Micro-ground powdered activated carbon for effective removal of natural organic matter during water treatment


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Abstract For the purpose of enhancing the adsorption of natural organic matter (NOM) from water sources, commercially available powdered activated carbon (PAC) was further ground to produce PAC of micrometre-sized particles, and the effects of PAC size on adsorption of NOM were investigated. The micrometre-sized PAC (median particle diameter, 0.8 and 3.8 µm) removed NOM much better than did as-received PAC (33 µm). Only one-tenth the dose of micrometre-sized PAC had the same effect as a full dose of the as-received PAC. The micro-grinding of PAC to micrometre sizes was effective at increasing its adsorption kinetics: adsorption of NOM to the micrometre-sized PAC reached 80% of equilibrium within only 1 min of contact time. The micro-grinding of PAC was also effective at increasing its adsorption capacity for NOM and polystyrene sulfonate-MW1800, but not for the small molecule phenol. This appeared to be due to an increase in mesopore surface area probably by fracture of ink-bottle pore structures during the micro-grinding. The micro-grinding enhanced the adsorption affinity of PAC for NOM that was strongly UV260-absorbent but not for NOM with low UV260 absorbance.

Keywords Activated carbon; adsorption; humic substances; natural organic matter

Introduction
Although adsorption by activated carbon is regarded as one of the best available technologies for removing dissolved contaminants such as natural organic matter (NOM) from drinking water, residence times at water treatment plants are not long enough for efficient use of activated carbon. When powdered activated carbon (PAC) is used in a treatment plant, the PAC–water contact time is typically 2 h or less, which is too short to allow maximum adsorption of most target compounds. In particular, NOM adsorption is slow and seldom reaches equilibrium (Sontheimer et al., 1983). When PAC adsorption is used for pretreatment before membrane filtration, PAC–water contact times are even shorter, and the carbon is discarded before the complete utilization of its adsorption capacity (Clark et al., 1996). A large PAC–water contactor may be a solution; however, using a large contactor would offset the advantages of the small footprint of membrane filtration equipment. Another strategy would be to use smaller PAC particles since they provide faster adsorption kinetics (Weber et al., 1983; Najim et al., 1990). PAC smaller than currently available products, for example micrometre-sized PAC, should permit shorter residence times or lower PAC dosages to be used in a pretreatment stage before membrane filtration. However, the effect of PAC particle size in this size range had not been quantified. The objective of this study was to investigate the effects of PAC size on removal of NOM by batch adsorption. We found that PAC micro-ground to micrometre sizes had increased adsorption capacity for NOM and also improved adsorption kinetics.
Materials and methods

Adsorbents and coagulant
Thermally activated wood-based PAC (Taikou-W, Futamura Chemical Industries Co., Ltd., Gifu, Japan) was used. Micrometre-sized PACs were obtained by grinding the PAC in a novel mill which is currently under development (NGK Insulators, Ltd.). To determine the effects of PAC size and the effectiveness of micrometre-sized PAC in adsorption experiments, we used both the ground PACs and the as-received PACs. All carbon powders were dried in an oven at 105°C and stored in a desiccator before use. The size distributions of the PACs (Figure 1) were determined with laser light-scattering instruments (LMS-30, Seishin Enterprise Co. Ltd. and Microtrac HRA, Nikkiso Co. Ltd., Tokyo, Japan). Pore-size distributions of the PACs were determined by the Dollimore method from nitrogen desorption data (Proserp VAS-3000, Seishin Enterprise Co. Ltd.). Poly-aluminum chloride (PACl, 10% Al₂O₃, 62.5% basicity, Sumitomo Chemical Co. Ltd., Tokyo) was used for coagulation treatment. The coagulant was diluted before use so as to add a fixed quantity to each experimental mixture.

