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Efficient extraction of bagasse hemicelluloses and characterization of solid remainder

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HIGHLIGHTS

- pH pre-corrected was studied and obtained high molecular weight of hemicellulose.
- Response surface model was established to optimize the extraction process.
- The yields of hemicellulose extracted increased from 33.77% to 43.38%.
- The species composition and purity (xylose 84.11%) of HE was analyzed by HPLC.
- The biggest balance between solid remainder and dissolved solid was obtained.

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ABSTRACT

To reduce the degradation of cellulose and obtain high molecular weight of hemicellulose from the extracts, pH pre-corrected hot water pretreatment was developed by employing sodium hydroxide (3.9 mol/L). The response surface model was established to optimize the extraction process. The species composition and purity of hemicellulose extract was analyzed by High Performance Liquid Chromatography (HPLC). The obtained solid remainder was analyzed by FTIR and SEM. The results showed that the component of xylose in hemicellulose extract was similar with commercial xylan. FTIR and SEM were shown to be able to evaluate solid remainder composition and surface characterization of the bagasse. The biggest balance between solid remainder and dissolved solid was obtained. Not only the yield of dissolved solid was improved, but the structure of solid remainder was also proved, which was beneficial to pulping and papermaking.

1. Introduction

The plant fibrous material contains about 15–35% of hemicellulose, and most of the hemicelluloses are extracted during the pulping stage. Calorific value of the hemicellulose is 13.6 MJ/kg, which is half of the lignin (Li et al., 2014). The kraft process in the modern pulp and paper making industry typically burns the extracted hemicellulose for steam. This kind of hemicellulose is underutilized, which is a great waste of resources. The fossil resources nearly dried up at present, it is particularly important for hemicellulose efficient utilization.

The existing pre-extraction methods mainly include physical method, chemical method and biological method. In concrete terms, there are dilute acid extraction (Walton et al., 2010; Wang et al., 2012), hot water extraction (Krogell et al., 2013; Liu, 2010; Liu et al., 2012), steam explosion extraction (Martin-Sampedro et al., 2014), alkali extraction (Sun et al., 2013) and dilute acid steam explosion (Sabiha-Hanim et al., 2015). The process condition of dilute acid extraction is hard to control, and the pulping yield will be reduced by the hydrolysis of cellulose. The structure of cellulose will be disrupted during the steam explosion extraction. The operating cost of alkali extraction is high for the employment of alkali and acid adding for pH adjustment. The hot water extraction develops with the purpose of reducing cost and environmental pollution, and hydrolysis of hot water extracts can be combined with the separation of solid materials. Shorter reaction time, higher concentration acid and higher temperature will produce more xylose monomer (Feria et al., 2012). The membrane filtration used for concentrated extract can avoid the employment of high concentration acid (Amidon and Liu, 2009). The ideal environment of extraction of woody biomass and separation of aromatic substances was acid medium (Krawczyk et al., 2013). Benko et al.

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found that the hemicellulose extraction yield (HEY) increased with the increase of hot water extraction temperature, but the molecular weight of polysaccharides decreased, as well as the hemicellulose damage increased (Benko et al., 2007).

In the previous work we found that, adding alkali could achieve effective in neutralizing the acids released during the pretreatment process. It could reduce the degradation of cellulose and obtain high molecular weight of hemicellulose from the extracts. This paper mainly focused on the efficient hot water extraction of hemicellulose. To reduce the degradation of cellulose and obtain high molecular weight of hemicellulose from extracts, pH pre-corrected hot water pretreatment was developed by employing sodium hydroxide (3.9 mol/L). The response surface model was established to optimize the extraction process. The species composition and purity of hemicellulose extract (HE) was analyzed by HPLC. The characterization and cross section morphology of raw material and solid remainder was analyzed by FTIR and SEM.

2. Methods

2.1. Raw material and chemicals

Bagasse was provided by a local sugar refinery (Guangxi, China). The pulp Kappa number was 10.1 and brightness was 31.9% ISO. 3.9 mol/L sodium hydroxide was prepared for controlling the pH of the solution. Xylan was used as a representative of the hemicellulose component and was purchased from Aladdin (China). All assay reagents were obtained from Sigma (USA). All the other chemicals employed in this work were purchased from Chong Qing Kawahigashi Chemical Co., LTD. (China). All of the chemicals were analytical grade.

