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Evaluation of ultrasonic pretreatment on anaerobic digestion of citrus orange peel waste for methane production

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Abstract

The study was performed in order to confirm and develop the possible use of orange peel waste in biogas production and to investigate ultrasonic pretreatment effect on enhancing biogas production. The inhibition by limonene present in the orange peel waste is the major challenge of biogas production from citrus waste, encountering this challenge was achieved by the removal of this substance using a steam distillation process. A batch anaerobic digestion experiment was performed at two thermal conditions thermophilic and mesophilic using a mixture of sludge and orange peel as a substrate in this study. In order to improve the solubilization of organic matter in the orange peels a mechanical pretreatment was applied: ultrasonification witch was carried out at a frequency of 37 kHz using an ultrasound cleaner for different exposure times 1 min, 5min, 10 min and 15 min which were investigated for the optimization. The obtained results of biogas production from the treated samples with the ultrasonic frequency showed a remarkable increase comparing with the untreated samples: 67% and 62% improvement after the ultrasonic pretreatment. Cumulative methane production of pretreated orange peel waste was the highest for the treatment times 1 and 10 minutes giving 970 mL.gTvs^{-1} and 671 mL.gTvs^{-1} for mesophilic and thermophilic phases respectively.

Keywords: Anaerobic Digestion, Biogas production, Limonene, Orange Peel, Ultrasonification;

1. Introduction

A large amount of citrus orange peel waste is generated every year due to the high production of citrus as a main fruit all over the world [1, 2]. A big percentage of this waste is still dumped every year causing environmental problems due to the accumulation of high organic content material [2, 3]. Therefore, it is necessary to propose an effective and suitable treatment for dealing with orange peel wastes, among them: biogas production by an anaerobic digestion process is highly desirable [4]. Actually, orange peel has been demonstrated by several studies that it is a potential source for biogas production [5].

Anaerobic digestion is an effective treatment technology that can be applied for municipal organic waste to stabilize organic matter [6]. It is a biological process allowing the conversion of biomass into biogas [7]. Anaerobic digestion consists of four stages Hydrolysis, acidogenesis, acitogenesis and methanogenesis [8]. Different groups of bacteria will dominate the different stages of digestion and products of one group will serve as feed for the next one [7, 8]. The biological hydrolysis step represents the rate limiting step of the Anaerobic digestion process [9], A potential solution to this problem is to introduce a pretreatment prior to the biogas production, in order to increase the biodegradability [8]. Many pretreatment methods were studied to accelerate the rate limiting step and increase the biogas production among them: ultrasonic, mechanical, chemical or thermal techniques resulting in bacterial cell wall disruption, disintegration and release of enzymes [6]. Sonication is an efficient mechanical pretreatment technology [10]: Ultrasonic wave is a pressure wave that propagates through a medium, resulting in vast amount of energy dissipation, and violent collapse of gas and vapor bubbles (termed "acoustic cavitations") the hydro mechanical shear forces produced by ultrasonic cavitations disrupt the cells in organic matter, leading to release of organic substances into the liquid phase [10, 11].

This research aims at studying the effect of ultrasonic pretreatment on biodegradability, methane potential and volatile solid removal efficiency during anaerobic digestion, its objective is also to investigate and evaluate the effect of thermal conditions on the process.

2. Materials and methods

2.1. Substrate and inoculums Sampling and Characterization

Sewage sludge used as the inoculums was obtained from the wastewater treatment plant (wwtp) of Oued El-Athmania Milla (Algeria) which mainly deals with effluents from domestic sources. Citrus waste was used as a substrate for biogas production, the orange peels were collected from household waste, it were then chopped (< 2mm) and homogenized prior to pretreatment.The characteristics of sludge and substrate fed to the digesters are presented in Table 1.

Table1: substrate and inoculums characterization

Parameters	Substrate	Inoculums
TS ($g.L^{-1}$)	15.09	70.04
TVSvs ($g.L^{-1}$)	14.65	27.01
SCOD ($mg.L^{-1}$)	9.926	33.088
Phosphorus ($mg.L^{-1}$)	0.632	0.679
TKN ($g.L^{-1}$)	0.012	0.0018
NH^{4+} ($g.L^{-1}$)	1.05	0.28
pH	4.36	7.34
TA ($mg.L^{-1}$)	-	1.312
TAC ($mg.L^{-1}$)	577.35	1.813
VFA ($g.L^{-1}$)	-	0.501
Protein ($mg.L^{-1}$)	76.9125	0.012

