Mesophilic anaerobic co-digestion of cheese whey with cow manure in batch reactor

Nassima Tirichine, Meryem Saber, Mohamed Khitous, Hakim Lounici, and Rabah Bouarab

Abstract− Anaerobic digestion is a biological process that takes place under very strict operating conditions, including a pH close to neutrality. This experimental work aims to study the effect of pH control on CH_4 production in mesophilic anaerobic co-digestion of cheese whey with cow manure. Two experiments were conducted in batch reactor, the first without pH adjustment and the second with pH adjustment. The results of the first co-digestion revealed an inhibition of the methanization process by acidification of the medium and accumulation of volatile fatty acids; whereas during the second co-digestion with pH adjustment using sodium bicarbonate (1M), the process was improved with methane levels (> 50%) in the biogas. The accumulated biogas volume was two times higher for the same operating time in the digester.

***Keywords*− Cheese whey, anaerobic co-digestion, pH control, cow manure, biogas.**

NOMENCLATURE

CW	Cheese Whey.
CM	Cow Manure.
TS	Total Solids.
VS	Volatile Solids.
Eh	Redox Potential.
COD	Chemical Oxygen Demand.
At	Total Alkalinity.
VFA	Volatile Fatty Acids.
DI	Digester I.
DII	Digester II.

I. INTRODUCTION

Cheese whey is the main waste or effluent generated by the dairy industry, and it has a very high organic matter content ranging from 57 to 140 g COD/L [1-3]. Therefore, the disposal of this by-product is a challenge for small and medium enterprises (SMEs) in the dairy industry that do not have any type of processing plant [2]. Indeed, the dairy industries annually produce hundreds of millions of kilograms of milk and derivatives, with world production estimated at 190 billion kg per year [4]. If we consider FAO statistics, cheese production (all kinds of cheese) reached 27,634 t in 2018, generating around 41,162 t of whey [5]. Anaerobic digestion is a particularly interesting solution for treating or pre-treating this effluent, because it offers an excellent solution both in terms of energy savings and depollution; whey processed through anaerobic digestion produces biogas which is considered valuable energy that can be converted into heat and electricity [1, 6, 7]. Some studies have been carried out with whey as a substrate or co to study anaerobic digestion, in particular those carried out by [1-2, 8-12]. However, some difficulties have been reported regarding the anaerobic digestion of cheese whey. The majority of these difficulties are due to the low alkalinity and rapid acidification of cheese whey which can deplete buffering capacity, leading to lower pH, buildup of volatile fatty acids (VFAs) and subsequent reactor failure [1, 7, 13, 14]. In this research work, we studied a very important parameter in anaerobic digestion which is the pH. For this, two digesters were started, one without pH correction and the second with pH correction using sodium bicarbonates. The whey was co-digested with cow manure as an inoculum or source of anaerobic bacteria. Various parameters have been monitored and analyzed and characterization methods are carried out in order to monitor the behavior of the digester over time.

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MATERIELS AND METHODS

A. Substrates

The effluent studied is the soft cheese whey generated by cheese dairy of Boudouaou (Algeria). It is made from a pressed cheese (Edam) and is still very rich in nutrients. Samples were taken from the coagulation tank and stored in 1 L plastic jerrican at 4°C until analyzed and processed in laboratory. Before each experiment, the substrate is removed from the freezer and defrosted at room temperature during 24 h. The cow manure used in this study comes from a private farm located in Bouzareah (Algeria).

The samples were made of fresh cow manure, and was directly weighed and put in the digesters. It is considered as an inoculum because it contains the microorganisms that will be used to degrade the nutrients contained in the whey. The main characteristics of cheese whey and cow manure are reported in Table I.

According to Table I, the whey contains a very high pollutant load, represented by a COD of 134 g O_2/L and has a fairly high level of fermentable organic solids, represented by the VS which is 98.3% [% MS]; which makes it a good substrate for producing biogas.

Table. I
Physicochemical characteristics of cheese whey and manure

Parameters	Cheese Whey	Cattle Manure
pH	6.4	8.1
Eh (mV)	23.1	-69.1
TS (%)	7	16
VS (% of TS)	98.3	86.7
COD (g L^{-1})	134	17.4
At (mg L^{-1})	-	1040
VFA (mg L^{-1})	37	11

B. *Analytical methods*

The system performance was tested by measuring biogas and methane productions, COD removing, total solids (TS), volatile solids (VS), total alkalinity At, pH, potential redox (Eh) and volatile fatty acids (VFA) concentrations. The influent and effluent pHs were measured from samples with a glass electrode pH meter (WTW InoLab pH Level 1). The total alkalinity (At) and the volatile fatty acids (VFA) were determined by titration at a pH of 4 and 3.5, respectively, according to the method described by Anderson [15]. All of the other analyses TS, VS, and COD were performed according to the Standard Methods [16, 17]. Biogas production of the system was determined daily by water displacement gas meter designed as a scaled measuring cylinders. Methane content biogas was measured using a gas analyzer Multitec 540.

