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Author(s)	Pan, Long; Matsui, Yoshihiko; Matsushita, Taku; Shirasaki, Nobutaka
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1 Superiority of wet-milled over dry-milled superfine powdered activated carbon
2 for adsorptive 2-methylisoborneol removal

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5 Long Pan ^a, Yoshihiko Matsui ^{b*}, Taku Matsushita ^b, Nobutaka Shirasaki ^b

6
7 ^a Graduate School of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan

8 ^b Faculty of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan

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10 * Corresponding author.

11 E-mail address: matsui@eng.hokudai.ac.jp

Abstract

Superfine powdered activated carbon (SPAC), which is produced from conventionally sized powdered activated carbon (PAC) by wet milling in a bead mill, has attracted attention for its high adsorptive removal ability in both research and practice. In this study, the performance of dry-milled SPAC was investigated. 2-Methylisoborneol (MIB), an earthy-musty compound commonly targeted by water treatment systems, was used as the target adsorbate. Dry-milled SPAC exhibited lower adsorptive removal of MIB than wet-milled SPAC, even when both SPACs were produced from the same PAC and were composed of particles of the same size. One reason for the lower removal of MIB by the dry-milled SPAC was a higher degree of aggregation in the dry-milled SPAC after production; as a result the apparent particle size of dry-milled SPAC was larger than that of wet-milled SPAC. The dry-milled SPAC was also more negatively charged than the wet-milled SPAC, and, owing to its higher repulsion, it was more amenable to dispersion by ultrasonication. However, even after the dry-milled SPAC was ultrasonicated so that its apparent particle size was similar to or less than that of the wet-milled SPAC, the dry-milled SPAC was still inferior in adsorptive removal to the wet-milled SPAC. Therefore, another reason for the lower adsorptive removal of dry-milled SPAC was its lower equilibrium adsorption capacity due to the oxidation during the milling. The adsorption kinetics by SPACs with different degrees of particle aggregation were successfully simulated by a pore diffusion model and a fractal aggregation model.

1. Introduction

Powdered activated carbon (PAC) is used widely in water treatment processes because of its ability to remove dissolved pollutants that cannot be removed by the conventional process of coagulation, sedimentation, and sand filtration (Cook et al. 2001, Li et al. 2003, Matsui et al. 2003, Shi et al. 2014). Recently, activated carbon with a much finer particle size than PAC (superfine powdered activated carbon, SPAC) has been intensively investigated, and SPAC is already being used in some water treatment plants (Bonvin et al. 2016, Ellerie et al. 2013, Heijman et al. 2009, Jiang et al. 2015, Matsui et al. 2007, Wang et al. 2011). Compared with PAC, which is composed of particles with diameters of tens of micrometers, SPAC, which consists of particles with diameters of no more than a few micrometers, has advantages with regard to both adsorption capacity and kinetics because of both its larger specific external surface area per unit of mass and the shortened diffusion distance within each carbon particle (Ando et al. 2010, Matsui et al. 2009, Matsui et al. 2015, Matsui et al. 2013, Sontheimer et al. 1988).

In all scientific studies and actual field applications to date, wet-milling systems have been used to produce SPAC. In wet-milling systems, the PAC is suspended in carrier water to make a slurry, and then the slurry is introduced into a bead mill to produce SPAC (Partlan et al. 2016). However, the production efficiency of such small-sized particles by this wet-milling system is limited because the viscosity of the carrier fluid, and thus the slurry concentration, must be low (Knieke et al. 2010, Schmidt et al. 2012). The low concentration of the slurry also increases the bulk volume of the SPAC and thus the cost of its transport after production. Even if SPAC is produced onsite in water treatment plants, the SPAC slurry has a large storage footprint.

In addition to wet-milling systems, dry-milling systems have recently become available that can successfully produce submicrometer-sized particles of various materials, such as intermetallics

(Suryanarayana 2001), boron (Jung et al. 2015), and boron carbides (Ramos et al. 2006). Unlike wet-milling systems, dry-milling systems utilize gas or steam, rather than a liquid, as the carrier of the particles during comminution by the milling medium. Compared with wet milling, dry milling mitigates the high production volume problem, reducing both the size of the storage footprint and the transport volume. In addition to these advantages, the dry-milling process can reduce the size of the milled particles at a higher rate and the particles may be less likely to become contaminated by milling medium residues, compared with the wet-milling process (Jung et al. 2015).

