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

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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, 2006). 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 sequen
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 bioferinery.

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(HSO₃)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) pretreatment temperature 170 °C, cooking for 40 min using an electrically heated oil bath (YRG 2-10 × 1.25, Nanjing JieZheng, China) and centrifugation, 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 adsorption 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:

\[ q_e = \frac{(C_0 - C_f)V}{W} \]  

(1)

\[ q_d = \frac{C_d V_d}{W_0} \]  

(2)

\[ D = \frac{C_d V_d}{(C_0 - C_f) V_i} \times 100\% \]  

(3)

\[ A = \frac{C_{ads} - C_{eq0}}{C_{eq0}} \times 100\% \]  

(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); \( C_{eq0} \) and \( C_{eq1} \) are the initial and equilibrium concentration of XOS in sample solution (mg/mL).

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

\[ S = \frac{C_{eq1}/C_{eq2}}{C_{ads}/C_{ads}} \]  

(5)

Table 1: Physical characteristics of the tested resins.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Classification form</th>
<th>Functional group</th>
<th>Skeleton</th>
<th>Average pore diameter (nm)</th>
<th>Particle diameter (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D301</td>
<td>Weak basic anion</td>
<td>-N⁺R₃</td>
<td>Styrene</td>
<td>30–80</td>
<td>0.3–1.25</td>
</tr>
<tr>
<td>D315</td>
<td>Weak basic anion</td>
<td>-NR₂,N⁺R₃</td>
<td>Acrylate</td>
<td>25–70</td>
<td>0.3–1.25</td>
</tr>
<tr>
<td>D354</td>
<td>Weak basic anion</td>
<td>-NR₂</td>
<td>Styrene</td>
<td>30–65</td>
<td>0.3–1.25</td>
</tr>
<tr>
<td>D380</td>
<td>Weak basic anion</td>
<td>-NR₂</td>
<td>Styrene</td>
<td>30–95</td>
<td>0.3–1.25</td>
</tr>
<tr>
<td>D396</td>
<td>Weak basic anion</td>
<td>-NR₂</td>
<td>Acrylate</td>
<td>30–80</td>
<td>0.3–1.25</td>
</tr>
<tr>
<td>D941</td>
<td>Weak basic anion</td>
<td>-NR₂</td>
<td>Acrylate</td>
<td>20–80</td>
<td>0.3–1.25</td>
</tr>
<tr>
<td>717</td>
<td>Strongly basic anion</td>
<td>-N⁺R₃</td>
<td>Styrene</td>
<td>5–10</td>
<td>0.3–1.25</td>
</tr>
</tbody>
</table>
where $S$ is separation factor of Mg-Ls and XOS, $C_{0S}$ and $C_{0E}$ is the concentration of XOS adsorbed to the resin and in supernatant when the adsorption equilibrium is reached (mg/mL), $C_{0s}$ and $C_{0e}$ is the concentration of lignosulfonate adsorb to the resin and in supernatant when the adsorption equilibrium is reached (mg/mL).

2.4. Adsorption kinetics tests under different pH values

The diluted spent liquor (25 g/L lignosulfonate) was adjusted to different pH values in the range of 3.0–5.0 using 1.0 M HCl or saturated Mg(OH)$_2$ solution. Then 1.0 g wet resin was added into 20 mL of each solution with flasks shaking at 150 rpm and room temperature for 8 h. Samples were collected periodically to determine the concentration of Mg-Ls in the solution till adsorption equilibrium reached. All experiments were carried out in duplicate.

2.5. Adsorption isotherm experiments

1.0 g of wet D354 resin was added into 20 mL of diluted spent liquor with different initial concentrations (1 g/L, 5 g/L, 10 g/L, 15 g/L, 20 g/L, 25 g/L, 30 g/L, 40 g/L, 50 g/L, 60 g/L, 75 g/L) of lignosulfonate. Adsorption isotherm experiments were conducted in flasks shaking at 150 rpm for 8 h at 25, 30, and 35 °C. The initial and equilibrium concentrations of Mg-Ls in liquid phase were determined respectively.

Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1907) models were employed to describe the adsorption behaviors:

Langmuir equation:

$$ q_e = \frac{q_m K_L C_e}{1 + K_L C_e} $$

(6)

Freundlich equation:

$$ q_e = K_f C_e^{1/n} $$

(7)

where $q_e$ is the adsorption capacity (mg/g resin), $C_e$ is the equilibrium concentration (mg/mL), $q_m$ is the theoretically calculated maximum adsorption capacity (mg/g), $K_L$ is the Langmuir constant, $K_f$ and $n$ are the Freundlich constants, $1/n$ is an empirical constant.

2.6. Fixed bed column experiments

The dynamic adsorption and desorption experiments were carried out on a fixed bed column (16 mm × 12 cm) wet-packed with 22.0 g D354 resin. The packed length of resin bed was 12 cm (height to diameter ratio was 7.5) and the bed volume (BV) was 24 mL.

In adsorption process, the pretreated spent liquor (21.5 g/L Mg-Ls) flowed through the top of the column at a flow rate of 0.4 mL/min by a peristaltic pump until attaining equilibrium and concentration of lignosulfonate in the elution solutions were monitored at selected time intervals.

For desorption process, after adsorptive equilibrium, the adsorbate-laden resin column was firstly washed with 100 mL distillated water to remove impurities (Charpe and Rathod, 2015), and then lignosulfonate recovery yield was evaluated by passing 10% NaCl and 2% NaOH solution through the column at the flow rate of 1.0 mL/min. Fractions were collected at selected times and the amount of lignosulfonate was measured. Dynamic adsorption and desorption process were performed at room temperature.

2.7. Separation of MBSP spent liquor components by D354 resin bed

After 24 mL of pretreated spent liquor (21.5 g/L Mg-Ls) was pumped through the column at the flow rate of 0.4 mL/min, deionized water passed through the column with the flow rate of 0.8 mL/min to wash out sugar component with a volume of 2.3 BV, and then 10% NaCl and 2% NaOH solution flowed through the column to strip lignosulfonate with a volume of 6 BV at the flow rate of 1.0 mL/min at room temperature. For the mass balance of process, the two collected fractions were further lyophilized respectively to a constant weight to calculate the mass and purity.

2.8. Analytical methods

The viscosity measurements of the spent liquor were operated by using RS6000 (HAAKER, German) equipped with a Regel C35/1’’ TIll and a cone plate C35/1’’ TIll. Measurements were conducted using a small sample adapter on solutions (0.25 mL) at 25 °C (Liu et al., 2015).

The amount of lignosulfonate in the solution was determined by the means of UV-Vis method on a UV-Visible spectrophotometer at 280 nm (Bhattacharya et al., 2005).

Glucose, xylose and several known inhibitors (formic acid, acetic acid, levulinic acid, furfural, and hydroxymethyl furfural (HMF)) in the solution were quantified using an HPLC system (1200 series, Agilent 1260) equipped with a Bio-Rad Aminex HPX-87H column (300 mm × 7.8 mm) as described by Ouyang et al. (2013).

For the total amount of XOS, 5 mL sample was hydrolyzed with 4% H$_2$SO$_4$ (w/w) and then hydrolyzed at 121 °C for 60 min. Thereafter, the amount of the increased monomeric xylose concentration was calculated to determine the total XOS (Xiao et al., 2013). Additionally, the composition analysis of XOS was conducted using a Dionex HP AEC system (Dionex ICS-3000) equipped with integrated pulsed amperometric detection (HPAE-PAD) at 30 °C. Eluent was provided at a rate of 0.3 mL/min (Ren et al., 2016).

3. Results and discussion

3.1. Properties of MBSP spent liquor and diatomite treatment

After MBSP, the components analysis of raw biomass and residual solid was conducted. MBSP led to changes in the structural of the pretreated material, which implied that a great amount of hemicellulose and lignin were removed from the solid (Ren et al., 2016). Table 2 presented the comparison of MBSP spent liquor before and after 0.5% diatomite treatment. After magnesium bisulfitrepretreatment, a large amount of Mg-Ls and XOS (about 86.61 g/L lignosulfonate and 10.05 g/L XOS) were found in spent liquor, which is close to previous reports (Ren et al., 2016; Yu et al., 2016). Meanwhile, the concentration of glucose and xylose was 1.37 and 5.13 g/L, respectively. Additionally, several known fermentation inhibitors were also discovered in spent liquor, such as acetic acid, furfural and HMF. Thereby, in order to avoid subsequent chromatographic column deterioration and blockage, preliminary adsorption treatment was conducted to remove some impurities and reduce viscosity of spent liquor.

