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Batch and Semi-Continuous Anaerobic Digestion of Industrial Solid Citrus Waste for the Production of Bioenergy

Erik Samuel Rosas-Mendoza [1], Andrea Alvarado-Vallejo [2], Norma Alejandra Vallejo-Cantú [2], Raúl Snell-Castro [3], Sergio Martínez-Hernández [4] and Alejandro Alvarado-Lassman [2,]*

[1] CONACYT-Tecnológico Nacional de México, Instituto Tecnológico de Orizaba, Av. Oriente 9, 852. Col., Emiliano Zapata, Orizaba C.P. 94320, Mexico; eriksamuelrm@hotmail.com

[2] División de Estudios de Posgrado e Investigación, Tecnológico Nacional de México, Instituto Tecnológico de Orizaba, Av. Oriente 9, 852. Col., Emiliano Zapata, Orizaba C.P. 94320, Mexico; alvaradov.andrea@gmail.com (A.A.-V.); nvallejoc@prodigy.net.mx (N.A.V.-C.)

[3] Departamento de Ingeniería Química, CUCEI-Universidad de Guadalajara, Blvd. Marcelino García Barragán 1421, Guadalajara C.P. 44430, Mexico; raul.snell@cucei.udg.mx

[4] Instituto de Biotecnología y Ecología Aplicada, Universidad Veracruzana, Avenida de las Culturas Veracruzanas 101, Col., Emiliano Zapata, Xalapa C.P. 91090, Mexico; sermartinez@uv.mx

* Correspondence: lassman@prodigy.net.mx

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Abstract: The aim of this paper is to describe a study of the anaerobic digestion of industrial citrus solid waste (ISCW) in both batch and semi-continuous modes for the production of bioenergy without the elimination of D-limonene. The study was conducted at the pilot plant level in an anaerobic reactor with a working volume of 220 L under mesophilic conditions of 35 ± 2 °C. Cattle manure (CM) was used as the inoculum. Three batches were studied. The first batch had a CM/ISCW ratio of 90/10, and Batches 2 and 3 had CM/ISCW ratios of 80/20 and 70/30, respectively. In the semi-continuous mode an OLR of approximately 8 g total chemical oxygen demand (COD)/Ld (4.43 gVS/Ld) was used. The results showed that 49%, 44%, and 60% of volatile solids were removed in the batch mode, and 35% was removed in the semi-continuous mode. In the batch mode, 0.322, 0.382, and 0.316 LCH_4 were obtained at $STP/gVS_{removed}$. A total of 24.4 L/d (34% methane) was measured in the semi-continuous mode. Bioenergy potentials of 3.97, 5.66, and 8.79 kWh were obtained for the respective batches, and 0.09 kWh was calculated in the semi-continuous mode. The citrus industry could produce 37 GWh per season. A ton of processed oranges has a bioenergy potential of 162 kWh, which is equivalent to 49 kWh of available electricity ($3.90).

Keywords: anaerobic digestion; industrial solid citrus waste; cattle manure; citrus industry; bioenergy potential

1. Introduction

Citrus belongs to the group of products with the highest world consumption, with oranges being the most consumed. According to the official data, currently around four million hectares are harvested [1], with the world's production of oranges being about 47.5 million tons [2]. In this context, Brazil (15.1%), China (7.3%), the European Union (5.8%), the United States (4.9%), and Mexico (4.4%) are the countries that produce the most oranges [2]. Approximately, 28.7 million tons (60%) are consumed as fresh oranges and 18.8 million tons (40%) are used in the citrus industry for the production of concentrated orange juice, essential oils, marmalades, jellies, potpourris, candied peel, jams, flavoring agents for beverages, health drinks, and essences that are used as food-grade products [3–5]. From the processing of oranges, 40–60% of the total tonnage of oranges is discarded as solid waste [6,7], so, worldwide, the citrus industry generates from 7.5 to 11.3 million tons of industrial solid citrus waste (ISCW) per year. The large amounts of ISCW that are produced and the peculiar characteristics of ISCW involve considerable constraints for their management due to both economic and environmental factors [8]. ISCW is characterized by a high water content (80%); acid pH (i.e., pH values in the range of 3–5) due to the presence of organic acids [9]; total solids (20.17%, wet basis); total mineral solids (0.87%, wet basis); volatile solids (19.31%, wet basis); chemical organic demand (1085 mgO_2/g, dry basis) [10]; and D-limonene, which is a toxic compound [11]. As a matter of fact, traditional citrus peel waste disposal strategies (e.g., incineration and landfilling) currently are insufficient and problematic in terms of environmental impacts and energy efficiency [9]. Some viable alternatives for treating this type of waste are anaerobic digestion and anaerobic co-digestion, which have strong potential benefits to contribute to both pollution control and energy recovery [12,13]. The main advantages of anaerobic digestion and anaerobic co-digestion are (i) environmental friendly solutions compared to other practices, (ii) organic waste with a low nutritional content can be degraded via co-digestion with different substrates in anaerobic reactors, (iii) improved methane yield because of the supply of additional nutrients from the co-digestates, (iv) more efficient use of equipment and cost-sharing by processing multiple waste streams in a single facility, and (v) the process produces biogas with a low cost, and this could be vitally important in meeting our energy needs in the future [14–16].

Therefore, a method to limit the inhibition of the process because it produces toxic compounds, such as D-limonene, consists of co-digesting citrus peel waste with other substrates to dilute the toxic compounds [5]. Anaerobic co-digestion, and also anaerobic digestion, produce a valuable biogas, mainly composed of methane (65–80%) and carbon dioxide (20–35%), and a wet residue (digestate) [17]. Methane has a heating power of 9.94 kWh/m^3 at standard temperature and pressure (STP) [18], but the heating power of biogas varies from 5.2 to 6.2 kWh/m^3 at STP [19]. Biogas has great potential for various applications, such as heating, combined heat and electricity [20], the improvement of the quality of transport fuel, and the replacement of natural gas for various uses.