Despite these merits of dry milling compared with wet milling for the production of fine milled particles, adsorption by dry-milled SPAC has not yet been investigated. Therefore, in this study, the adsorption performance of dry-milled SPAC was compared with that of wet-milled SPAC. To evaluate the adsorption ability of the SPACs, we chose 2-methylisoborneol (MIB) as a representative target compound for adsorptive removal. MIB, which is produced by the metabolism and biodegradation of actinomycetes and cyanobacteria (Watson et al. 2000, Westerhoff et al. 2005), is extremely refractory to removal by conventional water treatment processes (Srinivasan and Sorial 2011), and it is a conventional target compound of activated carbon adsorption processes during water treatment (Cook et al. 2001, Gillogly et al. 1998, Matsui et al. 2008, Matsui et al. 2013, Newcombe et al. 1997, Newcombe et al. 2002, Pendleton et al. 1997). The results of the comparison showed that the adsorption performance of the dry-milled SPAC was inferior to that of the wet-milled SPAC, so we further investigated the reasons for the different performances.

2. Materials and methods

2.1. Adsorbents

Two commercial wood-based PACs were obtained and designated PAC-S (Shirasagi, Osaka Gas Chemical Co., Osaka, Japan) and PAC-F (Futamura Chemical Co., Tokyo, Japan). Dry-milled SPACs for use in the experiments were produced by milling each PAC to the target size in a dry-milling system (SDA5, Ashizawa Finetech Ltd., Chiba, Japan; bead diameter, 1.5 mm; carrier, air), and wet-milled SPACs were separately produced in a wet-milling system (LMZ015, Ashizawa Finetech Ltd., Chiba, Japan; bead diameter, 0.1 mm; carrier, pure water). All activated carbons, including non-milled PACs, wet-milled SPACs, and dry-milled SPACs, were stored in a slurry (1%–5% w/v) made with pure water at 4 °C after vacuum conditioning to remove any air from the activated carbon pores. Aliquots of the dry-milled SPAC slurry were ultrasonicated (150 W, 19.5 kHz, 1 min for 50 mL carbon slurry) for dispersion. The SPACs were labeled according to the milling process used and the PAC (-S or -F) from which they were produced; for example, SPAC-S-D was produced by dry milling from PAC-S, and ultrasonicated dry-milled SPAC that was produced from SPAC-S-D was designated SPAC-S-DS (Table 1).

Particle size distributions of the SPACs and PACs were determined by using a laser-light scattering instrument (Microtrac MT3300EXII, Nikkiso Co., Tokyo, Japan). To measure the true particle size of the carbon samples, the samples were taken from the stock slurries and then pretreated by the addition of a dispersant (Triton X-100, Kanto Chemical Co., Tokyo, Japan; final concentration, 0.08% w/v) and subsequent ultrasonic dispersion before measurement with the Microtrac instrument. The apparent particle sizes were measured without this pretreatment. Elemental analysis to determine the oxygen content was performed on the SPACs by using an elemental analyzer (Vario EL Cube, Elementar Japan K.K., Yokohama, Japan) equipped with thermal conductivity and infrared detectors.

2.2. Adsorbate and working solutions

A stock solution of MIB (~900 µg/L) was prepared by dissolving pure MIB (Wako Pure Chemical Industries, Ltd., Osaka, Japan) in ultrapure water and then filtering the solution through a 0.2-µm pore size membrane filter (DISMIC-25HP; Toyo Roshi Kaisha, Ltd., Tokyo, Japan). Organic-free water was spiked with the MIB stock solution to obtain working solutions with MIB concentrations of around 1 and 4 µg/L, because MIB usually occurs naturally at concentrations lower than these concentrations. The working solutions were adjusted to pH 7.0 ± 0.1 with HCl or NaOH as required. The MIB concentration was detected by using deuterium-labeled geosmin (Wako Pure Chemical Industries, Ltd., Osaka, Japan) as an internal standard in a purge and trap concentrator (Aqua PT 5000 J; GL Sciences, Inc., Tokyo, Japan) coupled to a gas chromatograph–mass spectrometer (GCMS-QP2010 Plus; Shimadzu Co., Kyoto, Japan), where the m/z 95 and m/z 115 peaks were interpreted as corresponding to MIB and deuterium-labeled geosmin, respectively.