2.2. Analytical methods

Characteristics examined and measured to evaluate the digesters were: pH, total solids (TS), total volatile solids (TVS), alkalinity, Volatile fatty acid (VFA), Organic and ammoniac nitrogen (TKN and NH^{4+}), phosphorus, protein, soluble chemical oxygen demand SCOD. All this parameters were determined by standard methods used in water treatment (Standard Methods for Water and Wastewater Analysis (1998)).
Methane and carbon dioxide produced during the anaerobic digestions were measured by the water displacement method for the total biogas volume and using a KOH solution to determine CH_4 and CO_2 content in each BMP test.

2.3. Pretreatments and substrate preparation

Oils present in citrus wastes are known for their antimicrobial effect so to make sure that the anaerobic digestion process doesn't fail we used a steam distillation process to reduce the concentration of the oils and to ensure the stability of the anaerobic process. Distillation was carried out using a mixture of chopped orange peel and water with a ratio of 1:6 during one hour to make sure of a 90 % removal of essential oils from the orange peels based on a previous work of the authors [12].After the removal of the oils the substrate was pretreated using a mechanical pretreatment which is ultrasonification: carried out using ultrasonic homogenizer (Elmasonic S100) operating at a frequency of 37 kHz. It was applied on the orange peels for four different exposure times: 1, 5, 10 and 15 minutes. The process efficiency was evaluated by measuring the improvement of solubilization of substrate organic matter in terms of SCOD after the exposure to the ultrasonic frequency. The results are shown in table 2 below:

Table2: substrate characterization after ultrasonic treatment

Exposure time	SCOD (mg/l)
1 min	15441.17
5 min	17647.05
10 min	22058.8
15 min	22610.29

2.4. Experimental set up for methane potential (BMP test)

The batch experiments were carried out in glass bottles with a rubber septum as reactors each reactor contained a reacting volume which is a mixture of inoculums and substrate with a TVS ratio of 1:3 inoculums / substrate. BMP tests were performed in duplicate. The Mixture preparation was done according to the following procedure:

- Determine volumes of inoculums, substrate and distilled water (necessary to fill the reactors with a 1:3 ratio).
- Addition 10 mL of a nutrient solution.

After the preparation of the mixtures their pH is fixed at 7 by adding NAOH solution, the headspace in the reactors was flushed for few minutes in order to obtain anaerobic conditions in the reactors and then they were silledand placed in an incubators.

Table3: batch reactors feelings

	TS ($g.L^{-1}$)	TVS ($g.L^{-1}$)	Reacting volume(mL)	Inoculums volume(mL)
De-oiled orange peels	6.13	5.86	90	15

The experimental design for the anaerobic digestion of the orange peel waste was carried out using the pretreated substrate for two different thermal conditions so using two different incubators. The experimental setups were carried out simultaneously

- One operating with thermophilic conditions at 55°c temperature.
- The other using mesophilic conditions at 37°c temperature.

In order to determine the methane production obtained from the inoculums itself, we used a mixture of inoculums and water only and to evaluate the effectiveness the combined H_2O_2-Ultrasonic pretreatment on biogas production we used a non treated substrate.

2.5. Experimental set up for methane potential (BMP test)

The daily production of biogas from each digester was measured by the water displacement method by a column of acidified water (pH = 2). Throughout the experiment period, the bottles were shaken and moved around in the incubator once a day with a daily measurement of the produced biogas volume. The aim was to determine methane production from fresh substrate and therefore the methane produced from the controls was subtracted from the methane produced in the reactors containing samples.

Substrate Methane production = displaced liquid by sample – displaced liquid by blank.

The water displacement method allows us to determine the total biogas volume so to determine CH_4 and CO_2 content in each BMP test we used a KOH solution. The results present in this work shows the accumulated methane production during incubation, the gas measurement stops when no production could be observed.