In the last few years, various scientific articles have been published that focused on the anaerobic digestion and co-digestion of solid waste from oranges, but the studies reported in these articles have required either total or partial elimination of D-limonene to avoid its inhibitory effect during this biological process. Specifically, various substrates and co-substrates have been used for anaerobic digestion and co-digestion, such as biowaste, municipal waste, catering waste, and orange peel waste. As inoculums have been used, e.g., a mixture of sludge, co-digested municipal solid waste and melon residues digestate, and liquid digestate coming from a full-scale plant, among others. Some interesting papers in this area are: (1) Calabrò et al. [21], who indicated that orange peel waste can produce up to 370 $LCH_4/kgVS$ (under normal conditions) in mesophilic conditions and up to 300 $LCH_4/kgVS$ (under normal conditions) in thermophilic conditions, and the presence of increasingly high concentrations of essential oils temporarily inhibits methanogenesis. (2) Ruiz and Flotats [22] indicated that the biochemical methane potential values of the citrus waste that was tested (i.e., orange peel, mandarin peel, mandarin, pulp, and rotten fruit) were 354–398 $LCH_4/kgSV$ and that grinding the orange peel (2.5 g limonene/L) did not influence the potential value of biochemical methane. (3) Anjum et al. [23] studied the synergistic effect of co-digestion to enhance anaerobic degradation of catering waste and orange peel, and their findings indicated that the highest degradation of organic matter (49%) was achieved with co-digestion of catering waste and orange peel at a 50%/50% mixing ratio. (4) Calabró and Panzera [24] performed the anaerobic digestion of ensiled orange peel waste (OPW), and their findings indicated that the highest production was attained for samples of OPW ensiled for 37 days, with a value of 365 normal $mLCH_4/gVS$, and OPW ensiled for 7 days inoculated with sludge already adapted to the substrate yielded 513.7 normal $mLCH_4/gVS$ versus 187.2 normal $mLCH_4/gVS$ of the corresponding test using non-adapted inoculum.

Other works have proposed different strategies to minimize D-limonene's toxic effects on anaerobic digestion, i.e., the combination of recirculation and filtration can be a promising strategy for the anaerobic digestion of citrus waste at high OLRs [25]. Orange peel waste alkaline pretreatment after the addition of a moderate amount of granular activated carbon can render the anaerobic digestion of OPW sustainable as long as the organic loading does not exceed 2 gVS/L and the nutrients are supplemented [26]. Further, the addition and pre-treatment of zero valent iron/granular activated carbon enhance process stability up to a loading of 3 kgVS/m^3 d and increases the production of methane, even at a suboptimal pH [27]. Similarly, two-stage anaerobic digestion systems have replaced the use of other pretreatments and increased the concentration of methane (approximately 60% compared with about 50%) and volume (by 13%) relative to one-stage anaerobic digestion. The accumulated biogas yield was 0.79 L/gSVT and 0.49 L/gSVT for the methanogenic and control reactors, respectively [28].

Cattle manure is used extensively as an inoculum in many studies [29] or as a co-substrate due to its pH characteristics (7.25), chemical oxygen demand (COD) (24.85 mg/L), TS (189.8 mg/L), and VS (34 mg/L) [30]. In addition, cattle manure is used directly as fertilizer in agriculture, but this can cause environmental problems, such as foul odors and contamination of both soil and water [31].

Despite the efforts made by the scientific community in the search for new and better alternatives for the use of solid citrus waste, it remains a challenge to find new ways of treatments that can be implemented on an industrial scale. A practical and affordable way is to take advantage of its physicochemical properties of cattle manure by using it as an inoculum in the anaerobic digestion of these wastes. Thus, the objective of this paper is to report the results of a study of anaerobic digestion for the production of bioenergy in both the batch and semi-continuous modes of ISCW with CM, without the elimination of D-limonene.

2. Materials and Methods

The methods used in this work are explained in detail below.

2.1. Experimental Device

It was constructed an anaerobic reactor (AR) made of fiberglass with a wall thickness of 0.64 cm, a height of 1.04 m, and a total volume of 250 L. The AR had a working volume of 220 L and a 30-L biogas chamber. Fiberglass is known to be a good thermal insulator, to be inert to diverse substances (e.g., the volatile fatty acids produced during the anaerobic digestion), to have resistance to deformation, and to be stable at relatively high temperatures. The valves, tubes, and connectors were made of schedule 80 PVC material that had a diameter of 5.08 cm. As shown in Figure 1, the reactants were placed in the AR. In addition, during the operation of the AR, the mesophilic conditions (35 ± 2 °C) using a heating jacket with a capacity of 25 L capacity was kept with an automatic thermostat and a 600 L/h capacity recirculation submersible pump inside the water reservoir. The inoculum and the substrate were mixed through a recirculation system installed at the bottom of the AR. The recirculation system consisted of a reservoir tank and a Masterflex Cole-Parmer variable-velocity, peristaltic pump. The biogas was collected in an inverted water displacement system, and HCl was used to maintain the pH at approximately 5.5 in order to avoid the dissolution of CO_2 into the water.

2.2. Inoculum

CM was used as the source of inoculum for this study. The CM was obtained from a geomembrane reactor located at a cattle farm in the city of Orizaba in Veracruz, Mexico. After collection, the CM was filtered using a pore size of 2 mm to remove large particles. The CM was characterized according to the parameters shown in Table 1, after which it was used to inoculate the AR.

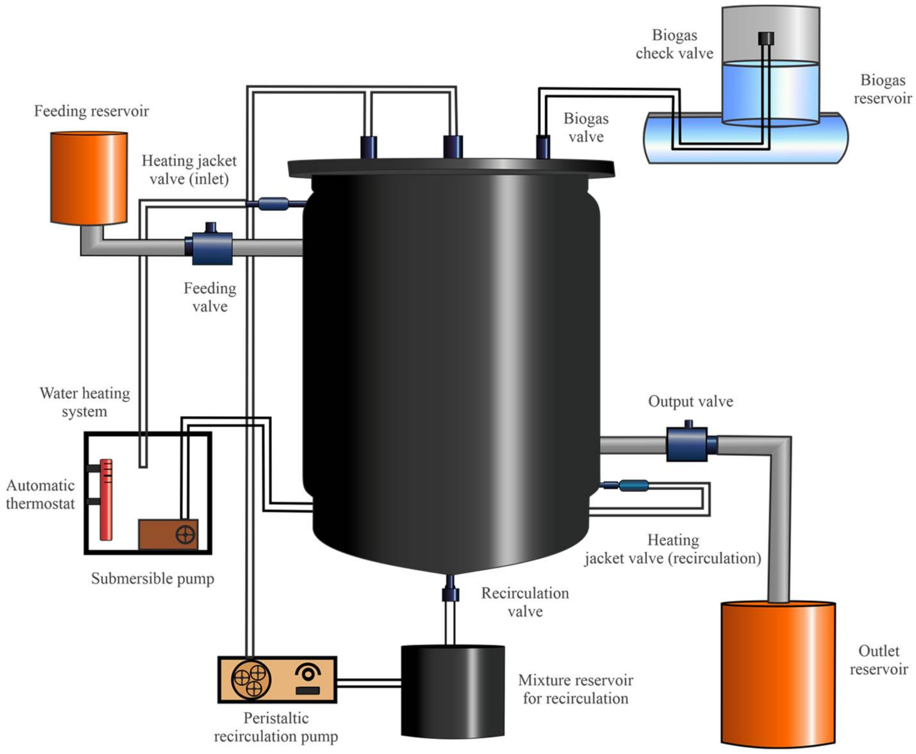

Figure 1. Anaerobic reactor for the digestion of industrial citrus solid waste (ISCW) with cattle manure (CM).

