VALORIZATION STUDY OF THE ORGANIC WASTE RESULTING FROM THE TOMATO CANNING BY METHANISATION

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In this work, the tomato canning waste from Adrar city -southwest of Algeria- are valued using anaerobic digestion (AD). The inoculum is used as an alkaline agent for pH adjustment. Six substrate to inoculum ratios of 0.25, 0.5, 1, 2, 3, and 4 are investigated under mesophilic conditions (37 ± 1 °C) for 45 days. The pH, chemical oxygen demand (COD), volatile solid (VS) reduction and volatile fatty acids/total alkalinity ratio (VFA/TA) are the measured parameters at the beginning and end of the digestion and the methane yield is daily measured. The best methane yield corresponds to the substrate to inoculum ratio of 0.5 with a CH_4 production of 260.98±7.24 mL/g VS.

Keywords: pH adjustment, Tomato canning waste, Substrate/inoculum ratio, Anaerobic digestion (AD), Biogas

1. Introduction

Since the 1970s, tomato (*Solanum lycopersicum*) culture has been grown in the Adrar region of southwestern Algeria. The generated waste from the tomato cannery (WTC) represents 4 to 13% of the weight of the tomato [1]. Nearly 90% of Adrar's WTC is discarded without any treatment and causes adverse environmental impacts and liquid releases of leachates into the basement by

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polluting the water table, unpleasant smells and greenhouse gas emissions. A part of the WTC, which accounts for almost 10%, is used to feed cattle (camels). Heuzé et al., [2] have shown that the use of tomato organic waste as livestock feed is not beneficial because of the low nutrient values.

Practically, there are several methods and solutions for recovering this organic waste, which permits the benefiting of their energy and protecting the environment. Anaerobic digestion is one of these promising solutions that combine several economic and environmental benefits. It makes it possible to recover bioenergy, which is the biogas mainly composed of CH_4 and CO_2 used as fuel, a digestate used as fertilizer for the agricultural soils and protects the environment against all pollution types [3]. In this context, Bacenetti et al., [4-5] have found that the use of the anaerobic digestion allows reductions of the climate change of 6.4% and ozone depletion of 13.4%.

The acidic nature of WTC (pH = 4.23) is a parameter limiting the use of this waste as a substrate in anaerobic digestion. Li et al., [6] have shown that the WTC negatively influences the anaerobic digestion process due to their acid pH. To adjust the acidic pH of the WTC, the addition of an alkaline agent is an adequate treatment solution. Alnakeeb et al., [7] and Calabrò et al., [8] have used an alkaline pretreatment with NaOH (pH = 11.13). The lime (pH = 12.3) can be used to the pH control by Zhang et al., [9].

The inoculum rich in the microbial population can improve anaerobic digestion by reducing the technical digestion time and increasing biogas production. Suksong et al., [10] have demonstrated that the use of an appropriate inoculum improves methane production and increases microbial activity. In addition to these advantages, the inoculum recovered from the lagoon station is the most favorable alkaline agent from the economic viewpoint, because it is recovered free of charge in Adrar city in the south of Algeria. Therefore, the relatively high pH inoculum (8.32) can be used as a source of alkalinity for pH adjustment of the WTC anaerobic digestion.

In this work, a valorization study of the waste of the tomato cannery (WTC) by anaerobic digestion is conducted. The objective of this work is the use of the inoculum as an alkaline agent to adjust the pH of WTC and minimize the digestion time and cost. To realize this objective, six substrate/inoculum ratios of 0.25, 0.5, 1, 2, 3, and 4 are experimented to obtain the best proportion of substrate/inoculum that gives the highest methane production.

2. Materials and methods

2.1. Substrate

The subject substrate of this study is the collected waste from Fouggara brand tomato cannery located in Reggane, south of Adrar city, in southwest Algeria. The substrate consists of skins, grains and peels. In order to avoid aerobic degradation of the substrate as well as its contamination by yeasts and mold, a drying process of the substrate is carried out directly after its collection using an indirect solar dryer. The obtained humidity after drying is less than 7%. The dried tomato waste was milled in a Janke and Kunkel micro mill to obtain particle sizes smaller than 500 μm [11].

