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Short Communication

Limited adsorption selectivity of active carbon toward non-saccharide compounds in lignocellulose hydrolysate

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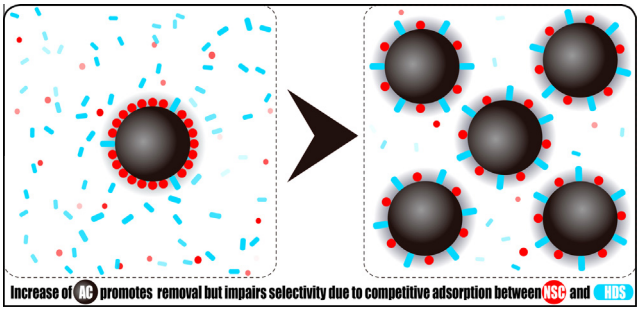
HIGHLIGHTS

- Wood hydrolysate contains abundant hemicellulose-derived saccharides (HDS).
- Activated carbon (AC) was used to purify HDS from non-saccharide compounds (NSC).
- Competitive adsorption between HDS and NSC resulted in limited selectivity.
- Adsorption of oligomeric HDS was dominant while monomeric HDS was negligible.

GRAPHICAL ABSTRACT



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ABSTRACT

Prehydrolysis of lignocellulose produces abundant hemicellulose-derived saccharides (HDS). To obtain pure HDS for application in food or pharmaceutical industries, the prehydrolysis liquor (PHL) must be refined to remove non-saccharide compounds (NSC) derived from lignin depolymerization and carbohydrate degradation. In this work, activated carbon (AC) adsorption was employed to purify HDS from NSC with emphasis on adsorption selectivity. The adsorption isotherms showed the priority of NSC to be absorbed over HDS at low AC level. However, increase of AC over 90% of NSC removal made adsorption non-selective due to competitive adsorption between NSC and HDS. Size exclusion chromatography showed that the adsorption of oligomeric HDS was dominant while monomeric HDS was inappreciable. The limited selectivity suggested that AC adsorption is infeasibility for HDS purification, but applicable as a pretreatment method.

1. Introduction

In the prehydrolysis-kraft process for dissolving pulp production, the majority of hemicellulose is dissolved into prehydrolysis liquor (PHL) (Krogell et al., 2013; Rissanen et al., 2014; Wang et al., 2015b). These hemicellulose-derived saccharides (HDS) in PHL are high value products but conventionally end up burning with concentrated black liquor for the recovery of chemicals and energy. In the view of biorefinery, the separation of HDS from PHL provides an alternative of PHL utilization with great economic and environmental benefits (Bujanovic et al., 2012; Chen et al., 2014). However, an effective and selective separation is required because a diverse set of non-saccharide compounds (NSC) from lignin depolymerization and carbohydrate degradation are present in PHL.

Various methods have been proposed to remove NSC from PHL. Adsorption by activated carbon (AC) is one of the most frequently used methods due to the remarkable adsorption capacity and the

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simplicity in operation (Liu et al., 2014). The adsorption of lignin and associated impurities by three commercial AC was investigated by Montané et al. (2006) for xylo-oligosaccharides separation from autohydrolysis liquor of almond shells. This work revealed that the increase of AC elevated the removal of lignin-derived species to 80%, but also resulted in significant carbohydrates loss. The study of Shen et al. (2012) showed strong affinity of lignin on AC surface, but great loss of oligosaccharides at the same time. The undesired loss of oligosaccharides was attributed to lignin–hemicellulose complex that a portion of the adsorbed oligomeric sugars on AC were covalently bonded to lignin. As well acknowledged, NSC in PHL includes phenolic compounds from lignin depolymerization, but also furfurals, HMF, and acetic acid from carbohydrates degradation. For bioconversion of HDS to ethanol, NSC is toxic to microorganisms and has to be eliminated. The study of Lee et al. (2011) demonstrated the sugar loss of 8.9% in the detoxification process at 2.5% AC. More importantly, the adsorption of HMF and furfural followed classical isotherm models but saccharides did not, which was inexplicable. Considering PHL is a multi-components system and the adsorption of organic solutes onto AC is a complex process, singular, binary and ternary systems were prepared by making a model PHL solution containing commercial available monosaccharides, xylan, lignin, and furfural (Fatehi et al., 2013). The results of AC absorption showed that the overall adsorption level of organics on AC was higher in multi-component than singular model systems, but the adsorption level of individual component was lower or higher as a result of competitive adsorption. Similarly, the competitive adsorption of furfural and phenolic compounds onto AC in fixed bed column was reported by Sulaymon and Ahmed (2007).

Since PHL contains multiple solutes, the presence of one component might promote or suppress the adsorption of other components, which affects the dynamic equilibrium and adsorption selectivity. To facilitate the study on competitive adsorption, all solutes in PHL were classified into two groups, namely HDS and NSC. HDS includes all monomeric saccharides and oligomeric saccharides. NSC includes mainly degradation products from lignin and carbohydrate in lignocellulose, e.g. phenolic compounds, furfural, HMF, acetic acid and formic acid. Such unrefined classification is quite simple but considered to be helpful for the evaluation of adsorption selectivity and the optimization of the separation process in a competitive and dynamic system.