Table 1. Characterization of cattle manure and industrial solid citrus waste.

Parameter	CM		ISCW	
	Mean	**Standard Deviation**	**Mean**	**Standard Deviation**
Total COD (g/L)	7.83	1.45	54.11	1.25
Soluble COD (g/L)	4.22	1.95	32.96	1.27
TS (g/L)	4.32	1.40	61.22	1.33
VS (g/L)	3.59	2.30	57.85	1.24
pH	7.45	0.18	4.46	0.17

2.3. Substrate

ISCW from a citrus processing plant in the municipality of Martínez de la Torre, Veracruz, Mexico was used as the substrate. This ISCW was generated at different points in the process of obtaining various products, such as fresh juice, concentrated juice, essential oil, and dry peel. ISCW was mixed before its final disposal, as part of the operating practices into the citrus processing plant. After, the ISCW samples were obtained, they were preserved at 4 °C. Then, the ISCW was cut into small pieces that were approximately 1–1.5 cm in length, and they were grinding to reduce the particle size for later physicochemical characterization. Table 1 shows the main parameters of the characterization of CM and ISCW.

All samples were analyzed in triplicate.

2.4. Methodology of the Experiment

The experiment consisted of three stages, as described below:

Stage 1. Inoculation, start-up, and stabilization of the anaerobic reactor with CM

The AR was inoculated with 160 L of fresh CM, and it was operated in a short batch mode over a period of seven days. Then, the start-up was initiated by extracting 140 L of CM, which left 20 L of CM along with a 200 L supply of fresh excreta, which ensured the availability of a working volume of 220 L of CM, and the AR was operated for 30 days. The reactor was stabilized by using two batches, each one for 30 days, and removing 200 L from the 220 L CM and adding 200 L of fresh CM into the reactor. In Stage 1, it was not necessary to regulate the pH, because, as shown in Table 1, the CM presented an almost neutral pH, and it was recirculated at a constant rate under mesophilic conditions at 35 ± 2 °C for a duration of 97 days.

Stage 2. Digestion stage of the ISCW with CM

After the previous stage, the AR was fed with ISCW, thus starting the anaerobic digestion process of the ISCW using CM in batch mode. Due to the low pH values of the ISCW, it was necessary to use a 3 M NaOH solution to increase the values to approximately 7.5 so the anaerobic digestion process could occur. The ISCW were fed at three different ratios because the bacteria inside the reactor had not adapted to the new substrate. Each ratio was evaluated as a batch, which means that one batch one corresponded to the CM/ISCW ratio of 90/10 (*v*/*v*), as shown in Table 2. Each batch was operated for 30 days with a total volume of 220 L of substrates.

Table 2. Anaerobic digestion of CM/ISCW.

Batch	CM/ISCW (%*V*/*V*)	CM Remaining in the Reactor (L)	Fresh ISCW (L)	Batch Duration (d)
1	90 / 10	198	22	30
2	80 / 20	176	44	30
3	70 / 30	154	66	30

Stage 3. Digestion stage in semi-continuous mode

After evaluating the anaerobic digestion process of the ISCW using CM in the batch mode, the adaptation of the inoculum to other conditions was proven. For this, the AR was maintained in recirculation for 15 additional days with the same CM/ISCW mixture used in the last stage, i.e., 70/30. Later, 44 L of the mixture was replaced by 44 L of fresh ISCW, and the remaining 176 L was used as an inoculum since it was perfectly adapted to degrade ISCW. This process was repeated four times, the first time for 5 days and 10 days each for the three remaining times. Thus, this digestion process took place during short periods of time, i.e., at the same conditions as Batch 2 of Stage 2.

To evaluate the operation of the AR in a semi-continuous mode, the CW/ISCW ratio was modified again, i.e., 90/10 was used. This last ratio was equivalent to manage an OLR of 8 $gCOD_T$/Ld, thus the AR was operated during two short periods of 10 days each one.

2.5. Analytical Determinations

The pH was determined by an Orion Model 250 A potentiometer. The total COD (COD_T) and the soluble COD (COD_S) were monitored every 24 h in both operational batches and semi-continuous modes using the colorimetric method [32]. Due to its nature, ISCW cannot be analyzed directly [33], and, for that reason, the particle size was reduced to less than 1 mm in a conventional blender with the aim of homogenizing the samples in order to avoid the obstruction of the measuring instruments. In order to conduct the COD_S, 12 mL of the sample were centrifuged in an HERMLE Z 383 centrifuge at 3500 rpm for 10 min, after which the supernatant was analyzed. The CODs of the digested samples were measured with a HACH spectrophotometer at 620 nm. The total solids (TS) and volatile solids (VS) were determined by the gravimetric method [32].

The composition of the biogas was determined using a Buck 310 gas chromatograph equipped with an All-Tech CRT I capillary column that was 6 inches long and had a diameter of 1/4 inch. The gas chromatograph detected CH_4, CO_2, O_2, and N_2. The 2 mL doses were injected directly into the gas chromatograph, helium at 70 psi was used as the carrier gas, the temperature of the column was 36 °C, and the temperature of the detector was 121 °C.

2.6. Bioenergy Potential of ISCW with CM

Bioenergy potential was calculated from the methane yields obtained during the anaerobic digestion of the industrial solid citrus waste with cattle manure in both batch and semi-continuous mode. The following conditions were assumed:

- ISCW had no physical or chemical pre-treatment to eliminate the D-limonene contained in the waste. This was done to maintain the same conditions that exist with industrial waste.
- In batch mode, three CM/ISCW ratios were considered, i.e., 90/10, 80/20, and 70/30. Each batch had a duration of 30 days.
- In semi-continuous mode, 22 L/day of fresh ISCW were fed, so, OLR 8 g total COD/Ld (4.43 gVS/Ld) was used. The experiment was conducted for a period of 10 days.
- The anaerobic digestion process in both the batch and semi-continuous cases was conducted at the mesophilic condition of 35 ± 2 °C.

The volume of methane generated by the anaerobic digestion (CH_4 AD) was calculated using Equation (1):

$$CH_4\ AD = (V_{AR})(VS_I)(VS_{\%})(Y_{CH4})(1 \times 10^{-5}) \quad (1)$$

where:

V_{AR}, is the volume of the anaerobic reactor (in liters) of the mixture (CM/ISCW) that was used.

VS_I, is the feeding concentration of the mixture (initial VS), expressed in g/L.

$VS_{\%}$, is the removal efficiency of the VS, expressed in %.

