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

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***Abstract*—** 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 500 mL of volume with four arrangements of the initial pH (pH=4; 5.5; 7; and 9.5) in mesophilic phase (T = 37 °C).

After the incubation period (48 days), the result show that the height efficiency of removal COD (about 94.8 %) was obtained for pH = 7, allowed by Reactor of pH=5.5, 74.3 %; pH=9.5 (70.54%) and finally pH=4 (15.97 %). Concerning the volatile solid, the removal efficiency was 62.51; 44.9;43.8 and 25.82 % for pH= 5.5; 7; 9.5 and 4 respectively. We can be concluding that the optimum pH anaerobic digestion of dairy waste is the neutral pH. The maximum production of biogas is very weak for the pH=4 (1661 mL) and (1700 mL) for the pH=5, 5. It is important for the pH=7 (2248 mL) and the pH=9.5 (2217 mL).

The results of the biogas yields show that: For test pH=4 and pH=5 the pH does not have any effect on the productions cumulated out of biogas finale but the kinetics was higher for the pH=5.5 and For test pH=7 and pH=9.5 the pH indeed does not have any effect on the production cumulated out of biogas finale nor in its speed of its obtaining the end values are of the same order of magnitude.

Point of considering composition in CH4 the variations in volume cumulated of the CH4 for test pH=4 and 5.5 account for the 2/3 of the total production out of methane compared to test pH=7 and pH=9.5.

***Keywords*—** Anaerobic Digestion, Biogas, Dairy effluents, Renewable Energy

I. Introduction

METHANISATION is a biological process which aims at producing, starting from organic waste, a biogas mainly made up of methane and carbon dioxide. Biogas can be valorised, inter alia, by cogeneration to produce an renewable energy in the form of electricity and of heat. This technique also induces the production of a residue called digestat.

Given the importance of this biogas energy terms (50-75% methane), several during the breakdown of a type given waste.several work were published these last years with an aim of determining the quantity of the biogas which can be produced during the degradation of a type of waste given. Several researchers studied the biodegradation of the various types of waste biodegradable through the measurement of the volume of the biogas produced, among this waste one can quote: solid fraction of manures [1], organic waste [2], produced muds of the stations of water treatment [3],municipal solid waste [4], agroalimentary waste [5], waste of factory of production of olive oil [6].

Others studied the influence of several parameters on the production of biogas. Such as the influence of the activity of the inoculum used during the test of biodegradation as well as the substrate ratio/inoculum [7], the influences of the physico-chemical pretreatments applied to waste [8], the influence of the granulometry of waste [9],and the influence of pH startup.

In this paper the biodegradability test is used to determine the effects of the initial pH of dairy wastewater in mesophilic temperature (37°C).

II. Materials And Methods

A. Methodologie

To make sure of a good progress of alkaline fermentation, a volume of inoculum and substrate was fixed successively 180 mL anaerobic mud recover to the secondary basin of the purification plant of the effluents urban of Constantine and 80 mL of the dairy wastewater. 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 N2. 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 (48 days).

B. Analytical methods

Liquid phase characterization was undertaken before and after anaerobic digestion experiments through the determination of pH, total solids (TS), total volatile solids (TVS), Alkalinity (TApH:6) and total alkalinity (TACpH4), chemical oxygen demand (COD), ammonia nitrogen (NH4+), total Nitrogen (NTK) and total phosphorus (Pt) according to Standard Methods (APHA, AWWA, WPCF, 1999). pH was determined using a pH-meter (Jenway 3510 PH meter) and

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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.responsible for obtaining any security clearances.

C. Characteristic of the liquid phase before incubation

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

TABLE I
CHARACTERIZATION OF THE LIQUID PHASE OF DIFFERENT REACTORS BEFORE INCUBATION

Parametrs	Unit	Initial characterization of each bottle
TA	mg CaCO3/L	741.6
TAC	mg CaCO3/L	920.4
ST	gTS/L	35.4
SVT	gTS/L	21.50
%SVT	%	60.6
CDO	mgO2/L	9493.7
NH_4^+	mgN/L	29.20
NTK	mgN/L	113.0
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.

III. RESULTS AND DISCUSSION

If you are using *Word*, use either the Microsoft Equation Editor or the *MathType* add-on (http://www.mathtype.com) for equations in your paper (Insert | Object | Create New | Microsoft Equation *or* MathType Equation). "Float over text" should *not* be selected.

