacement in agro-food farms. Apulia, a region in Southern Italy, concentrates 22% of farms and 57% of total national olive and olive oil production, resulting the leader producer of the Country. So that, a high quantity of biomass (olive pomace) can be recovered from the milling process. This study investigates the biogas production that occurs during the anaerobic digestion of olive pomace by means of an ultrasound pre-treatment or by means of green synthesis of ZnO Nanoparticles mixed with olive pomace, in order to facilitate its digestion or co-digestion. Measurement of dry matter and biogas produced volume during the anaerobic process were investigated starting from 3-phase and 2-phase olive pomace by means of high specific energy and low frequency ultrasound values. The results highlight a promising influence of ultrasound pre-treatment useful at increasing the biogas yield of olive pomace.

Keywords: Ultrasound pre-treatment, Biogas, Olive pomace, Green Synthesis, ZnO NPs;

1. Introduction

A precious economic and social resource for Mediterranean Countries is certainly represented by olive trees, especially for Apulia, a region in Southern Italy [1,2]. A great research effort is focused on the valorization of such resource, included the by-products of the olive oil production [3–6]. New technologies and new process for high-quality virgin

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Nomenclature

m_{H2O}^{add}	mass of water added to olive pomace
m_{TOT}^{i}	olive pomace initial mass
$\%M_i$	initial olive pomace moisture
$\%M_f$	final olive pomace moisture
t	sonication time
L_i	specific energy
m	olive pomace mass after water addition
P	ultrasonic bath power
2-POP	two phase olive pomace
3-POP	three phase olive pomace

oil production are developing fast [7–9], as well as new technologies are proposed for an energetic valorization of residues deriving from olive oil industry [6,10–12].

Among these residues, olive pomace has recently attracted increasing attention since it can be used for producing biogas via anaerobic digestion processes [11,13,14], other than heat and power via classical thermochemical conversion processes.. Olive pomace is composed of pit, olive pulp and olive mill wastewater. This by-product could represent a relevant source of pollution if discharged in the environment and not properly treated [15].

Recent findings have pointed out that a pre-conditioning of olive pomace with low-frequency (10-60 kHz) ultrasound techniques (US), can enhance the biogas production yield [16]. This is due to the influence of ultrasound treatment on the release of intracellular matter, promoting the rupture of the solids that are in the liquid medium [17–21]. The total solid surface in contact with the liquid phase is therefore increased and, as consequence, the chemical action of the inoculum is magnified [16,22]. There is a lack of research about the application of ultrasound to olive pomace. However, consolidated evidences about the beneficial effects of an ultrasound treatment can be found in extra virgin olive oil extraction process [16], as well as in sludge treatments [23–26].

Ultrasound (US) is a promising emerging technology that has already found application in the food industry [22]. The main reason relies on the mechanical effects generating during an ultrasound treatment and which are due to cavitation phenomena. When ultrasound are applied to a liquid medium, sinusoidal acoustic waves are produced and tiny gas bubbles grow within the fluid when the local pressure falls below the vapour pressure of the liquid [17,27]. If the bubble growth reaches a critical size, it implodes causing the phenomenon of cavitation. Generally speaking, the phenomenon of violent bubble implosions is characterized by extreme local conditions, such as high pressure differentials, shock waves and liquid jets [28].

On the other side, previous researches [29] demonstrated that the growth of methanogenic bacteria is dependent on Fe, Co, and Ni during enzyme synthesis. Some studies have been carried out to determine the requirements and optimal concentration for trace metals in pure culture of methane fermentation. Trace metals are essential constituents of cofactors and enzymes and their addition to anaerobic digesters has been shown to stimulate and stabilize the biogas process performance. Other studies reported that the presence of heavy metal ions (i.e., Cu, Zn, Fe, Ni, Co, Mo) during anaerobic biodegradation of organic matter is known to be fundamental for numerous reactions. However, high concentrations of these elements can inhibit the biological degradation process in anaerobic reactors. One of the problems with heavy metal compounds is that these elements are not biodegradable. Due to this, these compounds are known to accumulate, reaching potentially toxic concentrations for anaerobic bacteria. Some works concluded that addition of trace elements improves the anaerobic digestion [30].

