Chemical pretreatments of organic fraction of municipal solid waste for a sustainable valorization

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Abstract

Organic solid waste gains a lot of consideration in waste management due to both its potential environmental impacts and its suitability to achieve sustainability objectives. One of most widely applied treatment of organic solid waste is the anaerobic digestion, which also promotes renewable energy production. However, specific pretreatments of the substrates are needed to overcome the hydrolytic limiting step and to improve the quality of useful components during the process. Some of these pretreatments allow to convert the substrates in by-products, which could be properly employed in industrial processes. The aim of this work in studying the applicability of organic solvent pretreatment to convert organic solid waste in value-added chemicals. Differently composed organic samples were prepared and treated by acetic acid under various operating condition. Chemical-physical characteristics, biodegradability and structural changes were investigated to evaluate the efficiency of the pretreatment. The correlations among the resulting data were discussed in order to propose alternative and suitable uses of pretreated organic waste.

Keywords: organic solid waste, organic solvent, pretreatment, resource, value-added chemicals

1. Introduction

The organic solid waste management has become increasingly important during the years due to a growing awareness of the issues associated with their improper management. As the European Parliament established that the disposal in landfills must be the destiny of the only residues which cannot be recycled, reused or recovered (Directive 2008/98/EC), several innovative waste treatment technologies have been developed to provide solutions for the sustainable recovery of both energy and materials (Ripa *et al.*, 2017). The Circular Economy Package (EU COM 2/12/2015) emphasizes the necessity of the realization production and treatment systems (Pan *et al.*, 2015), in which the materials are used over and over again (Genovese *et al.*, 2017). They must be kept within the economy as new resources as long as this is possible (Geissdoerfer *et al.*, 2017). The organic fraction of municipal solid waste (OFMSW) could take part in the circular economy (Borrello *et al.*, 2017). This aim can be obtain through well-established processes such as the Anaerobic Digestion (AD), one of the most used treatments for organic waste recovery. The AD is considered an environmentally sympathetic process (Blake *et al.*, 2017), that stabilizes the organic waste producing renewable energy. The end products of AD are the biogas, rich of methane, and the digestate, a solid residue rich in nitrogen (Fisgativa *et al.*, 2016). The digestate is often intended for following composting processes in order to improve its fertilizer properties (Choong *et al.*, 2016). However, in some European countries, the most important barriers to the use of organic fertilizer is the difficulty in planning and use due to the lack of the regulations providing quality requirements or use guidelines (Case *et al.*, 2017). Although AD is considered an efficient technology for the OFMSW treatment, it presents some limitations such as the long time for the stabilization of organic matter and the low rate of biogas production. Suitable pretreatments (chemical, biological and physical) of the substrates are thus necessary to improve organic matter biodegradability and to accelerate the hydrolysis limiting step (Cesaro *et al.*, 2014). The application of pretreatments would be even more interesting if intended to take the greatest advantage from the organic substrate, converting it into both biogas and value-added products to be used within industrial applications. Such approach would indeed involve anaerobic processes along with various industrial sectors in integrated waste biorefinery (Mohan *et al.*, 2016). Recent studies have been focusing on the organic solvent treatment of lignocellulosic fraction (LF) to promote the fragmentation into its main components: cellulose, hemicelluloses and lignin. This fractions can be used for the production of bio-based products and biofuels or synthetized in aromatic compounds which can be used in the chemical industry (Zhang *et al.*, 2015; Sidiras & Salapa, 2015; Amnuaycheewa *et al.*, 2016; Narron *et al.*, 2016). As the OFMSW include a lignocellulosic component, which is the more complex to be degraded during anaerobic processes, a treatment with organic acid can to be also adopted to pretreat this substrate for its more efficient valorization within AD process. The application of the organic solvent pretreatment to substrates of AD process could promote the conversion of the OFMSW into value-added products, characterized by a greater market than waste based fertilizer. In this preliminary study, differently composed OFMSW samples were pretreated with an organic solvent under different operating conditions. The pretreatment conditions were identified in order to maximize the structural change of biomass as well as to minimize the treatment costs. The influence of pretreatment parameters on the substrates were determined experimentally at laboratory scale.

2. Materials and methods

2.1. Raw materials

For this study, OFMSW and LF were used as substrates. The composition of OFMSW was prepared in laboratory according to literature studies (Favaro *et al*., 2013, Alibardi&Cossu, 2015, Fisgativa *et al*., 2016). The LF was used as a control single substrate as well as to prepare a mixture with OFMSW: in the latter case, the samples contained 30% w/w of LF. After being collected, both substrates were ground to reduce the particles size, and stored at 4 °C until use. Table 1 reports the main characteristics of the substrates used for the experiments.

