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Characteristics of meso-particles formed in coagulation process causing irreversible membrane fouling in the coagulation-microfiltration water treatment

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ABSTRACT

In coagulation-membrane filtration water treatment processes, it is still difficult to determine the optimal coagulation condition to minimize irreversible membrane fouling. In microfiltration (MF), meso-particles (i.e., 20 nm–0.5 μm) are thought to play an important role in irreversible membrane fouling, especially their characteristics of particle number (PN) and zeta potential (ZP). In this study, a new nanoparticle tracker combined a high-output violet laser with a microscope was developed to identify the physicochemical characteristics of these microscopic and widely dispersed meso-particles. The effects of pH and coagulant dose on ZP and PN of micro-particles (i.e., >0.5 μm) and meso-particles were investigated, and then coagulation-MF tests were conducted. As the result, irreversible membrane fouling was best controlled for both types of membranes, while meso-particle ZP approached zero at around pH 5.5 for both types of natural water. Since PN was greatest under these conditions, ZP is more important in determining the extent of irreversible membrane fouling than PN. However, the acidic condition to neutralize meso-particles is not suitable for actual operation, as considering residual aluminum concentration, pipe corrosion, and chlorination efficiency. It is therefore necessary to investigate coagulants or other methods for the appropriate modification of meso-particle characteristics.

1. Introduction

Low-pressure membrane filtration methods facilitate simpler and more precise solid-liquid separation than sand filtration, and their introduction is therefore being considered at many water treatment plants. When introducing membrane filtration to water treatment processes, it is common to combine it with a preliminary coagulation process to remove dissolved organic matter and control membrane fouling (Gao et al., 2011; Huang et al., 2009; Matilainen et al., 2010; Singer, 1994). Also, because existing sand filter tanks can effectively be used as membrane submersion tanks, processing in which pre-coagulation and membrane filtration are combined is more often used in full-scale water treatment plants (as opposed to laboratories) than are ozone or activated carbon methods (Lebeau et al., 1998). However, although coagulation-membrane filtration processes are being considered as replacements for conventional water treatment processes, there are as yet no clear guidelines for optimal operation procedures when coagulation and membrane filtration are combined.

With sand filtration methods, it is important to optimize conditions such that turbidity and organic concentration are controlled. Optimal pH and coagulant dose are determined using jar tests. In most cases circumneutral conditions with a large dose of coagulants are used, to form large flocs (Amirtharajah and Mills, 1982). With membrane filtration methods, on the other hand, there is no need to sediment the flocs; instead they need only be larger than the membrane pore size. Thus these methods are more efficient than sand filtration because of the lower dose of coagulant

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required and smaller amount of coagulant sludge produced (Choi and Dempsey, 2004). In addition, floc formation and sedimentation basins are not required, so the size of processing facilities can be greatly reduced (Lebeau et al., 1998). A range of factors affect the process of membrane filtration and should be optimized, including the rate of removal of organic matter, turbidity, and the rate of membrane fouling. However, the conditions under which membrane fouling is best controlled differ from the optimal coagulation conditions obtained by jar tests (Choi and Dempsey, 2004; Kimura et al., 2008; Lee et al., 2000). In fact, optimal conditions are currently identified through a process of trial and error, by conducting membrane filtration tests under various coagulation conditions over an extended period of time. In order for the membrane filtration process to become more widespread, a method to replace the jar test that can simply and accurately explore the optimal coagulation conditions for pre-coagulation processing is crucial.

There are two types of membrane fouling: reversible and irreversible (Kimura et al., 2004). In reversible membrane fouling, there is a correlation between the fractal dimension of coagulation particles of 0.5 μm or greater (hereafter, micro-particles) and the rate of fouling. The mechanism that has been proposed to explain this is that floc strength increases with fractal dimension, and that any trans-membrane pressure (TMP) increase is thus inhibited by the formation of a coarse cake layer (Cho et al., 2005). It is however difficult to explain irreversible membrane fouling based on micro-particle behavior. This process is instead thought to be the result of microscopic particles with a particle size of 0.5 μm or less, which are close to or smaller than the membrane pore size (hereafter, meso-particles). Wiesner et al. (1989) calculated the balance between back-transportation speed and advection for each particle size, and proposed that particles around 0.1 μm in size are particularly likely to adhere to the membrane and are thus the primary culprits in membrane fouling. Furthermore, because physicochemical interactions between particles and the membrane surface are heavily involved in irreversible membrane fouling, we believe that in addition to rheological properties, physicochemical behaviors such as the effects of electrostatic force are instrumental in understanding the fouling mechanism of meso-particles.

