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**EFFECTS OF SUPER-POWDERED ACTIVATED CARBON PRETREATMENT ON  
COAGULATION AND TRANS-MEMBRANE PRESSURE BUILDUP DURING  
MICROFILTRATION**

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## ***Abstract***

*As a pretreatment for membrane microfiltration (MF), the use of powdered activated carbon (PAC) with a particle size much smaller than that of conventional PAC (super-powdered PAC, or S-PAC) has been proposed to enhance the removal of dissolved substances. In this paper, another advantage of S-PAC as a pretreatment for MF is described: the use of S-PAC attenuates transmembrane pressure increases during the filtration operation. The floc particles that formed during coagulation preceded by S-PAC pretreatment were larger and more porous than the floc particles formed during coagulation preceded by PAC pretreatment and those formed during coagulation without pretreatment. This result was due to increased particle–particle collision frequency and better removal of natural organic matter, which inhibits coagulation by consuming coagulant, before the coagulation reaction. The caked fouling layer that built up on the membrane surface was thus more permeable with S-PAC than with normal PAC. Both physically reversible and irreversible membrane foulings were reduced, and more stable filtration was accomplished with S-PAC pretreatment.*

**Keywords:** membrane fouling; membrane permeability; powdered activated carbon; pretreatment; flocculation; floc

## INTRODUCTION

Although water treatment systems that use low-pressure membrane technology (microfiltration, MF, and ultrafiltration, UF) have small footprints, completely separate suspended matter and bacteria, and require little maintenance and operational skill, they have disadvantages, such as energy consumption due to decreasing permeability caused by membrane fouling. In addition, dissolved substances such as disinfection byproducts and their precursors are not removed by this technology alone. The inability to remove dissolved substances is often addressed by pretreatment before filtration. Chemical coagulation and adsorption are the most popular pretreatments because they are inexpensive and are easy to use, and they have been extensively studied (Huang et al., 2009). A ferric or aluminum coagulant, powdered activated carbon (PAC) adsorbent, or both are added before membrane filtration (Mallevalle, 1996, Baudin et al., 2001), and the floc particles formed by coagulation and the PAC particles bearing the adsorbed dissolved substances are removed during membrane filtration.

Pretreatments reduce membrane fouling during filtration either by removing or modifying potential foulants (Carroll et al., 2000, Howe et al., 2006, Gray, 2008). For example, chemical coagulation aggregates particles and organic matter, and aggregation in turn limits pore blockage and enables the formation of a more porous cake that is easily removed by hydraulic cleaning (Lainé et al., 1989, Jack and Clark, 1998, Carroll et al., 2000, Park et al., 2002, Leiknes, 2004, Oh and Lee, 2005, Cho et al., 2005, Chen, et al., 2007, Fan et al., 2008). Physically reversible membrane fouling caused by cake resistance on the membrane depends straightforwardly on the coagulation conditions. At higher coagulant doses, a more permeable cake forms, or protection of the membrane from foulants is greater (Judd and Hillis, 2001, Pikkarainen et al., 2004, Choi and Dempsey, 2004). In the case of dead-end filtration, the

formation of a porous cake with large floc particles is key, and the optimum conditions for the production of large flocs that are resistant enough to shear stress to facilitate flow between aggregates have been quantified (Lee et al., 2000, Lee et al., 2005, Park et al., 2006, Park et al., 2007, Barbot et al., 2008). In contrast, physically irreversible membrane fouling is more complex and depends not only on coagulation conditions but also on the membrane material and the filtration conditions, including the membrane cleaning method (Lahoussine-Turcaud et al., 1990, Kimura 2008).

There has been some discussion about whether PAC itself fouls membranes as well as attenuating membrane permeability reduction (Yiantsios and Karabelas, 2001, Tomaszewska and Mozia, 2002). For example, Adham et al. (1991) reported that the addition of PAC to a UF process did not increase the rate of flux decline. Li and Chen (2004) reported that PAC pretreatment did not improve membrane permeability, because the fractions that were not adsorbed by PAC caused more fouling than the fractions that were adsorbed by PAC. The addition of PAC sometimes fouls the membrane, depending on the PAC–membrane interaction and the characteristics of the PAC cake-layer (Zhang et al., 2003, Mozia et al., 2005, Jang et al., 2006, Takizawa et al., 2008). However, the combination of chemical coagulation and PAC adsorption pretreatments has been shown to alleviate fouling (Jack and Clark, 1998, Haberkamp et al., 2007).

Due to the robustness of ceramic membranes, which allow high fluxes and rigorous cleaning methods, such membranes are increasingly being used as an alternative to polymeric membranes in the treatment of drinking water and wastewater. Ceramic membrane MF is becoming accepted for full-scale facilities, such as the 39,000 m<sup>3</sup>/d Hinogawa Water Treatment Plant near Kyoto, Japan, where poly-aluminum chloride coagulation is followed by short-duration flocculation and direct monolith ceramic membrane MF (Kanaya et al., 2007). A monolith ceramic membrane plant with a much larger capacity (170,000 m<sup>3</sup>/d) is being planned for

Yokohama, Japan. Ceramic membrane MF processes are usually designed to include pretreatment with a hydrolyzing metal coagulant (e.g., poly-aluminum chloride) followed by direct MF in dead-end mode (Loi-Brügger et al., 2006). Operational data of pilot plants and actual facilities have shown that water treatment processes using a ceramic membrane and chemical coagulation pretreatment are stable for dead-end filtration, even without long-duration flocculation and sedimentation. Pilot plant experiments and flow analysis have proved that monolith ceramic membranes show a unique flow pattern in the channels within the monolith element, causing extremely rapid flocculation in the channels during dead-end filtration. Most of the flocculated particles form a columnar cake with high permeability at the dead-end point (Yonekawa et al., 2004).

For pretreatment in ceramic membrane MF, the use of activated carbon with a particle size much smaller than that of conventional PAC (super-powdered PAC, or S-PAC) has been proposed to address the inability of the MF to remove dissolved substances (Matsui et al., 2004, Matsui et al., 2005). The small size of S-PAC, which enables faster adsorption kinetics (Matsui et al., 2009), enhances the adsorbate uptake rate over a limited retention time and thereby permits much shorter activated carbon–water contact times when used as a pretreatment for membrane filtration. Substantial enhancement of the adsorptive removal rate of geosmin has been achieved with S-PAC (Matsui et al., 2007). The addition of S-PAC does not result in fouling of the membrane; in fact, it alleviates transmembrane pressure (TMP) buildup in ceramic membrane MF. However, the filtration operation period of the reported experiments was relatively short, and the mechanism was not clearly explained. Therefore, further study is necessary to clarify the effect of S-PAC on TMP buildup in ceramic membrane MF with adsorption and coagulation pretreatments.

In this research, we conducted long-term pilot- and laboratory-scale experiments and compared the effects of S-PAC pretreatment, normal PAC pretreatment, and coagulation only (no PAC

pretreatment) on the permeability of a ceramic membrane during MF. We also discuss the mechanism of the S-PAC pretreatment effects.

## **MATERIALS AND METHODS**

### **Pilot-scale MF system**

A small membrane filtration pilot plant within the Kawai Water Purification Plant at Yokohama, Japan, was used for the experiments. The plant has three parallel MF lines that can be operated independently under different operational conditions. Each line has a small membrane module containing a tubular, ceramic monolith membrane element (nominal pore size, 0.1  $\mu\text{m}$ ; filtration area, 0.4  $\text{m}^2$ ; 55 channels; membrane diameter, 30 mm; membrane length, 1 m; Metawater Co., Nagoya, Japan), which was designed for small-scale experiments. (The membrane element used for the full-scale filtration plant has a membrane surface area of 25  $\text{m}^2$ , a diameter of 1800 mm, and a length of 1.5 m.) In the membrane filtration experiments, raw water from Lake Sagami (Kanagawa, Japan) was first introduced into the MF feed tank and then distributed to the MF lines after pH adjustment with diluted sulfuric acid. The S-PAC and PAC were added at inlets of the tube reactors at controlled dose rates. After contact with the adsorbent in the tube reactors, the coagulant (poly-aluminum chloride, PACl, Hieisyouten Co., Aichi, Japan) was added. PACl, S-PAC and PAC dose rates were determined by referring to the previous MF experimental results (Matsui et al., 2007). The flow of feed to the membrane module was configured in dead-end mode at a constant rate (filtration rate, 3  $\text{m}^3/\text{d} = 0.125 \text{ m}^3/\text{h}$ ) inside the module by positive pressure, the membranes were hydraulically backwashed periodically with the hypochlorite-injected membrane permeate at a pressure of 500 kPa, and the retentate was discharged by pressurized air.

