



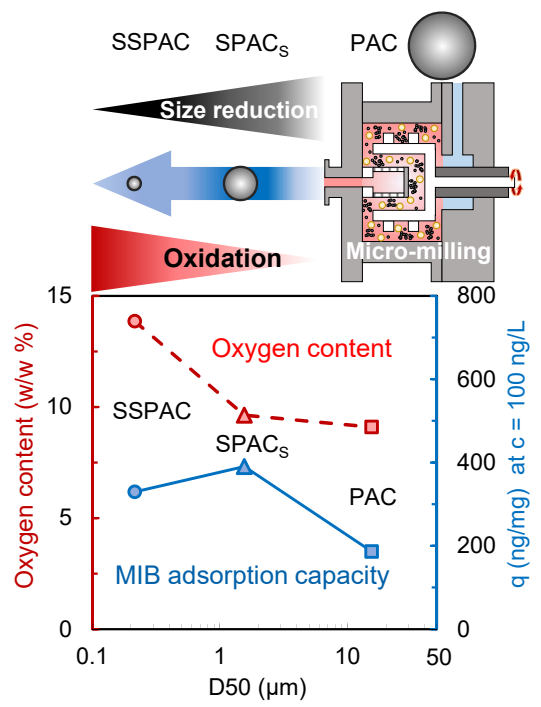
Title	Effects of decreasing activated carbon particle diameter from 30 μ m to 140 nm on equilibrium adsorption capacity
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Research Highlights

- Micromilling produced carbon particles with D50s as low as 140 nm.
- Adsorption capacity decreased as D50 decreased from a few micrometers to 140 nm.
- The adsorption capacity decrease was due to carbon oxidization during micromilling.
- Inhibition of carbon oxidation attenuated the decrease in adsorption capacity.
- Adsorption capacity was negatively correlated with particle oxygen content.



1 **Effects of Decreasing Activated Carbon Particle Diameter from 30 μm to 140 nm on**
2 **Equilibrium Adsorption Capacity**

3

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12

13 **Abstract**

14 The capacity of activated carbon particles with median diameters (D50s) of $> \sim 1 \mu\text{m}$ for
15 adsorption of hydrophobic micropollutants such as 2-methylisoborneol (MIB) increases
16 with decreasing particle size because the pollutants are adsorbed mostly on the exterior
17 (shell) of the particles owing to the limited diffusion penetration depth. However, particles
18 with D50s of $< 1 \mu\text{m}$ have not been thoroughly investigated. Here, we prepared particles
19 with D50s of $\sim 30 \mu\text{m}$ to $\sim 140 \text{nm}$ and evaluated their adsorption capacities for MIB and
20 several other environmentally relevant adsorbates. The adsorption capacities for low-
21 molecular-weight adsorbates, including MIB, decreased with decreasing particle size for
22 D50s of less than a few micrometers, whereas adsorption capacities increased with
23 decreasing particle size for larger particles. The oxygen content of the particles increased
24 substantially with decreasing particle size for D50s of less than a few micrometers, and
25 oxygen content was negatively correlated with adsorption capacity. The decrease in
26 adsorption capacity with decreasing particle size for the smaller particles was due to particle
27 oxidation during the micromilling procedure used to decrease D50 to $\sim 140 \text{nm}$. When
28 oxidation was partially inhibited, the MIB adsorption capacity decrease was attenuated. For
29 high-molecular-weight adsorbates, adsorption capacity increased with decreasing particle
30 size over the entire range of tested particle sizes, even though particle oxygen content
31 increased with decreasing particle size.

32

33 **Keywords**

34 MIB, micro-grinding, bead mill, oxygen content, oxidation

35

37 **1. Introduction**

38 Superfine powdered activated carbon (SPAC), which is produced by micromilling of
39 normal powdered activated carbon (PAC), is a new option for efficiently removing natural
40 organic matter, disinfection byproduct precursors, organic micropollutants, and taste and
41 odor compounds from water (Bonvin et al. 2016, Dunn and Knappe 2013, Heijman et al.
42 2009, Matsui et al. 2007, Matsui et al. 2004, Matsui et al. 2005, Wang et al. 2011). SPAC
43 offers many advantages over PAC, such as higher adsorption capacity (Ando et al. 2010,
44 Ando et al. 2011, Bonvin et al. 2016, Matsui et al. 2010), faster adsorption kinetics (Dudley
45 2012, Matsui et al. 2009a, Matsui et al. 2011, Wang et al. 2011), and the ability to attenuate
46 the buildup of transmembrane pressure when used before microfiltration (Ellerie et al. 2013,
47 Li 2014, Matsui et al. 2007, Matsui et al. 2009b).

48 The higher adsorption capacity of SPAC is of both practical and theoretical interest
49 because in previous studies it had been believed that adsorption occurred in the internal
50 pores of activated carbon (AC) particles and that equilibrium adsorption capacity was
51 therefore independent of particle size (Letterman et al. 1974, Najm et al. 1990, Peel and
52 Benedek 1980).