A. Characteristic of the liquid phase after incubation

TABLE II
CHARACTERIZATION OF THE LIQUID PHASE AFTER INCUBATION

reactor parametrs	pH=4	pH=5.5	pH=7	pH=9.5
pH	6.73	7.13	7.57	7.75
TA(Mgcaco3/l)	**800**	3250	4750	5800
TAC(Mgcaco3/l	2200	3900	5600	6400
AFG(Mgcaco3/l	1400	650	850	800
AFG/TAC	1.84	0.20	0.18	0.10
ST(g TS/l)	25.44	24.93	22.41	24.17
TVS(g TVS/l)	12.69	8.19	12.32	6.84
TVS(%)	49.88	32.85	54.97	56.14
TKN(mg/l)	254.44	249.28	224.07	241.71
NH_4^+(mg/l)	3.54	3.54	2.65	3.54
Pt (mg/l)	0.96	0.66	0.33	0.36
COD (mg/l)	7977.21	2384.94	493.44	2796.1

➢ PH Reactor

As shown in Table.2, the pH obtained after the incubation time in the mesophilic phase into the reactors of the test pH = 5.5 and pH = 4 successively is around 6.64 and 7.13 this means; that during the incubation period, the bacteria in the inoculum resisted until it's the pH back up to a near neutral pH which rendered the environment favorable to digestion. As regards the reactors pH = 7 and pH = 9.5 is obtained the pH is between 7.57 and 7.75 is a pH slightly above neutrality.

➢ Chemical oxygen demand removal efficiency

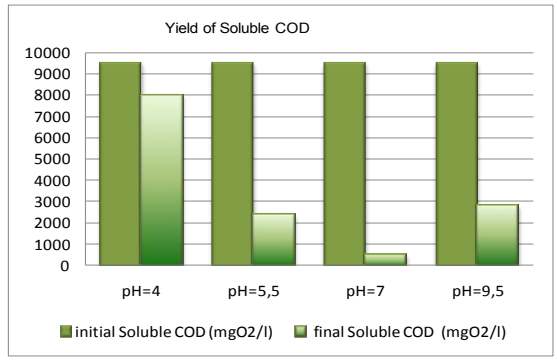

Fig1. Yield of elimination of COD

Fig 1 shown that there has been a considerable reduction in COD compared to those obtained prior to digestion for pH = 7and pH=5.5 with a yield 94 % and 70.54 respectively.

➢ Total solids and volatile solids removal efficiency

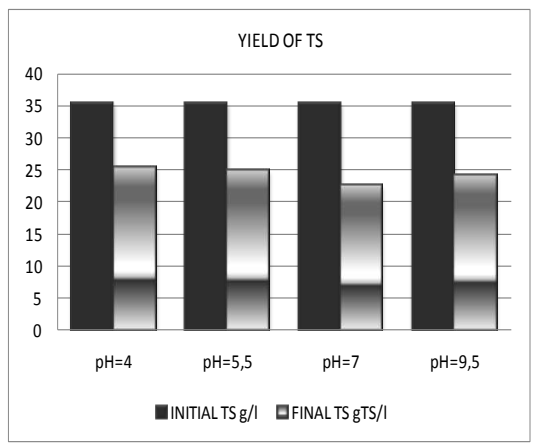

Fig2. Yield of elimination of TS

On Figure 2 shows the yields of elimination of total solids for the different tests of pH, we note that their values, TS after the incubation period is around 22 and 25 g / l, with a yield of 26-37% indicating that it tests neutral pH have the highest yield.

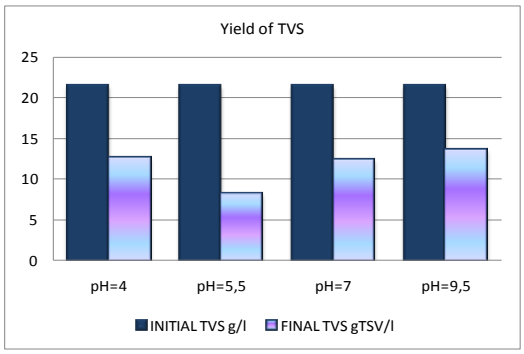

Fig3. Yield of elimination of TVS

On Figure 3 shows the yields of elimination of solides volatile (TVS) .The best performance of volatils solid (TVS) is 61.9 % corresponding to the test pH= 5.5 followed by the test pH=7,(42.69%), test PH=4 (40.93%) and for test pH= 9.5 (36.88%)