Nanoparticles have unique properties such as large surface area, high reactivity due to high surface area to volume ratio, high specificity, self-assembly and dispersibility [29–31]. Mu et al. [31] investigated four chemically synthesized metal oxides nanoparticles (nano-TiO_2, nano-Al_2O_3, nano-SiO_2 and nano-ZnO) and concluded that only nano-ZnO has inhibitory effects on methane generation, and the influence of nano-ZnO is dosage dependent. Lower nano-ZnO (6 mg/g-TSS) gave no impact on methane generation [30].

In this work experimental laboratory tests were performed with the purpose of assessing the effects that an ultrasound preconditioning of three-phase olive pomace (3-POP) can produce on the biogas yield in batch process. In addition, according to [32], the effect of synthesis of Green ZnO nanoparticles (ZnO NPs) on biogas production from two-phase olive pomace (2-POP) samples was assessed as well.

2. Materials and methods

With the aim of increasing the biogas production from olive pomace, an ultrasound pre-treatment was applied to 3-POP. Several samples were prepared starting from 3-POP provided by an Apulian oil mill. Part of these samples were pre-treated with ultrasound, while the remaining part followed a traditional procedure. Rumen liquid was added to all the samples, in order to promote the anaerobic digestion of the 3-POP. The samples were then placed in a thermally-controlled water bath to ensure mesophilic conditions during the digestion phase. The biogas production was constantly monitored for 43 days. The volume of the gas produced by the sonicated samples was compared to that obtained with the standard procedure. 5 mg of green synthesized ZnO NPs was added to 20 g of rumen liquid and 5 g of non-sonicated 2-POP. The biogas production was constantly monitored for 23 days.

2.1. Ultrasound pre-treatment

The ultrasound waves propagation within the fluid medium depends upon its water content [22]; for this reason the moisture content was kept constant for each sample of 3-POP. This typology of olive pomace is characterized by a lower water content then the 2-POP one (typically 55% against 70%. on wet basis). The 3-POP moisture was experimentally measured by means of an oven, in which the matter was kept for 24 hours at 105°C. The olive pomace moisture resulted equal to 54,16% wb. Therefore, before the ultrasound pre-treatment, 1,087 kg of water were added to 0,841 kg of olive pomace to reach 80% wb of moisture, according with the following expression:

$$\mathrm{m}_{\mathrm{H2O}}^{\mathrm{add}} = \frac{\mathrm{m}_{\mathrm{TOT}}^{\mathrm{i}} \times (\%\mathrm{M}_{\mathrm{i}} - \%\mathrm{M}_{\mathrm{f}})}{\%\mathrm{M}_{\mathrm{f}} - 1},$$

where m_{H2O}^{add} is the mass of water in kg needed to reach the desired moisture (80% by mass for the present case), m_{TOT}^{i} is the olive pomace initial mass in kg, $\%M_i$ and $\%M_f$ the olive pomace moisture before and after the water addition, respectively.

An ultrasound pre-treatment was applied to the moisturized olive pomace in order to enhance its anaerobic bioconversion, in accordance with the method proposed by Clodoveo et al. in [28]. Specifically, low-frequency and high-power ultrasounds (at a frequency of 37 kHz and with an installed power of 256 W) were generated by means of the Elmasonic P30H ultrasonic bath [28] depicted in Figure 1-(a).

The specific energy generated in the bath was set equal to 15 kJ/kg. This value was chosen according to Amirante et al. [22] and, in particular, it refers to the new Sono-Heat-Exchanger (SHE) technology, used for obtaining the highest virgin olive oil quality and yield. In the case of the SHE, the best result is obtainable working between 15-18 kJ/kg. For an economic point of view, it might be very continent to use the same machinery both for the extraction of olive oil and for the pre-treatment of the olive pomace. Therefore, in the present work, the value of the specific energy was set equal to that proposed in [22], allowing to verify if such a choice can be suitable for the pomace pre-treatment too. In addition, considering a circular economy approach, the produced biogas could be burned in combined heat and power generation plants [1,10,12,33], making the oil mill energetically autonomous.

