Bioresource Technology 159 (2014) 373–379

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

A combined adsorption and flocculation process for producing lignocellulosic complexes from spent liquors of neutral sulfite semichemical pulping process

Mehdi Dashtban [a,b], Allan Gilbert [b], Pedram Fatehi [b,*]

[a] Biology Department, University of Guelph, 50 Stone Road East, Guelph, Ontario N1G 2W1, Canada
[b] Chemical Engineering Department, Lakehead University, 955 Oliver Road, Thunder Bay, Ontario P7E 5E1, Canada

HIGHLIGHTS

- Lignocelluloses of NSSC pulping process was removed by adsorption and flocculation.
- Maximum turbidity and COD reductions of SL were 39% and 79%.
- Lignin and hemicellulose adsorptions reached 2.5 and 0.5 g/g for PDADMAC/SL/AC.
- MW of PDADMAC affected the properties of complexes and SL significantly.

ARTICLE INFO

Article history:
Received 8 January 2014
Received in revised form 27 February 2014
Accepted 1 March 2014
Available online 12 March 2014

Keywords:
Lignin
Hemicellulose
NSSC
Biorefinery
Adsorption

ABSTRACT

The spent liquor (SL) of a neutral sulfite semichemical pulping process contains lignocelluloses that are currently treated in a waste water system. In this work, an adsorption process using activated carbon (AC) was considered for isolating the lignin and hemicelluloses from SL. The maximum adsorptions of 0.9 g/g lignin and 0.43 g/g of hemicelluloses on AC were achieved under the conditions of 30 °C, pH 7 and 3 h with SL/AC weight ratio of 90. The addition of polydiallyldimethylammonium chloride (PDADMAC) to the SL/AC system significantly improved the adsorption of lignin to 2.5 g/g on AC. The molecular weight of PDADMAC considerably affected the results in that the higher MW PDADMAC led to less lignin, but more hemicelluloses, turbidity and chemical oxygen demand removals from the SL. The thermal analysis also revealed that the higher MW PDADMAC generated precipitates with a lower incineration temperature and heating value.

1. Introduction

The rising cost of energy, environmental concerns and tight competitions have led pulping processes to seek for process alternatives in order to reduce their production costs and/or produce materials with considerable profits (Dashtban et al., 2012; Saeed et al., 2011). In this context, many processes are under development to convert pulping operations to forest biorefineries (Fatehi et al., 2013a; van Heiningen, 2006).

In a neutral sulfite semichemical (NSSC) pulping process, wood chips are pretreated with sodium sulfite and carbonate to soften the structure of wood chips. Subsequently, the pretreated wood chips are disintegrated by mechanical refining (Benjamin et al., 1969; Dashtban et al., 2012). In this process, a part of lignin and hemicelluloses is separated from wood chips in a pretreatment process and dissolved in the spent liquor (SL), which is treated in the waste water system of the mill (Area et al., 2000a,b). Alternatively, these separated lignin and hemicelluloses of SL can be used as the feedstock for the production of value-added products, which will ultimately increase the revenue of this pulping process (Dashtban et al., 2012; van Heiningen, 2006). However, the SL is very dilute and contains cooking chemicals (i.e. inorganics) that hinder the direct use of SL for producing value-added chemicals in downstream processes (Fatehi et al., 2013a). To facilitate the application of these components, they should be first extracted from the SL. In the past, solvent extraction and ultrafiltration have been proposed for the extraction of hemicelluloses from the spent liquors of different pulping processes (Chen and Liu, 2007; Jonsson et al., 2008). However, these processes face some difficulties such as high operational costs and challenging solvent recovery, which make them industrially unattractive (Wallberg et al., 2003). On

* Corresponding author. Tel.: +1 807 343 8697; fax: +1 807 346 7943.
E-mail address: pfatehi@lakeheadu.ca (P. Fatehi).

http://dx.doi.org/10.1016/j.biortech.2014.03.006
0960-8524/

the other hand, an adsorption process showed promising results in isolating lignin and hemicelluloses from spent liquors of kraft-based dissolving pulp process (Fatehi et al., 2013a; Liu et al., 2011, 2012).

Activated carbons possess a porous structure and large surface area, and thus are suitable candidates for adsorption at industrial scales (Lashaki et al., 2012; Moreno-Castilla, 2004). In the past, activated carbons were used for removing different organic materials (i.e. phenols and hydrocarbons) from aqueous solutions (e.g. drinking water and/or wastewater) (Lashaki et al., 2012; Moreno-Castilla, 2004). In one study, activated carbon adsorbed 231, 204 and 245 mg/g of hemicelluloses, lignin and furfural on an activated carbon from a model pre-hydrolysis liquor (Fatehi et al., 2013a). These results, however, cannot be practically applied for simulating the adsorption performance of lignocelluloses of SL on activated carbon since the chemistry and compositions of PHL and SL are different. The first objective of this work was to evaluate the performance of an adsorption process in isolating the lignin and hemicelluloses from the spent liquor of an NSSC process. In fact, this is the first attempt to systematically isolate the lignocelluloses of SL using adsorption concept.

Alternatively, to improve the adsorption of lignocelluloses on activated carbons, a combination of adsorption (using activate carbon) and flocculation (using polydiallyldimethylammonium chloride (PDADMAC)) were employed in the past (Liu et al., 2012), and the results showed 83.3% lignin, 32.7% hemicelluloses and 100% furfural removals from PHL, respectively. In this context, the application of PDADMAC as a flocculant for the lignocelluloses of SL was investigated (Sitter et al., 2014). The second objective of this study was to systematically assess the performance of a combined adsorption and flocculation process in isolating the lignin and hemicelluloses from SL. However, this process cannot accommodate the separate adsorption of lignin or hemicelluloses on activated carbon.