Dynamic light scattering (DLS), light scattering, atomic force microscopes, and scanning electron microscopes have all been used in the investigation of the physicochemical behavior of microscopic particles (Buffle et al., 1998; Lead et al., 2006; Li et al., 1997; Perret et al., 1991; Tombacz et al., 1999). Because residual post-coagulation meso-particles are highly dispersed and therefore scatter light weakly, it is however extremely difficult to observe their particle characteristics underwater. Even with DLS, which is used in nano-particle characterization studies, the lower concentration limit for measurement is around 10 mg/L, and residual post-coagulation meso-particles, at a concentration of around 10,000 particles/mL, cannot be observed (Table S1). We have successfully detected, for the first time and with high sensitivity, underwater particles between 20 nm and 0.5 μm in size, by combining high-output short-wavelength laser light with an optical microscope, thus facilitating the measurement of zeta potential (ZP) and particle number (PN, lower bound 50,000 particles/mL) of meso-particles that remain after coagulation.

The purpose of this study was to describe the physicochemical behavior of meso-particles, which has to date been difficult to ascertain, and to identify the particular characteristics that affect irreversible membrane fouling. Meso-particles were operationally defined in this study as particles between 20 nm and 0.5 μm after fractionation of coagulated water, described in 2.2. Jar tests in detail. Using a polyaluminum chloride (PACl) with a basicity of 54.5% as coagulant, we varied the coagulation pH and PACl dose, measured the ZP and PN of the particles generated at coagulation, and compared the values for micro-particles and meso-particles. We also selected six sets of conditions from among the coagulation conditions tested, to conduct coagulation-MF tests using ceramic membranes and polyvinylidene fluoride (PVDF) membranes. This allowed us to identify the meso-particle characteristics that affect the rate of irreversible membrane fouling, and therefore propose a method for determining optimal coagulation conditions, based on meso-particle characteristics.

2. Materials and methods

2.1. Water samples and membranes

Water sampled from two representative bodies of surface water used as sources of drinking water in Japan (water A and water B) were used as raw water. Four hundred liters of water A and nine hundred liters of water B were collected, and large particles were removed using a 10 μm stainless steel cartridge filter. The characteristics of the two types of water are listed in Table 1. Water A was from a river which is about 59.5 km long and drains an area of 200 km^2. The level of organic matter in water A was very low compared to water B, as the total organic carbon (TOC) of water A was approximately one fourth of that of water B in Table 1. Water B was sampled from a water path running from a eutrophic lake. This lake's catchment area is approximately 220 km^2, which has recently been polluted by human sewage and agricultural fertilization. In addition, Table 1 showed that specific ultraviolet absorbance (SUVA) of water B was smaller than that of water A, which implies that water B contained much more hydrophilic organic matters including biopolymers (Kimura et al., 2014; Yamamura et al., 2014). We used two kinds of membranes for the filtration experiments: PVDF hollow fiber membrane (Asahi Kasei Chemicals, Japan) and ceramic monolith membrane (METAWATER, Japan). The nominal pore size of both membranes was 0.1 μm. For the PVDF membrane, 39 cm^2 of tiny-scale membrane modules were assembled with 10 fibers, each 10 cm in length. For the ceramic membrane, 53 of 55 holes in the 10 cm piece were filled with glue, leaving two holes with a combined surface area of 11 cm^2. The PVDF membrane used outside-in filtering and the ceramic membrane used inside-out filtering. Pure water permeability was determined for every module before it was used in the filtration experiments. ZP and PN of particles were examined through a series of jar tests under various pH and PACl doses.

2.2. Jar tests

The jar tests were performed at room temperature (18 ± 3 °C) using six standard 1 L beakers and a six-paddle jar test apparatus. We used PACl (10% as Al_2O_3) as the coagulant, at five different doses (0.3, 0.6, 1.0, 2.0 and 3.0 mg Al/L) with water A, and six doses (0.3, 0.6, 1.0, 2.0, 3.0 and 5.0 mg Al/L) with water B. We adjusted pH by adding 0.1 N sodium hydroxide or hydrochloric acid prior to the addition of PACl. The pH levels after PACl addition were 5.0, 5.5, 6.0, 6.5, 7.0, and 8.0. Mixing time was set at 3 min at 160 rpm (G

Table 1
Characteristics of the two types of surface water used in the tests.

	Water A	Water B
pH	7.9	8.0
TOC (Total organic carbon) (mg C/L)	1.1	4.3
UV_{254} (Ultraviolet absorbance at 254 nm) (cm^{-1})	0.023	0.080
SUVA (UV_{254}/TOC × 100) (L mg^{-1} m^{-1})	2.1	1.9
Turbidity (mg/L)	1.9	7.3
Alkalinity (mg $CaCO_3$/L)	9.9	70