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Pretreatment and Nanoparticles as Catalysts for Biogas Production Reactions in Pepper Waste and Pig Manure

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Abstract: The circular economy is based on using waste generated from any process to obtain products with zero residues' criteria. This research was focused on pepper waste from the polyphenolic extraction method. Pepper waste was evaluated in batch and semi-continuous regime anaerobic digestion, adding, as catalysts, absorbent nanoparticles and/or using pretreatment strategies. The best methane yields were obtained from SB1 (assay without pretreatment in pepper waste): 464 ± 25 NL kg VS^{-1} for batch assays; and from period II (1.47 g VS L^{-1} d^{-1}) of S2 (assay of pig manure and pepper waste with thermal pretreatment): 160 NL/kg VS^{-1} for semi-continuous experiments. However, a kinetic study showed a methane production rate higher for SB2 (assay with nanoparticles as catalyst) than SB1 in batch assays.

Keywords: nanoparticles; pretreatment pepper waste; kinetic; anaerobic process

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1. Introduction

Nowadays, the biorefinery concept is related optimizing the use of waste to obtain biofuels, energy, and high-added-value subproducts. Through this concept, it is possible fight against the climate change. Concretely, the European Commission has identified some priority areas where the European Directive from Renewables Energies [1] must act. A total elimination of waste generated by industries and the introduction of renewable energies in their processes can be regarded as appropriate measures undertaken to achieve some of the specific objectives against the climate change [2]. Particularly, in a region of Spain (Extremadura) where this research has been developed, there is a Regional Plan of Research, Technological Development, and Innovation [3]. This plan is focussed on economic priorities in the agrifood sector. For this reason, if waste from the agrifood sector is considered to be put to optimum use, we will be moving towards a more sustainable economy. According to the Spanish Statistics National Institute [4], there was 636,116 t of vegetable waste in Spain in 2020 from food and drink manufacturing industries and tobacco factories. A total of 26% in the production of fruits and vegetables in European countries in 2021 belong to Spain [5]. Furthermore, the amount of exported pepper from Spain exceeded 800,000 t in 2021, and in Spain, 1,500,000 t of pepper was produced in 2021 [6]. Normally, waste produced from pepper is around 50–60% of the total processed biomass [7]. The waste generated is usually employed as animal feed or discharged into landfills, leading to environmental degradation in the areas in which they are disposed of [8]. A strategic solution must be developed to manage the large amount of pepper waste produced in the country. Applying a biorefinery concept to pepper waste will be an excellent way to optimize the benefits. Different extraction methods can be carried out to achieve the valorization of this waste. High-added-value product can be obtained as polyphenolic and carotenoids compounds. A newly developed first-step extraction method offers an opportunity to obtain more degraded pepper waste to use as feed for microorganisms that produce biofuels—more concretely, biogas. The process to generate biogas is called anaerobic digestion (AD); it consists of degrading organic matter in the waste by specific microorganisms to produce biogas. Another product is generated in this process: digestate, which can be used as organic fertilizer. Digestate is a fertilizer containing odorless stabilized organic matter and NPK nutrients which have changed to mineral forms which are available for plants [9]. In this process, two or more residues can be employed, and this process is called anaerobic co-digestion (AC-D). There is a large number of studies concerning AC-D substrates employing vegetable waste with animal waste (i.e., slurry or cattle manure). An evaluation of pepper waste's addition in a co-digestion process with swine manure was developed by Riaño et al. [10]. In this study, the highest specific methane yield obtained under batch conditions was 309 N L CH_4 kg VS^{-1}, with a percentage of pepper waste in the mixture of 50% (on the VS basis). After AC-D under semicontinuous operation at different OLR values was studied, the method was shown to increase the specific methane yield by up to 86% compared to that obtained from a mono-digestion assay of swine manure (208 N L CH_4 kg VS^{-1} at 1.26 g VS $L^{-1}d^{-1}$). Li et al. [11] studied the AC-D of wood waste with pig manure and evaluated the methane production potential using a NaOH pretreatment in the wood waste. The obtained results showed that the methane yield was increased by 75.8% after NaOH pretreatment compared with the untreated wood waste. To improve the kinetics, different mechanisms can be employed, such as nanoparticles, bioelectrochemical applications, and nano-biochar. Madondo et al. [12] researched the application of bioelectrochemical systems and magnetite nanoparticles in sewage sludge for the improvement of organic content degradation. In this case, an enhanced methane percentage was obtained versus the control (88% versus 39%). A review [13] focused on the role of additive nano-biochar in the AC-D kinetic shows evidence of nano-biochar's value as a catalyst for enhancing biogas production. However, this review refers to the development of no-continuous operational modes. Semi-continuous operational modes using this kind of catalyst have not been so well studied. Magnetized nanoparticles (iron oxides and aluminum sulfate) were employed by Kweinor and Rathilal [14] to obtain a quicker reaction rate in the AC-D process of wastewater. The kinetic parameters calculated showed that the presence of these nanoparticles shortens the lag phase of the control system, with a kinetics rate of 0.285 d^{-1} for control and of 0.127 d^{-1} and 0.195 d^{-1} for iron oxides and aluminum sulfate nanoparticles, respectively.

