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Effect of Starting pH on the Produced Methane from Dairy Wastewater in Thermophilic Phase

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The experimental study was undertaken in order to evaluate the effects of the initial pH on the anaerobic digestion of dairy waste. The biodegradability tests were carried out in a series of reactor of 400ml of volume with four arrangements of the initial pH (pH= 4; 5.5; 7; and 9.5) in thermophilic phase (T = 55 °C). The dairy wastewater was the only source of organic carbon.
After the incubation period (50 days), the result show that the height efficiency of removal COD (about de 90.8 %) was obtained for initial pH = 7, allowed by Reactor of pH=9.5 79.64 %; pH=5.5 63.75 % and finally pH=4 (49.11%). Concerning the produced biogas it volume was: 163ml, 1000ml, 2000ml and 1500ml for pH= 4; 5.5; 7 and 9.5 respectively.
However the produced of CH_4 for pH=4 is negligible, for the pH=5.5 and pH=9.5 is slightly over 50 % and 75 % respectively compared to the production of the test pH=7
It can be concluded that dairy waste degradation in anaerobic process can happen optimum on range neutral pH.

1. Introduction

Energy production from the organic matter by means of anaerobic Digestion processes allow better waste management, preservation of the environment, development and diversification of energy resources.. Because of the important methane fraction in the produced biogas, between 50 to75 %, different research-works were undertaken last years with the objective of assessing produced biogas quantities during the degradation of a given waste.
One a very important factor affecting the anaerobic digestion of organic waste is the temperature (Angelidaki and Sanders 2004). Generally, anaerobic digestion process is operated under mesophilic or thermophilic condition, in which thermophilic digestion is reported to be the more efficient
Many researches in this field were presented, and a wide range of waste can be used as substrate for anaerobic digestion(Nallathambi 1997)**;** such as: (Angelidaki et al 2009), proposed a protocols for the determination of the bio-methane potential of organic solid wastes,(Moller et al 2004) used biodegradability test to determine Methane productivity of manure, straw , solid fractions of manure and waste of factory of production of olive oil (Fezzani and Bencheikh 2007), (Neves et al, 2006), used the biodegradability test to determine the bio-methane produced from codigestionof coffee waste and sewage sludge.
Other researchers have studied the influence of different parameters on biogas production; Such as the influence of the used inoculums activity on the biodegradation of the substrate as well as the substrate to inoculums ratio (Chen et al, 1996), Influence of inoculum to substrate ratio on the biochemical methane potential of maize in batch tests (Raposo et al, 2006) the influence of the granulometry of waste (Palmowski and Muller 2000).
In this paper the biodegradability test is used to determine the effects of the initial pH of dairy wastewater in thermophilic temperature (55 °C).

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2. Materials and methods

2.1 Methodology

Measures of methanogenic potential ((Biochemical Potential methanogenic or BMP) are performed following (Vedrenne et al 2005). Concretely, 400 mL of a substrate mixture inoculums and nutrient solution are introduced into a 570mL serum bottle.The quantity in substrate is calculated in order to obtain a ratio S/I equaling to 1.There are 4 anaerobic batch reactors with pH variation arrangement which are: Reactor of pH = 4, pH = 5.5, pH = 7, pH = 9.5 To adjust these pH use added NaOH and HCL 0.1M.
All the reactors batch are distributed between witnesses containing the inoculum only (the white), and tests which contain the mixture of the inoculum and of the substrate. These tests are doubled and the results are averaged over the two experimental measurements. After filling, the flasks are sealed with a rubber septum, and their atmosphere is purged with N_2. Measuring the volume of biogas produced during the times is performed by a column of water (pH = 2).
During all the period of digestion, the quantity of produced biogas was given the every day. The experiment continues until observation of a production of null biogas (50 days).

2.2 Analytical methods

Liquid phase characterization was undertaken before and after anaerobic digestion period through the determination of pH, total solids (TS), total volatile solids (TVS), Alkalinity (TA) and total alkalinity (TAC), volatile fatty acids (AFG), chemical oxygen demand (COD), ammonia nitrogen ($NH4^+$), total Nitrogen (NTK) and total phosphorus (Pt) according to Standard Methods (APHA, et al , 1998) pH was determined using a pH-meter (Jenway 3510 PH meter) and methane in the biogas was analyzed by a gas chromatograph (Arlo Erba strumentazione 4300 (fugueur,120 DFL) with a flame ionization, equipped with stainless steel column (4m long, 3mm outer diameter). The injector, detector and oven temperatures were 40, 80 and 120 ◦ C, respectively, where a 1mL gas sample was injected into the chromatograph using Helium as a gas carrier.

