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Pyrochars from bioenergy residue as novel bio-adsorbents for lignocellulosic hydrolysate detoxification

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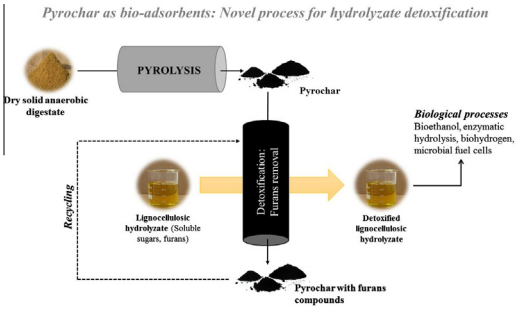
HIGHLIGHTS

- Pyrochar from digestate presented high surface area (>49 $m^2 g^{-1}$).
- At 40 g L^{-1}, more than 94% of furans compounds were removed.
- Pyrochars were effective in real lignocellulosic hydrolyzate detoxification.
- Pyrochars were selective towards furans compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

The robust supramolecular structure of biomass often requires severe pretreatments conditions to produce soluble sugars. Nonetheless, these processes generate some inhibitory compounds (*i.e.* furans compounds and aliphatic acids) deriving mainly from sugars degradation. To avoid the inhibition of the biological process and to obtain satisfactory sugars conversion level into biofuels, a detoxification step is required. This study investigates the use of two pyrochars derived from solid anaerobic digestates for the detoxification of lignocellulosic hydrolysates. At a pyrochar concentration of 40 g L^{-1}, more than 94% of 5-HMF and 99% of furfural were removed in the synthetic medium after 24 h of contact time, whereas sugars concentration remained unchanged. Furfural was adsorbed faster than 5-HMF by both pyrochars and totally removed after 3 h of contact. Finally, the two pyrochars were found efficient in the detoxification of corn stalks and Douglas fir wood chips hydrolysates without affecting the soluble sugars concentrations.

1. Introduction

The production of biofuels from lignocellulosic biomass by biological degradation is one of the routes that can contribute to a future sustainable bioenergy-based economy; the challenge is to find the appropriate microorganisms and enzymes that can convert lignocelluloses into bioenergy. Hence, the pretreatment of lignocellulosic biomass prior to biological attack is an essential step in order to increase lignocellulose accessibility and biodegradability. A large number of pretreatment methods have been developed until yet (Monlau et al., 2013). Chemical, physicochemical and thermo-chemical pretreatments are known to be effective on solubilization of carbohydrate polymers into soluble sugars (*i.e.* glucose, xylose, arabinose...) (Monlau et al., 2013; Sambusiti et al., 2013). However, these pretreatments generate also derived by-products, such as furans (*i.e.* furfural and 5-HMF) and aliphatic

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acids (*i.e.* acetic, formic and levulinic acids) (Monlau et al., 2014). Concentration of these compounds in lignocellulosic hydrolysates depends on various factors, including the type of biomass used, type of pretreatment and operational conditions applied (Monlau et al., 2014; Mussatto and Roberto, 2004; Barakat et al., 2012). Such compounds have been found to inhibit biological processes, (Palmqvist and Hahn-Hägerdal, 2000; Monlau et al., 2014). In general rules, the threshold inhibitory levels vary from microorganism to microorganism, but are generally around 1 g L^{-1}, whereas furfural was proved to be more toxic than 5-HMF (Monlau et al., 2014; Mussatto and Roberto, 2004). To avoid the inhibitory effect of furans and aliphatic acids, several processes for hydrolysate detoxification, including evaporation, adsorption on active charcoal, adsorption on ion exchangers, solvent extraction, alkaline treatment or enzymatic treatment, have been investigated (Mussatto and Roberto, 2004). Among these techniques, activated carbon adsorption has attracted attention due to its high sorption capacity (Zhang, 2011; Antoniou et al., 2014). Activated carbons (AC) are generally produced in two steps: char production through pyrolysis followed by a steam or chemical/thermal activation (Zabaniotou et al., 2014; Antoniou et al., 2014). The application of AC in lignocellulosic hydrolysate detoxification has been previously reported (Zhang, 2011; Sainio et al., 2011; Klasson et al., 2011, 2013). Nonetheless, the high production cost of AC remains often a limitation for it full-scale industrial implementation (Luo et al., 2015; Li et al., 2013).

A possible alternative is directly the use of pyrochar produced from lignocellulosic substrates and/or from bioenergy residues. Recently, Yao et al. (2012) have shown that a biological process like anaerobic digestion can play the role of "biological activation", by producing pyrochar with higher surface area. As the pyrochar production cost is considered no more than one tenth of AC, pyrochar produced from bioenergy residues could represent a low-cost adsorbent for detoxification processes (Luo et al., 2015). Until yet, pyrochar deriving from anaerobic residues (*i.e.* digestate) have been applied for organic or inorganics detoxification (*i.e.* heavy metals, dyes, herbicide...) (Sun et al., 2013; Inyang et al., 2012; Eibisch et al., 2015). Nonetheless, until now, no studies reported the use of anaerobically derived pyrochar for detoxification of hydrolysate containing soluble sugars and furan compounds and aliphatic acids.