### **Laboratory-scale MF system**

Figure 1 is a schematic diagram of the experimental setup for the laboratory-scale MF tests.

Water was fed to the system by a peristaltic pump. Either S-PAC or PAC was added at the inlet of the tube reactor. After contact with the activated carbon, the water was transferred to a second tube reactor, where the PACl (10% Al<sub>2</sub>O<sub>3</sub>, Taki Chemical Co., Hyogo, Japan) was added after dilution with pure water (Milli-Q Advantage, Nihon Millipore K.K., Tokyo, Japan) by a factor of 1 in 59,000 (diluted PACl was prepared every day to avoid deterioration due to excessive hydrolysis). The ceramic membrane element was the same as that used in the pilot-scale system, except that all but one of the 55 channels was plugged with glue. Filtration occurred at a constant flow rate (2 m/d = 0.083 m/h) in dead-end mode. The membranes were hydraulically backwashed repeatedly at a constant interval with the pure water (hypochlorite was added to the backwash water when NOM-containing water was used), which was stored in a pressurized tank at 500 kPa. While the filter was being backwashed, the membrane feed water was transferred to an optical particle counter (ZVM, Fuji Electric Systems Co., Tokyo, Japan), which covers a particle diameter range from 0.5 to 400 μm, for measurement of the size distribution of the floc particles. Before entering the optical particle counter, the membrane feed water was diluted with 5 parts pure water to satisfy the flow rate requirement and the requirement for maximum particle number counting. The optical particle counter was calibrated with polystyrene latex particles and covered a size range from 0.5 to 400 μm. Measurements were conducted several times, and the data were averaged to give the size distribution of the floc particles for a given set of coagulation–flocculation conditions.

Two types of water were used. Water containing inorganic ions but no natural organic matter (NOM) was artificially synthesized from pure water as a model membrane feed water; the

inorganic ion concentrations were adjusted to equal those of Lake Sagami water by adding reagent-grade salts (Wako Pure Chemical Industries, Osaka, Japan). The turbidity of the NOM-free water was adjusted to 0.3 mg/L with kaolin (Kanto Chemical Co., Tokyo, Japan). Water samples containing NOM were prepared from pure water, kaolin, and water from Lake Hakucho and the Chibaberi River (Hokkaido, Japan) after filtration through a membrane filter (nominal pore size, 0.45  $\mu\text{m}$ ). Dissolved organic carbon (DOC) and UV absorbance at a wavelength of 260 nm were quantified (DOC: Model 900, Sievers Instruments, Boulder, CO, USA; UV260: Model UV-1700, Shimadzu Co., Kyoto, Japan). PACl, S-PAC and PAC dose rates were determined after conducting some short-term preliminary experiments.

### **Activated carbon**

The S-PAC in the MF experiments was obtained by micro-grinding thermally activated, wood-based PAC (Taikou-W, Futamura Chemical Industries Co., Gifu, Japan) in a wet bead-mill. The median diameter of the as-received PAC was 7.6  $\mu\text{m}$ , and about 70% by volume of the PAC particles were larger than 5  $\mu\text{m}$ . Micro-grinding yielded a median diameter of 0.88  $\mu\text{m}$ ; the effective diameter was 0.22  $\mu\text{m}$ , and 70% by volume of the S-PAC particles were smaller than 1  $\mu\text{m}$ . No decant and other cleanup was conducted for the S-PAC and the PAC before use.

## **RESULTS AND DISCUSSION**

### **TMP buildup in pilot-scale MF experiment**

In previous studies, we found that better NOM and geosmin removal could be obtained with adsorption pretreatment using S-PAC instead of PAC in ceramic membrane MF (Matsui et al.,



2005, Matsui et al., 2007), and the S-PAC dose was at least 75% less than the PAC dose. We used these results to choose the adsorbent doses for the current experiments in the three parallel lines of the pilot-scale MF system to evaluate the effects of S-PAC and PAC on membrane permeability and fouling. An S-PAC dose of 1 mg/L was used for Line 1, and a PAC dose of 5 mg/L was used for Line 2. Line 3 was operated without activated carbon as a control. First, we evaluated the effect of S-PAC pretreatment by comparing the results for Lines 1 and 3. A lower rate of TMP buildup over 63 days of operation was observed for MF after S-PAC adsorption and coagulation pretreatments than for MF after coagulation pretreatment alone (the upper panel of Figure 2). For the first 30 days of operation, Line 3 showed only a slightly higher TMP than Line 1, and this slight difference may have been partly due to the difference in the initial permeability of the membranes. The difference in TMP between Line 3 and Line 1 increased as the operation was extended to 63 days. Lower rates of TMP increase when MF was preceded by S-PAC adsorption pretreatment were also observed in previous studies, but for shorter operational times of 6 and 22 days (Matsui et al., 2006, Matsui et al., 2007).

The lowering of the rate of TMP increase by S-PAC was confirmed by data obtained from another experiment, in which only two parallel lines of MF were operated: Line 1 with S-PAC and Line 3 without S-PAC. As shown in Figure 3, during MF without S-PAC pretreatment (Line 3), the TMP tripled (from 12 to 48 kPa) over the course of 54 days. In contrast, during MF with S-PAC pretreatment (Line 1), the TMP increase was substantially less over the operation period (the TMP increased from 12 to 18 kPa). Even though the coagulant dose for Line 1 was 0.5 mg-Al/L and lower than 0.8 mg-Al/L of Line 3, which could not have been beneficial for filterability, Line 1 exhibited a lower TMP increase over the operational period. Note that membrane fouling by S-PAC was not observed. We believe that the S-PAC adsorbed membrane-fouling substances, including some of the NOM, thereby attenuating the decrease in membrane permeability during filtration.

As shown in the upper panel of Figure 2, the adsorption pretreatment with normal PAC also lowered the TMP buildup rate. TMP buildup rates were similar for S-PAC pretreatment at 1 mg/L and PAC pretreatment at 5 mg/L. This similarity indicates that membrane-fouling substances were removed to a similar extent by S-PAC and PAC, even though the S-PAC dose was 20% of the PAC dose. As mentioned above, we previously found that similar NOM-removal efficiencies are obtained with PAC and with S-PAC at 1/4 the dose. Because NOM may have been a major membrane-fouling substance in the current system, the similar TMP buildup rates observed for the PAC (5 mg/L) and the S-PAC (1 mg/L) may have been due to similar adsorptive removal of membrane-fouling substances.

A closer look at the TMP rise over time (the small window in the upper panel of Figure 2) revealed a saw-toothed pattern in the TMP change. The amplitudes of the TMP increases in each batch filtration were almost the same for the S-PAC and PAC pretreatments (Lines 1 and 2), but the amplitudes were larger for coagulation only (Line 3). The drops in TMP were due to periodic cleaning of the membrane by hydraulic backwashing. Although most of the TMP increase that occurred during each batch filtration was physically reversible, the hydraulic backwashing procedure did not always restore the TMP to the initial value, because the membrane fouling could not be completely cleared. Therefore, there was a long-term buildup of TMP over the 63 days of operation. The reversible TMP increase in each batch filtration was calculated by subtracting the TMP after the backwash from the corresponding TMP just before the backwash, and the increases were plotted over the entire operation period (the lower panel of Figure 2). The amplitudes of the TMP increases due to physically reversible fouling were similar for MF with S-PAC (1 mg/L) and PAC (5 mg/L) pretreatments. The TMP increases were smaller for MF with adsorbent pretreatment (Lines 1 and 2) than without (Line 3). There are two possible explanations for this result: (1) substances that caused physically reversible fouling (such as NOM) were adsorbed by the activated carbon and (2) substances that caused physically

reversible fouling were greatly modified. The latter would indicate that the floc particles formed in the presence of adsorbent were more porous than the particles that formed in the absence of adsorbent, so that the caked fouling layer built up on the membrane surface was more permeable. Although our previous results may support the first explanation (Matsui et al., 2004, Matsui et al., 2005), evidence for the second explanation will be described in the next section. Our experiments indicated that the concern that the addition of S-PAC might accelerate TMP increase is unwarranted; we showed that the addition of S-PAC efficiently attenuated both reversible and irreversible membrane fouling.

