CHEMICAL ENGINEERING TRANSACTIONS
VOL. 99, 2023

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Sauro Pierucci, Flavio Manenti

ISBN 978-88-95608-98-3; **ISSN** 2283-9216

DOI: 10.3303/CET2399015

Biochar Enhances Anaerobic Digestion of Olive Mill Wastewater

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The anaerobic digestion of olive mill wastewater is severely hindered by the microbial toxicity of the effluent. Successful biodegradation is usually attained only by dilution and mixing with other organic wastes. In this work the addition of biochar has been investigated as an alternative to co-digestion. In batch tests, raw olive mill wastewater selectively inhibited methanogenic bacteria even at 1:10 dilution. Acidogenesis was not affected and further biodegradation was hindered by acidification and high hydrogen partial pressure. Methanogenesis resumed after 20 days and ended after 40 days from inoculation. Overall soluble COD removal was 32.9% with a methane yield of 2.35 ± 0.27 L STP/L of digestion medium. Treatment of wastewater with 15% (w/v) poplar biochar removed 71% of inhibitory polyphenolic compounds and effectively accelerated the onset of methanogenesis, with a reduced duration of 26 days. Biochar treatment of olive mill wastewater followed by anaerobic digestion led to a higher soluble COD removal (61.6%) with a slightly decreased biogas yield of 1.62 ± 0.30 L STP/L of digestion medium.

1. Introduction

Disposal of olive mill wastewater (OMW) on agricultural lands is a controversial question, mostly because of the contrasting effects of OMW on physicochemical (Comegna et al., 2022) and biological (Magdich, 2013) soil properties due to the high organic matter content and the large volumes produced in a short period of time.

Several practices and combined treatments have been proposed for OMW management, based on physicochemical or biological processes. Waste valorization should be preferred in line with current environmental regulations and recommendations (Morillo et al., 2009). In this respect, the anaerobic digestion (AD) process is an attractive technology because the production of biogas allows energy recovery. However, the exploitation of AD has some limitations due to the inhibition of methanogen growth, mainly due to the high concentration of polyphenolic components in OMW (Gonçalves et al., 2012).

Inhibition in AD can be counteracted either by reducing the concentration of the phenolic compounds by dilution (increasing the digester volume unless co-digestion with other agricultural waste is used to sustain process yield) or by removing the inhibitors. In the latter case, pre-treatments of OMW before AD can be envisaged to reduce the concentration of polyphenolic compounds by adsorption. Most of the treatment methods using adsorbent materials suffer several drawbacks, especially in terms of environmental impact, operational costs, and sensitivity to variable composition (Ioannou-Ttofa et al., 2017). By comparison, biochar seems to be a promising adsorbent material. Biochar is a pyrogenic carbon-rich material formed through the thermal decomposition of biomass feedstock under an oxygen-limited condition (Glaser et al., 2021). The charred organic material spans a continuum from light charring to charcoal to graphite (Di Rauso Simeone et al., 2018).

Paper Received: 14 January 2023; Revised: 30 March 2023; Accepted: 20 April 2023
Please cite this article as: Micoli L., Di Rauso Simeone G., Turco M., Toscano G., Rao M.A., 2023, Biochar Enhances Anaerobic Digestion of Olive Mill Wastewater, Chemical Engineering Transactions, 99, 85-90 DOI:10.3303/CET2399015