Knowing the installed power and the total mass to be treated, it was possible to calculate the sonication time needed to generate the selected specific energy. Namely, the 3-POP was processed for 1.88 min in order to reach the specific energy target. An important aspect to be avoided during the pre-treatment is the bacterial flora destruction. Thus, the thermal conditions of the bath during the experiments were constantly monitored with an infrared thermometer, as reported in Figure 1-(b) for ensuring temperatures lower than 40°C. In particular, the temperature during the ultrasound pre-treatment ranged between 17,5 °C and18,5°C.

2.2. Green synthesis of ZnO NPs

50 ml of distilled water were mixed with to 0.2 g of zinc acetate dihydrate and stirred for 10 min. 1.0 ml of aqueous wheat leaf extract was added to the above-mentioned solution followed by the addition of 2.0 M NaOH drop wise until the pH became 12 and a pale white aqueous solution was obtained. The mixture was stirred for 2 h. The obtained pale

white precipitate was isolated, washed several times with distilled water, followed by ethanol and dried at 80°C under vacuum overnight. For achievement of pure ZnO NPs, the obtained product was treated at 550 ^{0}C for 2 hours. The pale white powder of ZnO NPs was collected and used for the batch scale anaerobic digestion [32].

2.3. Anaerobic digestion test

After the ultrasound pre-treatment, the inoculum was added to all the samples (sonicated and non-sonicated), in order to promote the anaerobic digestion of the 3-POP. Each resulting sample was composed by 20 g of rumen liquid and 5 g of olive pomace. To work in mesophilic condition all the samples were randomly placed in the thermally-controlled water bath depicted in Figure 2. A temperature of 40°C was set and monitored during the experiments. The biogas produced was measured by means of a graduated syringe, with a capacity of 100 ml. Namely, the volume of the produced gas was given by the variations in the piston displacement of the syringe. The experiments were concluded when the biogas production rate was lower than 1%. The anaerobic digestion lasted 43 days.

(a) (b)

Figure 1 – Thermally controlled ultrasonic bath (a). Infrared thermometer used for monitoring temperature during the experiments (b).

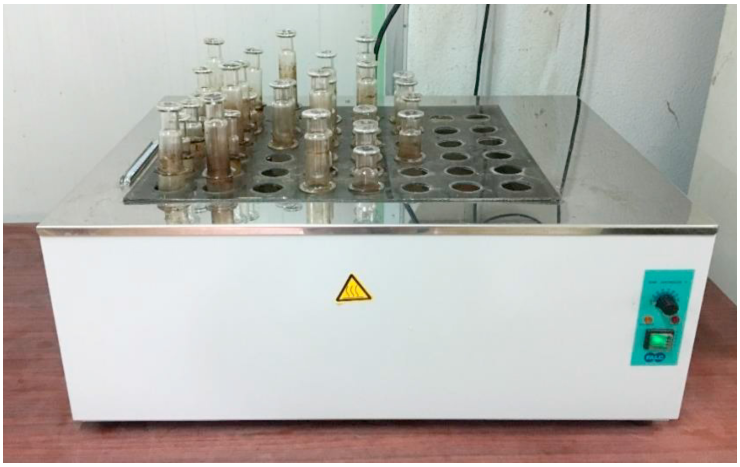

Figure 2 - Water Bath.

3. Results

3.1. Effect on biogas production

The biogas production was daily monitored for 43 days. As it is shown in Figure 3-(a), after the first ten days, the non-sonicated olive pomace biogas production resulted to be almost saturated, while in the case of the sonicated samples the biogas production kept increasing in the subsequent days. For the entire duration of the experiment, the production rate of the sonicated olive pomace samples resulted constantly higher than that of the non-sonicated ones. In addition, at the end of the 43th day, the production rate of the 3-POP sonicated samples was still slightly higher than zero (Figure 3-(b)).

