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Effects of three natural organic matter types on cellulose acetate butyrate microfiltration membrane fouling

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ABSTRACT

This study aimed to clarify the effect of interactions between membranes and natural organic matter (NOM), which is considered to be the major membrane foulant in wastewater treatment processes. Sodium alginate (SA), humic acid (HA) and bovine serum albumin (BSA) were used as NOM models. Hollow fiber membranes were prepared using cellulose acetate butyrate polymer (CAB). Filtration experiments were carried out using SA, HA and BSA solutions and the membrane fouling behavior was examined. NOM adsorption on CAB membranes was measured by quartz crystal microbalance with dissipation (QCM-D), where NOM solutions were flowed across CAB spin-coated quartz crystal sensors and adsorbed. SA showed more severe permeate flux decline during the early stage of filtration and lower recovery of permeate flux after backwashing compared with HA. The severe flux decline for SA was due to pore-plugging and cake formation with high molecular weight components. The BSA solution, with no high molecular components, showed a gradual permeate flux decline and resulted in lower permeate flux after 240 min filtration compared with HA. The gradual permeate flux decline with the BSA solution was due to ready adsorption of BSA on the CAB membrane.

1. Introduction

Membrane technologies such as microfiltration (MF) and ultrafiltration (UF) are attractive for drinking water and wastewater treatment due to complete particle removal, including microorganisms such as protozoa (Giardia and Cryptosporidium) [1,2]. The obstacle to more widespread use of membrane technology is membrane fouling, which decreases permeability, resulting in conservative design flux [3]. Some organic and inorganic materials in the feed water that accumulate on the membrane surface or within the pores during filtration are removed by periodical physical cleaning, such as backwashing and air-bubbling. Membranes for which performances cannot be recovered by physical cleaning only are treated by chemical cleaning using an oxidizer, alkali, and acid. Thus, membrane fouling causes increased operating costs, including energy and chemical consumption, and shortened membrane life, which limits widespread use of membrane technology [4,5].

Many studies have been carried out on characterizing membrane foulants and membrane fouling mechanisms. With respect to characterization of membrane foulants, natural organic matters (NOM), which are products of chemical and biological degradation of plant and animal residues [6], are considered the major membrane foulants [7]. In previous studies, it was reported that both hydrophobic NOM components, such as humic substances [8–11], and hydrophilic NOM components, such as polysaccharide- and protein-like substances [12–16], contributed to membrane fouling. It was also reported that synergy between hydrophobic and hydrophilic NOM [17] or NOM and inorganic matters [18,19] affected membrane fouling. With respect to membrane fouling mechanisms, Yuan et al. reported that large particles of humic acid played an important role in initial fouling during microfiltration of humic acid solutions [20]. Yamamura et al. conducted a pilot-scale microfiltration test on surface water and reported that membrane foulants changed from relatively large particles to small particles during filtration [21].

For better understanding and control of membrane fouling, more information about the effect of the interactions between NOMs and membranes on membrane fouling is required. Shäfer et al. examined the effect of colloid size on membrane fouling and found that the colloids with sizes closest to the membrane pore size caused the greatest flux decline [22]. A number of researchers examined adsorption of NOM on membranes [23–25]. Jucker et al. [23] and Jones et al. [24] reported that the adsorption of NOMs such as humic acid, fulvic acid and protein on the membrane surface was influenced by solution chemistry such as pH, ionic strength and presence of calcium. Quartz crystal microbalance with dissipation

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(QCM-D) monitoring is an attractive method for examining NOM adsorption on organic and inorganic surfaces [26–28]. When an NOM solution is passed through the flow chamber equipped with a polymer (e.g. poly(methyl methacrylate) [26] or polyethersulfone [27]) spin-coated quartz crystal sensor, the resonant frequency of the quartz crystal sensor decreases with adsorbed mass and information about adsorption extent and adlayer properties can be obtained. The QCM-D method is expected to be a powerful tool in clarifying the effect of NOM adsorption on membrane fouling.

The objective of this study was to elucidate the effect of interactions between membranes and NOMs on membrane fouling to improve understanding and control of membrane fouling. CAB polymer was used as a membrane material due to its good resistance to fouling, chemical tolerance and easiness in controlling of membrane structure [29]. We prepared hollow fiber membranes from CAB polymer via thermally induced phase separation and then compared membrane fouling by sodium alginate and BSA as models of hydrophilic NOMs with that by humic acid as a model of a hydrophobic NOM. Differences in membrane fouling behaviors for three types of NOMs were examined from the view point of the interaction between the CAB membrane and NOMs using QCM-D measurements.