2.3 Characteristic of the liquid phase before incubation

The physicochemical main features of the mixture (mud and dairy waste) in each reactors are deferred in table .1

Table 1: Characterization of the liquid phase of different reactors before incubation

Parametrs	Unit	Initial characterization of each bottle
TA	mg CaCO3/L	184
TAC	mg CaCO3/L	689.6
ST	gTS/L	33.5
SVT	gTS/L	20.20
%SVT	%	60.2
CDO	mgO2/L	8888.4
NH_4^+	mgN/L	57.7
NTK	mgN/L	121.7
Pt	mgP/L	1.68

Table 1, above presents the preliminary characterization of substrate (dairy waste and inoculums (sludge) mixture in different reactors. shows that it is rich in volatile matter (60.2 %). Which encourages the treatment of the latter by anaerobic biological process?
Similarly, the analysis results of alkalinity, ammonia nitrogen, organic nitrogen and phosphorus, are below the values that can inhibited the anaerobic digestion process.

3. Results and discussion

3.1 Characteristic of the liquid phase after incubation

pH Reactor

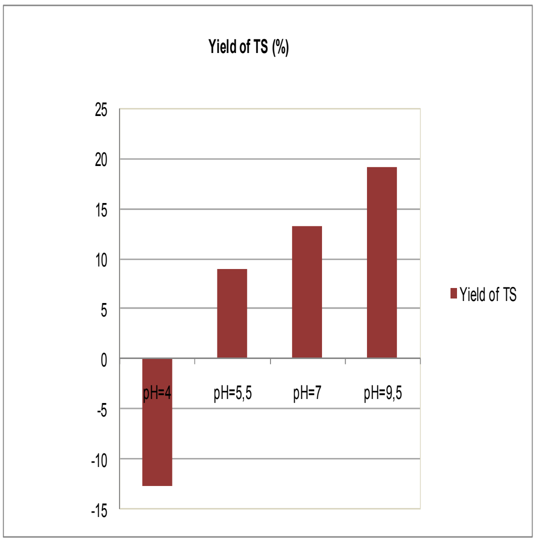
From Table (2), the pH value obtained after the incubation period in the reactor pH = 4 is between 5.35 and 5.41, this is an acid pH not favouring the anaerobic digestion. For reactors pH = 5.5, the pH is about de7.30 is a pH slightly higher than neutral, it means that there was ascended of pH made the environment favourable to digestion.

Table 2: characterization of the liquid phase after incubation

reactors parametrs	unit	pH=4	pH=5.5	pH=7	pH=9.5
pH	/	5.38	7.52	7.66	7.70
TA	Mg caco3/l	0,00	4110	5780	7120
TAC	Mg caco3/l	3100	4740	6260	7830
AFG	Mg caco3/l	3100	630	4,800	710
AFG/TAC	/	/	0.15	0.09	0.08
ST	g(TS)/L	37.87	30.57	29.13	27.13
TVS	g(TVS)/L	21.06	12.24	11.06	6.84
TVS%	/	55,64	40,04	37.96	25.21
TKN	mg/L	190.66	124.85	118.8	96.74
NH_4^+	mg/L	39.82	75.22	9292	61.95
Pt	mg/L	1.13	1.32	115	0.36
COD	mg/L	4482.44	3238.05	817.74	1808.91

than neutral, it means that there was ascended of pH made the environment favourable to digestion. Regarding the reactor pH = 7 and pH = 9.5, pH values obtained after the incubation period in thermophilic phase are around 7.75 is a pH slightly above neutral.It is usually considered that the optimum pH range for anaerobic digestion is between 6.7 and 7.3.