As a potential adsorbent from low-cost natural mineral (Fu and Wang, 2011), diatomite was used for the treatment of MBSP spent liquor. As expected, the transmittance of spent liquor increased obviously by diatomite treatment and the maximum transmittance of spent liquor was obtained with 0.5% diatomite pretreatment. Table 2 showed the change of spent liquor composition and viscosity after 0.5% diatomite treatment. XOS and xylose were the main soluble sugar in pretreatment.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Initial spent liquor</th>
<th>Treated spent liquor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose (g/L)</td>
<td>1.37 ± 0.06</td>
<td>1.20 ± 0.07</td>
</tr>
<tr>
<td>Xylose (g/L)</td>
<td>5.13 ± 0.11</td>
<td>3.63 ± 0.28</td>
</tr>
<tr>
<td>XOS (g/E)</td>
<td>10.05 ± 0.05</td>
<td>10.16 ± 0.15</td>
</tr>
<tr>
<td>Formic acid (g/L)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Levulinic acid (g/L)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Acetic acid (g/L)</td>
<td>5.02 ± 0.06</td>
<td>4.24 ± 0.03</td>
</tr>
<tr>
<td>HMF (g/L)</td>
<td>0.32 ± 0.06</td>
<td>0.23 ± 0.01</td>
</tr>
<tr>
<td>Furfural (g/L)</td>
<td>0.28 ± 0.03</td>
<td>0.21 ± 0.00</td>
</tr>
<tr>
<td>Mg-Ls (g/L)</td>
<td>86.61 ± 0.10</td>
<td>75.63 ± 0.76</td>
</tr>
<tr>
<td>Viscosity (mPas)</td>
<td>1.93</td>
<td>1.72</td>
</tr>
</tbody>
</table>
spent liquor. Diatomite treatment led to an obvious loss of xylose. It might contribute to the improvement of XOS purity. In addition, 12.68% of Mg-Ls and 15.54% of the acetic acid were removed from the spent liquor by diatomite treatment. Acetic acid is a major weak acid in spent liquor and the removal of acetic acid would facilitate subsequent chromatography. Besides these, other inhibitors and pigment were also adsorbed by diatomite at a certain extent, which led to the reduction of solution viscosity from 1.93 to 1.72 mPas. These results suggested that diatomite could indeed remove the partial impurities of spent liquor by adsorption, which would facilitate the following ion-exchange process.

3.2. Screening and selectivity study of resins

In order to acquire the best suitable resin for the separation of lignosulfonate and XOS from wheat straw MBSP spent liquor, the adsorption capacities, desorption and adsorption ratios of six macroporous resins and a gel type resin were evaluated and the results were listed in Fig. 1. Compared with other resins, resins D354 and D380 presented relatively higher adsorption capacities for Mg-Ls. For most resins, desorption ratio of Mg-Ls could reach near 100% except 717 resin (Fig. 1A). Thus it was clear that both D354 and D380 were the high effective exchange resins for removing lignosulfonate from spent liquor. Similar observation was also found in eliminating lignosulfonate from magnesium base acidic sulphite spent liquor (Fernandes et al., 2012). Furthermore, considering that a low level of adsorption ratio of XOS is needed for obtaining a high-purity lignosulfonate and avoiding the loss of XOS, the resin adsorption selectivity of Mg-Ls against XOS was tested by separation factor in order to determine the separation efficiency of lignosulfonate and XOS from spent liquor. As reported, a high selectivity is necessary for obtaining a high-purity of the product and the separation factor was much greater than 1 for all conditions studied (Zhang and Yang, 2015). As shown in Fig. 1B, compared with D380, D354 exhibited the lower adsorption ratio of XOS and owned a remarkable selectivity with separation factor of 111.60 in the complex spent solution. Therefore, D354 was selected as the optimum resin for further investigation.