Alkalinity is an important parameter in the AC-D process, mainly in a semi-continuous regime. High alkalinity (based on the equilibrium carbon dioxide–bicarbonate) provides an excellent buffer capacity of the digestion medium. VFA (Volatile Fatty Acids) accumulations or in pH values are avoided, according Smridhivej and Boyd [15]. When the feed of substrates added to the digester (organic load rate (OLR)) is increasing in the AC-D process, alkalinity and VFA must be controlled to avoid the inhibition of the process.

Due to the gap in the research related to the semi-continuous operational mode using diverse types of catalyst, the present study proposes to assess the performance and stability of assays employing pig manure and pepper waste in the AC-D, including absorbent nanoparticles and/or strategies of waste pretreatment, as catalysts. The obtained results are compared through different kinetic parameters calculated according to simulation models.

2. Results and Discussion

2.1. Chemical Characterization of Raw Materials

The assays developed in this research used different raw materials: pepper waste pretreatment (PWP) (with thermal pretreatment and/or nanoparticles), pig manure (PM), and pepper waste (PW). PWP with PM were studied in semi-continuous assays and PW with PM were employed in a pilot plant assay. PM, PW, and PWP were characterized before to start the studies, and results are shown in Table 1.

Table 1. Chemical parameters of raw materials determined.

Parameter	PM	PW	PWP
pH	7.70 ± 0.10	4.18 ± 0.04	4.10 ± 0.29
Redox potential, mV	−362 ± 23	−100 ± 1	206 ± 10
Alkalinity, mg $CaCO_3$ L^{-1}	9379 ± 75	-	-
N-NH_4, mg L^{-1}	1860 ± 85	870 ± 30	390 ± 80
C, %	2.23 ± 0.30	7.12 ± 0.19	7.63 ± 1.85
N, %	0.30 ± 0.03	0.36 ± 0.01	0.42 ± 0.09
C/N	7.32 ± 0.36	18.04 ± 1.37	18.71 ± 2.17
TS, %	5.71 ± 0.02	13.31 ± 0.29	17.17 ± 3.33
VS *, %	3.98 ± 0.12	12.32 ± 0.23	15.80 ± 3.14
Ca, ppm	2663 ± 48	1003 ± 21	1965 ± 18
Fe, ppm	209 ± 2	76 ± 1	120 ± 2
K, ppm	240 ± 30	2317 ± 25	1953 ± 4
Mg, ppm	1208 ± 11	439 ± 1	617 ± 4
Na, ppm	913 ± 2	64 ± 1	262 ± 3
P, ppm	1562 ± 7	473 ± 7	807 ± 46
Al, ppm	152 ± 7	81 ± 1	95 ± 5

* Total Volatile Solid over Total Solids.

As can be observed in Table 1, low values of pH from PW and PWP are presented. The alkalinity parameter value from PM is quite high to buffer the low pH values from pepper materials. If AC-D works with alkalinity values higher than 2000 mg $CaCO_3$ L^{-1}, as it does according to Flotats et al. [16], it indicates the stability of the process. The C/N proportion used in the feed must be close to 20–30 [17–20]; PW and PWP have values near to these values. The TS values of PW and PWP are very similar, and they are quite high. Moreover, the Total Volatile Solid is observed to be about 93 % of the TS. It entails a high potential of organic transformation of PW and PWP, as it is happened in research carried out by Arhoun et al. [21] (they developed AC-D of mixed sewage sludge and fruits and vegetable wholesale market waste).

2.2. Biochemical Methane Potential (BMP) of Different Strategies with PWP

Three assays were undertaken to find the most productive method: batch assay without pretreatment (SB1); batch assay with a determined absorbent nanoparticles dose (SB2); and batch assay with another determined absorbent nanoparticles dose and thermal pretreatment (SB3). Table 2 shows the BMP and the kinetic parameters. These results evidence that methane yield from SB1 is the highest of the studies carried out. Moreover, a thermal pretreatment of the PWP can be an adequate method to increase the methane average concentration in the biogas obtained. Gallego L. M. et al. [22] evaluated the empirical BMP through different models from some horticultural waste such as beet pulp and pear flesh; the obtained results (249 NL kg VS^{-1} and 318 NL kg VS^{-1} for beet pulp and pear flesh, respectively) were lower than the values obtained in this research. Kinetic parameters show higher R_{max} values for SB2 and SB3 than R_{max} for SB1. This probably means that the nanoparticles in the medium quickly support production methane rate.

Table 2. BMP and kinetic parameters for different studies developed with PWP.

Parameter	SB1		SB2		SB3	
Methane average yield, NL kg VS^{-1}	464 ± 25		331 ± 57		364 ± 49	
Methane average concentration, %	59 ± 2		56 ± 6		60 ± 1	
Replicates	R1	R2	R1	R2	R1	R2
R_{max}, Nm^3 kg VS^{-1} d^{-1}	0.64	0.75	0.82	1.51	0.85	1.00
l, d	2.82	1.56	0.77	1.29	-	-
R^2	0.9888	0.9757	0.9387	0.9727	0.9686	0.9766

Figures 1–3 illustrate the kinetic model fitting for the three studies. Two replicates were developed for each study. All of them are perfectly fitted to the modified Gompertz model because the regression coefficients are too elevated.

