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Article

Optimization of the process of methane production from wheat straw and bovine manure co-digestion by ultrasound disintegration and physicochemical treatments

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Abstract: Biomass is an attractive energy source that can be used for production of heat, power, and transport fuels, and when produced and used on a sustainable basis, can make a large contribution to reducing greenhouse gas (GHG) emissions. Anaerobic digestion (AD) is a suitable technology for reducing organic matter and generating bioenergy in the form of biogas. This study investigates the factors allowing the optimization of the process of biogas production from the co-digestion of wheat straw (WS) and bovine manure. The statistical analysis of the experiments carried out show that ultrasonic processing plays a fundamental role by sonication density and solids concentration leading to improved characteristics of WS by reducing particle size and increasing concentration of soluble chemical oxygen demand. The higher the sonicating power used, the more the waste particles are disrupted. The optimality obtained under mesophilic conditions for WS pretreated with 4% w/w (weight by weight) H_2O_2 at temperature 36 °C under 10 minutes of ultrasonication at 25 kHz improves the methane yield by 64%.

Keywords: lignocellulosic biomass; wheat straw; anaerobic digestion; chemical pretreatment; ultrasound pretreatment; biogas enhancement.

1. Introduction

Anaerobic digestion (AD) of biomasse residues is considered the best sustainable option to generate sufficient green energy to meet world demand and ensure an adequate future supply of clean energy and fuel [1–2]. Agricultural biomass is abundantly found in nature, such as wheat straw (WS). However, this latter is used as livestock feed, discarded carelessly, or burnt in an open field which involves serious environmental problems [3]. WS can be effectively treated by AD which is one of the most promising technologies with the potential to convert various biomasses to biogas [4]. However, the lignocellulosic material contained in the WS being resistant to microbial attacks, the AD process is considerably slowed down [5]. Therefore, a WS pretreatment is necessary to improve its biodegradability by hydrolysis of its lignocellulosic recalcitrant components [6]. Pretreatment aims to enhance accessibility to the three main components of lignocellulose (cellulose, lignin, and hemicelluloses) and increase biodegradation rate and overall main product yield in AD [7].

The impact of different pretreatment methods on biomass degradability is extremely different and mostly depends on the feedstock characteristics [6–7]. Several biomass pretreatments have been studied such as grinding [8], ultrasound [9–10], chemical processes [3–11–12], biological technique [13–14] and thermal methods [1–15].

Due to the crystallinity reduction and mass transfer increase, grinding involves the breakdown of biomass size and crystallinity which improves the hydrolysis process [10]. Chemical reagents are predominantly used for pretreatment of lignocellulosic materials because of their low cost and high efficacy [16].

Alkaline pretreatment involves the addition of bases to biomass, such as sodium and potassium hydroxide, which lead to an increase in the internal surface of biomass, a decrease in crystallinity, a destruction of links between lignin and other polymers and a lignin breakdown. Alkaline pretreatment can delignify biomass by oxidation with high carbohydrate retention. This allows the breaking of the ester and ether bonds between

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lignin and carbohydrates [17]. Up to now, NaOH and KOH are the most effective alkali-treatments for improving biomass digestibility. NaOH pretreatment has proven to be effective to improve digestibility and increase the methane yield [5]. However, due to concerns over sodium discharge in the process effluent which is difficult to be recycled, may limit its application on a commercial scale [9].

To improve biogas production, hydrogen peroxide that is a strong oxidant has been used for biomass pretreatment [17]. It has a significant advantage of leaving no residues in the biomass because it degrades into oxygen and water and hardly forms secondary products [18]. H_2O_2 promotes the production of HOO^- anion, which in turn promotes the production of hydroxyl (•OH) and superoxide (O^{2-}) radicals leading to high delignification [10].

Ultrasound disintegration (US) pretreatment disrupts the cell wall structure, increases the specific surface area, and reduces the degree of polymerization by compression and cavitation effects [19]. The cavitation produced due to the pulsating high-frequency ultrasonic waves penetrates the polysaccharides and disrupts the mesh of cross-linking polymers that faclitate biomass degradation [17]. Cavitation is the formation of a violent collapse of bubbles in the liquid, which can induce several transformations. The main effects of cavitation phenomena include the free radical formation, such as hydroxyl radical generated due to the decomposition of water molecules [20].

This study aims to improve the methane production from WS by coupling several pretreatments. To the best of our knowledge, coupling the US to grinding and chemical pretreatment using NaOH and H_2O_2 solutions has been weakly studied for lignocellulosic degradation to improve biogas and biomethane production.

The remainder of this paper is organized as follows:

Section 2 is devoted to the materials and methods used. In this Section, analytical methods, pre-treatments and biomechemical methane potentieal tests are presented. Particular attention is focused on the ultrasound pre-treatment.

In Section 3, the results obtained are analyzed and discussed in depht.

This work ends with conclusions as well as perspectives on the role of biomass and its potential contribution to the world's future energy demand.

2. Materials and Methods

2.1 Substrate and inocula

WS was taken from the stables of Hussein Dey slaughterhouse in the city of Algiers (Algeria). Bovine manure (BM) was taken from the stable of the same slaughter-house. Sewage sludge (SS) was taken from the wastewater treatment plant of Baraki-Algiers.