3.3. Adsorption kinetics under different solution pH values

The pH of the solution is the most important parameter influencing the adsorption performance (Zhang et al., 2008; Wu et al., 2012). Thus the adsorption behaviors of Mg-Ls on resin D354 at different pH value of solution were presented in Fig. 2. On the one hand, the adsorption capacity increased sharply during the initial 1 h and reached equilibrium at about 6 h. Thus the later adsorption isotherm tests should be run for 8 h to ensure complete equilibration. On the other hand, since the initial pH value of the adsorption solution determines the extent of ionization of lignosulfonate, the pH value of solution showed an obvious effect on the adsorption affinity (Li et al., 2011; Zhao et al., 2011). It was clear that more Mg-Ls were adsorbed at pH 3.5–4.0. D354 resin is a kind of macroporous adsorbent with weak base group (tertiary amine group). Thus it is supposed to preferentially adsorb the Mg-Ls in its ionic form. Ionization degrees of lignosulfonate in solution under different pH values are related to the sulfuric, carboxylic and phenolic groups of lignosulfonate. In the low pH range, the decrease of pH resulted in a drop of adsorption capacity, which might also be caused by the incomplete ionization of lignosulfonate. However, when the pH value of solution was higher than the P_{ka} of acetic acid (P_{ka} = 4.76), more acetic acid was protonized and the adsorption of acetic acid on D354 resin occurred. It significantly limited the adsorption capacity of lignosulfonate, which could lead to a decreased amount of adsorbed lignosulfonate at higher pH value.

To summarize, considering that the natural pH of spent liquor (pH 3.5) was close to the optimal pH for lignosulfonate adsorption, it was hence chosen for all the later experiments. It also suggested that a future industrial implementation of recovery of XOS and lignosulfonate from wheat straw MBSP spent liquor will not require an additional operation of pH adjustment.

3.4. Static adsorption isotherms

Lignosulfonate adsorption isotherms were further determined to obtain information on the capacity of D354 resin at 25, 30 and 35 °C.
respectively. When changing the initial lignosulfonate concentrations of spent liquor from 1 to 75 g/L, the equilibrium distribution of lignosulfonate between the resin and solution phase was shown in Fig. 3. The amount of adsorbed lignosulfonate increased with increasing equilibrium lignosulfonate concentration. When the initial concentration of lignosulfonate was about 47.2 g/L, the lignosulfonate uptake reached the saturation plateau. Additionally, the adsorption capacity decreased with increasing temperature, which indicated that the adsorption is a thermopositive process (Zhao et al., 2011). It indicated that the adsorption process could be performed at room temperature.

To fit the experimental equilibrium data, the Langmuir and Freundlich equation were used and Table 3 summarized the adsorption isotherm parameters. The Langmuir adsorption isotherm is the best-known isotherm that assumes monomolecular layer adsorption with a homogeneous distribution of adsorption energies and without mutual interaction between adsorbed molecules (Langmuir, 1918). The Freundlich equation is used to model multilayer adsorption and adsorption on heterogeneous surfaces (Freundlich, 1907). The adsorption of Mg-Ls on D354 presented a typical Langmuir adsorption because $R^2$ was larger than 0.97 for all experiments. It hence meant that the adsorption of Mg-Ls by D354 assumed monolayer coverage of the adsorption surface and no further adsorption occurred at the same site when it was occupied. The maximum adsorption capacity was achieved to 389.61 mg/g at 25 °C. Additionally, 1/n in Freundlich equation were all between 0.1 and 0.5, which indicated that the adsorption process could take place easily (Li et al., 2011), and that resin D354 is suitable for recovery of lignosulfonate from wheat straw MBSP spent liquor.

### Table 3

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_m$</td>
<td>$K_L$</td>
</tr>
<tr>
<td>25</td>
<td>389.609</td>
<td>0.156</td>
</tr>
<tr>
<td>30</td>
<td>382.817</td>
<td>0.103</td>
</tr>
<tr>
<td>35</td>
<td>381.900</td>
<td>0.082</td>
</tr>
</tbody>
</table>

3.5. Adsorption and desorption of lignosulfonate on a fixed bed column

Considering that ion-exchange process is generally operated in a fixed bed column in practical applications, dynamic adsorption and desorption tests were performed on a fixed bed column (16 mm × 12 cm) using D354 resin. Fig. 4A showed the dynamic breakthrough curve under flow rate of 0.4 mL/min with initial Mg-Ls concentration of 21.5 g/L. The dynamic breakthrough curve showed...
little growth up to feeding solution of 48 mL (corresponding to 120 min) and then increased sharply until reaching adsorption equilibrium at 850 min. It meant that when 340 mL of sample solution was fed onto resin column, the adsorption process reached adsorption equilibrium for lignosulfonate. Under such conditions, the resin demonstrated a higher dynamic adsorption capacity of 190.28 mg/g. Compared to higher adsorption capacity under static condition, the decrease of adsorption capacity was due to insufficient contact time and limitation of diffusivity of lignosulfonate. Similar result was also observed in the separation of glycyrrhizin acid from licorice root extract (Charpe and Rathod, 2015).