2.3. Batch adsorption tests

The adsorption kinetics was investigated by means of batch tests with efficient mixing. A working solution of water and MIB was placed in a beaker (1 L or 3 L). After the addition of a specified amount of SPAC or PAC slurry, aliquots were withdrawn at intervals and filtered immediately through 0.2-µm membrane filters (DISMIC-25HP, Toyo Roshi Kaisha, Tokyo, Japan) for analysis of the MIB concentration.

For the adsorption equilibrium tests, aliquots (110 mL) of the working solutions (hereafter, water samples) containing MIB (1 ± 0.2 µg/L) were transferred to 120-mL vials. Specified amounts of SPAC or PAC were immediately added (0.3–1.8 mg/L), and the vials were manually shaken and then agitated on a mechanical shaker for 1 week at a constant temperature of 20 °C. Preliminary experiments confirmed that the adsorption equilibrium of MIB was reached after 1 week of contact

(Matsui et al. 2013, Matsui et al. 2012). Control tests of water samples that did not contain carbon (i.e., blanks) were also conducted to confirm that changes in the blank MIB concentration during long-term mixing were negligible. After 1 week of shaking, the water samples were filtered through 0.2- μm pore size membrane filters, and then MIB concentrations in the aqueous phase were measured. Solid-phase concentrations of MIB were calculated from the mass balance.

2.4. Pore diffusion model for the batch adsorption process

These experimental data of adsorption kinetics were simulated with a pore diffusion model (PDM, see SI) that was modified to incorporate adsorbent particle aggregation. In the model, each adsorbent particle aggregate is treated as a single adsorbent unit; thus, for simplicity, diffusion in interparticle pores between the adsorbent particles composing the aggregate and diffusion in the pores of the individual adsorbent particles are merged. Although the shell adsorption model is used to simulate the different isotherms of PAC and wet-milled SPAC (Matsui et al. 2013, Matsui et al. 2014), it is not yet possible to use this model to simulate the different isotherms of wet-milled and dry-milled SPACs, which have a similar particle size. Therefore, because of its wide application and simplicity, we decided to use the Freundlich model.

The apparent density (ρ) and porosity (ε) of an aggregate in PDM equation can be estimated by using fractal theory (Elimelech et al. 2013) as follows:

$$\frac{\rho}{\rho_p} = \frac{1 - \varepsilon}{1 - \varepsilon_p} = \left(\frac{d_p}{d}\right)^{3-\beta} \quad (1)$$

where ρ is the apparent density of an aggregate (g/L), ρ_p is the apparent density of the adsorbent particles composing the aggregate (g/L), ε_p is the porosity of the adsorbent particles composing the aggregate (cm), ε is the porosity of the aggregate (cm), d_p is the diameter of the adsorbent particles

composing the aggregate (cm), d is the diameter of the aggregate (cm), and β is the fractal dimension (dimensionless).

3. Results and discussion

3.1. Comparison of MIB removal between wet-milled and dry-milled SPAC

Wet-milled and dry-milled SPACs were intentionally produced with similar true particle size distributions (Supplementary Information, SI; Fig. 1S). For example, the median true diameter (D_{50}) of SPAC-S-D was 1.24 μm , whereas that of SPAC-S-W was 1.28 μm (Table 1). However, the MIB adsorption kinetics of SPAC-S-D and SPAC-S-W differed (Fig. 1); the MIB removal rate of SPAC-S-D was obviously lower than that of SPAC-S-W. Wet milling of PAC-S improved MIB removal (Fig. 1, SPAC-S-W vs. PAC-S), consistent with results reported previously (Matsui et al. 2009, Matsui et al. 2013), whereas dry milling did not result in any improvement in MIB removal (SPAC-S-D vs. PAC-S). Compared to the MIB removal rate of PAC-F, the rates of both SPAC-F-D and SPAC-F-W were higher. However, the adsorption kinetics of SPAC-F-D was inferior to that of SPAC-F-W, despite their similar true particle size distributions (Table 1).