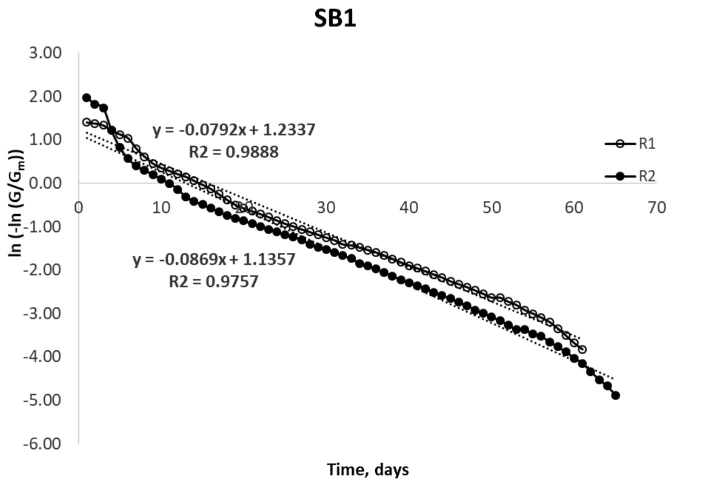

Figure 1. Experimental results fitted to the modified Gompertz model for SB1.

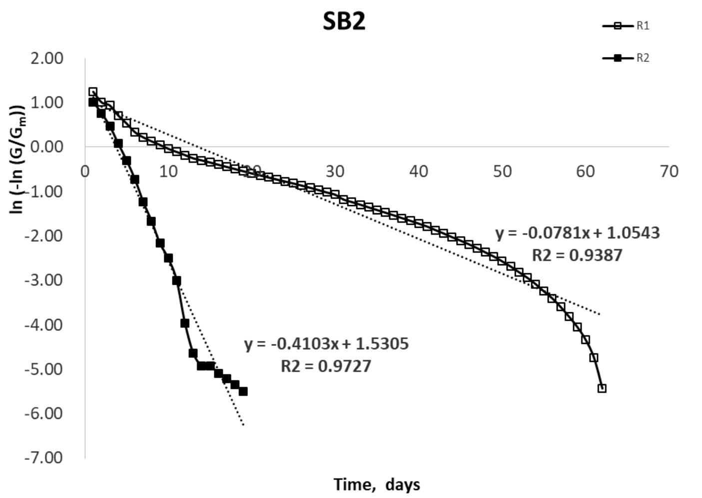

Figure 2. Experimental results fitted to the modified Gompertz model for SB2.

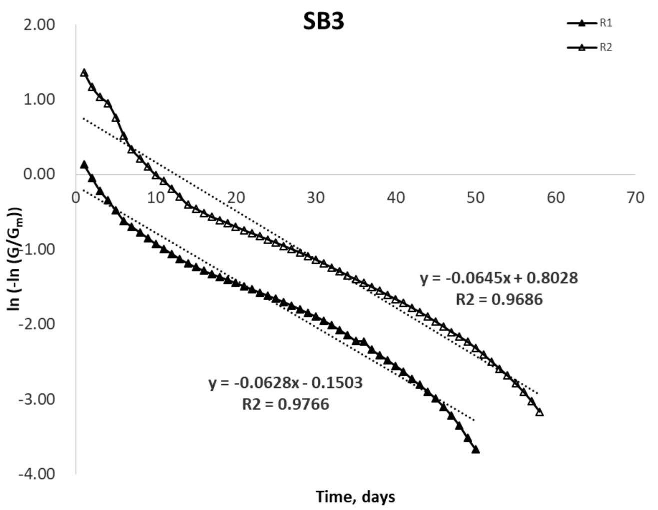

Figure 3. Experimental results fitted to the modified Gompertz model for SB3.

There is no lag phase (*l*) in SB3 because a previous pretreatment has been developed, and the experimental results fitted to the kinetic model were taken after this pretreatment. Regarding the lag phase from SB1 and SB2, the values obtained present more elevated values in SB1 than SB2. This fact seems to indicate that the nanoparticles' presence improves the methane production in the first stage. The lag phase average values of sorghum and corn stover (0.190 d and 2.648 d, respectively) obtained by González et al. [23] are the lowest in this research and very close the experimental to values of this work. Chiappero et al. [24] employed different biochars as catalysts during AD of mixed wastewater sludge, and the kinetic parameter R_{max} for the modified Gompertz model ranged between 0.014 and 0.034 Nm^3 kg VS^{-1} d^{-1}, i.e., lower values than results obtained in this work.

2.3. Different Pretreatment for Assays Semi-Continuous with PM and PWP

Assays were developed with three different conditions: S1: PM with PWP; S2: PM with PWP and thermal pretreatment; and S3: PM with PWP developing thermal pretreatment and nanoparticles use (the employed dose (0.015 g g VS^{-1}) was the most productive for batch assay). In Figure 4, we observe influence of the treatment carried out to increase the methane production for OLR (period I to III). The methane volume represented in Figure 4 seems very similar for periods II and III. A light difference can be seen in period I, obtaining the highest production for S2 and the lowest production for S1; this means that the nanoparticles are not increasing the methane production in the AC-D for period I (Table 3 does not show rises of methane production when nanoparticles are employed neither). Chen et al. [25] studied two types of magnetic nanoparticles (Ni ferrite nanoparticles and Ni Zn ferrite nanoparticles). They found a stimulation of anaerobic digestion in synthetic municipal wastewater with a certain type of nanoparticles but an inhibition of another type of nanoparticles was added to the anaerobic digestion medium. The values of methane yields and kinetic parameters are represented in Table 3.