Total solids and volatile solids removal efficiency



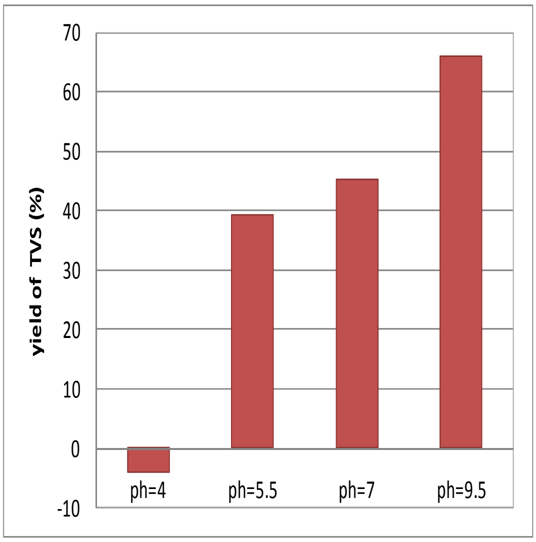


Figure 1: removal efficiency of TS

Figure 2: removal efficiency of TVS

The figures represent yields of elimination of TS and TVS. The best performance of volatils solid (TVS) is 62 % corresponding to the test pH= 9.5. For a pH = 4, we note that the total solids were increased compared to those obtained before incubation which gave a negative return. This increase can be justified by the conversion of microorganism's endogenous phase.

Chemical oxygen demand removal efficiency

Figure 3 shown that there has been a considerable reduction in COD compared to those obtained prior to digestion for pH = 7and pH=9.5 with a yield 90.80 % and 79.64 respectively.

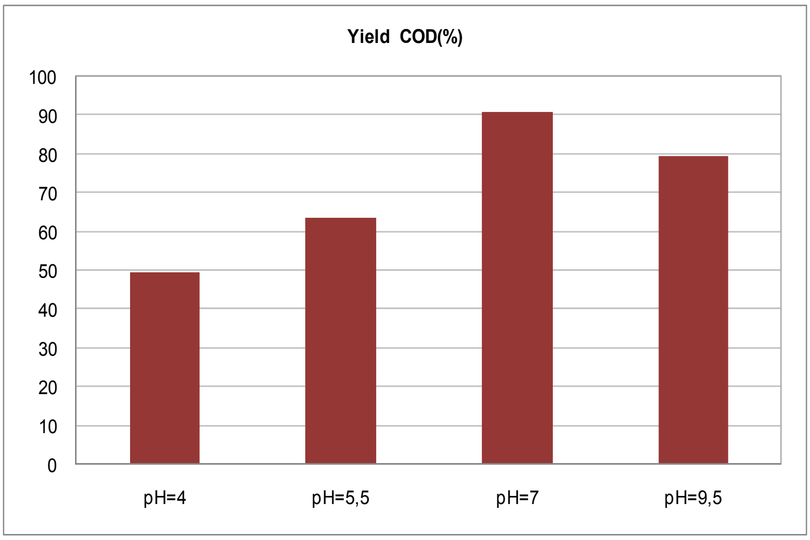


Figure 3: Removal efficiency concentration of COD

3.2 Cumulated biogas volume obtained from substrate

The cumulated biogas produced from organic fraction of dairy wastewater, in thermophilic phase was presented in figure 4

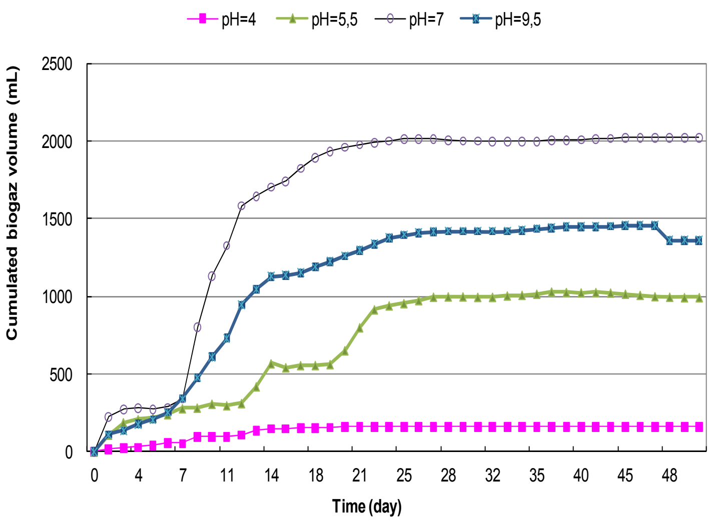


Figure 4: Cumulated biogas volume of dairy waste (T=55 ° C)

The cumulated produced biogas from organic fraction of dairy waste, in thermophilic phase (T = 55 ° C) was presented in Figure 4. It should be noted that the biogas production of dairy waste was calculated after eliminating the inoculum effect. The production is maintained until the 50^{th} day.

