ANAEROBIC DIGESTION OF TOMATO PROCESSING WASTE: EFFECT OF ALKALINE PRETREATMENT

CALABRÒ P.S.[1], GRECO R.[1], EVANGELOU A.[2] and KOMILIS D.[2]

[1] Department of Civil, Energy Environmental and Materials Engineering, Università Mediterranea di Reggio Calabria, via Graziella loc. Feo di Vito, 89122 Reggio Calabria, Italy, [2] Department of Environmental Engineering, Democritus University of Thrace, Xanthi, 671 00, Greece
E-mail: dkomilis@env.duth.gr

ABSTRACT

Tomato (*Solanum Lycopersicum*) is the second most highly produced vegetable in the world, with an estimated generation of 164 Mt within 2013; about 50 Mt are cultivated for the processing industry that generates various by-products (pomace, skins and seeds) that represent 4-13% of a typical tomato or a total amount of around 3 to 6 Mt/year. Tomato processing waste (TPW) is often dumped or landfilled near processing sites generating liquid emissions, odors and methane emissions due to an uncontrolled anaerobic fermentation. The use of tomato waste for biomethane production through anaerobic digestion has been also proposed with an estimated production in the range 199-384 $NmlCH_4/gVS$.

TPW is characterized by acidity (pH around 4) and is relatively rich in protein and fat. Fibre content is high: crude fibre is in the 33-57 % DM range, while lignin content has been reported to be around 4%.

Alkaline pretreatment to neutralize the TPW and to enhance methane generation is investigated in this work.The objective of the research activity presented in this paper is to assess if a mild alkaline pretreatment carried out at 20°C with a duration of either 4 and 24 hours and a limited NaOH dosage (1 or 5%) can be beneficial to the anaerobic biodegradability of tomato waste in terms of neutralization of the acidity, increase of substrate accessibility and faster kinetics of the process.

The results indicate that the neutralization of the pH is possible only if the highest NaOH dosage for 24 hours is used. With reference to the specific methane production, data obtained in this study (320 NmL/gVS on average) are in agreement with those previously reported in literature. Statistical analysis demonstrates that there is no statistical difference between untreated and treated samples in terms of specific methane production. Hypothesizing a first-order kinetic for biologic methane production, calculated kinetic constants shows that the alkaline pretreatment leads to a slower kinetic of the anaerobic process.

According to the results of this paper, TPW is a suitable substrate for anaerobic digestion, moreover an alkaline pretreatment should be considered only in those cases where the buffering capacity is insufficient for preventing the acidification of the anaerobic sludge linked to the use of TPW.

Keywords: alkaline pretreatment, anaerobic digestion, biochemical methane potential, kinetics, tomato waste.

1. Introduction

Tomato (*Solanum Lycopersicum*) is the second most produced vegetable in the world, with about 164 Mt produced only in 2013 (FAOSTAT, 2015); one quarter of the total production is directed to the industry (Tomato news, 2014).The transformation of tomato generates various by-products (pomace, skins and seeds) representing about 4-13% of the processed material (Ventura *et al*., 2009) that corresponds to around 2 to 5 Mt/year. If tomato transformation by-products are not further processed or used, they become tomato processing waste (TPW), that is often dumped near productions sites causing impacts on soil and groundwater, odour problems and, due to uncontrolled anaerobic fermentation, CH_4 emissions in the atmosphere (Encinar *et al*., 2008).

The use of tomato waste for biomethane production through anaerobic digestion has been also proposed with reported yields that range from 199 to 384 NmL CH_4/gVS (Gunaseelan, 2004; Ward *et al*., 2008; Dinuccio *et al*. 2010; Gonzàlez-Gonzàlez and Cuadros, 2013). TPW is acidic (pH around 4.5) and is relatively rich in protein and fat. The acidic pH of TPW is likely a limitation for its use as a substrate for anaerobic digestion. Therefore, either the codigestion with other substrates or, if this is not feasible for technical-economic reasons, a neutralisation pretreatment could be considered beneficial (Bouallagui *et al*, 2009). Alkaline pretreatment (with NaOH, KOH, lime, ammonia, and urea) before the anaerobic digestion has been widely studied in the past. No information seems to appear in the literature on the effect of alkaline pretreatment on the anaerobic digestion of TPW.