3. Results

3.1. Substrate characterization after steam distillation and ultrasonic pretreatment

Table 4: Pretreated substrate characterization

		TS ($g.L^{-1}$)	TVS ($g.L^{-1}$)	TVS (%)	SCOD ($g.L^{-1}$)	Pt ($g.L^{-1}$)	TKN (g.L-^{1})	NH_4^+ ($g.L^{-1}$)	TAC ($g.L^{-1}$)	VFA ($g.L^{-1}$)	Protein ($g.L^{-1}$)
Pretreated substrate	1min	5.8	5.7	98	44	0.21	0.8	0.56	0.15	0.15	0.005
	5min	5.75	5.5	96	45	0.18	1.4	0.42	0.15	0.15	0.0087
	10min	5.2	5.08	97	47	0.57	2.2	0.42	0.2	0.2	0.013
	15min	5.1	4.8	95	55	0.15	2.4	0.42	0.125	0.125	0.015

3.2. Effect of ultrasonification on substrate solubilization

SCOD increment (solubilization) has been adopted as a measure of ultrasonic disintegration efficiency, and supposed to improve biodegradability. The figure 1 shows the values of SCOD after ultrasonic pretreatment for the different exposure times.

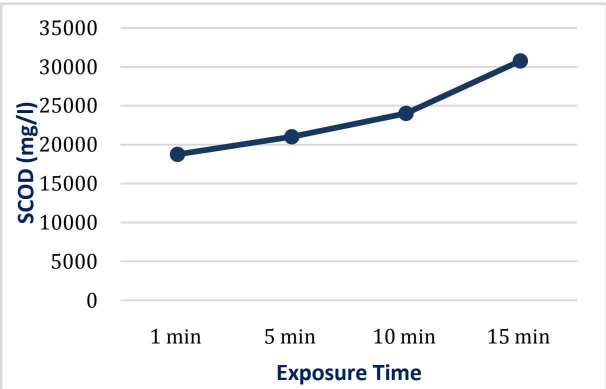

Figure1. Substrate solubilization after ultrasounds

The results showed that the solubilization of the organic matter in the orange peels is increasing with the increase of exposure time (figure 1). Were we obtained an improvement of 9926 mg/l to 15441.17mg/l, 17647.05 mg/l, 22058.8 mg/l and 22610.29 mg/l for 1, 5, 10 and 15 minutes respectively giving us an improvement in solubilization percentage of 37%, 43%, 55%, and 56% respectively. And that led us to conclude that the ultrasonification exposure time plays an important role in increasing the solubilization of the organic matter. These studies reported that maximum solubilization (56%) in terms of SCOD was obtained for the sample treated with 15 minutes of exposure comparing with the non treated sample.

3.3. Biogas production

The results are shown as the accumulated biogas production during the incubation time. The Figures 3 and 4 shows the cumulative volume of biogas produced for both treated and untreated samples along with the control: inoculums.

The specific biogas production is an important parameter for the expression of the capacity of the waste to produce biogas; it is expressed in terms of volume of produced biogas relatively to the mass of substrate in terms of the total volatile solids $mL.gTVS^{-1}$.