Biochar is rich in aromatic carbon and minerals and is commonly used as a soil conditioner (Bong et al., 2020). It is also characterized by high surface area and porosity, which confer it significant sorbent capacity for organic and inorganic compounds through various mechanisms such as adsorption, aromatic-π interaction and electrostatic interactions. (Lehmann and Joseph, 2015). The addition of biochar for the enhancement of AD is motivated not only by the adsorbing properties towards inhibiting compounds, but also by the pH buffering capacity (Wang et al, 2018) and by the ability to act as an redox-active carrier for the immobilization of bacterial cells (Chen et al. 2014).
In this perspective, the aim of the present work was to investigate the effects of a biochar treatment on the AD of OMW. The attention was focused on the possible improvements in process efficiency by evaluating COD removal, biogas yields and overall kinetics.
The effect of biochar treatment was quantified in batch digestion tests. The experimental setup was similar to that suggested for biomethane potential (BMP) tests (Holliger et al. 2016) except for the so-called S/X ratio. Low substrate to solids ratios are usual in BMP tests, since the inoculated sludge is used to overcome nutrient imbalance and inhibitory compounds of the tested substrate. In our tests, in order not to mask the inhibitory effect of OMW, an high substrate to solids ratio was used. Furthermore, ammonium chloride was added to the digestion mixture, given the low nitrogen content of the substrate.

2. Materials and methods

2.1 Materials

OMW was collected in a three-phase olive mill located in Ostuni (Italy). All samples were stored at -20 °C until anaerobic digestion tests. OMW was characterized according to APAT standard methods (APAT, 2003) (Table 1).

Table 1. Characterization of olive mill wastewater

Properties	Mean ± St.dev.
pH	5.00 ± 0.03
Dry matter, %	8.0 ± 0.2
Organic C, g kg^{-1}	55.0 ± 0.8
TKN, g N L^{-1}	0.82 ± 0.01
sCOD[a], g L^{-1}	91.7 ± 0.5
tCOD[b], g L^{-1}	98.6 ± 0.7
TPC[c], g L^{-1}	3.3 ± 0.1

[a]sCOD: soluble COD; [b]tCOD: total COD; [c]TPC: total phenolic compounds

Biochar was produced from poplar wood in a downdraft, open top gasifier by AGT (Advanced Gasification Technology, Cremona, Italy). Biochar (B) was used as powder with a granulometry in the range 0.05-0.5 mm. Further physical and chemical properties of B are reported in De Pasquale et al. (2012) and Rao et al. (2017).
The inoculum used in AD batch tests was collected in a mixed poultry and cattle slurry digester located in Eboli (Italy).

2.2 Phenolic compounds removal

Adsorption of phenolic compounds by B was evaluated in 15% (w/v) shaken suspensions of B in OMW. Suitable volumes of OMW (20 mL) were treated with 3 g of B in 30 mL polyethylene tubes on an orbital shaker (150 rpm) at 25 °C for different incubation times (0, 7, 10, 15, and 20 days). Samples of OMW without B were kept as controls. All samples were centrifuged at 3500 rpm for 10 min at the end of each incubation time and total phenolic compounds (TPC) were measured according to the procedure described by Greco et al. (2006). Experiments and analyses were carried out in triplicate.

2.3 OMW treatment with biochar

Before AD process OMW was also treated with B by mixing OMW and 15% B (w/w) with orbital shaker for 21 days at 30 °C. This sample was named B-treated OMW.

2.4 Anaerobic digestion tests

AD tests were conducted in a 750 mL glass batch reactor connected to a MilliGascounter® flow-meter (type MGC-1, from Ritter, Bochum, Germany) for biogas production measurements. The digestion mixture included 50 mL of inoculum (6% dry matter), 50 mL of OMW or B-treated OMW, 400 mL of tap water, and 1.91 g of NH_4Cl (corresponding to a final concentration of 1 g NH_4^+-N L^{-1}).

The overall fermentation volume was 500 mL with an initial pH value around neutrality. The anaerobic conditions were ensured by bubbling nitrogen at the flow rate of150 mL min^{-1} for 20 min through the digestion mixture; in addition, 2 mL with 0.8 mmol mL^{-1} of Na_2S were added to remove the residual dissolved oxygen.
During the AD test temperature was kept constant at 35 ± 1 °C and the mixture was gently stirred at 60 rpm. pH of digestion medium was checked on liquid samples withdrawn during all the run. When pH changed from neutrality more than 0.5 (medium generally acidifies when fermentation starts), it was adjusted by adding 1 M NaOH in order to maintain pH around neutrality, optimal for the methanogenic bacteria growth (Tezel et al., 2011).
Biogas production measurements, in terms of cumulative volumes and flow rates, were recorded by an on-line data acquisition system with an accuracy of approx. ± 3%. The biogas produced was then collected in gas sampling bags and analyzed by a Shimadzu GC-2014 gas-chromatograph equipped with a TCD detector and a molecular sieve packed column (Carboxen-1000 Supelco®, from Merck, Darmstadt, Germany).