C. *Experimental setup*

Experimental studies were performed in anaerobic reactor with a total volume of 5 L (Figure 1). The reactor was heated with water bath equipped with a temperature controller (LAUDA E200) to maintain a constant temperature of 38 °C. After that cheese whey and cow manure were filled to the reactor at 50/50 (V/V) with water, the reactor inlet was closed to prevent air leakage. After 24 hours, we start the samples in the two digesters and the monitoring of the parameters.
The biogas produced is measured with a gas meter and stored in a special bag for analysis by a biogas analyzer.

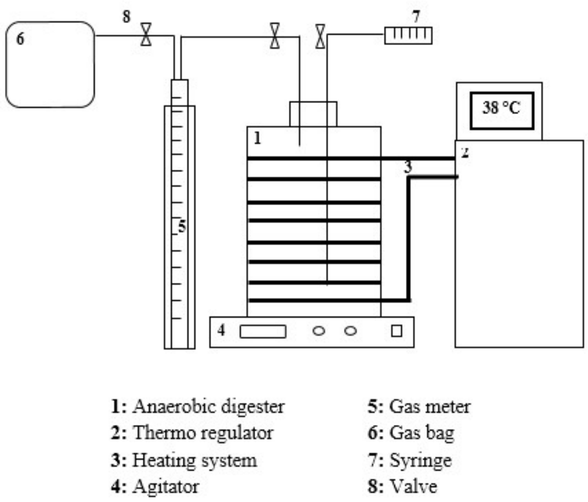

Fig. 1. Experimental set-up: Anaerobic digester (5L), gas meter (250mL) and storing bag (2L)

D. *Digester Startup*

The physico-chemical characteristics of the two digesters before starting are given in Table II. The two experiments were, carried out in order to study the effects of pH on the reactor performances.
According to Table II, we notice that the mixture of cheese whey at 7% TS, and cow manure at 16% (Table I) with water, gives us TS of 7% for both digesters DI and DII.

Table. II
Main characteristics of digester I and digester II

Parameters	Digester I	Digester II
pH	6.5	6.5
Eh (mV)	-8.7	-8.1
TS (%)	7	7
VS (% of TS)	87.1	87.1
COD (g L^{-1})	35. 319	35. 182
At (mg L^{-1})	1600	1400
VFA (mg L^{-1})	1.02	2.4

II. RESULTS AND DISCUSSION

A. *pH control and measurement*

pH of raw cheese whey and cow manure was 6.4 and 8.1 respectively (Table I). Mixing the two substrates with water gives us a pH of 6.5 in DI and DII (Table II). No adjustment was made for the pH in the first digester whereas the pH in the second digester was adjusted to the setpoint of 6.0 by the addition of 1M sodium bicarbonate solution.

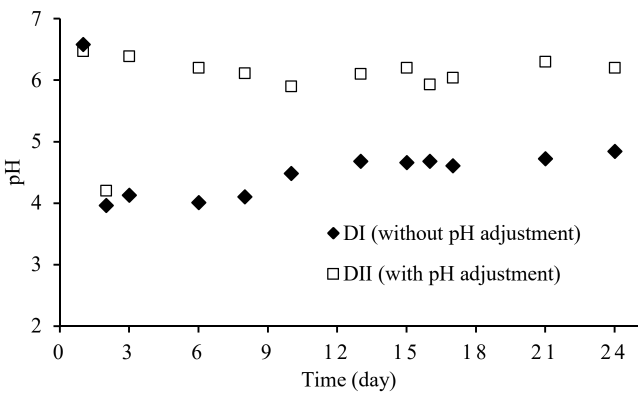

Fig. 2. pH behavior during anaerobic co-digestion of cow manure and cheese whey with and without pH adjustment

Fig. 2 shows the evolution of pH for both anaerobic co-digestion processes (without and with adjustment of pH). For first experiment, the pH decreased with time reaching 3.96 after 48 hours and then remained around values between 4.01 and 4.84. For the experiment with adjustment of pH, the pH decreased reaching 4.2 before adding sodium bicarbonate. However, when the 1M of sodium bicarbonate was added to digester, the pH increased with time reaching an average value of 6.39 after 3 days.

