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Comparisons of membrane fouling and separation efficiency in protein/polysaccharide cross-flow microfiltration using membranes with different morphologies

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ABSTRACT

The membrane fouling and filtration performance of Bovine serum albumin (BSA)/dextran cross-flow microfiltration using membranes with different morphologies are analyzed and compared. Three 0.1 μm hydrophilic membranes made of mixed cellulose ester (MCE), polyvinylidene fluoride (PVDF) and polycarbonate (PC) were used in these experiments. The MCE and PVDF membranes had sponge-like structures, while the PC membrane had uniform straight-through circular pores. The membrane morphology, cross-flow velocity and transmembrane pressure effects on the filtration flux; membrane fouling and solute transmissions are discussed. The filtration flux increases with increasing cross-flow velocity or transmembrane pressure. The PVDF membrane produced the highest filtration flux, while the MCE membrane exhibited the lowest. A 15–30% difference in filtration flux may be obtained due to different membrane selection. Comparing various filtration resistances, the cake resistances of PVDF and PC membranes are almost the same but much higher than that for the MCE membrane, especially under high pressure. The membrane blocking resistance sequence is MCE > PVDF > PC membrane. The membrane blocking resistance of MCE and PVDF were quite similar due to their sponge network structures. Membrane fouling was analyzed using SEM and CSLM. BSA aggregates deposited onto the membrane surfaces, while dextran molecules adsorbed on the membrane surface and the membrane pore walls. More BSA/dextran mixtures were observed on the PVDF membrane. The PC membrane fouling was due mainly to pore coverage. Dextran molecules were more likely to deposit onto PVDF and MCE membranes. Both BSA and dextran transmission decreased with increasing cross-flow velocity. Increases in transmembrane pressure lead to lower BSA but higher dextran transmission. The PVDF membrane exhibited the highest solute transmission, while the PC membrane resulted in the lowest. All membranes exhibited higher selectivity for the BSA/dextran mixture under higher pressures, especially the PC membrane.

1. Introduction

Microfiltration is one of the most efficient methods used for primary separation in biological production processes. Fermentation broth mixtures contain microbial cells, proteins and polysaccharides, which are separated or concentrated using microfiltration. Because of the high product selectivity, high separation efficiency and high system integration flexibility advantages, microfiltration has attracted the attention of many researchers and engineers to research new microfiltration system development. However, membrane fouling due to solute adsorption, particle deposition or membrane blocking often occurs and significantly decreases the filtration flux or separation selectivity [1,2]. Alleviating membrane fouling through membrane selection or modification, process manipulation or module design is an important approach to achieving optimum operation.

Previous researchers have expended great effort in understanding the membrane filtration of bio-products, especially for the separation of proteins or polysaccharides after microbial cell removing. Tracey and Davis [3] and Bowen et al. [4] reported that the membrane pore size and protein concentration played the most important roles in membrane fouling in microfiltration of pure BSA. The membrane fouling types changed from internal blocking into cake formation after a period of filtration [3–5]. Besides the hydrodynamic conditions, Huisman et al. [6] conducted BSA cross-flow ultrafiltration using membranes with different

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Nomenclature

C_b	solute concentration in feed (kg/m^3)
C_p	solute concentration in filtrate (kg/m^3)
q_s	pseudo-steady filtration flux (m^3/m^2 s)
R	filtration resistance (m^{-1})
R_c	filtration resistance due to cake formation (m^{-1})
R_{cp}	filtration resistance due to concentration polarization layer (m^{-1})
R_{if}	filtration resistance due to membrane internal fouling (m^{-1})
R_m	filtration resistance of clean membrane (m^{-1})
R_t	total filtration resistance (m^{-1})
T	solute transmission defined by Eq. (2) (%)
u_s	cross-flow velocity (m/s)

Greek letters

ΔP	filtration pressure (Pa)
μ	filtrate viscosity (kg/s m)

molecular weight cut-off (MWCO). When a membrane with small MWCO (MWCO < 30 kDa) was used, the early stage membrane fouling was determined by the interaction between the protein and membrane, while that in the later period was dependent on the interactions between protein molecules. The membrane MWCO played a trivial effect on the membrane fouling when a membrane with large MWCO was used. The interactions between protein functional groups are important factors affecting membrane fouling, especially in protein mixture ultrafiltration [7]. Iritani et al. [7] and Ouammou et al. [8] indicated that the protein zeta potential or electrostatic interaction was an important property in determining membrane fouling in bio-mixture ultrafiltration. Different approaches for protein membrane filtration were proposed in previous literatures. Blatt et al. [9] claimed that the membrane fouling in protein ultrafiltration depended strongly on the transmembrane pressure. The concentration polarization layer presented an important role under low pressures, while solute molecules deposited onto the membrane surface or adsorbed into the wall surface in membrane pores were important under high pressures. A gel layer formed on the membrane surface could be described appropriately using a gel-polarization model in such conditions [2,10].

