Chemical Engineering Journal 295 (2016) 268–277

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Fouling behavior of dissolved organic matter in nanofiltration membranes from a pilot-scale drinking water treatment plant: An autopsy study

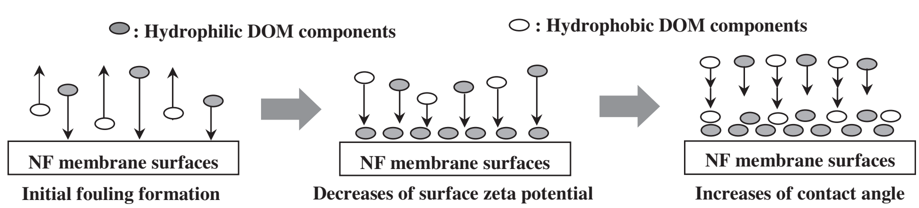
Kangmin Chon [a,b], Jaeweon Cho [c,*]

[a] Jeju Global Research Center (JGRC), Korea Institute of Energy Research (KIER), Haemajihaean-ro 200, Gujwa-eup, Jeju-si, Jeju-do 63357, Republic of Korea
[b] School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Cheomdan-gwagiro 261, Buk-gu, Gwangju 61005, Republic of Korea
[c] School of Urban and Environmental Engineering, Ulsan Institute of Science and Technology (UNIST), UNIST-gil 50, Ulju-gun, Ulsan 44919, Republic of Korea

HIGHLIGHTS

- Fouling characteristics of NF membranes can be changed by a CC–MF process.
- Hydrophilic DOM and inorganic scaling govern fouling formation of NF membranes.
- Variations in surface properties of NF membranes dominate fouling behavior of DOM.
- Hydrophilic DOM contributes to initial fouling formation of the NF membranes.
- Adsorption of hydrophobic DOM may intensify subsequent fouling formation of NF membranes.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 January 2016
Received in revised form 19 February 2016
Accepted 13 March 2016
Available online 17 March 2016

Keywords:
Combined coagulation and microfiltration process
Dissolved organic matter
Drinking water treatment plant
Membrane autopsy
Nanofiltration

ABSTRACT

This study investigated the fouling behavior and mechanisms of nanofiltration (NF) membranes fed with surface water pre-treated using a combined coagulation and microfiltration (CC–MF) process in a pilot-scale drinking water treatment plant through membrane autopsies and characterization of the desorbed foulants. The CC–MF process removed hydrophobic DOM components preferentially and mitigated biofouling of the NF membranes efficiently. This clearly shows that the fouling characteristics of the NF membranes can be influenced by the CC–MF process. The fouling formation of the NF membranes was dominated by chemically removable DOM components primarily consisting of hydrophilic fractions and inorganic scaling. However, the surfaces of the fouled NF membrane (contact angle = 65°) were more hydrophobic than those of the virgin NF membrane (contact angle = 57°). This is attributed to the differences in the fouling behavior of hydrophobic and hydrophilic DOM components in relation to the surface features of the NF membranes (i.e., surface zeta potential and contact angle). The initial formation of organic fouling layers on the NF membranes surfaces was caused by deposition of hydrophilic DOM components, which can decrease electrostatic repulsive forces between humic substances and the negatively charged NF membrane surfaces by reducing the negative surface zeta potential. Therefore, hydrophobic DOM components accumulated more readily onto the NF membrane surfaces. The covering hydrophilic organic fouling layers with hydrophobic fractions may intensify the subsequent adsorption of hydrophobic DOM components on the NF membrane surfaces by increasing the contact angle.

* Corresponding author. Tel.: +82 52 217 2833; fax: +82 52 217 2819.
E-mail address: jaeweoncho@unist.ac.kr (J. Cho).

http://dx.doi.org/10.1016/j.cej.2016.03.057
1385-8947/

1. Introduction

Integrated membrane systems consisting of microfiltration (MF)/ultrafiltration (UF) followed by reverse osmosis (RO) or nanofiltration (NF) are becoming indispensable for drinking water treatment since they efficiently remove both waterborne pathogens and various water contaminants, such as dissolved organic matter (DOM), heavy metals, metalloids, and trace organic contaminants (i.e., disinfection byproducts, pharmaceuticals, personal care products, and endocrine disrupting chemicals) [1–4]. Despite of great advances in membrane technologies (i.e., improvement of membrane properties related to permeate flux and fouling resistance), the practical application of integrated membrane systems is still limited by membrane fouling caused by adsorption, accumulation or precipitation of organic and inorganic constituents on the membrane surfaces [5]. Membrane fouling is a major contributor to increases in operating costs due to decreasing permeate flux, elevating transmembrane pressure (TMP), and frequent chemical cleaning, which may shorten the lifetime of membranes [5–7]. Therefore, the identification of membrane foulants and their fouling mechanisms is necessary to develop optimal pre-treatment, backwashing, physical and chemical cleaning procedures for mitigation of membrane fouling [8].