3. Results and Discussion

3.1 Adsorption of phenolic content by biochar

Before starting the anaerobic digestion tests, the potential adsorption capability of B to remove phenolic compounds from OMW was evaluated.
The time course of TPC in OMW during the treatment with B was monitored (Figure 1). The initial TPC of OMW was 3.3 g L^{-1} and after 20 days of B treatment the residual TPC dropped to about 1.0 g L^{-1} (70% decrease). Any possible variation of the TPC content due to other than adsorption on B could be excluded because no significant differences were observed in the control test without B over the incubation time. The results confirmed that B is a good sorbent for phenolic compounds, in accordance with the results of Rao et al. (2017), that showed the high efficiency of B in phenol removal.

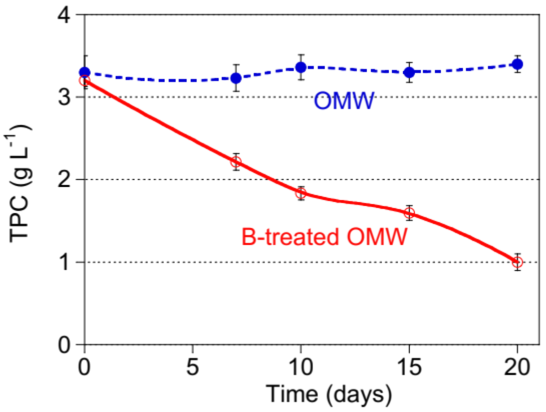

Figure 1. Time course of TPC concentration during 20 days of treatment with and without B.

3.2 Anaerobic digestion tests

A batch of B-treated OMW was used as substrate for the following AD tests. B was not removed before AD because of the potential beneficial effects on digester management: i) some biodegradable organic compounds adsorbed on B can be still made available to digestion; ii) B has some buffering capacity and can ease pH control; iii) the removal of suspended solids can be postponed at the end of treatment.
AD tests were carried out using OMW and B-treated OMW in the same experimental conditions. Figure 2 shows the cumulative volumes of biogas at standard temperature and pressure (STP, 0 °C and 1 atm) produced during the digestion process for each test. The qualitative trends of the two tests were very different. Gas and liquid phase analysis allowed the identification of different metabolic phases due to the changes in the population of microbial consortium during the AD test.
Biogas evolution data from the run with OMW (Figure 2, dashed line) presented a sequence of well-separated phases, namely a prevalently acidogenic phase followed by a long lag phase, and at last the methanogenic phase.
The initial biogas production occurred in two days (~320 mL). The initial biogas composition was about 24 % H_2, 61 % CO_2, and 15% CH_4, by volume (Figure 3). At the same time, pH of the digestion medium dropped from the initial values of 6.0-6.5 down to about 5.0-5.5. This can be attributed to the prevalence of acidogenic phase in which bacteria consume the organic substrate and produce H_2, CO_2 and VFA.

The scarce activity of methanogenic bacteria gave rise to H_2 and VFA accumulation with consequent pH decrease (Tezel et al., 2011).
Notwithstanding the pH correction to neutrality, a lag phase followed about 17-18 days long, without any significant biogas production. The presence of phenolic compounds could be responsible for the inhibition of methanogenic species growth in the OMW test (Gonçalves et al., 2014).
The biogas production became again appreciable after 19-21 days, when exponential growth of acetogenic and methanogenic bacteria started with the associated production of CH_4 and CO_2. At first, the volume of biogas increased exponentially then volume approached to a constant value (~1660 mL) in about 35-40 days. During this phase the produced biogas contained mainly CH_4 (80-85% v/v) and CO_2 (Figure 3).

