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Simultaneously separation of xylo-oligosaccharide and lignosulfonate from wheat straw magnesium bisulfite pretreatment spent liquor using ion exchange resin

Lei Liu[a,b], Jiwei Ren[c], Yitong Zhang[a], Xinlu Liu[a], Jia Ouyang[a,d,*]

[a] *College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, People's Republic of China*
[b] *School of Biology and Environment, Nanjing Polytechnic Institute, Nanjing 210048, People's Republic of China*
[c] *College of Forestry, Nanjing Forestry University, Nanjing 210037, People's Republic of China*
[d] *Key Laboratory of Forest Genetics and Biotechnology of the Ministry of Education, Nanjing Forestry University, Nanjing 210037, China*

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ABSTRACT

For wheat straw, an ideal bio-refinery process is that all three major components of biomass could be efficiently utilized to make high value chemicals, MBSP could directly convert the hemicelluloses and lignin into xylo-oligosaccharides and lignosulfonate. However, these value-added compounds still present in spent liquor and thus should be isolated as an individual product. In present work, a simple and efficient ion exchange process was developed for separating xylo-oligosaccharides and lignosulfonate simultaneously from spent liquor. D354 resin was selected for its high adsorption capacity of magnesium lignosulfonate and remarkable selectivity. 93.09% of XOS and 98.03% of lignosulfonate were recovered from the treated spent liquor in a fixed bed column with D354 resin. Overall, 1 L of MBSP spent liquor could coproduce 9.5 g XOS and 74 g lignosulfonate. These results offer an opportunity for complete and effective utilization of biomass by a novel integrated process coupling of MBSP and ion-exchange process.

1. Introduction

During the past two decades, the conversion of agricultural wastes has drawn much attention for environmental problems and economic reasons (Sun and Cheng, 2002). However, due to their lignocellulosic nature, these wastes are difficult to be utilized directly (Alvira et al., 2010; Yu et al., 2014). In general, a pretreatment process is needed for isolating their three main components (hemicellulose, cellulose and lignin). A number of pretreatment methods have been developed for effective utilization of the agricultural waste (Sun and Cheng, 2002; Mussatto et al., 2008; Lan et al., 2013). But most of them are applied to make biomass amenable to enzyme hydrolysis by biomass deconstruction. They inevitably lead to the degradation of hemicelluloses or lignin and the efficient utilization of low-cellulose fractions is always an issue for commercialization of biomass bio-refining (Zhang, 2008). Therefore, in order to achieve the maximum benefit from these wastes, an ideal pretreatment should be developed to give separate streams that may be used for different high value-added productions (Yu et al., 2016).

In this background, a few studies on biomass utilization began to concern for co-utilization of lignin and hemicellulose (Huang et al., 2016). Auto-hydrolysis pretreatment using water as the only reagent seemed to demonstrate a better utilization of the biomass than many traditional pretreatments (Vargas et al., 2015; Michelin and Teixeira, 2016). By this pretreatment, hemicelluloses fraction could be depolymerized to xylo-oligosaccharides (XOS) simultaneously (Nabarlatz et al., 2007; Vargas et al., 2015). XOS is more valuable than xylose as a novel sweetener and functional foods (Garrote et al., 2008; Huang et al., 2016). Thus this pretreatment could improve the utilization of biomass by co-producing XOS. However, the valued outlet of lignin is still a key issue for the complete utilization of biomass. On the other hand, as a by-product of the pulping industry, lignosulfonate has been successfully used in various applications, such as a water reducing agent for concrete admixture (Ouyang et al., 2011), dispersants (Yang et al., 2014) and surfactant (Lou et al., 2014). Recent researches indicated that lignosulfonates also could be prepared by sulfomethylation of lignin (Zhu et al., 2015; Huang et al., 2016). Thus after acid pretreatment of wheat straw, further sulfomethylation treatment of pretreated wheat straw could remove lignin and recover lignosulfonate as a cement water reducer (Zhu et al., 2015). Additionally, lignosulfonate also could be produced from enzymatic hydrolysis residue via sulfomethylation after a mild auto-hydrolysis pretreatment and sequent

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* Corresponding author at: College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, People's Republic of China.
E-mail address: hgouyj@njfu.edu.cn (J. Ouyang).

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enzymatic hydrolysis (Huang et al., 2016). These novel integrated processes provide us an opportunity that coproduction of XOS and lignosulfonates might be a potential economical way for biomass biorefinery.

Recently, a kind of magnesium bisulfite pretreatment (MBSP) has been developed derived from sulfite pulping (Yu et al., 2016). By this pretreatment, 85.85% hemicellulose and 81.98% lignin from corn stover could be removed at the same time, which obviously improved the enzymatic hydrolysis yield. Meanwhile, a large amount of high-valued XOS and lignosulfonate were co-produced in spent liquor (Ren et al., 2016; Yu et al., 2016). Currently, there have been a few studies focused on the separation of lignin fractionation from spent liquor via surfactant or surfactant and calcium treatments (Shi et al., 2012; Cave and Fatehi, 2015). But there is little information on the effective separation of lignosulfonate and XOS simultaneously. Hence, with the objective of maximizing the use of wheat straw MBSP spent liquor, this work investigated the performance of various anion-exchange resins in isolating lignosulfonate and XOS from spent liquor. It is believed that this work is the first report on the use of anion-exchange resin for the separation of lignosulfonate and XOS simultaneously. Meanwhile, a novel integrated process was established for complete and effective utilization of biomass.