2.2. Inoculum preparation

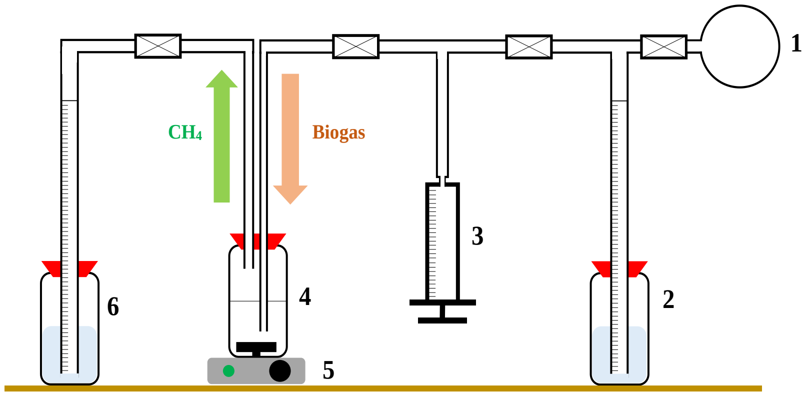
The inoculum was recovered by decantation from a batch digester that operates at 37 °C for two months treating the dried sludge recovered from the lagooning station of the Adrar city. Thereafter, a quantity of 40 g VS of inoculum was introduced into each reactor. According to the potential bio-methane protocol, a reactivation and degassing operation for seven days at 37 °C was carried out before launching the experiments [12].

2.3. Reactor preparations

Batch digesters in the glass vials form with a capacity of 1000 mL (800 mL of useful volume) were used in the experimental tests. The experiment was launched for eight reactors. Seven reactors were filled with constant inoculum initial loads of 40 g VS/L as mentioned in Section 2.2. Six of these seven reactors were supplied by the substrate with quantities of 10, 20, 40, 80, 120 and 160 g VS/L which correspond to the substrate/inoculum ratios of 0.25, 0.5, 1, 2, 3 and 4 to guarantee a wide range of this ratio. The seventh reactor was used as a blank (inoculum without waste) to determine the methane yield/g VS. The methane volume obtained from the blank reactor was subtracted from that obtained by the reactors containing the different substrate to inoculum ratios [13]. The eighth digester contains only 40 g VS/L of tomato waste, which was used as a control. Each reactor was completed to 800 mL with tap water. Two digesters that contain only the WTC substrate and the inoculum were used as control and blank respectively. The reactors were hermetically closed and incubated in a thermostatically controlled water bath at 37 ± 1 °C [14]. In order to avoid stratification, the manual agitation of the reactors for one minute was applied 3 times a day [15]. All digesters are prepared in triplicate, and the average of the three results was considered.

2.4. Biochemical potential of methane

The substrate to inoculum ratio influence on the methane production from the tomato waste was evaluated using the biochemical methane potential test following the protocol described by Angelidaki et al., [12]. The displaced liquid method was used for measuring the volume of the produced biogas [16]. Fig. 1. In order to minimize the dissolution of CO_2, the biogas was measured using a burette immersed in a saturated NaCl solution (10 g/L of NaCl and acidified by the addition of HCl at pH = 2) [17].



(1) Unfiltered biogas flask - (2) Saturated solution (Nacl 10g/L pH = 2) - (3) Syringe - (4) Filtration of CO_2 – (5) Magnetic agitator - (6) methane

Fig. 1. Measurement of the volume of biogas and methane.

The produced biogas passes through a bottle that captures CO_2 (filled with sodium hydroxide solution (3 mol/L)). After the CO_2 removal, the remaining volume represents the produced CH_4 that converts to the standard conditions (temperature and pressure (STP)) [17].

2.5. Analytic method

Total solids (TS) and volatile solids were determined before feeding the digesters and at the experiment end according to the standard method, 2540 G [18]. Total alkalinity, volatile fatty acids and chemical oxygen demand were determined at the digestion start by sampling from the digesters using a 50 ml syringe after one hour of launching the reactors. The same measurements by the same means were made at the digestion end. The COD was measured by closed reflux titrimetric according to the standard method 5220 C [18]. Total alkalinity (TA) was measured according to the standard method 2320 B 4c [18]. Volatile fatty acids (VFA) were measured according to the method described by Dilallo et al., [19] and Anderson et al., [20] using titrimetric method and the results were expressed in acetic acid equivalent. The pH values were measured using a model pH-meter (HANNA HI 8314).

