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Enhancing the biomethane production from tannery wastewater by thermal pretreatment

O. Achouri[1]*, A. Panico[2], M. Bencheikh-Lehocine[3], K. Derbal[3], F. Pirozzi[4]

[1]Process Engineering Faculty, Environmental Engineering Department, University of Constantine 3, Ali Mendjeli Nouvelle Ville, Constantine, ALGERIA
[2]Telematic University Pegaso, Piazza Trieste e Trento 48, 80132, Naples, ITALY
[3]Process Engineering Department, National Polytechnic School of Constantine, Bp 75, A, Nouvelle Ville RP, Constantine, ALGERIA
[4]Department of Civil, Architectural and Environmental Engineering, University of Naples Federico II, via Claudio 21, 80125, Naples, ITALY

*Corresponding author: wafaachouri@gmail.com; Tel.: +213 551 29 32 36.

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ABSTRACT/RESUME

Abstract: *Anaerobic Digestion (AD) is often chosen as a suitable treatment for tannery wastewater (TWW) since this waste stream is rich in organic matter. Nevertheless, the high organic load and the presence of compounds commonly used in the leather production process and responsible for inhibiting the biological activity (e.g. chromium and sulphide) limit the full capitalization of the whole potential in producing biomethane from this low-cost and interesting source of renewable energy. Pretreatment of substrates is considered by most as the solution to overcome this negative aspect as a higher biomethane production in a shorter time is expected after that. Actually in this study three different temperatures have been tested, in detail, 90, 80, and 70 °C, to pretreat a real TWW prior to a mesophilic AD process conducted in a series of batch biomethane potential (BMP) tests aimed at evaluating the optimum temperature that can result in increasing the soluble COD content and consequently the AD performance .*

After the pretreatment, the soluble COD concentration increased from a minimum of 11% to a maximum of 80%: which resulted in an increase of the biomethane production compared with the raw substrate. The highest temperature (90°C) investigated gave the highest increasing in soluble COD but had a negative effect on AD process performance, as the final production of biomethane was 178 ml CH_4/g TVS, more than 4 folds less than the maximum yield of 891 ml CH_4/g TVS obtained from the sample pre-treated at 80°C where the increase in soluble COD was by 57%.

These results highlight the critical aspect of the thermal pretreatment: the increase of temperature can enhance the biomethane production as well as reduce it, therefore the choice of the most suitable temperature depends strongly on the characteristics of the substrate and it can be made only through experimental tests.

I. Introduction

Anaerobic Digestion (AD) is commonly used to treat high organic load wastewaters, stabilize sludge from municipal wastewater treatment plants and process organic solid wastes of different origins [1]. When AD is operated at full scale, not only it prevents the environmental pollution, but also it can be used as a system to produce sustainable energy and recover nutrients. [2]

In the past, many studies have been conducted on the AD process with the aim of improving its performance as well as maximizing the biogas production and pre-treatment methods, in particular, those using the effect of heating, are resulted in the most promising [4].

Actually, a thermal pretreatment leads to pathogen removal, reduces the viscosity in the digesting matrix [5] and promotes the cells break [6; 7]. Furthermore, high temperatures destroy lignin bonds [7; 9] and convert complex lipids and proteins into lower molecular weight compounds [10], thus improving the hydrolysis of particulate organic matter and consequently the substrate biodegradability [11]. Costs for heating the substrate represent the critical aspect of this method if the biogas produced by AD is not enough to supply with power the heating system [7]

Ivet et al [12] investigated the effect of a low-temperature pretreatment (70 ◦C) on the efficiency of thermophilic AD of primary and secondary settlement wastewater sludges: the study was aimed at optimizing the process time ranging from 9 to 72 hours in terms of volatile dissolved solids (VDSs), volatile fatty acids (VFAs) and biogas production through thermophilic batch tests. The results showed an initial enhancement of organics solubilization (VDS increased nearly 10 times after 9 h), followed by a gradual generation of VFA (from 0 to about 5 g L-1 after 72 h). Biogas production increased up to 30%. A similar work was conducted by Mottet et al [11], where wastewater activated sludge (WAS) was thermally pretreated at a higher temperature, i.e. 110, 165 and 220°C. 165 °C was found to be the optimal condition for the thermal pretreatment resulting in an increase of chemical oxygen demand (COD) and volatile solids (VS) solubilization by 18 and 15% respectively as well as an enhance of biodegradability ranging from 47 and 61%. Nevertheless, extremely high-temperature treatment promoted the production of slowly and hardly biodegradable compounds, like Amadori compounds and melanoidins [11].

