Evaluating submicron-sized activated carbon adsorption for microfiltration pretreatment

Y. Matsui*, T. Sanogawa*, N. Aoki**, S. Mima** and T. Matsushita*

*Department of Civil Engineering, Gifu University, Yanagido 1-1, Gifu 501-1193, Japan

**Research & Development Department, NGK Insulators, Ltd., Maegata-cho 1, Handa 475-0825, Japan
(E-mail: *y-matsui@cc.gifu-u.ac.jp*; *j3101016@guedu.cc.gifu-c.ac.jp*; *n-aoki@ngk.co.jp*; *s-mima@ngk.co.jp*; *taku_m@cc.gifu-u.ac.jp*)

Abstract Submicron powdered activated carbon (PAC) rapidly adsorbed natural organic matter (NOM) fromwater samples: a batch test of the adsorption kinetics showed that the NOM concentration dropped substantially within 15 s and then leveled off. In a tubular flow reactor test, NOM removal after a 15 s contact time was almost the same as removal values attained at longer contact times. Laboratory-scale and bench-scale pilotplant ceramic microfiltration (MF) experiments with submicron PAC adsorption pretreatment were conducted to evaluate NOM removal and to examine the effect of the PAC on filterability. The laboratory scale MF experiment revealed that PAC adsorption pretreatment could be accomplished with a detention (2.4 s) that was much shorter than the time expected from the adsorption kinetics test. This result suggests that adsorption pretreatment for MF could be accomplished by adding the submicron PAC directly into the feed line to the membrane and that installation of a special PAC contactor before the membrane unit is unnecessary. Although micron PAC rather than submicron PAC was used unintentionally in the pilot plant experiment, these PAC showed much better NOM removal than normal PAC, and no adverse effects, such as transmembrane pressure buildup and reversible or irreversible membrane fouling, were observed.
Keywords Humic substances; membrane; natural organic matter; particle size; powdered activated carbon

Introduction

Because of their durability, ceramic membranes have attracted considerable attention in the field of drinking water treatment in Japan. Although microfiltration (MF) with ceramic membranes offers the advantages of lower pressure and lower energy consumption than tighter membranes, the membranes cannot exclude particles with diameters smaller than tens of nanometres, such as viruses and dissolved natural organic matter (NOM).

The addition of a metal coagulant, powdered activated carbon (PAC), or both to a membrane-filtration influent is a simple, cost-effective way to remove contaminants that cannot be removed by the membrane itself (Clark *et al.*, 1996; Wiesner and Laîné, 1996). The presence of these additives would also minimize any reduction in the permeability of the membrane and thereby reduce the frequency of the hydrodynamic or chemical membrane-cleaning procedures that are conventionally used to maintain permeate flux. Because of chemical and mechanical stability of ceramic membranes, the use of additives in the influent is particularly beneficial for ceramic MF. When coagulation pretreatment is used, a long detention time is not needed for coagulation/flocculation, because micro-floc particles form rapidly and can be retained by the membrane; therefore, the advantages of the small footprint of membrane filtration systems are not lost. In contrast, PAC adsorption requires a large contactor to ensure sufficient utilization of the adsorption capacity of PAC, and the use of a large contactor offsets the advantages of the small footprint. Recently, our research group proposed using micron to submicron PAC to speed up adsorption (Matsui *et al.*, 2004) and thus permit capacity utilization at shorter contact times. Laboratory-scale MF experiments showed that PAC adsorption pretreatment for

MF can be accomplished with a detention time of 1 min and that the amount required is one-fourth that required for normal PAC (Matsui *et al.*, 2005). The ceramic membrane used in our studies is appropriate for small PAC because the membrane has a narrow distribution of pore sizes and therefore completely excludes even submicron PAC particles.

We report herein the results of submicron PAC adsorption–ceramic MF experiments designed to further reduce the PAC contact time. We also conducted a bench-scale pilot-plant MF test to determine whether addition of submicron PAC led to transmembrane pressure (TMP) buildup or membrane fouling.

Materials and methods

Water samples

Water from the Toyokawa River in Aichi, Japan, was used, except in the batch kinetics test, in which water from Takkobu Lake, Hokkaido, was used. Water samples were collected and transported in polyethylene tanks and stored at 4 °C. Total organic carbon (TOC) and the ultraviolet absorbance at 260 nm (UV_{260}) were monitored to quantify bulk NOM concentrations in the samples (TOC measurement, Model 810, Sievers Instruments, Boulder, CO, USA; UV_{260} absorption, Model UV-160A, Shimadzu Corp., Kyoto, Japan). These values were measured after membrane filtration (0.45 μm PTFE membrane filter) for all the water samples except the MF permeates.