This result highlighted that the olive pomace produces more biogas in a faster way when preconditioned by an ultrasound pre-treatment. Indeed, according to Gianico et al. in [16], ultrasound pre-treatment resulted effective in solubilizing the organic matter (up to 22% and 72% Soluble Chemical Oxygen Demand increase) and the polyphenols (up to 46% and 150% increase) present in olive husks.

3.2. Effect of ZnO NPs on 2-POP

The morphology and distribution of nanoparticles were further characterized using Transmission Electron Microscope (TEM). TEM analysis (Figure 4) shows that the green synthesized ZnO NPs particle size ranged between 12 nm and 37 nm. The TEM images demonstrate the internal structure of the nanoparticles and provide more accuracy on their size. All the TEM characterization was carried out one day after the preparation process.

Total Solids (TS) in the olive pomace vary from 21 to 49 % with average value 34.47 %. On the other hand, the determination of C and N content was obtained using CHN628 Instrument. The measurement method is based on complete and instantaneous oxidation (dynamic flash combustion) of the samples [34], with their conversion from organic substrates to gaseous products. C/N ratio varies in the range of 37 to 58, largely outside the range of 20-30 that indicated as optimum range in literature [35].

According to Figure 5, during the first week the production volume of the 2-POP mixed with ZnO NPs was still slightly higher than the standard 2-POP, which indicated the catalytic activities of ZnO NPs on the methanogenesis bacteria at the beginning of the experiment. The experimental results were obtained after a period of 23 days when the production rate of 2-POP was zero, and the overall volume production of the standard 2-POP resulted higher than that of the 2-POP mixed with the ZnO NPs.

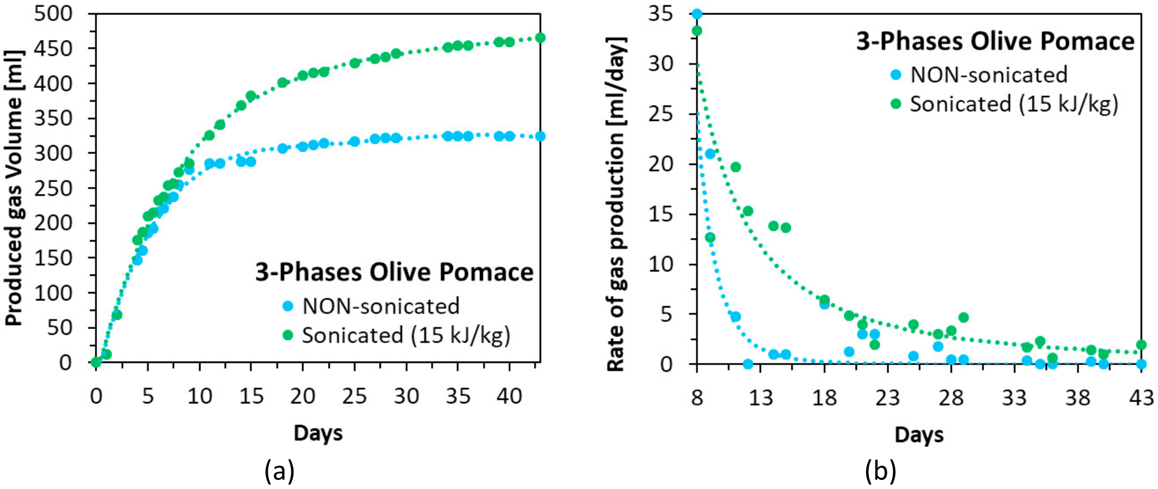

Figure 3 – 3-POP biogas volume daily production (a). 3-POP production rate from day 8 (b).