3.2. Comparison of particle sizes between wet-milled and dry-milled SPACs

According to the theory of adsorption kinetics, the adsorptive removal by carbon particles is enhanced by a reduction of the carbon particle size because (1) the specific outer surface area of the particles is increased, leading to a higher rate of adsorbate uptake from the bulk phase into pores; and (2) the internal radial diffusion distance within a carbon particle is shortened, thus increasing the mass flux

rate. Therefore, to identify the reasons for the different MIB removal rates by wet-milled and dry-milled SPACs, we focused on the carbon particle size.

The results presented in section 3.1 are those based on the true carbon particle diameters of each SPAC, determined after the addition of dispersant and ultrasonication. However, carbon particles in a suspension may exist as aggregates rather than as discrete particles (Bonvin et al. 2016). Thus, although the wet-milled and dry-milled SPACs had the same true particle size distribution, the apparent particle size distributions in the suspensions used for the experiments were not necessarily the same because the degree of aggregation might have differed between wet- and dry-milled SPACs.

Research on SPAC adsorption in membrane filtration systems has reported aggregated forms of SPAC on the membrane surface (Ellerie et al. 2013). During our adsorption kinetics experiments, however, direct observation of the particles in the suspension for particle size measurement was not possible because of the very low carbon concentration, the small particle sizes, and the high-speed movement of the particles in the stirred vessel. Therefore, we used non-pretreated samples to evaluate apparent SPAC particle diameters. In addition, the sonicator attached to the Microtrac instrument was switched off during the measurements. To minimize as much as possible any flow or mixing effect from the instrument on the particle size measurement, each measurement was conducted soon after signal stabilization, which took place around 30 to 40 s after the carbon sample was transferred from the stock bottle to the instrument. The resulting apparent particle diameter distributions (Fig. 2) clearly revealed the presence of aggregates in the SPAC slurry. The extent of aggregation differed between dry- and wet-milled SPACs; SPAC-S-D and SPAC-F-D were aggregated to a higher degree than SPAC-S-W and SPAC-F-W.

Moreover, the apparent particle size distribution of the dry-milled carbons did not change in relation to the mixing time during the adsorption experiment (SI, Fig. 2S). Although the same mixing

conditions were used as in the adsorption tests, the carbon concentration of the suspension used for the particle size measurement was 30 times the concentration used in the absorption experiment because of the detection limit of the Microtrac instrument. Higher concentrations of particles lead to more frequent particle–particle collisions, and the collision frequency determines the aggregation rate (Baalousha 2009, Christian et al. 2008, Phenrat et al. 2007). Therefore, the fact that the particle size distribution was not changed by the mixing even at the higher concentration suggests that during the adsorption experiments the apparent carbon particle size probably remained unchanged by the mixing as well.

The mass transfer process in activated carbon adsorption involves of two general mechanisms: (i) external mass transfer across the liquid film surrounding the carbon particle, and (ii) radial intraparticle diffusion through pores (Sontheimer et al. 1988). When carbon particles are aggregated, the interparticle spaces act as pseudopores through which molecules must diffuse to reach the external surfaces of the individual particles. Thus, when the particles are aggregated, the total diffusive pass length is lengthened and the available external surface area and number of particles are both smaller, all of which reduce the adsorption rate. Therefore, the slower MIB removal rate by the dry-milled SPAC compared with that by the wet-milled SPAC should be related to the different degree of aggregation between the SPACs.