Y_{CH4}, is the methane yield obtained from the anaerobic co-digestion process, in LCH_4 at STP/gVS_{rem}.

1×10^{-5} is a conversion factor to express the methane generated by AD in m^3 at standard temperature and pressure (STP). Bioenergy potential was estimated using Equation (2):

$$BEP = (CH_4\ AD)(HP_{CH4}) \quad (2)$$

where:

HP_{CH4}, is the heating power of methane at standard temperature and pressure, 9.94 kWh/m^3 at STP [18].

From the bioenergy potential, the amount of electricity that can be used was calculated using Equation (3) based on the energy conversion efficiency (η) of a commercial generator, i.e., 30% [34], and 1×10^{-2} is a conversion factor that was used to express electricity in kWh. The remaining 70% corresponds to thermal energy.

$$\text{Electricity} = (BEP)(\eta)(1 \times 10^{-2}) \quad (3)$$

The cost of electricity tariff (ET) in Mexico is approximately 0.08 USD/kWh [35], so Equation (4) can be used to calculate the cost of electricity provided by the anaerobic digestion process:

$$\text{Cost} = (\text{Electricity})(ET) \quad (4)$$

3. Results and Discussion

The results presented in this section are explained according to the research methodology, i.e., Stage 1: inoculation, start-up, and stabilization of the anaerobic reactor with CM; Stage 2: digestion stage of the ISCW with CM; and Stage 3: the digestion stage in the semi-continuous mode. In addition, an estimate of the bioenergy potential from anaerobic digestion process is presented. The findings of each stage are described below:

3.1. Inoculation, Start-Up, and Stabilization of the Anaerobic Reactor with CM

In this stage, only cattle manure was used, i.e., for inoculation (7 days), start-up (30 days), and stabilization of the anaerobic reactor (two batches at 30 days per batch).

During the inoculation, the pH values remained stable, ranging between 6.95 and 7.81, while the total COD decreased from 7.5 to 3.6 g/L, and the soluble COD decreased from 4.7 to 2.5 g/L. The initial TS value of 5.14 g/L decreased to a final level of 3.7 g/L, and the values of VS were 3.7 at the beginning and 1.6 g/L at the final of the inoculation. Subsequently, during the start-up, the pH at the inlet was 7.69, and it was 6.71 at the outlet. The initial and final values of the total COD were 6.5 and 1.45 g/L, respectively. Likewise, there was a decrease in the soluble COD from 2.97 to 0.84 g/L, and the TS and VS values varied from 4.36 to 2.76 g/L and from 2.74 to 1.11 g/L, respectively. Finally, in the stabilization, the pH was equal to the value in the previous phases, i.e., very close to 7. The CM used to feed the AR maintained an average total COD of 7.35 g/L and an average soluble COD of 3.8 g/L. Each batch presented 79 and 88% of total COD removal, with a similar tendency for the removals of soluble COD, TS, and VS. The accumulated biogas was quantified as approximately 72.6, 659, 647, and 741 L in the inoculation, start-up, and stabilization phases (two batches), respectively. Baek et al. [36] found that the biochemical methane potential of the cattle manure though mono-digestion can produce around 109.2 L/kgVS. These same researchers concluded that co-digesting cattle manure with food waste and pig manure proved effective in accelerating the initiation of anaerobic digestion, which suggested that the co-digestion strategy could be applied to promote the start-up of a digester to treat cattle manure. Usually manure is considered to be an output product in livestock systems, which leads to the idea that it is simply residual; however, manure should be considered to be a valuable product because of its nutrients and biogas potential [37]. Alatriste-Mondragón et al. [13], mention that the main wastes most used in co-digestion processes are municipal wastewater sludge, the organic fraction of municipal solid waste and cattle manure. Cattle dung proved to be beneficial to achieve enhanced biogas production with supplementation of four residues: compost, landfill waste, paddy soil and kitchen waste [38]. Silva and Abud [39], evaluated the use of bovine manure as inoculum in the vinasse biodigestion process, using 0.5, 3.0 and 5.5% of manure.

3.2. Digestion Stage of the ISCW with CM

After conditioning the inoculum during Stage 1, the anaerobic reactor was operated in three batches at the conditions shown in Table 2, i.e., using the ISCW as the substrate and the CM as the inoculum.

Regarding the monitoring of the pH, the three batches were fed so as to regulate the pH of their respective CM/ISCW relationships with values close to 7.5. During the 30 days of operation, the pH remained relatively stable, finally reaching values below 7, as shown in Figure 2. However, in Batch 3 during the first six days, a decrease in pH was observed, and it reached 5, which may have been due to the bacterial medium's being affected by the increased ISCW feed. In order to avoid greater levels of acidification, an extra addition of NaOH solution was required, which successfully stabilized the pH, as had been the case in the previous batches. Continuing with the analysis of Batch 3, despite having suffered a significant initial change in pH, the bacteria regained their activity, and the anaerobic digestion process was not inhibited. In anaerobic digestion or co-digestion, pH is an important operating parameter, and, in this experiment, the pH oscillated between values that were close to 7, i.e., in a range of 6.80 to 7.58. Ward et al. [40], found that the ideal range of pH for anaerobic digestion was 6.8−7.2. Lee et al. [41] reported that methanogenesis occurs efficiently in an anaerobic reactor at pH values between 6.5 and 8.2. Marín-Peña et al. [42] also reported that pH values in the range of 7.0–7.5 favor the methanogenic stage of anaerobic digestion. In addition, during the anaerobic co-digestion of 50% orange peel with 50% catering waste, Anjum et al. [23] observed that the pH was in the range of 6.38–7.01 between days 39 and 42, which is the optimum range for methanogenesis.

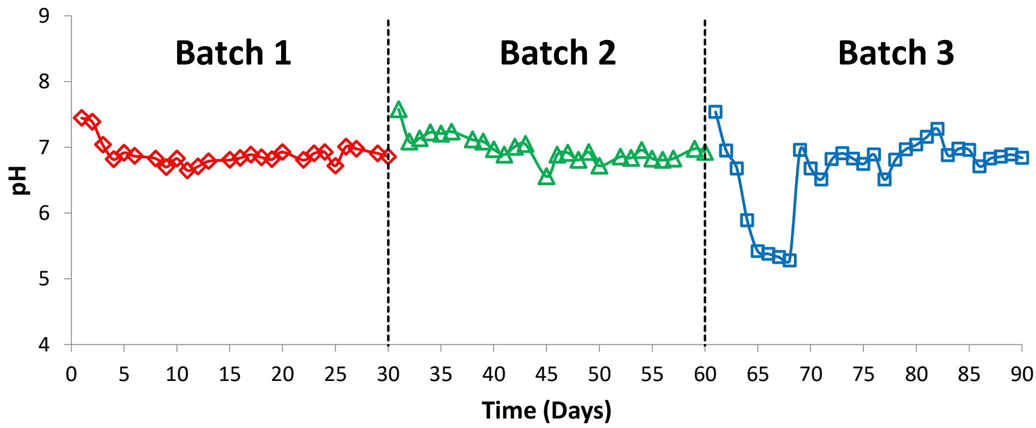

Figure 2. Values of pH during the digestion of SCW with CM.