53 Previous investigations have reported that the change in the AC particle size caused by
54 micro-milling does not result in any substantial change in the internal pore area (Ando et
55 al. 2010, Matsui et al. 2014, Pan et al. 2017). Therefore, the higher adsorption capacity of
56 SPAC is not related to the internal pore area. More recently, the higher adsorption capacity
57 has been explained in terms of the shell adsorption model (SAM), which holds that
58 adsorbates are adsorbed mainly on the exterior (shell) of particles owing to the limited
59 diffusion penetration depth (Ando et al. 2011, Matsui et al. 2011, Matsui et al. 2013, Matsui

60 et al. 2014). The decrease in particle size upon micromilling increases the exterior surface
61 area, thus enhancing adsorption capacity, as long as the particle radius is larger than the
62 diffusion penetration depth, which depends on the adsorbate and the AC. For example, it
63 has been shown that 2-methylisoborneol (MIB), a taste and odor compound that is a target
64 of water treatment processes, penetrates to a depth of 4–6 μm in some coconut-shell-based
65 and wood-based PACs and that SPACs (particle radius, 0.5–1 μm) produced from the PACs
66 have higher MIB adsorption capacities than the PACs (particle radius, 5–10 μm) (Matsui
67 et al. 2015, Matsui et al. 2014).

68 The SAM also suggests that if the adsorbate penetration depth is a few micrometers,
69 adsorption capacity may not increase when the AC particle radius is decreased from a few
70 micrometers to less than a micrometer. However, adsorption capacities and characteristics
71 of ACs in this particle size range have not been thoroughly investigated. Micromilling is a
72 new nanotechnology that has enabled production of particles with median diameters (D50s)
73 from the submicrometer range down to hundreds of nanometers, and even smaller (Mende
74 et al. 2003, 2004). This technology has been applied to materials such as corundum (Stenger
75 et al. 2005), aluminum nitride (Jia et al. 2015, Qiu et al. 2006), $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (Han et al. 2012),
76 barium sulfate (Patel et al. 2014), silica (Patel et al. 2015), and crystalline pyrene (Flach et
77 al. 2016). Our research group (Pan et al. 2015, Pan et al. 2017) and others (Amaral et al.
78 2016, Partlan et al. 2016) have produced AC particles with D50s of 200–250 nm.

79 Several full-scale SPAC–microfiltration plants are already being used for drinking
80 water production (Kanaya et al. 2015); in these plants, SPAC with D50s of 1–2 μm is
81 produced onsite and added before membrane filtration. The use of smaller particles (e.g.,
82 150-nm diameter) might enhance adsorptive removal efficiency.

83 In this study, we produced ACs with D50s of 30 μm to 140 nm and evaluated the effects
84 of particle size on their adsorption capacities for various adsorbates.

85 **2. Experimental**

86 2.1 ACs

87 Five commercially available PACs (Carbons A–E, Table 1) were milled normally (see
88 sec. 2.2.1) to produce SPACs and submicrometer SPACs (SSPACs). The PACs, SPACs,
89 and SSPACs were given unique four-part designations specifying particle size, parent PAC
90 (A–E), production method, and batch number (where applicable). For the first term, PAC
91 designates particles with D50s of 12.0–28.0 μm ; SPAC_L, D50s of 3.80–8.10 μm ; SPAC_S,
92 D50s of 0.794–1.80 μm ; and SSPAC, D50s of 0.137–0.230 μm . The third term (used only
93 for SPAC_L, SPAC_S, and SSPAC) indicates the production method: “N” for normal milling,
94 “NET” for extended-time normal milling, “OI” for oxidation-inhibiting milling, and “R” for
95 rinsing with pure water (see sec. 2.2 and Tables S1 and S2). For example, SSPAC-C-N-2
96 is the second batch of an SSPAC produced from PAC-C under normal milling conditions.

97

98 2.2 SPAC and SSPAC production

99 SPAC_L was produced with a closed-chamber ball mill (Nikkato, Osaka, Japan) with 5-
100 and 10-mm-diameter balls. SPAC_S and SSPAC were produced with a bead mill with a re-
101 circulation system (LMZ015, Ashizawa Finetech, Chiba, Japan) with (0.1- or 0.3-mm-
102 diameter ZrO₂ beads. The next two sections describe the milling procedures.

103

104 2.2.1 Normal milling

105 As-received PACs (designated as, e.g., PAC-A) were slurried in pure water (Milli-Q
106 Advantage, Millipore, Bedford, MA, USA) at a concentration of ~15% (w/w) and then
107 milled in the ball mill at <45 rpm for 4–5 h to afford particles with D50s of 3.03–3.90 μm
108 (designated as, e.g., SPAC_L-A-N). The slurry was collected from the chamber of the ball
109 mill with pure water and then diluted to ~1% (w/w).

110 The diluted AC slurry (400 mL) was then milled with the bead mill with 0.3-mm-
111 diameter beads at a rotational speed of 2590 rpm in recirculation mode for 20–30 min to
112 afford particles with D50s of <1.47 μm but >0.915 μm (designated as, e.g., SPAC_S-A-N).
113 AC particles with D50s of 137–198 nm were produced from SPAC_L or SPAC_S using the
114 bead mill with 0.1-mm-diameter beads at 3884 rpm in re-circulation mode for 1.5–2 h. In
115 additional experiments, the milling time was extended to 5–7 h. During milling, the slurry
116 was kept at <28 °C by means of a cooling system.