Therefore, the objective of this work was to assess if an alkaline pretreatment carried out at 20°C, with a duration of either 4 and 24 hours and with a limited NaOH dosage (1% or 5%), could be beneficial to the anaerobic biodegradability of TPW. Biochemical methane potential (BMP) experiments were carried out in duplicate and obtained results were modelled with first order kinetics to evaluate the effect of alkaline treatment on methane generation rates.

2. Materials and methods

Approximately 2 L of TPW were obtained from a small plant located in the province of Reggio Calabria (Italy) that processes tomatoes to obtain tomato puree. The received sample was distributed in 250 mL glass digestion flasks, closed with caps. In each flask, the TPW samples were soaked in NaOH solutions at different dosages (1 and 5 gNaOH/100 gTS) with a total solid concentration of about 120 gTS/L. The flasks were maintained at 20 °C for either 4 or 24 h in an incubator, according to the experimental design of Table 1. Note that sample (a) is the TPW as received without any addition of water, while sample (A) is the control obtained after adding the same amount of water that had been added to the other samples.

Table 1: Characteristics of untreated and treated TPW

Sample	NaOH dosage [gNaOH/100gDM]	Incubation time [h]	TS [% WM]	VS [%DM]	pH achieved after pretreatment	COD [mg/g_{DM}]
a[1]	0	0	16.5	94.6	4.3	N.A.
A[1]	0	24	10.9	92.1	4.6	1180
B	5	4	13.2	90.9	9.6	1000
C	1	24	10.9	90.3	4.5	1035
D	5	24	12.4	89.8	7.1	1030

[1]: controls in which no NaOH was added. Results from reactor A were used in subsequent calculations to calculate net BMP.

Total solids (TS), volatile solids (VS), pH and COD (for the pretreated samples) were determined according to standard procedures (APHA *et al*., 2005). Ultimate analysis (C, H, N, S) of the control and of the pretreated samples was performed with an elemental analyzer (Thermo-Electron, USA, model: EA-1110, CHNS-O) according to Komilis *et al*. (2012). Biochemical methane potential (BMP) tests were performed in duplicate under mesophilic conditions (35±0.5°C). Tests were performed using a custom made method that is a modification of that described in Schievano *et al*. (2008). The CH_4 content is calculated by transferring 100 mL biogas into a second OxiTop® using a syringe and a tube immersed in 0.3 L of a 3M NaOH solution (Schievano *et al*., 2008) for assuring CO_2 removal. Biogas measurements in the first bottle were calculated via the ideal gas law using the pressure readings while, the pressure increase in the second bottle was converted, using the ideal gas law, to moles of CH_4 generated.

All samples were inoculated with an anaerobic sludge that was taken from the second stage of a digester the operated under mesophilic conditions and fed on agro-residuals (cattle manure, chicken manure, agriculture residuals and other industrial residues coming from the transformation of agriculture products such as olive and oranges). The inoculum had a solid content of 49.0 gTS/L and 34.4 gVS/L. Immediately after sampling, inoculum was sieved (<1mm) to remove large fibrous materials (e.g. straw) and was then kept under endogenous anaerobic conditions at 35 °C for about 10 days to reduce non-specific biogas generation. Each batch was prepared by mixing 50 ml of inoculum with 50 ml of distilled water, then, immediately at the end of the pretreatment period, substrate was added by keeping an inoculum to substrate ratio (ISR, on a VS basis) at around 2.5. Around 0.75 gTS of substrate were placed in each BMP bottle. The net specific biochemical methane production (BMP) was calculated as follows:

$$BMP = \frac{(V_{CH4,s} - V_{CH4,blank})}{VS_s \cdot V_s} \quad (1)$$

where: BMP in NmL CH_4 / g VS; V_{CH4} is the 30 d gross methane production from all treatments (substrate + inoculum) in NmL CH_4; $V_{CH4,blank}$ is the 30 d methane production of the inoculum in NmL CH_4; VS_s is the concentration of volatile solids from the feedstock in the bottle at the beginning of the test (g VS/L) and V_S is the liquid volume (L) in the BMP bottle.