2.2 Analytical methods

COD (Chemical Oxygen Demand), total solids (TS), volatile solids (VS), volatile fatty acids (VFAs), total alkalinity (TA), and pH were determined according to the Standard Methods of APHA [21].

Before analyzing heavy metals (HM) contained in BM and SS, the samples were mineralized by microwave Milestone ETHOS One Sk-10 High-Pressure Rotor.

Analysis of HM for both BM and SS was carried out by spectrometry atomic absorption (SAA) flame,240FS Agilent.

The WS morphologies were observed using Quanta Scanning Electron Microscope (SEM).

2.3 Grinding pretreatment

Grinding is a size reduction operation used for biomass pretreatment that increases the reactivity and does not release any effluents. Particle size reduction increases the available surface area and reduces the cellulose crystallinity. After the grinding, the fine powder is collected using a series of superimposed sieves. The dry WS with a diameter of 0.65–1.25 mm was collected and stored in a plastic bag at ambient temperature (around 25°C) until further experimentation.

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2.4 Ultrasound pretreatment

An ultrasonic wave is a mechanical and elastic wave, which propagates through fluid, solid, gaseous or liquid media. The frequency range of ultrasound is between 20 kHz and 10 THz (One Tera Hertz = 1 THZ = 1000 GHz = 10^{12} Hz),

Depending on the application, two criteria for classification of ultrasonic waves can be considered: the ultrasonic power and the frequency of the wave.

For a low power (less than 1 W), there is no interaction other than vibratory with the matter and ultrasound does not induce changes in the medium through which it passes. This concerns all applications of non-destructive testing [22] for frequencies ranging from 20 kHz to 10 MHz, and medical diagnosis, as well as ultrasound imaging [23,24,25] and Doppler [26] for frequencies above 1 MHz.

When the ultrasonic power is sufficient (a few Watts) and at relatively low frequencies, the passage of the ultrasonic wave is accompanied by non-linear physical phenomena and associated chemical transformations. We speak then of power ultrasound whose emission is likely to modify the medium through which it passes.

These ultrasounds are also used in the medical field but with a therapeutic aim to destroy benign or malignant lesions (tumors, calcifications, stones...) and, in the industrial field, as for example the disintegration of waste. It is this last application which is used, in our work, as a very effective pre-treatment of disintegration at a frequency of 25kHz: it is what we call ultrasonication disintegration.

Ultrasound disintegration (US) pretreatment allows material to be broken down on a finer scale than grinding. US involves creating pressure waves, resulting in the formation of cavitation bubbles in the liquid which disrupts the cell wall structure and increases the specific surface area [19,20].

Figure 1. The experimental setup used for US pretreatment.

Figure 1 shows the prototype experimental setup used in the ultrasonic disintegration pre-treatment of wheat straw.

2.5 Biochemical methane potential (BMP) tests

BMP tests were performed under mesophilic conditions (36 °C) in a batch digester of 500 mL as a working volume. Figure 2 shows the experimental set-up used for this purpose. At the beginning of each experiment, the digester was flushed with N_2 gas for 4 min to ensure anaerobic conditions. The biomethane production was measured daily by the liquid displacement method, with the use of acidic solution at pH2 (bottle 5 in Figure 2) to prevent the possible dissolution of CO_2 and 3M NaOH solution (bottle 4 in Figure 2) to capture CO_2.

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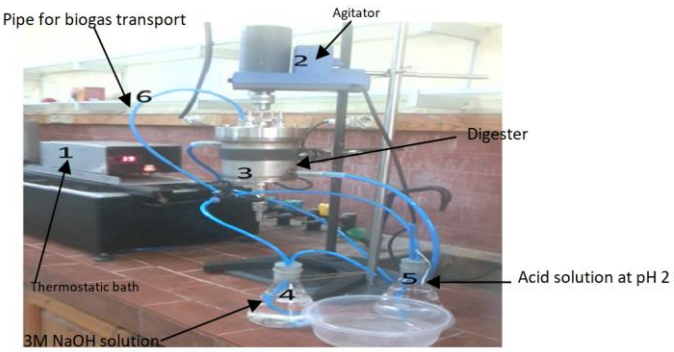

Figure 2. The experimental setup used for BMP tests.

3. Results and discussions

3.1 Effect of heavy metals present in the considered inocula on AD

Heavy metals (HM) are present in municipal sludge in significant concentrations and the most frequently found are copper (Cu), zinc (Zn), lead (Pb), iron (Fe), and nickel (Ni) [27–28]. The industry is the primary source of HM in urban wastewater (UWW) and represents up to 50 % of the total HM content in SS [29]. Domestic sources are mainly associated with the leaching from plumbing materials (Cu and Pb) gutters and roofs (Cu and Zn) and galvanized materials. Detergents and cleaning products (containing Cd, Cu, and Zn), cosmetics, perfumes, and body care products (containing Zn) are another source of HM in UWW [30]. HM in manure by-products are derived directly from the animal diet and indirectly from the ingestion of contaminated soil and during manure collection [31]. Many essential metals (e.g. Cu, Zn, and Fe) are required for the activation or functioning of many enzymes and coenzymes in AD. The order of HM composition in methanogenic microorganisms cells was found to be Fe>Zn≥Ni>Cu [32]. HM are not biodegradable but they can accumulate in the substrate in a toxic concentration amount. Otherwise, excessive amounts of HM can lead to the inhibition of anaerobic microorganisms [33].

