

AD-504**Ultrasonication pre-treatment as a tool to boost COD solubilization and biogas production in anaerobic digestion****M. Biasiolo*, F. Mazzolini, C. Giotto, C. Cavinato**

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Abstract: Anaerobic digestion is a well-known and widely recognized biological process that allows a direct waste-to-energy nexus, through the conversion of organic wastes into biogas. Depending on the wastes used as a substrate and on their degradability, kinetics and process yields may vary consistently, affecting the economic sustainability of the process. Pre-treatments of the organic substrates may boost their degradability, enhancing and speeding up biogas production. The application of ultrasonication has been widely studied to increase the hydrolysis rate in anaerobic digestion processes. In this study, a mixture of Poultry Manure (PM) and Sewage Sludge (SS) was treated at different ultrasonic densities (180, 340, 500, and 1000 W L⁻¹). The overall highest increase in the soluble COD was obtained at 1000 W L⁻¹, with a degree of disintegration of 23.6 %. The treated wastes were then tested to define their biological methanation potential (BMP) and to define their hydrolysis coefficient. The outcomes of the test indicate a significant increase in the specific methane production and the hydrolysis activity (+ 22.8 % and + 32.3 %, respectively).

Keywords: Pre-treatment; ultrasonication; co-digestion

Introduction

The correct management of sewage sludge is pivotal to ensure the environmental and economic sustainability of wastewater treatment plants (WWTPs). Despite being relatively rich in putrescible organic matter and nutrients, maximizing its potential may require the adoption of specific process strategies, such as chemical-physical pre-treatment or co-digestion. Poultry manure stands out as one of the most abundant and economically viable materials, with a high nutrient content, and may be successfully combined with sewage sludge to complement and balance the nutrient ratio of the organic mixture (Sillero et al., 2022). Among different mechanical pre-treatment, ultrasonication has been widely studied for its potential to increase the hydrolysis rate in anaerobic digestion processes, attracting significant interest for its simple operation, short retention time, absence of chemical addition, and minimal by-product formation (Pilli et al., 2020).

This study aims to investigate the impact of ultrasonication as a pre-treatment to maximize the hydrolysis activity and the biogas production yields of an anaerobic digestion process co-digesting poultry manure and sewage sludge, focusing on the application of different ultrasonic densities to the waste mixture.

Material and Methods

The Poultry Manure (PM) used in this study was provided by a zootechnic industry. The Sewage Sludge (SS) was collected from a gravity static thickener at a municipal wastewater treatment plant (WWTP). The organic waste mixture (PM+SS mixture) was prepared by mixing poultry manure and sewage sludge in a 1:9 ratio, on fresh matter basis. The digestate used for the BMP test, collected in the same WWTP from a full-scale mesophilic anaerobic digester, was sieved with a 2 mm mesh sieve and degassed in an oven at 39°C for one week, to obtain a homogeneous inoculum.

Table 1 Chemical-physical characterization of inoculum and substrates.

	Total Solids (g _{TS} kg _{FM} ⁻¹)	Total Volatile Solids (g _{TVS} kg _{FM} ⁻¹)	sCOD (g _{O2} L ⁻¹)	tCOD (g _{O2} kg _{FM} ⁻¹)
Anaerobic Inoculum	34.9 ± 0.3	19.2 ± 0.1	-	-
Sewage Sludge	26.6 ± 0.8	19.6 ± 0.4	5.6 ± 0.6	25.7 ± 0.9
Poultry Manure	470 ± 1	355 ± 6	97 ± 5	500 ± 9
PM+SS mixture	56 ± 2	43 ± 2	10.2 ± 0.6	69 ± 4

Table 1 shows the chemical-physical characteristics of the involved matrices. Total Solids and COD content analyses were performed according to APHA standard methods.

The ultrasonication pre-treatment was carried out using a probe-type ultrasonicator (GET:WAVE, Everywave srl, Italy) and a 400 mL vessel (working volume of 250 mL). The sonicator was set at 20 kHz and the power supplied was regulated to achieve ultrasonic densities of 180, 340, 500, and 1000 W L⁻¹.