Coagulant and adsorbents

The coagulant, polyaluminium chloride (PACl, 10% Al_2O_3, 62.5% basicity, Sumitomo Chemical Co., Tokyo, Japan), was diluted before use, and a fixed quantity was added to each experimental mixture. Submicron PAC was obtained by grinding thermally activated wood-based PAC (Taikou-W, Futamura Chemical Industries Co., Gifu, Japan). We used both the submicron PAC and the as-received (normal) PAC to determine the effects of PAC size and the effectiveness of the submicron PAC in adsorption experiments. All PAC was dried in an oven at 105 °C and stored in a desiccator before use. Particle-size distributions of the PAC were determined using laser-light scattering instruments (LMS-30, Seishin Enterprise Co., Tokyo; and Microtrac HRA, Nikkiso Co., Tokyo, Japan).

Batch adsorption tests

Batch tests of NOM adsorption were conducted using water from Takkobu Lake. Before PAC was added to a beaker containing the water sample, an aliquot was withdrawn from the beaker to determine the initial NOM concentration. After the addition of a specified amount of PAC, aliquots were withdrawn at intervals and filtered immediately through a 0.45 μm membrane filter for NOM concentration analysis. The absence of PAC particles in the membrane permeates was confirmed.

Adsorption test using a tubular flow reactor

A flow-through tube contactor with multiple sampling ports was used to determine the change of NOM concentration at contact times less than 1 min. The NOM solution flowed through the tube (length, 20 m), and PAC was injected at a port close to the solution inlet. Water samples were withdrawn from ports at various hydraulic detention times and applied immediately to membrane filters for PAC–water separation.

MF systems

A laboratory-scale experimental setup and a MF bench-scale pilot plant were used for MF experiments with PAC adsorption and coagulation pretreatments. In the laboratory-scale experiments, river water was fed into a system with three parallel lines (Figure 1)
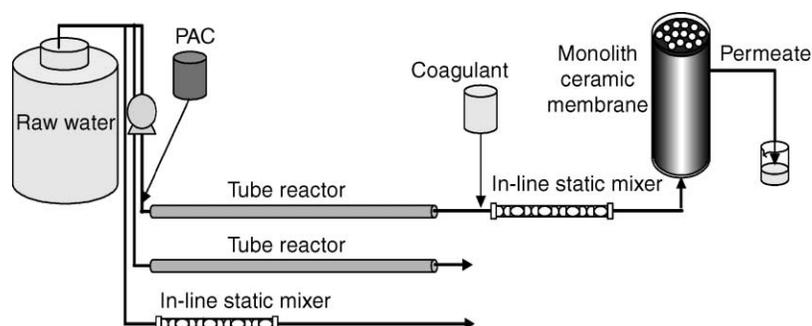
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Figure 1 Schematic of the PAC adsorption/coagulation/MF systems

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for PAC adsorption, PACl coagulation, and MF at a constant flow rate using a peristaltic pump. After a PAC contact time ranging from 2.4 s to 6.3 min, the water was transferred to an in-line static mixer, where the coagulant was added. PAC was injected at a dosing rate of 3 mg/L, and the PACl dose was set at 3 mg-Al/L. Two mixing units were used to vary the PAC contact time: an in-line mixer with a detention time of 2.4 s and a tube reactor with detention times of 10 s, 30 s, 1 min, and 6.3 min. After coagulation, the water was fed into the MF module (multichannel tubular, nominal pore size $= 0.1 \mu$m, NGK Insulators, Nagoya, Japan) in dead-end mode. The flow of feed to the membrane module was maintained at a constant rate (1.5 m/d $= 62.5 \mathrm{L \cdot m^{-2} \cdot h^{-1}}$) inside the channels by positive pressure. A new or chemically cleaned membrane was used for each experiment to eliminate any effects of historical fouling, and the filtration lasted for 5 h without hydraulic backwashing.

A MF bench-scale pilot plant with three parallel lines was used to compare transmembrane pressure (TMP) buildup and permeation quality at various PAC sizes. The system was operated for 6 d with hydraulic backwashing every 2 h.