Firstly, HM concentrations were determined in the inocula. Table 1 shows the observed metals concentrations in BM and SS, compared to those required for AD microorganisms.

Table 1: Metals concentrations for BM and SS compared with the concentrations of metals required for AD.

Metals concentrations mg/Kg	Cu	Zn	Pb	Ni	Mn	Cr	Co
BM (our study)	18.27	43.40	02.01	12.09	25.88	32.64	02.34
BM [31]	21.00	115	02.10	09.00	111	20.00	01.70
BM [34]	31.04	126.33	02.24	-	-	01.09	-
SS (our study)	*72.50*	*491.24*	05.00	15.76	30.14	50.40	02.11
SS [31]	54.70	294	02.47	15.00	142	75.10	04.10
SS [30]	44.70	360	10.40	03.80	136	08.00	01.80
required for AD [35]	64	-	200	30	55	52	20
required for AD [36]	10	60	-	100	3	-	75

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It appears in table 1 that for the SS, Cu, and Zn values (72.50 and 491.24 mg/Kg respectively) exceed the necessary concentrations for the growth of the methanogenic microorganisms. Methanogens are a key group in AD, because when methanogenic activity is inhibited the process is blocked at the acidogenesis step leading to incomplete degradation of the organic matter and accumulation of VFAs [7]. Also, HM toxicity is one of the main causes of bioreactor problems which can disrupt the enzyme function and lead to significant AD inhibition [23].

Secondly, to specify the inhibitory effect of these metals, two ADs were carried out for 10 days with the inocula considered and during which the pH, the VFAs, and the TA were measured. To ensure the reproducibility of results each experiment was conducted in duplicate and the results are depicted in Figure 3.

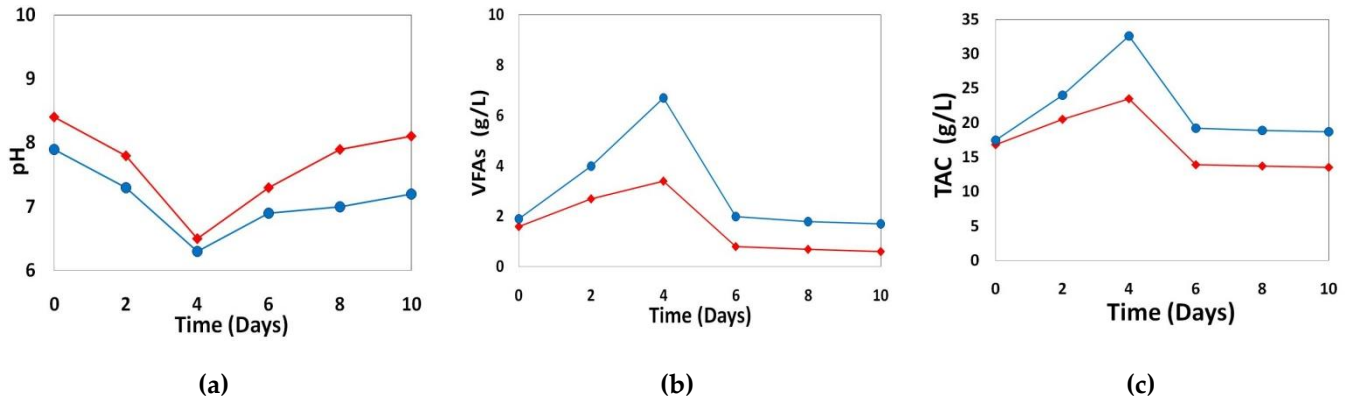

Figure 3: (a) pH; (b) VFAs and (c) TAC variation for BM (♦) and SS (●) during AD.

The pH is one of the most significant parameters for the stability of AD, which could affect the activity of acidogenic and methanogenic micro-organisms [37]. For both inocula, Figure 3 (a) shows that during the first step of the AD process (1st-4th day), pH decreases from 8.4 to 6.5 and 7.9 to 6.3, respectively for BM and SS. This is due to the increased production of VFAs from 1.6 to 3.4 g/L and 1.9 to 6.7 g/L, respectively for BM and SS (Figure 3 (b)). This result is in agreement with those obtained by Nandi et al [37] and Mota et al [38]. Indeed, at the beginning of the process (hydrolysis step) the extracellular enzymes, which are produced by hydrolytic microbes, decompose complex organic polymers to simple soluble monomers. Proteins, lipids, and carbohydrates are hydrolyzed to amino acids, long-chain fatty acids, and sugars, respectively. These small molecules are then converted by acetogenic bacteria to a mixture of VFAs and other minor products such as alcohol [39]. The main VFAs presents during the AD process are acetic, butyric, and propionic acids, which are commonly accumulated at the start-up period in the AD [40]. In the second step of AD (5th - 6th day) we observed an increase in pH value to 7.3 for BM and 6.9 for SS and diminution of VFAs to 0.8 for BM and 1.8 g/L for SS. This complies with the results obtained by Blasco et al [41]. This is explained by the value buffer of pH and the consumption of the VFAs by bacteria [42]. During this step, the acetogenic bacteria convert the VFAs to acetate, carbon dioxide, and hydrogen. These latter provide direct substrates for methanogenesis which correspond to the last step for the AD process for methane production. Finally, during the third step (7th - 10th) of the AD process, we noted a pH values stabilization around 8 and 7 respectively for BM and SS. The equilibrium values of VFAs were about 0.65 and 1.75 CH_3COOH g/L for BM and SS. These results are in agreement with those observed by Rinco et al [42].