117

118 2.2.2 Oxidation-inhibiting milling

119 As-received PACs were dried in a vacuum chamber for at least 1 h, and then the
120 chamber was filled with N₂ at atmospheric pressure. The PACs in the N₂-filled chamber
121 were rinsed with pure water three times. The PACs obtained in this way are designated as,
122 e.g., PAC-C-R.

123 The rinsed PAC slurries were adjusted to a concentration of ~15% (w/w) with pure
124 water, transferred to the ball mill filled with N₂ gas, and milled under the conditions used
125 for normal milling. Because collecting the AC slurries under N₂ after milling was difficult,
126 they were collected in air, but as quickly as possible. The collected slurries were adjusted
127 to a concentration of ~1% (w/w) with pure water. The dissolved oxygen concentration was

128 then reduced to <1 mg/L by allowing N₂ gas to diffuse into the slurries for >1 h. The slurries
129 obtained in this way are designated as, e.g., SPAC_L-C-OI.

130 SPAC_S-OI was produced by bead milling of SPAC_L-OI under conditions in which the
131 slurry was purged with N₂ (Fig. 1); otherwise, the milling conditions were the same as those
132 used for normal bead milling. After milling, the slurries were kept under vacuum for >1 h
133 and then placed under N₂ at atmospheric pressure. The slurries obtained in this way are
134 designated as, e.g., SPAC_S-C-OI.

135 SSPAC-OI was produced by bead milling SPAC_L-OI (400–500 mL) under N₂ purging,
136 similar to those used to produce SPAC_S, for 3–4 h at 2590 rpm with 0.1- or 0.3-mm-
137 diameter beads.

138 All the AC slurries were stored at 4 °C after vacuum conditioning to remove air from
139 the pores.

140

141 2.3 AC characterization

142 Particle size distributions of all the ACs were measured by laser-light scattering
143 (Microtrac MT3300EXII, Nikkiso, Tokyo, Japan) in transmission mode. Samples of stock
144 slurries were pretreated with a dispersant (Triton X-100, Kanto Chemical, Tokyo, Japan;
145 final concentration, 0.08% w/v) and ultrasonically dispersed (150 W, 19.5 kHz, 4 min for
146 50 mL AC slurry) before measurement.

147 SSPAC particles were observed by field emission scanning electron microscopy (JSM-
148 7400F, JEOL, Tokyo, Japan) at an accelerating voltage of 5.0 kV and a working distance
149 of 3.0 mm. The particles were not precoated, because the thickness of the coating layer
150 might have hindered accurate observation. SPAC_L, SPAC_S, and PAC particles were not

151 observed microscopically, because images of these particles had already been obtained
152 (Ando et al. 2010) and because the particles sizes were visually confirmed.

153 The oxygen, hydrogen, nitrogen, and sulfur contents of the ACs were determined by
154 elemental analysis (Vario EL Cube, Elementar Japan, Yokohama, Japan) with thermal
155 conductivity and infrared detection. For this purpose, the AC slurries were dried by a
156 vacuum cooling method to prevent oxidation during drying. Before elemental analysis, the
157 dried samples were placed in small tin capsules and weighed out. The capsules containing
158 sample were stored in an acrylic container under a vacuum. After atmospheric pressure N₂
159 was introduced to the box, the capsules were promptly transferred to the elemental analyzer.
160 The oxygen content was measured in O mode, and the other elements were measured in
161 CHNS mode. Ash contents were determined by igniting oven-dried AC samples in a muffle
162 furnace at 550 °C. Averages of triplicate measurements are reported for each AC.

163

164 2.4 Adsorbates and working solution

165 MIB was the main target compound in this study. MIB concentrations were determined
166 in two ways. Either the *m/z* 95 peak of MIB was detected with a purge-and-trap concentrator
167 (Aqua PT 5000 J, GL Sciences, Tokyo, Japan) coupled to a gas chromatograph–mass
168 spectrometer (GCMS-QP2010 Plus, Shimadzu, Kyoto, Japan) using geosmin-*d*₃ (*m/z* 115)
169 as an internal standard. Or the *m/z* 108 peak of MIB was detected by headspace solid-phase
170 microextraction (PAL RSI 85, Agilent Technologies Japan, Ltd., Tokyo, Japan) coupled to
171 a gas chromatograph–mass spectrometer (7820A/5977 E MSD, Agilent) using 2,4,6-
172 trichloroanisole-*d*₃ (*m/z* 195) as an internal standard.