Total COD and soluble COD varied from batch to batch depending on the amount of ISCW that was added. Thus, as shown in Figure 3, the total COD values at the beginning of the three batches were 19.78, 25.18, and 37.34 g/L, respectively. After 30 days of operation, the total COD removals for the three batches were 58%, 50%, and 62%, respectively. Similarly, 60%, 57%, and 35% of the soluble COD were removed from Batches 1, 2, and 3, respectively. Figure 4 shows that, as the CM/ISCW ratio increases, a wider relative difference exists between the total COD and the soluble COD. Anjum et al. [23] noted that, after 42 days of the digestion process, the highest decrease in insoluble COD, i.e., from 30,080 to 14,720 mg/L, was observed at the 50% orange peel ratio with catering waste. This means that 51% of insoluble COD was transformed into soluble COD. Comparing this findings with the results of the present work, the digestion process of ISCW using CM is adequate.

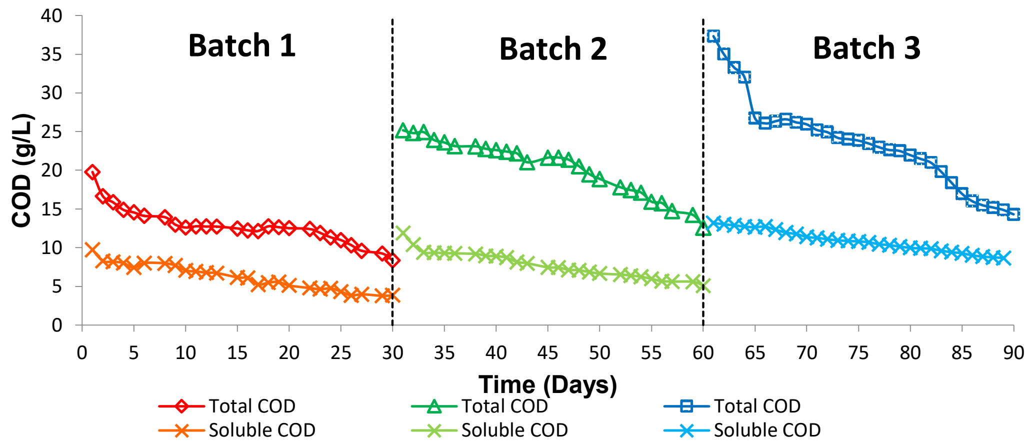

Figure 3. Behavior of the total chemical oxygen demand (COD) and soluble COD.

However, the addition of ISCW resulted in increases in the volatile solids concentrations and the total concentrations of each batch. Figure 4 shows that the TS values at the beginning of each batch were 15.17, 19.66, and 27.75 g/L, respectively, and they had removal levels of 53, 49, and 58%, respectively. As expected, the VS levels followed a trend similar to the trend of the TS levels, with removal percentages of 49, 44, and 60%, respectively. In considering other types of substrates, Li et al. [43] reported that the initial concentration of the substrate influences the mesophilic anaerobic digestion of solid, organic, municipal waste, as was the case for Batches 1, 2, and 3 in terms of both COD and solids. Thus, comparing these findings with the literature, Anjum et al. [23], found that the co-digestion of catering waste and orange peel at a 50% ratio presented 66% of the organic matter removal efficiency (volatile solids) and 55% of total solids, but the experiment was conducted only for a period of 80 days.

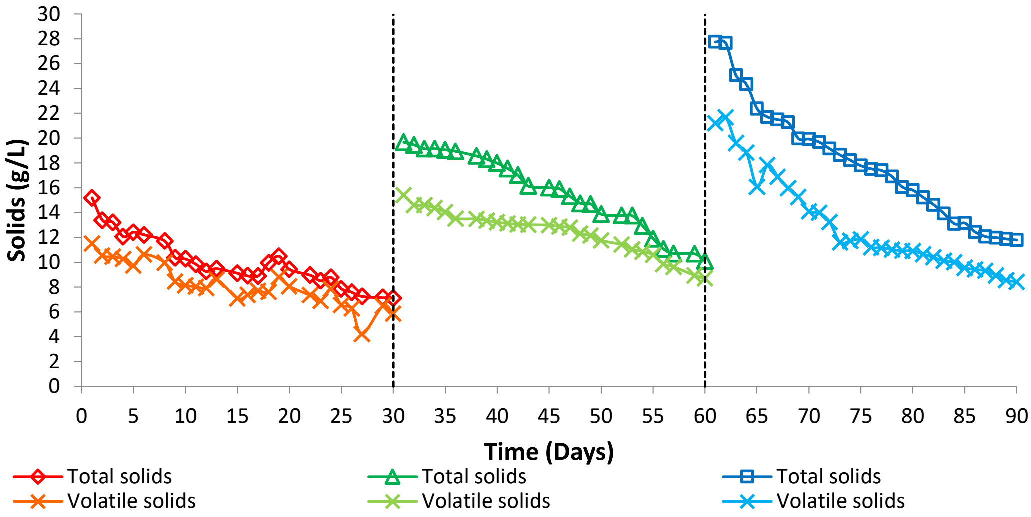

Figure 4. Degradation profiles for total solids (TS) and volatile solids (VS) during digestion in the batch mode.

While the bacteria were adapting to the ISCW that was added, Batch 1 showed low levels of biogas production during the initial days of the experiment. Then, an increase was observed until Day 8, and, later, 29 L was reached at 18 days. Batch 2 reacted similarly, but it had higher biogas production during the first days of operation than the previous batch, which was attributed to the increase of the concentration of ISCW. The highest production of 28 L was reached on day 43. However, Batch 3 was affected from 61 to 71 days due to the new increase in the concentration of ISCW. However, Figure 5 shows that, from day 73 forward, this batch showed a very clear recovery, and it reached its highest point of 28 L on day 80. The biogas that accumulated in the three batches was 550, 606, and 467 L, respectively. The highest quantity of biogas was accumulated in Batch 2, followed by Batches 1 and 3. The maximum methane yield for the three batches were 0.305, 0.337, and 0.331 LCH_4 at STP/g total COD_{rem}, respectively. These same methane yield expressed in terms of volatile solids for Batches 1, 2, and 3 presented averages of 0.322, 0.382, and 0.316 LCH_4 at STP/gVS_{rem}, respectively. Despite the elevated concentrations of organic material, the bacterial medium was capable of adapting and degrading this type of waste, thereby generating high methane yields. SRTs of 300, 150, 100 days for Batches 1, 2 and 3, respectively; were calculated.