Compared to BM, SS showed a lower pH value and more significant VFAs production. As the VFAs production in the hydrolysis step occurs at a faster rate than their assimilation in acetogenesis or methanogenesis step, the methanogenic activity of micro-organisms is inhibited [16–36]. Of all microorganisms in the overall consortium for the anaerobic conversion of organic matter to methane, Archaea is commonly considered as the most sensitive to toxicity [43].

As it can be seen in (Figure 3 (c)) the TA variation is inversely proportional to pH. The first step of AD (1st-4th day) is characterized by an increase in the TA values

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(expressed in $CaCO_3$ concentration) from 16.8 to 23.5 g/L and 17.5 to 32.6 g/L, respectively for BM and SS. Also, for BM and SS, pH decreases to restore the alkalinity conditions which lead to the outbreak of the methanogenesis step [44]. During the methanogenesis step (5^{th} - 6^{th}day), the TA value decreases to 13.9 g/Lfor BM and 19.2 g/L for SS. Alkalinity is known to be a critical buffering factor for neutralizing VFAs during methanogenesis by VFAs consumption [37]. In the third step (7^{th} - 10^{th}), the TA stabilization occurs and final values were around 13.6 g/L and 18.8 g/L for BM and SS respectively, indicating that the AD process already reached stability. These results conform with those observed by Montusiewicz et al [27]. Based on the results obtained above that showed significant inhibition of AD due to the high concentration of Cu and Zn in SS, we maintained BM as inoculum for the rest of the study.

3.2 Effect of NaOH and H_2O_2 concentration on WS pretreatment

In order to evaluate the effect of WS pretreatment on the AD, NaOH (0.5, 1, 2, 4% w/w) and H_2O_2 (1, 2, 4, 8% w/w) solutions were experimented. The pretreatment evaluation is measured by the quantity of dissolved organic matter in solution. 2 g of biomass sample was added to 200 mL of solution and made under moderate agitation (250 rpm) for 1h.

According to the solution concentration, results illustrated in Figure 4 show that, compared to WS hydrolysis with water, the pretreatments with NaOH and H_2O_2 improve the amount of dissolved organic matter. However, it seems that a 4% H_2O_2 solution corresponds to the optimal value which leads to 1410 mgO_2/L of COD. However, higher H_2O_2 concentrations influence negatively the decomposition process. H_2O_2 pretreatment of lignocellulosic biomass breaks down lignin and hemicellulose and releases a cellulose fraction with high degradability to the anaerobic microorganisms [43]. Otherwise, H_2O_2 has a significant advantage because it avoids toxic residues in the biomass and it degrades into oxygen and water [18]. Even NaOH pretreatment can degrade the carbohydrates, cellulose, and hemicelluloses improving the biomass digestibility, it generates Na as residue that can be toxic for methanogenic microorganisms [5–18].

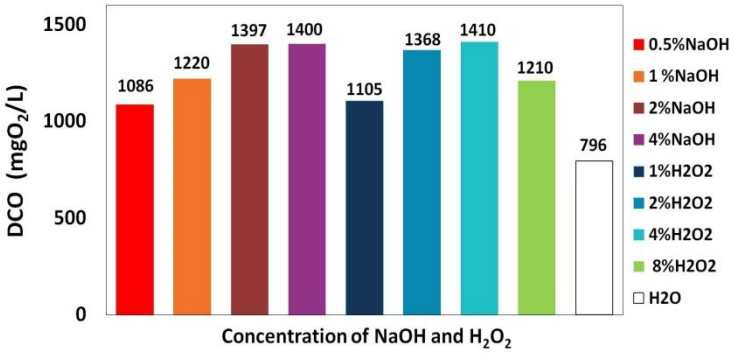

Figure 4. Effect of NaOH and H_2O_2 concentration on COD released.

3.3 Effect of coupling US with NaOH and H_2O_2 pretreatment

US pretreatment employs ultrasonic radiation to breakdown the complex network of polymerization in biomass. Cavitations produced due to the pulsating high-frequency ultrasonic waves penetrate polysaccharides and disrupt the mesh of cross-linking polymers facilitating better biodegradation [17]. The pretreatment results of the coupling 30 min of the US with NaOH and H_2O_2 are deferred in Figure 5.

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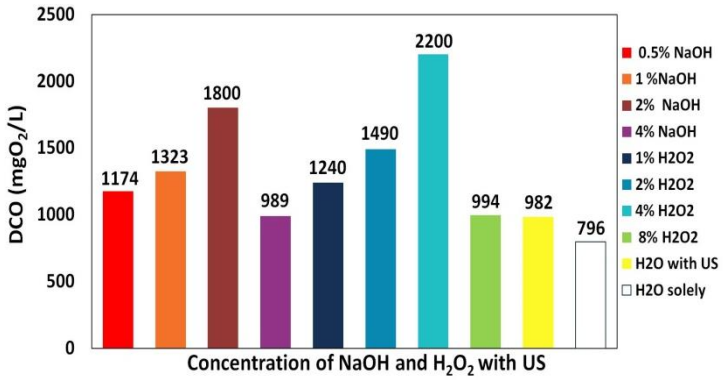

Figure 5. Effect of coupling US pretreatement with NaOH and H_2O_2 on COD released.

