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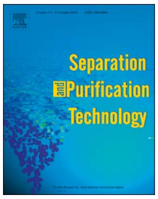

Autopsy study of irreversible foulants on polyvinylidene fluoride hollow-fiber membranes in an immersed microfiltration system operated for five years

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ABSTRACT

Membrane autopsies were performed to understand causes of irreversible fouling on fouled membranes that were used for five years to treat surface water. The results of the autopsies of the membranes taken from the 1st and 2nd stages, i.e., a dual stage configuration to obtain 99% water recovery, showed that fouling layers occurred in both stages and severe fouling of the 2nd stage membrane was obvious. The severe flux decline in the 2nd stage illustrated the importance of the feed water quality. Compositional analyses by scanning electron microscopy with energy dispersive X-ray spectroscopy noted a great increase in the amount of Al on the 2nd stage membrane. Infrared spectra revealed that carboxylic acids, polysaccharide, and aromatic compounds originating from the feed water remained in the membrane. This study suggests that coagulation pretreatment should be implemented with great care because large amounts of Al remain on the membrane surface. In addition, cleaning should be performed in response to both organic and inorganic foulants. The fouling layer on the membrane captured the substantial amounts of inorganics such as Al in addition to organic foulants such as polysaccharide/protein-like compounds.

1. Introduction

Low-pressure membrane (LPM) processes such as microfiltration and ultrafiltration have been applied extensively in water treatment plants to produce high-quality drinking water for a few decades. In particular, outbreaks of water-borne pathogens such as Cryptosporidium and Giardia lamblia in the late 1980s and 1990s accelerated this application due to the great rejection of particulate matter [1]. Low-pressure membrane systems were installed worldwide and several pilot plants were demonstrated in the 2000s in Asian countries. Numerous capacities of membrane plants were built in the late 2000s and operated for several years in Korea. Recently, membrane replacement for these plants occurred because of regular examination for long-term operation, contract termination, warranty of membrane performance, or difficulties in meeting required water production.

Efficient operation of the membrane processes has been hindered by fouling that occurred inevitably because of accumulation of particles, organic matter, and microorganisms, which enter along with feed water. Major foulants of drinking water plants in which LPMs were applied were identified as organic colloids and particulate matter in surface water [2]. The organic colloids, with sizes between 1 nm and 1 µm, in surface water included organic macromolecules such as polysaccharide and humic substances and their clusters such as cellular debris. Kimura et al. [3] operated a pilot-scale ultrafiltration plant for five months and found that polysaccharide-like organic matter in raw water had great affinity to the membrane and caused irreversible fouling.

Coagulation pretreatment has been frequently applied to reduce foulants such as particles and organic matter and to increase permeability [4]. However, the excess doses of inorganic coagulants could yield an effect of compressing the electric double layer on a negatively charged membrane surface and facilitating adsorption of natural organic matter on the membrane surface [5]. Dong et al. [6] noted that in-line coagulation could expedite formation of a cake layer on the membrane by coagulant flocs, in which NOM was adsorbed and thus settling of floc might further improve reduction of fouling. Much research is needed to predict and control fouling based on an understanding of membrane fouling mechanisms and the interactions of

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membranes with numerous substances encountered in filtration.

Continuous or intermittent aeration has been also applied to reduce fouling in an immersed membrane system. While the air bubbles injected from the bottom of the reactor are ascending, the membrane fibers are aroused by fluid flow, which produces bulk shear rate and physical scrubbing effects. Although aeration is a frequently used method to reduce fouling, high energy requirement from air blower needs to be improved. Intermittent aeration has been developed to reduce energy cost. Fouling reduction effects by aeration were different depending on water quality such as marked effect at higher solid concentration, air intensity, and uniformity of air distribution through the length of fiber. Lee and Kim [7] revealed that recovery of permeate flux was highest in the membrane located near the source of aeration after chemical cleaning.

Backwash or chemical wash during the membrane filtration process has been regularly used to mitigate fouling [5]. The produced water, i.e., filtrate, is used during regular backwash and a chemical, such as sodium hypochlorite, is sometimes added to the filtrate for enhanced backwash, with the intention of removing organic accumulation [2,8]. Although backwash or enhanced backwash can recover water flux, gradual decline of flux occurs. To increase water permeability recovery, extensive chemical cleaning is applied every 6 or 12 months. Periodic chemical cleaning is intended to remove foulants that form a cake layer on the membrane surface and are adsorbed on the membrane as filtration occurs [8,9].

Yet, membrane permeability continues to deteriorate and membrane operation is eventually terminated even though rigorous chemical cleaning has been applied. To date, few studies have sought reasons for why membranes significantly lose their permeability even though chemical cleaning has been regularly applied and what foulants are on the surfaces of the membranes at the termination of membrane operation due to the fouling. Several studies have used autopsy of fouled membranes to explain reasons for different fouling mechanisms depending on pretreatment [10], to understand fouling phenomena with irregular adsorption of organic matter [11], and to study fouling of a spiral wound reverse osmosis (RO) membrane operated for 1 year [12]. Various analytical tools for autopsy used in the literature included zeta potential, X-ray diffraction analysis (XRD), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX) [13].

