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Chemical pretreatment of lignocellulosic agroindustrial waste for methane production

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A B S T R A C T

This study investigates the effect of different chemical pretreatments on the solubilization and the degradability of different solid agroindustrial waste, namely winery waste, cotton gin waste, olive pomace and juice industry waste. Eight different reagents were investigated, i.e. sodium hydroxide (NaOH), sodium bicarbonate ($NaHCO_3$), sodium chloride (NaCl), citric acid (H_3Cit), acetic acid (AcOH), hydrogen peroxide (H_2O_2), acetone (Me_2CO) and ethanol (EtOH), under three condition sets resulting in treatments of varying intensity, depending on process duration, reagent dosage and temperature. Results indicated that chemical pretreatment under more severe conditions is more effective on the solubilization of lignocellulosic substrates, such as those of the present study and among the investigated reagents, H_3Cit, H_2O_2 and EtOH appeared to be the most effective to this regard. At the same time, although chemical pretreatment in general did not improve the methane potential of the substrates, moderate to high severity conditions were found to generally be the most satisfactory in terms of methane production from pretreated materials. In fact, moderate severity treatments using EtOH for winery waste, H_3Cit for olive pomace and H_2O_2 for juice industry waste and a high severity treatment with EtOH for cotton gin waste, resulted in maximum specific methane yield values. Ultimately, the impact of pretreatment parameters on the different substrates seems to be dependent on their characteristics, in combination with the specific mode of action of each reagent. The overall energy balance of such a system could probably be improved by using lower operating powers and higher solid to liquid ratios.

1. Introduction

Anaerobic digestion is a biological process, in which a microbial consortium degrades organic substrates in the absence of oxygen. This process is comprised of four main steps, namely hydrolysis, acidogenesis, acetogenesis and methanogenesis, and results in the production of biogas, mainly composed of CH_4 and CO_2, and digestate. Anaerobic digestion has been widely used as an organic waste stabilization method, while lately it has been intensively studied as a promising alternative to traditional energy production technologies, due to its limited environmental impacts (Ariunbaatar et al., 2014; Zheng et al., 2014). This technology is characterized by a high potential for energy recovery, which makes it more efficient in terms of energy generation from organic materials, compared with other biological and thermo-chemical processes. The use of more sustainable energy sources instead of fossil fuels has nowadays become necessary, in order to effectively reduce greenhouse gas emissions. Anaerobic digestion represents a viable option for such a purpose, since it captures and utilizes the methane that would otherwise be naturally produced through the decomposition of organic materials deposited in landfills, and ultimately be released in the atmosphere (Bolado-Rodríguez et al., 2016; Song et al., 2014; Zheng et al., 2014).

Agricultural and agroindustrial waste and by-products represent viable feedstock for anaerobic digestion systems. Their use for such purpose is considered advantageous, since they are highly available in large amounts, while they can also be characterized as renewable and low cost resources (Fernández-Cegrí et al., 2012; Zhao et al., 2014; Zheng et al., 2014). Agroindustrial activities are particularly important in Mediterranean countries, since they represent a significant sector of the economy. Among the most widespread and profitable activities of this region, are the wine and olive oil production industries, as well as the citrus fruits, especially oranges, and cotton processing activities, with all of them resulting in the generation of large amounts of waste materials (Pellera and Gidarakos, 2016). However, the performance of anaerobic digestion of such substrates is often limited, due to their

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Nomenclature

AcOH	acetic acid [where, Ac: acetyl, i.e. CH_3CO-]
BI	biodegradability index (%)
BMP	biochemical methane potential
CGW	cotton gin waste
E_C	specific energy consumption (kJ/kg VS)
E_M	specific energy corresponding to the energy produced from the pretreated samples in the form of methane (kJ/kg VS)
E_Q	specific energy corresponding to the energy produced in the form of heat (kJ/kg VS)
E_T	specific energy profit of the pretreatment (kJ/kg VS)
EtOH	ethanol
H_2O_2	hydrogen peroxide
H_3Cit	citric acid
JW	juice industry waste
Me_2CO	acetone
NaCl	sodium chloride
$NaHCO_3$	sodium bicarbonate
NaOH	sodium hydroxide
OP	olive pomace
sCOD	soluble chemical oxygen demand (mg O_2/g VS)
SMY	specific methane yield expressed as volume of methane per gram of VS added (mL $CH_{4,\ STP}$/g VS_{added})
SMY_P	specific methane yield expressed as volume of methane per gram of VS of pretreated substrate (mL $CH_{4,\ STP}$/g VS_P)
SMY_{Raw}	specific methane yield expressed as volume of methane per gram of VS corresponding to raw substrate (mL $CH_{4,\ STP}$/g $VS_{consumed}$)
STP	standard temperature and pressure
TMP	theoretical methane potential (mL CH_4/g VS)
TOD	theoretical oxygen demand (mg O_2/g VS)
TPH	total phenols (mg GAE/g VS and mg GAE/L)
TS	total solids (%)
VS	volatile solids (%)
WW	winery waste
Y_{TS}	mass yield for the pretreatment process based on total solids ($gTS_{pretreated\ sample}$/$gTS_{raw\ sample}$)
Y_{VS}	mass yield for the pretreatment process based on volatile solids (g $VS_{pretreated\ sample}$/g $VS_{raw\ sample}$)
Y_{Wet}	mass yield for the pretreatment process based on wet sample ($gWet_{pretreated\ sample}$/$gWet_{raw\ sample}$)