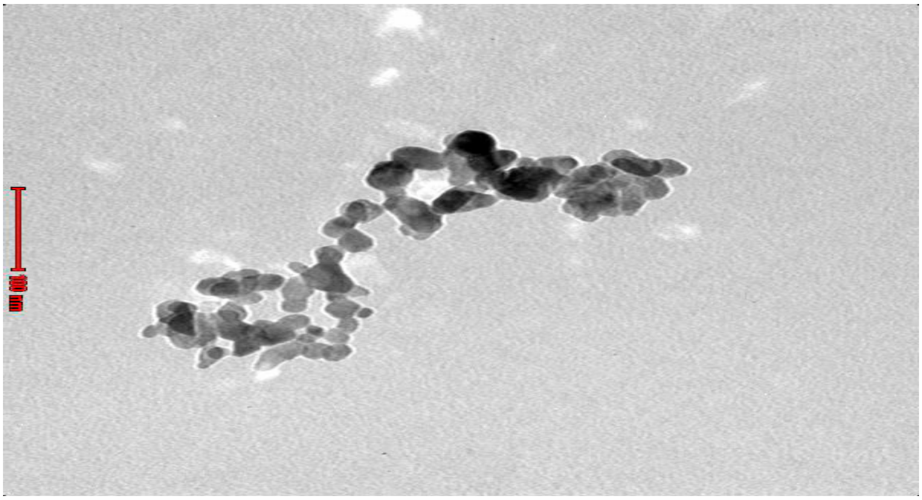

Figure 4 - Green synthesized ZnO NPs TEM analysis.

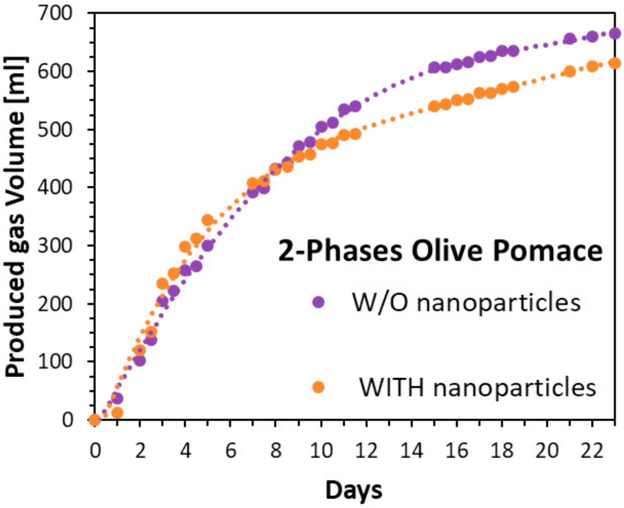

Figure 5 - Biogas Volume Daily production from 2-POP biomass with and without ZnO NPs.

4. Conclusions

This experimental activity aimed at ascertaining the effects that an ultrasound preconditioning of three-phase olive pomace can induce on biogas production during anaerobic digestion. Laboratory tests were performed on a 3-POP provided by Apulian oil mills. Part of the realized samples was treated with low frequency and high specific energy ultrasound, while the remaining part followed a standard procedure. The effective ultrasound waves propagation within the fluid medium depend upon the water content, so that the same moisture (80% by mass) was ensured for each sample of 3-POP. An ultrasound pre-treatment was dispensed to the olive pomace in order to enhance its anaerobic bioconversion. The specific energy generated was set equal to the optimal value obtained from preliminary analyses, namely 15 kJ/kg. Therefore, 1.88 minutes were necessary to reach the specific energy target with 256 W. After the ultrasound pre-treatment, rumen liquid was added to all the samples, in order to promote the anaerobic digestion of the 3-POP. The samples were then placed in a thermally-controlled water bath to ensure mesophilic conditions during the digestion phase and the biogas production was constantly monitored for 43 days.

After the first ten days, the non-sonicated olive pomace biogas production resulted to be almost saturated, contrariwise to what was observed in the case of the sonicated samples, for which the biogas production kept increasing in the subsequent days. For the entire duration of the experiment, the production rate of the sonicated olive pomace samples resulted constantly higher than that of the non-sonicated ones. In addition, at the end of the 43th day, the production rate of the 3-POP sonicated samples was still slightly higher than zero.

This result highlighted that the olive pomace produces more biogas in a faster way when preconditioned by an ultrasound pre-treatment.

This experiment also studied the ZnO NPs effect on 2-POP biogas volume production. During the first week the production volume of the 2-POP mixed with ZnO NPs was still slightly higher than the standard 2-POP, but at the end of the 23th day overall volume production of the standard 2-POP resulted higher than that of the 2-POP mixed with the ZnO NPs.

