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Increased biogas production from wheat straw by chemical pretreatments

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ABSTRACT

This work investigated the effect of three different chemical pretreatment methods on the biogas production from the anaerobic digestion of wheat straw. The lignocellulosic material was separately pretreated using i) the organic solvent N-methylmorpholine N-oxide (NMMO) at 120 °C for 3 h, ii) the organosolv method, employing ethanol as the organic solvent at 180 °C for 1 h and iii) using an alkaline pretreatment with NaOH at 30 °C for 24 h. All the pretreatments were effective in increasing the biomethane production yield of wheat straw. In particular, the cumulative biomethane production yield of 274 mL CH_4/g VS obtained with the untreated feedstock was enhanced by 11% by the NMMO pretreatment and by 15% by both the organosolv and alkaline pretreatment. The three pretreatment methods had a different impact on the chemical composition of the straw. NMMO hardly changed the amount of carbohydrates and lignin present in the original feedstock. Organosolv had a major impact on dissolving the hemicellulose component, whereas the alkaline pretreatment was the most effective in removing the lignin fraction. In addition to the increased biogas yields, the applied pretreatments enhanced the kinetics of biomethane production.

1. Introduction

In response to the increase of the global demand for renewable energy, the anaerobic digestion (AD) technology has attracted wide attention in the last few years. The biogas generated from the AD of lignocellulosic materials, such as agricultural waste, has the potential to address the energy needs while providing multiple environmental benefits [1]. Wheat is among the three most cultivated crops worldwide, with a global production of 729 Tg in 2014 [2]. Considering a straw to grain ratio of 1.5 [3], more than one billion tons of wheat residues are produced annually. The large availability, together with the relative low-cost, makes wheat straw a sustainable feedstock for the production of biofuels [4]. However, similarly to any other lignocellulosic substrate, the conversion of wheat straw to biogas is hampered by the complex structure of this material. Specifically, the accessible surface area, the crystallinity of the cellulose and the lignin content limit the digestibility of the lignocellulosic matter [5]. Therefore, a pretreatment prior to AD is required in order to overcome the limitation posed by the hydrolysis rate [6].

An extensive number of techniques have been investigated to pretreat lignocellulosic materials, based on physical, chemical, and biological approaches, with the main goal of increasing the biogas yields [7]. Compared to physical and biological methods, chemical pretreatments have received larger attention because they are usually less expensive and result in faster rates and better efficiencies in enhancing the degradation of complex organic materials [8,9]. Recently, novel pretreatment methods employing organic solvents, such as N-methylmorpholine N-oxide (NMMO) and the organosolv technique, have been tested, proving to be successful in increasing the biogas yields from lignocellulosic materials [10]. On the other hand, alkaline pretreatments have been studied for many years for their ability to increase the accessibility of the carbohydrate portion to the microorganisms, thus enhancing the methane yields [11,12].

Several cellulose solvents have been investigated in the last years, since they offer advantages such as a decrease of the cellulose crystallinity, a minimum loss of fermentable sugars, short

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pretreatment times and relatively low energy requirements [13]. However, the effectiveness of different pretreatments on a specific substrate has rarely been compared within the same study in terms of enhancement of the biomethane production yields and variation of the lignocellulosic composition of the original feedstock. Due to the high variability in the chemical composition of lignocellulosic materials [4], comparing results from different studies is particularly challenging.

Among the different cellulose solvents, NMMO is particularly attractive since it is already employed in industrial processes for the production of cellulose fibers. Beyond being non-toxic, it is fully biodegradable and recyclable up to 98% [14]. The organosolv method is based on the pretreatment of the lignocellulosic materials with organic solvents, such as low boiling point alcohols, in order to achieve the chemical breakdown of the lignin fraction by cleavage of ether linkages and its subsequent dissolution [15]. The main advantages of this method are the easy recycling of the pretreatment solvent by distillation and the recovery by precipitation of a highly pure lignin fraction, which is an economically valuable byproduct with various applications in the chemical industry or as a fuel [16]. The alkaline pretreatment uses bases, with NaOH being the most popular, to render the lignocellulosic matrix easily degradable for the microbes, through the removal of portions of lignin and hemicellulose [7]. The main mechanism of this method is the saponification and cleavage of the linkages between lignin and carbohydrates [17]. Thus, the alkaline pretreatment leads to an increase of the accessible surface area and porosity, structural swelling, a decrease of the cellulose crystallinity and the disruption of the lignin structure [7].

This work aimed to compare the effects of NMMO, organosolv and NaOH pretreatment on the lignocellulosic composition of wheat straw and the biomethane yields from its subsequent AD. While alkaline pretreatments have been successfully applied to pretreat wheat straw, NMMO and organosolv have up to now not yet been tested for the enhancement of AD of this agricultural residue. Biomethane potential (BMP) tests and compositional analyses were performed on the untreated and pretreated wheat straw to evaluate the effectiveness of the three different pretreatment methods. The AD process was further assessed by evaluating the kinetics of biomethane production and analyzing the trends of volatile fatty acids (VFA) production along the AD process.