complex lignocellulosic composition. Cellulose, hemicellulose and lignin are the main components of lignocellulosic materials and among them, lignin is the most resistant to biodegradation, constituting the barrier preventing access of the microbes to cellulose (Fernández-Cegrí et al., 2012). The main structural and compositional characteristics of lignocellulosic biomass, which affect their degradability, are cellulose crystallinity, accessible surface area, degree of cellulose polymerization, presence of lignin and hemicellulose, and degree of hemicellulose acetylation. In order to overcome these obstacles, treatment is frequently applied prior to anaerobic digestion of such substrates (Zheng et al., 2014). The objective of any pretreatment method is to disrupt the complex structure of lignocellulosic materials, by reducing the crystallinity as well as the degree of polymerization of cellulose, partially polymerizing and removing hemicellulose, altering and removing lignin and increasing the surface area and porosity of the materials (Behera et al., 2014; Singh et al., 2015). A pretreatment process should be able to achieve an improvement in the digestibility of the treated material, while minimizing environmental pollution, having low energy requirements and limiting the production of potentially inhibiting degradation products, such as organic acids, furan derivatives and phenol compounds (Banerjee et al., 2016; Bolado-Rodríguez et al., 2016). Pretreatment methods, depending on their basic mode of action, can primarily be categorized as physical, chemical and biological, with each category including several separate technologies (Bolado-Rodríguez et al., 2016).

Compared with the other methods, chemical pretreatments are considered very promising, since they can be quite effective in degrading more complex-structured substrates (Behera et al., 2014; Song et al., 2014). Such methods can be performed by applying a variety of chemical processes of different natures. Chemical pretreatments with alkaline reagents involve the use of compounds such as sodium hydroxide, calcium hydroxide and aqueous ammonia (Liew et al., 2011; López González et al., 2013; Pellera et al., 2016; Sambusiti et al., 2013; Song et al., 2014), while in pretreatments with acid reagents both inorganic and organic acids, such as sulfuric acid, hydrochloric acid, phosphoric acid, acetic acid, citric acid, oxalic acid and maleic acid, are used (Amnuaycheewa et al., 2016; Assawamongkholsiri et al., 2013; Lim et al., 2013; Monlau et al., 2013; Scordia et al., 2011; Song et al., 2014; Tian et al., 2016). Oxidative treatments include ozonation (Ariunbaatar et al., 2014) and treatment with peroxides, with their majority particularly focusing on hydrogen peroxide (Monlau et al., 2012; Silverstein et al., 2007; Song et al., 2014). Other types of chemical pretreatments can utilize organic solvents (Kabir et al., 2014), as well as inorganic salts (Banerjee et al., 2016; Kang et al., 2013; Liu et al., 2009). The effectiveness of such pretreatments on different substrates, is highly dependent on the type of substrate, as well as on the type of method being used. In fact, different results will be obtained when treating different materials with the same pretreatment, as a result of the complexity and variability in lignocellulosic structures (Kang et al., 2013; Sambusiti et al., 2013; Zheng et al., 2014). At the same time, variations will also be observed in the results obtained through different pretreatments of the same substrate, since each method acts on different parts of the material (Song et al., 2014). Consequently, the investigation of various combinations of pretreatment methods and substrates is very useful for better understanding the particular effects of different treatments on specific types of materials. The present study makes a significant contribution to this challenging topic.

This study investigates the effect of chemical pretreatment on four of the most widespread solid agroindustrial waste of the Mediterranean region, namely winery waste (WW), cotton gin waste (CGW), olive pomace (OP) and juice industry waste (JW). The main objective was to determine the impact of such a treatment on the solubilization of these materials, as well as on their degradability under anaerobic conditions for methane production. For this purpose, a number of batch assays were conducted, in which different reagent dosages, process durations and temperatures were adopted. Pretreatment was applied using eight different chemical reagents, i.e. NaOH, $NaHCO_3$, NaCl, H_3Cit, AcOH, H_2O_2, Me_2CO and EtOH, in order to also determine the influence of different reagent natures (alkaline, acidic, saline, oxidative, organic) on the final results. Materials solubilization was assessed by analyzing the liquid fractions obtained after pretreatment for soluble chemical oxygen demand and total phenols concentrations, while Biochemical Methane Potential (BMP) assays were adopted for determining the methane potential of solid pretreated samples.

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