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# Specific investigation of irreversible membrane fouling in excess of critical flux for irreversibility: A pilot-scale operation for water treatment

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ABSTRACTS

Based on a long-term operation in excess of the critical flux for irreversibility, irreversible membrane fouling, caused by constituents in surface water, was investigated for a pilot-scale operation of two different hollow-fiber ultrafiltration (UF) membranes. Among the cleaning reagents tested (i.e., sodium hypochlorite, sodium hydroxide, and citric acid) sodium hypochlorite showed the ideal performance in permeability restoration (approximately 80%) of both UF membranes, indicating that organic matter played an important role in irreversible fouling. Chemical analysis of hydrophobic/hydrophilic fractionation, fluorescence excitation–emission matrices, liquid chromatography with organic carbon detection, and Fourier-transform infrared spectroscopy were applied to examine fractions of organic matter that caused the irreversible fouling. All analyses indicated that humic acid- and fulvic acid-like materials were more related to the irreversible foulants than protein-like materials under the high-flux conditions. In particular, aromatic protein and humic-like organic materials were largely responsible for the irreversible membrane fouling. Additionally, Fe, Al, and Ca may have contributed to the irreversible fouling to some degree. Through conducting similar investigations under pilot- or large-scale operating conditions, it should be possible to use an appropriate membrane with minimal irreversible fouling.


## 1. Introduction

Filtration processes in the treatment of surface water are the fastest growing membrane technology. However, membrane fouling represents one of the major disadvantages and challenges of this technology [1]. Membrane filtration performance in terms of flux, intermittent physical cleaning techniques (e.g., backwash), and chemical cleaning are highly dependent on the quality of the raw water. Flux reduction or transmembrane pressure (TMP) increase due to the accumulation of material on the membrane surface is generally referred to as "membrane fouling" [2,3]. For membranes with a hollow fiber configuration, membrane fouling is partially reversible by applying backwash, which removes the majority of the accumulated matter. Membrane manufacturers have developed backwash procedures specific to their membrane types and configurations that use permeation or aeration. Following a backwash, membranes recover most of their permeability and the flux increases. The frequency and duration of backwashes are adjusted depending on the raw water quality and, generally, both are increased when the raw water turbidity load increases.

Nevertheless, membrane fouling is not entirely reversible by intermittent backwash procedures over long operation periods. As the number of filtration cycles increases, the irreversible fraction of membrane fouling also increases. To obtain the desired production flow rate or flux, an increase in TMP is required [4–6]. When this pressure reaches the maximum pressure allowed by the mechanical resistance of the membrane, chemical cleaning of the membrane is required for the membrane to recover most of its initial permeability. Regardless of the membrane system used, chemical cleaning is typically cumbersome and requires the shutdown of the unit for several hours during washing. This results in a reduction in the overall plant capacity and produces waste, which may be difficult to dispose of. Moreover, repeated chemical cleaning may affect the membrane's life [7]. Chemical cleaning should thus be limited or avoided, if possible. For these reasons, irreversible membrane fouling represents a significant limitation to membrane filtration of surface waters.

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Classical theories based on the analysis of gel layer formation and accumulation of particulate matter do not completely explain the irreversibility of membrane fouling. A previous study [4] reported that the adsorption of low-molecular-weight molecules, smaller than the membrane pore size, could lead to significant irreversible membrane fouling. It was suggested that hydrophilic membranes were better suited to the filtration of surface waters, because adsorption phenomena are driven by interactions between natural organic matters (NOMs) and membranes. NOM, composed of humic substances and non-humic materials, in surface waters was demonstrated to be the foulant responsible for membrane fouling in several studies [8–15]. However, it is unclear which fraction(s) and functional group(s) of these NOMs in surface waters cause irreversible membrane fouling. Thus, further studies are needed with a special emphasis on irreversible fouling in the treatment of surface water.

Currently, exceeding the threshold flux or critical flux for irreversibility conditions (termed "high TMP condition" or "high flux condition" here) are most relevant for the industrial applications of surface water treatment to obtain large amounts of permeate water within a short filtration time. However, many reports have also described phenomena involved in irreversible fouling under low TMP or flux conditions during short-term operations [6,10,11,16]. It still remains uncertain whether these results can be applied to the irreversible fouling that may occur during long-term operations with high TMP or flux conditions. Based on the results obtained on the critical flux for irreversibility in our previous study [17], two different hollow-fiber ultrafiltration (UF) membranes were tested for long-term pilot-scale filtration of surface water at a flux exceeding the critical flux for irreversibility. The primary objective of this study was to evaluate the recovery of water permeability by chemical cleaning with various oxidizing, alkaline, and acidic solutions. In this study, the constituents in raw water and the composition of the desorbed membrane foulant that cause irreversible membrane fouling under high-flux conditions were investigated and discussed. In addition, an investigation of characteristic components that cause irreversible fouling was also conducted to establish new cleaning protocols for fouling control.