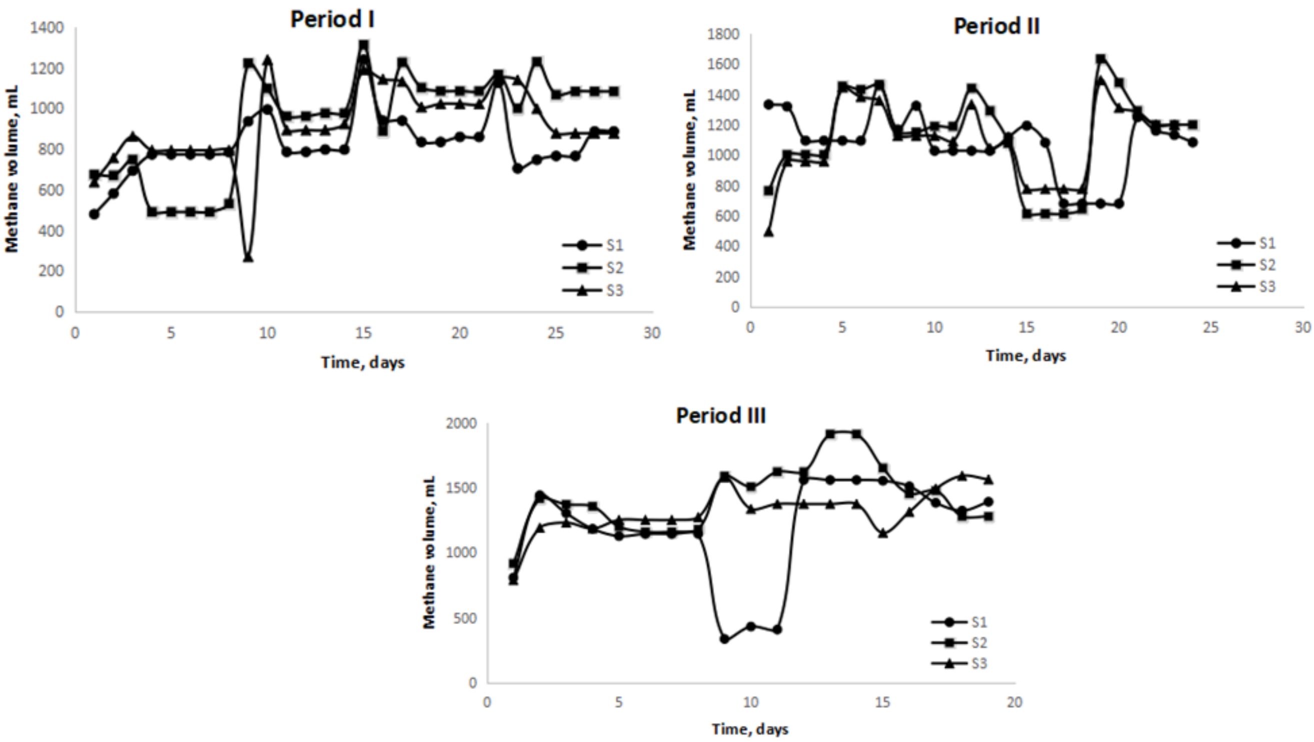

Figure 4. Methane volume evolution for different periods.

Table 3. Methane yield and kinetic parameters obtained in semi-continuous assays.

Period	Period I	Period II	Period III
		S1	
Methane yield, NL kg VS^{-1}	139	149	149
k_B, g COD L^{-1}		4.42	
U_{max}, d^{-1}		1.03	
k_2, d^{-1}		0.73	
		S2	
Methane yield, NL kg VS^{-1}	158	160	156
k_B, g COD L^{-1}		4.98	
U_{max}, d^{-1}		1.49	
k_2, d^{-1}		0.90	
		S3	
Methane yield, NL kg VS^{-1}	153	156	155
k_B, g COD L^{-1}		4.33	
U_{max}, d^{-1}		1.31	
k_2, d^{-1}		0.64	

According with the catalyst effect of the nanoparticles and the thermal pretreatment, the kinetic parameters' reaction constants—k_B and k_2—for each kinetic model fitted are shown in Table 2. The highest values of reaction constants belong to S2. This corresponds to the assay with the most elevate methane yield (S2). In any case, the reaction constant obtained in this work are higher than values of reactions constant obtained by other authors; 0.25 g COD g VS^{-1} d^{-1} has been reported by De la Lama D. et al. [26] for "alperujo" in semi-continuous anaerobic digestion of the thermally pretreated medium.

As can be seen in Figures 5 and 6, experimental results from the cumulative methane production of the S1 and S2 experiments are perfectly fitted to the Stover–Kincannon and second-order models because their regression coefficients are elevated (0.9999, 0.9822, and 0.9772).