173 On the basis of environmental relevancy, molecular size, and hydrophobicity, nine
174 other adsorbates were tested in addition to MIB: geosmin (log K_{ow}, 3.57; 182 Da),

175 dimethylphosphorothidate-oxon (DMTP-oxon; log Kow, 0.77; 286 Da), benzothiazole (log
176 Kow, 2.09; 135 Da), phenol (log Kow, 1.46; 94 Da), *para*-nitrophenol (log Kow, 1.91; 139
177 Da), salicylic acid (log Kow, 2.06; 138 Da), poly(styrenesulfonic acid sodium salt) with an
178 average molecular weight (MW) of 210 Da (PSS-210), PSS-1100 (average MW, 1100 Da),
179 and SNOM (Suwannee River natural organic matter, International Humic Substance
180 Society). Note that the log Kow values listed above are from EPI Suite™ database (ver. 4,
181 U.S. Environmental Protection Agency). Geosmin concentrations were determined by a
182 method similar to that used for MIB; *m/z* 112 was attributed to geosmin. DMTP-oxon was
183 quantified by hybrid quadrupole-orbitrap mass spectrometry (Q Exactive, Thermo Fisher
184 Scientific, Waltham, MA, USA) combined with liquid chromatography (UltiMate3000 LC
185 systems, Thermo Fischer Scientific) using mepronil as an internal standard (DMTP-oxon,
186 *m/z* 287; mepronil, *m/z* 270). The other adsorbate concentrations were measured by UV–
187 vis spectrophotometry (UV-1800, Shimadzu, Kyoto, Japan) at 269.5, 252, 296, 317, and
188 261 nm for phenol, benzothiazole, salicylic acid, *para*-nitrophenol, and PSS-210/PSS-1100,
189 respectively.

190 Except for PSS-210 and PSS-1100 (Sigma-Aldrich, St. Louis, MO, USA), all chemical
191 reagents were purchased from Wako Pure Chemical Industries (Osaka, Japan). The working
192 solution was organic-free water with the ion composition used in previous research (Table
193 S3) (Matsui et al. 2015, Pan et al. 2016). The working solutions were adjusted to pH 7.0 ±
194 0.1 with HCl or NaOH as required. The solution pH was maintained constant during
195 adsorption tests probably due to bicarbonate buffer.

196

197 2.5 Batch adsorption tests

198 For each target adsorbate, an aliquot (100 or 110 mL) of working solution containing
199 the adsorbate was transferred to a 110-mL vial; AC was immediately added; and the vial

200 was manually shaken and then agitated on a mechanical shaker for 1 week or 3 days at
201 20 °C in the dark. Preliminary experiments confirmed that adsorption equilibrium was
202 reached within 1 week for the MIB–PAC combination (Matsui et al. 2013, Matsui et al.
203 2012), 3 days for MIB–SPAC/SSPAC, and 1 week for the other 8 adsorbates (for all the
204 ACs). Control tests of blank solutions containing adsorbates but no AC confirmed that
205 changes in adsorbate concentration during long-term mixing were negligible. After shaking,
206 water samples were filtered through a 0.2- μm -pore-size membrane filter
207 (polytetrafluoroethylene, DISMIC-25HP, Toyo Roshi Kaisha, Tokyo, Japan) to remove the
208 AC, and then the adsorbate concentration in the filtrate was measured. Complete removal
209 of SSPAC required two filtrations. Preliminary tests confirmed that MIB did not adsorb on
210 the filter and that SSPAC was completely removed by the filtration. Solid-phase
211 concentrations of adsorbates were calculated from mass balances.

212

213 **3. Results and discussion**

214

215 3.1 SPAC and SSPAC production by normal micromilling

216 SSPACs with D50s of 137–198 nm were produced by the milling methods described
217 in sec. 2.1, and SSPAC production with good reproducibility was verified both from the
218 particle size distribution (Fig. S1) and by scanning electron microscopy (Fig. 2). The
219 characteristics of the normally milled ACs are listed in Table S1.

220

221 3.2 Effects of particle size on MIB adsorption capacity

222 Equilibrium MIB adsorption isotherms were determined for Carbons A with D50s of
223 12.0–0.198 μm (Fig. S2). The MIB adsorption capacity of each AC was quantified in terms
224 of the solid-phase concentrations (designated as q) in equilibrium with liquid-phase
225 concentrations of 50 and 100 ng/L, after fitting of the isotherm data to the Freundlich model.

226 The effects of particle size on MIB adsorption capacity are depicted in Fig. 3a. Reduction
227 of D50 from 12.0 μm (PAC-A) to 1.47 μm (SPAC_S-A-N) doubled the adsorption capacity,
228 but the MIB adsorption capacity did not increase when D50 was decreased further: the MIB
229 adsorption capacity of SSPAC-A-N (D50: 198 nm) was ~85% of that of SPAC_S-A-N.

230 A decrease in adsorption capacity in going from SPAC_S to SSPAC was also observed
231 for the other ACs. For example, the adsorption capacity of SSPAC-B-N was ~90% of that
232 of SPAC_S-B-N, the adsorption capacity of SSPAC-C-N was 51–93% of that of SPAC_S-C-
233 N, and the adsorption capacity of SSPAC-D-N was ~90% of that of SPAC_S-D-N (Fig. 3b–
234 d, respectively). The adsorption capacity of SSPAC-D-N_{ET}, which was produced by milling
235 for extended time, was 65–75% of that of SPAC_S-D-N. In the case of Carbons E, the
236 adsorption capacity started to decrease with particle size when D50 was <3.90 μm ; the
237 adsorption capacity of SSPAC-E-N was ~74% of that of SPAC_L-E-N (Fig. 3e). A similar
238 trend was reported in a study of atrazine removal with microfiltration membrane precoated
239 with SPAC (Amaral et al. 2016). In that study, adsorption capacity decreased as D50 was
240 reduced from ~300 to ~200 nm for one of the three studied ACs and as D50 was reduced
241 from ~600 to ~500 nm for another AC, although the authors of the paper did not comment
242 on the trend.