3.3. Verifying the reasons for lower MIB removal by dry-milled SPAC

To verify the effects of aggregation on the adsorption kinetics, the dry-milled carbons were ultrasonicated to disaggregate them and decrease their apparent particle size. The apparent particle size of the ultrasonicated dry-milled SPACs (SPAC-S-DS and SPAC-F-DS) became smaller; in fact, the apparent particle sizes of SPAC-S-DS and SPAC-F-DS were even smaller than those of the wet-

milled carbons SPAC-S-W and SPAC-F-W (Fig. 3). SPAC-S-DS and SPAC-F-DS showed higher MIB removal rates than SPAC-S-D and SPAC-F-D, respectively (Fig. 4). The adsorption kinetics of the dry-milled SPACs was thus clearly improved after they were pretreated by ultrasonication. Therefore, aggregation can explain in part the low MIB removal rates of the (non-sonicated) dry-milled SPACs.

However, the MIB removal attained by the ultrasonicated dry-milled SPACs was still lower than the removal attained by the corresponding wet-milled SPACs, even though the ultrasonicated dry-milled SPACs were less aggregated and their true particle size distributions were similar to those of the wet-milled SPACs. The difference in MIB removal between the ultrasonicated dry-milled SPACs and the wet-milled SPACs suggests that there is another reason, in addition to aggregation, for the lower MIB removal ability of the dry-milled SPACs.

In addition to adsorption kinetics, adsorption capacity affects adsorptive removal. Therefore, we examined the MIB adsorption isotherms of the carbons (Fig. 5). SPAC-S-W and SPAC-F-W both had higher capacities than their parent carbons (PAC-S and PAC-F, respectively). This result is in agreement with previous findings that adsorption capacity is increased when the carbon particle diameter is decreased from a few tens of micrometers to a few micrometers (Ando et al. 2010, Ando et al. 2011, Matsui et al. 2012). Dry milling, however, did not increase the adsorption capacity: the adsorption capacities of SPAC-S-D and SPAC-F-D were nearly the same as those of their parent carbons (PAC-S and PAC-F, respectively). The contact time between the carbon and water was sufficient for even the PACs to reach adsorption equilibrium; therefore, the adsorption capacities of the dry-milled SPACs were not influenced by particle aggregation. Dunn and Knappe (2013) have suggested that interparticle pseudopores formed as a result of SPAC particle aggregation might act as additional mesopores and thus increase the adsorption capacity relative to that of the corresponding

PAC. However, we observed an opposite effect: the dry-milled SPACs, which were more severely aggregated, had lower adsorption capacities than the wet-milled SPACs.

Previous investigations of PACs before and after wet milling have reported that the change in the carbon particle size caused by wet milling does not result in any substantial change in the internal pore area (Ando et al. 2010, Matsui et al. 2014). Therefore, the dependency of the adsorption capacity on the carbon particle size is not related to the internal pore area. In the present study, the internal pore area, which was measured as the Brunauer-Emmett-Teller (BET) surface area, could not explain the adsorption capacity differences: SPAC-S-W and SPAC-F-W both had higher capacities than their parent carbons, even when the solid-phase concentrations in the isotherms were normalized by the BET surface area (i.e., the mass of adsorbed MIB was divided by the BET surface area; SI, Fig. 3S).

The increased adsorption capacity of smaller sized carbon particles can be explained by the shell adsorption model. According to this model, the adsorbate molecule penetrates the carbon particles only a certain distance (Matsui et al. 2011). If the carbon particle radius is substantially larger than this penetration distance, adsorption sites in the interior region of the carbon particle are not utilized (Matsui et al. 2015). As a result, the equilibrium adsorption capacity increases as the carbon particle size decreases until the particle radius becomes much smaller than the penetration distance. Once the particle radius is much smaller than the adsorbate penetration distance, as in the case of the SPACs, the adsorption capacity becomes independent of particle size and is then mainly determined by the pore surface chemistry (Li et al. 2002, Matsui et al. 2015, Quinlivan et al. 2005). Therefore, the different adsorption capacities of the wet-milled and dry-milled SPACs might reflect differences in the chemical characteristics of the pore surfaces due to the different milling methods. One possible cause of different pore surface chemical characteristics might be oxidation during milling, which would cause the carbon to become more hydrophilic (Partlan et al. 2016); the carbon became oxidized during dry milling. In fact, the dry-milled SPACs had a higher oxygen content than the wet-milled

SPACs (SPAC-S-D: $10.17\% \pm 0.36\%$ vs. SPAC-S-W: $6.29\% \pm 0.18\%$; SPAC-F-D: $6.37\% \pm 0.27\%$ vs. SPAC-F-W: $4.35\% \pm 0.16\%$), indicating that the dry-milled SPACs probably had more oxygen-containing functional groups and were thus more hydrophilic. These characteristics would cause the adsorption capacity of the dry-milled SPACs to be lower than that of the wet-milled SPACs.