Water samples
Water samples from Takkobu Lake, Hokkaido, Japan, and from Kiso River, Aichi, Japan, were used as source waters containing NOM. The water samples were collected and transported in polyethylene tanks, and stored at 4°C until use in experiments; we refer to the samples as Takkobu water 1, Takkobu water 2, Kiso water 1, and Kiso water 2 according to the sampling date and storage period. Total organic carbon (TOC) and ultraviolet absorbance at 260 nm (UV₂₆₀) were used to quantify bulk NOM concentration (TOC measurement: Model 810, Sievers Instruments, Inc., Boulder, CO, USA; UV₂₆₀ absorption: Model UV-160A, Shimadzu Co., Kyoto, Japan). The molecular weight (MW) distributions of NOM in the sample waters were determined by high-performance size-exclusion chromatography [L7110 (Hitachi, Ltd., Tokyo, Japan); packed column: GL-P252 (Hitachi, Ltd.); eluent: 0.02 mol L⁻¹ Na₂HPO₄ + 0.02 mol L⁻¹ KH₂PO₄]. PSS (MW 1800, 4600, and 6500) was used for calibration. UV absorbance at 260 nm (L4000, Hitachi, Ltd.) and TOC (Model Turbo, Sievers Instruments, Inc.) of the column effluent were measured continuously. Phenol (Wako Pure Chemical Industries, Ltd., Osaka, Japan) and sodium polystyrene sulfonate (PSS) of molecular weight 1,800 (Polysciences Inc., Warrington, PA, USA) were used for comparing equilibrium adsorption capacities of the PACs. These com-

![Figure 1](https://iwaponline.com/ws/article-pdf/4/4/155/417496/155.pdf)
pounds were dissolved in ultrapure water (Milli-Q Gradient A10 System, Millipore Co., Bedford, MA, USA) and the pH was adjusted to 7.0 ± 0.1 with HCl or NaOH.

**Batch adsorption and coagulation tests**

Batch tests were conducted to analyze NOM removal by the different PACs and coagulation treatment. After addition of a certain amount of PAC to a 500-mL water sample and mixing for 1 or 10 min, coagulant was added, mixed rapidly for 2.5 min, and then mixed slowly for 2.5 min. Samples were withdrawn before and after addition of the coagulant and were filtered immediately through a 0.45-µm membrane filter for analysis of the NOM concentration in the liquid phase.

**Equilibrium and kinetic adsorption tests**

Batch kinetic tests were conducted with efficient mixing. Before the addition of PAC to a beaker containing 1 or 2 L of water sample containing NOM, samples were withdrawn to determine the initial NOM concentration. After addition of a certain amount of PAC, samples were withdrawn at intervals and filtered immediately through a 0.45-µm membrane filter for analysis of NOM concentration. The bottle-point technique was used to determine adsorption isotherms of NOM, phenol, and PSS. Sample waters (100 mL) containing PAC were withdrawn from the beaker used for the kinetic tests and transferred to 125-mL vials. The vials were agitated on a shaker for 1 to 3 weeks. Blanks were included to determine the initial concentration. The liquid-phase concentrations were measured every few days or weekly by filtering the water samples through a 0.45-µm membrane filter, until attainment of adsorption equilibrium was confirmed. The amount of NOM, phenol, or PSS adsorbed per unit mass of PAC (solid-phase concentration) was determined according to the mass balance equation: \( q \cdot C_c = C_0 - C \), where \( q \) and \( C \) are the solid-phase and liquid-phase concentrations in equilibrium, respectively, \( C_0 \) is the initial liquid-phase concentration, and \( C_c \) is the adsorbent concentration.

**Results and discussion**

Figure 2 shows the results of a batch adsorption–coagulation experiment in which NOM concentrations in terms of UV absorbance (260 nm) and TOC are plotted as a function of PAC dose. As expected, micrometre-sized PACs removed more NOM than equal doses of as-received PAC. Use of micrometre-sized PAC enabled a large reduction in the dosage: nearly identical removal percentages were attained with 4 mg L\(^{-1}\) of 0.8-µm PAC, 8 mg L\(^{-1}\) of 3.8-µm PAC, and 40 mg L\(^{-1}\) of 33-µm PAC. The effect of PAC size on adsorptive removal of NOM can be explained in two ways: adsorption kinetics and equilibrium. The usual explanation for size effects during adsorption is that, with a smaller porous adsorbent,
(i) the diffusion pathway from the external surface of the particle to its inside is shorter and (ii) the external particle surface area per gram of adsorbent is higher, both of which enhance adsorption rate. Figure 3 shows the fractional approach, \((C_0 - C)/(C_0 - C_\infty)\), of NOM adsorption by PAC to equilibrium, where \(C\) is the concentration of NOM, \(C_0\) is the initial concentration, and \(C_\infty\) is the equilibrium concentration. The 0.8-\(\mu\)m PAC reached 80% (by UV\(_{260}\)) and 60% (by TOC) of equilibrium at 1 min of contact time. In contrast, the 33-\(\mu\)m PAC reached only 35% (by UV\(_{260}\)) and 28% (by TOC) at 60 min. These results confirmed that micro-grinding of PAC drastically enhanced the adsorption rate and that a contact time of only 1 min is enough for adsorptive removal of NOM from water samples.