Carrère and al. [13] studied the effect of heat treatment (70-190 ° C) on AD of pig manure to maximize methane production in batch biomethane potential (BMP) tests at the mesophilic condition: methane potential of manure soluble fraction increased with the temperature whereas temperatures higher than 135 °C were necessary to improve the methane potential of the total fraction.

Ariunbaatar et al.[14] examined the effects of thermal pretreatment on food waste (FW) by heating the substrate constituting by FW either singularly or mixed with inoculum at 50, 60, 70 and 80 °C with different operating times: the results showed that the better improvements in biomethane production by 44–46% were achieved with a thermophilic pretreatment at 50°C for 6–12 h and a thermal pretreatment at 80°C for 1.5 h; thermophilic pretreatments at higher temperatures (>55°C) and longer operating times (>12 h) yielded a higher soluble chemical oxygen demand (CODs) but had a negative effect on the methanogenic activity [14]

Pontoni et al [15] investigated the effect of thermal pretreatment on the AD of aromatic compounds present in olive oil mill wastewater (OMWW); in BMP tests at a laboratory scale, samples of OMWW pretreated at mild (80 ± 1 °C), intermediate (90 ± 1 °C) and high temperature (120 ± 1 °C) were studied; the results showed an increase by 34% in specific methane production (SMP) for OMWW treated at the lowest temperature and a decrease by 18% for treatment at the highest temperature, The total phenols (TP) and total COD removal efficiency was for both the highest at 80 °C (i.e. 62.7% and 63.2% for TP and COD, respectively) and lowest at 120 °C (i.e. 44.9% and 32.2% for TP and COD, respectively).

On the basis of these positive results, and in the view of improving the efficiency of the AD process performed on tannery wastewater (TWW), in this study, thermal pretreatments were conducted on a real tannery wastewater prior AD and the effect of pretreatment was evaluated by biomethane production and COD removal.

II. Materials and methods

II.1. Substrate

TWW was collected from the Tannery Manufacturer DMD spa located in Solofra, Italy. Wastewater was composed of two waste streams produced during the skin treatment: the first stream was produced by the pretanning step (soaking, fleshing, unhairing, liming, etc...) and the second from the main tanning step (chrome tanning followed by synthetic tanning) and dyeing. The mixture used in the experiments was obtained mixing the previously mentioned streams according to a ratio of 50:50 in volume (v/v). The resulting mixture was stored at 4°C in the fridge before further use. The characteristics of the raw wastewater are shown in table1.

TABLE 1. *Characterization of tannery wastewater*

Parameters	Values[1]
pH	3.23
TS	15300
TVS	5860
COD_t	23718.67
COD	20612.5
SO_4^{-2}	1309.5
Cl^-	4299.1
S^{-2}	380
Total Cr	150
NH3-H	22.90

[1]All values are expressed as mg/L except for pH

II.2. Inoculum

Activated sludge from a municipal wastewater treatment plant located in Nola, Italy, was used as inoculum. It was degassed for 30 days at a temperature of 35° C in air-tight batch reactors in anaerobic conditions. This operation was necessary to adapt the inoculum to the new operating conditions (i.e. anaerobic) and ensure the complete degradation of residual organic matter present in the sludge.

II.3 Thermal treatment

In the present study, TWW was thermally pretreated at three different temperatures: 90, 80 and 70°C and then used as a substrate in biomethane potential (BMP) tests. The thermal pretreatment process was performed using a drying oven (ARGO LAB TCN115, ITALY): 1000 mL samples of TWW were placed in 2000 mL heat resistant glass bottle and treated for 30 minutes at the different temperatures mentioned before. After cooling, samples were collected and chemically analyzed for evaluating total and soluble COD to evaluate the effect of the heat treatment on solubilization of organic solids.

