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Influence of hemicellulose aggregate and gel layer formation on flux and retention during nanofiltration of alkaline solutions

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Abstract

Nanofiltration of process liquors from viscose-type textile fibre production was investigated using a laboratory-scale crossflow test apparatus. Feed solutions contained about 200 g/l sodium hydroxide and a high concentration of hemicellulose as a contaminant originating from the raw material wood. The effects of various pretreatments and the addition of reagents on flux, retention and irreversible fouling were studied. Reagent addition affected the solution state of hemicellulose thus purposely provoking aggregate formation. Dynamic light scattering and turbidity measurements were used to track the evolution of hemicellulose aggregates. Aggregation generally coincided with distinct flux decline during nanofiltration thus indicating that this phenomenon may result in the build-up of gel layers at the membrane surface. Partial neutralisation with sulfuric acid caused extremely severe fouling, whereas methanol addition had a minor effect. The impact of heat treatment and oxidative degradation of hemicellulose on nanofiltration performance was attributed to changes in molar mass distribution.

Keywords: Fouling; Hemicellulose; Aggregation; Gel layer; Dynamic light scattering

1. Introduction

The production of viscose-type cellulosic textile fibres from wood generates large amounts of caustic soda waste liquors containing 200 g/l sodium hydroxide and dissolved hemicellulose as a contaminant. Hemicellulose is a collective term for polysaccharides originating from the raw material wood and their degradation products, e.g.

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sugar acids and hydroxycarboxylic acids. In the process liquors studied here, the high molar mass fraction mainly consists of 4-O-methylglucuronoxylan [1]. Hemicellulose is an undesired component in the viscose fibre production process because it deteriorates both processability and fibre quality. To maintain a certain hemicellulose concentration in the process liquors part of the hemicellulose has to be removed from the process with simultaneous minimisation of caustic soda losses. The purification of these process liquors by nanofiltration (NF) is a challenge not only because of the high corrosiveness of caustic soda but also due to the high concentration of organic solutes (chemical oxygen demand above 40,000 mg/l). Fouling is a critical issue of this process that reduces flux and leads to the need for rigorous cleaning procedures.

Carbohydrate chains in solution are able to interact with each other e.g. via hydrogen bonds thus forming different conformations and types of aggregates. The observation that xylans have a strong tendency to self-associate was first reported by Blake and Richards [2]. Several researchers investigated size exclusion chromatography (SEC) as a technique to detect xylan aggregates in dimethyl sulfoxide (DMSO)/water mixtures [3,4]. The mechanism of aggregation is not only influenced by the molar mass of the xylans but also by the nature and the occurrence of substituents such as acetyl groups and lignin residues. It was proposed that there is a relationship between xylan aggregation in aqueous solution and the formation of xylan structures on cellulose surfaces [4].

Massucco [5] modified the properties of ultrafiltration membranes by generating an irreversibly compressed hemicellulose gel layer under increased pressure. These gel layers adhered to the membrane surface even at high shear forces and reduced pressures and caused a permanent increase in retention at reduced flux. Aqueous suspensions of the acid-insoluble xylan fraction showed gelation at concentrations above 15–16 wt.% [6]. Gelation of the bulk phase has also been observed in solutions of hemicellulose in DMSO/water mixtures [7]. It is therefore suggested that aggregation phenomena of hemicellulose in solution play an important role in the formation of gel layers during nano- and ultrafiltration.

Fouling phenomena during nanofiltration of polysaccharide solutions have been studied using both model substances [8–10] and real effluents from the pulp and paper industry [8,9]. It was observed that anionic substances were retained better and fouled less due to charge repulsion effects especially at high pH where most of the membranes are negatively charged as well. Flux decline was more distinct when using more open membranes particularly if they were permeable to the model substance [8]. In nanofiltration of real effluents a gel or cake layer formed that was controlled by crossflow velocity. The fouling layer disappeared upon rinsing the system, irreversible fouling was therefore found to be low [9].

The aim of the present study was to relate hemicellulose composition and supramolecular structure to nanofiltration performance parameters such as permeate flux, retention of hemicellulose and decrease in pure water permeability. A series of experiments was carried out using a laboratory-scale crossflow membrane test equipment. The evolution of hemicellulose aggregates was studied by dynamic light scattering (DLS) and turbidity measurements. The formation of aggregates and gel layers was purposely provoked by partial neutralisation and by addition of reagents that affect the solution state of hemicellulose such as copper cations or methanol. Hemicellulose composition and molecular structure were influenced by heat treatment and oxidative degradation.

2. Experimental

2.1. *Test equipment, operating procedures and membranes used*

Nanofiltration was carried out in laboratory scale with a flat-sheet crossflow membrane test