3. Results and discussions

3.1. pH

The hydrogen potential is one of the most important parameters affects the DA process stability. Wellinger et al., 2013 [21] have confirmed that an optimum and uniform pH presents one of the basic conditions must be met to enable the bacteria to degrade the substrate efficiently. Pishgar, 2015 [22] has concluded that the pH range of 6.5-7.5 provides an environment suitable for most anaerobic bacteria including methanogenic bacteria. Moreover, a considerable diminution in the risk of bacteria methanogens inhibition is recorded when the pH is adjusted between 7.0 to 8.0 [23].

The initial pH value of tomato waste (control) is acidic (pH = 4.23) which provides a not suitable environment for methanogenic bacteria and provokes inhibition of these bacteria in the control digester [23]. Whereas, the initial pH value of the inoculum (blank) is alkaline (8.32), which made it possible used to adjust the acid pH of the tomato waste and to contribute to overcoming the inhibition of the anaerobic digestion (AD) process. This is confirmed by the initial pH values of 7.36, 7.24, 7.03, 6.86, 6.33 and 6.05 obtained in the reactors containing the substrate to inoculum ratios of 0.25, 0.5, 1, 2, 3 and 4 respectively, where these pH values are higher than that of the control reactor (4.23). Fig. 2.

The substrate to inoculum ratios of 0.25, 0.5, 1 and 2 have allowed the initial pH adjustments of 7.36, 7.24, 7.03 and 6.86 respectively, these pH values are in the optimal range that can promote the microbial activity of methanogenic bacteria [22]. While the substrate to inoculum ratios of 3 and 4 led to initial pHs below 6.5 with values of 6.33 and 6.05 respectively, which can negatively influence the AD process [22]. Fig. 2.

The final pH value of the tomato waste (control) decreased to 4.17 due to the high production of VFAs that causes the inhibition of the process during the experiment [21]. In contrast, the final pH value of the inoculum (blank) increased to 8.48 due to its protein content that can be allowed to maintain the pH during the AD process [6]. The final pH value of the reactors containing the substrate to inoculum ratios of 0.25 and 0.5 maintain their initial pH close to neutrality with values of 7.33 and 7.31 respectively that are in the range of the optimal pH of methanogenic bacteria. This is explained by the balance achieved between the bacteria forming acid and acetate with that forming methane. Fig. 2. Tao et al., [24] have reported that the efficiency and stability of AD processes are ensured by the balance between microbial groups.

Finally, the reactors containing the substrate to inoculum ratios of 1, 2, 3 and 4 have encountered a remarkable decrease in pH values of 6.39, 5.38, 5.62 and 5.56 respectively, which are outside the optimal pH range of methanogenic bacteria (<6.5). In addition, these values are the result of developed imbalances. Fig. 2. Kawai et al., [25] have reported that an accumulation of acetic and butyric acid leads to a decrease in pH value.

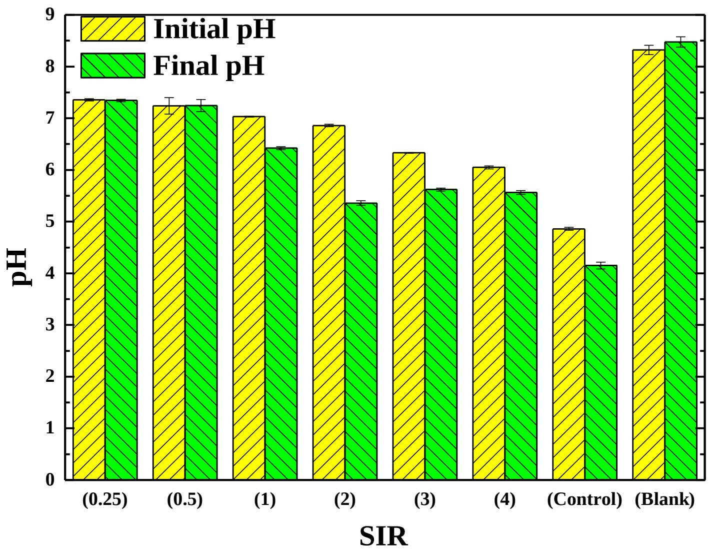


Fig. 2. Initial and final pH of anaerobic digesters of the tomato canning waste at different substrate to inoculum ratios (SIR).