II.4. BMP test

According to a previous work of the authors [16] on the treatment of TWW by AD, a ratio Inoculum/substrate (I/S) equal to 1.5 (m/m) in terms of total volatile solids (TVS) was used for performing BMP tests.

Experiments were carried out in 1000 mL serum Schott (Germany) bottles with air-tight caps equipped with a system composed of capillary pipe and valve useful to collect biogas. Different volumes of pretreated as well as untreated (as control test) samples of wastewater were mixed with a fixed 100 mL volume of anaerobic sludge according to have for all BMP tests the same I/S ratio: micro and macronutrients were also added to each sample. Furthermore, tap water was added up to have a working volume of 600 ml.

BMP tests were performed in duplicate on both untreated and pretreated substrates. A further BMP test was conducted with inoculum and no TWW to measure the biogas produced by inoculum during the endogenous phase; in all BMP tests, the initial pH was adjusted at 7 by adding properly small volumes of NaOH solution (1N). All values used for each BMP test are listed in Table 2.

Before starting the BMP tests, the head space of each reactor was flushed with nitrogen gas to remove oxygen and to set anaerobic conditions, and then the bottles were hermetically closed for preventing the entrance of air into the reactors.

***Table 2.** Composition of each BMP test*

	TVS(mg/L)	Volume(mL)	Tap water(mL)	Nutriments (mL)
Inoculum (control)	20610	100	480	20
Raw water	5860	334.5	245.53	20
70°C	5805	336.7	243.30	20
80°C	5780	337.7	242.28	20
90°C	3710	470.4	109.65	20

Bottles were kept at 35°C in a temperature-controlled water bath. Daily production of biogas was measured by the technique of displacement of the water: an acid solution of (1N) HCl with 2% NaCl was used. The BMP tests were stopped when no significant biogas production was detected.

II.5. Analytical methods

The composition of TWW was analyzed measuring the following parameters (see Table 1): pH; total solids (TS); TVS; alkalinity; total chemical oxygen demand (CODt); soluble chemical oxygen demand (CODs). All measurements were conducted according to the standard analytical methods for water and wastewater (APHA, AWWA, and WEF).
The sulphide content was analyzed by oxidation with an excess of iodine solution of 0.025 N .A solution of thiosulfate 0.025 N was used for titration. SO42- and Cl- concentrations were measured by 761 Compact IC Ω Metrohm (JASCO, Switzerland), total Cr was measured using the Atomic Adsorption Spectrometer (Spect AA. VARIAN, Australia) and biogas composition was

assessed by Gas Chromatography (Varian Star 3400 Australia) The rate of COD solubilization was calculated by the following equation (1)

$$COD\ solubilization\ (\%) = \frac{\text{soluble COD measured after pretreatment}}{\text{total COD measured after pretreatment}} \text{x}100 \quad (1)$$

III. Results and discussion

III.1 Effects of thermal pretreatment on COD solubilization

Results from the thermal pretreatment are listed in table 3.

***Table 3.** Effect of Thermal Pretreatment*

Temperature	Increase	Removal		
	COD_S %	NH3-H%	TS%	TVS %
70°C	23.87	35.94	2.15	0.94
80°C	57.00	25.85	2.19	1.36
90°C	81.36	15.72	10.06	36.68

The effect of thermal pretreatment on COD solubilization and COD_s was evaluated (Figure. 1): a value of 71% COD_s compared to COD_t (SCOD=14843.9 mg/L) was measured in the untreated TWW. In all thermally pretreated samples the fraction of COD_s compared to COD_t increased up to 95% in the sample pretreated at 80°C (i.e. COD_s=28599.0 mg/L). This result indicates that the organic particulates in TWW were liquidized to soluble carbohydrates, lipids, and proteins or converted into lower molecular weight compounds by thermal pretreatment.