243 According to the SAM, adsorbent particle size affects MIB adsorption capacity when
244 the adsorbent radius is substantially larger than the adsorbate penetration depth (Matsui et
245 al. 2013, Matsui et al. 2014). Under these circumstances, the increase in the external surface
246 area of the adsorbent particles with decreasing particle size results in increased adsorption
247 capacity. Therefore, the higher adsorption capacity of PAC-A (12.0 μm) relative to that of
248 SPAC_S-A-N (1.47 μm) was likely due to this mechanism. That the adsorption capacity did
249 not increase with decreasing particle size for D50s of <1.47 μm (i.e., from SPAC_S-A-N to
250 SSPAC-A-N) suggests that the particle radii of both of these ACs were smaller than the

251 MIB penetration depth and that all of the internal pores of the particles were utilized for
252 MIB adsorption. Once the internal pores are completely utilized, adsorption capacity is
253 independent of particle size. The change in the AC particle size caused by micromilling
254 would not result in any substantial change in the internal pore structure (Ando et al. 2010,
255 Matsui et al. 2014, Pan et al. 2017). Moreover, any structural changes in internal pores
256 could not explain the phenomena that MIB adsorption capacity decreased while PSS-1100
257 adsorption capacity increased, as described in the section 3.6. Under these circumstances,
258 pore surface chemistry strongly would affect adsorption capacity (Li et al. 2002, Matsui et
259 al. 2015, Quinlivan et al. 2005).

260

261 3.3 Oxygen content of AC

262 Oxygen-containing complexes on the AC surface alter surface hydrophobicity and
263 affect the adsorption capacity for organic compounds, including MIB (Moreno-Castilla
264 2004, Pendleton et al. 1997, Song et al. 2010). The number of oxygen-containing complexes
265 is reflected by the AC oxygen content (% [w/w]), which is thus highly correlated with MIB
266 adsorption capacity (Li et al. 2002, Matsui et al. 2015).

267 The oxygen content of Carbons A increased with decreasing particle size (Fig. 4a), and
268 the increase was particularly large when D50 dropped to $<1 \mu\text{m}$. The external surface of
269 AC particles is usually more oxidized than the interior because oxygen diffuses very slowly
270 in the abundant, narrow internal pores (Boehm 2002). Micromilling in the bead mill, which
271 was used to produce particles with D50s of $<1 \mu\text{m}$, brought the particle interior into contact
272 with oxygen in the water, possibly hastening oxidation. That the drop in MIB adsorption
273 capacity was coincident with a substantial increase in oxygen content (Figs. 3 and 4)
274 suggests that the drop in MIB adsorption capacity was due to carbon oxidation.

275 Wood-based Carbons A–C (i.e., PAC-A, PAC-B, and PAC-C) were produced by the
276 same manufacturer, and were marketed under the same specification and brand name.
277 However, they were produced in different batches, and were received in our laboratory at
278 different times. In addition, the times from receipt to experimental use (stock periods)
279 differed, decreasing in the order PAC-A (~7 years) > PAC-B (~1 year) > PAC-C (<6
280 months). This order is consistent with the order of decreasing oxygen content: PAC-A
281 (9.1%) > PAC-B (7.2%) > PAC-C (2.0%) (Fig. 4a–c). This finding is in line with a report
282 that AC is oxidized very slowly in air (Billinge et al. 1984, Boehm 2002). For these three
283 PACs, the order of decreasing MIB adsorption capacity was opposite the order of
284 decreasing oxygen content: that is, adsorption capacity decreased with carbon age in the
285 order PAC-C > PAC-B > PAC-A (Fig. S2). Although characteristics other than oxygen
286 content might also be related to the adsorption capacity difference between the three
287 carbons, these data is consistent with the idea that carbon oxidation decreased MIB
288 adsorption capacity (Considine et al. 2001).

289 For Carbons A–C, the sources of which had different oxygen contents, oxygen content
290 increased as the particle size was decreased by micromilling with the bead mill (Fig. 4a–c).
291 The same was true of Carbon D, a wood-based AC produced by a different manufacturer,
292 and Carbon E, a coal-based AC produced by a third manufacturer (Fig. 4d,e). The oxygen
293 content increased further when the milling time was extended from 1.5–2 to 5–7 h (compare
294 SSPAC-D-N and SSPAC-D-N_{ET} in Fig. 4d). Because the external surface of AC particles
295 is believed to be more oxidized than the interior (Boehm 2002, Partlan et al. 2016), overall
296 particle oxidation would have increased as particle size was decreased by micromilling.
297 That oxygen content increased with decreasing particle size for all five kinds of ACs used
298 in this study is consistent with this understanding.