Results and discussion

Adsorption kinetics

To determine the speed of NOM uptake by the submicron (volumetric median sizes, 0.8 μm) PAC, we conducted a batch experiment. A rapid concentration decline was observed (Figure 2): by the time the first sample was withdrawn after 1 min of contact
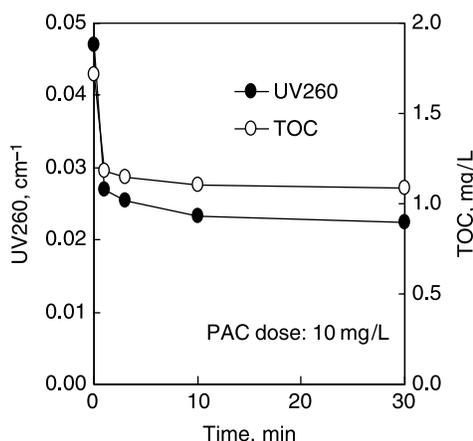

Figure 2 Variation of NO0M concentration with contact time in the batch adsorption kinetics test, 0.8 μm PAC (Takkobu Lake water)

time, the NOM concentration had already dropped, and it remained almost unchanged thereafter. (The NOM concentrations gradually decreased over a period of several weeks, probably owing to slow diffusion into micropores in the PAC particles (Peel and Benedek, 1980). The concentration at 3 weeks, which we assume to be the equilibrium concentration, was in fact below the concentration measured at 30 min.) If we assume that the utilizable adsorption capacity of the PAC is the capacity that can be utilized during a contact time of 30 min, the data indicate that NOM uptake was so fast that a contact time of 1 min was sufficient for utilization of the adsorption capacity. The data suggested that the contact time could be shortened further, but in the batch test, the sampling interval could not be shortened below 1 min, because the sampling itself and the subsequent filtration took about 10 s, which created non-negligible error when the sampling time interval was shortened to less than 1 min.

To circumvent this problem, we used a flow-through tube contactor with multiple sampling ports, as described previously. PAC contact times were controlled by removing water samples from the ports at different hydraulic detention times. The NOM concentration measured after 15 s of PAC contact time was nearly identical to the concentrations measured after 0.5–9.6 min of PAC contact (Figure 3). Because velocity in a tubular reactor is parabolically distributed rather than uniform across the cross section, the laminar flow in a tubular reactor does not produce a plug flow reactor condition; hence, the residence times of individual PAC particles in the reactor are not equal.

Nonetheless, the data show that NOM removal was not dependent on the average residence time of PAC at contact times ranging from 15 s to 10 min, and the data also suggest that PAC adsorption with a contact time of only 15 s would be feasible as a pretreatment for membrane filtration.

NOM removal by MF with adsorption and coagulation pretreatment

These results indicated that the submicron PAC had a dramatically enhanced adsorption rate relative to normal PAC and that a contact time of 15 s should be sufficient for adsorptive removal of NOM during pretreatment for MF. To confirm this, we conducted laboratory-scale MF operations with coagulant and submicron PAC pretreatments (Figure 1). PAC was added before coagulant dosing, and various PAC contact times (from 2.4 s to 6.3 min) were compared. NOM removal with a PAC contact time of only 0.5 min was almost the same as that with contact times of 1 min and 6.3 min (Figure 4).
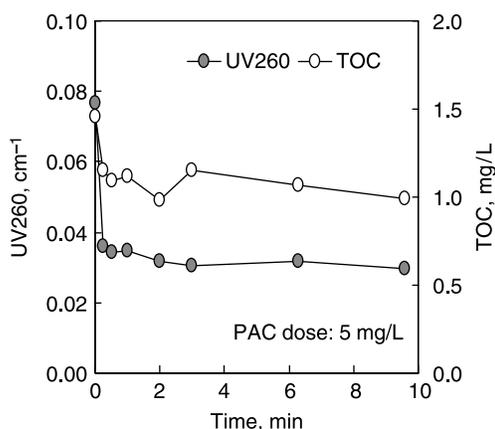