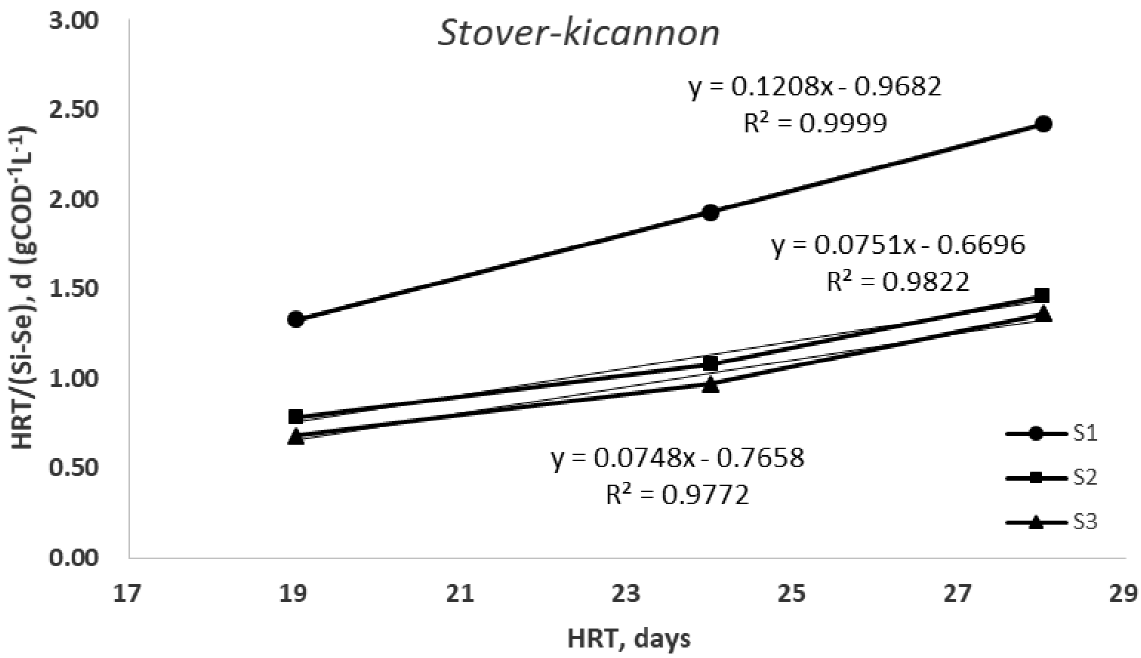

Figure 5. Experimental results fitted to the Stover–Kincannon model for semi-continuous experiments.

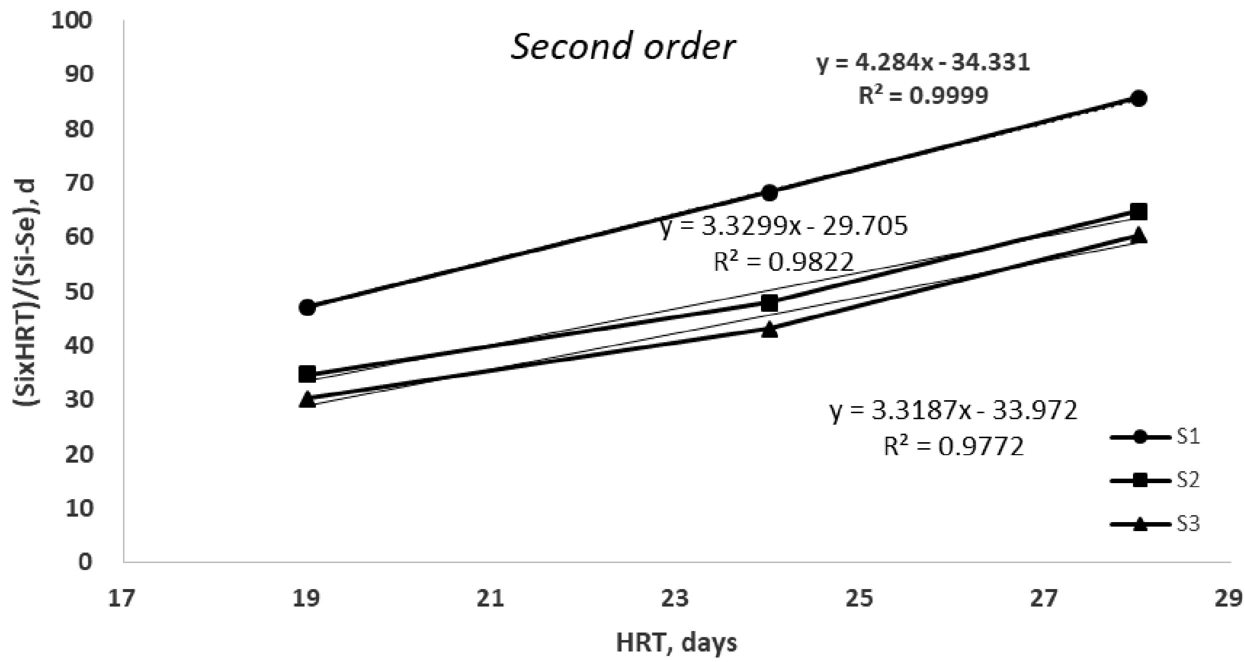

Figure 6. Experimental results fitted to the second-order model for semi-continuous experiments.

2.4. Effect of OLR on Different Parameters

The interactions study of certain parameters in the AC-D process and the studied values of OLR are represented in Figures 7 and 8. An expected, direct interaction is presented in alkalinity when the OLR is increased; this means that the process stability is increasing until 1.88 g VS L_D^{-1} d^{-1} for the three assays developed. This behavior was found in a work carried out by Parralejo et al. [27], where the AC-D process in semi-continuous assays was evaluated for OLR ranged 1.2–1.8 g VS L_D^{-1} d^{-1} for different mixtures of animal manure or nitrogen-rich biomass. However, the VS parameter evolution with OLR shows a light decrease in the second period (and small increases in methane yield (Table 3)). VFA and ammonia nitrogen parameters exhibit a direct interaction with the OLR evaluated in the most of assays developed. This is a normal behavior when the organic matter is enhanced. Nevertheless, the values of VFA and ammonia nitrogen are below the threshold values for the stability of the processes (4000 mg L^{-1} and 5000 mg L^{-1} for ammonia nitrogen and VFA, respectively) [28].