Thus, the main objectives of this study were the following:

(i) Determination of the physicochemical characteristics of pyrochars derived from biogas residues.
(ii) Optimization of the pyrochar concentration and adsorption time for furans removal of a synthetic medium.
(iii) Study of the detoxification process on a full-scale derived lignocellulosic hydrolysate (*i.e.* corn stalks, Douglas-fir wood chips).

2. Method

2.1. Feedstocks

Solid digestates used for pyrochars production were collected from two full-scale biogas plants located in Southern Italy (Puglia region). The two anaerobic digesters worked at mesophilic conditions and were fed with a mixture of energy crops, crops residues and manure. The characteristics of the first anaerobic digester (AD1) were: digester volume of 3720 m^3, feeding of 56 t FM d^{-1} and an Hydrolytic Retention Time (HRT) of 62 days. The characteristics of the second anaerobic digester (AD2) were: digester volume of 5840 m^3, feeding of 120 t FM d^{-1} and an HRT of 53 days. Once collected, digestate samples were dried overnight at 105 °C, prior to physicochemical characterization and pyrolysis experiments.

Table 1
Main chemical characteristics of solid digestates (AD1 and AD2) (values correspond to mean ± SD of measurement performed in duplicate).

Parameters	AD1	AD2
TS (g 100 g^{-1} FM)	29.7 (±1.1)	24.0 (±0.3)
VS (g 100 g^{-1} TS)	72.1 (±0.9)	71.2 (±0.2)
Ash (g 100 g^{-1} TS)	12.7 (±1)	10.0 (±0)
C (g 100 g^{-1} TS)	42.5 (±0.24)	43.0 (±0.07)
H (g 100 g^{-1} TS)	6.1 (±0.03)	6.2 (±0.03)
N (g 100 g^{-1} TS)	1.4 (±0.12)	1.3 (±0.03)
Cellulose (g 100 g^{-1} TS)	17 (±0.8)	17 (±0.9)
Hemicelluloses (g 100 g^{-1} TS)	10.1 (±1.4)	12.2 (±1.7)
Proteins (g 100 g^{-1} TS)	8.8 (±0.75)	8.1 (±0.2)
Klason lignin (g 100 g^{-1} TS)	31.9 (±1.8)	34.0 (±1.2)
Cri (%)	76.4	53.8

Corn stalks and Douglas-fir wood chips, used for hydrolysate production, were collected from a farm and a cooperative company (Brassac Industries) located in the south of France, respectively.

2.2. Lignocellulosic hydrolysates production

Corn stalks and Douglas-fir wood chips hydrolysates were obtained through a diluted acid pretreatment performed in a batch reactor Paar® 5500 (Anton Paar, USA) with a total volume of 500 mL, equipped with a thermal heater, a manometer, a temperature controller and a stirrer system (Anton Paar, USA).

The hydrolysate from corn stalks was obtained by soaking sample (7.5 gTS) in 100 mL of H_2SO_4 solution (5% w/w) at 150 °C for 30 min (30 min was required to reach the desired test temperature), under stirring conditions. The pressure reached the value of 6 bar when sample was heated at 150 °C.

The hydrolysate from Douglas-fir wood chips was obtained by soaking sample (10 gTS) in 200 mL of H_2SO_4 solution (0.52% v/v) for one night at ambient temperature. Then, the soaked sample was pretreated at 190 °C for 7.5 min (1 h was required to reach the desired test temperature), without stirring. The pressure reached the value of 8 bar when sample was heated at 190 °C. After pretreatments, samples were centrifuged at 5000 rpm for 15 min at room temperature and the separated hydrolysate fractions were collected.

2.3. Pyrochars production

Pyrolysis experiments were performed in a quartz rotary kiln reactor, fed with 10 g of dry solid digestate. Then, the reactor was purged with nitrogen under steady flow (100 mL min^{-1}) for 30 min to ensure an oxygen free environment. The experiments were carried out at 600 °C, with a heating rate of approximately 20 °C min^{-1} at atmospheric pressure and inert atmosphere, while the residence time at the maximum temperature was 10 min. Pyrochar was weighted after collection and dried overnight at 105 °C for further physicochemical characterization.

2.4. Analytical determinations

Total Solids (TS), Volatile Solids (VS) and ash were determined according to the APHA standard method (APHA, 2005). The pH of pyrochars was measured after the addition of de-ionized water (mass ratio 1:20). The solution was then hand-shaken and allowed to stand for 5 min before measuring the pH, using a pH meter (Mettler Toledo FE20®).

Cellulose, hemicelluloses and klason lignin content was measured using a strong acid hydrolysis method adapted from NREL protocol (Sluiter et al., 2007). The C, H and N content was determined using an elementary analyzer Elementar VarioMacroCube.