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Synergistic effects in combined fouling of a loose nanofiltration membrane by colloidal materials and natural organic matter

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Abstract

Fouling of nanofiltration (NF) membranes in water treatment and wastewater reuse applications is often caused by both colloidal materials and dissolved organic matter. However, most past mechanistic studies on NF membrane fouling have focused on either colloidal fouling or organic fouling. In this study, the performance of a 'loose', low salt rejection NF membrane during combined fouling by both colloidal materials and dissolved natural organic matter (NOM) was compared with that during colloidal fouling and organic fouling alone. A significant synergistic effect was observed during combined fouling, manifested as considerably higher flux decline rate than what expected based on the sum of colloidal and organic fouling alone. Microscopic analysis of the colloid/organic foulant layer structure confirmed faster foulant accumulation on the membrane surface, indicating a mechanism of hindered back diffusion of colloidal and organic foulants. The membrane flux decline during combined fouling was also found to depend on solution chemistry and colloidal particle size. Notably, the effects of these factors are different from those during fouling by colloidal materials or dissolved organic matter alone.

Keywords: Nanofiltration; Colloidal fouling; Colloid; Natural organic matter; Organic fouling; Combined fouling; Hindered back diffusion

1. Introduction

Nanofiltration (NF) is an attractive process in water treatment and wastewater reuse because of its high rejection of multivalent ions and dissolved organic compounds, and because it requires a much lower operating pressure than reverse osmosis. However, like other membrane filtration processes, fouling is a major problem in the efficient operation of NF systems. Membrane fouling causes deterioration of both the quantity and quality of treated water, and consequently results in higher treatment cost. In water and wastewater treatment, NF membranes are subject to fouling by colloidal materials (referred to as colloidal fouling) as well as by dissolved organic compounds (referred to as organic fouling), which are not removed by the pretreatment processes.

Membrane fouling by colloidal materials is governed by concentration polarization and cake layer formation on the membrane surface. For membranes with high intrinsic resistance, i.e., nanofiltration and reverse osmosis, the resistance of the cake layer is often insignificant compared to that of the membrane itself. However, the increase in osmotic pressure due to the enhanced concentration polarization of salt ions within the colloidal cake layer – a phenomenon referred to as cake-enhanced osmotic pressure – may result in rapid flux decline during cake layer development [1–3]. The formation of the colloidal cake layer is affected by physicochemical properties of the membrane surface (surface charge, roughness, and hydrophobicity), characteristics of the colloidal material (particle size and charge), solution chemistry (solution pH and ionic strength), and system hydrodynamics (cross-flow velocity and transmembrane pressure) [4–9]. The surface charges of the membrane and the colloidal particles determine the electric double layer interactions between the membrane surface and the colloidal foulant as well as those among colloidal particles, which strongly depend on the total ionic strength and pH of the feed solution [9]. Par-

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ticle size, cross-flow velocity, and transmembrane pressure are found to affect the thickness, porosity, and permeability of the cake layer [7,9]. Colloidal deposition on the membrane surface was also found to be enhanced by membrane surface roughness [10,11]. For chemically inert colloidal materials, such as silica, colloidal particles are held in the cake layer by non-specific interactions (mainly electric double layer interactions) and transmembrane pressure. Consequently, for such cases, fouling is mostly reversible.

Organic fouling is more complicated because specific interactions between chemical functional groups on the membrane surface and those of the organic foulants may occur. Therefore, physicochemical characteristics of organic foulants – charge, chemical functionality, and molecular conformation – play a very important role in organic fouling. Organic fouling of polymeric membranes was also found to be affected by the ionic composition of the feed solution. One phenomenon that has been reported in a myriad of studies is enhancement of organic fouling by divalent cations. Divalent cations, such as Ca^{2+} and Mg^{2+} have been shown to increase organic fouling rate by forming complexes with natural organic matter (NOM), a major foulant in natural water [12–21]. A recent study on NOM fouling mechanisms found that Ca^{2+} was able to induce specific membrane–NOM and NOM–NOM interactions, which results in a dense, cross-linked organic fouling layer, and consequently rapid flux decline [22].