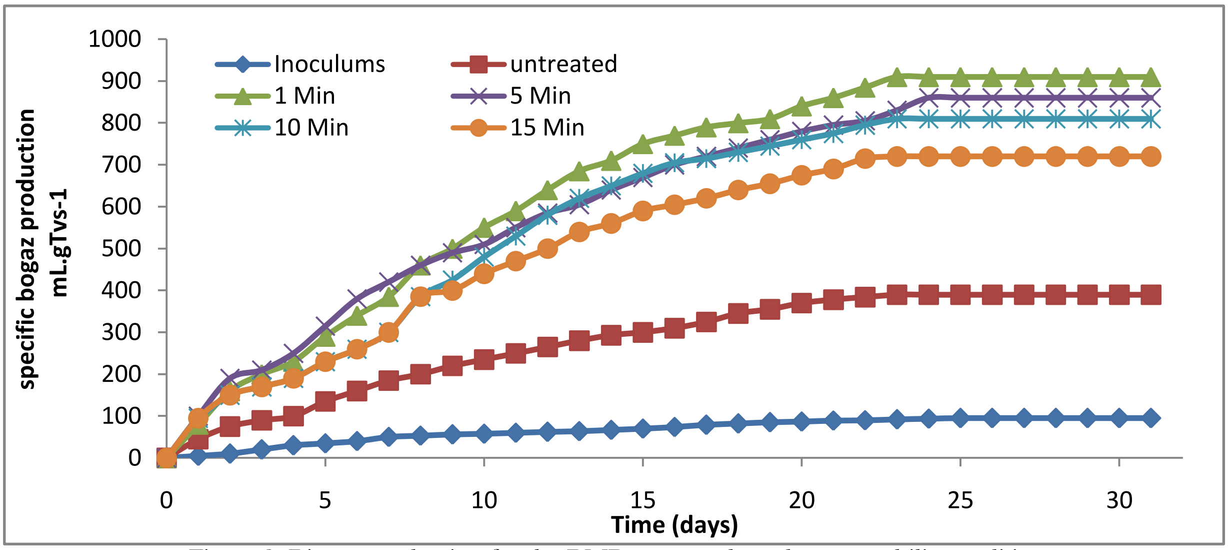

Figure 2. Biogaz production for the BMP tests conducted at mesophilic conditions

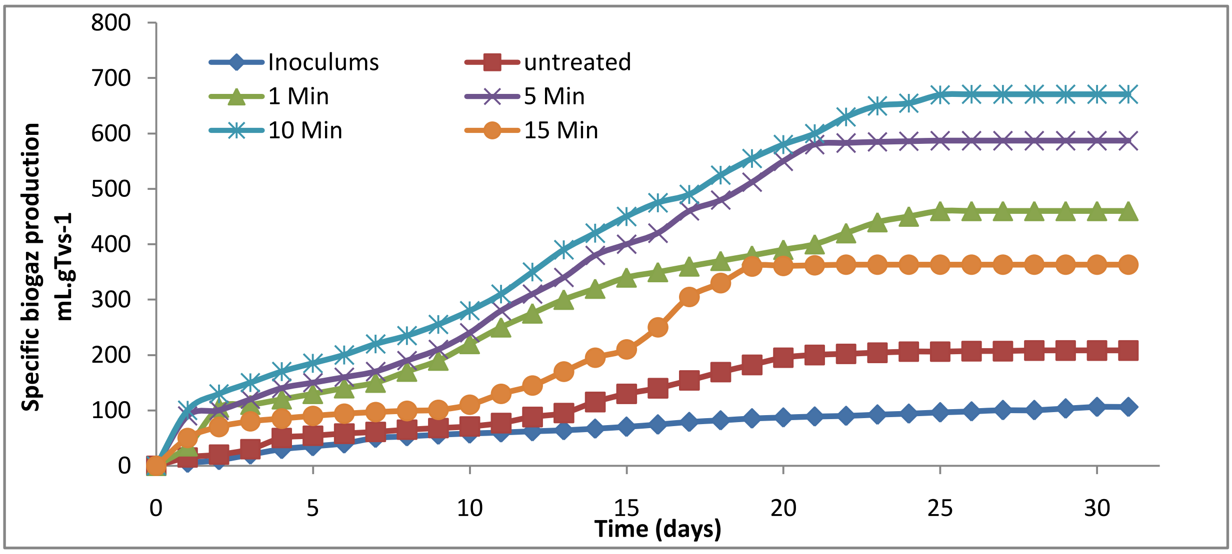

Figure 3. Biogaz production for the BMP tests conducted at thermophilic conditions

The Figures 2 and 3 shows the cumulative volume of biogas produced for the ultrasonically pretreated samples for different exposure times (1, 5, 10 and 15 minutes) after 30 days of incubation time.

The cumulative methane production from samples pre-treated with the ultrasonic frequency were significantly higher than the non-treated sample going up to 62% and 68% in case of the highest biogas productions for mesophilic and thermophilic conditions respectively. Reducing particle size by the ultrasonic frequency is likely the largest contributor to enhancing methane production that was observed in the current study. Results are consistent with prior studies [13, 14] that indicated that gas production rates from anaerobic digestion of ultrasonically pretreated sludge were higher than those for untreated sludge. It is seen that methane productions were not proportional to treatment times (1, 5, 10 and 15 minutes) when comparing the results obtained from the two thermal conditions.

Results from the 30 days BMP assays indicated methane production was in around 65% higher for the ultrasonic pretreated samples comparing with the control. In case of th mesophilic phase methane yields were found to increase with shorter treatment treatmenttime :a 1 minute exposure time gave a 970 mL.gTvs^{-1} production wich is by far the highest in all BMP tests. contrary to the tests conducted at thermophilic phase where the highest production was registered for a 10 minute exposure time giving 671 mL.gTvs^{-1} production. So we can say that the results were not very conclusive regarding choosing the optimal exposure time.

3.4. Digestate characterization

Total solids and total volatile solids removal are presented after the digestion process for both experimental set ups: the mesophilic and the the thermophilic one along with SCOD removal.