299

300 3.4 Controlling oxidation during SPAC and SSPAC production

301 The increase in oxygen content as milling progressed suggests that milling introduced
302 oxygen-containing functional groups, which would increase the carbon hydrophilicity and
303 thus decrease MIB adsorption capacity. Therefore, if oxidation during milling could be
304 inhibited, the adsorption capacity decrease could be attenuated. We investigated various
305 methods for producing less-oxidized SSPAC with D50s of <230 nm (Table S2, Fig. S1).
306 The oxygen contents of Carbons C and D are presented in Fig. 5 (Fig. S3).

307 Oxidation-inhibiting milling (sec. 2.2.2) inhibited oxidation as D50 was reduced from
308 2.65–8.11 μm to 174–230 nm. Specifically, oxidation-inhibiting milling to produce SSPAC-
309 C-OI increased oxygen content by only $2.2 \pm 0.5\%$ (w/w) (Fig. 5c), whereas normal milling
310 to produce SSPAC-C-N increased oxygen content by $3.4 \pm 1.2\%$ (Fig. 4c). The oxygen
311 content increase in going from SPAC_L-D to SSPAC-D by oxidation-inhibiting milling was
312 $2.0 \pm 0.2\%$ (Fig. 5d), which was approximately half the increase due to normal milling (3.8
313 $\pm 0.1\%$; Fig. 4d).

314 We also measured the hydrogen, nitrogen, sulfur, and ash contents of ACs produced
315 by normal milling and oxidation-inhibiting milling (Fig. S4). Like oxygen content,
316 hydrogen content increased with decreasing particle size. When the particles were milled,
317 the ratio (increase in oxygen content, in moles)/(increase in hydrogen content, in moles)
318 ranged from 2/3 to 3/2. This result suggests that hydroxyl and/or carboxyl groups formed
319 on the carbon surface, an additional indication that milling increased carbon hydrophilicity.
320 The ash contents in PAC-B-R, SPAC_S-B-OI, SSPAC-B-OI, and SSPAC-B-N were
321 somewhat lower than those in PAC-B and SPAC_S-B-N. This result may have been due to
322 the effect of rinsing and dilution of the AC slurry with pure water; rinsing and dilution
323 would have washed out inorganic materials, including metals. However, this small change

324 in ash content did not affect MIB adsorption capacity: the MIB adsorption isotherm of PAC-
325 C-R did not differ substantially from that of PAC-C (Fig. S5).

326

327 3.5 Correlation between oxygen content and MIB adsorption capacity

328 We have suggested that the low MIB adsorption capacities of the SSPACs produced
329 by normal milling resulted from carbon oxidation. In a final test, SSPACs with low oxygen
330 content (SSPAC-C-OI) and with high oxygen content (SSPAC-C-N) were produced from
331 the same PAC, and their MIB adsorption capacities were determined. SSPAC-C-OI
332 exhibited higher adsorption capacity than SSPAC-C-N (Figs. S2 and S6). Moreover, there
333 were strong negative correlations between oxygen content and MIB adsorption capacity
334 (Fig. 6). These results clearly indicate that the low MIB adsorption capacity of normally
335 milled SSPAC produced relative to that of SPACs was due to increased oxygen content,
336 which increased carbon hydrophilicity.

337 The plots in Fig. 6 include data for AC particles with D50s from 137 nm to 1.64 μm
338 (i.e., all the SPACs and SSPACs). The correlation shown in the figure clearly means that
339 adsorption capacity was unrelated to particle size in this range, suggesting that the entire
340 particle, including internal pores, was accessible to MIB molecules, as suggested by the
341 SAM (sec. 3.1). Oxygen content is a good indicator of MIB adsorption capacity of particles
342 with D50s of $< \sim 1 \mu\text{m}$ (SPACs and SSPAC). This agrees with a previous finding that SPAC
343 hydrophilicity, as indicated by oxygen content, is the main determinant of adsorption
344 capacity for hydrophobic compounds such as geosmin (Matsui et al., 2015).

345 The oxygen content of SSPAC-OI was lower than that of SSPAC-N but was still higher
346 than that of the SPACs from which SSPACs were produced. That is, oxidation was not
347 completely prevented by oxidation-inhibiting milling. The highest adsorption capacity was

348 attained with SPACs having a D50 of ~ 1 μm . The energy required to reduce D50 to $< \sim 1$
349 μm would not offer any increase in adsorption capacity. Therefore, SPAC with a D50 of a
350 few micrometers (~ 1.5 μm for Carbons A–D, ~ 4.0 μm for Carbon E) is a more reasonable
351 choice for MIB removal from the viewpoint of high MIB adsorption capacity and
352 reasonable energy consumption.

353

354 3.6 Effect of particle size on adsorption of other adsorbates

355 We observed that adsorption capacity for MIB, a hydrophobic low-MW compound
356 ($\log K_{ow}$, 3.31; 168 Da), increased in going from PAC to SPAC and decreased in going
357 from SPAC to SSPAC. To determine whether this trend held for other adsorbates, we
358 conducted adsorption equilibrium tests on several environmentally relevant compounds
359 with various hydrophobicities and MWs. The adsorption capacities for these compounds
360 were quantified in terms of the solid-phase concentrations (q) in equilibrium with two
361 liquid-phase concentrations in the experimentally observed range (Fig. S6). Then we
362 evaluated the relationship between adsorption capacity and particle size (Fig. S8).