Equilibrium adsorption tests also revealed that the adsorption capacity of PAC depends on its particle size. Figure 4 shows adsorption isotherms of NOM. In the high liquid-phase concentration range, the adsorption capacity of 0.8-\(\mu\)m PAC was higher than that of 33-\(\mu\)m PAC, indicating that micro-grinding increased the adsorption capacity of PAC for NOM. Weber et al. (1983) have also conducted isotherm experiments to see the particle size effect of granular activated carbon (GAC) on NOM adsorption capacity and reported that smaller particles have greater capacity for adsorbing NOM. In their experiments, however, the adsorption might not reach or closely approach true equilibrium, since large GACs with 100/200, 40/60, and 20/25 US sieve sizes (150/75 \(\mu\)m, 425/250 \(\mu\)m, and 850/710 \(\mu\)m) were used, and adsorption isotherms were obtained after short contact time of 2 weeks when considering the GAC size. Nonetheless, the observed large capacity difference seemed to be due to a true capacity difference. Our adsorption tests used PACs much smaller than GACs, and the achievement of adsorption equilibrium was confirmed by 3 weeks of agitation.

![Figure 3](image1.png)  
**Figure 3** Batch kinetic tests of Takkobu water 1: in \((C_0 - C)/(C_0 - C_\infty)\), \(C\) is the NOM concentration, \(C_0\) is initial concentration, \(C_\infty\) is equilibrium concentration. PAC dose was 2 mg L\(^{-1}\)

![Figure 4](image2.png)  
**Figure 4** Adsorption isotherms of NOM by UV\(_{260}\) (Left) and TOC (Right) in Takkobu water 1
Therefore, the observed difference in adsorption capacity between the PACs with different sizes should reflect true differences in capacity for different particle sizes.

Other researchers have reported that the adsorptive capacity of activated carbon for low-MW pure chemicals is not affected by grinding or by the carbon particle size (Derick and Beckmann, 1969; Letterman et al., 1974; Peel and Benedek, 1980; Najim et al., 1990). Therefore we also investigated the effect of carbon particle size on its equilibrium adsorption capacity for pure chemicals of known MW: PSS, MW 1800 (PSS-1.8k), and phenol, MW 94. The results confirmed that the adsorption capacity for the smaller molecule, phenol, did not change, or even became slightly lower after PAC particle size was reduced (Figure 5). Adsorption of the larger molecule, PSS-1.8k, however, was clearly higher for PACs of smaller sizes (Figure 6).

The MWs of the NOM in the sample waters ranged from 1,400 to 3,500 (Figure 7). Applying the relationship between hydrodynamic size and MW for humic substances

![Figure 5](image_url) Adsorption isotherm of phenol

![Figure 6](image_url) Adsorption isotherm of PSS-1.8k

![Figure 7](image_url) Molecular weight distribution of NOMs in the sample waters
(Buffle, 1988), we estimated the radius of NOM with MWs of 1,400–3,500 to be about 1.0–1.6 nm. Assuming that the adsorbable pore size is 1.5 times the hydrodynamic size (Summers and Roberts, 1988), the adsorbable pore radius of our NOMs was 1.5–2.4 nm. This estimate for the adsorbable pore sizes of the NOMs is in agreement with other findings (Lee et al., 1981; Pelekani and Snoeyink, 1999). By applying the same estimation approach to PSS-1.8k (since the coiled configuration and diffusion characteristics of PSS are similar to those of NOM; Beckett et al., 1987), we estimated that the adsorbable pore radius of PSS-1.8k was 1.7 nm; however, the true size of PSS-1.8k in our test solutions may be greater than this value, because the low ionic strength of the solution would unravel the coiled configuration of the PSS molecule, making it bulkier.

We compared the pore-size distributions in the micro-ground and as-received PACs (Figure 8). The micro-ground PAC showed a larger surface area than the as-received PAC for pore sizes >1.5 nm in radius. Since the hydrodynamic radii of NOM (1.5–2.4 nm) and PSS–1.8k (≥1.7 nm) are in this range, these molecules can access these pores in the PAC and be adsorbed. The lack of a PAC size effect on phenol adsorption (Figure 5) can be attributed to the adsorbable pore radius of the phenol molecule being 0.5 nm and to our finding that no substantial difference between the micro-ground and the as-received PACs in total surface area was found for pore sizes >0.7 nm (Figure 6). These data clearly indicate that micro-ground PAC particles expose new areas of the mesopore surface not previously accessible to PSS-1.8k and NOM molecules, as noted previously (Randtke and Snoeyink, 1983).

