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Seasonal variation of effective chemical solution for cleaning of ultrafiltration membrane treating a surface water

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ABSTRACT

Water treatment using ultrafiltration (UF) membranes is gaining popularity world-wide, but the problem of membrane fouling needs to be addressed. We investigated the characteristics of membrane foulants by conducting two long-term filtration experiments using surface water from the Chitose River. The membrane was made of polyacrylonitrile and had a molecular weight cut-off of 100 kDa. The experiments were conducted in February 2004 Winter operation (Run 1) and October 2005 Summer operation (Run 2), when feed water characteristics were considerably different. Despite this, rates of physically irreversible fouling were similar. By measuring pure water permeability before and after chemical cleaning, we found that acidic or chelate solutions were most effective for cleaning the membrane from Run 1, whereas an alkaline solution was more effective for that from Run 2. Analysis of the chemical solutions that effective worked for canceling the fouling revealed that acidic cleaning in Run 1 extracted iron, carbohydrate and humic acid, while alkaline cleaning in Run 2 extracted carbohydrates. These results indicates that the iron, carbohydrates and humic acid caused the physically irreversible fouling in Run 1, and carbohydrates were mainly responsible in Run 2. Based on the findings obtained in this study, it was suggested that the most important foulants and the most effective chemical cleaning agents may differ substantially between seasons.

1. Introduction

The use of membrane technology in drinking water treatment is increasing, partly because it can achieve complete removal of pathogens such as *Cryptosporidium* [1]. The main obstacle for wider application of this technology is membrane fouling. Despite routine cleaning to mitigate fouling, using methods such as periodic backwashing, organic and inorganic substances accumulate in the membrane over time and eventually cause membrane fouling. This fouling may be physically irreversible or it may be chemically reversible [2]. Chemical membrane cleaning is expensive, reduces the membrane's lifespan and necessitates specialized disposal of the spent cleaning agents [3]. It is therefore desirable to minimize the frequency of chemical cleaning. Before this can be achieved, however, it is necessary to understand the fouling process.

Natural organic matter (NOM), composed of non-biodegradable organic compounds including humic substances, has been shown to be the major constituent that causes fouling of membranes used for water treatment [2,4–9]. However, because of the heterogeneous and fluctuating nature of NOM, it is not yet known which fraction of NOM in the feed water causes physically irreversible membrane fouling. Yuan et al. and Katsoufidou et al. suggested that the hydrophobic fraction is largely responsible [6,7], but Kimura et al. and Yamamura et al. have recently found that the hydrophilic fraction is the primary culprit [8,9].

Furthermore, the quality and constituents of natural water vary substantially throughout the year. In the storm season, for example, the hydrophobic fraction of NOM is dominant in natural water [10], and at lower temperatures the content of algal organic matter increases [11]. Membrane fouling in drinking water production processes is likely to depend on the nature of the NOM in the feed water; as a result, different constituents may be responsible for fouling in different seasons. Although many studies have examined the difference in membrane fouling caused by NOM collected from different water sources, the influence of seasonal variation in feed water has not been adequately addressed.

Here we examine seasonal variation in feed water with respect to two factors: (i) the recovery in water permeability of fouled membranes as a result of chemical cleaning; and (ii) the characteristics of the foulants responsible for physically irreversible fouling.

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To do this we conducted experiments involving long-term filtration of surface water using an ultrafiltration (UF) membrane.

2. Materials and methods

2.1. Membrane filtration experiments

Experiments were conducted at the Kamiebetsu Water Purification Plant using Chitose River surface water as raw water. A polyacrylonitrile (PAN) membrane with a molecular weight cut-off of 100 kDa (Toray, Tokyo, Japan) was used in this study. The membrane was housed in a vessel and operated under pressure using an outside-in flow pattern. Using this membrane, two filtration experiments were conducted for 30 days, starting at the beginning of February 2004 (Run 1) and the beginning of October 2005 (Run 2). Both runs were conducted at the same experimental site, with an identical experimental setup and run cycles. The filtration flux was set at a constant value of 0.65 $m^3\ m^{-2}\ d^{-1}$, and periodic physical cleaning was carried out as follows: 30 min filtration followed by 30 s air scrubbing and then 60 s hydraulic backwashing.

