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Journal of Membrane Science 258 (2005) 43–54
journal of MEMBRANE SCIENCE
www.elsevier.com/locate/memsci

Biofouling potential of various NF membranes with respect to bacteria and their soluble microbial products (SMP): Characterizations, flux decline, and transport parameters

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Received 11 October 2004; received in revised form 18 February 2005; accepted 21 February 2005

Abstract

A problem of considerable concern in membrane filtration processes is biofouling with microorganisms and their soluble microbial products (SMP). This work focused on NF membrane biofouling by either bacteria (biotic filtration/biofouling) or SMP (abiotic filtration/biofouling); the former was analyzed using NF membrane filtration, the concept of concentration polarization (CP), and the convection–diffusion–electrophoretic model (CDE), using *Flavobacterium lutescens* bacteria, with the latter investigated through NF membrane filtrations using SMP extracted from the bacteria. Four different NF membranes were tested: piperazine versus *meta*-phenylene diamine (MPD)-based polyamide thin-film composite (TFC) membranes. Through membrane characterizations, including contact angle, surface charge, SEM, and AFM, the MPD-based NF membranes exhibited relatively hydrophobic and higher roughness compared to the piperazine-based NF membranes. The convection–diffusion–electrophoretic migration model, in conjunction with the CP concept, could demonstrate the electrostatic interaction of bacteria against trans-membrane pressure during filtration. With increasing operating pressure, the CP thickness of the bacteria boundary layer decreased due to compaction of the CP layer. The CP layers of bacteria for the MPD-based membranes having relatively high negative surface charges, were less compacted in thickness due to electrostatic repulsion between the membrane surfaces and bacteria. All membranes exhibited high repulsive forces with the extended DLVO (XDLVO) approach, due to the high AB interaction energy in an aquatic system. To evaluate the interactions between the membrane surface and bacteria during filtration, the Hamaker constants of various NF membranes were also determined by measuring the contact angle between the membrane surface and bacteria. NF membranes with greater hydrophobicity and roughness exhibited higher biofouling potential in terms of membrane–bacteria interactions identified from the Hamaker constants estimation. From SMP (extracted from *F. lutescens* at a decay condition) characterizations, some portions of colloidal NOM (i.e., with higher molecular weights) were revealed to be comprised of SMP through the IR spectra analysis. Also, they were found to have high hydrophilicity and biodegradability from XAD resins and BDOC measurements, respectively. When the SMP were compared to other macromolecules (bovine serum albumin, colloidal NOM, and Suwannee River NOM) in terms of fouling through membrane fouling experiments, they provided high membrane fouling potential. Various transport parameters (mass transfer coefficient, membrane selectivity, and solute permeability) of the SMP were determined by irreversible thermodynamic models combined with the film model to quantitatively investigate the SMP behaviors in NF membranes [S. Lee, G. Amy, J. Cho, Sherwood correlations for natural organic matter (NOM) in nanofiltration (NF) membranes and its applicability, J. Membr. Sci., 240 (1–2) (2004) 49–65]. Relatively hydrophobic and rougher membranes (i.e., MPD-based NF membrane) exhibited higher selectivity, in terms of SMP, compared to relatively hydrophilic membranes.

Keywords: Soluble microbial products (SMP); Nanofiltration; Convection–diffusion–electrophoretic model (CDE model); Hamaker constant; Biofouling; Colloidal NOM

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1. Introduction

Many researchers have studied membrane processes to produce safe and delicious tap water. Biofouling with bac-

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doi:10.1016/j.memsci.2005.02.025

teria and their soluble microbial product (SMP) is a significant problem. Bacteria in aquatic systems have high biofouling potential in membrane processes due to cell growth and produces by-products (i.e., SMP). They can also provide serious problems in terms of the flux and removal efficiency during filtration. To control these problems, it is most important to understand the physico-chemical interactions between both bacteria–membrane and membrane–SMP. The adhesion behavior of bacteria onto the membrane surface was investigated by surface thermodynamics and the DLVO (Derjaguin–Landau–Verwey–Overbeek) theory. These have been used to explain the adhesion potential of *Paenibacillus polymyxa* bacteria on minerals with thermodynamics and extended DLVO (XDLVO) theory [2]. The thermodynamics approach cannot account for bacteria adhesion onto minerals due to an inadequate description of the electrostatic interaction. Meanwhile, the XDLVO theory can partially illustrate the adhesion behavior between minerals and bacteria. The Hamaker constants between bacteria and the membrane surface can be calculated using contact angle measurements to estimate a quantitative interaction force (i.e., attraction) between two [3]. With a comprehension of the interaction between bacteria and a membrane, an understanding of biofouling potential with bacteria could be obtained. The accumulation of bacteria onto the membrane surface was analyzed with the convection–diffusion–electrophoretic (CDE) migration model. The CDE model can be applied to either charged protein or macromolecules to evaluate the electrostatic interaction with the membrane surface [4].