➢ Ammonia nitrogen and azote organic

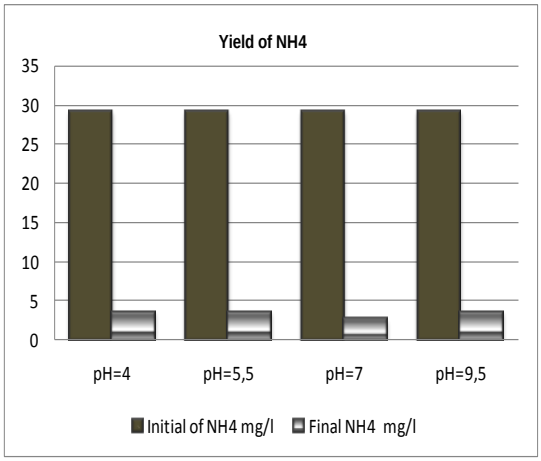

Fig4. Yield of elimination of $NH4^{+}$

Figure 4 shows that the final values of the concentration of ammonia nitrogen is considerably low compared to the initial concentrations, translates into removal efficiencies of ammonia which is very high, between 85.14 and 91%.

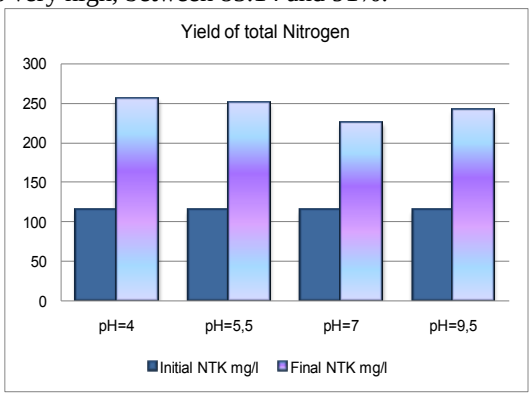

Fig5. Yield of elimination of NTK

According to values of total nitrogen residues, were initially obtained from the order 113mg / l. After the incubation period, these values are doubled and varying between (206-260mg / l). In this set we can say that the total nitrogen contents are unstable between the beginning and the end of incubation for four pH tested. Although these values appear to be high, they are low compared to the values that inhibit the process of anaerobic digestion (2000mg/l) for both ammonia nitrogen as organic nitrogen. [11].

➢ Total phosphorus removal efficiency

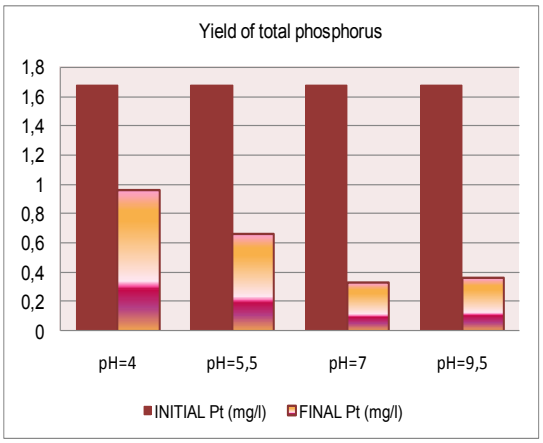

Fig6.Yield of elimination of total pophorus

The elimination yields of total phosphorus are very high for wholes reactors tested ranging from 40 to 80% knowing that the best performance remains that of the reactor at a starting pH equal to 7.

B. Variation of cumulative volume in biogas from (dairy waste)

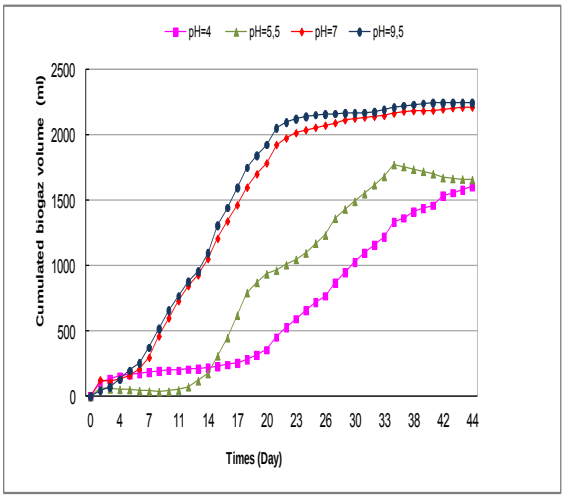

Fig.7. Cumulated biogas volume of dairy waste

The cumulated produced biogas from organic fraction of dairy waste, in mésophilic phase (T = 35° C) was presented in Figure 8. It should be noted that the biogas production of dairy waste was calculated after eliminating the inoculum effect.