### **TMP buildup in laboratory-scale MF experiment**

We also studied the effect of S-PAC pretreatment using a laboratory-scale MF setup. A particle counter was built into the setup so that the size distribution of floc particle entering the membrane could be monitored. For each batch filtration, the TMP increase caused by physically reversible membrane fouling was measured. Long-term TMP buildup caused by physically irreversible fouling was not studied, because the operation period of the laboratory-scale experiment was shorter than that of the pilot-scale experiment, owing to the limited amount of stored raw water.

#### 1) Effect of activated carbon pretreatment on floc particle size

For a preliminary test, the size distributions of floc particles produced in the tube reactor of the laboratory-scale MF setup were measured by using the particle counter (MF was not conducted), and the effect of S-PAC and PAC addition on flocculation was studied. The flocculation experiments were conducted by changing the length of the reactor tube [and thus the mixing time and the resulting  $GT$  (the product of the velocity gradient,  $G$ , and mixing time,  $T$ ) value]. The floc size increased with increasing  $GT$  value, and S-PAC enhanced flocculation for  $GT$

values larger than 19,000 (below this value, no flocculation was observed; Figure 4). Larger floc particles were clearly formed when S-PAC was added; the floc particles were smaller for PAC and even smaller for coagulation alone. The increased flocculation rates observed with S-PAC and PAC relative to the rates for coagulation alone can be explained by the increased volume concentration of particles, according to the orthokinetic flocculation theory. This theory holds that the particle–particle collision frequency, and thereby the rate of flocculation, increases proportionally with the volume concentration of particles to be flocculated (e.g., Elimelech et al., 1998). However, we expected to observe identical flocculation rates with S-PAC and PAC, because we thought that the volume concentration of activated carbon particles in the S-PAC system would be equal to that in the PAC system from the standpoint of mass conservation. However, the flocculation rates were not the same. The addition of S-PAC enhanced flocculation more than PAC at the same dose. Aggregates adopt a fractal structure when growing, so that aggregates formed starting from small primary particles have more porous and thus a higher effective floc volume than aggregates that form from large primary particles; the higher effective floc volume increases the collision frequency, which in turn leads to more-rapid aggregation. As consequence of the fractal structure, the floc density,  $\rho$ , decreases appreciably as the particle size,  $d$ , decreases (Tambo and Watanabe, 1979, Elimelech et al., 1998):

$$\rho \propto d^{d_F-3} \quad (1)$$

where  $d_F$  is the mass fractal dimension.

The mass is kept constant during the coagulation, and the total volume fraction,  $\emptyset$ , is related to the density,  $\rho$  (Oles, 1992, Serra and Casamitjana 1998):

$$\rho \propto 1/\emptyset \quad (2)$$

Therefore,

$$\emptyset \propto d^{3-d_F} \quad (3)$$

For a typical mass fractal dimension value of 2 (Tambo and Watanabe, 1979, Tambo and Francois, 1991, Elimelech, et al., 1998), the total volume concentration of floc particles increases roughly in proportion with the increase of floc particle size. Figure 5 shows the change of the total volume concentration of floc particles, which was calculated from the data obtained with the particle counter, during the course of floc growth; floc growth was quantitatively indexed by the median diameter of the floc particles. The total volume concentration increased substantially with floc growth, and the total volume concentration increased with floc size with a slope of 1 on a log–log scale, which indicates the fractal structure with a fractal dimension of 2. Moreover, the total volume concentration of floc particles was larger in the S-PAC system than in the PAC system even though the S-PAC and PAC doses were the same. This result proves that the aggregates formed starting from smaller primary particles had more porous and thus a greater effective floc volume. We concluded that this was the mechanism by which the addition of S-PAC increased the collision frequency and enhanced flocculation more than did PAC.

We also conducted flocculation experiments using NOM-containing water. Interestingly, the effect of activated carbon on flocculation was more prominent for NOM-containing water than for NOM-free water: small floc particles were formed for the GT values in the tested range in the presence of the PAC and for coagulation alone. For example, floc particles with a median diameter of 200  $\mu\text{m}$  were formed with S-PAC addition at a GT value of 55,000, whereas PAC addition produced floc particles with a 25  $\mu\text{m}$  median diameter at the same GT value (Figure 4, right panel). With NOM-free water and a GT value of 57,600, the median diameter of the floc particles formed was 200  $\mu\text{m}$  with S-PAC addition and 110  $\mu\text{m}$  with PAC addition (Figure 4, left panel). Higher NOM removal by S-PAC may have been the reason for this result. NOM (humic substances in particular) is removed by coagulation and thus consumes coagulant.

Therefore, coagulation of turbidity and activated carbon particles could be hindered by the presence of NOM, but S-PAC adsorbed humic substances efficiently before the start of the coagulation reaction and enhanced coagulation. Higher NOM removal efficiency was observed for S-PAC than for PAC, although NOM removal efficiencies for both S-PAC and PAC were low, and the difference was not great in terms of either DOC content or UV<sub>260</sub> value (Figure 6). The low NOM removals can be explained by the low content of humic substances in the NOM, as indicated by the low SUVA (specific ultraviolet absorbance) value of 1.6 L/(mg·m). Finally, we believe that the merit of S-PAC in terms of coagulation and flocculation arose from two effects, one chemical and one physical: enhanced coagulation by the removal of coagulant-consuming NOM and enhanced flocculation caused by increased particle–particle collision frequency, respectively.

## 2) Effect of floc particle size on TMP during MF

Next we conducted MF experiments to see how floc particle size affected membrane permeability during MF. First, NOM-free water was used to evaluate the effect of floc particle size in the absence of NOM as a membrane foulant. When the system was dosed with S-PAC and PAC alternately every 2 days, the TMP changed as shown in the upper panel of Figure 7. Reversible TMP increases in each batch filtration differed for the S-PAC and PAC pretreatments (the lower left panel of Figure 7). At the beginning of the operation, S-PAC (2 mg/L) was injected into the water, and the reversible TMP increase was 0.5–0.9 kPa. After PAC (2 mg/L) was substituted for S-PAC on day 2, the reversible TMP increase increased to 1.0–1.4 kPa. When S-PAC was substituted for PAC again on day 4, the reversible TMP increase decreased. Overall, the reversible TMP increase was smaller when the water was treated with S-PAC than when it was treated with PAC, which indicates the superiority of S-PAC for reducing physically reversible membrane fouling. The size distributions of the floc particles entering the membrane differed for the two activated carbons (the lower right panel of Figure 7): larger floc

particles were formed when the water was treated with S-PAC than when it was treated with PAC. This result indicates that the attenuation of TMP buildup was attributable to the formation of larger floc particles, which we believe would give the layer caked on the membrane surface greater porosity and greater permeability. Furthermore, according to the results shown in Figure 5, floc particles formed in the presence of S-PAC were more porous and less compact than those formed in the presence of PAC, and this difference should have contributed to making a more permeable filter cake. The ability of S-PAC to attenuate the TMP increase was more clearly observed for the NOM-containing water, as expected from the effect on coagulation and flocculation described in the previous section. The TMP increase was reduced when S-PAC was added to the system, but a higher TMP increase was observed when PAC was added (the upper and lower left panels of Figure 8). The floc particles that entered the membrane after S-PAC addition were much larger than those that entered the membrane after PAC addition (the lower right panel of Figure 8).

In the pilot-scale MF experiment, S-PAC at 1 mg/L and PAC at 5 mg/L showed similar TMP increases, as described in the previous section. Given these results, we compared the changes in TMP at low S-PAC and high PAC doses (S-PAC = 0.5 mg/L and PAC = 2 mg/L) in the laboratory-scale MF system. Neither the TMP increase for the entire operation period nor the reversible TMP increase for each batch filtration differed between S-PAC and PAC (the upper and lower left panels of Figure 9). Examination of the particle-size distribution data revealed that floc particles of similar size distributions were formed with 0.5 mg/L S-PAC and 2 mg/L PAC (the lower right panel of Figure 9). Therefore, the TMP increase in each batch filtration was highly controlled by floc particle size and probably did not greatly depend on the size of the original particles added.

