Separation and Purification Technology 187 (2017) 380–388

Contents lists available at ScienceDirect

Separation and Purification Technology

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

Influence of prefiltration on membrane performance during isolation of lignin-carbohydrate complexes from spent sulfite liquor

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ARTICLE INFO

Article history:
Received 22 December 2016
Received in revised form 25 April 2017
Accepted 14 June 2017
Available online 29 June 2017

Keywords:
Galactoglucomannan
LCC
Fouling
Prefiltration
Spent sulfite liquor
Ultrafiltration

ABSTRACT

In this study, we examined the isolation of lignin-carbohydrate complexes (LCCs) from sodium-based spent sulfite liquor, in conjunction with minimization of membrane fouling. We screened 3 polysulfone (PS) membranes with cutoffs of 100, 50, and 25 kDa, respectively. Flux and retention for the 100- and 50-kDa membranes had the same order of magnitude, indicating that these properties were determined by fouling that formed on the membrane—not pore size. The PS membrane with the 50-kDa cutoff performed best in terms of flux and retention of lignin-carbohydrate complexes and experienced the least membrane fouling.

Two prefiltration methods were used to decrease the fouling of the 50-kDa membrane: a 0.2-μm PS microfiltration membrane and dead-end filtration with 10-um filter cloth and a 4 wt% mixture of kieselguhr (diatomite) and spent sulfite liquor prior to filtration.

Prefiltration of the SSL with microfiltration increased the flux 3-fold and decreased the fouling grade from 49% to 7.2%. Dead-end filtration effected a 16% increase in flux and a fouling grade of 17%. The retention of LCC during microfiltration was high, which resulted in a loss of high-molecular-weight products, whereas the loss of LCC during dead-end filtration was negligible.

A 50-kDa PS membrane performed best with regard to the recovery of lignin-carbohydrate complexes from spent sulfite liquor. Also, dead-end filtration is a promising method for eliminating membrane fouling.

1. Introduction

Spent sulfite liquor (SSL) is a waste stream that is generated in the manufacture of pulp in the sulfite process. The treated SSL is usually concentrated in evaporators before being sent to a recovery boiler where the pulping chemicals are recovered and the organic materials are incinerated to produce power and heat [1]. The solids content in SSL is 8–14% by weight, of which lignosulfonates, hemicelluloses, monosaccharides, and pulping chemicals are the major constituents [1,2]. Studies on the composition of dissolved wood components have established the existence of lignin that is covalently bound to polysaccharides [3–6]. Lawoko et al. [7] discovered that lignin binds to all major polysaccharides in the plant wall, demonstrating that extracted lignin-carbohydrate complexes (LCCs) have a wide array of compositions, depending on the extraction method and plant type. Giummarella et al. [8] discovered that the carbohydrates linked to lignin in spruce were mainly arabinoglucuronoxylan and galactoglucomannan (GGM) The main lignin-carbohydrate linkages detected were benzyl ether (xylan) and phenyl glycosidic (mannan). The LCC structures were not uniform, meaning that significant differences existed in the LCC structures, because of the lignin part of the LCC. The study confirmed the observations made by Lawoko et al. [7]. Similar observations were made by Du et al. [9], where three major LCC fractions were detected in the spruce-based raw material, that is, in mannan, glucan and xylan enriched fractions. All of the mentioned fractions had a high molecular weight and were practically insoluble in dioxane/water mixtures. Possible applications for LCCs have been presented in several studies, which have shown that LCCs can be used in the production of gas-barrier films [10], for polymeric surfactants and as drug carriers [11]. Thus, the isolation and fractionation of LCCs are important for research and development of future products.

The separation and purification of the wood polymers has garnered significant interest, because many applications are being developed for the use of these components. Membrane filtration has become a common method for the fractionation and isolation of wood components from various waste streams. Al Manasrah

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http://dx.doi.org/10.1016/j.seppur.2017.06.031
1383-5866/

et al. [12] examined the possibility of using ultrafiltration (UF) membranes for the recovery of GGMfrom pressurized hot water extracts of spruce sawdust. In their study, the GGM retention rate was 88%, the purity was 63%, and the recovery rate was 70%, with an 86% reduction in volume. The purity improved further with diafiltration of the filtrate through the complete removal of monosaccharides and a portion of the xylan. Other studies have shown that UF membranes can be used to recover and purify lignosulfonates from SSL [13–15]. These reports compared various membranes and concluded that polysulfone membranes with a molecular-weight cutoff (MWCO) over 10 kDa were optimal in terms of flux, rejection of lignosulfonates, and high temperature tolerance versus cellulose-acetate and fluoropolymer membranes.

