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The use of thermochemical and biological pretreatments to enhance organic matter hydrolysis and solubilization from organic fraction of municipal solid waste (OFMSW)

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ABSTRACT

The introduction of the anaerobic digestion for the treatment of the organic fraction of municipal solid waste (OFMSW) is currently of special interest. The main difficulty in the treatment of this waste fraction is its biotransformation, due to the complexity of organic material. Therefore, the first step must be its pretreatment for breaking complex molecules into simple monomers, to increase solubilization of organic material and improve the efficiency of the anaerobic treatment in the second step. The hydrolysis stage is considered the rate-limiting step for the anaerobic digestion of solid wastes. Thus, in this paper thermochemical and biological pretreatments were performed to accelerate the hydrolytic processes by means of a fast organic matter solubilization of industrial OFMSW.

The thermochemical pretreatments were conducted in oxidizing and inert atmospheres and sodium hydroxide was employed as an alkaline agent. On the other hand, the biological pretreatments were performed using mature compost, fungus *Aspergillus awamori* and activated sludge from a conventional WWTP as enzymatic agents.

The results from the thermochemical pretreatment indicate that the best conditions for organic matter solubilization were 180 °C, 3 g NaOH/L and 3 bar. Increments of soluble chemical oxygen demand (COD) of approximately 246% can be achieved in these conditions. In the case of biological pretreatments, the mature compost showed the maximum hydrolytic activity with an increase of COD of 51% for the lower inoculation percentage (2.5%, v/v).

1. Introduction

Anaerobic digestion can be an attractive option, both as a disposal route and as a source of alternative energy. In the last few years, much effort has been made at introducing anaerobic digestion processes for treating the organic fraction of municipal solid waste (OFMSW). However, the main obstacle in spreading this technology is the lower biodegradation rate of solid wastes (due to the chemical composition and structure of lignocellulosic materials) in comparison to liquid ones. Generally, the methanogenic stage is the rate-limiting step of the anaerobic digestion processes of liquid wastes. However, studies on the anaerobic digestion of primary sludge and organic complex substrates have concluded that the hydrolysis of organic matter to soluble substrate is the rate-limiting step for solid waste degradation [1]. Therefore, physical, chemical or biological pretreatment methods (or their combination) are required, in order to reduce the rate of such a limiting step.

Thus, in his work on cellulose fermentation, Pavlostathis [2] found a negligible accumulation of hydrolyzed products in the reactor and concluded that the conversion of cellulosic matter to soluble products was the rate-limiting step in the overall process. Lee and Donaldson [3] also observed a low concentration of soluble compounds in cellulose fermentation processes and thus, the hydrolytic stage was considered the limiting stage of the process as well. By means of activity assays of soluble and insoluble fraction of slaughterhouse effluents (considered complex wastes for their ruminant remains and fat content), Galisteo et al. [4] determined that the hydrolysis of organic-complex material was also a limiting stage of the degradation process.

Hence, several methods have been developed to improve the biodegradability of complex wastes through the application of different types of pretreatments: physical, chemical, biological and combinations of them [5–15]. For complex substrates such as lignocellulosic materials, pretreatment causes a deep modification in the structure of complex material and a decrease in the degree of poly-

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Table 1
Physicochemical characterization of the industrial OFMSW.

Parameter	Data
pH	7.98
Density (kg/m^3)	650
Alkalinity (g $CaCO_3$/L)	18.13
Ammonia (g NH_3-N/L)	0.79
Total nitrogen (g/kg)	29.0
TS (g/g sample)	0.71
VS (g/g sample)	0.16
DOC (mg/g)	11.90
Total VFA (mgAcH/L)	32.65

merization, thus weakening the molecular bonds between lignin and carbohydrates and increasing the superficial area of particulate wastes.

This paper examines thermochemical alkaline and three biological pretreatments applied to organic fraction of municipal solid waste (OFMSW) in order to enhance waste hydrolysis so as to increase both the anaerobic biodegradability and overall degradation rate of the waste. The pretreatments mentioned above were expected to be particularly effective for industrial OFMSW with large-sized particles from a municipal solid waste treatment plant.