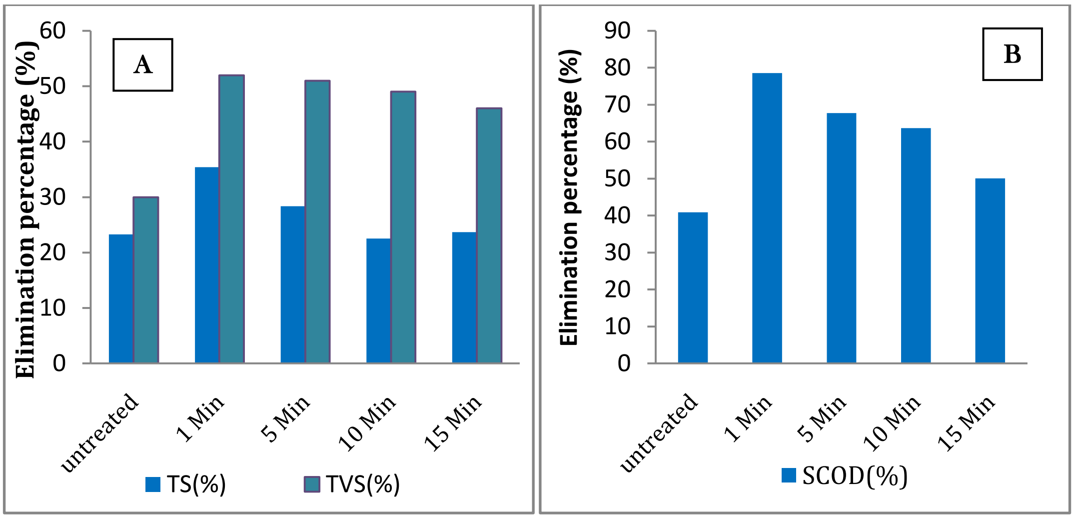

Figure 4 (A, B). TS, TVS and SCOD removal percentages after AD for the BMP tests conducted at mesophilic conditions

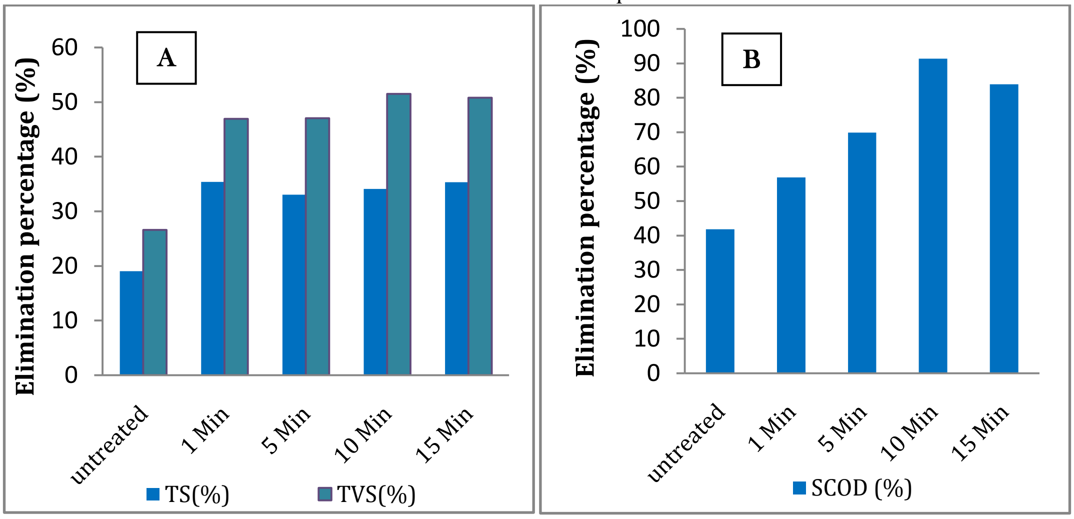

Figure 5 (A, B). TS, TVS and SCOD removal percentages after AD for the BMP tests conducted at thermophilic conditions

The results obtained show a remarquable improvement in the degradation of organic matter for both thermal conditions. The treatment efficiency for the removal of organic matter comparing with the untreated sample was very satisfying and in coherence with biogas production for all the treated samples see figures 4 (A, B) and 5 (A, B).

4. Conclusion

This study indicates that ultrasonic pretreatment is an effective treatment for this kind of substrate enhancing its biodegradability, methane potential and volatile solid removal efficiency during anaerobic digestion. Conducting the experiment at mesophilic temperature gave a higher production than the thermophilic one. As a result the use of ultrasonic pretreatment shows merit for increasing methane production from the process.

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