2. Materials and methods

2.1. Substrate and inoculum

Wheat (*Triticum aestivum*) straw was harvested from agricultural fields in the province of Salerno (Italy). Before use, the straw was cut into pieces with a size smaller than 4 mm. The inoculum was a digestate from a full-scale AD plant located in the same province, treating buffalo manure and residues from a dairy factory. The main physicochemical characteristics of both the wheat straw and the inoculum are reported in Table 1, while Table 2 gives the carbohydrates and lignin content of the raw wheat straw.

Table 1
Characteristics of the raw wheat straw and the inoculum.

	Wheat straw	Inoculum
TS (%)[a]	93.1 ± 0.1	5.1 ± 0.1
VS (%)[a]	76.8 ± 1.1	3.4 ± 0.0
TKN (g N/kg TS)	11.2 ± 0.2	51.0 ± 0.4
COD (g/kg TS)	1169.6 ± 71.4	1312.3 ± 47.6

[a] Based on wet weight.

Table 2
Carbohydrates and lignin composition of the untreated and pretreated wheat straw.

Pretreatment conditions	Glucan (%)[a]	Xylan (%)[a]	Galactan (%)[a]	Arabinan (%)[a]	Lignin (%)[a]
Untreated	31.0 ± 1.0	15.5 ± 0.3	0.3 ± 0.0	2.6 ± 0.7	18.3 ± 0.1
NMMO	31.7 ± 0.2	15.1 ± 0.1	0.3 ± 0.1	2.3 ± 0.1	17.9 ± 0.2
Organosolv	36.3 ± 0.9	6.1 ± 0.2	0.2 ± 0.0	3.1 ± 0.9	15.8 ± 0.5
Alkaline	36.0 ± 0.1	9.7 ± 0.1	0.2 ± 0.1	2.0 ± 0.3	11.6 ± 0.2

[a] Based on dry weight.

2.2. Pretreatments of wheat straw

Three different chemical pretreatment methods were conducted in this study, namely NMMO, organosolv and alkaline pretreatment. The chosen pretreatment conditions were based on previous studies performed on lignocellulosic materials [11,18,19]. Fig. 1 shows the experimental flow adopted.

The NMMO pretreatment was performed using an NMMO aqueous solution (Sigma-Aldrich, Germany), which was concentrated to 85% (w/w) from the commercial 50% (w/w) solution by using a rotary evaporator (Büchi Rotavapor R-114, Switzerland). 92.5 g of the obtained NMMO solution were added to 7.5 g of wheat straw in a 500 mL Erlenmeyer flask, which was placed in an oil bath and heated at 120 °C for 3 h, while stirring every 10 min. Propyl gallate (0.625 mg per g NMMO) was added to prevent oxidation of the solvent. Immediately after the pretreatment, boiling deionized water was added as antisolvent in order to stop the reaction. The pretreated straw was then placed on textile bags and repeatedly washed with boiling deionized water until a clear filtrate was achieved.

The organosolv pretreatment was performed using ethanol as organic solvent. 150 mL of 50% (v/v) ethanol were added to 15 g of wheat straw in a high-pressure stainless steel vessel (Sigma-Aldrich, Germany) with a working volume of 300 mL. The vessel was then sealed and placed in a TCF 50 PRO convection oven (ArgoLab, Italy), where it was heated at a rate of 3 °C/min up to 180 °C, which was maintained for 60 min. Afterwards, the vessel was cooled in an ice bath. The pretreated straw was then removed and washed with 100 mL ethanol and subsequently with deionized water until obtaining pH 7.0 in the liquor.

The alkaline pretreatment was performed using sodium hydroxide. In a 500 mL bottle, 16 g of wheat straw were soaked in 100 mL of 1.6% (w/w) NaOH solution. The bottle was then incubated at 30 °C for 24 h. After the pretreatment, the straw was filtered and air-dried until further use.

2.3. BMP tests

BMP tests were performed in triplicate under mesophilic (37 ± 2 °C) conditions. The biomethane production was measured by the liquid displacement method, as described by Esposito et al. [20] and modified as in Mancini et al. [19]. Serum bottles (Wheaton, USA) of 125 mL were loaded with 45 g of inoculum and 1 g of untreated or pretreated wheat straw to obtain an inoculum to substrate ratio of 1.5 g VS/g VS. To reach 70 mL of working volume, 20 mL of tap water were added into each bottle. One triplicate of blank samples containing only inoculum and tap water was also prepared in order to determine the biomethane production of the inoculum, which was then subtracted from the production of the straw samples. For VFA analysis, 0.5 mL of the liquid phase was sampled daily from each batch bottle during the first 10 d of BMP test, except for day 1 and 6.