B. *Redox evolution*

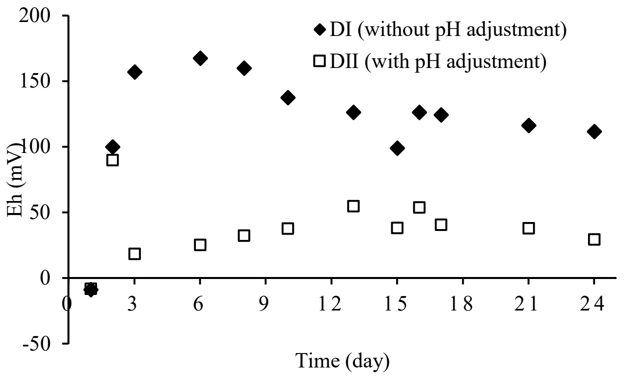

Fig. 3. Eh behavior during anaerobic co-digestion of cow manure and cheese whey with and without pH adjustment

Figure 3 shows the evolution of the redox potential for the two experiments. At start-up, the reduction potentials (Eh) were -8.7 mV and -8.1 mV for DI and DII, respectively. After 48 hours of anaerobic co-digestion, the potentials reached 100 and 90 mV for DI and DII, respectively. After 72 hours, the redox potential increases to 157 mV in the unadjusted digester (DI), and decreases to 18.5 mV in the adjusted digester (DII). This last value indicates correct bacterial activity in the digester (DII). This result is similar to that given by the literature where reduction potentials of 0 to 50 mV are generally measured for digesters in full activity [18].

C. *VFA control*

Volatile fatty acids are short chain fatty acids derived from microbial fermentation during anaerobic digestion. They are in continuous production and consumption during anaerobic digestion, and their monitoring can help us delineate the different stages of anaerobic digestion. Indeed, a too high concentration of VFA is toxic for bacteria and harms the proper operation of the digester hence the importance of their control.

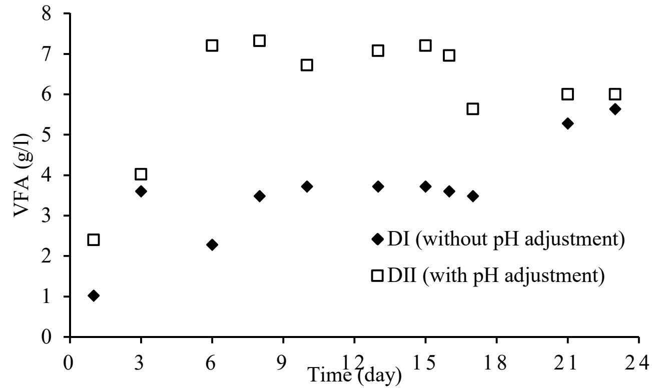

Fig. 4. VFA behavior during anaerobic co-digestion of cow manure and cheese whey with and without pH adjustment

Fig. 4 illustrates volatile fatty acids concentration evolution (expressed in g/L) as a function of the co-digestion time. The evolution curve of the VFA in the digester I, without pH adjustment can be divided into two phases; Phase 1, observed during first 3 days of digestion, with high production of VFA from 1 g/L to 3.6 g/L. This phase corresponds to the hydrolysis and acidogenesis phase; Phase 2, during this phase, the AGV values remained low, around 3 g/L from the 8th to the 17th day, with a maximum of 5.64 g/L on the 23rd day. This is due to the stopping of whey hydrolysis and acetogenesis as well, which led to an inhibition of the methanation process. As a result, a slowing and stopping of CH_4 production was recorded (Fig. 6).

While the evolution of VFA in the digester II, with pH adjustment can be divided into three phases; Phase 1, observed during the first 6 days since the beginning of digestion, with a high production of VFA (from 2.4 g / L on the first day to 7.2 g/L on the 6th day). This phase corresponds to the hydrolysis and acidogenesis reactions. Phase 2, starts from the 6th to the 15th day when stabilization of VFA concentrations around 7.2 mg/L is observed. It is the acetogenesis phase; Phase 3, from the 15th day, the VFA concentrations decrease from 7.2 to 5.64 mg/L. This phase corresponds to the beginning of methane production (Fig. 6). This is the methanogenesis phase.

D. Alkalinity

The total alkalinity of an anaerobic digester is a measure of its ability to neutralize excess of organic acids and maintain a constant pH [14].