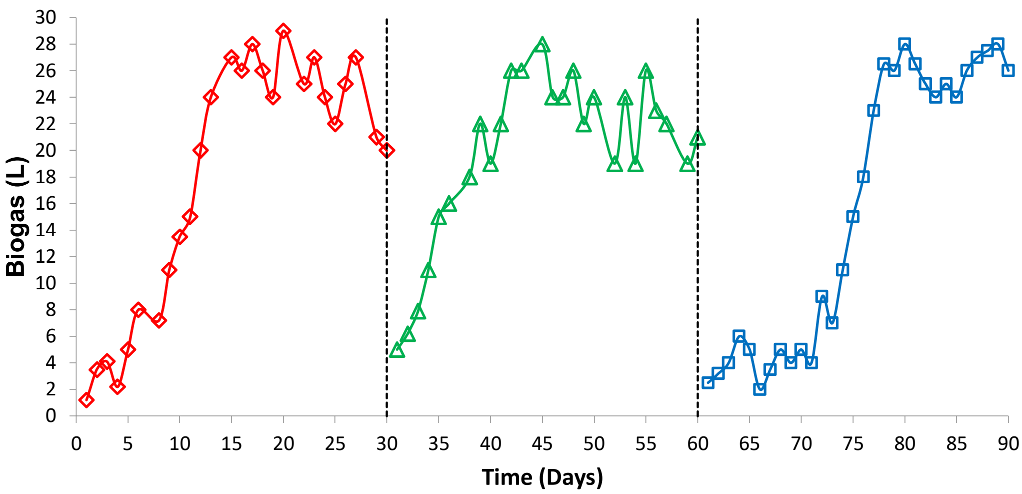

Figure 5. Biogas production in the digestion stage in batch mode.

Calabrò et al. [21] reported a methane yield of about 0.396 LCH_4/gVS (under normal conditions) in 30 days, utilizing a co-digestion process on orange peel waste (50%) with biowaste (50%), but they extracted a large amount of the D-limonene present in the fresh residue. This yield was higher than that obtained in this work, but the difference is due to the proportions of the citrus waste that were used and the fact that the remaining D-limonene was eliminated during the pretreatment. Similarly, Ruiz and Flotats [22], found that the biochemical methane potential obtained for orange peel samples was an average 356 LCH_4/kgVS over a period of 28 days. Finally, the concentration of essential oils, in orange peel waste, is 5.4 g/kg, being 90–98% D-limonene [44]. The concentrations of D-limonene above 200 mg/kg has an inhibitory effect on anaerobic digestion of citrus peel [22]. The inhibitory effect of essential oils (up to 2 g/L) on anaerobic digestion of orange peel waste under mesophilic conditions results in a methane yields up to 370 LCH_4 at STP/kgVS [21].

Table 3 presents a summary of the results of the anaerobic digestion process compared with common studies.

Table 3. Summary of the current findings with other common studies.

Parameter	Current Findings			Reference					
	Batch 1	**Batch 2**	**Batch 3**	**[10]**	**[21]**	**[22]**	**[23]**	**[24]**	**[28]**
Inoculum	Cattle manure	Cattle manure	Cattle manure	Granular sludge	Mixture of sludges	Digestate from cow manure digesters	Co-digested municipal solid waste and melon residues digestate	Liquid digestate	Mesophilic anaerobic sludge
Substrate	ISCW	ISCW	ISCW	Orange peel waste	Orange peel waste	Citrus waste of different origins	Catering waste	Industrial orange peel waste	Industrial orange peel waste
Co-substrate	-	-	-	-	Biowaste	-	Orange peel	-	-
Stages	Single-stage	Single-stage	Single-stage	Single-stage	Single-stage	Single-stage	Single-stage	Single-stage	Two-stage
Ratio	90/10	80/20	70/30	-	50/50	2.6	50/50	0.3	Orange peel/Inoculum/Water 35/26/39
Reactor volume (L)	250	250	250	3.5	0.5	2	0.5	1.1	4.3
Period (d)	30	30	30	5	30	28	42	37	25.8
Temperature (°C)	35 ± 2	35 ± 2	35 ± 2	37	35 ± 0.5	38	30 ± 1	35 ± 0.5	35
pH	6.86–7.45	6.98–7.58	6.84–7.50	6.70–8.60	-	-	6.38–7.01	7.58–7.65	7.00–8.00
COD_T removed (%)	58	50	62	84–90	-	75	49	-	-
COD_S removed (%)	60	57	35	-	-	77	51	-	-
TS removed (%)	53	49	58	-	-	-	55	-	-
VS removed (%)	49	44	60	-	-	11	66	-	-
Y_{CH4} (LCH_4/gVS)	0.322	0.382	0.316	0.230	0.396	0.354–0.398	1.06 L/dt_{subs}	0.365	0.79

3.3. Digestion Stage in Semi-Continuous Mode

After the completion of the digestion in batches over a period of 30 days, it was necessary to verify the performance of the inoculum and evaluate the digestion of the waste in a shorter operating period. The reactor was operated with an 80/20 ratio, but this was done according to the conditions established in Table 4.

Table 4 shows that the percentage of total COD and VS removed from short Batch 1 was low, and this was due to the short time the bacteria had to degrade the organic material. Thus, it was necessary to increase the degradation time for the subsequent short batches, in which there was a significant increase in the removal percentages, with similar behavior observed for the degradation in the other parameters, i.e., total COD and VS, in short Batches 2 and 3. However, removal efficiencies decreased drastically for short Batch 4, which probably was due to the fact that there was a short time period in which to digest the CM/SCW ratio of 80/20. At standard temperature and pressure, the maximum methane yields for each short batch were 0.103, 0.164, 0.117, and 0.134 LCH_4 per gram of total COD_{rem}, respectively. However, the average methane yields for each batch, according to the VS readings, were 0.052, 0.104, 0.074. and 0.297 LCH_4 at STP/gVS_{rem}, in which it was observed that the methane yields for the last batch were high compared to the low percentages for the removal of total COD and VS. STRs from 25 to 50 days were calculated.

Table 4. Evaluation of digestion over short periods of time.