Although pretreatment by coagulation/flocculation or low pressure membrane filtration can remove most particulate matter, fine colloidal materials and dissolved organic foulants can escape the pretreatment. Therefore, NF membranes are always exposed to both fine colloids and dissolved organic compounds. However, because of the complex nature of natural and waste waters, almost all mechanistic studies on membrane fouling in water and wastewater applications have focused on one foulant type, usually colloidal foulant or organic foulant, for the purpose of simplicity. It is very important to understand the effect of colloid–NOM interactions on the mechanisms of NF membrane fouling by both colloidal materials and dissolved organic matter, i.e., combined fouling.

The study presented here aims to unravel the mechanisms of combined organic/colloidal fouling of NF membranes. The effects of foulant characteristics, solution chemistry, and filtration system configuration on combined fouling of NF membranes were systematically investigated. Results demonstrate significant synergistic effects during fouling of NF membranes when both colloidal materials and dissolved organic matter are present in the feed water.

2. Materials and methods

2.1. Model NF membrane and membrane characterization

A thin-film composite nanofiltration membrane, NF-270 (FilmTec Corp., Minneapolis, MN), was tested. Membrane samples were stored in deionized water at 4 °C, with water replaced regularly. All membrane samples were rinsed thoroughly with deionized water prior to use. The surface morphology of the membrane was analyzed using a Multimode atomic force microscope (AFM) (Digital Instruments, Santa Barbara, CA). Imaging was performed in tapping mode in deionized water using an oxide sharpened SiN probe (Veeco Metrology Group, Santa Barbara, CA). Membrane surface roughness was determined by AFM image analysis on a $10\,\mu m \times 10\,\mu m$ surface area. Zeta potential of the membrane surface was determined by streaming potential measurements conducted with an electrokinetic analyzer (BI-EKA, Brookhaven Instruments Corp., Holtsville, NY) under all solution conditions tested in the fouling experiments [23–25].

2.2. Model foulants

Suwannee River humic acid (SRHA) standard (International Humic Substances Society, St. Paul, MN) was used as the model organic foulant. It has been thoroughly characterized and used in numerous fouling studies [13,26–28]. Stock solution (1 g/L) was prepared by dissolving the SRHA powder as received in deionized water and adjusting the pH to 8.2 with NaOH to ensure complete dissolution. The stock solution was then stored in a sterilized amber glass bottle at 4 °C.

The model colloidal foulants used are two types of silica colloids with different particle sizes: MP3040 and SNOWTEX® (ST-XL) (Nissan Chemicals, Westheimer, TX). Both colloids are spherical in shape and the average diameters of the colloids are 300 nm for MP3040 and 30–40 nm for ST-XL. Concentrated stock suspensions of silica were stored at 4 °C. Before use, the stock suspension was hand shaken to agitate all visible precipitate, and then sonicated for at least 15 min to ensure good dispersion of the colloids. The concentration of the stock suspension was routinely monitored following the same dispersing procedure.

2.3. Solution chemistry

The solution conditions tested in the fouling experiments were carefully chosen to represent typical natural waters. Table 1 summarizes the solution conditions used in this study. All fouling experiments were conducted at a total ionic strength of 10 mM with various ionic compositions. Feed solution pH was kept at 8.1 in all experiments by adding 1 mM $NaHCO_3$ and a small amount of NaOH. In some experiments, $CaCl_2$ or $MgCl_2$ (Fisher Scientific, Pittsburgh, PA) was added at a concentration of 1 mM to study the effect of divalent cations on fouling. The desired total ionic strength was obtained by adjusting the concentration of NaCl (Fisher Scientific). A constant SRHA concentration of 20 mg/L was used in all experiments involving organic foulants. The concentration was confirmed by measuring the total organic carbon (TOC) of the feed solution with a TOC analyzer (Shimadzu Corporation, Kyoto, Japan) and comparing the measured value with that calculated from the mass concentration of SRHA and its organic carbon content provided by the International Humic Substances Society. Colloidal concentration used in all experiments involving colloids was 100 mg/L. The high organic and colloidal concentrations were chosen to accelerate the fouling process.