References

[1] Amirante R, Clodoveo ML, Distaso E, Ruggiero F, Tamburrano P. A tri-generation plant fuelled with olive tree pruning residues in Apulia: An energetic and economic analysis. Renew Energy 2016;89:411–21.

[2] Amirante R, De Palma P, Distaso E, Tamburrano P. Thermodynamic analysis of small-scale externally fired gas turbines and combined cycles using turbo-compound components for energy generation from solid biomass. Energy Convers Manag 2018;166. doi:10.1016/j.enconman.2018.04.055.

[3] Clodoveo ML, Dipalmo T, Schiano C, La Notte D, Pati S. What's now, what's new and what's next in virgin olive oil elaboration systems? A perspective on current knowledge and future trends. J Agric Eng 2014;45:49–59.

[4] Amirante R, Cassone E, Distaso E, Tamburrano P. Overview on recent developments in energy storage: Mechanical, electrochemical and hydrogen technologies. Energy Convers Manag 2017;132:372–87.

[5] Amirante R, Coratella C, Distaso E, Tamburrano P. A small size combined system for the production of energy from renewable sources and unconventional fuels. Energy Procedia, vol. 81, 2015. doi:10.1016/j.egypro.2015.12.090.

[6] Clodoveo ML, Paduano A, Di Palmo T, Crupi P, Moramarco V, Distaso E, et al. Engineering design and prototype development of a full scale ultrasound system for virgin olive oil by means of numerical and experimental analysis. Ultrason Sonochem 2017;37. doi:10.1016/j.ultsonch.2017.01.004.

[7] Amirante P, Clodoveo ML, Tamborrino A, Leone A, Paice AG. Influence of the crushing system: phenol content in virgin olive oil produced from whole and de-stoned pastes. Olives Olive Oil Heal Dis Prev Acad Press London, UK 2010:69–76.

[8] Amirante P, Clodoveo ML, Tamborrino A, Leone A, Dugo G. Oxygen concentration control during olive oil extraction process: a new system to emphasize the organoleptic and healthy properties of virgin olive oil. VI Int. Symp. Olive Grow. 949, 2008, p. 473–80.

[9] Amirante P, Clodoveo ML, Tamborrino A, Leone A. A new designer malaxer to improve thermal exchange enhancing virgin olive oil quality. VI Int. Symp. Olive Grow. 949, 2008, p. 455–62.

[10] Amirante R, De Palma P, Distaso E, Pantaleo AM, Tamburrano P. Thermodynamic analysis of a small scale combined cycle for energy generation from carbon neutral biomass. Energy Procedia, vol. 129, 2017. doi:10.1016/j.egypro.2017.09.213.

[11] Tekin AR, Dalg\iç AC. Biogas production from olive pomace. Resour Conserv Recycl 2000;30:301–13.

[12] Amirante R, De Palma P, Distaso E, La Scala M, Tamburrano P. Experimental prototype development and performance analysis of a small-scale combined cycle for energy generation from biomass. Energy Procedia 2017;126:659–66. doi:10.1016/j.egypro.2017.08.294.

[13] Riggio V, Comino E, Rosso M. Energy production from anaerobic co-digestion processing of cow slurry, olive pomace and apple pulp. Renew Energy 2015;83:1043–9.

[14] Katsoni A, Mantzavinos D, Diamadopoulos E. Sequential treatment of diluted olive pomace leachate by digestion in a pilot scale UASB reactor and BDD electrochemical oxidation. Water Res 2014;57:76–86.

[15] Chartzoulakis K, Psarras G, Moutsopoulou M, Stefanoudaki E. Application of olive mill wastewater to a Cretan olive orchard: effects on soil properties, plant performance and the environment. Agric Ecosyst Environ 2010;138:293–8.

[16] Gianico A, Braguglia CM, Mescia D, Mininni G. Ultrasonic and thermal pretreatments to enhance the anaerobic bioconversion of olive husks. Bioresour Technol 2013;147:623–6.