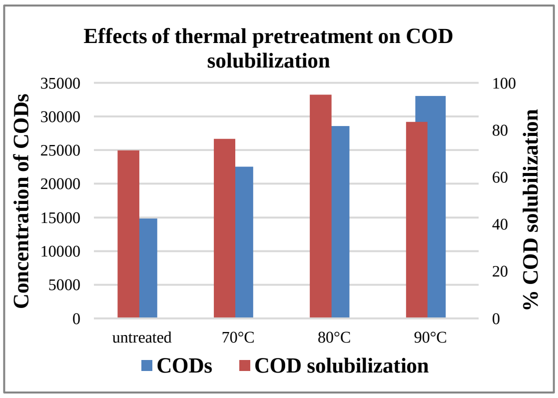


***Figure1.** Effects of thermal pretreatment on COD solubilization*

III.2. Impact of thermal pretreatment on the anaerobic digestion of tannery wastewater

Cumulative volumes of biomethane produced during the AD process from substrates pretreated at different temperatures are shown in Figure 2.

At the beginning of the incubation, the biomethane production from all BMP tests was low and increased progressively after 15 days of incubation.

The cumulated biomethane production curves in Figure 1 show a trend really similar to those obtained from substrates rich in lipids [17]: a low biomethane production rate on the first days of incubation could be reasonably attributed to the longer times required by lipids to be hydrolyzed and turned to be biologically converted to biomethane TWW are actually rich in lipids [19].

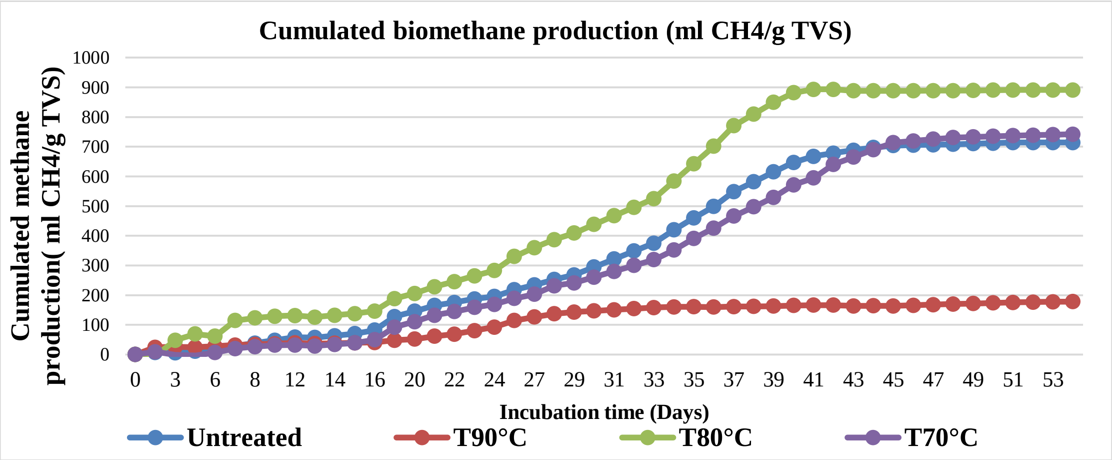


***Figure 2.** Cumulated biomethane production (ml CH4/g TVS)*

The daily production of methane from the pretreated substrate at 90° C showed very low values, i.e.178 ml CH4 / g TVS, this temperature had a negative effect on AD process performance, as already found by Ariunbataar et al. [14]. Pretreatments of FW at higher temperatures (>80°C) could reduce the production of biomethane, giving values lower than expected, due to the loss of organic substances by volatilization as well as the formation of chemical bonds that result in the agglomeration of organic solids making them less available for microorganisms.