The production is maintained until the 48th day. We notice that the maximum production out of biogas is very weak for the tests pH=4 and pH=5.5 it is important for the pH = 7 and pH = 9.5. If we consider the curve of pH 7 and the pH = 9.5 pH has no effect on the cumulative final biogas production either in its rapidity of his obtaining.

Concerning the curve of pH = 4 and pH = 5.5 is noted that the pH n 'has no effect on the final cumulative biogas production, but the kinetic was higher for pH = 5.5. The final values of biogas are 2217 mL, 2248 mL 1700 mL and 1661 mL corresponding to the test pH = 7, pH = 9.5, pH = 5.5 and

pH = 4 respectively.

Scientific papers, addressing optimization of anaerobic digestion, recall the importance of starting pH between 6.5et8.5 [11]. Thus a gap of this pH range is generally indicative of a malfunction of the digester, and an accumulation of acid or alkaline compounds,this is confirmed with the test pH = 4 and 5.5, by against for pH = 9.5 it was expected that the yield and kinetics of the cumulative biogas production, is lower than the test pH = 7. Referring to the result of the final pH was observed that the pH of the test pH = 9.5 is around 7.75, so close to neutral, practically the same as the test of pH = 7.

C. Variation of Cumulative gas (CH4) and(CO2)

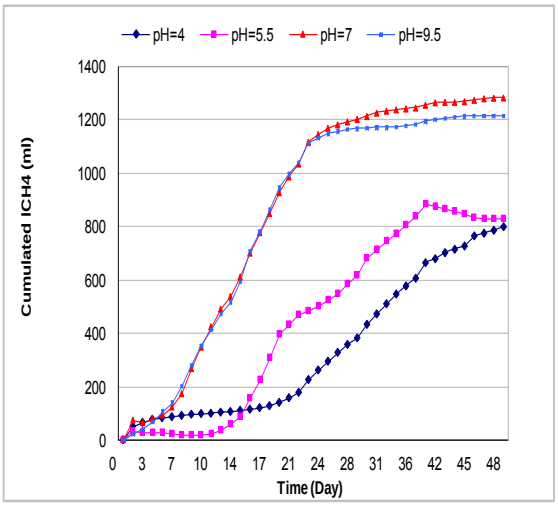

Fig.8. Cumulated CH4 volume

The variations in volume cumulated in CH4 according to figure (8) for the test of the pH= 4 and 5.5 are weak compared to the test of the pH = 7 and the pH = 9.5 and account for the 2/3 of the total production out of methane of the test pH=7.

In addition one notices for the curve of the pH = 7 and the pH = 9.5 a slight difference on the cumulated production of the final CH4 which is respectively 1294 mL and 1214 mL.

Indeed a consequent production out of methane reflects the good performance of this last. In the same way for the produced volume of carbon dioxide, see Figure 9.

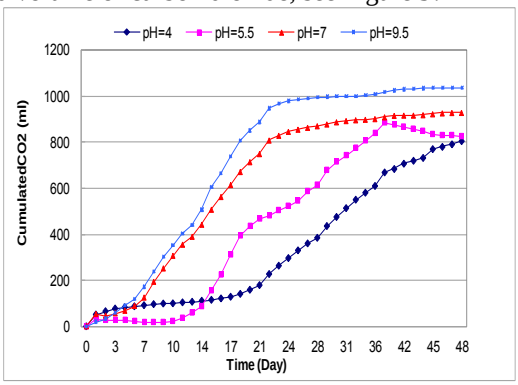

Fig.9. Cumulated CO2 volume

IV. Conclusion

The result show that the height efficiency of removal COD (about 94.8%) was obtained for initial pH = 7, allowed by Reactor of pH=5.5 74.3%; pH=9.5 (70.54%) and finally pH=4 (15.97%). Concerning the volatile solid, the removal efficiency was 62.51; 44.9; 43.8 and 25.82% for pH= 5.5; 7; 9.5 and 4 respectively.

The variation in the volume of accumulated biogas while eliminating the effect of the inoculum is [49 58ml/jour]. The production continues until the 48th day.