2. Methods

2.1. Materials

Commercial AC DARCO G60 in powder form with 100 mesh particle size was supplied by Sigma–Aldrich, Inc. DARCO G60 has a total surface area of 600 m^2/g with mean pore radius of 25 Å. The methylene blue adsorption of DARCO G60 was 15 g/100 g (Hung et al., 2007).

2.2. PHL preparation

PHL was prepared in laboratory using a circulation type laboratory pulping digester with a reaction vessel of 20 L in size (Greenwood Instruments, LLC. Canada). Prehydrolysis of 1.0 kg wood chips of *Populus*×*euramericana* 'Neva' was conducted at 170 °C for one hour with wood to water ratio of 1:6 (w/w) (Wang et al., 2015a). At the end of prehydrolysis, PHL was collected at the reaction temperature of 170 °C from a drain valve which was connected to a condenser. The chemical compositions of PHL were listed in Table 1. HDS in PHL consisted of oligosaccharides and monosaccharides with a total concentration of 13.09 g/L. NSC consisted of a variety of organics resulted from lignin depolymerization and carbohydrates degradation. Soluble lignin, main constituents of NSC, was composed by a inhomogeneous mixtures with high polydispersity, thus intractable to be quantified except some low-molecular-weight phenolic compounds as listed in Table 1. To obtain accurate amount of NSC, total dissolved solid (TDS) was measured, and NSC was quantified by an indirect way to be 7.82 g/L as the difference of TDS (20.91 g/L) and HDS (13.09 g/L). This way, some volatile substances other than water in PHL were excluded from NSC because TDS was measured on 105 °C dry weight basis.

2.3. AC adsorption

Adsorption experiments was conducted in batch mode. Aliquots of 20 ml of PHL were filtered through o.22 μm nylon membrane and placed in 100 ml test tubes. Appropriate amount of AC was added from 0.1 to 2.0 g with various AC levels of 5, 10, 20, 40, 50, 60, 80, 90, and 100 g/L. The tubes were capped and placed in an air bath at 25 °C, attached perpendicularly with clamps to a horizontal revolving shaft that had a rotating speed of 60 rpm. After 2 h, the tubes were removed from the bath and the mixture was centrifuged at 12,000 rpm for 10 min to remove AC. Aliquots of supernatant liquid were filtered through a 0.22 μm nylon syringe filter, placed in an encapsulated vial, and stored at 5 °C until analysis.

2.4. Analytical methods

TDS was measured on a 105 °C dry weight basis (Sluiter et al., 2008). Soluble lignin was determined via UV/Vis spectroscopy at 240 nm with absorptivity of 25 L/g cm after appropriate dilution of PHL with 3% H_2SO_4 (w/w) (Crocker, 2008).

Monosaccharides in PHL were determined using a Dionex (Sunnyvale, CA) HPLC system (ICS-5000) equipped with a GP40 gradient pump, an anion exchange column (CarboPac PA20 and a guard) and an ED40 electrochemical detector (Wang et al., 2015b). Aliquot of 25 μL was injected manually after passing through a 0.2 μm nylon syringe filter. Gradient was set as 2 mM NaOH isocratic with a step to 200 mM NaOH at 10 min to regenerate the column at a flow rate of 0.5 mL/min and 25 °C. Monosaccharides were quantified with reference to standards using the same analytical procedure. Oligosaccharides were determined by an indirect method based on quantitative acid hydrolysis of the liquid samples with 4% w/w of H_2SO_4 at 120 °C for 60 min according to NREL technical report (Sluiter et al., 2006). The concentrations of oligosaccharides were reported as the increase of monosaccharides.

The concentration of 4-hydroxybenzoic acid, vanillin, syringaldehyde, guaiacol, formic acid, acetic acid, levulinic acid, furfural, and HMF were measured using a Shimadzu LC-20T HPLC system equipped with a Waters C18 symmetry column (4.6 × 150 mm, 5 μm) and a UV detector. Samples were run at 30 °C and eluted at 1.0 mL/min^{-1} with a gradient elution mode of mobile phase A and B as detailed in Electronic annex Table S1. Mobile phase A was a mixture of 0.02 mol/L NaH_2PO_4 and acetonitrile with a volume ratio of 95:5 at pH 2.8 adjusted by H_3PO_4. Mobile phase B was a mixture of acetonitrile and methanol with a volume ratio of 50:50. All analyses were carried out in duplicates at a minimum. The average data were reported. The standard deviations were calculated as measurement errors.

The molecule weight distribution of the HDS and NSC in liquid samples was analyzed by size exclusion chromatography (SEC) on an HPLC system comprising Shimadzu LC-20T, Shimadzu SB-803 HQ column (8 × 300 mm, 6 μm), UV detector and refraction index (RI) detector using 0.05 mol/L KNO_3 as mobile phase at 0.5 mL/min