In this study, autopsies were performed to examine irreversible foulants on the surfaces of fouled membranes that were obtained from a microfiltration (MF) plant in operation. Some modules were taken out from the system for autopsies since the recovery of flux of the module was not reached to the designated value, i.e., 50% of initial permeability after cleaning-in-place had been performed according to the chemical cleaning protocols prepared by the manufacturer. Autopsies of the membranes were performed by analyzing fouled surface by optical image analysis, field-emission scanning electron microscopy (FE-SEM), and atomic force microscopy (AFM) and by evaluating deposits detached from the fouled membranes using Fourier transform infrared spectroscopy (FTIR) for organic foulants, and inductively coupled plasma atomic emission spectrometry (ICP-AES) for inorganic foulants.

2. Materials and methods

2.1. Immersed MF membrane system

A schematic diagram of the immersed hollow-fiber membrane system in operation for water treatment is shown in Fig. 1. The membrane system has a capacity of 25,000 m^3/day. Feed water withdrawn from the Han River was pumped to the coagulation tank. The effluent from the in-line coagulation was piped to the immersed hollow-fiber membrane system. The immersed membrane systems were installed in six tanks. The system was configured for two-stage microfiltration, such that the concentrate from the 1st stage entered the 2nd stage. The 1st five tanks treated feed water and the last tank was used to filter the concentrate of the 1st five tanks, thus it was a dual-stage configuration. Five tanks, with 90% water recovery, were used for the 1st stage filtration, and the last tank, again with 90% water recovery, treated the concentrates from the 1st stage; therefore, this dual-stage system could achieve total water recovery of 99%.

The MF hollow-fiber membranes were composed of polyvinylidene fluoride (PVDF) materials with braid reinforcement (KOLON Industries, Inc., Korea). Detailed specification of the microfilter is summarized in Table 1. The filtration mode was an outside-in flow pattern. Nominal pore size of the hollow-fiber membranes in this study was 0.1 μm. The inside- and outside- diameters of the hollow fibers were 0.8 mm and 2.0 mm, respectively. The total effective length of the hollow-fiber MF membrane for each module was 1 m, and the surface area of a membrane was 20 m^2 per unit module. The hollow fiber was horizontally oriented in the module. In a tank, 10 skids were installed; a skid consisted of 20 modules. A module located in the fourth tank of the 1st stage and a module of the 2nd stage were taken out after five years of operation. The modules in the middle of the tank were selected after visual inspection and consulting with the operators in service. A module from each stage taken from the skid immediately brought to the laboratory in a container filled with distilled water. Membranes specimens for autopsy were then cut from both the 1st and also from 2nd stages and prepared depending on the specific analyses. The fibers and sampling parts where were suspected to severe fouling were selected to elucidate reasons of flux reduction.

2.2. Operating conditions and cleaning procedure

The MF system was installed at a water treatment plant, for which water was drawn from the Han River (Seoul, Korea). The total organic carbon (TOC) concentrations of the raw water were ranged from 2.1 and 2.4 mg/L and the suspended solids (SS) were varied from 2.3 mg/L to 22.4 mg/L at the intake site. The high SS values generally appeared in summer during the rainy season. The turbidity measured at the inlet of the MF system also showed the high valued due to the rainfalls. The turbidity reached its maximum value of 338 NTU on July 23, 2013. The water qualities including organic and inorganic compounds are summarized in Table 2. Compared to the particle and organic matter, inorganic ions such as total dissolved solids (TDS) and sulfate showed relatively constant concentrations.

The poly aluminum chloride (PAC) coagulant (17 vol%) was injected into the feed water to remove particulate matter. The coagulant doses also varied, from 1.1 mg/L to 30.0 mg/L, depending on water quality parameters such as turbidity and organic carbon concentrations. The average coagulant dose of 9.3 mg/L for the MF was similar to the dose used for the water treatment plant, in which conventional processes such as rapid mixing, flocculation, and sedimentation were applied.

The membrane filtration was operated as constant TMP mode. Intermittent aeration was applied from the bottom of the tank. The aeration cycle was 1 min of operation and 5 min of idle period. The normalized air flowrate was 0.3 $Nm^3/m^2/h$. The flux of the 1st stage was maintained at the range of 20–35 $L\,m^{-2}\,h^{-1}$ for three years and gradually decreased and reached to 15 $L\,m^{-2}\,h^{-1}$ before the termination of operation. The flux of the 2nd stage was followed a similar pattern to the flux of the 1st stage. It started at the flux of 10–17 $L\,m^{-2}\,h^{-1}$ and was decreased approximately to half of the initial flux after five years of operation.

The cleaning procedure was conducted followed by the manufacturer's instruction. Backwash was conducted with permeate for 30 s at an interval of fifteen minutes. Enhanced backwash was also applied every day for fifteen minutes with 20 mg/L of sodium hypochlorite. Chemical cleaning was scheduled for every April and October, i.e., generally twice a year. During chemical cleaning, chemical agents were