3.4. Quantifying the impacts of aggregation and adsorption capacity on adsorptive MIB removal

3.4.1. Model simulations describing experimental data

To evaluate separately and quantitatively the impacts of adsorption capacity and particle aggregation on adsorption kinetics, we conducted PDM simulations. The PDM parameter values were determined for each carbon by independent experiments (SI, Table 1S). The unknown model parameters were the pore diffusion coefficient (D_p) and the fractal dimension (β). We searched for a single set of values for these unknowns that best described all the experimental adsorption kinetics data of the four differently sized carbons (PAC and SPACs). Because markedly different adsorption kinetics were exhibited by PAC-S and the SPACs produced from it (see Figs. 1 and 4), we focused on this series of carbon samples. The final objective of the modeling was to evaluate quantitatively the effect of particle aggregation and adsorption capacity on adsorptive MIB removal for a given carbon–water contact time and carbon dosage. Therefore, we searched for a single set of model parameters, including the pore diffusion coefficient, that could successfully describe the experimentally determined adsorption kinetics of PAC-S, SPAC-S-W, SPAC-S-D, and SPAC-S-DS.

We found that a pore diffusion coefficient of 1.55×10^{-6} cm/s and a fractal dimension of 2.75 resulted in the best fit to the experimental data (Fig. 6 and SI Fig. 5S and Table 2S). The diffusivity of a MIB molecule in water, estimated by the Hayduk–Laudie correlation method (Lyman et al. 1990), was 5.39×10^{-6} cm/s (see SI). By applying equation (3) (Sontheimer et al. 1988), therefore, the tortuosity

was calculated to be 3.5 from the pore diffusion coefficient (1.55×10^{-6} cm/s) and the diffusivity. This value is plausible for tortuosity in activated carbon (Sontheimer et al. 1988).

$$D_p = \frac{D_M}{\chi} \quad (3)$$

where D_M is diffusivity in water (cm²/s) and χ is tortuosity (dimensionless).

The fractal dimension of aggregates should be between 1.5 and 3 (Avnir et al. 1984, Elimelech et al. 2013, Logan 1999). Therefore, the best-fit value of 2.75 is also reasonable and not inconsistent with the abovementioned range. The fractal dimension of 2.75 suggests tightly aggregated particles, which is consistent with observations (SI, Fig. 9S). Thus, the PDM modified to consider adsorbent aggregation by incorporating fractal theory successfully described the adsorption kinetics of SPACs with different degrees of aggregation.

3.4.2. Effects of adsorbent aggregation and adsorption capacity

To quantify separately the impacts of adsorbent aggregation and adsorption capacity on adsorption kinetics, we conducted a series of four model simulations (cases I–IV). As the point of departure, we used the case of MIB removal by the dry-milled carbon, SPAC-S-D, which had a low adsorption capacity and a large apparent carbon particle size owing to severe aggregation, compared with that of the wet-milled carbon SPAC-S-W. Model simulations were conducted in which the apparent particle size of SPAC-S-D (case I, median diameter, 14.2 μ m) was replaced with smaller sizes (case II, median diameter, 2.42 μ m; case III, median diameter, 1.24 μ m) to see how a particle size reduction due to disaggregation would enhance MIB removal. In addition, a simulation was conducted by replacing the SPAC-S-D isotherm with that of SPAC-S-W, which had a higher adsorption capacity (case IV). The particle size distribution of case II was based on the apparent size distribution of SPAC-S-D

