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Adsorption of lignocelluloses of model pre-hydrolysis liquor on activated carbon

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HIGHLIGHTS

- Pre-hydrolysis liquor was prepared using commercial sugars, lignin and furfural.
- Furfural and xylose had the highest and lowest adsorption levels on AC.
- Experimental results were most fitted into Langmuir and pseudo-second order models.
- Addition of PDADMAC to pre-hydrolysis liquor increased the adsorption on AC.

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ABSTRACT

The main objective of this work was to study the adsorption behavior of various components dissolved in the pre-hydrolysis of kraft process on activated carbon. In this work, model prehydrolysis liquor (PHL) solutions (MPHL)s were prepared via mixing various commercially available monosugars, xylan, lignin and furfural; and their adsorption performance on activated carbon (AC) was investigated. In singular (one component) MPHL/AC systems, furfural had the maximum and xylose had the minimum adsorption, and the adsorption of monosugars was basically similar on AC. Also, polydiallyldimethylammonium chloride (PDADMAC) was added (0.5 g/l) to singular xylan or lignin MPHL/AC system, which increased the lignin and xylan adsorptions to 350 and 190 mg/g on AC, respectively.

1. Introduction

Today, pulp and paper industry has remarkably lost its market in North America due to a substantial decrease in the consumption of some paper grades, e.g. newsprints. The production of value-added chemicals from raw materials or the wastes of pulp industry is an alternative to increase the revenues of pulping process, which will convert it to a biorefinery plant (Huang et al., 2010; Kaylen et al., 2010).

In the production of dissolving pulp based on kraft technology, the pre-hydrolysis liquor (PHL), which is produced via steaming wood chips, is currently mixed with black liquor and sent to recovery boiler, i.e. wasted (Saeed et al., 2012; Shi et al., 2011). However, PHL contains approximately 3–5% organics that can be utilized in the production of value-added chemicals (e.g. additives from hemicelluloses and phenolic compounds from lignin), but the noticeable water content of PHL makes its possible downstream processes unattractive (Kohnke et al., 2008; Ren et al., 2009; Saeed et al., 2012; Silva et al., 2011). In the past, a solvent extraction has been employed in laboratory scales to isolate lignocelluloses from various spent liquors (Liu et al., 2011). However, the present problem of solvent recovery constrained the commercialization of this technology. Alternatively, ultrafiltration has been used for separating the lignocelluloses from spent liquors. However, its unselectivity and inefficiency limited its industrial application (Wallberg et al., 2003). Alternatively, adsorption concept was employed to separate the lignocelluloses of spent liquors (Chaichanawong et al., 2010; Radovic et al., 2000). It was previously shown that activated carbon (AC) was an efficient adsorbent for the lignocelluloses of PHL (Liu et al., 2012). Although the changes in the experimental conditions varied the performance of AC for adsorbing lignocelluloses from industrial PHL (Liu et al., 2011), they did not help identify the adsorption performance of each individual component on AC. This

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is because PHL is a mixture of different lignocelluloses, and the adsorption of one component was followed with that of others (Liu et al., 2011). On the other hand, the adsorptions of furfural and lignin dissolved in various solutions have previously been assessed on AC (Berson et al., 2005; Fierro et al., 2008; Sahu et al., 2008; Srivastava et al., 2006), but they were not carried out under the conditions of PHL, e.g. concentrations. As such, those results cannot be practically applied to predict the adsorption performance of lignocelluloses of PHL on AC. The first objective of this work was to study the adsorption behavior of each individual component of PHL on AC.

As PHL is a mixture of different organics (Li et al., 2010; Saeed et al., 2011), the presence of one component, e.g. lignin, might affect the adsorption of other components, e.g. xylan, on AC. The second objective of this study was to evaluate if the presence of different organics, namely xylose, xylan, lignin and furfural, would affect their individual adsorption on AC.

It was previously reported that industrially produced PHL contains approximately 10 g/l mono-sugars (xylose, rhamnose, fructose, glucose, galactose, mannose and arabinose), 10 g/l lignin, 10–15 g/l oligo-sugars, 10 g/l acetic acid and less than 10 g/l furfural (Saeed et al., 2012). It was also reported that acetic acid was not adsorbed on AC (Liu et al., 2011), thus was excluded from this study. In this work, various commercially available sugars, lignin and furfural were mixed in order to produce a model PHL (MPHL) at low concentrations, and the adsorption performance of these components assessed on AC in singular, binary and ternary MPHL systems under different process conditions.

2. Methods

2.1. Materials

Analytical grades of xylose (D-(+)-xylose, >99%), rhamnose (L-rhamnose monohydrate, >99%), fructose (D-(−)-fructose, >99%), glucose (D-(+)-glucose, >99%), galactose (D-(+)-galactose, >99%), mannose (D-(+)-mannose, >99%), arabinose (L-(+)-arabinose, >99%), xylan (from beech), poly(β-D-xylopyranose[1→4]), kraft lignin (low sulphonated degree, 4% sulfur), furfural (>99%), were all purchased from Aldrich company and diluted to 40 g/l solution (pH 7) prior to use. The molecular weight of these components was reported as obtained from Aldrich. Polydiallyldimethylammonium chloride (PDADMAC) solution (20% weight) with a molecular weight ranging from 400 to 500 kDa was also purchased from Aldrich Company and used as a flocculant and for charge density analysis. Standard solutions (1 mol) of HCl and NaCl, as well as the powder of Na_2CO_3, $NaHCO_3$ (>99%), and Na_2SO_4 (>99.0%, anhydrous, granular) were purchased from Aldrich company. Activated carbon (animal bone charcoal) was obtained from Carvao ativado do Brasil Ltda.