The volume concentrations of floc particles were 3.8 ppm for S-PAC at 0.5 mg/L and 2.0 ppm for PAC at 2.0 mg/L (data not shown). That is, the volume concentration of floc particles was higher for S-PAC at 0.5 mg/L than for PAC at 2.0 mg/L, although the mass concentration was lower. This result clearly shows that the floc particles formed after the addition of S-PAC had higher porosity and thus should have had higher permeability as they built up on the membrane surface. We next examined the effect of floc particle size on the TMP buildup rate with different flocculation times by changing the length of the reactor tube (and the resulting GT value), which produced different sizes of floc particles. Two flow lines with different detention times for coagulation and flocculation were set up and used alternately every 2 days in an experiment. One flow line had a GT value of 24,000, and the other had a GT value of 57,600. The membrane filtration experiment started with the high GT value (57,600). At this GT value, the reversible TMP increase for each batch filtration was less than 0.1 kPa (the upper and lower left panels of Figure 10). After 2 days of operation, the coagulation–flocculation condition was changed to the low GT value (24,000), and higher rates of TMP buildup (about 3 kPa) were observed. The TMP buildup declined when the GT value was increased again. This GT-value–related change in the TMP buildup rate was repeated every time the GT value was changed. The median size of floc particles formed at GT = 57,600 was 160  $\mu\text{m}$ , whereas it was 15  $\mu\text{m}$  at GT = 24,000 (the lower right panel of Figure 10). These data clearly show that the size of floc particles entering the membrane affected the reversible TMP increase and the permeability of the cake layer formed on the membrane. In this paper, the effects of S-PAC pretreatment on coagulation and TMP buildup during microfiltration were discussed mainly by focusing on floc particle size. Coagulation, however, is basically complex phenomena, which is better understood by floc particle size and other characteristics. More studies are still needed.

## CONCLUSIONS



- 1) The addition of S-PAC did not reduce membrane permeability. Instead, the S-PAC attenuated the long-term (63 days) TMP buildup that could not be reversed by hydraulic backwashing. The addition of PAC also attenuated the long-term TMP buildup, but at a dose that was 5 times the S-PAC dose. The better TMP attenuation ability of S-PAC may have been due to the fact that S-PAC removed NOM more efficiently than PAC or coagulation alone.
- 2) Because the addition of S-PAC or PAC resulted in the formation of larger floc particles, the reversible TMP increase during each filtration cycle was mitigated by pretreatment with S-PAC or PAC.
- 3) Addition of S-PAC depressed reversible TMP increases more effectively than did addition of PAC because larger, more permeable floc particles were formed with S-PAC than with PAC at the same dose. Larger, more permeable floc particles were formed with S-PAC because of the increased volume concentration due to the fractal effect and the increased frequency of particle–particle collisions.
- 4) Another reason for the difference in floc particle size may have been differences in the degree to which NOM hindered coagulation: more NOM may have been adsorbed by S-PAC than by PAC and by coagulation alone. As a result, more of the coagulant may have been available for effective coagulation.

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## REFERENCES

- Adham, S. S., Snoeyink, V. L., Clark, M. M. and Bersillon, J. L. (1991) Predicting and verifying organics removal by PAC in an ultrafiltration system. *J. Am. Water Works Assoc.* 83(12), 81–91.
- Barbot, E., Moustier, S., Bottero, J.Y. and Moulin, P. (2008) Coagulation and ultrafiltration: Understanding of the key parameters of the hybrid process. *J. Membr. Sci.* 325, 520–527.
- Baudin, I., Campos, C. and Laîné, J.M., (2001) Removal of organic matter by the PAC-UF process: first two years of a full-scale application, *Water Sci. & Technol.: Water Supply* 1(4), 253–263.
- Carroll, T., King, S., Gray, S.R., Bolto, B.A. and Booker, N.A. (2000) The fouling of microfiltration membranes by NOM after coagulation treatment. *Water Res.* 34(11), 2861–2868.
- Chen, Y., Dong, B.Z., Gao, N.Y. and Fan, J.C. (2007) Effect of coagulation pretreatment on fouling of an ultrafiltration membrane. *Desalination* 204, 181–188.
- Cho, M.-H., Lee, C.-H. and Lee, S. (2005) Influence of floc structure on membrane permeability in the coagulation-MF process, *Water Sci. & Technol.* 51(6–7), 143–150.
- Choi, K. Y.-j. and Dempsey, B.A. (2004) In-line coagulation with low-pressure membrane filtration. *Water Res.* 38(19), 4271–4281.
- Elimelech M., Williams, R., Gregory, J. and Jia, X. (1998) Particle deposition and aggregation. Butterworth-Heinemann.
- Fan, L., Nguyen, T., Roddick, F.A. and Harris, J.L. (2008) Low-pressure membrane filtration of secondary effluent in water reuse: pre-treatment for fouling reduction. *J. Membr. Sci.* 320, 135–142

- Gray, S.R., Ritchie, C.B., T. Tran, T., Bolto, B.A., Greenwood, P., Busetti, F. and Allpike, B. (2008) Effect of membrane character and solution chemistry on microfiltration performance. *Water Res.* 42(3), 743 – 753.
- Haberkamp, J., Ruhl, A.S., Ernst, M. and Jekel, M. (2007) Impact of coagulation and adsorption on DOC fractions of secondary effluent and resulting fouling behavior in ultrafiltration. *Water Res.* 41(17), 3794 – 3802.
- Howe, K.J., Marwah, A., Chiu, K-P. and Adham, S.S. (2006) Effect of coagulation on the size of MF and UF membrane foulants. *Environ. Sci. Technol.* 40(24), 7908–7913.
- Huang, H., Schwab, K. and Jacangelo, J.G. (2009) Pretreatment for low pressure membranes in water treatment: a review. *Environ. Sci. Technol.* 43(9), 3011–3019.
- Jack, A. M. and Clark, M. M. (1998) Using PAC-UF to treat a low-quality surface water. *J. Am. Water Works Assoc.*, 90(11), 83–95.
- Jang, H.-N., Lee, D.-S., Park, M.-K., Moon, S.-Y., Cho, S.-Y., Kim, C.-H. and Kim, H.-S. (2006) Effects of the filtration flux and pre-treatments on the performance of a microfiltration drinking water treatment system, *Water Sci. & Technol.: Water Supply* 6 (4), 81–87.
- Judd, S.J. and Hillis, P. (2001) Optimization of combined coagulation and microfiltration for water treatment. *Water Res.* 35(12), 2895–904.
- Kanaya, S., Fujiura, S., Tomita, Y. and Yonekawa, H. (2007) The world's largest ceramic membrane drinking water treatment plant. *Proc. AWWA Membrane Technol. Conf.*, Tampa, FL, USA.
- Kimura, K., Maeda, T., Yamamura, H and Watanabe, Y. (2008) Irreversible membrane fouling in microfiltration membranes filtering coagulated surface water. *J. Membr. Sci.* 320, 356–362
- Lahoussine-Turcaud, V., Wiesner, M.R., Bottero, J.-Y. and Mallevalle, J. (1990) Coagulation pretreatment for ultrafiltration of a surface water. *J. Am. Water Works Assoc.* 82(12), 76–81.

Lainé, J.-M., Hagstrom, J. P., Clark, M. M. and Mallevialle, J. (1989) Effects of ultrafiltration membrane composition. *J. Am. Water Works Assoc.* 81(11), 61–67.

Lee, J.D., Lee, S.A., Jo, M.H., Park, P.K., Lee, C.H. and Kwak, J.W. (2000) Effect of coagulation conditions on membrane filtration characteristics in coagulation-microfiltration process for water treatment. *Environ. Sci. Technol.* 34(17), 3780–3788.

Lee, S.A., Fane, A.G. and Waite, T.D. (2005) Impact of natural organic matter on floc size and structure effects in membrane filtration. *Environ. Sci. Technol.* 39(17), 6477–6486.

Leiknes, T., Odegaard, H. and Myklebust, H. (2004) Removal of natural organic matter (NOM) in drinking water treatment by coagulation-microfiltration using metal membranes, *J. Membr. Sci.* 242 (1–2), 47–55.

Li, C.-W. and Chen, Y.-S. (2004) Fouling of UF membrane by humic substance: Effects of molecular weight and powder-activated carbon (PAC) pre-treatment. *Desalination* 170, 59–57.

Loi-Brügger, A., Panglisch, S., Buchta, P., Hattori, K., Yonekawa, H., Tomita, Y. and Gimbel, R. (2006) Ceramic membranes for direct river water treatment applying coagulation and microfiltration. *Water Sci. & Technol.: Water Supply* 6(4), 89–98.