Among several mechanisms suggested for the increase in accessible pores as a result of grinding (Weber et al., 1983), the fracture of ink-bottle-type constrictions is worth considering. Not all mesopores are accessible to large adsorbate molecules, because of ink-bottle constrictions in the internal pores of adsorbents. We produced micrometre-sized PACs by grinding as-received PACs, so fractures could have occurred at constricted pathways so as to open the way to interior pores, making them accessible to large adsorbate molecules. The pore-size distributions shown in Figure 8 were obtained from nitrogen desorption data; therefore, if ink-bottle constrictions were present in the adsorbent, the size of the interior pores that are on the other side of the constriction would falsely be regarded as the size of the constriction (Adamson, 1990). After some ink-bottle structures are fractured, such interior pores are determined as being larger than before fracturing, which, in effect, increases the total surface area of larger pores. Considering that pores having a 10–20-nm radius showed the greatest increase in surface area after micro-grinding (Figure 8), it is not improbable that micro-grinding PAC to the level of 500 nm radius could alter pore structures in this size range.

![Figure 8](https://iwaponline.com/ws/article-pdf/4/4/155/417496/155.pdf)
Other characteristics seen in Figure 4 are that, in the low liquid-phase concentration range, the adsorption capacity of 0.8-µm PAC was lower than that of 33-µm PAC, and the slope of the log–log plot is steeper for 0.8-µm PAC. A possible reason for the lower adsorption capacity of the 0.8-µm PAC could be the heterogeneity of the NOMs in our samples, namely, that a fraction of NOM is more weakly adsorbable to the 0.8-µm PAC than the other NOM. Figure 9 shows the change in specific UV absorbance (SUVA, UV260/TOC) of NOM adsorbed to the PAC vs. amount of PAC added. The SUVA of the NOM adsorbed to 33-µm PAC was closer to the SUVA of raw water than was the SUVA of NOM adsorbed to 0.8-µm PAC. In addition, the SUVA value of NOM adsorbed to 0.8-µm PAC decreased with increasing PAC dosage. These findings indicate that 0.8-µm PAC preferentially adsorbs NOMs having high UV absorbance and suggest that the NOM in our samples was a heterogeneous population in terms of adsorption to 0.8-µm PAC. If so, characteristics of a multicomponent isotherm should be seen for adsorption of NOM by the 0.8-µm PAC.

One characteristic and diagnostic feature of a multicomponent isotherm is a dependency of the isotherm on the initial adsorbate concentration (Sontheimer et al., 1988; Matsui et al., 1998). For the as-received PAC (33-µm PAC), we did not find evidence for an initial concentration dependency in Figure 10. For the micro-ground PAC (3.8-µm PAC), however, the isotherm at a higher initial NOM concentration (UV = 0.02 cm⁻¹) may differ from
that at a lower initial NOM concentration ($\text{UV} = 0.01 \text{ cm}^{-1}$) (Figure 10). This observation of the initial concentration dependency of the isotherm also supports the above-mentioned interpretation that NOM in our samples is heterogeneous with respect to adsorption to 0.8-µm PAC. The results in Figure 9 also suggest that micro-grinding of PAC would not be effective for enhancing adsorption of NOM composed mainly of substances with low $\text{UV}_{260}$ absorbance. In fact, little if any effect of PAC size on NOM adsorption was seen for a water sample with low SUVA (Figure 11).

**Conclusions**

Micro-grinding of as-received PAC to form micrometre-sized PAC particles enhanced its ability to adsorb NOM with high $\text{UV}_{260}$ absorbance, owing to changes in both capacity and kinetics. Micrometre-sized PAC (0.8 µm) at a dosage of 4 mg L$^{-1}$ showed the same NOM removal as the as-received PAC (33 µm) at ten times the dosage. Because of the increase in outer surface area and the decrease in PAC particle radius, the micrometre-sized PAC reached 80% of adsorption equilibrium within only 1 min of contact time. An increase in adsorption capacity was observed for NOM and PSS-1.8k (large molecules) but not for phenol (small molecule). The pore-size distribution data explained the adsorption capacity increase well. The results obtained in this research suggest that use of micrometre-sized PAC in water treatment should permit not only lower PAC dosages but also shorter PAC contact times, which are especially important for its use as a pretreatment before membrane filtration.

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**References**