Compared to the chemical pretreatment solely, for low concentrations of NaOH and H_2O_2, the exposition of the substrate to the US significantly increases its decomposition. Indeed the US has various effects on the organic matter such as mechanical effects and creation of free radicals with very high oxidant capacity.

The attack of the WS lignocellulose by hydrogen peroxide seems better than that with sodium hydroxide. However, for strong concentrations of both NaOH and H_2O_2, the US decrease this decomposition, because the solubilized organic matter is mineralized by hydroxyls radicals produced.

US pretreatment augments the oxidative power of H_2O_2 [9]. Thus, a mass concentration of 4% w/w of H_2O_2 seems the optimal value with a COD value of 2200 mgO_2/L. The delignification of WS with a low concentration of H_2O_2 4% w/w was promoted due to the production of the HOO^- anion, which in turn promoted the production of hydroxyl (•OH) and superoxide (O_2^-) radicals. Similarly, the promotion of radicals with ultrasound enhanced solubilized lignin degradation [3–17].

3.4 Effect of reaction time for H_2O_2 coupled with US pretreatment

Figure 6 depicts the effect of the reaction time according to released COD under the optimal conditions previously determined 4% w/w H_2O_2 coupled with the US while varying the treatment time from 5 to 45 minutes.

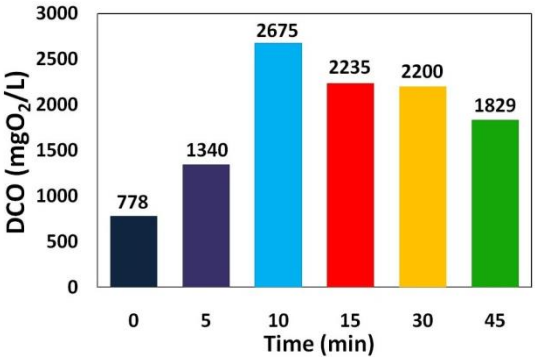

Figure 6. Effect of reaction time for H_2O_2 coupled with US pretreatement on COD released.

The obtained results show that the solubilized organic matter of the substrate depends on the pretreatment time. The optimal COD value 2675 mg O_2/L was reached after 10 min of pretreatment, which implies that the discharges imposed on the substrate are powerful and rapidly degrade the lignocellulosic biomass. Beyond 10 min, the COD value decreased and reached 1829 mg O_2/L after 45 min. This result could be explained by the degradation of the COD solubilized by the hydroxyl radicals present in the solution [10].

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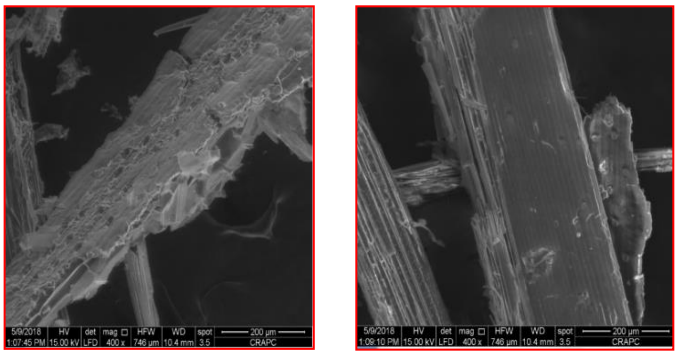
3.5 SEM observations

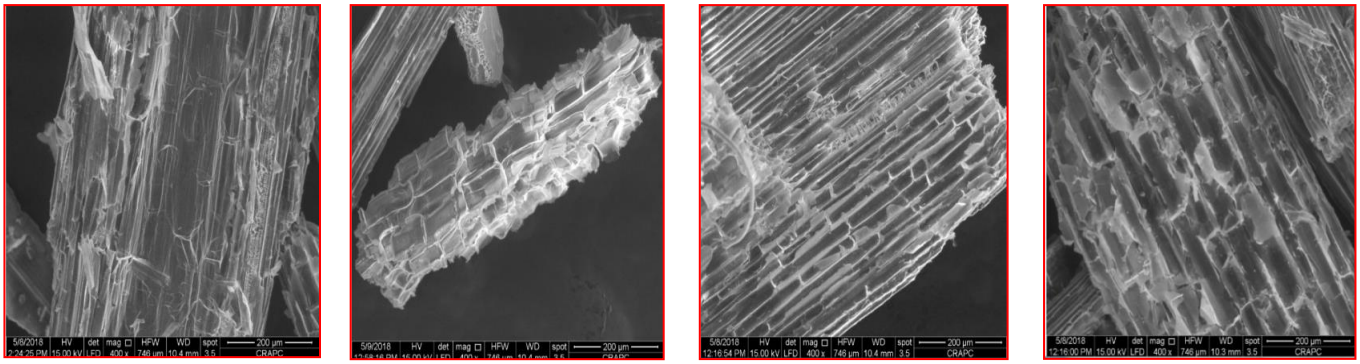
To observe the structural changes of WS after the pretreatments, SEM analysis was conducted. The morphological features of raw WS (Figure 7 (a)) shown a regular and compact surface structure with fibers arranged in bundles. After both NaOH and H_2O_2 pretreatments coupled with ultrasound (Figure 8) the surface of the WS samples, which is mainly composed of lignin and hemicellulose, was destroyed. The lignin and hemicellulose of pretreated WS samples were partially removed and broken, resulting in the exposure of internal structures. After that, WS became loose and scattered, and exhibited fiber porosity on its surface compared to the raw WS. These results are similar to those obtained by Zheng et al [3]. These observed results demonstrate that pretreatment could destroy the cellulose-hemicellulose-lignin network, removing some of the external fibers and there by accelerating the biodegradation process [18–44].