2. Materials and methods

2.1. Methodology

Assays of thermochemical and biological pretreatments were carried out to accelerate the hydrolytic rate and increase the anaerobic biodegradability of the OFMSW from an 880 t/d industrial MSW treatment plant called *Las calandrias* in Jerez de la Frontera (Cadiz, Spain). The average particle size of the waste selected for this study was 30 mm and its characterization is shown in Table 1. Importantly, the morphology of the waste used in the experiments has not been altered in any way, i.e., the waste has not been processed by drying or milling. The OFMSW had completely the original features of industrial waste.

The thermochemical pretreatments carried out used sodium hydroxide (NaOH) as an alkaline agent. In this case, the operative variables to be studied were: temperature, pressure, NaOH dosage and type of atmosphere (inert (N_2) or oxidizing (synthetic air)) according to the experimental conditions reported in the literature [16–21].

In the case of biological pretreatments, different enzymatic agents were tested: activated sludge from municipal and conventional WWTP placed in Puerto Real (Cadiz, Spain), mature compost from the *L. calandrias* plant and finally, fungus *Aspergillus awamori*. This fungus has been elected since it is a variety of *Aspergillus niger*, biological-hydrolytic agent widely used and referenced in the literature [6]. The operational variable in these assays was the percentage of inocula in terms of volume.

The effect of the pretreatments performed on organic matter solubilization has been measured in terms of dissolved organic carbon (DOC), dissolved volatile solids (DVS), total volatile fatty acids (TVFA) and soluble chemical oxygen demand (sCOD). TVFA was determined according to Riau et al. [22]. Individual C2–C7 volatile fatty acids (VFA), including iC4, iC5 and iC6, were measured by a gas chromatograph (Shimadzu GC-17 A) equipped with a flame ionization detector (FID) and a capillary column filled with Nukol (polyethylene glycol modified by nitroterephthalic acid). DVS, DOC and sCOD were determined according to *Standard Methods* [23].

Table 2
Design of experiments.

Thermochemical pretreatments		Biological pretreatments
Variable	Value	Inoculum percentage (%, v/v)
T (°C)	120–150–180	
Pressure (bar)	1–5–10	2.5, 5.0, 7.5 and 10
Dose of NaOH (g/L)	1–3–5	

2.2. Thermochemical pretreatments

The experiment was conducted according to a 3^n-type factorial design (3 being the number of the variable and "n" being the number of levels of each variable tested). The variables were temperature, pressure and alkaline agent dosage, as described in the planning sheet shown in Table 2. The factorial design established 27 experiments.

The assays were carried out in a 1 L non-stirred pressure vessel (Parr^{TM}, series 4600-4620) equipped with two proportional-integral-derivative (PID) controllers for temperature and pressure fitting. The pressure was regulated by means of a pneumatic overpressure valve activated by a compressor. A heating jacket was also employed to warm the system.

Each reactor was filled to 60% of its capacity with OFMSW containing a total solids (TS) concentration of 30%. The alkaline agent was applied by means of a 10 M-NaOH solution. The operation time was 30 min in all cases established as optimal for this waste [24].

The inert and oxidizing atmospheres were achieved using N_2 and the air supply from a gas cylinder, respectively.

2.3. Biological pretreatments

Three biological agents (mature compost, the fungus *A. awamori* and waste activated sludge) were used. The inocula concentrations for each of these were 2.5% (v/v); 5% (v/v); 7.5% (v/v) and 10% (v/v). In all cases, the operation time was 24 h established as optimal for biological pretreatment with the same of OFMSW [24].

Four 1 L stainless steel reactors operating in batch mode without agitation were used to conduct the assays. The reactors had a top gas exit to evacuate the gases generated during the hydrolysis stage.

2.3.1. Mature compost

The reactors were loaded to 60% of their volume with industrial OFMSW containing 30% of TS. The mature compost (density = 0.58 g/mL) came from a windrow composting system, which consisted in a pile of MSW and municipal WWTP anaerobically digested sludge (17:3) on a wet basis (10,889 kg of OFMSW mixed with 993 kg of sludge). The inoculum characteristics are detailed in Table 3.

Table 3
Features and composition of the compost pile in dry base.

Parameter	Data
OFMSW (kg)	10.889
Sludge (kg)	993
pH	7.27
NH_4^+ (mg/g)	0.008
Conductivity (mS/cm)	4.92
Organic matter (%)	25.24
Carbon (%)	14.63
NO_3^- (mg/g)	0.14
N_{total} (%)	0.74
DOC (mg/g)	21.41
P_2O_5 (mg/g)	0.26
C/N ratio	19.7