Mallevialle, J., (1996) *Water Treatment Membrane Processes*, McGraw-Hill, New York, NY, USA.

Matsui Y., Fukuda Y., Murase R., Aoki N., Mima S., Inoue T. and Matsushita T. (2004) Micro-ground powdered activated carbon for effective removal of natural organic matter during water treatment. *Water Sci. & Technol.: Water Supply* 4(4), 155–163.

Matsui Y., Murase R., Sanogawa T., Aoki N., Mima S., Inoue T. and Matsushita T. (2005) Rapid adsorption pretreatment with submicron powdered activated carbon particles before microfiltration. *Water Sci. & Technol.* 51(6–7), 249–256.

Matsui, Y., Sanogawa, T., Aoki, N., Mima, S. and Matsushita, T. (2006) Evaluating submicron-sized activated carbon adsorption for microfiltration pretreatment. *Water Sci. & Technol.: Water Supply* 6(1), 149–155.

- Matsui, Y., Aizawa, T., Kanda, F., Nigorikawa, N., Mima, S. and Kawase, Y. (2007) Adsorptive removal of geosmin by ceramic membrane filtration with super-powdered activated carbon. *J. Water Supply Res. Technol.-AQUA* 56(6-7), 411-418.
- Matsui, Y., Ando, N., Sasaki, H., Matsushita, T. and Ohno, K. (2009) Branched pore kinetic model analysis of geosmin adsorption on super-powdered activated carbon. *Water Res.* 43(12), 3095-3103.
- Moziá, S., Tomaszewska, M. and Morawski, A.W. (2005) Studies on the effect of humic acids and phenol on adsorption-ultrafiltration process performance. *Water Res.* 39(2-3), 501-509.
- Oh, J.-I. and Lee, S.H., (2005) Influence of streaming potential on flux decline of microfiltration with inline rapid pre-coagulation process for drinking water production. *J. Membr. Sci.* 254, 39-47.
- Oles, V. (1992) Shear-induced aggregation and breakup of polystyrene latex particles. *J. Colloid & Interface Sci.* 154(2), 351-358.
- Park, P.-k., Lee, C.-h., Choi, S.-J., Choo, K.-H., Kim, S.-H. and Yoon, C.-H. (2002) Effect of the removal of DOMs on the performance of a coagulation-UF membrane system for drinking water production. *Desalination* 145, 237-245.
- Park, P.K., Lee C.H. and Lee, S. (2006) Variation of specific cake resistance according to size and fractal dimension of chemical flocs in a coagulation-microfiltration process. *Desalination* 199, 213-215.
- Park, P.K., Lee, C.H. and Lee, S. (2007) Determination of cake porosity using image analysis in a coagulation-microfiltration system. *J. Membr. Sci.* 293, 66-72.
- Pikkarainen, A.T., Judd, S.J., Jokela, J. and Gillberg, L. (2004) Pre-coagulation for microfiltration of an upland surface water. *Water Res.* 38(2), 455-465.
- Serra, T. and Casamitjana, X. (1998) Structure of the aggregates during the process of aggregation and breakup under a shear flow. *J. Colloid & Interface Sci.* 206(2), 505-511.
- Takizawa S., Zhao, P., Ohgaki S. and Katayama, H. (2008) Kinetic analysis of PAC cake-layer formation in hybrid PAC-MF systems. *Water Sci. & Technol.: Water Supply* 8 (1), 1-7.

Tambo, N. and Watanabe, Y. (1979). Physical characteristics of flocs I, the floc density function and aluminium floc. *Water Res.* 13, 409–419.

Tambo, N. and Francois, R.J. (1991) Mixing, breakup, and aggregate characteristics. In *Mixing in Coagulation and Flocculation* ed. A. Amirtharajah, M. M. Clark, R. R. Trussell. Am. Water Works Assoc.

Tomaszewska, M. and Mozia, S. (2002) Removal of organic matter from water by PAC/UF system. *Water Res.* 36(16), 4137–4143.

Yiantsios, S.G. and A.J. Karabelas, A.J. (2001) An experimental study of humid acid and powdered activated carbon deposition on UF membranes and their removal by backwashing. *Desalination* 140, 195–209.

Yonekawa, H., Tomita, Y. and Watanabe, Y. (2004) Behavior of micro-particles in monolith ceramic membrane filtration with pre-coagulation. *Water Sci. & Technol.* 50(12), 317–325.

Zhang, M., Li, C. and Benjamin, M.M. and Chang, Y. (2003) Fouling and Natural Organic Matter Removal in Adsorbent/Membrane Systems for Drinking Water Treatment. *Environ. Sci. Technol.* 37, 1663–1669.

## Figure captions

Figure 1. Laboratory-scale MF system.

Figure 2. Temporal variations of TMP (upper panel) and reversible TMP increase for each batch filtration (lower panel) for Lines 1–3 of the pilot-scale MF system (PACl dose = 0.8 mg-Al/L, S-PAC/PAC contact time = 2 min, coagulation time = 2 min,  $G = 200 \text{ s}^{-1}$ ,  $GT = 24,000$ ,  $\text{pH} = 6.8$ , MF flux = 3 m/d, backwash interval = 3 h, Lake Sagami water, turbidity = 5–31 NTU, average turbidity = 10 NTU, TOC = 1.1–1.5 mg/L, average TOC = 1.2 mg/L). The small window in Panel A shows temporal variation of TMP on days 8–10.

Figure 3. Temporal variation of TMP for Lines 1 and 3 of the pilot-scale MF system (S-PAC contact time = 2 min, coagulation time = 2 min,  $G = 200 \text{ s}^{-1}$ ,  $GT = 24,000$ ,  $\text{pH} = 6.8$ , MF flux = 3 m/d, backwash interval = 3 h, Lake Sagami water, turbidity = 6.1–69 NTU, average turbidity = 17 NTU, TOC = 0.7–1.5 mg/L, average TOC = 1.0 mg/L).

Figure 4. Variation of median diameter of floc particles with GT value: (left panel) NOM-free water and (right panel) NOM-containing water (PACl dose = 1 mg-Al/L, S-PAC/PAC contact time = 21 s,  $G = 160 \text{ s}^{-1}$ ,  $T = 1\text{--}8 \text{ min}$ ,  $GT = 9600\text{--}76,800$ ; NOM source: Lake Hakucho water,  $\text{DOC} = 4.6 \text{ mg/L}$ ,  $\text{UV}_{260} = 0.075 \text{ cm}^{-1}$ ).

Figure 5. Relationship between volume concentration of total floc particles and median diameter of floc particles (left panel) NOM-free water and (right panel) NOM-containing water. (Experimental conditions are described in Figure 8.)

Figure 6. Comparison of NOM removal performances of S-PAC and PAC for the MF influent (S-PAC and PAC doses = 2 mg/L, PACl dose = 1 mg-Al/L, S-PAC/PAC contact time = 21 s, coagulation time = 4 min,  $G = 160 \text{ s}^{-1}$ ,  $GT = 38,400$ ; NOM source: Lake Hakucho water,  $\text{DOC} = 4.6 \text{ mg/L}$ ,  $\text{UV}_{260} = 0.075 \text{ cm}^{-1}$ ).

Figure 7. TMP (upper panel), reversible TMP increase for each batch filtration (lower left panel), and floc size distributions of MF influent (lower right panel) in the laboratory-scale MF system with alternating addition of S-PAC and PAC (S-PAC and PAC doses = 2 mg/L, PACl dose = 1 mg-Al/L, S-PAC/PAC contact time = 21 s, coagulation time = 4 min,  $G = 160 \text{ s}^{-1}$ ,  $GT = 38,400$ , MF flux = 0.083 m/h, backwash interval = 8 h, NOM-free water).

Figure 8. TMP (upper panel), reversible TMP increase for each batch filtration (lower left panel), and floc size distributions of MF influent (lower right panel) in the laboratory-scale MF system with alternating addition of S-PAC and PAC (S-PAC and PAC doses = 2 mg/L, PACl dose = 1.5 mg-Al/L, S-PAC/PAC contact time = 21 s, coagulation time = 4 min,  $G = 160 \text{ s}^{-1}$ ,  $GT = 38,400$ , MF flux = 0.083 m/h, backwash interval = 4 h, NOM-containing water; NOM source: Chibaberi River water, DOC = 1.8 mg/L,  $UV_{260} = 0.06 \text{ cm}^{-1}$ ).