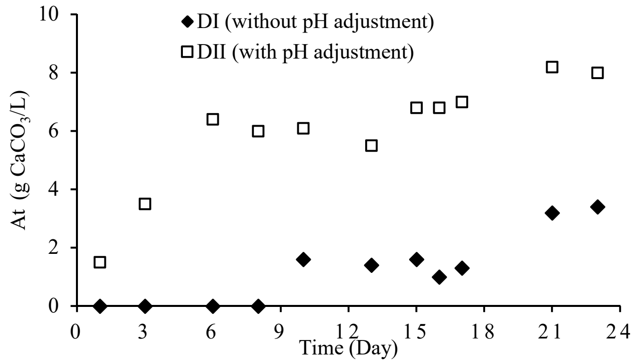

Fig. 5. At behavior during anaerobic co-digestion of cow manure and cheese whey with and without pH adjustment

For an operational digester, a total alkalinity of 2.5 to 5 g/L $CaCO_3$ is recommended [19] According to Grady and Lim (1980) [20], the use of sodium bicarbonate to control pH can have toxic effects that will inhibit microorganisms if the concentration exceeds 8000 ppm sodium (the equivalent of 8 g/L). In digester II (with pH adjustment with 1M sodium bicarbonate), although total alkalinity values of 8 and 8.2 g $CaCO_3$ /L were observed, there was no apparent inhibition by the sodium ion as indicated by the methane production fig. 6 with a methane content of 45%. These results are similar to those obtained by Ghaly (1999) [14]. Because total alkalinity is the sum of all alkali elements, it varies significantly with the endpoint of the pH used [14]. The pH values in digester I (without pH control) being less than or close to 4.5, the total alkalinity was therefore zero during the first 8 days. Then the alkalinity increases gradually until reaching 3.4 g/L after 23 days of anaerobic co-digestion. This is explained by the buffering power of cow manure which tends to neutralize the acidified medium.

E. *Biogas and methane production*

The fig. 6 shows the cumulative volume of biogas and methane levels produced by both anaerobic co-digestion of whey with cow manure (with and without pH adjustment). The total biogas production obtained by the digester II is much higher than that obtained by the digester I; it reached 11.5 L for the digester II and 5.7 L for the digester I. This difference is due to the different behaviors of the two digesters: the evolution of the pH, the alkalinity and the VFA concentration.

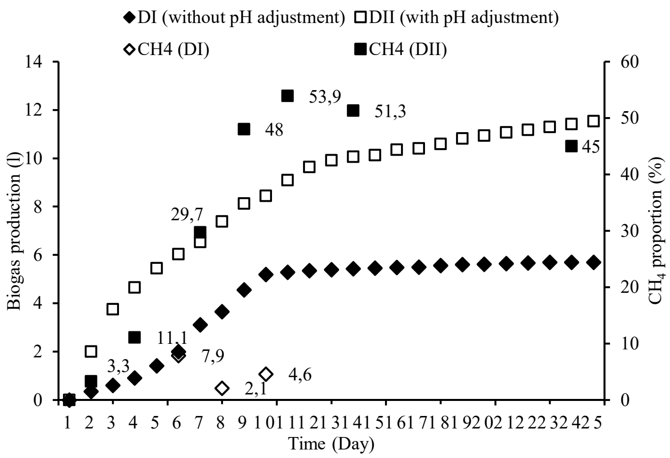

Fig. 6. Process performance during anaerobic co-digestion of cow manure and cheese whey with and without pH adjustment

Methane production

In the digester II, where we made regular pH adjustments, the methane content gradually increased over time to reach a maximum of 53.9% on the 11th day of anaerobic digestion, and 51.3% on the 15th day. While in the first digester, the methane content reached a maximum of 7.9% on the 7th day, and then dropped to 2.1% after the 8th day, stopping abruptly after 10 days of anaerobic digestion, due to the process inhibition.

In conclusion, the digester II worked properly including the four phases of the anaerobic digestion process. This is mainly due to the control and adjustment of the pH.

III. CONCLUSION

The effect of pH adjustment by the use of sodium bicarbonate on the performance of a mesophilic anaerobic digester was studied. It has been found necessary to control the pH of the digester during anaerobic co-digestion of acid whey with cow manure. Without pH control, the very low pH (3.3) inhibited the methanogenic process and the biogas produced contained very little methane. The pH inhibition of the methanogens was irreversible and the digester I did not recover (no methane production). While in the second digester, where we made adjustments, the pH was restored, and it was able to increase the methane production in the biogas, until 50% of CH_4. As a result, the biogas production reached 11 L in 25 days with a maximum methane content of 54% after the 11th day of co-digestion.

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