3.2. Chemical oxygen demand

COD represents the quantity of oxygen required to oxidize the organic and inorganic matter contained in the digestion solution [26]. A significant COD removal at the digestion end indicates a good functioning of the AD process with an intense activity of methanogenic bacteria that is due to the weak presence of inhibitors [27].

The initial COD values of 15520, 19520, 23843, 27442, 28344 and 32882 mg O_2/L obtained by the digesters containing the substrate to inoculum ratios of 0.25, 0.5, 1, 2, 3 and 4 respectively, show that the increase in the substrate loading in these reactors leads to an increase in the COD values. Fig. 3. The same results and findings are found by Raposo et al., [28].

At the digestion end, a significant COD removal is recorded for the reactors containing the substrate to inoculum ratios of 0.25, 0.5, 1, 2, 3 and 4 with rates of 51.8, 61.68, 26.04, 32.13, 42.64 and 29.63% respectively. Fig. 3. The COD removal indicates the conversion of organic carbon from the hydrolysis phase to biogas and the consumption of a part of the volatiles solid by microorganisms [29]. The highest COD removal of 51 and 61% are obtained by the reactors containing the substrate to inoculum ratios of 0.25 and 0.5 respectively. In comparison with the literature, the maximum COD removal of 50.18% is obtained by Kumar et al., [30] using a substrate to inoculum ratio of 0.5 and the Azolla pinnata as substrate.

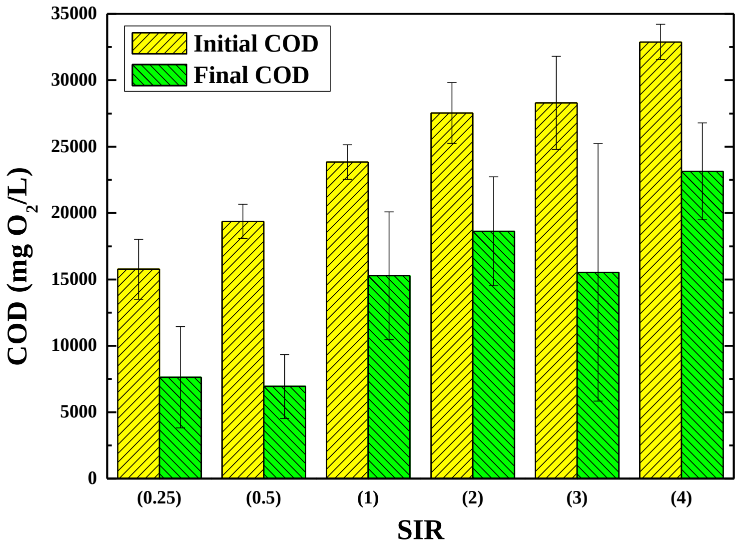


Fig. 3. Initial and final COD of anaerobic digesters of the tomato canning waste at different substrate to inoculum ratios.

3.3. Volatile solid removal

The volatile solid removal represents the ratio of the difference of initial and final volatile solids divided by the initial volatile solids; this rate indicates a good bioconversion inside the digesters when the removal rate is high. Conversely, it indicates a bad biomass bioconversion when it is low. VS removal represents the organic compound consumption of the digestate during the AD process [31].

The VS removals with values of 52.95, 49.11, 48.63, 32.11, 29.29 and 24.06 are obtained the reactors that contain the substrate to inoculum ratio of 0.25, 0.5, 1, 2, 3 and 4 respectively. The VS removals are important for the substrate to inoculum ratios of 0.25, 0.5 and 1, which probably shows the bioconversion of the organic compound into biogas in these reactors due to their favorable pH [21-22]. The same results are found by Liu et al., [32]. Low VS removals were obtained by the reactors containing the substrate to inoculum ratios of 2, 3 and 4 (Fig. 4).

In addition, the conversion of the organic compound to biogas has not been achieved [33], which was caused by the acid pH that causes an inhibition in these reactors and leads to methane yields considerably lower [34].