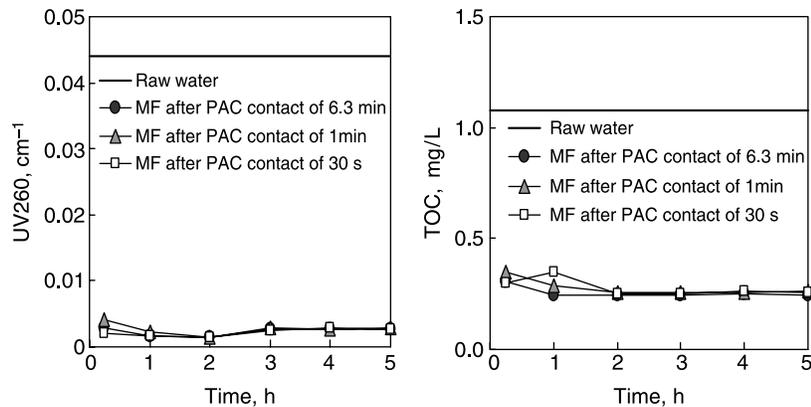**Figure 3** Variation of NOM concentration with contact time in the tubular flow reactor, 0.8 μm PAC

Figure 4 Effect of PAC contact time on NOM removal by MF with adsorption–coagulation pretreatments. Dosages of 0.8 μm PAC and coagulant were 3 mg/L and 3 mg/L as Al, respectively

In the next experiment, we reduced the PAC contact time further, to 2.4 s. Surprisingly, the PAC contact time of 2.4 s yielded the same permeate water quality as the contact times of 10 and 30 s (Figure 5). These results suggested that rapid pretreatment for MF could be accomplished by dosing with PAC just in front of the membrane and that the installation of a PAC contactor prior to the membrane unit is unnecessary.

We also conducted long-term tests using a membrane bench-scale pilot plant to observe the effect of PAC particle size on TMP and permeate water quality. In this pilot-plant operation, the membrane was backwashed every 2 h.

Two types of PAC were used: normal PAC (median diameter, 8.8 μm) and micron PAC (1.2 μm). (We had planned to use submicron PAC particles, but because we did not obtain the particle-size measurement until after the membrane pilot-plant experiment had been completed, we did not realize until too late that we had actually produced micron PAC.) The NOM concentrations (both in terms of UV_{260} and TOC) in the membrane permeate subjected to coagulation and normal-PAC adsorption pretreatments were almost identical to the concentrations obtained by coagulation pretreatment alone (Figure 6). Whereas the normal PAC did not contribute to NOM removal, the addition of 1.2 μm PAC actually decreased the NOM concentration in the permeate in terms of both UV_{260} and TOC.

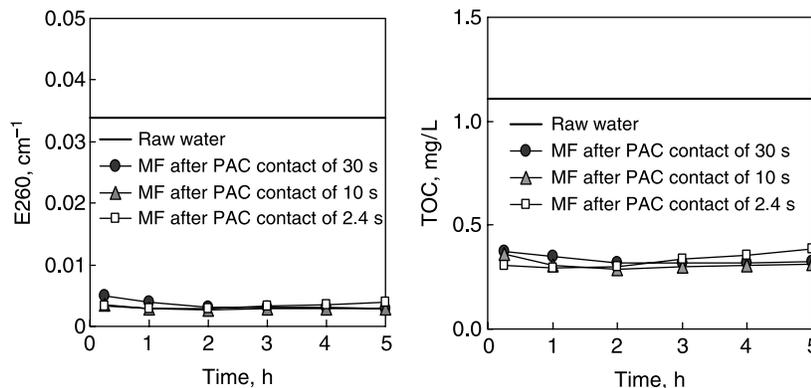**Figure 5** Effect of PAC contact time on NOM removal by MF with adsorption–coagulation pretreatments. Dosages of 0.8 μm PAC and coagulant were 3 mg/L and 3 mg/L as Al, respectively
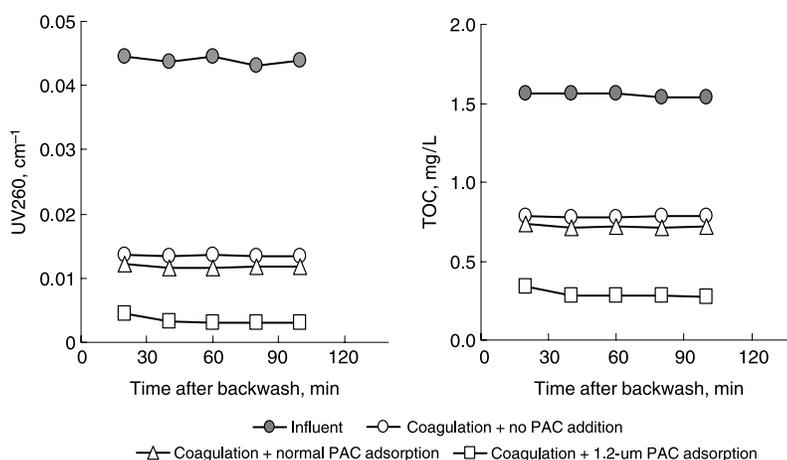
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Figure 6 Effect of PAC contact time on NOM removal by MF with coagulation-adsorption pretreatments (bench-scale pilot plant experiment: PAC and PACl dosages were 1.3 mg-Al/L and 20 mg/L, respectively. Membrane pore size was 0.1 μm. The filtration rate was 5.6 m/d $= 62.5$ L·m^{-2}·h^{-1})