2. Experimental

2.1. Materials

Cellulose acetate butyrate (CAB, Mw = 65,000, Daicel Chemical Industries, Japan) was used as a membrane material. The substitution degrees of acetyl and butyryl groups were 2.04 and 0.71, respectively. Triethylene glycol (TEG, Wako Pure Chemical Industries, Japan) was used as a diluent for membrane preparation via thermally induced phase separation. The sodium alginate filtration solution was prepared by mixing sodium alginate (Aldrich Chemical Co., Milwaukee, WI) with sodium bicarbonate (Wako Pure Chemical Industries) as a buffer. The humic acid (Aldrich Chemical Co.) solution was also prepared with sodium bicarbonate. The bovine serum albumin (BSA) solution was prepared by mixing BSA with a sodium dihydrogen phosphate/disodium hydrogen phosphate buffer solution at pH 7 (all reagents from Wako Pure Chemical Industries). All chemicals were used without further purification.

2.2. Preparation of hollow fiber CAB membrane

Hollow fiber membranes were prepared using a batch-type extruder via thermally induced phase separation (TIPS) under the preparation conditions shown in Table 1. CAB polymer and TEG were placed into a vessel equipped with a stirrer and heated to 443 K. The mixture was then blended for 1 h and held for 2 h to remove air bubbles from the polymer solution. The homogeneous polymer solution was fed to a spinneret with a gear pump using N_2 gas pressure. The spinneret consisted of an inner tube with a diameter of 0.83 mm and an outer tube with a diameter of 1.58 mm. The hollow fiber was extruded from the spinneret with TEG as an inner coagulant and was introduced into a water bath at 323 K, where phase separation proceeded and the porous structure was solidified. The hollow fiber was wound at a take-up speed of 0.21–0.26 m/s. Finally, residual TEG in the membrane was extracted by water.

Table 1
Preparation conditions for the hollow fiber membranes.

Spinneret size (mm)	1.58/0.83 (outer/inner diameter)
Polymer solution	CAB (25 wt.%)-TEG
Solution temperature (K)	443
Polymer solution flow rate (m/s)	0.17–0.19
Inner coagulant	TEG
Inner coagulant flow rate (m/s)	0.17–0.19
Inner coagulant temperature (K)	298
Take-up speed (m/s)	0.21–0.26
Air gap (mm)	0
Bath composition	Water
Bath temperature (K)	323

2.3. SEM observation

The hollow fiber membrane was freeze–dried (FD-1000 freeze dryer, EYELA, Japan). The dry hollow fiber membrane was immersed into liquid nitrogen, broken, and treated by Au/Pd sputtering. Scanning electron microscope (SEM, Hitachi Co., JSM-5610LVS, Japan) images of the outer and inner surfaces of the hollow fiber membrane were measured at an accelerating voltage of 15 kV.

2.4. Filtration experiments

A diagram of the filtration-backwashing experiments with the single hollow fiber module is shown in Fig. 1. Feed solution was pumped into a module packed with a single hollow fiber of length of about 110 mm (effective membrane area = 3.5×10^{-4} m^2). Cross-flow filtration was carried out from the outer surface to the inner surface of the hollow fiber at a transmembrane pressure of 50 kPa and a cross-flow rate of 0.04 m/s. For each filtration experiment, deionized (DI) water was initially permeated and the pure water permeability J_0, was measured. Feed solution, consisting of 50 mg/L sodium alginate and 0.5 mmol/L sodium bicarbonate as a buffer solution (pH 8), was filtered and the permeability of the sodium alginate solution, J, was measured. After filtration for 1 h, backwashing with DI water was carried out for 1 min at a pressure of 100 kPa. The filtration-backwashing cycle was repeated four times. During filtration of sodium alginate, concentrations of sodium alginate in the feed and permeate were measured using a total organic carbon (TOC) meter (Shimadzu Co., TOC-V, Japan). Rejection of sodium alginate was calculated as:

$$\text{Rejection}\,(\%) = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

where C_0 and C are the TOC in feed and permeate, respectively.

Filtration experiments for solutions containing 50 mg/L humic acid and BSA were carried out in a same way on feed solutions prepared as described in Section 2.1. The rejections of humic acid and BSA were calculated according to Eq. (1) by measuring the absorbance at wavelengths of 254 nm and 280 nm, respectively, with a spectrometer (Hitachi Co., U-2000, Japan).

2.5. Apparent molecular weight distribution measurement

Apparent molecular weight distributions for the solutions of sodium alginate, humic acid and BSA solutions were measured by the membrane fractionation method using ultrafiltration and microfiltration membranes [10,20,30]. 50 mg/L of sodium alginate, humic acid and BSA solutions prepared in the manner described in Section 2.1 were used as feeds. Three kinds of ultrafiltration membranes used were Amicon® ultra with nominal molecular weight limits (NMWLs) of 30, 50 and 100 kDa (Millipore). Microfiltration membranes with pore sizes of 0.1 and 0.45 μm were also used (Durapore® membrane filter, Millipore). The concentrations in the feed and permeate for sodium alginate, humic acid and BSA were measured as described above and the apparent molecular weight distributions were calculated from the resultant rejections using the ultrafiltration and microfiltration membranes.