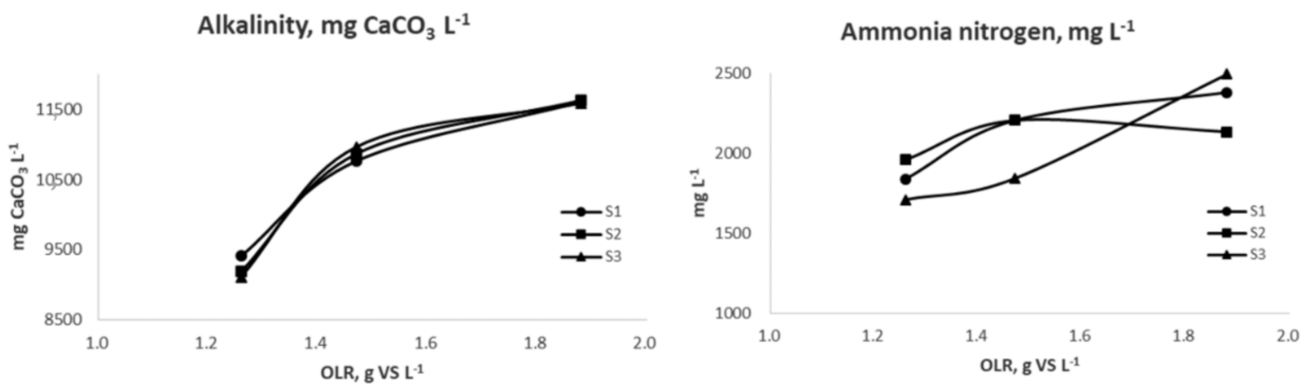

Figure 7. Alkalinity (**left**) and ammonia nitrogen (**right**) effects on OLR developed in semi-continuous assays.

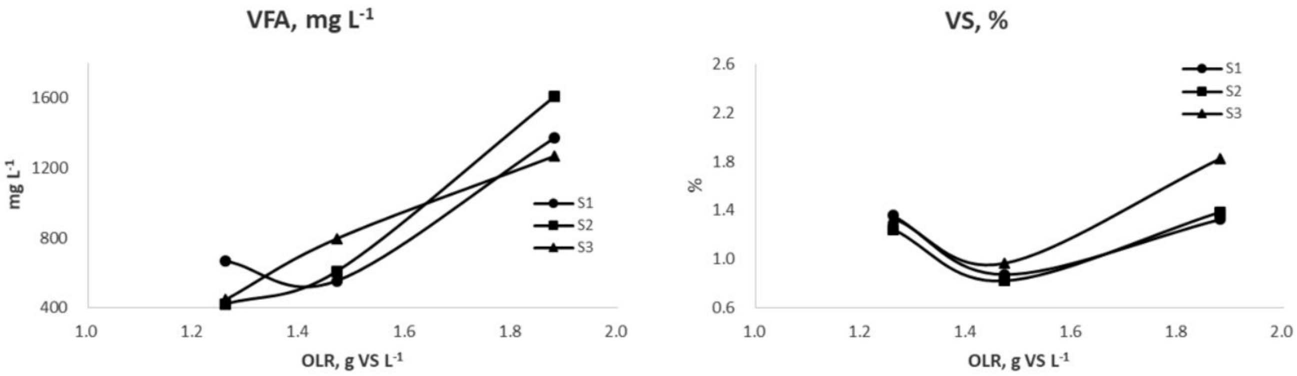

Figure 8. VFA (**left**) and VS (**right**) effects on OLR developed in semi-continuous assays.

2.5. Digestate Pilot Plant Experiment

An experiment in a pilot plant was carried out for two OLR values (period I and II). In this experiment, a semi-continuous AC-D for PW and PM was assessed. Methane yield and digestate composition were evaluated for each OLR studied, and the results are shown in Table 4.

Table 4. Methane yield and digestate composition for experiment carried out in pilot plant.

Parameter	Period I	Period II
pH	7.91 ± 0.10	7.95 ± 0.05
Redox potential, mV	−388 ± 12	−409 ± 9
Alkalinity, mg $CaCO_3$ L^{-1}	10,892 ± 2	10,340 ± 37
Methane yield, NL kg VS^{-1}	173 ± 45	264 ± 55
C, %	1.06 ± 0.03	2.20 ± 0.20
N, %	0.21 ± 0.01	0.37 ± 0.02
C/N	4.98 ± 0.15	6.02 ± 1.14
Ca, ppm	779 ± 4	2259 ± 9
Fe, ppm	75 ± 2	230 ± 2
K, ppm	1317 ± 28	2467 ± 29
Mg, ppm	526 ± 2	1121 ± 3
Na, ppm	669 ± 2	596 ± 6
P, ppm	359 ± 10	1052 ± 15
Al, ppm	40 ± 2	157 ± 2
Zn, ppm	34 ± 1	141 ± 1
Cu, ppm	10 ± 1	38 ± 1
Cr, ppm	<5	<5
Ni, ppm	<5	<5

Higher methane yield is obtained for period II (elevate OLR employed) than for period I. This difference in S1 was observed in assays carried out in laboratory conditions. It could be due to the pepper substrate being pretreated and the organic matter being degraded in the pretreatment process. All values of the elements showed in Table 4 are higher for period II than the values of elements for period I, and in any case, the values for period II are correct for the development of the AC-D process because the methane yield has an adequate value. If the digestates obtained for two periods are evaluated as fertilizer, N, P, and K nutrients are the most important. Normally, P and K are often expressed as P_2O_5 and K_2O, respectively. In Table 5, the nutrient compositions assimilable by plants are exposed along with a fertilizer classification for digestates according to the Spanish standard [29].