The hydrolysis with the only H_2O coupled with the US (Figure 7 (b)) caused minimal changes on the surface of the WS samples. The surface was relatively smooth and showed minimal destruction compared to that using both NaOH and H_2O_2 pretreatments coupled with the US. The WS structures of samples after both NaOH and H_2O_2 pretreatments coupled with the US were destroyed indicating the efficiency of these pretreatments. However, despite the efficiency of NaOH pretreatment coupled with the US, this pretreatment generates residues that can probably oxidize the desirable structures like sugars, VFAs, and alcohols that inhibit the AD process [37].



(a) **(b)**

Figure 7. (a) SEM photo of raw WS; (b) SEM photo of pretreated WS with H_2O and US solely.



(a) **(b)** **(c)** **(d)**

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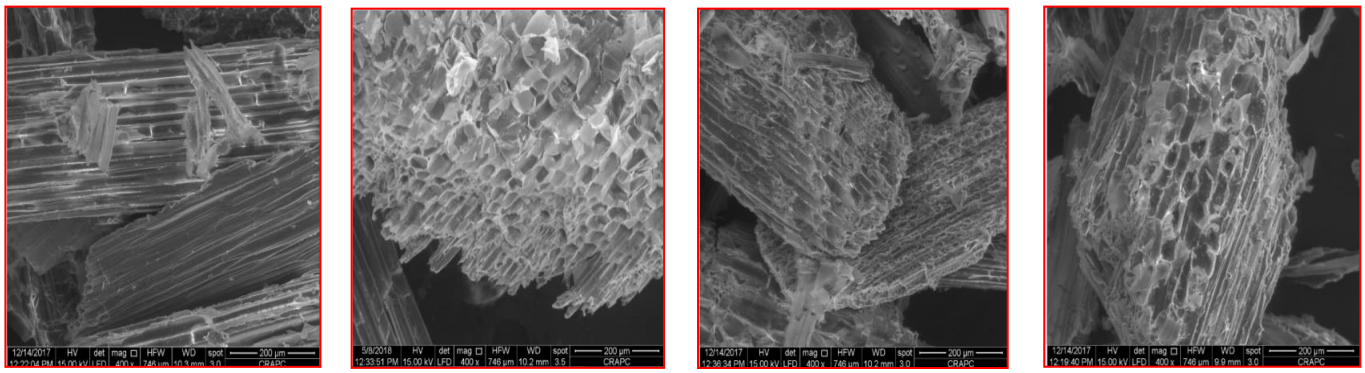

(e) (f) (g) (h)

Figure 8. SEM photo for pretreated WS with chemical solution and 10 min of US: (a) 0.5%NaOH; (b) 1% NaOH; (c) 2% NaOH; (d) 4% NaOH; (e) 1% H_2O_2; (f) 2% H_2O_2; (g) 4% H_2O_2 and (h) 8 % H_2O_2.

3.6 Impact of H_2O_2 pretreatment coupled with the US on biogas and methane production

To determine the influence of coupling H_2O_2 to the US pretreatment on biogas and methane production we carried out two AD experiments. One experiment with pretreated WS under the optimal conditions determined previously 4% w/w H_2O_2 and 10 min of US and another with raw WS. For these BMP tests, each experiment was conducted in duplicate to ensure the reproducibility of results which are presented in figure 9 and table 2.

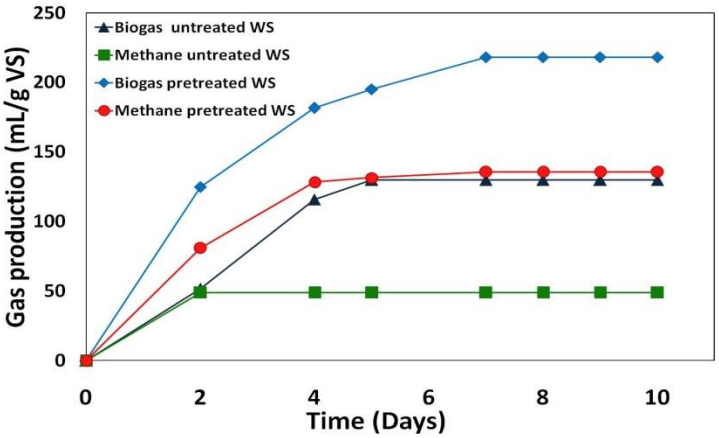

Figure 9. Cumulative volumes of biogas and methane for pretreated and untreated WS, during the AD process.