SMP can be defined as organic materials produced by microorganisms, such as bacteria and algae. Noguera et al. [5] defined SMP as “the pool of organic compounds that result from substrate metabolism and biomass decay during the complete mineralization of simple substrates”. Although SMP are major organic compounds in wastewater systems, they consist of some portions of organic matters from natural surface water. Many researchers have performed characterizations of SMP in terms of their size, biodegradability, and toxicity using various different methods. Boero et al. [6] used ^{14}C-labelled compounds to determine the molecular weight (MW) distribution of SMP using batch ultrafiltration cells. Schiener et al. [7] measured the MW of SMP. The SMP was found to exhibit a bimodal distribution, with 30% having MW <1 kDa and 25% >100 kDa. In this work, a high performance size exclusion chromatography (HP-SEC) method was used to measure the MW distribution of SMP with UV, fluorescence, and DOC detectors. Another characteristic parameter of SMP is their chelating property; Kuo and Parkin [8] have shown that SMP have typical chelating functional groups, such as carboxylates, hydroxyls, phenols, and amines. These chelating functional groups react with metal ions in surface water to form metal complexes. The biodegradability of SMP has been investigated with respect to the residual COD. Parkin and McCarty [9] identified the biodegradable SMP fraction ranged from 0 to 60%. Barker et al. [10] investigated the biodegradability of SMP with different MW values. The SMP with relatively high and low MW were found to be more easily degraded under aerobic and anaerobic conditions, respectively. SMP were also found to be more toxic than effluent organic compounds (EfOM) with respect to mutagenic responses [11]. Extracellular polymeric substances (EPS) can be differentiated from SMP by their location (either inside/surface or outside) of the bacterial cell [12]. Thus, membrane filtration can be categorized by either a biotic or abiotic fouling experiment where either bacteria/combined EPS or SMP, respectively, are involved.

The objectives of this study were: (1) to investigate NF membrane biofouling under biotic condition, using concentration polarization (CP) with bacteria accumulation and the convection–diffusion–electrophoretic model with bacteria, (2) to investigate NF membrane fouling under biotic condition with respect to the interaction between bacteria and the membrane surface in terms of the Hamaker constant, and (3) to characterize the SMP and NF membranes using various methods, and to relate the characterized results to NF membrane biofouling under abiotic conditions.

2. Theory

2.1. Convection–diffusion–electrophoretic migration model

To demonstrate the transport phenomenon of charged solutes during filtration, the convection–diffusion model combined with electrostatic concept was used. This is a simplified form of the extended Nernst–Plank model (Eq. (1)), which can illustrate the behaviors of ions in both NF and RO membranes.

$$JC_i - D\frac{\mathrm{d}C_i}{\mathrm{d}x} - \mu_i C_i \frac{\mathrm{d}\psi}{\mathrm{d}x} = JC_\mathrm{p} \tag{1}$$

where D is the diffusivity of charged solute, and varies depending on the chemical conditions, such as pH and ionic strength; the diffusivity was calculated by the Stokes–Einstein equation. μ_i is the electrophoretic mobility of the solute and ψ is the electric potential of the charged membrane; ψ can be simplified by the Debye approximation ($\psi = \psi_0 \exp(-\kappa x)$).

The electric field of a charged surface is expressed as Eq. (2):

$$E_x = -\frac{\mathrm{d}\psi}{\mathrm{d}x} \tag{2}$$

where E_x is the electric field at the distance (x) from the membrane surface.

Because of the difficulty in measurements of surface potential, the zeta potential (ψ_z) was measured, which is the surface potential at the shear plane. The electric field at the membrane wall (E_z) is as followed:

$$E_\mathrm{z} = -\kappa\psi_\mathrm{z} \tag{3}$$