Short Batch	Operation (Days)	ISCW Fed to the Anaerobic Reactor (L)	Initial Total COD (g/L)	Removed Total COD (%)	Initial VS (g/L)	Removed SV (%)
1	5	44	13.58	30	11.98	48
2	10	44	12.17	47	10.46	67
3	10	44	14.25	40	12.96	67
4	10	44	17.86	12	10.01	16

Once the evaluation of the short batches was completed, the operation of the reactor in semi-continuous feeding mode began with a daily 22-L dose of fresh ISCW in order to keep the organic loading rate (OLR) at approximately 8 g total COD/Ld (4.43 gVS/Ld). During the adaptation phase, an average of 8.03 g/L of total COD was used, while, during the stabilization phase 8.35 g/L of total COD was used.

Figure 6 shows a similar behavior in the removal of total COD and VS in the adaptation and stabilization phases, presenting average values of 29% for total COD in the adaptation phase and 24% in the stabilization phase. For the removal of VS, the adaptation phase presented 25%, while the stabilization phase presented 35%. The generation of biogas for the adaptation and stabilization phases were, on average, 21.6 L/d and 24.4 L/d, respectively, with about 34% methane.

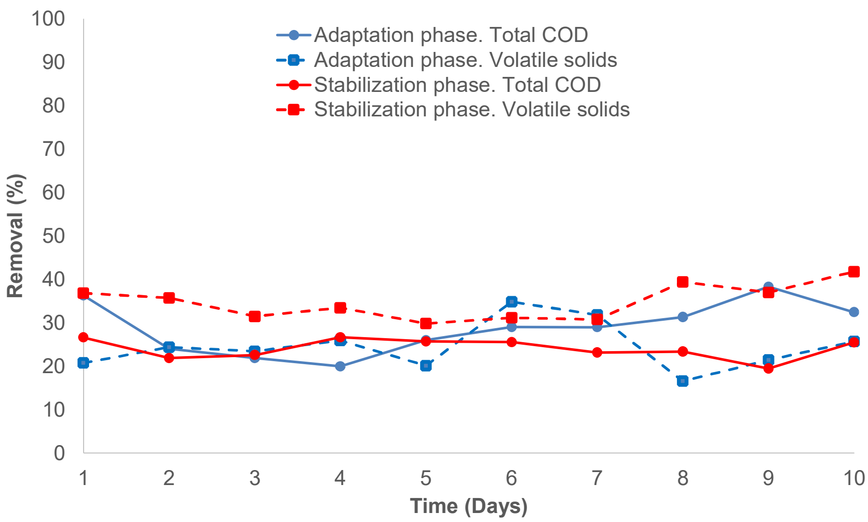

Figure 6. ISCW feeding in semi-continuous mode in both the adaptation and stabilization phases: percent of total COD and VS removed.

Operating in the semi-continuous mode, an SRT of 10 days was obtained, which is in accordance with those described by Martín et al. [10], who found an 84–90% level for the COD removal at an OLR of 1.20–3.67 gCOD/Ld. When they increased the load to 4 gCOD/Ld, they observed a strong inhibition of COD. However, the methane yield was 0.27–0.29 LCH_4 at STP/$gCOD_{add}$. In contrast with this study, Martín et al. [10] conducted their experiments at thermophilic conditions with an SRT of 25 days.

While the removal of total COD and VS, as well as the methane yield, were lower in the semi-continuous mode than in the batch mode, the anaerobic reactor can treat up to 220 L of ISCW in 10 days, whereas only 22 L were fed during 30 days in the batch mode.

This finding highlights the adaptation of a specialized inoculum for the treatment of greater volumes of ISCW in shorter periods.

3.4. Bioenergy Potential from Anaerobic Digestion

Equation (1) was used to calculate the volume of methane generated by anaerobic digestion. For Batches 1, 2, and 3, 220 L of the CM/ISCW mixture were fed with 90/10, 80/20, and 70/30 ratios, respectively. The initial concentrations of total VS for the three batches were 11.52, 15.41, and 21.19 g/L, respectively. The percentages of VS removed, which were obtained experimentally after 30 days of operation for each batch, were 49%, 44%, and 60%, and the maximum methane yields were 0.322, 0.382, and 0.316 LCH_4 at STP/gVS removed. Thus, the methane generated by AD for each batch was 0.40, 0.57, and 0.88 m^3 at STP, respectively. In the semi-continuous mode, an average of 8.35 g/L of total COD was fed, and it was equivalent to 4.63 g/L of VS, reaching 35% of VS removed, with 0.024 LCH_4 at STP/gVS removed, all during a period of 10 days. The methane generated by AD in semi-continuous mode was approximately 0.01 m^3 at STP.

Bioenergy potential was estimated using Equation (2) for Batches 1, 2, and 3, and the values of 3.97, 5.66, and 8.79 kWh were obtained, respectively, during 30 days for each batch. To conduct the experiments in batch mode, it was necessary to supply fresh ISCW, and, for Batches 1, 2, and 3, approximately 10, 20, and 30 kg of fresh ISCW, respectively, were supplied. Therefore, the specific bioenergy potential from a kg of fresh ISCW was 0.40, 0.28, and 0.29 kWh/kg fresh ISCW for each batch. The bioenergy potential in the semi-continuous mode was calculated as 0.09 kWh during a period of 10 days, as shown in Figure 7. It is important to mention that, although in semi-continuous mode a much lower bioenergy potential was obtained compared to batch mode, the retention time to treat 220 L of ISCW was 10 days, which is equivalent to 22 L of ISCW/day, and to treat 22 L of ISCW in batch mode (Batch 1), 30 days were required.

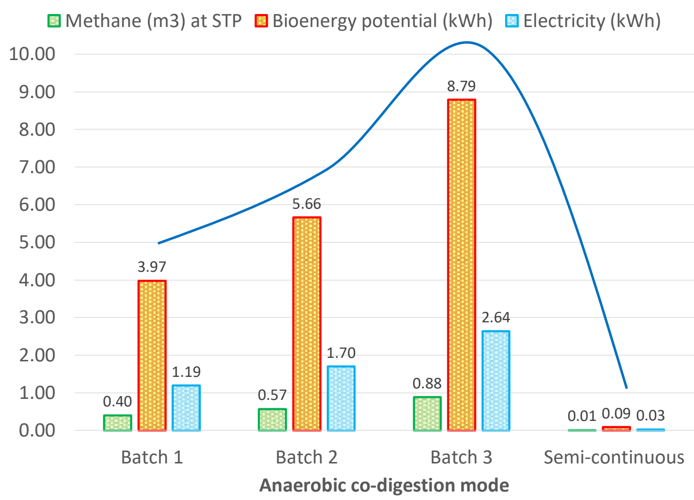

Figure 7. Bioenergy potential derived from anaerobic digestion ISCW with cattle manure (batch and semi-continuous modes).

