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Separation and concentration of hydroxycinnamic acids in alkaline hydrolyzate from rice straw by nanofiltration

Yun Li [a,b], Benkun Qi [a], Jianquan Luo [a], Rashid Khan [a,b], Yinhua Wan [a,*]

[a] State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China
[b] University of Chinese Academy of Sciences, Beijing 100049, PR China

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ABSTRACT

Alkali pretreatment could cause the degradation of the lignin of lignocellulose, releasing hydroxycinnamic acids and phenolic aldehydes into the hydrolyzate. Hydroxycinnamic acids (ferulic and p-coumaric acids) found in alkaline lignocellulosic hydrolyzate are high value-added products. Their separation and concentration from phenolic aldehydes were investigated using nanofiltration (NF) membrane with model solution and practical hydrolyzate. The effect of main operating parameters such as feed pH, permeate flux, NaCl concentration and the synergistic effect of pH and salt on the retentions of phenolic acids and aldehydes in the model solution were studied. Results indicated that the separation performance of hydroxycinnamic acids from aldehydes was optimal at neutral pH. All the phenolics retentions decreased with increasing NaCl concentration, especially for aldehydes. Salt and pH acted synergistic effect on phenolic aldehydes retention. When the practical alkaline hydrolyzate was treated under concentration–diafiltration mode, the mass percentage of hydroxycinnamic acids reached as high as 91.4%. This work demonstrated that NF could accomplish the separation and concentration of hydroxycinnamic acids from practical alkaline lignocellulosic hydrolyzate.

1. Introduction

The lignocellulosic biomass such as rice straw is an abundant and renewable carbohydrate source. Biofuel produced from lignocellulosic materials had attracted great attention all over the world. However, one of the major barriers from lignocellulosic biomass to ethanol is the recalcitrance of lignocellulose. Alkali pretreatment could remove most of lignin to produce reactive cellulosic fiber for enzymatic attack and make cellulose more accessible to hydrolytic enzymes for conversion to glucose. During alkali pretreatment, hydroxycinnamic acids (ferulic and p-coumaric acids) were released by cleaving the ester linkages with polysaccharides and the ether linkages with lignin [1–3]. Besides hydroxycinnamic acids, a large quantity of alkali-soluble lignin and a small amount of phenolic aldehydes, e.g. vanillin and syringaldehyde, were also produced. Hydroxycinnamic acids (ferulic and p-coumaric acids) play an important role in health promotion and disease prevention, such as antioxidant, antimicrobial, anti-inflammatory and anticancer [4,5].

Due to the high value-added of these hydroxycinnamic acids, their separation and purification from biomass alkaline hydrolyzate have attracted growing attention all over the world. However, it is difficult to purify hydroxycinnamic acids from the alkaline hydrolyzate due to the complex components of hydrolyzate. Ou et al. [6] applied activated carbon adsorption to purify ferulic acid from sugarcane bagasse alkaline hydrolyzate. However, they found that purification of ferulic acid from alkaline hydrolyzate by activated charcoal was not feasible due to the strong adsorption of pigments to charcoal. In addition, the adsorption selectivity of activated charcoal to ferulic acid was poor as it could also adsorb other phenolics present in the hydrolyzate. Moreover, Salgado et al. [7] investigated the ferulic acid purification from alkaline hydrolyzate of agro-industrial wastes by activated charcoal adsorption and found that the adsorption efficiency of activated charcoal was nearly 40%, indicating that the loss of hydroxycinnamic acids was quite high during the adsorption process. Therefore, it is of significance to find an efficient purification strategy to separate hydroxycinnamic acids from alkaline hydrolyzate of biomass.

Nanofiltration (NF) is a cost-competitive and environment-friendly separation technology, which can efficiently separate low molecular weight solutes via size exclusion and charge effect. It has been used in biomass biorefinery for concentration of sugars and removal of pretreatment inhibitors [8,9]. For example, Luo et al. [10] applied NF integrated with laccase pretreatments to

* Corresponding author.
E-mail address: yhwan@ipe.ac.cn (Y. Wan).

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remove phenolic acids from model monosaccharides solution. In addition, Zhao et al. [11] employed ultrafiltration (UF) and NF to concentrate ferulic acid from corn bran hydrolyzate obtained by alkaline-ethanol aqueous solution pretreatment. However, compared to corn bran hydrolyzate, the composition of the alkaline hydrolyzate of lignocellulose is much more complex, and various phenolic aldehydes are produced together with hydroxycinnamic acid. Therefore, it is necessary to investigate the separation of hydroxycinnamic acids and phenolic aldehydes by NF for this application. To the best of our knowledge, this is the first systematic study regarding the separation and purification hydroxycinnamic acids from the alkaline hydrolyzate of cellulosic biomass by NF.

In the present study, the feasibility of separating and concentrating hydroxycinnamic acids (ferulic and p-coumaric acid) in alkaline hydrolyzate from rice straw using NF was investigated, with focus on the effects of operation conditions (especially flux, pH and NaCl concentration) on the separation of hydroxycinnamic acids from phenolic aldehydes in the alkaline hydrolyzates. In addition, the effects of operating mode on separation performance and the membrane fouling were examined in detail. In this work, both model solution and practical alkaline hydrolyzate were used in order to clarify the separation mechanisms and to evaluate the practicability in industry.