2.2. pH pre-control experiment

The optimal dosage of sodium hydroxide (the end pH) was determined by the single factor analysis. The hot water extraction was carried out at an oil-bathed reactor, with four 1100 mL stainless steel cylindrical reactors in it. Bagasse was treated with pure water, at a ratio of 5:1. The dosage of the sodium hydroxide is 1–7% under the condition of the highest temperature 170 °C, and holding for 60 min. At the end of the desired reaction time, the reactors was removed from oil bath and quickly cooled down under cold running water for about 10 min. The alcohol precipitation was employed for separation and purification of hemicellulose (Ruiz et al., 2013). The solid and liquid were separated by 0.45 nm membrane filtration system, 95% anhydrous ethanol were added to the filtrate in order to obtain the high-molecular weight of hemicellulose. The precipitated hemicellulose was obtained by centrifugal separation and freeze drying.

2.3. Extraction experiment design and optimization of hemicellulose extract

The optimal parameters of hot-water extraction hemicellulose were obtained by response surface design experiment (Table 1). Taking the hemicellulose extract yield as index, response surface of three factors three levels was taken to optimize the condition with the highest temperature, holding time and sodium hydroxide dosage. The accuracy and reliability of the model was evaluated by analysis of significance, correlation and variance (Ma et al., 2013). Real and normalized values of the operational variable temperature (x_1), times (x_2), sodium hydroxide dosage (x_3) and results obtained for the responses on the hemicellulose extract yields (% HEY) were shown in Table 4.

Table 1
Response surface analysis and level design.

Horizontal encoding	Variables		
	Temperature (x_1) (°C)	Times (x_2) (min)	Sodium hydroxide dosage (x_3) (%)
−1	150	40	2
0	170	60	4
1	190	80	6

2.4. Acid hydrolysis of hemicellulose extract for determination of chemical composition

The main sugar component was determined by hemicellulose extract hydrolysis according to Ruiz et al. (2013) with a slight modification. In order to compare the chemical composition of the hemicellulose extract hydrolysate, a commercial xylan (99%) was used as reference material. 640 mg hemicellulose extract was suspended in 2 mol/L sulfuric acid and placed the tube in a boiling water bath for 3 hours. The resulting supernatant was filtered through a 0.2 μm sterile membrane filter. The reaction products i.e., xylose, glucose, arabinose, mannose and galactose (Peng et al., 2012) were quantified by HPLC in a Waters e2695 (USA) chromatograph equipped with a refractive index detector and symmetry shield TM RP18 (4.6 mm × 250 mm, 5 μm) column. The basic method and process was as follows: 50 μL monosaccharide sample was taken under different concentration, and then adding 0.4 mL 1-2 phenyl-3-methyl-5-pyrazolone (PMP) methanol solution and 0.4 mL sodium hydroxide. Put the tubes in a 70 °C vibration water bath for 1.5 h. Adding water to 2 mL after the solutions was neutralized by hydrochloric acid. Adding 10 mL trichloromethane and put it into a vortex mixer treating for 1 min. The resulting supernatant was then filtered through a 0.45 μm sterile organic membrane filter. Chromatographic separation was performed with the mobile phase of 0.02 mol/L ammonium acetate and acetonitrile (82%/18%). The detection wavelength was 250 nm, and the column temperature was kept at 25 °C, with a flow rate of 1.0 mL/min for 35 min.

2.5. Characterization of solid remainder by Fourier-transform infrared

FTIR spectra of the bagasse fiber were measured on a Nexus 470 spectrometer (HP, USA) using 16 scans and frequency range of 500–4000 cm^{-1}. Signal averages were obtained at a resolution of 4 cm^{-1}. Samples were mixed with KBr in a ratio of 1:10 mg (Bagasse:KBr) and pressed under vacuum to form pellets (Yuan et al., 2010). Two specimens of the samples were tested, and the results were averaged (González et al., 2011).

2.6. Morphological characterization

The cross section morphology of raw material and solid remainder was observed by SEM (S-3400 N, Hitachi, Japan). The bagasse powder was fractured in liquid nitrogen and then coated with gold before test. SEM micrographs of ×100, ×500 and ×1000 magnifications were used.

3. Results and discussion

3.1. Raw material composition analysis

The chemical composition of bagasse was previously analyzed by Ruiz (Ruiz et al., 2011), containing cellulose of 45.28%, lignin of 22.39%, hemicellulose of 22.13% and ash of 1.01%. The chemical composition of traditional hot-water extraction (TP) and hot water