2.2. Characterization of AC

The BET surface area of AC was determined via nitrogen adsorption/desorption isotherms using a BELSORP-max (BEL Inc). About 0.1 g (o.d.) of AC was pretreated at 120 °C and 10^{-7} Torr overnight for contamination removal. Afterwards, the measurement was carried out using Nitrogen, as a probe, at 77 K overnight. The isotherm data was recorded in a relative pressure of P/P_0 in the range of 10^{-7}–0.99999 and then the BET specific surface area of AC was determined from the adsorption isotherms.

The acidic and basic groups of AC were determined by following the Boehm's method (1996): this method is based on acid/base titration of carbon acidic or basic centers. First, 0.6 g of adsorbent was added to 15 ml of 0.1 mol/L $NaHCO_3$, Na_2CO_3, NaOH or HCl solutions and the mixtures were shaken for 24 h at room temperature. Then, 5 ml of supernatant was titrated with 0.1 mol/L of HCl or NaOH solution at room temperature (Kato et al., 2007).

2.3. Charge density analysis

The charge density of organic materials was determined using a Particle Charge Detector, Mütek PCD 03 titrator (Herrsching, Germany) with a PDADMAC solution (1 mM), as previously demonstrated (Liu et al., 2011).

2.4. Model pre-hydrolysis liquor (MPHL) preparation

As explained in the introduction, industrial PHL contains less than 5 wt%. organics containing monosugars, xylan, lignin and furfural (Saeed et al., 2012). MPHL singular solutions were prepared via diluting xylose, xylan, lignin and furfural solutions (40 g/l) to different concentrations, i.e. 5, 10, 15, 20 and 30 g/l.

Hardwood is the main raw material for the production of kraft-based dissolving pulp process, and thus the main hemicellulose of PHL is xylan (Liu et al., 2011; Saeed et al., 2012). Therefore, xylan was one component of all binary and ternary MPHL solutions. By mixing 40 ml of xylan solution (20 g/l) with 40 ml of xylose, lignin or furfural solutions (20 g/l), 80 ml of MPHL binary solutions (20 g/l) were prepared (thus, the concentration of each component was 10 g/l in the binary MPHL solutions). By mixing 40 ml of xylan solution (30 g/l) with two of the three 40 ml of xylose, 40 ml of lignin and 40 ml of furfural solutions (30 g/l), 120 ml of ternary MPHL solution of 30 g/l was produced (thus, the concentration of each component was 10 g/l in the ternary solutions). The pH of all solutions was 7, as this was the optimum pH for the adsorption of lignocelluloses of industrial PHL on AC (Liu et al., 2011; Sahu et al., 2008; Srivastava et al., 2006).

2.5. Adsorption on AC

To investigate the adsorption performance of various monosugars, i.e. xylose, mannose, fructose, arabinose, galactose, glucose and rhamnose, two different concentrations of 5 and 15 g/l monosugars were prepared in singular MPHL solutions, and 50 ml of these solutions were mixed with 1 g of AC for 120 min. To investigate the adsorption isotherms of xylan, xylose, lignin and furfural on AC, 50 ml of xylan, xylose, lignin and furfural singular MPHL solutions having various concentrations were mixed with 1 g of AC for 360 min. To investigate the adsorption kinetic of xylan, xylose, lignin and furfural on AC, 50 ml of the singular MPHL solutions (20 g/l) were mixed with 1 g of AC and mixed for various time intervals. To investigate the effect of salt on the adsorption, 50 ml of the MPHL singular solutions (20 g/l) were mixed with 1 g of AC for 360 min, while the concentration of Na_2SO_4 was ranged from 0 to 0.4 mol. Na_2SO_4 salt was selected, as it presents in black liquor of the kraft process and can easily contaminate industrial PHL.

Alternatively, to assess the adsorption performance of binary and ternary MPHL solutions on AC, 50 ml of the binary or ternary MPHL solutions were mixed with 1 g of AC for 360 min. All the aforementioned experiments were conducted at pH 7, room temperature in 250-mL Erlenmeyer flasks and shaken for 120 min in a New Brunswick water bath shaker. After mixing, the supernatants were separated from the MPHL/AC systems via filtering with Whatman cellulose nitrate membranes (0.45 μm pore size). The supernatants were kept for sugar, lignin and furfural analyses. All the above analysis was repeated 5 times and the average values were reported. In this work, the experiments were conducted 5 times, the average values were reported and the variations in the results were stated in Tables 1 and 2 and Figs. 1–3. Also, the experimental results were fitted