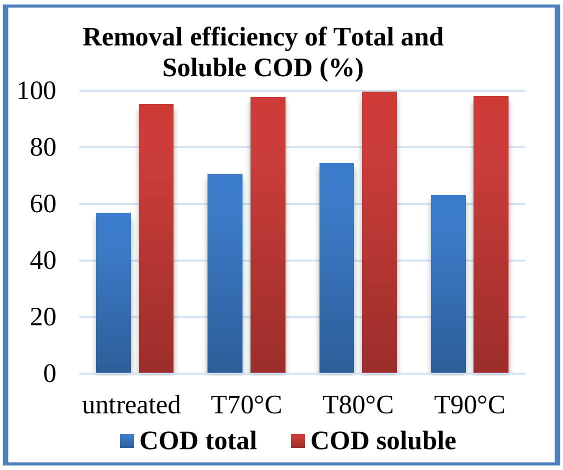
Substrate thermally pretreated at 80°C showed the highest specific methane production since the beginning of the experiment. The cumulative specific methane volume after 54 days of incubation was 891 mlCH4/gTVS, a value 25% higher than that obtained at the same day of incubation from the untreated substrate that achieved a total specific volume of 714 ml CH4 / g TVS. Although lower than 80°C, also the substrate pretreated at 70°C resulted in a biomethane production higher than untreated TWW.

III.3 The impact of thermal pretreatment on the characteristics of digestate

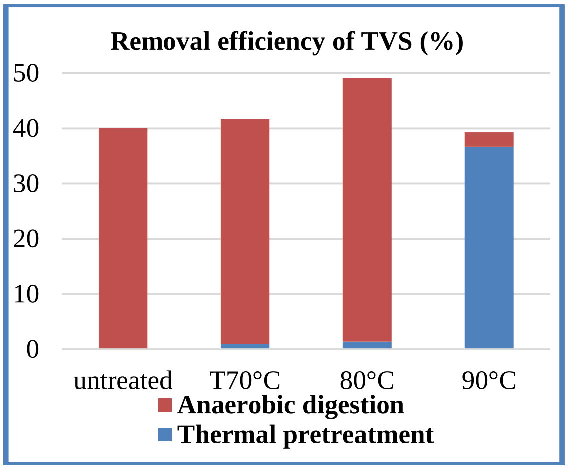
Accordingly, to the methane production, the maximum total COD (COD_t) removal was achieved in the BMP test fed with the substrate pretreated at 80°C. The COD_t removal efficiency ranged from 56% for the untreated TWW to 70 and 74% with TWW pretreated at 70 and 80°C respectively: an increase by around 30% was therefore achieved thanks to the thermal pretreatment at those temperatures. This result confirms the positive effect of thermal pretreatment on biodegradability of organic solids and consequently on AD process performance of TWW by optimizing the biomethane production and making TWW less harmful when discharged into the environmental after treatment.

Considering the soluble fraction of COD (COD_s) all BMP tests showed high removal efficiency ranging from 95% for the untreated TWW to 99.5% for the pretreated TWW at 80°C.(see Figure 3)

The low performance of AD process in terms of biomethane production conducted on substrate pretreated at 90°C can be easily explained considering that after pretreatment the substrate lost 36.68% of TVS by volatilization and therefore the biomethane yield was lower when compared to other BMP tests because produced from the residual amount of TVS. In the figure, 3 are shown the removal efficiency of organic solids measured in terms of COD and TVS during the whole cycle of treatment, i.e. thermal pretreatment followed by AD. The maximum removal efficiency was obtained with the TWW pretreated at 80°C in agreement with the results previously presented, resulting in a total removal efficiency of 49%, obtained summing 1.4% after pretreatment to 47.6% after AD



(A)



(B)

Figure 3. *Removal efficiency of total and soluble COD (A) and TVS (B)*

IV. Conclusion

This study has shown the positive as well as contrasting results from thermal pretreatment of TWW prior AD process. Compared to untreated TWW, a heating pretreatment at 80°C resulted in an increase by 25% and 31% of biomethane production and COD_t removal, respectively. Nevertheless, 10°C more in the pretreatment were sufficient to lead the process at experiencing an evident underperformance as resulted from the BMP tests filled with substrate pretreated at 90°C

The results presented in this paper are promising for the careful use of thermal pretreatment on tannery wastewater prior AD in order to increase the biomethane production and to promote the organic solids removal.

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