The US mechanically disrupt the cell structure of WS and promote the release of free radicals as •OH, •HO_2, •H [18–19]. As hydrogen peroxide is a strong oxidant, it degrades lignin to soluble compounds with low molecular weights. As these latter are more accessible to the anaerobic microorganisms, the biogas and the biomethane production is improved [43].

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Table 2: Methane production yield for pretreated and untreated WS

	Pretreated WS	**Untreated WS**
Biogas (mL/g VS)	218	130
Methane (mL/g VS)	136	49
Methane (%) in biogas	62	38
Methane improvement (%) for pretreated WS	64	/

During the first step of AD (1st-4th day) the Figure 8 shows that for both treated and untreated WS, the volume of biogas and methane produced increases. This corresponds to the beginning of the AD process (hydrolysis phase) during which large polymer molecules are broken down into simple soluble monomers. Proteins, lipids, and carbohydrates are hydrolyzed to amino acids, long-chain fatty acids, and sugars. As lignin is a hydrophobic heteropolymer in nature, it degrades very slowly and most of its degradation remains incomplete. This phase is flowed by the acetogenesis during which different monomers (sugar, long-chain fatty acids, and glycerol) are converted into alcohols and short chain of fatty acids by the acidogenic microorganism. Throughout this period, alcohol and short chains of fatty acids are converted into acetate, carbon dioxide, and hydrogen. After that, the produced acetate is used as a substrate by methanogenic bacteria for methane production during the methanogenesis phase. The last step (5th - 6th day) shows the stabilization of biogas production and the end of the methane, The accumulation of hydrogen develops significant pressure which blocks the activity of acetogenic bacteria that stop acetate production. Due to the symbiotic relation between acetogenic and methanogenic bacteria, these latter utilize this hydrogen in methane production and significant hydrogen pressure does not occur [38–45].

Consequently of what was been explained above and compared to the untreated US, table 2 indicates that pretreated WS produces more biogas and biomethane than untreated WS. This corresponds to an improvement of 40% and 64%, respectively for biogas and methane production. Besides, it appears that treated WS products more methane 62% than untreated one 37%. It appears that the treatment of WS accelerates the hydrolysis rate which depends on the nature of the substrate and the size of a substrate particle [45]. Indeed, WS pretreatment with 4% w/w H_2O_2 coupled with 10 min of US allowed releasing the organic matter contained in the biomass to make it accessible to microorganisms. This leads to the performance improvement of AD and the increase in methane production yield [5]. Otherwise, untreated WS inhibits the AD process due to its high content of lignocellulosic material which makes it resistant to microbial attack [5–38].

3.7 Effect of the filtrate resulting from the pretreatment of WS with H_2O_2 coupled with the US on the biogas production

In this part of our work, we studied in the optimal conditions (4% H_2O_2 and 10 min US) the use of the filtrate resulting from the WS pretreatment on biogas and methane production. The experiment was conducted in duplicate to ensure results reproducibility. Figure 10 and table 3 show the obtained results.

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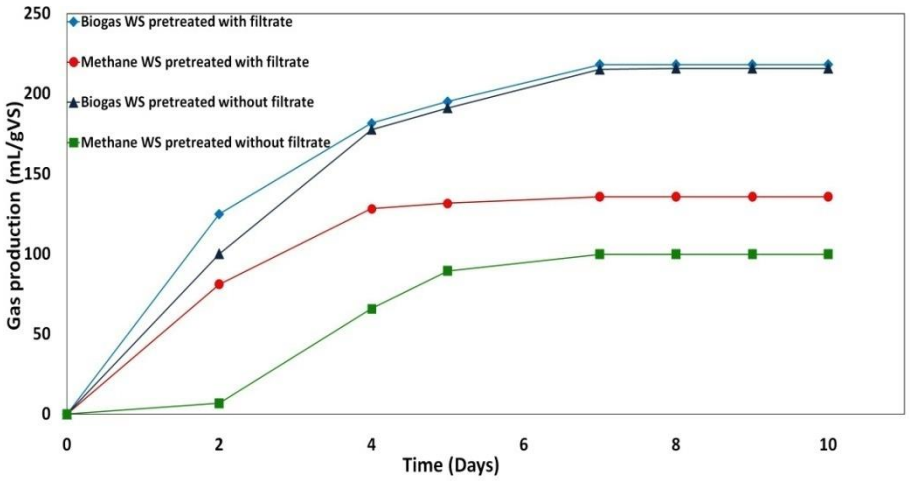

Figure 10. Cumulative volumes of biogas and methane for AD of pretreated WS with and without filtrate.

Table 3: Methane product yield for AD of WS pretreated with filtrate and WS pretreated without filtrate.

	Pretreated WS with filtrate	**Pretreated WS with water**
Biogas (mL/g VS)	218	215
Methane (mL/g VS)	136	100
Methane (%) in biogas	62	46
Methane improvement (%) for pretreated WS with filtrate	26	/

It appears in figure 10 that the biogas production is almost the same for both cases, while methane generation is more important when the filtrate is used instead of water. AD of pretreated WS with the filtrate increase by 26% than that with water. This is explained by the presence in the filtrate of solubilized organic matter resulting from the WS pretreatment. Indeed, this latter partially breaks down lignin and hemicelluloses and releases to the microorganisms cellulose fraction with high degradability [3].