The anaerobic digestion process was assumed to follow first order kinetics (Angelidaki *et al*., 2009; Sambusiti *et al*., 2013a,b). The first order kinetic constant was estimated by fitting experimental data to the following equation:

$$BMP(t) = BMP_{t\rightarrow\infty} \cdot (1 - exp^{-k_h \cdot t}) \quad (2)$$

where: BMP (t) (Nml CH_4/g VS) is the cumulative methane production at time t, $BMP_{t\rightarrow\infty}$ (Nml CH_4/g VS) is the asymptotic methane production, k_h (d^{-1}) is the first order kinetic constant and t (d) is the time. Based on the above, the individual cumulative methane measurements collected during the experimental period were fitted to equation (2) to calculate k_h and $BMP_{t\rightarrow\infty}$. The regression modelling was done with an Excel® spreadsheet using the least squares method after applying the Solver® optimization routine.

3. Results and discussion

Figure 1 shows the specific methane production of each treatment and for each replicate separately. The fitted equation is based on the aforementioned first order kinetic model (R^2 was always higher than 0.94 in all fittings). It is noted that this first order kinetic profile, with a very short methane generation lag phase, has been also observed with other acidic organic wastes studied with BMP experiments, such as citrus wastes (Forgács *et al*., 2012). Table 2 presents the ultimate analysis of all substrates.

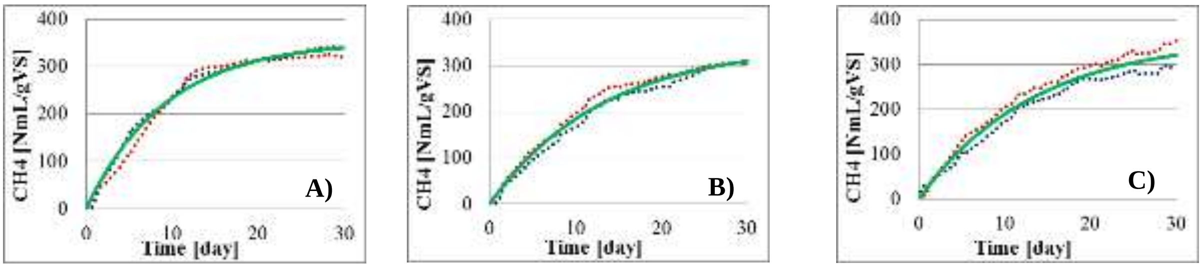

Figure 1: Actual measurements (the dotted values shown are from 2 replicate reactors per treatment) and fitting of the modeled methane production (solid lines) for: A) untreated TPW; B) 5% NaOH - 4h TPW; and C) 5% NaOH - 24h TPW.

Table 2: Ultimate analysis' results and derived empirical formulas

Sample	NaOH dosage [gNaOH/100gDM]	Incubation time [h]	C (%DM)	N (%DM)	H (%DM)	O[1] (%DM)	Empirical formula
A	0	24	43.4[a]	2.56[a]	8.44[a]	37.7	$C_{20}H_{46}O_{13}N$
B	5	4	39.3[b]	1.96[b]	8.48[a]	41.1	$C_{23}H_{61}O_{18}N$
C	1	24	40.4[ab]	2.48[a]	7.84[a]	39.6	$C_{19}H_{44}O_{14}N$
D	5	24	39.6[ab]	2.13[ab]	8.58[a]	39.5	$C_{22}H_{56}O_{16}N$

[1]: Oxygen content was indirectly calculated by the difference of the sum of C, H, N, S from the VS content. No sulfur was detected in any of the samples.
Means on the same column that share the same letter indicate statistical similarity at $p < 0.05$ based on Tukey´s test with n=5.

Table 3 summarizes the experimental and modelling results. According to Table 3, the methane yield was comparable to that reported in the scientific literature for other organic wastes (Gunaseelan, 2004; Ward *et al*., 2008; Dinuccio *et al*. 2010; Gonzàlez-Gonzàlez and Cuadros, 2013). Moreover the BMP results, in a similar manner to the characterization results, clearly demonstrated that the alkaline pretreatment did not influence significantly BMP_{exp}, $BMP_{t\to\infty}$. The average BMP_{exp} from all treatments (including the control) was 320 NmL/gVS. Interestingly, however, a reduction in the rate of methane production (see kinetic constants of Table 3) was observed for all treated samples compared to the control. In fact, the time for reaching 75% of the experimental final BMP increased from about 10 days (untreated sample) to about 15 days (sample treated with 5% NaOH for 24 hours).