(ultrasonicated carbon), and the distribution of case III was based on the apparent size distribution measured after both the addition of dispersant and ultrasonication (completely dispersed carbon). We then compared the simulated MIB removal rates among the cases (Fig. 7). Compared with case I, MIB removal was improved in case II, and further improved in case III, and these improvements were obtained within a short contact time. However, by about 30 min of contact time, the MIB removal curves of cases II and III merged. Therefore, even if the carbon particles are aggregated so that the apparent particle size is twice the true particle size, the effect of that aggregation on MIB removal is small after a contact time of 10 min or longer. Moreover, only a small effect of particle aggregation was seen in wet-milled carbon, SPAC-S-W, when moderately aggregated carbon particles (case V, apparent particle size 3 times that of case VI, the true size). The MIB removal of these two cases became similar after 30 min of carbon–water contact (SI, Fig. 6S). Therefore, when SPAC is used for water treatment, its particle size should be measured and its degree of aggregation should be determined. If, for example, the SPAC particles are aggregated such that the aggregate size is much more than twice the true particle size, disaggregation, for example by ultrasonication, should be considered as an easy way to improve the adsorptive removal performance.

In addition to carbon particle aggregation, the dry-milled SPAC (SPAC-S-D) had the disadvantage of low adsorption capacity. When the SPAC-S-D isotherm was replaced with the SPAC-S-W isotherm (case IV), MIB removal was further improved (Fig. 7). The improvement resulting from the increased adsorption capacity achieved by changing the isotherm was moderate compared with that achieved by disaggregation. However, the gap between the case III and case IV curves was almost constant, regardless of the contact time. Thus, an increase in adsorption capacity is necessary to improve MIB removal for carbon–water contact times longer than about 20 min.

3.5. Stability after disaggregation

As discussed in section 3.4.2, for more efficient MIB removal, the disaggregation of SPAC particles, for example by ultrasonication, is recommended. To investigate the effectiveness of disaggregation, we conducted an experiment to see how long a time the dispersed state of the ultrasonicated SPAC would be maintained and whether re-aggregation would occur after disaggregation by ultrasonication. The stocks of wet-milled and dry-milled SPAC were stored in a slurry after ultrasonication, and samples were withdrawn at intervals and their apparent size distributions were measured to determine whether the median diameters (D_{50}) of the ultrasonicated SPACs changed with storage time after ultrasonication (SI, Fig. 7S). The results showed little change in D_{50} after storage; thus, the ultrasonicated SPACs maintained their initial dispersed state. These results indicate that the aggregations of dry-milled and wet-milled SPAC is a temporary state that can be reversed by ultrasonication.

In addition, ultrasonication was more effective in dry-milled SPACs than in wet-milled SPACs. The apparent size of the dry-milled SPAC after ultrasonication (SPAC-F-DS) was smaller than that of the wet-milled SPAC after ultrasonication (SPAC-F-WS) (Table 1), even though (1) the true size distribution of the dry-milled SPAC was similar to that of the wet-milled SPAC and (2) the apparent size of the dry-milled SPAC was larger before ultrasonication. Therefore, the dry-milled SPAC may be more amenable to dispersion by ultrasonication, and its size may become closer to the true size after ultrasonication. The ratio of the median apparent size after ultrasonication to true size (Table 1) was smaller for SPAC-F-D than for SPAC-F-W, and the ratio was slightly smaller for SPAC-S-D than for SPAC-S-W. The zeta potential values, and thus the relative charge, of the dry-milled SPACs were lower than those of the wet-milled SPACs in suspensions with a wide range of pH values (SI, Fig. 8S). The more negative charge of the dry-milled SPACs compared with the wet-milled SPACs is in accordance with our finding that the dry-milled SPACs had a higher oxygen content, and thus

more negatively charged oxygen-containing functional groups, than the wet-milled SPACs. Thus, there may be stronger repulsion between dry-milled SPAC particles than between wet-milled SPAC particles, with the result that the dry-milled SPAC particles are more easily dispersed by ultrasonication. The higher degree of aggregation of the dry-milled SPAC compared with the wet-milled SPAC immediately after the milling might be related to the production conditions. Liquid bridge forces due to moisture in the air used as the carrier of the particles might have induced aggregation of the dry-milled SPACs. Also an interparticle force such as the van der Waals' force might also have acted as a bridge force. The aggregation of the dry-milled SPACs would be maintained in the absence of external dispersion forces such as ultrasonication.