2. Materials and methods

2.1. Materials and reagents

The wheat straw used in experiments was harvested from Lianyungang in Jiangsu province, China. Before pretreatment, it was air-dried, crushed, and sieved to achieve the fraction between 20 and 80 mesh sizes. The samples were stored at room temperature until use. Diatomite was purchased from Tianjin Fuchen Chemical Reagent Factory (Tianjin, China). All other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

Resins D301 and 717 were purchased from Shanghai Huazhen Technology Co., Ltd. (Shanghai, China); D354, D380, D396, D941, D315 were purchased from Zhengzhou Qinshi Science and Technology Development Co., Ltd. (Zhengzhou, China). The physical characteristics of the tested resins were presented in Table 1. Before use, these resins were soaked with 1 mol/L NaCl to transform to the Cl^- form, followed by a washing step using deionized water before use. All resins (D301, D315, D354, D380, D394, and D941) are macroporous type except for 717, which is gel type resin.

2.2. Preparation and treatment of MBSP spent liquor

The wheat straw was mixed with 4% (w/v) $Mg(HSO_3)_2$ at ratio of solid to liquid 1:4 in a 1.25 L sealed stainless steel tank, and subjected to pretreatment temperature 170 °C, cooking for 40 min using an electrically heated oil bath (YRG 2-10 × 1.25, Nanjing JieZheng, China) with glycerol. After pretreatment, the reactors were placed in cold water immediately to terminate the reaction, spent liquor was separated from the pretreated solid residue by solid-liquid separation (Ren et al., 2016). Thereafter, 0.5% (w/w) diatomite was added to the MBSP spent liquor and the mixture was stirred for 2 h at room temperature (Caliskan et al., 2011). After diatomite treatment, the mixture was centrifuged with 6000 rpm for 20 min to remove sediments and the supernatant was collected for further reserved at 4 °C in order to facilitate subsequent ion exchange resin treatment.

2.3. Screening of resins for separation of lignosulfonate and XOS from MBSP spent liquor

All test resins were screened through static adsorption and desorption experiments. Prior to adsorption test, the wheat straw spent liquor was diluted by deionized water to achieve a 25 g/L lignosulfonate solution. The adsorption experiment was performed as follows: 1.0 g pretreated test resin was placed in a 100 mL conical flask, and then 20 mL of the diluted spent liquor (25 g/L lignosulfonate) was added. The flasks were shaken at 150 rpm and 25 °C in a constant temperature oscillator at for 8 h till adsorption equilibrium reached. The amount of lignosulfonate and XOS in supernatant after adsorption was analyzed respectively. The desorption process was carried out as follows: the test resin particles were washed with deionized water for three times and separated with spent liquor by filtration, the adsorbed resins were then desorbed with 20 mL 10%NaCl and 2%NaOH solution at 150 rpm for 8 at 25 °C. Finally, the amount of lignosulfonate and XOS in desorption solution was analyzed respectively. The static adsorption and desorption experiment for each resin was carried out in duplicate.

The adsorption capacity, desorption capacity, desorption ratio and adsorption ratio of magnesium lignosulfonate and XOS were calculated according to the following equations:

$$q_e = \frac{(C_0 - C_e)V_i}{W} \tag{1}$$

$$q_d = \frac{C_d V_d}{W} \tag{2}$$

$$D = \frac{C_d V_d}{(C_o - C_e)V_i} \times 100\% \tag{3}$$

$$A = \frac{C_{xos0} - C_{xos1}}{C_{xos0}} \times 100\% \tag{4}$$

where q_e is the adsorption capacity of Mg-Ls (mg/g resin); q_d is the desorption capacity of lignosulfonate (mg/g resin); D is the desorption ratio of lignosulfonate (%); A is the adsorption ratio of XOS on resin; C_0 and C_e are the initial and equilibrium concentrations of lignosulfonate in the solution, respectively (mg/mL); V_i is the volume of the initial sample solution (mL); W is the weight of the tested wet resin (g); C_d is the concentration of lignosulfonate in desorption solution (mg/mL); V_d is the volume of the desorption solution (mL); C_{xos0} and C_{xos1} are the initial and equilibrium concentration of XOS in sample solution (mg/mL).

Separation factor of resins is calculated according to the following equation:

$$S = \frac{C_{b1}/C_{b2}}{C_{a1}/C_{a2}} \tag{5}$$

Table 1
Physical characteristics of the tested resins.

Resin	Classification form	Functional group	Skeleton	Average pore diameter (nm)	Particle diameter (mm)
D301	Weak basic anion	$-N^+R_3$	Styrene	30 – 80	0.3–1.25
D315	Weak basic anion	$-NR_2$,$-N^+R_3$	Acrylate	25–70	0.3–1.25
D354	Weak basic anion	$-NR_2$	Styrene	30–65	0.3–1.25
D380	Weak basic anion	$-NR_2$	Styrene	30–95	0.3–1.25
D396	Weak basic anion	$-NR_2$	Acrylate	30–80	0.3–1.25
D941	Weak basic anion	$-NR_2$	Acrylate	20–80	0.3–1.25
717	Strongly basic anion	$-N^+R_3$	Styrene	5–10	0.3–1.25