Table 3: BMP results, theoretical methane yields and calculated kinetic coefficients

Substrate	BMP_{exp} [NmL/gVS][1]	Difference[2] [%]	$BMP_{t\to\infty}$ [NmL/gVS] [3]	k_h [d^{-1}] [3]
Untreated (A)	330 ± 10	-	353	0.110
5% NaOH - 4h (B)	305 ± 1	-7.6	344	0.076
1% NaOH - 24h (C)	335 ± 20	+1.5	354	0.097
5% NaOH - 24h (D)	324 ± 29	-1.8	358	0.075

[1]: Methane yield after 30 days of incubation based on duplicate runs (mean ± STD).
[2]: Deviation between the BMP of each run and the BMP of the control (untreated sample).
[3]: $BMP_{t\to\infty}$ and k_h are calculated via the kinetic modelling.

4. Conclusions

Alkaline pretreatment of TPW did not affect methane yield in any of the treatments in comparison to the control. The average net methane production of all treatments (including the control) was 320 NmL CH_4/g VS. On the other hand, alkaline pretreatment reduced the rate of methane generation, compared to the control, probably due to the high pH achieved (reactor B) or due to a likely accumulation of salts.

REFERENCES

1. Angelidaki, I, Alves, M., Bolzonella, D., Borzacconi, L., Campos, J.L., Guwy, A.J., Kalyuzhnyi, S., Jenicek, P and van Lier, J.B., (2009), Defining the biomethane potential (BMP) of solid organic wastes and energy crops: a proposal protocol for batch assays. Water Sci. Technol., 59.5, 927-934.
2. American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF), (2005), Standard Methods for the Examination of Water and Wastewater. 21th Edition, American Public Health Association, Washington, D.C.
3. Bouallagui. H., Lahdheb, H., Ben Romdan, E., Rachdi, B., Hamdi, M., (2009) Improvement of fruit and vegetable waste anaerobic digestion performance and stability with co-substrates addition. Journal of Environmental Management, 90, 1844–1849.

4. Dinuccio, E., Balsari, P., Gioelli, F., Menardo, S. (2010), Evaluation of the biogas productivity potential of some Italian agro-industrial biomasses. Bioresource Technol., 101, 3780–3783.
5. Encinar, J.M., Gonzàlez, J.F., Martìnez, G., (2008), Energetic use of the tomato plant waste. Fuel Process. Technol., 89, 1193 -1200.
6. FAOSTAT, (2015), Statistical database of the Food and Agriculture Organization of the United Nations. Internet site: http://faostat3.fao.org/.
7. Forgács, G., Pourbafrani M., Niklasson, C., Taherzadeh, M., Sárvari Hováth, L. (2012), Methane production from citrus wastes: process development and cost estimation. J. Chem. Technol. Biotechnol, 87, 250-255.
8. González-González, A., Cuadros, F. (2013), Continuous biomethanization of agrifood industry waste: A case study in Spain. Process Biochem., 48, 920-925.
9. Gunaseelan, V.N., (2004), Biochemical methane potential of fruits and vegetable solid waste feedstocks. Biomass Bioenerg., 26, 389 – 399.
10. Komilis, D., Evangelou, A., Giannakis, G., Lymperis, C. (2012), Revisiting the elemental composition and the calorific value of the organic fraction of municipal solid wastes. Waste Manage. 32, 372-81.
11. Sambusiti, C., Monlau, F., Ficara, E., Carrere, H., Malpei, F. 2013a. A comparison of different pre-treatments to increase methane production from two agricultural substrates. Appl. Energ., 104, 62 - 70.
12. Sambusiti, C., Ficara, E., Malpei, F., Steyer, J.P., Carrère, H. 2013b. Effect of sodium hydroxide pretreatment on physical, chemical characteristics and methane production of five varieties of sorghum. Energy, 55, 449-456.
13. Schievano, A., Pognani, M., D'Imporzano, G., Adani, F. (2008), Predicting anaerobic biogasification potential of ingestates and digestates of a full-scale biogas plant using chemical and biological parameters. Bioresour. Technol. 99, 8112–8117.
14. Tomato news, 2014. About the tomato processing industry. Internet site: http://www.tomatonews.com/resources.html
15. Ventura, M.R., Pieltin, M.C., Castanon, J.I.R. (2009), Evaluation of tomato crop by-products as feed for goats. Anim. Feed Sci. Tech., 154, 271-275.
16. Ward, A.J., Hobbs, P.J., Holliman, P.J., Jones, D.L. (2008), Optimisation of the anaerobic digestion of agricultural resources. Bioresource Technol., 99, 7928 – 7940.