The maximum biogas production is very low for pH 4 (1661ml) and (1700ml) for pH = 5.5. It is important for pH = 7 (2248ml) and pH 9.5 (2217ml).

The results show that biogas yields:

- For the tests of the pH=4 and pH = 5 pH has no effect on cumulative in the final biogas but the kinetics was higher for pH = 5.5 productions
- Tests for pH = 7 and pH = 9.5 pH has no effect on production or cumulative final biogas or in the rapidity of obtaining it. Indeed the final values are of the same order of magnitude.
- From the point of view of composition CH4 variations in cumulative volume of CH4 for testing pH = 4 and Figure 5.5, representing two thirds of the total methane production compared to tests of pH 7 and pH = 9.5. Tests for pH = 4 and pH = 5 pH has no effect on cumulative in the final biogas but the kinetics was higher for pH = 5.5 productions.
- For the tests of the pH = 7 and pH = 9.5 pH has no effect on the final cumulative production in biogas nor in the speed of graduation. Indeed, the final values are of the same order of magnitude.

From the point of view of composition CH4 variations in cumulative volume of CH4 for testing pH = 4 and Ph= 5.5, representing two thirds of the total methane production compared to tests of pH 7 and pH = 9.5.

References

[1] Z. Mladenovska, H. Hartmann, T. Kvist, M. Sales-Cruz, R. Gani and B.K. Ahring, Thermal pretreatment of the solid fraction of manure: impact on the biogas reactor performance and microbial community, Water Science & Technology Vol 53 No 8 pp 59–67 2006. http://dx.doi.org/10.2166/wst.2006.236

[2] Hansen, T. L., Schmidt, J. E., Angelidaki, I., Marca, E., Jansen, J. C., Mosbæk, H. & Christensen, T. H. 2004 Measurement of methane potentials of solid organic waste. Waste Manage. 24(4), 393–400. http://dx.doi.org/10.1016/j.wasman.2003.09.009

[3] Lin, J. G., Ma, Y. S., Chao, A. C. & Huang, C. L. 1999 BMP test on chemically pretreated sludge. Bioresour. Technol. 68(2), 187–192. http://dx.doi.org/10.1016/S0960-8524(98)00126-6

[4] Owens, J. M. & Chynoweth, D. P. 1993 Biochemical methane potential of municipal solid-waste (MSW) components. Water Sci. Technol. 27(2), 1–14

[5] Fezzani, B., Ben Cheikh, R., 2007, Thermophilic anaerobic co-digestion of olive mill wastewater with olive mill solid waste in a tubular digester, Chemical Engineering Journal 132, 169–179. http://dx.doi.org/10.1016/j.cej.2006.12.017

[6] Erguder T.H., Tezel U., Guven E., Demirer G.N., 2001. Anaerobic biotransformation and methane generation potential of cheese whey in batch and UASB reactors. Waste Manage., 21 (7), 643-650. http://dx.doi.org/10.1016/S0956-053X(00)00114-8

[7] Neves, L., Oliveira, R. & Alves, M. M. 2004 Influence of inoculum activity on the bio-methanization of a kitchen waste under different waste/inoculum ratios. Process Biochem. 39(12), 2019–2024 http://dx.doi.org/10.1016/j.procbio.2003.10.002

[8] Perez Lopez, C., Kyrchmayr, R., Neureiter, M. & Braun, R. 2005 Effect of physical and chemical pre-treatments on methane yield from maize silage and grains. In proceedings of the International Symposium on Anaerobic Digesion of Solid Waste (ISAD-SW) 2005. Copenhagen, Denmark, August 31- Septmeber 3, 2005, p. 204–208.

[9] Palmowski, L. M. & Muller, J. A. 2000 Influence of the size reduction of organic waste on their anaerobic digestion. Water Sci. Technol. 47(12), 231–238.

[10] Vedrenne F., Béline F. & Bernet N. Evaluation of the methane production of livestock wastes: ultimate productivity and organic matter characterization, 4th international symposium on Anaerobic Digestion of Solid Waste, Copenhague, 31 août- 02 septembre 2005, 218-225.

[11] DJELAL Hayet, POIGNANT Emeline et BRAU Lucie 2009,' Mise en place d'un pilote industriel sur le site de la station d'épuration d'une laiterie pour optimiser le traitement de leurs effluents Récents Progrès en Génie des Procédés – Numéro 98 – (2009).