Several dextran membrane filtration results were proposed. Vernhet and Moutounet [11] carried out the cross-flow microfiltration of red wine and indicated that polysaccharides were the major foulants. Garcia-Molina et al. [12] studied the ultrafiltration of dextran suspensions. They found a fouling layer was formed on the membrane surface to control the filtration rate and the filtration rate increased with increasing transmembrane pressure. Hwang and Huang [13] investigated membrane fouling in blue dextran cross-flow microfiltration using PC membranes with different pore sizes. They found that the membrane pore sizes were reduced by dextran adsorption and proposed a theoretical model to estimate the fouled pore sizes under various conditions. Proteins and polysaccharides were primarily responsible to membrane fouling in membrane bioreactors [14]. However, little is currently known about the fouling mechanisms. When protein/polysaccharide mixtures were prepared to simulate the bio-product of fermentation broths and filtered in microfiltration, the filtration flux was much lower than that in pure component filtration [15,16]. This was attributed to the more compact structure of the fouled layer formed by multi-component [15]. Hwang and Sz [16] found that membrane fouling was due mainly to dextran adsorption into the membrane pores in BSA/dextran binary suspension cross-flow microfiltration. A hydrodynamic model coupled with macromolecular coil-stretch behavior was proposed to estimate the mean pore size and fouled layer depth under various operating conditions. Hwang and Sz [17,18] indicated that the major filtration resistances were caused by the deposition of BSA aggregates onto the membrane surface and the adsorption of dextran molecules into the membrane pores. The dextran concentration, original membrane pore size and transmembrane pressure effects on the filtration performance were discussed.

Different components separated in the fermentation broth play different roles in membrane fouling during microfiltration. The variety of physical and chemical characteristics of various foulants causes the fouling phenomena to be complex and difficult to analyze. However, selecting a suitable membrane as the filter medium is an essential approach to achieving efficient operations. The fouling extent and pattern depend significantly on the membrane physical and chemical properties, such as surface morphology, pore size (distribution), functional groups, surface charge density and hydrophobicity. For instance, Hwang and co-workers [19–21] studied the effect of membrane morphology on the particle fouling during microfiltration. They proposed an analyzed method to establish membrane blocking charts for relating the blocking index, filtration rate and particle accumulation [20]. The critical conditions at which the membrane fouling changed from pore blocking to cake filtration depended markedly on the membrane morphology [21]. Kim et al. [22] defined the characteristics of commercial membranes and claimed that the performance of a microfiltration was mainly controlled by the nominal structure. Ho and Zydney [23] studied the effects of surface morphology and pore structure of membranes on the initial rate of protein fouling. Pore blockage caused by the deposition of large protein aggregates occurred on the surface of membranes with straight-through pores. The rate of blockage was a strong function of membrane porosity. However, membranes with interconnected pores were fouled more slowly because the fluid could flow around the blocked pores through the interconnected pore structure. Yao et al. [14] studied the combined influences of proteins and polysaccharides on dead-end microfiltration using PVDF and PC membranes. They revealed that the initial fouling rate of PVDF membrane was lower than that of track-etched PC membrane, except when the protein/polysaccharides had a ratio of 500:100 mg/L. The results showed that the cake resistance rather than pore adsorption was the main fouling mechanism for both membranes during filtration and both membranes showed higher polysaccharide rejection than protein rejection. Dizge et al. [24] studied the influence of the membrane type and pore size in activated sludge cross-flow microfiltration. Their experimental data showed that the filtration flux was affected strongly by the membrane surface roughness and membrane pore structure. However, the pore size effect on the filtration flux might have contrary tendencies for different membrane types.

In this article, the main effort was devoted to study the effects of membrane morphology on the performance of cross-flow microfiltration of protein/polysaccharide mixtures. BSA and dextran were selected as typical protein and polysaccharide filtration samples. Three hydrophilic membranes manufactured from different materials were used as the media to filter BSA and dextran mixtures. The membranes had similar nominal pore sizes and other