2. Material and methods

2.1. Raw material and chemicals

Rice straw was collected from Jingzhou, Hubei Province, China. The naturally dried rice straw was chopped to 1–2 cm size. It was then milled, screened to collect the fraction of 0.5–1 mm size and dried at 50 °C for 24 h before use. The water content was 4.0%. The main compositions of the raw rice straw in dry solids were as follows: glucan 39.7%, xylan 15.7%, arabinan 3.4%, acid-soluble lignin (ASL) 3.3%, acid-insoluble lignin (AIS) 17.4% and ash 6.9%.

Ferulic acid, p-coumaric acid, vanillic acid, vanillin, syringaldehyde and p-hydroxybenzaldehyde were of analytical grade reagent and purchased from J&K Scientific Ltd, Beijing, China.

2.2. Preparation and UF of alkaline hydrolyzate from rice straw

Rice straw was pretreated with 0.5 M NaOH solution at a solid: liquid ratio of 1:10 (w/w) at 120 °C for 2 h. Then, the pretreatment slurry was separated into liquid fraction and solid fraction with 300 mesh filter cloth in the vacuum filter. The obtained liquid fraction was further ultrafiltrated with a 5000 Da molecular cut-off ceramic membrane (TiO_2–ZrO_2, TAMI, France) to remove soluble compounds with high molecular weight such as lignin and hemicellulose, which could cause severe membrane fouling for subsequent purification of hydroxycinnamic acids by NF. UF was performed at 50 °C with a constant transmembrane pressure (TMP, 0.1 MPa) and a cross-flow velocity of 5 m s^{-1}. The permeate of UF was collected for analysis of phenolics content and used for concentration and diafiltration experiments of NF as described in Section 2.5.

2.3. Preparation of model solutions

Model solutions were prepared by dissolving ferulic acid, p-coumaric acid, vanillic acid, syringaldehyde, p-hydroxybenzaldehyde and vanillin in 0.5 M NaOH solution to obtain a mixture solution. The concentrations of phenolics in model solutions were selected based on the practical alkaline rice straw hydrolyzate obtained from Section 2.2. The pH of model solution was adjusted by adding HCl.

2.4. Membrane and experimental set-up

Commercially available NF 270 membrane (Dow FilmTech, USA) was employed in the present study. The virgin NF membrane was soaked in 50% (v/v) ethanol solution for 10 s and then washed with deionized water in order to release the conserving solvent. Then the membrane was soaked in deionized water for at least 24 h before use.

The experimental set-up for NF was the same as described in detail elsewhere [8], consisting of a liquid chromatographic pump (LC-20AT, Shimadazu Corp., Kyoto, Japan), an injection column (Superloop 50 mL, Pharmacia, Sweden), a pressure sensor (MLH040BSB09A, Honeywell, USA), a self-made stirred-cell filter with a working volume of 12.5 mL, and a magnetic stirrer. The effective membrane surface area of NF membrane disc in NF cell was 4.52×10^{-4} m^2.

2.5. Filtration procedure

A fresh NF 270 was used in each set of NF experiments. The soaked membrane disc was compacted inside the cell by filtering deionized water at 400 L m^{-2} h^{-1} (The TMP was equal to 30 bar) for 30 min to minimize pressure effect on the membrane performance. Approximately 50 mL model solution was injected into the injection column and then pumped into the filtration cell. NF experiments were performed at room temperature. The effects of feed pH, permeate flux and NaCl concentration and the possible synergistic effect of pH and NaCl on the performance of the NF process, in terms of retention and TMP, were investigated in the experiments. Before and after the NF of the model solution, the pure water permeability of membrane was measured in order to determine the irreversible fouling of the used membrane.

Concentration operation was performed by continuously feeding the practical alkaline hydrolyzate into the cell at constant permeate flux of 106.2 L m^{-2} h^{-1} until the TMP reached 40 bar. While in the subsequent diafiltration operation, deionized water was pumped continuously into the cell filter at constant permeate flux of 106.2 L m^{-2} h^{-1}.

2.6. Characterization of membrane fouling

Before and after the NF experiments, the surface of membrane was characterized by Scanning electron microscopy (SEM, JSM-6700F, JEOL, Japan), Fourier transformer infrared (FTIR, Thermo Scientific Nicolet iS 50, USA) and contact angle (CA, OCA20, Dataphysics, Germany) to analyze the fouling features of the used membrane.

2.7. Analysis methods

2.7.1. HPLC analysis

Phenolics were determined by liquid chromatography (Shimadzu Corp., Kyoto, Japan), equipped with a C_{18} Column (4.6 × 250 mm, TC-C_{18}, Agilent, USA) and an UV detector (SPD-20A, Shimadzu Corp., Kyoto, Japan) at 320 nm. The mobile phase was acetonitrile/water (20:80) and 1% acetic acid (v/v) at a flow rate of 1 mL min^{-1}. The injection volume was 20 μL. The determination was carried out at room temperature.