Figure 9. TMP (upper panel), reversible TMP increase for each batch filtration (lower left panel), and floc size distributions of MF influent (lower right panel) in the laboratory-scale MF system at a reduced adsorbent dose of S-PAC and a full dose of PAC (PACl dose = 1 mg-Al/L, S-PAC/PAC contact time = 21 s, coagulation time = 4 min,  $G = 160 \text{ s}^{-1}$ ,  $GT = 38,400$ , MF flux = 0.083 m/h, backwash interval = 6 h, NOM-free water).

Figure 10. TMP (upper panel), reversible TMP increase for each batch filtration (lower left panel), and floc size distributions of MF influent (lower right panel) in the laboratory-scale MF system at different GT values (S-PAC dose = 2 mg/L, PACl dose = 1 mg-Al/L, S-PAC/PAC contact time = 21 s,  $GT = 24,000 = 320 \text{ s}^{-1} \times 1 \text{ min} + 160 \text{ s}^{-1} \times 30 \text{ s}$  or  $GT = 57,600 = 320 \text{ s}^{-1} \times 1 \text{ min} + 160 \text{ s}^{-1} \times 4 \text{ min}$ , MF flux = 0.083 m/h, backwash interval = 8 h, NOM-free water).



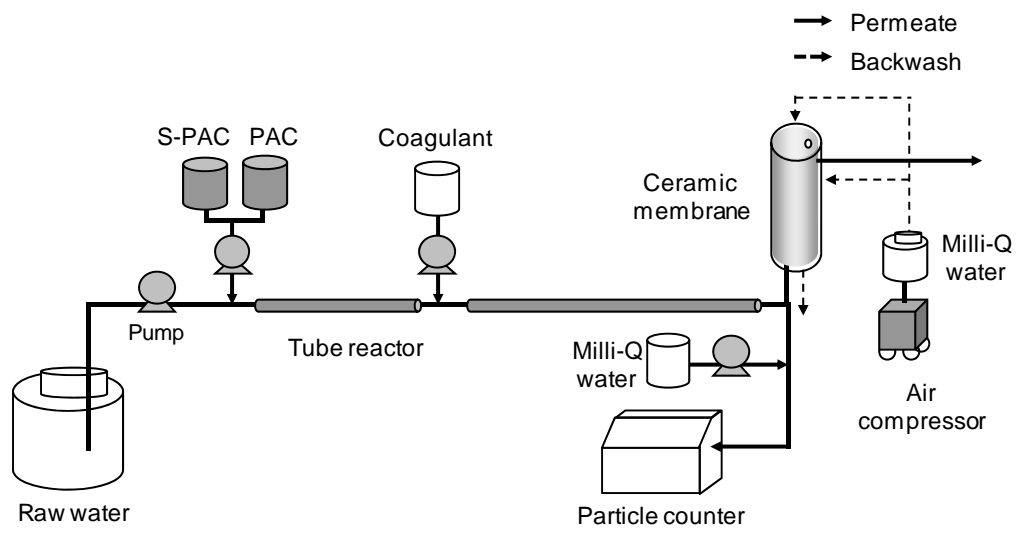


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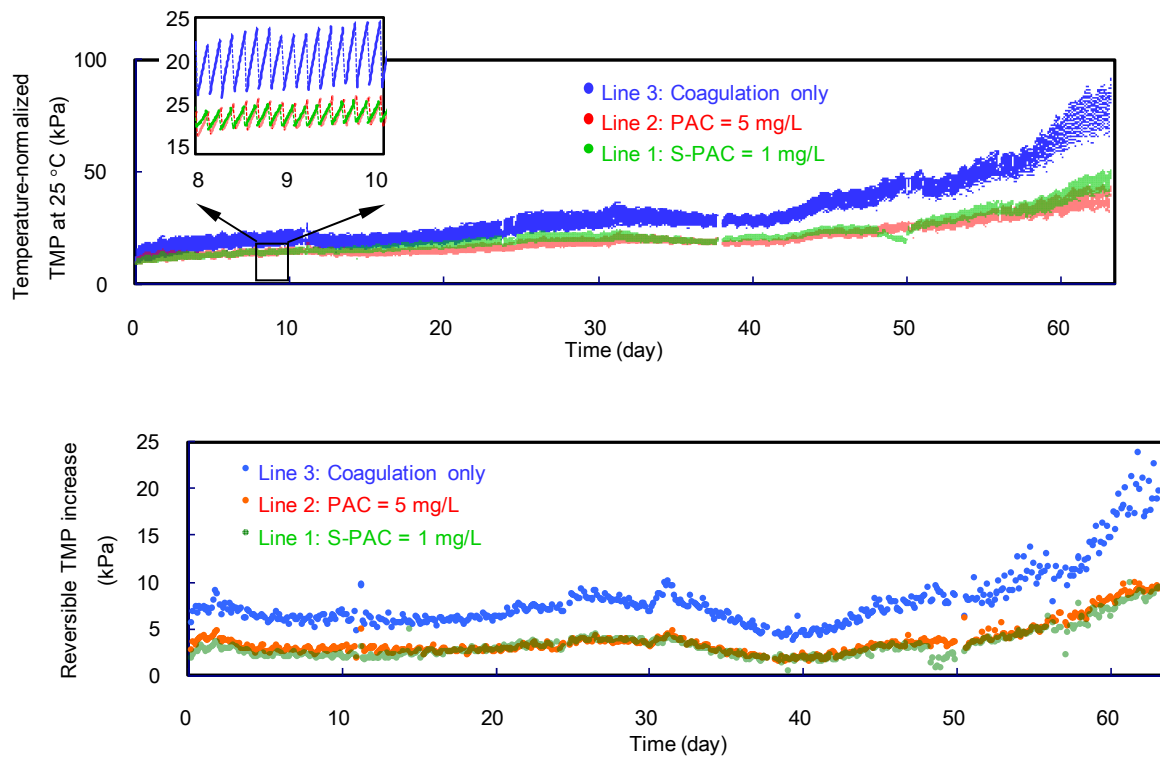


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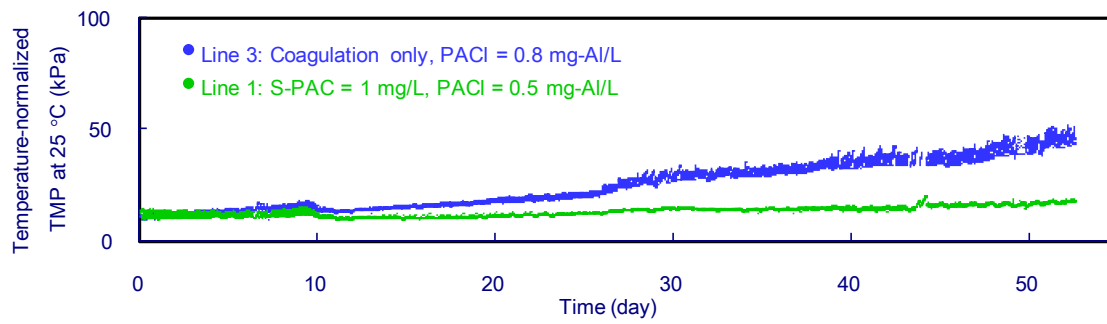


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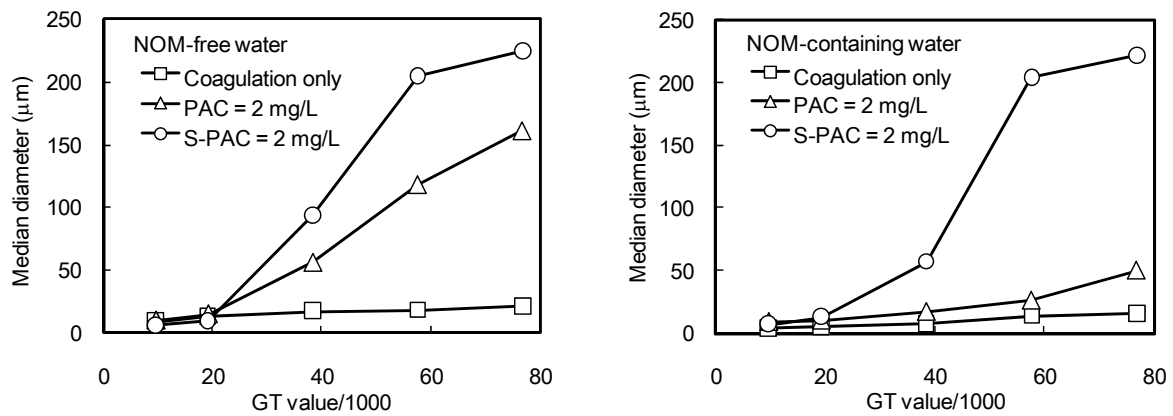