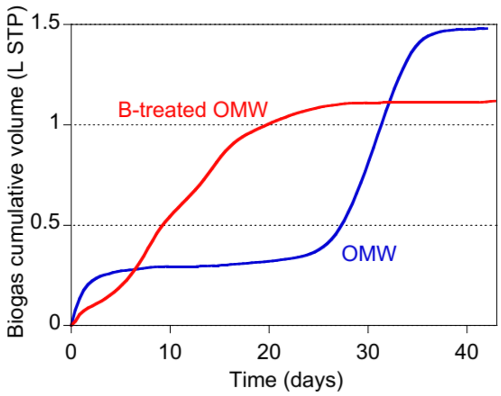

Figure 2. Cumulative biogas volumes produced during AD of OMW and B-treated OMW.

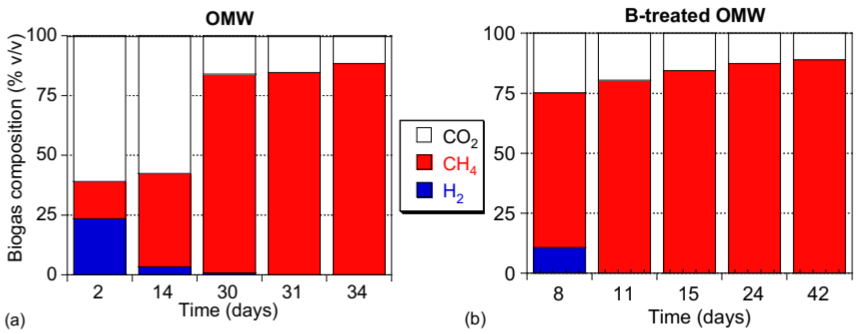

Figure 3. Biogas composition (CO_2, CH_4, H_2) at different days during AD of (a) OMW and (b) B-treated OMW.

In contrast to run with OMW, during the AD of B-treated OMW, the trend of cumulative biogas volume (Figure 2, solid line) did not show a neat separation between metabolic phases. The onset of the methanogenesis was faster, since after 8 days H_2 concentration was lower (~11% v/v) and CH_4 higher (~64% v/v) than those observed for the OMW run (Figure 3). Then, the biogas production continued at high rates and produced biogas contained mainly CH_4, in the range 80-89% v/v, and CO_2 the remaining (Figure 3). After about 24-26 days biogas production stopped and the final cumulative volume was about 1220 mL (Figure 2, solid line). This behavior can be explained by the fact that the B based pre-treatment reduced the TPC concentration, thus avoiding the initial inhibition of methanogenic bacteria.
The digestion medium with B-treated OMW had an initial pH in the range 7.2-7.3. In contrast to the run with OMW, pH did not change significantly during the fermentation with B-treated OMW, due to the buffering action of B (Wang et al., 2018).

3.3 Evaluation of biodegradation by COD balance

Even though the run with B-treated OMW approached biogas volume plateau faster than with OMW (~26 versus ~40 days), volumetric methane and hydrogen yields were significantly lower (Table 2). A comparative evaluation could be performed with the aid of some measured COD values.
From the theoretical biogas yields per gram of digested COD (0.35 L CH_4/g COD and 1.4 L H_2/g COD at STP) and from the measured volumetric yields (Table 2) an overall COD removal by AD can be calculated.

Table 2. Biogas yields and soluble COD removals.