In the classification of the Spanish standard, "fertilizers A" are those that have the lowest amount of Zn, Cu, Cr, and Ni. The plant nutrients' availability amounts to 55%, 64%, and 92% for N, P_2O_5, and K_2O, respectively [30].

Table 5. Nutrient composition assimilable by plants of digestates from period I and II.

Parameter	Period I	Period II
Assimilable N content, %	0.12	0.20
Assimilable P_2O_5 content, %	0.80	2.33
Assimilable K_2O content, %	1.01	1.89
Fertilizer classification [28]	A	A

3. Materials and Methods

3.1. Evaluated Raw Materials

This research employed pig manure (PM) and pepper waste as raw materials, both without pretreatment (PW) and pretreated (PWP). PM was collected from a pig farm located in Guadajira (Badajoz, Spain) (+38°51′9.6768″, −6°40′15.5418″). PW was provided by a frozen vegetable factory. PW was composed of stem, peduncle, and seeds, so the heterogeneous waste was mixed and chopped via mechanical pretreatment to obtain a homogeneous paste. Moreover, PWP was subjected to the polyphenols extraction method to achieve optimization in the waste valorization. Polyphenols extraction employed water as solvent and ultrasound bath to be as close as possible to the most environmentally friendly techniques. PM was stored at room temperature; PW homogeneous paste was frozen, and the extraction method of PW to obtain PWP was carried out weekly. An inoculum was employed to help the development of the specific microorganisms. The inoculum used in assays consisted of a mixture of completely degraded organic material with a high content of methanogenic microorganisms. The inoculum was composed of a mixture of prickly pear and pig manure.

3.2. Digester Used and Experimental Design

Laboratory and pilot plant digesters were employed in this research, both made of stainless steel, with a central agitator electrically operated and adjustable by a potentiometer to obtain the mixture of substrates, and a thermostat to control the temperature inside the digesters. Laboratory digesters are coated with an outer jacket through which hot water circulates to maintain the constant temperature of the substrate, and pilot plant digester has an inner coil surrounding the walls for the hot water. The total volumes of laboratory and pilot plant digesters are 6 L and 2000 L, respectively, but the used volumes for these experiments were 4.5 L and 1500 L, respectively. In this study, a mesophilic temperature range (38 °C) was employed. At the beginning, three batch assays were developed (Table 6) to establish the influence of the nanoparticles' dose and the thermal pretreatment presence: SB1 batch assay of PWP; SB2 batch assay of PWP with a determined absorbent nanoparticles dose (0.064 g g VS^{-1}); and SB3 batch assay of PWP with another determined absorbent nanoparticles dose (0.015 g g VS^{-1}) and thermal pretreatment.

The ratio of inoculum to PWP was 1:2 on VS basis. The nanoparticles used belong to a small factory (Smallops), located in Badajoz (Extremadura, Spain), that manufactures the product from organic waste. Three semi-continuous assays were carried out (S1 to S3). The studied fed were S1: PM with PWP; S2: PM with PWP developing thermal pretreatment; S3: PM with PWP developing thermal pretreatment and nanoparticles use. The working procedure from semi-continuous regime assays consisted of a daily feeding of the substrate mixture. A hopper on the top of the digesters with a ball valve was employed to introduce the substrate mixture, and another valve located on the side of the digester was used to extract the digestate. Three different OLRs (1.26 g SV $L_D{}^{-1}$ d^{-1}; 1.47 g SV $L_D{}^{-1}$ d^{-1}; and 1.88 g SV $L_D{}^{-1}$ d^{-1}) were studied for each assays set. Each OLR evaluated was considered a study period. Table 6 shows the experimental design. Finally, a pilot plant experiment was carried out, studying a mixture of 50% of PM and 50% of PW (on VS basis).

Table 6. Experimental design in assays sets evaluated.

Assay	OLR, g VS LD−1 d−1	Mixture Composition/Feed	Hydraulic Retention Time (HRT), d
SB1	-	Inoculum–PWP (ratio: 1:2)	-
SB2	-	Inoculum–PWP (ratio: 1:2) with nanoparticles (0.064 g g VS^{-1})	-
SB3	-	Inoculum–PWP (ratio: 1:2) with nanoparticles (0.015 g g VS^{-1}) and thermal pretreatment	-
S1	Period I: 1.26	50% PM and 50% PWP (on VS basis)	28
	Period II: 1.47		24
	Period III: 1.88		19
S2	Period I: 1.26	50% PM and 50% PWP (on VS basis) with thermal pretreatment	28
	Period II: 1.47		24
	Period III: 1.88		19
S3	Period I: 1.26	50% PM and 50% PWP (on VS basis) with thermal pretreatment and nanoparticles (0.015 g g VS^{-1})	28
	Period II: 1.47		24
	Period III: 1.88		19