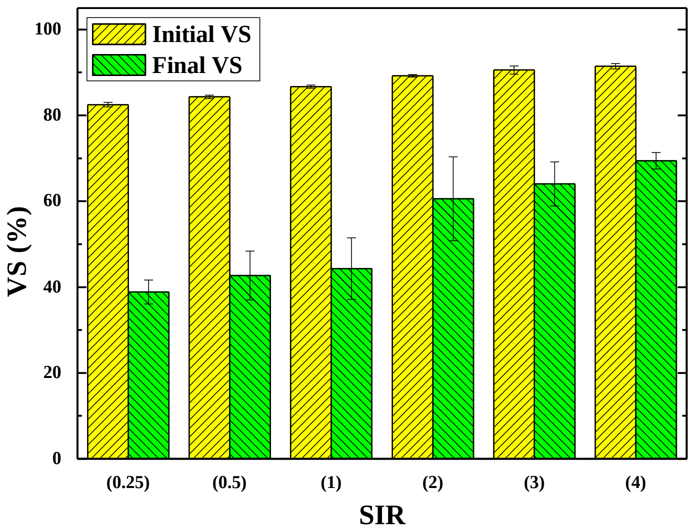


Fig. 4. Initial and final VS of anaerobic digesters of the tomato canning waste at different substrate to inoculum ratios.

3.4. Volatile fatty acids / total alkalinity ratio

The VFA/TA ratio is the indicator of the digestion process stability. Rasapoor et al., [35] have divided the AD process stability according to three ranges of the VFA/TA ratio, a stable process for VFA/TA <0.4; an unstable process for 0.4 < VFA/TA <0.8 and a significantly unstable process for VFA/TA > 0.8.

At the start-up of the digestion, the VFA/TA ratios of 0.28, 0.31 and 0.38 are recorded for the substrate to inoculum ratios of 0.25, 0.5 and 1 respectively, indicate stable processes of AD, probably due to the initial buffer capacity produced by a large amount of inoculum in these reactors. VFA/TA ratio values of 0.41, 0.44, 0.47 and 0.52 were measured at the start of the experiment for the digesters containing the substrate to inoculum ratios of 2, 3, 4 and the control respectively, indicate unstable processes of AD in these reactors. Fig. 5. Li et al., [6] have proved that the sufficient quantity of inoculum can provide a sufficient number of microorganisms with a high buffering capacity that allows ensuring the AD process stability.

At the end of digestion, the reactors containing the substrate to inoculum ratios of 0.25 and 0.5 kept the ratio of VFA/TA less than 0.4 with values of 0.18 and 0.23 respectively. These reactors have a decrease in VFA/TA ratios indicating the conversion of VFAs to biogas and permit to avoid acidification and the inhibition in these reactors, and represent a stable AD process. The reactors containing the substrate/inoculum ratio of 1, 3 and 4 have known an increase in the VFA/TA ratio with values of 0.45, 0.62 and 0.64 respectively, indicating an unstable process. Finally, final VFA/TA ratios exceeding 0.8 were recorded in the reactors with the substrate/inoculum ratio of 2 and the control indicating a significantly unstable process in these reactors. Fig. 5. The same results and findings are found by Feng et al, [36] and Feng et al, [37].

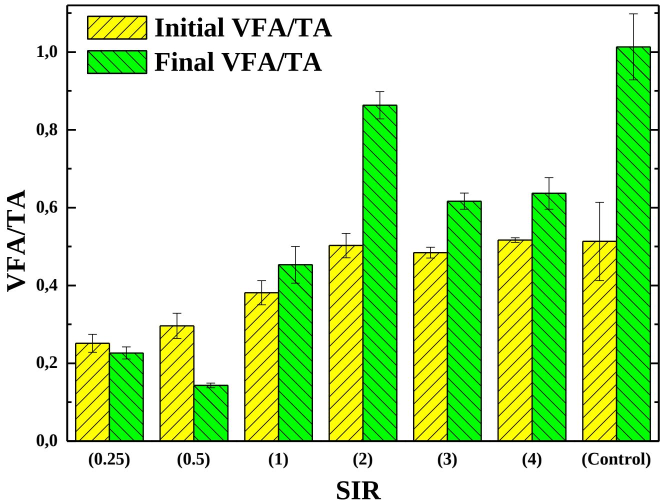


Fig. 5. Initial and final VFA/TA ratio of anaerobic digesters of the tomato canning waste at different substrate to inoculum ratios.