In this work, the lignin and hemicelluloses were systematically isolated from SL by means of adsorption or a combined system of adsorption/flocculation. In fact, this system is introduced for the first time ever to isolate the lignin and hemicelluloses from NSSC spent liquors. The isolated materials can be considered as fuel of the NSSC process or filler for use in the corrugated medium papers. In other words, the product of this process (i.e. precipitates of adsorption process) can be directly used as a value-added material in the NSSC process. More importantly, the reduction in the lignocellulose content of SL will lead to a lower load in the waste water system of the mill, which will help reduce the production costs of the NSSC process.

2. Methods

2.1. Materials

The analytical grades of furfural (>99%), acetic acid (>99%), glucose (>99%), activated carbon (catalog number#AC404045000), polydiallyldimethylammonium chloride (PDADMAC) with two molecular weights of 100–200 and 400–500 kDa, and poly vinylsulfate potassium salt (PVSK with the molecular weight of 170 kDa) were purchased from Sigma Aldrich. The spent liquor (SL) was received from an NSSC pulping process located in eastern Canada. In the NSSC process, wood chips are pretreated with sodium sulfite and carbonate with liquid to wood ratio of 5 (kg/kg) for 15–18 min at 180 °C prior to mechanical refining the treated wood chips. The SL is the supernatant of the pretreatment stage that was collected via filtering the pretreated wood chips prior to refining.

2.2. BET and charge density analyses

The BET surface area of AC was determined according to the previously described method (Fatehi et al., 2013a). Briefly, the AC surface area was determined via nitrogen adsorption/desorption isotherms using a Quantachrome Instrument, Nova 2200e, Florida, USA, using 0.1 g (o.d.) of AC. The AC was pretreated at 120 °C and 10^{-7} Torr overnight for contamination removal. The charge density analysis of AC was carried out using a particle charge detector, Mütek PCD-04 titrator (Herrsching, Germany) with a PDADMAC or PVSK solution (5 mM) as previously described (Liu et al., 2011).

2.3. Adsorption

To study the impact of pH on the adsorption performance of AC, the pH of original SL (5.7) was adjusted to 3.0 by adding 4 wt.% H_2SO_4 or to 7.0, 9.0 or 11.0 by adding 1 M NaOH solution. Then, the SLs were centrifuged at 2000 rpm (448 g) for 10 min to remove any precipitates due to the pH change. Subsequently, 1 g of AC was added to 30 g of these SLs in 250 mL Erlenmeyer flasks and incubated at 30 °C for 3 h at 100 rpm in a Boekel water bath shaker. To study the adsorption isotherm, various masses (15, 30, 45, 90, 120 and 180 g) of SL (with optimal pH of 7) was mixed with 1 g of AC at 30 °C and shaken for 180 min in the water bath shaker. To study the adsorption kinetics, 1 g of AC was mixed with 90 g of SL (having pH of 7) and incubated at 30 °C for various time intervals (10, 20, 30, 45, 60, 180, 360 and 1440 min) in the water bath shaker. Alternatively, the control of each sample was prepared (i.e. SL having the same pH, but without mixing with AC) and incubated under the same experimental conditions. After incubating, the SL samples were centrifuged at 2000 rpm (448 g) for 10 min so that the treated AC could be easily separated. The supernatants were kept for hemicelluloses, lignin, turbidity and chemical oxygen demand (COD) analyses. All of the above adsorption experiments were repeated three times and the average values were reported in this work. Also, the precipitates of the experiments conducted with 90 g of the SL (having pH of 7) and 1 g of AC at 30 °C for 3 h and 100 rpm was collected for TGA, calorimetric and CHNS analyses. As there is no method to determine the lignin and hemicelluloses of SL together, the lignin and hemicellulose concentrations were determined separately, and discussed in this work separately (Figs. 1–4).

2.4. Combined adsorption/flocculation

To improve the adsorption of lignin and hemicelluloses on AC, a combined adsorption and flocculation experiment was considered.

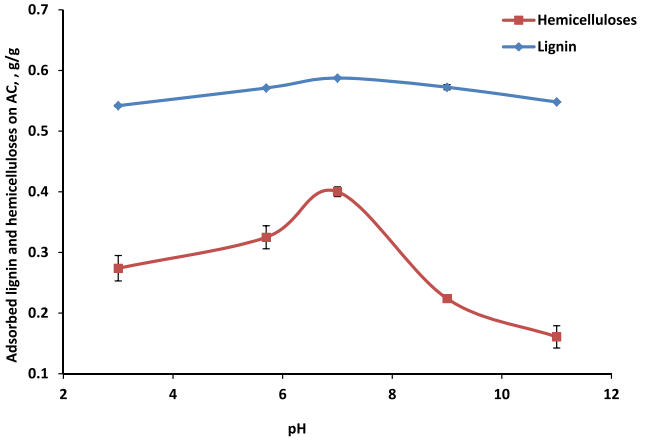

Fig. 1. Effect of pH on the adsorption performance of lignin and hemicelluloses of SL on AC (conducted at 30 °C, SL/AC wt. ratio of 30 at 100 rpm for 24 h).