3.3. Analytical Methods

APHA standard methods [31] were employed to characterize the substrates used. Drying the sample to a constant weight in an oven (JP Selecta Digitheat, Barcelona, Spain) at 105 °C for 48 h (2540 B method) and at 550 °C for 2 h in a muffle oven (Hobersal 12PR300CCH, Hobersal Furnaces & Ovens Technology, Barcelona, Spain) using an inert atmosphere (2540 E method) were the means employed to determine total solids (TS) and volatile solids (VS) in the samples analyzed. Specific electrodes were employed to measure the pH and redox potential values of the digestion medium connected to a pH meter (Crison Basic 20, Hach lange Spain S.L.U., Barcelona, Spain). To determine the alkalinity of the medium, method 2320 was employed; for the chemical oxygen demand (COD), method 410.4 was employed [32]; for ammonia nitrogen (N-NH_4) by volumetric titration, the E4500-NH_3 B method was employed; and for total volatile fatty acids (VFA), to Buchauer's volumetric method was employed [33]. The ratio between N and C nutrients was analyzed by a True-Spec CHN Leco 4084 elementary analyzer (ECO empowering results, Madrid, Spain, according to the UNE-EN 16948 standard for biomass analysis C, N, H [34]. A constant monitoring of the biogas volume and its composition was carried out with an Awite System of Analysis Process series 9 analyzer (Bioenergie GmbH, Awite Bioenergie GmbH, Langenbach, Germany) (composed of different sensors to detected methane, carbon dioxide, hydrogen, hydrogen sulfide, and oxygen concentration). The gas meter (Ritter model MGC-1 V3.2 PMMA, Awite Bioenergie GmbH, Langenbach, Germany) was employed to measure the biogas produced, which was stored in Tedlar bags. The biogas volume produced was corrected at standard conditions (0 °C, 101,325 kPa). The digestate was featured by spectroscopy using an ICP-OES Varian 715 ES (Agilent Technologies, Santa Clara, CA, USA).

3.4. Evaluation of Substrate Removal Kinetic Models

For batch assays, experimental results have been fitted to a kinetic model called a modified Gompertz [14]. For semi-continuous assays, based on the substrate removal rate, Grau second-order multicomponent and modified Stover–Kincannon models have been employed as kinetic models [26]. For the Grau second-order multicomponent model when multicomponent substrates are evaluated, the substrate removal rate can be expressed according to Equation (1):

$$\frac{-dS}{dt} = k_{n(s)} \cdot X \cdot \left(\frac{S_e}{S_i}\right)^n \tag{1}$$

where $-dS/dt$ is the substrate removal rate; k_n (s) is the reaction constant; X is the concentration of the microorganisms, which ca be assumed as constant; S_e is the substrate concentration at any time; and S_i is the initial substrate concentration.

Integrating Equation (1) for $n = 2$ and linearizing it, the following linear expression is obtained (Equation (2)):

$$\frac{(S_i \cdot HRT)}{(S_i - S_e)} = HRT + \frac{S_i}{k_s \cdot X} \tag{2}$$

The value of the second-order reaction constant can be obtained by the plot of the $(S_i{\cdot}HRT)/(S_i - S_e)$ versus HRT. The term HRT is the hydraulic retention time value for each set assay.

In the modified Stover–Kincannon model, the substrate removal rate is expressed as a function of the OLR as follows in Equations (3) and (4):

$$\frac{dS}{dt} = \frac{(S_i - S_e)}{HRT} \tag{3}$$

$$\frac{dS}{dt} = \frac{U_{\max} \cdot \left(\frac{S_i}{HRT}\right)}{k_B + \left(\frac{S_i}{HRT}\right)} \tag{4}$$

where *dS/dt* is the substrate removal rate; k_B is the reaction constant; $U_{\max}$ is the maximum substrate removal rate; S_i and S_e are the substrate concentrations explained above; and *HRT* the hydraulic retention time, as has been specified before. When Equations (3) and (4) are equalized and integrated and the resulting expression is linearized, Equation (5) is obtained, as follows:

$$\frac{HRT}{(S_i - S_e)} = \frac{k_B}{U_{\max}} \cdot \frac{HRT}{S_i} + \frac{1}{U_{\max}}. \tag{5}$$

Experimental results fitted to Equation (5) give a linear expression where the reaction constant can be obtained from the slope.

4. Conclusions

A comparison between batch and semi-continuous assays have been developed concerning AC-D processes in pig manure and pepper waste, including absorbent nanoparticles and/or pretreatment strategies as catalysts. For batch assays, kinetic parameters specify that the presence of nanoparticles in the medium quickly supports the methane production rate (higher R_{max} values for SB2 and SB3 than R_{max} for SB1, and the lag phase is lowest for SB2). The studied influence of the pretreatment carried out in the methane production for the OLRs the evaluated OLRs (period I to III) via semi-continuous assays shows slightly more elevated values for the thermal pretreatment assay (160 NL kg VS^{-1}). Direct interaction among alkalinity, VS, ammonia nitrogen and VFA parameters, and the OLR has been found. Finally, digestates from experimental pilot plants evaluated for two OLR values have been assessed and classified, according the Spanish standard, as the fertilizer with the lowest heavy metal concentration and assimilable N, P_2O_5, and K_2O content of 0.12%, 0.80%, and 1.01% for period I, and 0.20%, 2.33%, and 1.89% for period II, respectively. However, this kind of fertilizer must be extensively studied before being applied to different crops.

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