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Separation of lignocelluloses from spent liquor of NSSC pulping process via adsorption

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ABSTRACT

Hemicelluloses and lignin present in the spent liquor (SL) of neutral sulfite semichemical (NSSC) pulping process can potentially be converted into value-added products such as furfural, hydroxymethylfurfural, levulinic acid, phenols and adhesives. However, the direct conversion of hemicelluloses and lignin of SL into value-added products is uneconomical due to the dilute nature of the SL. To have a feasible downstream process for utilizing lignocelluloses of SL, the lignocelluloses should initially be separated from the SL. In this study, an adsorption process (via applying activated carbon) was considered for isolating the dissolved lignin and hemicelluloses from the SL of an NSSC pulping process. Under the optimal conditions of pH, SL/AC weight ratio, time and temperature of 5.7, 30, 360 min and 30 °C, the maximum lignin and hemicellulose adsorptions were 0.33 and 0.25 g/g on AC. The chemical oxygen demand (COD) and turbidity of the SL were decreased by 11% and 39%, respectively, as a result of lignocellulose adsorption on AC. Also, the incineration behavior of the SL-treated AC was studied with a thermo-gravimetric analysis (TGA).

1. Introduction

The depletion and rising price of oil as well as environmental concerns have challenged the production and use of oil-based chemicals (Dashtban et al., 2009, 2012). The substitution of oil-based chemicals with bio-based chemicals was proposed as an alternative to address these difficulties. In this regard, the production of bio-based chemicals and biofuel in biorefinery scenarios from biomass has attracted great attentions (Fatehi, 2013).

In an NSSC pulping process, wood chips are initially treated with chemicals in order to soften the structure of wood chips, and subsequently the pretreated wood chips are refined by mechanical disintegration (Benjamin et al., 1969). The main product of this process is corrugated medium paper, while the hemicellulose and lignin dissolved in the spent liquor (SL) of the pretreatment stage are handled in the wastewater systems (i.e. the lignocelluloses are wasted) (Dashtban et al., 2012). However, these lignocelluloses could be used as feedstock for the production of value-added chemicals (e.g. furfural, hydroxymethylfurfural, levulinic acid, phenols or adhesives), which would in turn increase the revenues of this pulping process (Dashtban et al., 2012; Saeed et al., 2011).

However, the SL is very dilute, and its direct use as a raw material for producing value-added chemicals is infeasible (Fatehi et al., 2013a). One alternative to address this difficulty is to extract lignocelluloses from the SL in order to facilitate their applications in various products. Different strategies were proposed for serving this purpose including solvent extraction (Chen and Liu, 2007), ultrafiltration (Jonsson et al., 2008), and adsorption using activated carbons (AC) (Liu et al., 2011a, b). Although solvent extraction was previously applied for isolating lignocelluloses at lab scales (Liu et al., 2011a, b), the challenges associated with solvent recovery make its commercialization unattractive (Fatehi et al., 2013a). Ultrafiltration was also unselective and inefficient in separating the lignocelluloses from spent liquors (Egüés et al., 2012; Wallberg et al., 2003).

Previously, adsorption process showed promising results in separating lignocelluloses from various spent liquors (Fatehi et al., 2013a,b,c; Liu et al., 2011a, b, 2012). Adsorption is a well-established process for removing organic materials (e.g. phenols and hydrocarbons) from aqueous solutions (e.g. drinking water and/or wastewater) at industrial scales (Lashaki et al., 2012; Moreno-Castilla, 2004; Symons, 1978). In this respect, extensive research was carried out to investigate the adsorption of different phenolic compounds (i.e. gallic acid, *p*-hydroxybenzoic acid and syringic acid) dissolved in various wastewaters on activated carbon (Garcia-Araya et al., 2003; Gonen and Aksu, 2003; Moreno-Castilla, 2004; Ravi et al., 1998; Sulaymon and Ahmed, 2008, 2013).

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Furthermore, the adsorption of lignocelluloses on activated carbon (Fatehi et al., 2013a), calcium carbonate (Fatehi et al., 2013b) and calcium oxide (Shi et al., 2012) from pre-hydrolysis liquor (PHL) of a kraft-based dissolving pulp process was assessed in the past. However, as PHL and SL have different properties and compositions, the results of these studies cannot be practically applied to simulate the adsorption performance of lignocelluloses of SL on AC. In this paper, the adsorption performance of lignocelluloses dissolved in the SL of an NSSC pulping process on activated carbon was analyzed for the first time, which could ultimately help develop an integrated process for producing value-added chemicals from the lignocelluloses of the SL. It will also help reduce loads to the wastewater system of the NSSC process. To achieve this goal, the adsorption of lignocelluloses of SL on two activated carbons was initially investigated, and the adsorption conditions were optimized for the selected activated carbon. The impact of the adsorption process on the COD and turbidity of SL was also investigated. Furthermore, the incineration behavior of treated AC with lignocelluloses was assessed.