363 Going from SPACs-A-N (1.47 μm) to SSPAC-A-N (0.20 μm) did not decrease
364 adsorption capacity for PSS-1100 and SNOM, which have high MWs (>1000 Da, Fig. S8);
365 in fact, adsorption capacity consistently increased with decreasing particle size. This result
366 is consistent with previous findings indicating that adsorption capacity for high-MW
367 compounds increases with decreasing AC particle size (Ando et al. 2010, Ando et al. 2011).
368 For high-MW compounds, the penetration depth was smaller than the radii of adsorbents
369 such as PAC and SPAC (Ando et al. 2010); therefore the interior of those adsorbents were
370 inaccessible to those adsorbates, and adsorption occurred only at the external particle
371 surface. In these circumstances, adsorption capacity increases with decreasing adsorbent
372 particle size.

373 For the other 7 compounds, all of which had MWs of <300 Da, adsorption capacity
374 decreased when D50 was decreased to < ~1 μm , as was the case for MIB. For all the
375 adsorbates, the adsorption capacities of SSPAC-A-N (0.20 μm) were lower than those of
376 SPAC_s-A-N (1.47 μm) (Figs. 7 and S8). The magnitude of the adsorption capacity decrease
377 depended on the adsorbate, but we were unable to identify the adsorbate property that
378 explained the magnitude of the decrease. For example, the magnitude of the decrease was
379 not correlated to adsorbate log Kow ($R^2 < 0.02$, Figs. 7 and S9a). The adsorption capacity
380 of SSPAC-A-N for geosmin (log Kow, 3.57), which is at least as hydrophobic as MIB (log
381 Kow, 3.31), was 30% lower than that of SPAC_s-A-N. The adsorption capacity of SSPAC-
382 A-N for DMTP-oxon (log Kow, 0.77), which is hydrophilic, was also 30% lower than that
383 of SPAC_s-A-N. For Carbons B (i.e., SPAC_s-B-N and SSPAC-B-N), the magnitude of the
384 adsorption capacity decrease was not correlated with adsorbate log Kow (Fig. S9b,c). The
385 lower adsorption capacity of SSPAC relative to that of SPAC_s was due to the higher
386 hydrophilicity of SSPAC, as indicated by the higher oxygen content (sec. 3.5). The
387 differences in the magnitude of the adsorption capacity decrease in going from SPAC_s to
388 SSPAC for the eight compounds (MIB plus the seven adsorbates other than PSS-1100 and
389 SNOM) indicate that the adsorption capacities for these compounds had different
390 sensitivities to carbon hydrophilicity (oxygen content).

391 Different sensitivities to carbon hydrophilicity have been reported in other studies,
392 although these studies did not involve SPAC or SSPAC. For example, a study comparing
393 the adsorption capacities of AC for a hydrophobic compound, trichloroethene (log Kow,
394 2.42; 131 Da), and a hydrophilic compound, methyl *tert*-butyl ether (log Kow, 0.94; 88 Da),
395 indicated that the decrease in adsorption capacity associated with increased carbon
396 hydrophilicity was more pronounced for the hydrophilic compound (i.e., the adsorbate with
397 the lower log Kow) (Li et al. 2002). However, a study involving several fatty acids,

398 including propanoic acid (log Kow, 0.33; 74.1 Da), valeric acid (log Kow, 1.39; 102 Da),
399 enanthic acid (log Kow, 2.42; 130 Da), and pelargonic acid (log Kow, 3.42; 158 Da),
400 revealed that the decrease in adsorption capacity associated with increased carbon
401 hydrophilicity was not necessarily greater for hydrophobic adsorbates with high log Kow
402 values than for hydrophilic adsorbates with low log Kow values (Kaneko et al. 1989). Water
403 likely adsorbs as clusters around the hydrophilic sites on the carbon surface (Pendleton et
404 al. 1997). As the number of hydrophilic sites increases, water clusters tend to extend over
405 hydrophobic sites, which prevents hydrophobic adsorbates, such as MIB, from accessing
406 the hydrophobic sites on the carbon surface. Increased formation of water clusters on
407 hydrophilic sites also reduces the energy of interaction between hydrophilic adsorbates,
408 such as DMTP-oxon, and the carbon surface (Kaneko et al. 1989, Li et al. 2002). Although
409 adsorption capacity for both hydrophobic and hydrophilic adsorbates decreases with
410 decreasing carbon hydrophobicity, the mechanisms of the decreases for the two types of
411 adsorbates are likely to differ, which in turn would lead to differences in the sensitivity of
412 adsorption capacity to carbon hydrophobicity.

413

414 **4. Conclusions**

415 (1) Micromilling produced AC particles with D50s as low as 137 nm.

416 (2) MIB adsorption capacity decreased with decreasing particle size for ACs with D50s of
417 less than a few micrometers. This decrease in adsorption capacity was due to carbon
418 oxidization during micromilling.