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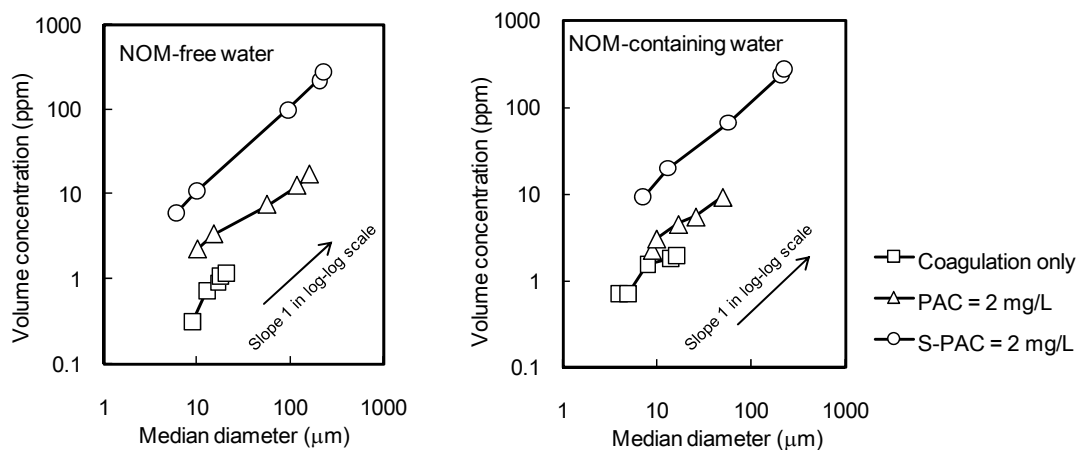


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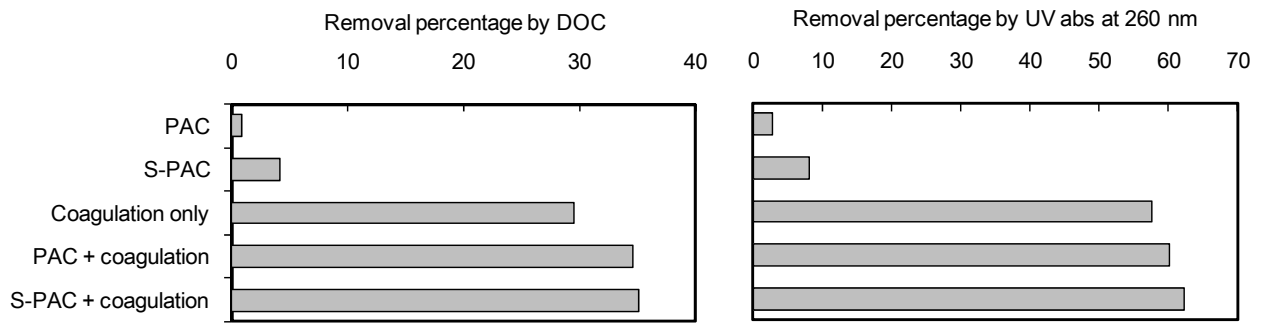


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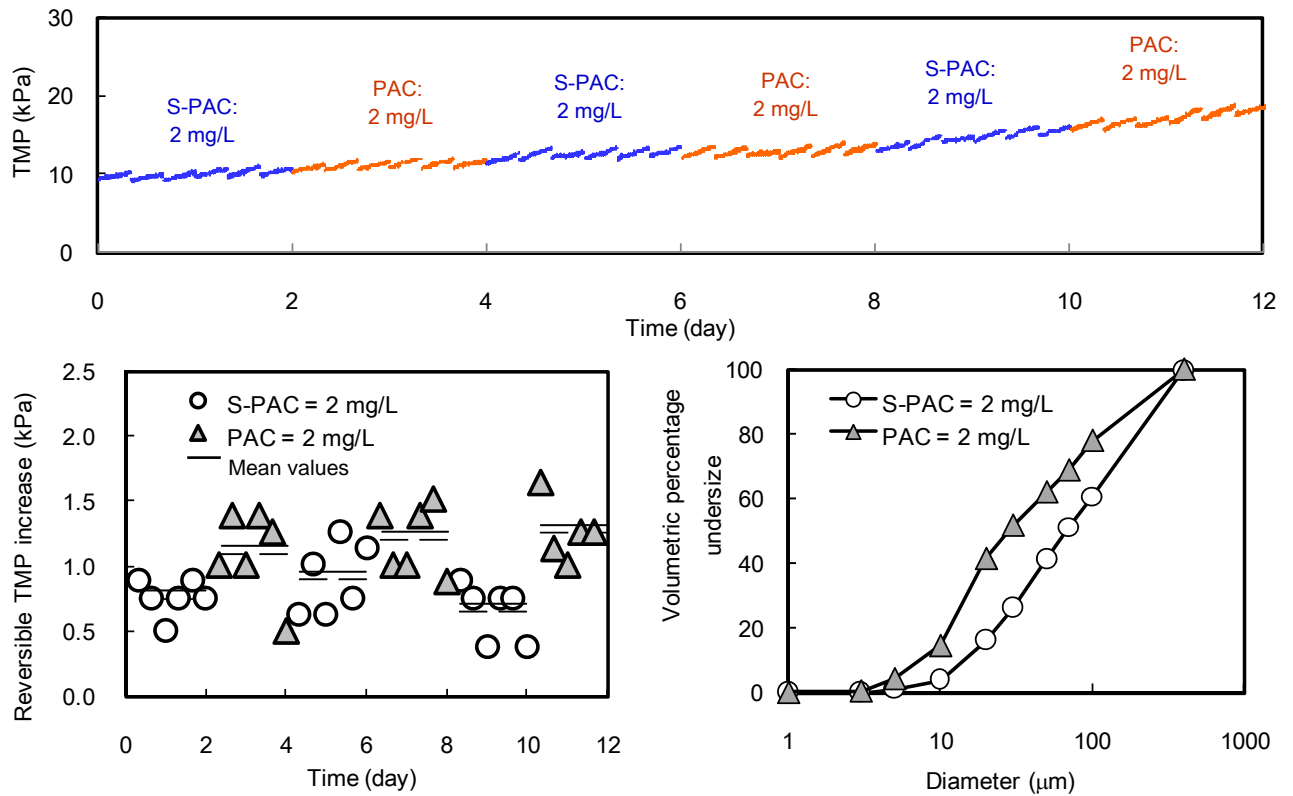