From the bioenergy potential, using Equation (3) the amount of electricity that can be available for use was obtained, and it was 1.19, 1.70, and 2.64 kWh for Batches 1, 2, and 3, respectively, while 0.03 kWh was obtained for the semi-continuous mode. The thermal energy values derived from the bioenergy potentials were 2.78, 3.96, and 6.15 kWh for the aforementioned batches, and it was 0.06 kWh for the semi-continuous mode. The costs of consuming these amounts of electricity were estimated by Equation (4), and they were 0.10, 0.14, and 0.421 USD for each respective batch and 0.002 USD for the semi-continuous mode.

The citrus processing plant mentioned previously was used as a case study, and it had a processing capacity per season (124 days) of 230,000 tons of oranges, which is equivalent to about 1850 tons per day. From each ton of oranges processed, 0.5 to 0.6 tons of ISCW were generated, which is equivalent to about 925 tons of ISCW per day and 115,000 tons of ISCW per season. Using the results obtained from the bioenergy potential in batch mode, it can be assumed that the citrus industry could produce 46, 33, and 34 GWh per season using Batches 1, 2, and 3, respectively, resulting in an average of 37 GWh per season. In terms of available electricity, there would be 14, 10, and 10 GWh for each batch, respectively, and, on average, 11 GWh per season, which is equivalent to 1.1, 0.8, and 0.8 million USD per season, with an average of 0.9 million USD per season. As a consequence, one ton of ISCW has a bioenergy potential of approximately 324.5 kWh, corresponding to 97 kWh of electricity (7.8 USD). In other words, a ton of processed oranges has a bioenergy potential of 162 kWh and could provide 49 kWh of electricity equivalent to 3.9 USD. Koppar and Pullammanappallil [45] conducted an analysis of the bioenergy potential using 270 wet tons/day of orange peel waste, and they found that 106 GWh/year could be obtained, which would be equivalent to 78 GWh in a season of 270 days, as was analyzed in their case study. With a 25% conversion efficiency, 26 GWh/year of electricity could be obtained, i.e., 19.5 GWh in a season of 270 days.

For the calculation of the bioenergy potential on an industrial scale, it is possible to consider the use of a single reactor and the information obtained from the anaerobic digestion of the waste, however; this would be a hypothetical case, since the reactor would have to be of considerable volume. A practical alternative to solve this could be through the implementation of modular reactors, so that when the amount of solid waste produced by the citrus industry increases or decreases, modular units would be available to cover both treatment and energy demands. On the other hand, as previously mentioned, this work was focused on the treatment of solid orange waste, whose season is 124 days, i.e., from January to April. The rest of the year the citrus plant continues processing lemons (May to October), grapefruit (September to December) and tangerine (December). As can be seen, there are solid citrus wastes throughout the year, which have similar characteristics, so there would be raw material available for the anaerobic digestion process, in the case of an annual operation.

4. Conclusions

A study was conducted of the anaerobic digestion of citrus solid waste in both the batch mode and the semi-continuous mode without the elimination of D-limonene. Cattle manure was used as the inoculum, and once stabilized through two batches of 30 days each, it reached values in the range of 79–88% removal of COD, with similar values of other parameters, such as soluble COD, total solids, and volatile solids with the pH maintained at about 6.71. The accumulated biogas was quantified as being in the range of 647 to 741 L.

In batch mode, industrial solid citrus waste was treated by means of anaerobic digestion, with the previously conditioned inoculum (CM), using ratios CM/ISCW 90/10 (Batch 1), 80/20 (Batch 2), and 70/30 (Batch 3) with a retention time of 30 days for each batch. The values of pH were around 7, the total COD removals were 58%, 50%, and 62%, the soluble COD removals were 60%, 57%, and 35%, the total solids removals were 53%, 49%, and 58%, and the volatile solids removals were 49%, 44%, and 60%. The maximum methane yields were 0.305, 0.337, and 0.331 LCH_4 at STP/g of total COD removed, which was equivalent to 0.322, 0.382, and 0.316 LCH_4 at STP/gVS removed. All of these values are for each respective batch.

The same inoculum that was used in batch mode also was used in the semi-continuous mode to treat 22 L of ISCW per day, equivalent to an OLR of around 8 g total COD/Ld. The semi-continuous mode was proved over a 10-day period. The total COD removal was 24%, and the volatile solids removal was 35% on average, while maintaining a pH value around 7. The biogas generation that was obtained was 24.4 L/d, which was about 34% methane. The semi-continuous mode presented disadvantages compared to the batch mode, but the 22 L of ISCW that were digested in Batch 1 in semi-continuous mode during a 30-day period were treated in only one day.

Bioenergy potentials of 3.97, 5.66, and 8.79 kWh were obtained for Batches 1, 2, and 3, respectively, and 0.09 kWh was calculated in the semi-continuous mode. With these findings, it can be assumed that the citrus industry could produce 46, 33, and 34 GWh per season using Batches 1, 2, and 3, respectively, with an average of 37 GWh per season. This implies that, at an industrial level, it is feasible to operate the anaerobic digestion process, so, a ton of processed oranges has a bioenergy potential of 162 kWh and could provide 49 kWh of electricity equivalent to 3.9 USD.As a part of our future work, a general analysis of the anaerobic digestion process will be conducted using both solid and liquid waste (effluents) from the citrus industry, with attention to priority areas, such as energy and the environment. In addition, the biodegradation of the D-limonene concentration inside the reactor will be monitored in order to study in depth the inhibitory effects and its effect on biogas production.

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Abbreviations

AD	Anaerobic digestion
AR	Anaerobic reactor
BEP	Bioenergy potential
CH_4 AD	Volume of methane generated by the anaerobic digestion
CM	Cattle manure
CO_2	Carbon dioxide
COD	Chemical oxygen demand
COD_{add}	Chemical oxygen demand added
COD_{rem}	Chemical oxygen demand removal
COD_S	Soluble chemical oxygen demand
COD_T	Total chemical oxygen demand
d	Day
ET	Electricity tariff
g	Grams
GWh	Gigawatt-hour
HCl	Hydrochloric acid
HP_{CH4}	Heating power of methane
ISCW	Industrial solid citrus waste
kg	Kilogram
kWh	Kilowatt-hour
L	Liter
LCH_4	Liters of methane
m^3	Cubic meter
η	Energy conversion efficiency
N_2	Molecular nitrogen
O_2	Molecular oxygen
OLR	Organic loading rate
OPW	Orange peel waste
pH	Potential of hydrogen
psi	Pound per square inch

PVC	Polyvinyl chloride
SRT	Solid retention time
STP	Standard temperature and pressure
TS	Total solids
USD ($)	United States dollars
V_{AR}	Volume of the anaerobic reactor
VS_I	Initial concentration of the VS
$VS_{\%}$	Removal efficiency of the VS
VS	Volatile solids
Y_{CH4}	Methane yield

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