3.5. Daily yield of methane

After 24 hours of digestion, methane production is recorded in all reactors. The highest CH_4 yields measured after the first day are obtained by the substrate to inoculum ratios of 2 and 3 that exceed 30 mL CH_4/g VS/day, and then they decrease rapidly to near zero (0.5 – 1 mL CH_4/g VS/day) from the fourth day to the digestion end. Methane yield of 15.83 mL CH_4/g VS/day is measured for the reactor contains the substrate to inoculum ratio of 4 during the first day, and then they decrease rapidly until reaching nearly zero values from the third day. This is due to the high VFA accumulation that has led to the irreversible acidification within the reactors of the substrate to inoculum ratios of 2, 3 and 4 because the methane production has not been regenerated [38-39]. Fig. 6. In this context, Zuo et al., [40] have demonstrated that high methane yield during the first days of digestion is due to the presence of easily degradable fractions in the substrate.

A large production is recorded during the second day in the reactor of the substrate to inoculum ratio of 1, then it is entirely reduced to values lower than 1 mL CH_4/g VS/day during the period of 4^{th} to 12^{th} day. A new production of methane is observed in the same reactor during the period of the 13^{th} to the 19^{th} day. This new production is mainly due to the possible consumption of VFA. The short time of this new production is the result of the insufficient quantity of the inoculum in the digester, the nature of the acidic pH and the increase of the VFA/TA ratio. Fig. 6.

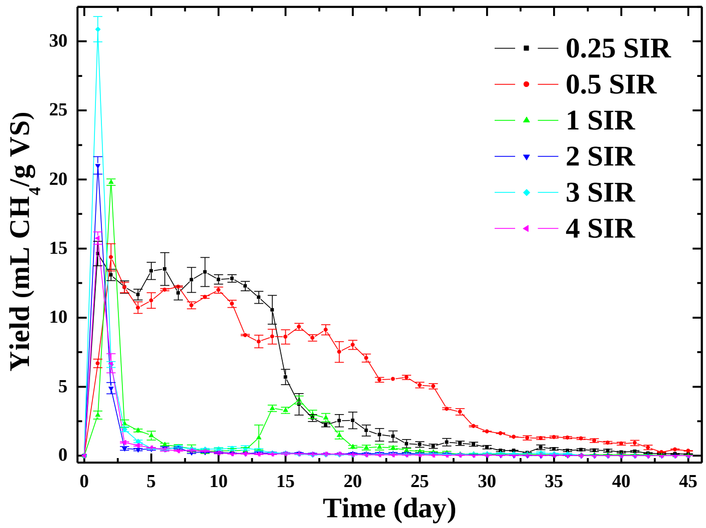


Fig. 6. Daily yield of methane of anaerobic digesters of the tomato canning waste at different substrate to inoculum ratios.

The methane yield obtained for the substrate to inoculum ratios of 0.25 and 0.5 is around 12 and 10 mL CH_4/g VS/day respectively during the first 15 days. This production is decreased to values below 4 mL CH_4/g VS/day in the remaining digestion period for the substrate to inoculum ratio of 0.25, and is around 7 mL CH_4/g VS/day in the period from 16^{th} to 25^{th} day of digestion for the substrate to inoculum ratio of 0.5, then decreases to values below 4 mL CH_4/g VS/day for the remaining period of the digestion. The maintaining of the biogas production in the reactors contained the substrate to inoculum ratios of 0.25 and 0.5 is due to the inoculum availability (microbial population), the pH stability around a neutral pH, the high COD and VS removals and the keep of VFA/TA ratio less than 0.4 [34]. Fig. 6.

3.6. Accumulated yield of methane

The accumulated methane yields of 56, 32, 48 and 29 mL CH_4/g VS are obtained by the reactors containing the substrate to inoculum ratios of 1, 2, 3 and 4 respectively. These methane yields don't exceed 60 mL CH_4/g VS that represents only 11-21% of the optimal accumulated methane yield. Moreover, the biogas production was stopped in the first week probably due to their acid pHs and unstable processes that provoke an inhibition in these reactors. The same results are obtained by Pellera et al., [39] for the juice industry waste (pH= 4.62), they found that the inhibition was produced for a substrate to inoculum of 2 with an acid pH of 5.11. They have obtained for this case an accumulated methane yield of 34 ml CH_4/g VS that represents only 8% of the optimal accumulated methane yield.