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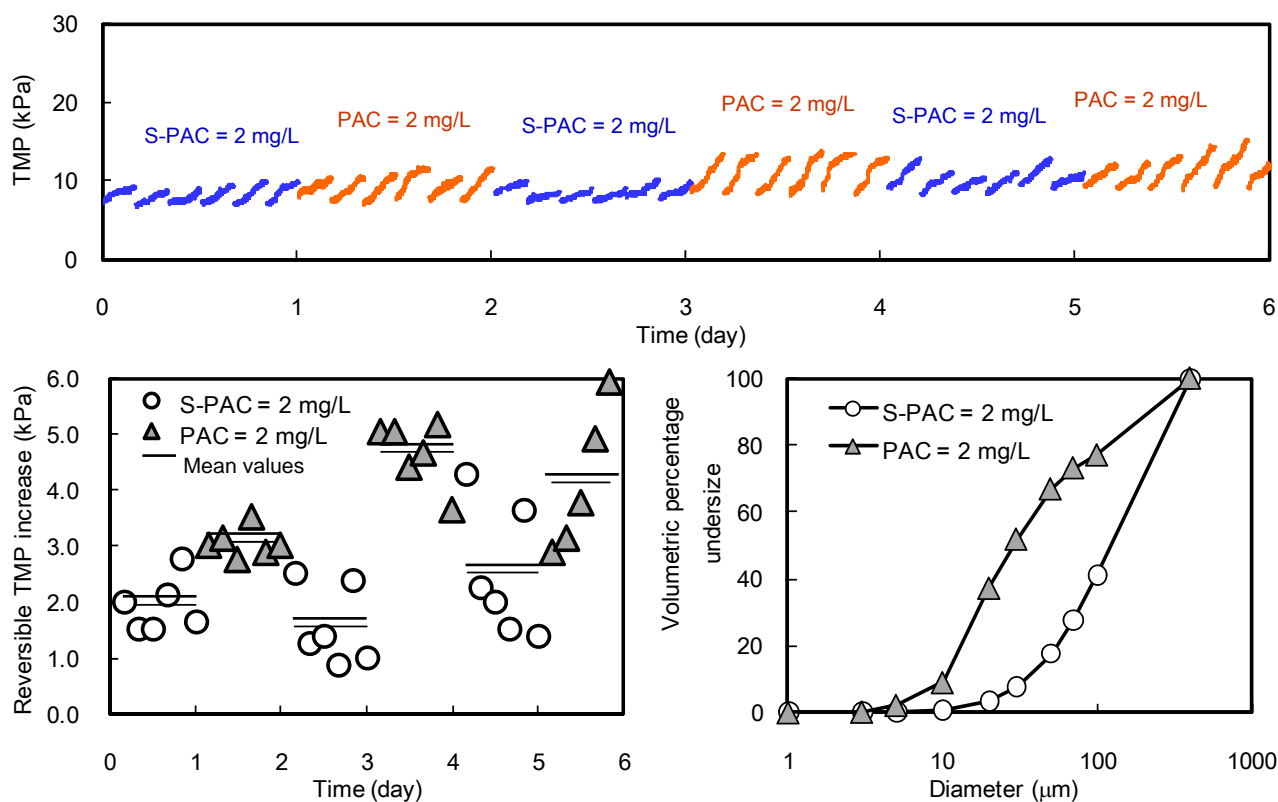


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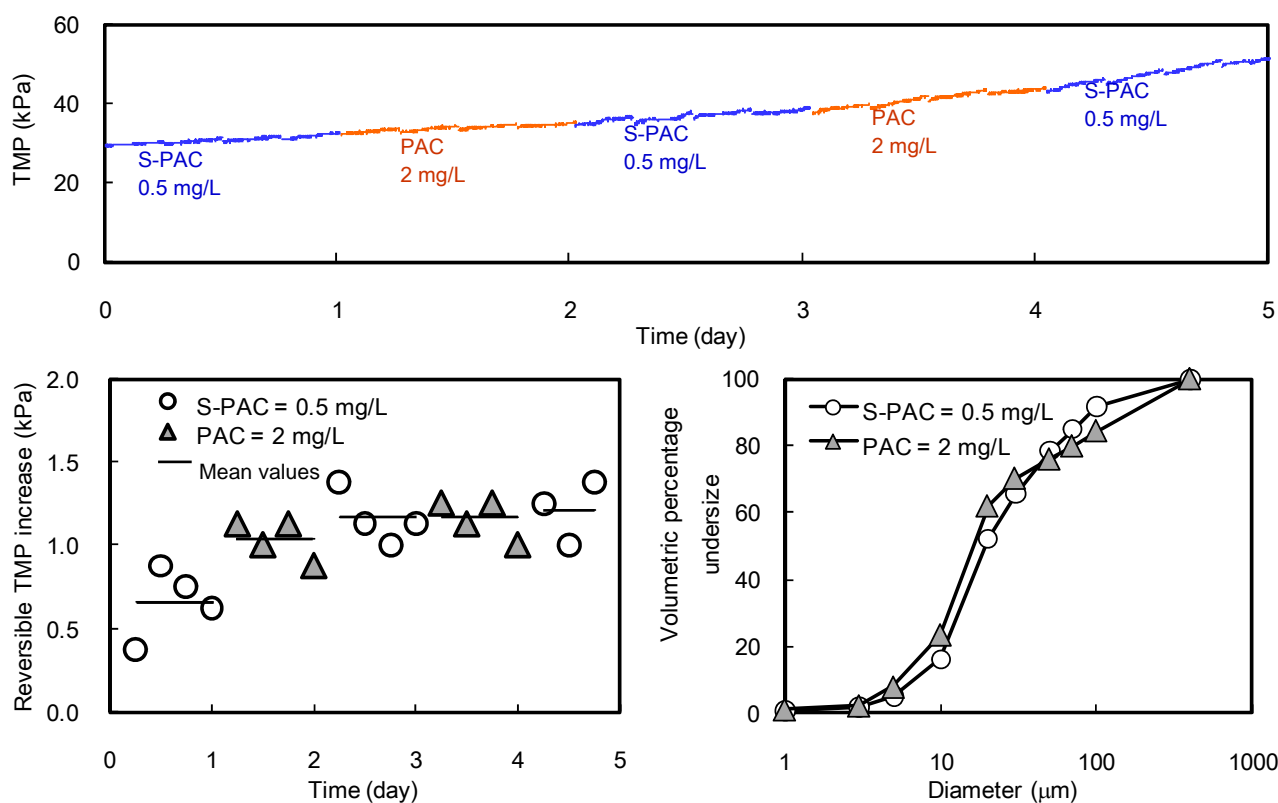


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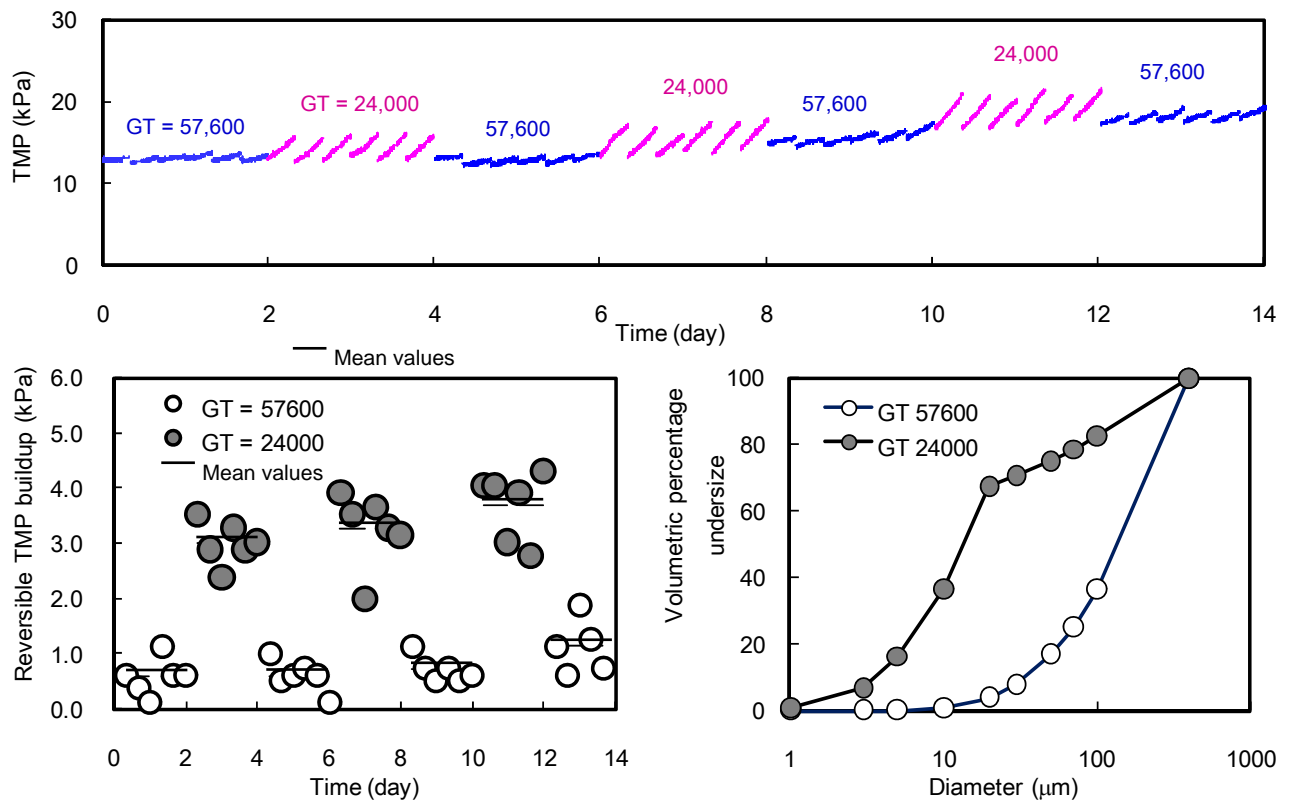


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