During the pre-treatment, the temperature was maintained at 30 ± 1 °C using an iced bath. Samples were collected after 1, 2.5, 5, 10, and 15 min for COD determination. After the 15-minutes pre-treatment, the sample obtained was stored at -20 °C.

The degree of disintegration (DD, %) was determined as:

$$DD (\%) = \frac{COD_{UC} - COD_0}{COD_{NaOH} - COD_0} \quad (1)$$

where COD₀ (g_{O2} L⁻¹) is the soluble COD of the untreated sample, COD_{UC} (g_{O2} L⁻¹) is the soluble COD of the ultrasonicated sample, and COD_{NaOH} (g_{O2} L⁻¹) is the soluble COD of the sample after addition of 1 M NaOH for 24 h at room temperature.

The BMP test was performed in duplicate using 1 L glass bottles, with 400 mL of inoculum, an F/M ratio of 0.3, and a temperature of 39 °C. The experiment lasted a total of 24 days. During the test, the biogas daily production was measured with a water displacement cylinder, and its composition was analysed using a portable biogas analyser (MCA100 SynH2, ETG Risorse e Tecnologie, Italy).

Results and Conclusions

Table 2 shows the soluble COD concentration, the degree of degradation, and the maximum solubilization rate of the treated and untreated substrate. All conditions resulted in a significant increase in the soluble COD of the waste mixture, with the highest increase obtained after 15 min at 500, and 1000 W L⁻¹: 18.4 g_{O2} L⁻¹ (+ 79.5 %), and 19.6 g_{O2} L⁻¹ (+ 91.4 %), respectively.

Table 2 Effect of ultrasonic pre-treatment on COD solubilization and degree of disintegration.

	soluble COD (g _{O2} L ⁻¹)	Degree of disintegration (%)	Maximum solubilization rate (g _{O2} L ⁻¹ min ⁻¹)
Control condition	10.2 ± 0.6	-	-
180 W L ⁻¹	15.4 ± 0.9	13.1 ± 0.8	1.8 ± 0.9
340 W L ⁻¹	16.8 ± 0.5	16.5 ± 0.5	3.0 ± 0.9
500 W L ⁻¹	18.4 ± 0.8	20.5 ± 0.9	4.4 ± 0.8
1000 W L ⁻¹	19.6 ± 0.4	23.6 ± 0.5	5.7 ± 0.7

Figure 1 shows the trend of the degree of disintegration (DD, %) and the COD solubilization rate (g_{O2} L⁻¹ min⁻¹) during the test. The ultrasonic pre-treatment was capable of solubilizing a significant fraction of the available COD of the PM+SS mixture, ranging between 13 and 24 % of the maximum COD achievable by chemical disintegration. It is worth mentioning that the COD solubilization rate (g_{O2}

$\text{L}^{-1} \text{min}^{-1}$) reached its maximum value at the beginning of the procedure for all tested conditions, suggesting that the pre-treatment is mostly effective within the first minute.