[17] Amirante R, Distaso E, Tamburrano P. Experimental and numerical analysis of cavitation in hydraulic proportional directional valves. Energy Convers Manag 2014;87:208–19.

[18] Roy RA. Cavitation sonophysics. Sonochemistry and Sonoluminescence 1999;524:25–38.

[19] Seya PM, Desjouy C, Béra J-C, Inserra C. Hysteresis of inertial cavitation activity induced by fluctuating bubble size distribution. Ultrason Sonochem 2015;27:262–7.

[20] Desjouy C, Fouqueray M, Lo CW, Seya PM, Lee JL, Bera J-C, et al. Counterbalancing the use of ultrasound contrast agents by a cavitation-regulated system. Ultrason Sonochem 2015;26:163–8.

[21] Santos HM, Lodeiro C, Capelo-Mart\'\inez J-L. Power ultrasound meets protemics. Ultrasound Chem Anal Appl 2008:107–27.

[22] Amirante R, Distaso E, Tamburrano P, Paduano A, Pettinicchio D, Clodoveo ML. Acoustic cavitation by means ultrasounds in the extra virgin olive oil extraction process. Energy Procedia 2017;126:82–90.

[23] Rokhina E V, Lens P, Virkutyte J. Low-frequency ultrasound in biotechnology: state of the art. Trends Biotechnol 2009;27:298–306.

[24] Castrillón L, Fernández-Nava Y, Ormaechea P, Marañón E. Optimization of biogas production from cattle manure by pre-treatment with ultrasound and co-digestion with crude glycerin. Bioresour Technol 2011;102:7845–9.

[25] Climent M, Ferrer I, del Mar Baeza M, Artola A, Vázquez F, Font X. Effects of thermal and mechanical pretreatments of secondary sludge on biogas production under thermophilic conditions. Chem Eng J 2007;133:335–42.

[26] Barber WP. The effects of ultrasound on sludge digestion. Water Environ J 2005;19:2–7.

[27] Amirante R, Distaso E, Tamburrano P. Sliding spool design for reducing the actuation forces in direct operated proportional directional valves: Experimental validation. Energy Convers Manag 2016;119:399–410.

[28] Clodoveo ML, Durante V, La Notte D. Working towards the development of innovative ultrasound equipment for the extraction of virgin olive oil. Ultrason Sonochem 2013;20:1261–70.

[29] Qiang H, Lang D-L, Li Y-Y. High-solid mesophilic methane fermentation of food waste with an emphasis on iron, cobalt, and nickel requirements. Bioresour Technol 2012;103:21–7.

[30] Abdelsalam E, Samer M, Attia YA, Abdel-Hadi MA, Hassan HE, Badr Y. Influence of zero valent iron nanoparticles and magnetic iron oxide nanoparticles on biogas and methane production from anaerobic digestion of manure. Energy 2017;120:842–53.

[31] Mu H, Chen Y, Xiao N. Effects of metal oxide nanoparticles (TiO2, Al2O3, SiO2 and ZnO) on waste activated sludge anaerobic digestion. Bioresour Technol 2011;102:10305–11.

[32] Hassan SSM, El Azab WIM, Ali HR, Mansour MSM. Green synthesis and characterization of ZnO nanoparticles for photocatalytic degradation of anthracene. Adv Nat Sci Nanosci Nanotechnol 2015;6:45012.

[33] Amirante R, Distaso E, Tamburrano P. Novel, cost-effective configurations of combined power plants for small-scale cogeneration from biomass: Design of the immersed particle heat exchanger. Energy Convers Manag 2017;148. doi:10.1016/j.enconman.2017.06.047.

[34] Friis JC, Holm C, Halling-Sørensen B. Evaluation of elemental composition of algal biomass as toxical endpoint. Chemosphere 1998;37:2665–76.

[35] Grönroos A, Kyllönen H, Korpijärvi K, Pirkonen P, Paavola T, Jokela J, et al. Ultrasound assisted method to increase soluble chemical oxygen demand (SCOD) of sewage sludge for digestion. Ultrason Sonochem 2005;12:115–20.