4. Conclusions

(1) Dry-milled SPAC removes MIB at a lower rate than wet-milled SPAC. There are two reasons for this: compared with wet-milled SPAC, (i) dry-milled SPAC is more severely aggregated and (ii) its adsorption capacity is lower.

(2) Wet-milled SPAC is only moderately aggregated, so the effect of the aggregation on its adsorptive removal of MIB is small. Dry-milled SPAC is severely aggregated, and this aggregation lowers its adsorptive removal of MIB, in particular when the carbon–water contact time is short (< 20 min).

(3) Dry-milled SPAC is more easily disaggregated by ultrasonication than wet-milled SPAC, although it aggregates more severely after production. The high disaggregation tendency of dry-milled SPAC is due to the high negative surface charge of the carbon particles. SPACs do not become re-aggregated once after they are disaggregated.

(4) The low adsorption capacity of dry-milled SPAC compared with wet-milled SPAC is likely due to oxidation during milling.

(5) The pore diffusion model modified to consider adsorbent aggregation by incorporating fractal theory could successfully describe the adsorption kinetics of SPACs with different degrees of aggregation with a single set of parameter values.

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Figure 1. Adsorption kinetics of MIB by PACs and dry-milled and wet-milled SPACs (MIB initial concentration $C_0 = 1.25 \pm 0.15 \mu\text{g/L}$; carbon dosage, 3 mg/L, except 3.7 mg/L for SPAC-S-W. C = MIB concentration at each measurement time).

Figure 2. True and apparent SPAC size distributions

Figure 3. Apparent particle size distributions of the dry-milled SPACs, the ultrasonicated dry-milled SPACs, and the wet-milled SPACs

Figure 4. Adsorption kinetics of the dry-milled SPACs, the ultrasonicated dry-milled SPACs, and the wet-milled SPACs (MIB initial concentration, $1.25 \pm 0.15 \mu\text{g/L}$; carbon dosage, 3 mg/L, except 3.7 mg/L for SPAC-S-W)

Figure 5. Adsorption isotherms of the PACs, the wet-milled SPACs, and the dry-milled SPACs.

Figure 6. Simulated (lines) and experimentally observed (symbols) adsorption kinetics of PAC-S and the SPACs produced from it (MIB initial concentration, $1.25 \pm 0.15 \mu\text{g/L}$; carbon dosage, 3 mg/L, except 3.7 mg/L for SPAC-S-W).

	Aggregation degree	Median diameter (μm)	Adsorption isotherm
I	Original aggregation	14.24	SPAC-S-D
II	After ultrasonication	2.42	
III	Complete dispersion	1.24	
IV	Complete dispersion	1.24	SPAC-S-W

Figure 7. Model simulations of four cases of MIB removal by SPAC-S-D (MIB initial concentration, 1 $\mu\text{g/L}$; carbon dosage, 3 mg/L).

Table 1. SPACs and PACs classified by size and milling method

Designation	Original carbon	Production method	Median diameter D ₅₀ (μm)		Apparent size/ true size
			True size (measured after the addition of dispersant and ultrasonication)	Apparent size (measured with no pretreatment)	
PAC-S	PAC-S	Non-milled	11.8	13.8	1.17
SPAC-S-W		Wet milling	1.28	3.80	2.96
SPAC-S-WS		Wet milling followed by ultrasonication		2.61	2.03
SPAC-S-D		Dry milling	1.24	14.2	11.48
SPAC-S-DS		Dry milling followed by ultrasonication		2.42	1.95
PAC-F	PAC-F	Non-milled	27.5	36.5	1.33
SPAC-F-W		Wet milling	1.21	3.42	2.83
SPAC-F-WS		Wet milling followed by ultrasonication		2.41	2.00
SPAC-F-D		Dry milling	1.22	10.3	8.41
SPAC-F-DS		Dry milling followed by ultrasonication		1.99	1.63