The dynamic desorption curve on D354 resin was obtained for investigating the recovery of lignosulfonate. 10% NaCl and 2% NaOH solution was selected as eluent to strip lignosulfonate adsorbed on resin D354 herein. As shown in Fig. 4B, when desorption rate was set at 1.0 mL/min, the volume of desorption solution was about 6 BV and the recovery yield of lignosulfonate reached 71.11%. Moreover, after 1.0 mL/min, the volume of desorption solution was about 6 BV and the desorption rate was set at 0.4 mL/min, deionized water passed through the column to strip lignosulfonate with a volume of 6 BV at the flow rate of 0.8 mL/min and Na-Ls was washed out by deionized water. The recovery yield of lignosulfonate was about 60.09% (Wang et al., 2013). Therefore, this process made it possible to fully use MBSP spent liquor by D354 resin. Therefore, a novel integrated process coupling of MBSP and ion-exchange process has the potential for complete and profitable utilization of biomass.

3.6. Recovery of lignosulfonate and XOS from MBSP spent liquor

Based on the above fixed bed column experiments, 24 mL of pretreated spent liquor (21.5 g/L Mg-Ls) was pumped through the column at the flow rate of 0.4 mL/min, deionized water passed through the column with the flow rate of 0.8 mL/min to wash out sugar component with a volume of 2.3 BV, and then 10% NaCl and 2% NaOH solution flowed through the column to strip lignosulfonate with a volume of 6 BV at the flow rate of 1.0 mL/min at room temperature. The separation profiles of lignosulfonate and XOS was conducted as Fig. 5 presented. XOS was firstly eluted by deionized water in 0–54 mL (Fig. 5A) and subsequently sulfonate ions was stripped by lignosulfonate desorption solution in 55–200 mL (Fig. 5B). As shown in Fig. 5, the elution profiles of lignosulfonate and XOS indicated that the recovery yield of XOS and lignosulfonate could reach 0.1% and 98.03% respectively. It suggested that XOS and lignosulfonate were completely isolated from MBSP spent liquor by ion-exchange herein. Moreover, the comparison of the molecular distribution of XOS before and after ion-exchange process revealed that anion-exchange process did not change the allocation proportion of XOS with different degrees of polymerization (DP). After ion exchange, XOS in the DP range of 2–4 (X2, X3 and X4) still occupied 87.13% of XOS components (X2-X6). The goal of this work was to establish a simple and economical way for isolating lignosulfonate and XOS from wheat straw MBSP spent liquor. As shown in Fig. 6, based on our process, 20 mL crude spent liquor (containing 1.73 g Mg-Ls and 0.20 g XOS) could produce 1.48 g Na-Ls with purity of 91.92% and 0.19 g XOS with purity of 60.09%. The results indicated that 85.55% of lignosulfonate and 93.09% of XOS were successfully isolated and recovered from crude spent liquor. Taking into account that the prices of XOS (depending on the purity) and lignosulfonate with purity about 90% in China are approximately $22–50 kg⁻¹ (Otieno and Ahring, 2012) and $9.85 kg⁻¹ at present, 1000 mL of MBSP spent liquor could produce 9.5 g XOS and 74.0 g lignosulfonate, which respond to $0.21–0.48 and $0.73 respectively. Both XOS and lignosulfonate are potential high valued products, which could directly enter the market. Compared to a conventional bioethanol, our process made it possible to fully use MBSP spent liquor by efficient recovery of XOS and lignosulfonate simultaneously for the first time.

4. Conclusions

In this work, a feasible and effective method for simultaneously separation and purification of lignosulfonate and XOS from wheat straw MBSP spent liquor was successfully established. D354 resin was selected for its high adsorption capacity of 389.61 mg/g resin for Mg-Ls and remarkable selectivity with separation factor of 111.60 at 25 °C and natural pH of spent liquor. The recovery yield of 93.09% XOS and 98.03% lignosulfonate could be achieved using a fixed bed column with D354 resin. Therefore, a novel integrated process coupling of MBSP and ion-exchange process has the potential for complete and profitable utilization of biomass.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2017.09.207.

References