AD test	Biogas L L^{-1}	CH_4 L L^{-1}	H_2 L L^{-1}	Final sCOD g L^{-1}	sCOD removal[b] %
OMW	3.81 ± 0.21	2.35 ± 0.27	0.19 ± 0.11	6.15 ± 0.79	32.9
B-treated OMW	2.21 ± 0.25	1.62 ± 0.30	0.12 ± 0.04	3.52± 0.55	61.6

[a] Liters of gas at STP per liter of digestion medium.
[b] Evaluated on loaded sCOD, i.e. 9.17 g L^{-1} deriving from 10% OMW (v/v) used in digestion medium.

For the OMW digestion, an overall COD removal of 6.86 ± 0.76 g L^{-1} can be calculated from the cumulative volumes of CH_4 and H_2. COD removal calculated from biogas production can be compared with that calculated from measured COD balance. Initial and final COD of the OMW digestion batch (comprehensive of suspended solids) were 14.38 ± 0.25 and 8.66 ± 0.47 g L^{-1}, respectively, giving an overall COD removal of 5.72 ±0.53 g L^{-1}. Given the large experimental error in biogas volumes and the COD measurement of particulate solid suspensions (from inoculum and biomass), the agreement with the value estimated from biogas yields was considered satisfactory.
From the measured volumetric yields of the B-treated OMW digestion (Table 2), an overall COD removal by AD of 4.72 ± 0.86 g L^{-1} can be calculated. We were not able to directly check this value with measured COD data from B-treated OMW digestion batch due to high interference of B on COD measurements. The COD removal was evaluated on added sCOD basis, i.e. by recalling that the initial sCOD of OMW was 91.7 g L^{-1} and 10% (v/v) OMW (both OMW and B-treated OMW) was added to the digestion medium: thus, about 9.17 g L^{-1} were potentially available for biodegradation. The inoculum COD was negligible and in any case not biodegradable, as verified by separated AD test. After removing suspended solids, soluble COD (sCOD) of OMW digestate was about 6.15 g L^{-1}, corresponding to 32.9% removal of initial sCOD in the digestion medium. Conversely, sCOD at the end of digestion of B-treated OMW was about 3.52 g L^{-1} (61.6% sCOD was removed). The removal of sCOD from B-treated OMW was therefore 9.86 – 3.52 = 6.34 g L^{-1} , much higher than the value 4.72 g L^{-1}, calculated from biogas production. Sequestration by B of part of biodegradable organic content could be responsible of the resulting difference.
The results obtained with B-treated OMW can be compared with other pretreatments based on physicochemical and biological methods as reported in the literature. Most successful physicochemical methods include heat treatment, ultrasounds, and advanced oxidation processes, i.e. ozonation, Fenton process, electrochemical oxidizing methods (Ioannou-Ttofa et al. 2017). Biological methods include aerobic pretreatments with the endogenous microflora or with added fungi (Ioannou-Ttofa et al. 2017). All the pretreatments aim to reduce the phenolic content and improve the anaerobic digestion of the organic content of OMW (Gunay and Karadag, 2015). Even if the listed pretreatments succeed to obtain comparable or higher phenolics and COD removals, they are all more energy-consuming than the pretreatment with B (even the biological aerobic pretreatment consumes considerable amounts of energy to aerate for the required treatment time).

4. Conclusions

The results of present work showed that the biochar treatment improves the efficiency of anaerobic digestion of OMW by accelerating biogas production and improving COD removal. The biochar treatment was found to be able to remove most of phenolic compounds responsible for the microbial toxicity of OMW. Methanogenesis of biochar-treated OMW was no more inhibited, thus removing the long lag phase after initial acidogenesis. Part of biodegradable COD could be adsorbed by biochar and no more available for digestion, giving rise to lower biogas yields. However, the combined treatment (biochar followed by AD) ensured a higher sCOD removal than AD of OMW alone (~61.6% vs ~32.9%), still allowing for a fair energy recovery by biogas production.

Acknowledgements

This work was part of the project “Mitigation of the environmental impact of olive mill waste water through sustainable bioprocess with energy recovery” funded by the Università degli Studi di Napoli Federico II, Finanziamento Ricerca di Ateneo.

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