2.2. Tests performed on fouled membranes at termination of filtration experiments

To investigate the constituents responsible for physically irreversible fouling, the foulant was desorbed from the membranes at the termination of each filtration experiment as in the following. When the experiment was terminated, the fouled membrane was removed from the vessel. The membrane fibers were immediately taken to the laboratory in a container filled with distilled water. First, each membrane fiber was manually wiped with a sponge and thoroughly rinsed with distilled water, to minimize the risk of the accumulated cake causing physically reversible fouling in subsequent tests. Based on visual inspection, no accumulated cake remained on the membrane after wiping with a sponge. Membrane modules of 40 cm^2 of membrane area were assembled, and pure water permeability of the fouled membrane was measured by applying 30 kPa of pressure difference. Filtration was continued until a constant permeate flow rate was achieved (usually within 15 min). After measuring pure water permeability, the membrane modules were soaked in various chemical solutions at 20 °C for 24 h. The chemical solutions used for cleaning were Milli-Q water, NaCl (0.1 M), NaOH (pH 12), HCl (pH 2), EDTA (20 mM) and oxalic acid (0.5%). The increase in pure water permeability as a result of chemical cleaning was determined, and the chemical solutions containing the foulant desorbed from the membranes were analyzed. Membrane specimens that were not used for assembling the membrane modules were divided into two groups which were soaked in a solution of either NaOH (pH 12) or HCl (pH 2). Because a large number of membrane specimens was available, this process enabled extraction of sufficient organic matter for nuclear magnetic resonance (NMR) analysis.

2.3. Analytical methods

The samples were filtered through 0.45 μm polytetrafluoroethylene (PTFE) membranes. Concentrations of dissolved organic carbon (DOC) were determined using a Total Organic Carbon (TOC) analyzer (TOC-5000, Shimadzu, Kyoto, Japan). Ultraviolet (UV) absorbance was measured with a spectrophotometer (U-2000, Hitachi, Tokyo, Japan). Concentrations of metals were determined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (ICPS-7500, Shimadzu, Kyoto, Japan). Organic matter contained in the isolates was fractionated using the hydrophobic/hydrophilic fractionation method [12] to obtain three fractions: hydrophobic (HPO), hydrophilic (HPI) and transphilic (TPI). Solid-state cross polarization/magic-angle spinning carbon-13 (CPMAS ^{13}C) NMR spectra of the membrane foulants were obtained using a Brucker MSL300 at 75.47 MHz with a spin rate of 8 kHz and a pulse width of 4.5 μs for the 90° pulse. Contact time was set to 1 ms. Acquisition time and recycle delay were 30 ms and 4 s, respectively.

3. Results and discussion

3.1. Seasonal variation in feed water characteristics

Concentrations of organic matter were considerably different in the two filtration experiments (Table 1). Although the concentration of DOC was low in Run 2, specific ultraviolet absorbance (SUVA) of the feed water in Run 2 was much higher than that in Run 1. Based on the SUVA values, it is likely that the feed water in Run 2 contained more hydrophobic organic matter than that in Run 1 [13]. This was in accordance with the results of the hydrophobic/hydrophilic fractionation.

Based on the CPMAS ^{13}C NMR spectra of the organic matter isolated from the feed waters (Fig. 1), it is likely that the characteristics of organic matter in the feed water varies considerably with season. A large peak associated with carbohydrates [14,15] was seen at 75 ppm in both NMR spectra. The spectra in Fig. 1 are, however, inconsistent with the results of the hydrophobic/hydrophilic fractionation, which suggested that more than half of the organic matter in the feed water was hydrophobic (Table 1). This discrepancy may be explained by the heterogeneous nature of NOM. Some fractions of NOM may have both carbohydrate and humic characteristics [15,16]. For both runs, the presence of aromatic carbon was indicated by peaks around 110–165 ppm [15,16]. These peaks were minor in the spectrum for Run 1 but were pronounced in the spectrum for Run 2, indicating that the feed water for Run 2 contained more aromatic humic substances than that for Run 1.

3.2. Development of membrane fouling in the filtration experiments

A rapid increase in trans-membrane pressure (TMP) at the beginning of Run 1 (Fig. 2) was caused by the failure in operation of the air compressor used for air scrubbing. This was followed by a decrease in TMP, caused by physical cleaning.

Interestingly, the rates of occurrence of fouling were almost the same in the two runs, despite the substantial differences in the characteristics of the feed water. As described in the experimental section, the degree of physically irreversible fouling were estimated at the end of each run. These results were very similar: approximately 70% of the total filtration resistance at the end of the long-term experiment was attributed to physically irreversible fouling in both cases. This suggests that the physically irreversible fouling in both experiments occurred as a result of similar processes and substances, but further analysis of the membranes showed this not to be the case.

3.3. Membrane cleaning with chemical cleaning agents

The ratio of pure water flux after chemical cleaning (J_1) to the flux before chemical cleaning (J_0) is used to express the degree to which pure water permeability was restored by chemical cleaning (Fig. 3). Because chemical cleaning was done following manual removal of the accumulated cake, we can conclude that this change in water permeability was a result of the removal of substances causing physically irreversible fouling.

The chemical solutions that were most effective differed between the two runs (Fig. 3), despite the similar rates of fouling. In Run 1, acidic (HCl and oxalic acid) and chelate (EDTA) solutions