Table 1. Characteristics of substrates used in this study

Parameter	LF	OFMSW+LF
pH [-]	6,2 ± 0,1	6,9 ± 0,2
TS [%]	26,1 ± 6,3	32,3 ± 5,5
VS [%TS]	50,3 ± 3,9	58,5 ± 4,1
sCOD [mg/l]	15.180 ± 3.657	17,2 ± 1,8
C/N [-]	19.210 ± 4.481	13,2 ± 2,0

2.2. Pretreatment methods

The organic acid pretreatment of the substrates was carried out in 300 ml flask with specified solid - liquid ratio (Sindhu *et al*., 2010; Sannigrahi *et al*., 2010; Amnuycheewa *et al*., 2016). 30 grams of organic waste were immersed in a formic acid/water solution and pretreated in an autoclave for 70 minutes, at either 80°C or 120°C. Preliminary tests were performed using waste samples pretreated with 15% acid formic/water solution at 120°C, in absence (A) and in presence (B) of 1% sulfuric acid as catalyst. Based on the obtained results, further preliminary tests were carried out either reducing the acid concentration or the operating temperature as follows:

- 5% formic acid/water solution at 120°C (C);
- 15% formic acid/water solution at 80°C (D).

After each pretreatment, the liquid fraction was separated from the solid one by vacuum filtration using glass filter (Zhang *et al*., 2016) and stored at 4°C until use. The solid fractions were analyzed in terms of pH, Total Solid (TS), Volatile Solid (VS), soluble Chemical Oxygen Demand (sCOD), C, H and N. The liquid fractions were analyzed in terms of Volatile Fatty Acid (VFA) concentration.

2.3. Analytical methods

pH was measured by pHmeter (model HI 99121, Hanna Instruments). TS, VS and COD were evaluated according to Standard Methods (APHA, 1998). The content of C, H, and N were obtained by an elemental analyzer (Organic Elemental Analyzer, Flash 2000, Thermo Finningan). VFA were analyzed through Standard Distillation Method 5560C and their concentrations were expressed as acetic acid equivalents.

3. Results and discussions

The characteristics of both the solid and liquid fractions of the substrates pretreated in absence (A) and presence (B) of sulfuric acid are listed in Table 2.

Table 2. Characteristics of substrates pretreated without catalyst (a) and with catalyst (b)

Substrates	Fraction	TS [%]	VS [%TS]	sCOD [mg/l]	C/N ratio
LF (A)	Solid	19,9 ± 5,8	30,3 ± 4,5	32.620 ± 4.230	30,3
	Liquid	5,1 ± 5,9	18,6 ± 5,4	18.930 ± 5.130	-
OFMSW + LF (A)	Solid	22,6 ± 4,6	37,7 ± 4,1	49.870 ± 5.052	35,3
	Liquid	8,8 ± 4,3	20,5 ± 3,9	27.460 ± 4.963	-
LF (B)	Solid	20,8± 3,2	32,5 ± 3,3	44.550 ± 3.390	29,3
	Liquid	6,4± 3,1	20,5 ± 7,8	16.880 ± 7.120	-
OFMSW + LF (B)	Solid	23,5± 5,6	27,5 ± 6,1	41.630 ± 4.980	32,1
	Liquid	7,9± 3,4	22,8 ± 6,8	201.120 ± 5.560	-

The LF and the LF+OFMSW used in the experiments were characterized by an average VS concentration of 50,3%TS and 58,5%TS and a soluble COD (sCOD) concentration of 15.180 mg/l and 19.210 mg/l, respectively. The characteristics of the mixed sample (OFMSW+LF) were, thus, comparable with those obtained for the control LF samples in terms of both VS and sCOD. After the organic solvent pretreatment without catalyst, the solid fractions of the same samples were both found to be characterized by a lower VS content of around 30,3%TS and 37%TS for the LF and the LF+OFMSW, respectively. In the presence of the catalyst, similar values, of approximately 32,5%TS for the LF and 27,5%TS for the LF+OFMSW, were obtained. Conversely, sCOD concentration increased after the organic solvent pretreatment in all samples. This indicates that the application of the pretreatment, with or without the catalyst, can provide significant solubilisation effects on the substrates. The C/N ratio values of solid fractions were also comparable among differently pretreated samples and set around the optimal one for AD processes, that should range between 20 or 30 (Li *et al*., 2011; Karthikeyan *et al*., 2012). The liquid fractions were also analyzed in terms of VFA concentration. All samples showed significant amounts of VFA. As shown in Figure 1, for the mixed OFMSW+LF samples the detected concentration value was 71.785 mgAC/l in the absence of catalyst, higher than the value obtained in the presence of catalyst (57.471 mgAC/l).