Isolation of LCCs from wood is a relatively new approach, necessitating more research. Lawoko et al. [6] developed a procedure to separate LCCs into several fractions with varying compositions for analytical purposes; however, for industrial separation, a simpler method is needed. Westerberg et al. [16] combined membrane filtration and an adsorption-based process for polymeric resins, isolating LCCs and upgrading GGM. The downsides of this approach were the adsorption process, in which the separation capacity was limited, and the degradation of sorbent material, which was costly. A combination of precipitation with diafiltration has been presented in several research papers showing an effort to develop a method for universal fractionation and purification of LCCs (glucan-lignin, glucomannan-lignin and xylan-lignin) [9,17–19]. Glucan-lignin was precipitated in the first step by dispersing the dimethyl sulfoxide and tetrabutylammonium hydroxide dissolved sample in deionized water. The addition of barium hydroxide to the supernatant precipitated the glucomannan-lignin. The xylan-lignin complex was precipitated by the addition of hydrochloric acid after removal of the glucomannan-lignin precipitate. All of the precipitates were freeze-dried and washed using a diafiltration setup. The method was claimed to yield high purities of the different fractions and was suitable for lab-scale experiments.

Economically, using membranes that result in a high product yield and can withstand the harsh environment of various solvents is critical for membrane filtration as a long-term separation method. Another important economic factor is the decrease in irreversible fouling on the membranes, which can in turn limit the capacity of the process and shorten the lifespan of membranes.

Understanding the fouling phenomenon can help in choosing the proper pretreatment method to minimize fouling without sacrificing product yield. Hermia [20] proposed a combined blocking filtration law that can be used to characterize the blocking mechanism that acts on the membrane during constant pressure filtration (Eq. (1)):

$$\frac{d^2t}{dV^2} = \alpha\left(\frac{dt}{dV}\right)^{\beta} \tag{1}$$

where α and β are assume different values, depending on the type of fouling; see Table 1.

Table 1
α and β values for various blocking mechanisms. K_A is the membrane surface area that is blocked per volume permeating through the membrane. K_B is the decrease in membrane pore cross-sectional area per volume permeate. K_C is the area of the deposited cake. u_0 is the mean initial velocity of the permeate, A_0 is the membrane area, and R_r is the hydraulic cake resistance.

Blocking mechanism	α	β
Complete	$K_A u_0$	2
Standard	$(2\,K_B/A_0^{1/2})u_0^{1/2}$	3/2
Intermediate	K_A/A_0	1
Cake	$(R_r K_C/A_0^2)u_0^{-1}$	0

Complete blockage of the membrane occurs when every particle that arrives to the surface blocks a pore, with no superposition of particles [21,22]. Particles that adsorb to the inner pore walls diminish the pore radius and in turn decrease the flux—referred to as the standard blocking mechanism. Intermediate blocking exists when particles deposit themselves onto the membrane surface or other particles, thus shrinking the available membrane area and, consequently, the flux. When the available membrane surface is completely blocked, particles will deposit solely onto other particles, causing cake formation.

Bowen et al. [21] used the blocking filtration law to analyze fouling mechanisms during the microfiltration of bovine serum albumin. One condition of this law was noise-free data during the numerical differentiation, which was solved by fitting the experimental data to a polynomial and using the fitted data for the numerical differentiation. Vela et al. [23] studied the applicability of the blocking filtration law to the ultrafiltration of PEG, demonstrating that the model was applicable to cases in which the transmembrane pressure was low and the cross-flow velocity was high. In other cases, the results lay outside of the specified range of the model and thus had no physical meaning. Many advanced models have also been studied during the last 20 years; however, these models are not frequently used by engineers or in industrial applications [24].

Pretreatment prior to membrane filtration decreases fouling and increases the flux [25–27]. Krawczyk et al. [26] compared two prefiltration methods: microfiltration and dead-end filtration with kieselguhr (diatomite) as a filtration aid. Using these methods, the flux increased from 70 to 225 and 440 L/m^2 h after dead-end filtration and microfiltration, respectively. The loss of hemicellulose during microfiltration was substantial (only 4% was recovered), whereas that during dead-end filtration was negligible.

The aim of this study was to fractionate and purify high-molecular-weight and GGM-rich LCCs by membrane filtration. Irreversible fouling on the membranes was characterized per Bowen [21]. The impact of two prefiltration methods (microfiltration and dead-end filtration with kieselguhr) was also examined with regard to minimizing membrane fouling.

2. Materials and methods

2.1. Spent sulfite liquor (SSL) solution

The raw material was sodium-based SSL that was provided by Domsjö Fabriker (Örnsköldsvik, Sweden), which was collected after the first step in the pulping of softwood (60% Picea abies and 40% Pinus sylvestris). The composition of the raw material is presented in Section 3.1.

2.2. Equipment and experimental procedure

2.2.1. Membranes

The membranes, obtained from Alfa Laval Nordic A/S (Søborg, Denmark), were made of polysulphone with a polypropylene support. The membranes and their specifications are listed in Table 2.

2.2.2. Membrane filtration set-up

The screening study was performed using the equipment in Fig. 1a. The set-up consisted of a 15-L tank with an immersion heater (Backer, Elektro-Värme AB, Sösdala, Sweden), regulated by a temperature control unit (Model MCM, Shinko Technos Co., Ltd, Osaka, Japan), and two digital pressure gauges (DCS40.0AR, Trafag AG, Bubikon, Switzerland) on the feed and retentate side, respectively. The pressure was adjusted with a needle valve on the retentate side, and the flow was set with a positive displacement pump