2. Materials and methods

2.1. Materials

The analytical grades of furfural (>99%), acetic acid (>99%) and glucose (>99%) were obtained from Sigma Aldrich. Activated carbons with two different grades were purchased from Fisher Scientific (AC1: catalog number 05690B) and Sigma Aldrich (AC2: catalog number C2764). Polydiallyldimethylammonium chloride (PDADMAC) with a molecular weight ranging 100–200 kDa was purchased from Sigma Aldrich, while polyvinylsulfate potassium (PVSK) with a molecular weight of 170 kDa was purchased from Wako Chemicals Ltd., Japan. Both PDADMAC and PVSK were dissolved in 0.05% wt. solutions for a charge density analysis. The industrially produced SL (pH 5.7) was received from an NSSC pulping process located in eastern Canada.

2.2. Characterization of AC

The BET surface area of AC was determined via nitrogen adsorption/desorption isotherms using a Nova 2200e. At first, 0.05 g (o.d.) of ACs was treated overnight at 120 °C and 10^{-7} Torr for contamination removal, and the analysis was conducted on the pretreated ACs (Fatehi et al., 2013a). Furthermore, elemental analysis was performed using a Vario EL Cube Instrument (Germany) according to the method established previously (Fadeeva et al., 2008). In this method, the AC samples were weighed and loaded in an integrated carousel. First, the AC samples were flushed with a carrier gas (He). Subsequently, the combustion of ACs was carried out, which was followed by the reduction of the combusted gases so that the produced gases could be identified with the instrument and eventually elemental balance of the ACs could be developed (Fadeeva et al., 2008). On the other hand, the charge density analysis of ACs was carried out using a particle charge detector, Mütek PCD-04 (Herrsching, Germany) with a PDADMAC and PVSK solutions (5 mM), as previously described (Liu et al., 2011a).

2.3. AC adsorption process

The adsorption performance of hemicelluloses and lignin from SL on the ACs was assessed under different conditions. At first, 1 g of ACs was added to 30 g of SL in 250 mL Erlenmeyer flasks and incubated at 30 °C for 360 min at 100 rpm in a Boekel Scientific water bath shaker. Afterwards, the samples were centrifuged at 2000 rpm for 10 min so that supernatants (treated SL) could be separated from the ACs. The supernatants were kept for hemicelluloses, lignin, turbidity and chemical oxygen demand (COD) analyses. A comparison between the lignocelluloses of SL before and after the adsorption experiments was considered for determining the amount of lignocelluloses adsorbed on ACs. The pH of the SL after the adsorption was tested, and the results showed that the pH of SLs was negligibly changed during the adsorption experiments. These results assisted in identifying the more efficient AC (i.e. AC2). Subsequently, the effects of SL/AC ratio, pH, time and temperature of the adsorption experiment on the performance of the selected AC were investigated. To investigate the effect of pH on adsorption, the pH of SL (5.7) was adjusted to a lower value (pH 3.0) by adding 4% H_2SO_4 or a higher value (pH 11.0) by adding NaOH (1 M). Identical SL samples with the same pH value, but without any AC2 treatment, were prepared as control samples for comparison. The impact of dosage on the adsorption was studied using the selected AC2 by varying the weight ratios of SL to AC (e.g. 45, 90, 120 and 180) at the optimal pH (5.7), temperature (30 °C) and time (360 min). The kinetic of adsorption was studied using AC2 with the SL/AC weight ratio of 30 at pH 5.7 and 30 °C but at different adsorption time intervals. To investigate the effect of temperature, the adsorption experiment was conducted at a temperature range of 30–70 °C, while the pH, time and SL/AC wt. ratio were 5.7, 90 min and 30, respectively. All the above adsorption experiments were repeated 3 times and the average values are presented in this paper.

2.4. Hemicellulose analysis of SL

To measure the hemicelluloses content of SL (before and after treating with AC), all the oligomeric sugars were converted to monomeric sugars via treating the samples with 4 wt% sulfuric acid at 121 °C for 1 h in an oil bath (Fatehi et al., 2013a). Then, the sugar concentration of the SL samples was determined via using a microplate-based method by applying 3,5-dinitrosalicylic acid (DNS reagent), as described in the literature (Dashtban et al., 2011).

2.5. Ash and lignin analyses of SL

The ash content of the SL was determined according to TAPPI T412, while the lignin content of SLs was determined according to TAPPI UM 250 with a UV spectrophotometry (GENESYS 10S UV–Vis) at 205 nm (Liu et al., 2011a,b).

2.6. Furfural and acetic acid analyses of SL

Furfural and acetic acid contents of SL were determined with ^{1}H NMR using a Varian Unity Inova 500 MHz spectrometer according to a previously established method (Liu et al., 2011a; Saeed et al., 2012a,b). Furfural and acetic acid standard solutions were prepared to generate calibration curves required for determining furfural and acetic acid concentrations in SLs.

2.7. Turbidity and COD analyses

The turbidity and chemical oxygen demand (COD) of the original SL and the SL that corresponded to the optimal adsorption experiment (30 SL/AC wt. ratio, pH 5.7 at 30 °C for 360 min) were determined in order to identify maximum effect of AC treatment on the SL (Saeed et al., 2011). The COD analysis of the aforementioned SL samples was carried out using a COD kit (0–1500 mg/L) obtained from CHEMetrics Inc., USA, according to ASTM D1252-06. In this set of experiments, the SLs were mixed with the premixed chemicals (as received from CHEMetrics) and then incubated in a block digester at 150 °C for 2 h. Afterwards, the absorbency of the samples was determined at 620 nm. The turbidity of the SL samples was