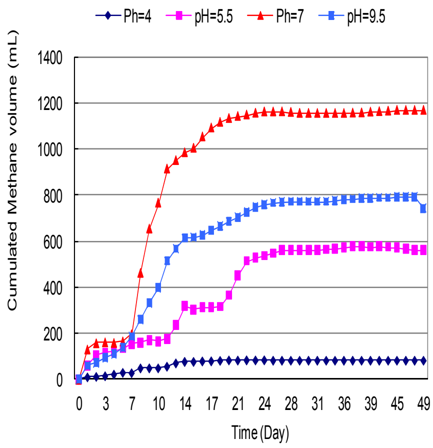
We notice that the biogas production is negligible for test pH = 4, it is important for a test pH = 7 and represents twice the production test of pH = 5.5.

The final values of biogas are 2000 mL, 1500 mL 1000 mL and 162 mL corresponding to the test pH = 7, pH = 9.5, pH = 5.5 and pH = 4 respectively.

This result confirms the results of articles that address the pH of between 6.5 and 8.5 startup that gives the best efficiency degradation of organic matter. (Vedrenne et al 2005).

3.3 Cumulated methane and carbon dioxide obtained from dairy waste

The variations in cumulative volume of CH4 in Figure 5 for test pH = 5.5 and pH = 9.5 are small compared to the test pH = 7. Thus the total production of methane in the test pH = 5.5 represents half of the total production of methane compared to test pH = 7 and 2/3 compared to the test pH = 9.5 with respect to the pH test = 4 the total méthane production is negligible. In the same way for the produced volume of carbon dioxide, see Figure 6.



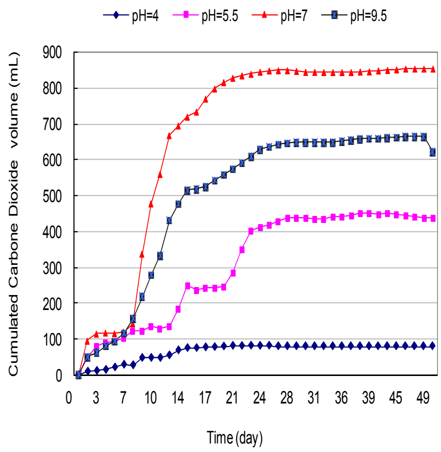


Figure 5: Cumulated CH4 volume (T=55 ° C) *Figure 6: Cumulated CO₂ volume (T=55 ° C)*

3.4 Biogas Composition

Figure 7, represents the average composition of biogas expressed as a percentage of methane and carbon dioxide.

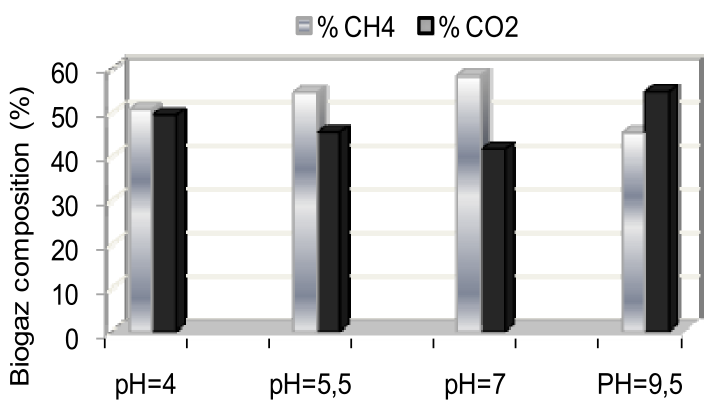


Figure 7: Biogas composition,

The percentages of methane in reactors tested are 58.3%, 54.5%, 50.7% and 45.4%. Corresponding to the test pH =7, pH = 9.5, pH = 5.5 and pH = 4 respectively.

4. Conclusion

Based on this research during 58 days, the maximum methane production is negligible for, pH=4 (50ml) and (500ml) for pH = 5.5. It is important for pH = 7 (1200ml) and pH 9.5 (800ml).
Qualitatively, the percentages of methane in four reactors tested are 58.3 %, 54.5 %, 50.7 % and 45.4 %. Corresponding to the test pH =7, pH = 9.5, pH = 5.5 and pH = 4 respectively.
It can be concluded that dairy waste degradation in anaerobic process can happen optimum on range neutral pH.

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