## 2. Materials and methods

### 2.1. Experimental setup

The pilot-scale plant used for this study was installed in an existing water treatment facility, as described in our previous study [17]. The pilot plant was fed with raw water as influent, taken from the Imjin River in the North Han River Basin in South Korea. The influent was pumped directly from a receiving well to the influent raw water tank of the pilot plant, which was located within the water treatment plant near the Imjin River. As shown in Fig. 1, each pilot system contained one cassette consisting of three full-scale membrane modules. Each polyvinylidene fluoride (PVDF) hollow-fiber UF membrane module supplied by Cheil Industries Inc. (membrane A) and Zenon Environmental Inc. (membrane B) was submerged in a separate water tank (1.2 $m^3$). The nominal pore sizes of membranes A and B were 0.03 μm and 0.04 μm, respectively, with overall membrane surface areas of 37.9 $m^2$ and 40.8 $m^2$, respectively, and membrane lengths of 1.9 m. Membrane A was newly developed and is not yet commercially available, thus a membrane B having similar characteristics based on the nominal pore size, membrane surface area, and membrane length to membrane A was also used in this study for comparison. More details with respect to the membrane properties are provided separately [17]. Filtration operation was stopped at the allowable TMP of 70 kPa suggested by the supplier. The TMP was measured using Sensys SSGC (South Korea) pressure sensors, and a PC running the Wonderware InTouch (USA) software, controlled by a peristaltic pump, automatically setting the constant flux for the desired experimental test. All TMP data were adjusted to 20 °C equivalent values, considering the change in water viscosity.

### 2.2. Operating conditions

The two membrane systems were operated under a dead-end filtration mode with cross-flow of air, combined with frequent draining of the membrane tank. Specific aeration was applied using a dedicated blower (DBR-043, Korea) with an airflow rate of 0.3 N $m^3$ $h^{-1}$ $m^{-2}$. The membranes were cleaned systematically with chemicals prior to operation. Chemical cleaning for the removal of organic and inorganic matter involved soaking the membrane modules in 1000 mg $L^{-1}$ NaOCl solution and 5000 mg $L^{-1}$ citric acid solution for 12 h, respectively. The operation, which exceeded the critical flux for the irreversibility of membranes A and B for the accumulation of irreversible foulants, was conducted for 3 months. After every filtration for 14.5 min, the flow rate of the backwash water was 1.2 times of the filtration flux for 30 s without any chemicals. When the TMP increased rapidly during the period of operation, manually cleaning methods of backwashing and draining membrane tank were also carried out to reduce the pressure and continue the operation. In this study, both membranes were cleaned by manually backwashing and were rinsed thoroughly with treated water, a step carried out to minimize the influence of the accumulated foulant and cake causing reversible fouling in the subsequent tests. By visual inspection, neither accumulated foulant nor cake was found on either membrane following the manually cleaning methods used. After measuring the pure water permeability using each membrane module, each membrane module was soaked in chemical solutions of sodium hypochlorite (NaOCl: 1000 mg $L^{-1}$), sodium hydroxide (NaOH: pH 12), and citric acid (pH 2) for 24 h (Fig. 1). Then, the chemical solutions, containing foulants desorbed from the membranes, were analyzed in terms of their organic and inorganic constituents. Additionally, the recovery of pure water permeability by chemical cleaning was determined using both membrane modules.

### 2.3. Irreversible fouling investigation

Influent raw water samples were analyzed three times per week for a 3-month period prior to the tests carried out in the present study. The total organic carbon (TOC) and dissolved organic carbon (DOC) concentrations were analyzed using a GE 5310C (USA), and $UV_{254}$ absorbance was evaluated using a HACH DR/4000 (USA). Before $UV_{254}$ absorbance and DOC measurements were performed, all samples were filtered through 0.45-μm hydrophilic PTFE membranes (Advantec Toyo Kaisha, Ltd., Japan) because adsorption of organic matter to these membranes was negligible. The pH and temperature of the influent were recorded regularly with a DYS DWA-2000A/pH (Korea). The turbidity and $Cl_2$ concentration were also observed with a HACH SC200 (USA). The Fe, Mn, Al, and Ca concentrations of the inorganic matter were measured using a PerkinElmer Optima 8300 ICP-OES (USA), according to the standard 3120B digestion method [18]. The desorbed samples from the fouled membranes were diluted with deionized (DI) water to adjust the detection limit for all measuring devices. To obtain other information on the organic matter, in addition to TOC, DOC and $UV_{254}$, fluorescence excitation–emission matrices (EEMs) of the samples from the cleaned membranes were generated using a TECAN XFLUOR4 SAFIRE II (Germany). The range of excitation wavelengths was between 230 and 400 nm, while the emissions ranged from 280 to 650 nm. Readings were taken at 5-nm increments in the emission and excitation ranges. Fractionation of