DOM components comprising aromatic and aliphatic hydrocarbons have been identified as a main constituent of foulants in membrane processes for drinking water treatment [1,6]. Although many studies have investigated the fouling behavior of DOM in many types of membranes with various feed water characteristics, the interactions between DOM components and membrane surfaces have not been properly identified due to the inherent complexity of DOM [9]. During the past decade, coagulation coupled to MF/UF membranes have been widely used as a pre-treatment for NF and/or RO membranes as pre-treatment is an essential step to control the fouling formation by DOM in high-pressure membranes (i.e., NF and/or RO membranes) [10]. Her et al. [6] demonstrated that ozonation can increase the degree of membrane fouling by hydrophilic DOM components and enhance biofouling onto the membrane surfaces. A recent study found that DOM bound to silica or calcium strongly contributes to the fouling formation of NF and RO membranes receiving UF membrane-treated groundwater [11]. However, because structural and functional characterizations of DOM are time-consuming and labor intensive, there have been few comprehensive studies on the effects of variations of physicochemical properties of DOM by pre-treatments on the formation of membrane fouling [12].

Numerous researchers have conducted fouling experiments with laboratory-scale filtration units to extend the understanding of the fouling formation in membrane processes for drinking water treatment [13,14]. Nevertheless, their fouling mechanisms have not yet been clearly revealed as laboratory-scale fouling tests performed under controlled operating conditions cannot fully reflect the fouling phenomena taking place in the practical implementation of membrane processes (i.e., pilot-scale or full-scale drinking water treatment plants (DWTPs)). Therefore, pilot-scale or full-scale experiments are necessary to consider the effects of changes in feed water qualities, efficiencies of pre-treatment, and operating conditions on the fouling development in membrane processes for drinking water treatment. A membrane autopsy is considered to be a powerful diagnostic tool since it can provide valuable insights into the nature of the deposited foulants on the membrane surfaces and fouling behavior closely associated with the membrane and feed water characteristics and thereby help improve the performance of membrane systems [15]. However, only few autopsy studies of NF membrane modules used in pilot-scale or full-scale DWTPs have been performed due to their long duration and high costs [1,16]. In addition, most previous autopsy studies have primarily focused on the RO membranes used for brackish water and/or seawater desalination [17,18]. Based on these reasons, a fundamental understanding of fouling characteristics in NF membrane processes fed with the permeates of a combined coagulation and MF (CC–MF) process for drinking water treatment, including possible fouling behavior and primary types of foulants, has yet to be comprehensively established.

The main objective of this study is to provide deeper insights into the fouling behavior and mechanisms of NF membranes in a pilot-scale DWTP. Therefore, DOM in the feed, treated surface water, and the deposited foulants on the NF membranes surfaces were rigorously characterized by various analytical methods to investigate the influence of changes in DOM characteristics by the CC–MF process on the fouling characteristics of the NF membranes. Furthermore, variations in surface morphologies and properties of the NF membranes associated with varying feed water qualities were identified through membrane autopsies and directly correlated to the observed fouling behavior and mechanisms to elucidate the role of DOM in the fouling formation of the NF membranes for drinking water treatment.

2. Materials and methods

2.1. Description of the pilot-scale DWTP

As represented in Fig. 1, a pilot-scale DWTP consisting of a CC–MF process and NF membranes was operated for nearly 1 year under continuous operating conditions at Anyang DWTP (Anyang, Gyeonggi-do, Korea). Surface water (250 m^3/day) from Paldang Dam located in the upper stream of Han River (Gyeonggi-do, Korea) was coagulated with poly aluminum hydroxy chloro sulfates (PAHCSs; $Al_{13}(OH)_{28}Cl_9SO_4$; Samgoo Chemical Industry, Ansan, Gyeonggi-do, Korea) and directly filtered by two parallelly connected polyvinylidene fluoride (PVDF) hollow fiber MF membrane modules with a nominal pore size of 0.05 μm (HIFIM-75, H_2L, Anyang, Gyeonggi-do, Korea), which were operated in dead-end mode. The MF membrane modules (effective surface area of each module = 75.0 m^2) were backwashed using sodium hypochlorite solution (NaOCl; concentration = 4 mg/L) with air stripping every 40 min for 60 s to remove aggregates from the MF membrane surfaces and consecutively drained for 20 s to remove remaining sodium hypochlorite solution and then refilled with fresh water for 30 s. The MF permeates were further treated by a 2-stage NF membrane system (recovery rate = 75%) using spiral wound type polyamide thin-film composite (PA TFC) NF membrane modules with a molecular weight cut off (MWCO) of 210–310 daltons (Da) (NE90, Doray Chemical, Seoul, Korea). The first stage consists of four NF membrane modules and the second stage has two NF membrane modules (effective surface area of each module = 7.9 m^2). The physicochemical properties of the MF and NF membranes are provided in Table 1 [19].

2.2. Preparation of samples

2.2.1. Water samples

Three different types of water samples (i.e., surface water from Paldang Dam (feed water), the permeate of the CC–MF process (CC–MF permeate), and the permeate of the NF membranes (NF permeate)) were collected from the tested pilot-scale DWTP to investigate the removal of organic and inorganic contaminants by the pilot-scale DWTP and changes of DOM characteristics in the feed and treated waters. Prior to analyses, all the collected water samples were pre-treated by glass fiber filters with a nominal pore size of 0.7 μm (GF/F, Whatman, Clifton, NJ, USA).