TMP is an important issue when using such small PAC, so we evaluated TMP build-up over 6 d of operation, during which PAC was added to two membrane filtration systems (Figure 7). We started to add the PAC after the MF system had been operating for 7 d at a much higher filtration flux than that of normal operation.

Therefore, at the time of PAC addition, the TMP values were already rather high. However, during the 6 d after the PAC was added, the changes in the TMP values for the normal PAC and the micron PAC were the same. Moreover, when the TMP values observed during operations without PAC were compared to those with PAC, no difference in the trend of TMP buildup was observed.

The saw-toothed shape of the TMP curves was due to periodic cleaning of the membrane by hydraulic back-flushing, and the TMP increases represented by each of the spikes (indicating TMP increases after a backwash until just before the next backwash) were due to reversible fouling. In terms of reversible fouling, no large difference was observed between operations with and without PAC: short-term changes in the TMP values after hydraulic backwashing for the operation with PAC addition were no larger than the changes seen in the absence of PAC. These results indicate that neither the
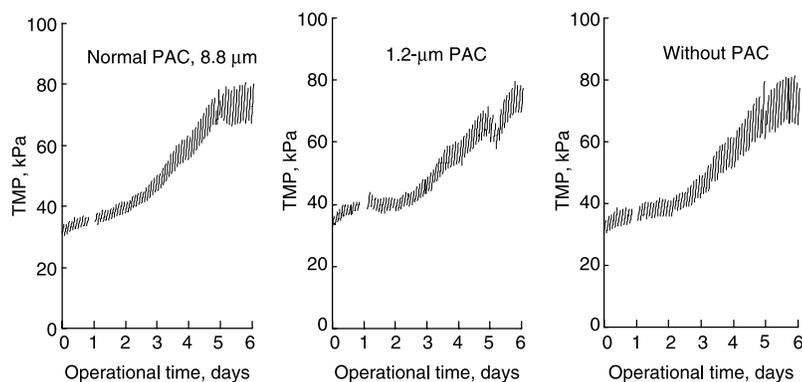

Figure 7 Transmembrane pressure (TMP) buildup during operation of MF (bench-scale plant experiment: PAC and PACl dosages were 1.3 mg-Al/L and 20 mg/L, respectively. Membrane pore size was 0.1 μm. Filtration rate was 5.6 m/d)

normal PAC nor the 1.2 μm PAC increased reversible or irreversible membrane fouling. Overall, submicron PAC not only required only a short contact time but also had an enhanced ability to adsorb NOM without negatively influencing TMP buildup or membrane fouling.

Conclusions

(1) Submicron PAC showed extremely fast NOM-adsorption kinetics: the kinetics studies using the batch reactor and the tubular flow reactor suggested that PAC adsorption pretreatment for MF could be accomplished with a detention time of 15 s.

(2) Detention times ranging from 2.4 s to 6.3 min in the presence of submicron PAC as a pretreatment before MF did not affect the water quality of the membrane permeate. The application of submicron PAC permitted an extremely short pretreatment contact time, which suggests that a PAC contactor would be unnecessary. PAC can be directly dosed to the MF feed line without a reduction in the effectiveness of adsorptive removal.

(3) The addition of 1.2 μm PAC as well as normal PAC did not accelerate TMP increases between backwashes or induce long-term TMP increases, which suggests that they did not act as reversible or irreversible foulants.

Acknowledgements

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