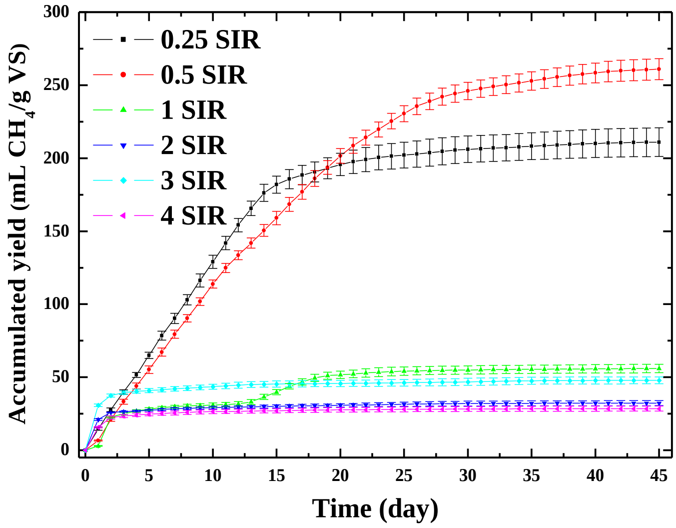


Fig. 7. Accumulated yield of methane of anaerobic digesters of the tomato canning waste at different substrate to inoculum ratios.

The reactor with the substrate to inoculum ratio of 1 has known a new production during the period from the 13th to the 21st day. The lowest accumulated CH_4 yield of 28.53±1.74 mL CH_4/g VS is obtained by the substrate to inoculum ratio of 4. The nature of the acidic final pH, the low COD and VS removals and the high VFA/TA ratios in the reactors of the substrate to inoculum ratios of 1, 2, 3 and 4 are the responsible of produced inhibitions in these reactors and consequently failure process. In other words, this instability is induced by an imbalance in the bioavailability of acidogenic and methanogenic microorganisms [40], this imbalance slows the syntrophic metabolism of fermentation intermediates (alcohol, propionate and VFA ... etc.), inhibits the methanogenic phase, increases VFA and NH_3, and results lower pHs [42-43]. An acceptable CH_4 accumulated yield of 210.97±9.78 mL CH_4/g VS is obtained by the substrate to inoculum ratio of 0.25. The optimal accumulated methane yield is obtained for the substrate to inoculum ratio of 0.5 (260.98±7.24 mL CH_4/g VS). Fig. 7. The best methane yield of the human fecal material of 254 ml CH_4/g VS is obtained by a substrate to inoculum ratio of 0.5 as reported by Michael O Fagbohungbe et al., [38].

4. Conclusions

The present study focuses on the valorization study of the organic waste outcome from the tomato canning in the Adrar city using the anaerobic digestion technic. Experimental anaerobic digestion tests were carried out at the laboratory of the renewable energy research unit in the Saharan Medium - Adrar - Algeria. The inoculum of the lagooning station of the Adrar city is used as an alkaline agent for pH adjustment. Six substrate to inoculum ratios of 0.25, 0.5, 1, 2, 3, and 4 were studied experimentally. In this work, the stability of the anaerobic digestion process was assessed based on the pH and VFA/TA ratio measurements. A VFA/TA ratio (<0.4) was recorded according to a substrate to inoculum ratio of 0.5 and a favorable pH at the beginning and end of the digestion indicating the buffer capacity of the inoculum. A COD removal of 61.68 %, as well as an VS removal of 49 % were obtained by the same substrate to inoculum ratio, due to the bioconversion of the organic compounds into biogas during the anaerobic digestion process. These results confirm the stability of the anaerobic digestion in the reactor containing the substrate to inoculum ratio of 0.5 and allow the obtain the optimal cumulative methane yield of 260.98 ± 7.24 mL CH_4/g VS.

Finally, based on the obtained results, it is recommended to use the inoculum with a substrate to inoculum ratio of 0.5 for the anaerobic digestion of tomato waste according to the following advantages: Allow the reduction of the digestion time due to their richness in methanogenic bacteria; Allow the acid pH adjustment of the tomato waste; Allow the reduction of the anaerobic digestion cost, since it is recovered free of charge in comparison with other alkaline agents; Allow obtaining an acceptable methane yield.

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