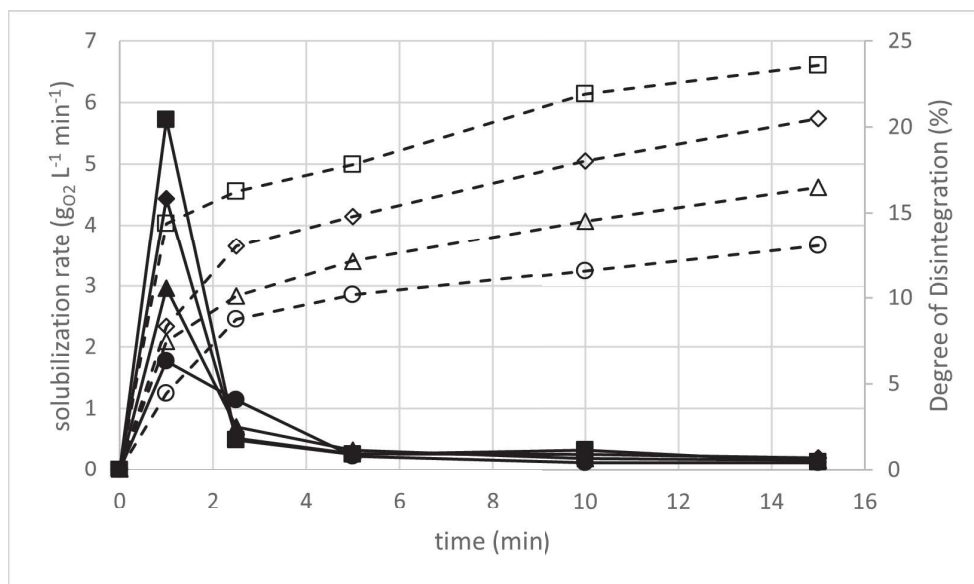


Figure 1 Ultrasonic treatment performance as solubilization rate ($\text{gO}_2 \text{L}^{-1} \text{min}^{-1}$, solid dots) and degree of disintegration (DD, %, hollow dots). 180 W L^{-1} (●, ○); 340 W L^{-1} (▲, △); 500 W L^{-1} (◆, ◇); 1000 W L^{-1} (■, □).

To define the effect of the ultrasonic treatment in enhancing the biodegradability of the PM+SS mixture and the yields of its conversion to methane, a BMP test was performed. Figure 2 shows the Specific Methane Production ($\text{Nm}^3_{\text{CH}_4} \text{t}_{\text{TVS}}^{-1}$) of the treated and untreated substrates. In all the pre-treated conditions, higher values of SMP were achieved, with the highest one obtained at 500 and 1000 W L^{-1} : 307.7 (+ 22.8 %) and 303.0 (+ 21.6 %) $\text{Nm}^3_{\text{CH}_4} \text{t}_{\text{TVS}}^{-1}$, respectively. These values are slightly higher than the increase in CH_4 yields obtained by other authors when applying ultrasonication to the mono-digested substrates: + 15 % (Zhao et al., 2023) for sewage sludge and + 19 % (Anacleto et al., 2022) for poultry manure.

The achievement of higher SMP values for ultrasonic-treated substrates is most likely due to the enhanced hydrolysis coefficient, which reached the highest values at 500 and 1000 W L^{-1} : 0.409 (+ 28.8 %) and 0.420 (+32.3 %) d^{-1} , respectively.

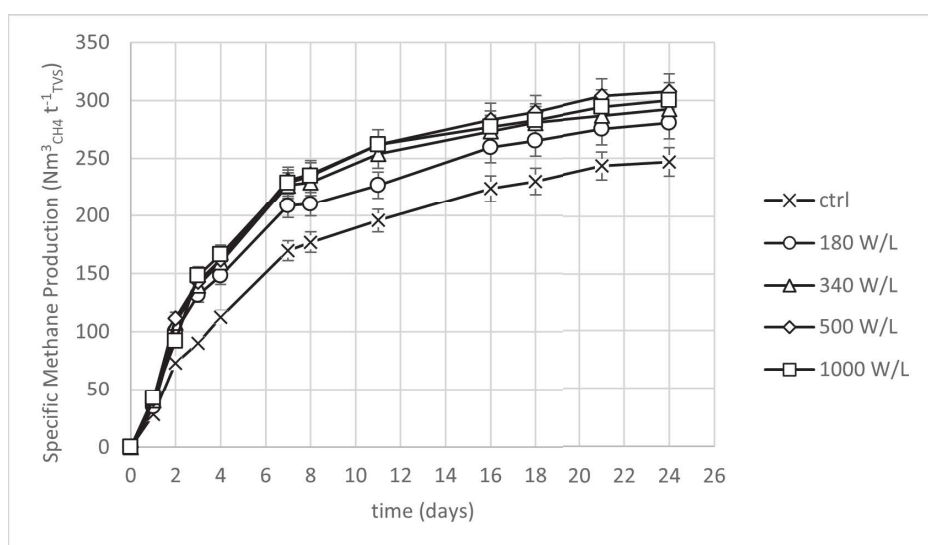


Figure 2 Ultrasonic Specific Methane Production ($\text{Nm}^3_{\text{CH}_4} \text{t}^{-1}_{\text{TVS}}$). Control condition (X); 180 W L^{-1} (○); 340 W L^{-1} (△); 500 W L^{-1} (◇); 1000 W L^{-1} (□).

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