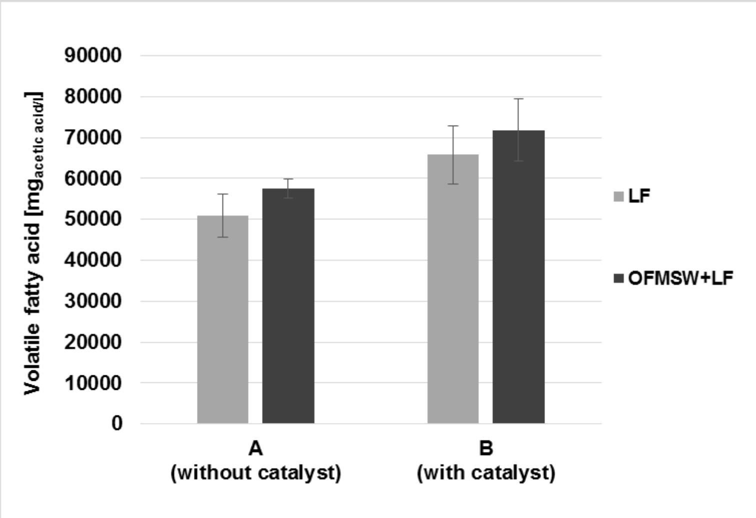

Figure 1. Volatile fatty acid of the samples pretreated in the presence (A) and in the absence (B) of catalyst

It is well known that the VFA concentration usually starts to increase during the first steps of AD process (Gerardi *et al*., 2003). The pretreatment may have promoted a preliminary hydrolysis phase which is generally considered the limiting step of AD (Cesaro *et al*., 2013). The organic solvent pretreatment is expected to involve the delignification of the lignocellulosic biomass in the investigated substrates (Kumar *et al*., 2009). In particular, it should break down the crystalline structure of the lignocellulosic substrates in order to allow the hydrolysis of the cellulose fraction (Kumar *et al*., 2009). Further tests are thus ongoing to verify the effect of the solvent pretreatment on the initial lignin content of the investigated samples.The excess of the VFA concentration in the liquid fractions of pretreated samples can be inhibitory to the biomass in the anaerobic digester (Franke-Whittle *et al*., 2014), as their stability is reported to occur for VFA concentration below 1.500 mg/L (Angelidaki *et al*., 2005). Therefore, the solid fraction of the pretreated samples could be a convenient substrate in the AD process (Wang *et al*., 2014), whereas the liquid fractions could be suitably destined to the recovery of VFA for industrial applications. VFA-rich substrates can indeed be used as building blocks in order to produce different kinds of bio-chemicals, such as biopolymers, aldehydes, ketones, bulk chemicals, pharmaceuticals (Mohan *et al*., 2016). Preliminary results showed that the presence of the catalyst does not have a key-role in defining pretreatment yields.Although the use of catalysts could lead to slightly higher methane yields in a following AD process (Mancini *et al*., 2016), working without sulfuric acid would be more effective from an operational and economic point of view. Therefore, other tests, carried out as a first attempt of operating condition optimization, did not use sulfuric acid as catalyst. The solid fraction of the mixed OFMSW + LF samples that were pretreated at 120°C, with the 5% formic acid/waster solution (C), were characterized by sCOD concentrations comparable with the samples pretreated at 80°C, with the 15% formic acid/water solution (D). These sCOD values were slightly lower than the one obtained pretreating the sample at 120°C with 15% acid solution (A). This may means that the reduction of the acid concentration or the operating temperature had the same significant effect on the solubilization of the substrate. The C/N ratio values of substrates pretreated under operating conditions C and D were comparable with other substrates. However, it would seem that the pretreatment at 80°C with 15% acid solution (D) promotes a slightly higher accumulation of VFA on the substrates than the other operating conditions. The data obtained in the present work represent a screening activity to define the operating parameters of interest for the OFMSW pretreatment with organic solvents. On this basis, further tests will involve the pretreatment optimization, with reference to the possible use of the solid fractions from pretreated samples within AD processes. To this end, the determination of the lignin content and its evolution during the pretreatment will be evaluated as well.

4. Conclusion

The results of this study present the advantages of using formic acid pretreatment for the OFMSW valorisation. The pretreatment improves the fractionation of the OFMSW, the solubilization of organic matter and the hydrolysis of the lignocellulosic biomass. This preliminary investigation confirmed that both the acid formic concentration and the operating temperature used during the pretreatment play a key role. However, results further pointed out that the proper combination of these parameters can lead to a cost-effective and feasible application of this pretreatment for OFMSW valorization. Further tests are needed to optimize the pretreatment, varying the investigated operating conditions as well as including further ones, like the pretreatment duration, in order to promote the integration of AD processes within organic waste biorefineries.

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