4. Conclusions and perspectives

Renewable bioenergy sources are taking a major role as sustainable fossil fuel. AD is a main treatment for reducing the organic matter contained in WS and generating at the same time, methane-rich biogas.

The present study indicates that the excessive amounts of HM present in sewage sludge, especially Cu and Zn with values of 72.50 and 491.24 mg/Kg respectively which exceed the necessary concentrations for the growth of the methanogenic microorganisms (60 mg/Kg and 64 mg/Kg for Cu and Zn respectively) leading to significant inhibition of methane production.

Through the optimization of various pretreatments of WS, we observed that the pretreatment with 4 % w/w H_2O_2 under 10 min of the US is the most effective. This latter led to the optimal solubilization of recalcitrant matter constituting the WS and corresponding to the COD value of 2675 mg O_2/L.

The biochemical methane potential (BMP) tests carried out at mesophilic conditions resulted in an increase of methane content 62% in the biogas for pretreated WS with 4% w/w H_2O_2 with 10 min of US. BMP tests showed also that this pretreatment improved the methane yield by 64%.

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The use of filtrate from American pretreatment, instead of water, leads to an increase in methane production of 62% in the biogas and a methane yield of 26%.

The choice of using straw is justified by its high calorific value of about 14.5 MJ/kg while that of wood in nature is 10.8 MJ/kg and that of urban waste and fibrous residues such of sugar cane is only 7.77 MJ/kg.

Figure 11 shows the methanization process. It consists of the degradation, under the action of bacteria, of organic materials (or substrates) such as agricultural materials and livestock effluents (plant biomass, manure, slurry), green and household bio-waste, waste from the food industry, and sludge from wastewater treatment plants. This reaction, called anaerobic digestion (in the absence of oxygen), produces biogas and digestate.

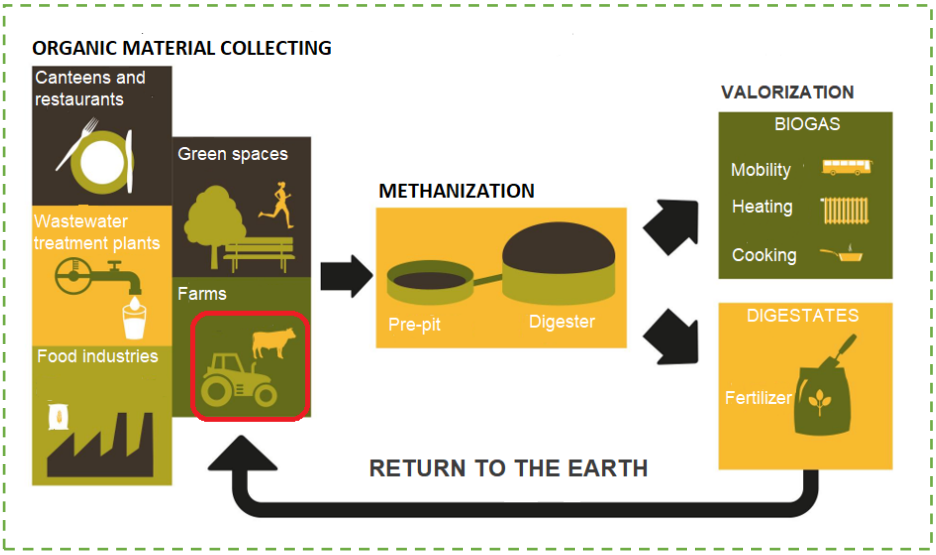

Figure 11. Methanization process

Methanization, or the production of biogas from agricultural waste and residues, as part of a circular economy approach, meets two major challenges: the production of renewable energy to replace fossil fuels and contribute to a future 100% renewable energy system, and support for the transition of the agricultural sector through the implementation of agro-ecological practices.

Biomass is the latest renewable energy to be exploited, subject to sustainability criteria. More than 10% of the EU (European Union)'s final energy consumption would come from biomass, which would then represent half of the total consumption of renewable energy in Europe. According to the European Union (https://ec.europa.eu/eurostat/fr/web/energy/data/energy-balances), by 2030 the use of biomass (final energy) will be 19 EJ (1 EJ = 10^{18} joules), the % of biomass in the final energy consumption is 19%, and the % of renewables in the final energy consumption will be 41%.

The world's energy production has entered a transitional phase that will require us to significantly reduce our consumption of fossil fuels, which are sources of greenhouse gases and whose resources are not inexhaustible.

Today, the only renewable alternative to fossil fuels for the production of liquid fuels, lubricants and basic molecules for chemistry is biomass.

Some countries, such as the Netherlands, have reservations about the sustainability of this energy source. However, we must defend the renewable character of biomass when it is managed intelligently. This resource uses a cheap and widespread primary energy. It can therefore be collected locally (wood, vegetable and food waste). In fact, it

has the advantage of being dependent on a local market, unlike oil and gas (of fossil origin) which are dependent on international markets.

The future of biogas must be seen in the context of the global energy system. Several directions can be considered depending on the pace of technological innovation, the ambition of energy policies, market dynamics and societal trends.

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