419 (3) Partial inhibition of carbon oxidation during micromilling attenuated the decrease in
420 MIB adsorption capacity.

421 (4) For attaining high MIB adsorption capacity without unnecessary consumption of energy
422 for micromilling, SPAC with a D50 of 1–4 μm is a reasonable choice.

423 (5) The adsorption capacity decrease with decreasing AC particle size for particles with
424 D50s of less than a few micrometers was observed for all eight low-MW adsorbates.
425 The magnitude of the decrease depended on the adsorbates, but the relationship could
426 not be explained simply by differences in adsorbate hydrophilicity.

427 (6) For SNOM and PSS-1100, adsorption capacity increased with decreasing adsorbent
428 particle size (i.e., in going from PAC to SSPAC).

429 (7) AC underwent oxidation during long-term storage, and the resulting increase in oxygen
430 content could be associated with decreases in adsorption capacity for compounds such
431 as MIB.

432

433 **Acknowledgments**

434

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441

442 **Appendix. Supplementary Information**

443 Table S1-S3 and Figures S1–S9 are available in the online version at #####.

444

445

446 **References**

- 447 Amaral, P., Partlan, E., Li, M., Lapolli, F., Mefford, O.T., Karanfil, T. and Ladner, D.A. (2016)
448 Superfine powdered activated carbon (S-PAC) coatings on microfiltration membranes:
449 Effects of milling time on contaminant removal and flux. *Water Research* 100, 429-438.
- 450 Ando, N., Matsui, Y., Kurotobi, R., Nakano, Y., Matsushita, T. and Ohno, K. (2010)
451 Comparison of natural organic matter adsorption capacities of super-powdered activated
452 carbon and powdered activated Carbon. *Water Research* 44(14), 4127-4136.
- 453 Ando, N., Matsui, Y., Matsushita, T. and Ohno, K. (2011) Direct observation of solid-phase
454 adsorbate concentration profile in powdered activated carbon particle to elucidate
455 mechanism of high adsorption capacity on super-powdered activated carbon. *Water*
456 *Research* 45(2), 761-767.
- 457 Billinge, B.H.M., Docherty, J.B. and Bevan, M.J. (1984) The desorption of chemisorbed
458 oxygen from activated carbons and its relationship to ageing and methyl iodide retention
459 efficiency. *Carbon* 22(1), 83-89.
- 460 Boehm, H.P. (2002) Surface oxides on carbon and their analysis: a critical assessment.
461 *Carbon* 40(2), 145-149.
- 462 Bonvin, F., Jost, L., Randin, L., Bonvin, E. and Kohn, T. (2016) Super-fine powdered
463 activated carbon (SPAC) for efficient removal of micropollutants from wastewater
464 treatment plant effluent. *Water Research* 90, 90-99.
- 465 Considine, R., Denoyel, R., Pendleton, P., Schumann, R. and Wong, S.-H. (2001) The
466 influence of surface chemistry on activated carbon adsorption of 2-methylisoborneol from
467 aqueous solution. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*
468 179(2-3), 271-280.
- 469 Dudley, L.-A. (2012) Removal of Perfluorinated Compounds by Powdered Activated
470 Carbon, Superfine Powder Activated Carbon, and Anion Exchange Resin.
- 471 Dunn, S.E. and Knappe, D.R. (2013) DBP Precursor and Micropollutant Removal by
472 Powdered Activated Carbon [Project# 4294].
- 473 Ellerie, J.R., Apul, O.G., Karanfil, T. and Ladner, D.A. (2013) Comparing graphene, carbon
474 nanotubes, and superfine powdered activated carbon as adsorptive coating materials for
475 microfiltration membranes. *Journal of Hazardous materials*, 261, 91-98.
- 476 Flach, F., Konnerth, C., Peppersack, C., Schmidt, J., Damm, C., Breitung-Faes, S.,
477 Peukert, W. and Kwade, A. (2016) Impact of formulation and operating parameters on

478 particle size and grinding media wear in wet media milling of organic compounds – A case
479 study for pyrene. *Advanced Powder Technology* 27(6), 2507-2519.

480 Han, S.-W., Shin, J.-W. and Yoon, D.-H. (2012) Synthesis of pure nano-sized $\text{Li}_4\text{Ti}_5\text{O}_{12}$
481 powder via solid-state reaction using very fine grinding media. *Ceramics International*
482 38(8), 6963-6968.

483 Heijman, S.G.J., Hamad, J.Z., Kennedy, M.D., Schippers, J. and Amy, G. (2009)
484 Submicron powdered activated carbon used as a pre-coat in ceramic micro-filtration.
485 *Desalination and Water Treatment* 9(1-3), 86-91.

486 Jia, L., Kondoh, K., Imai, H., Onishi, M., Chen, B. and Li, S.-f. (2015) Nano-scale AlN
487 powders and AlN/Al composites by full and partial direct nitridation of aluminum in solid-
488 state. *Journal of Alloys and Compounds* 629, 184-187.

489 Kanaya, S., Kawase, Y., Mima, S., Sugiura, K., Murase, K. and Yonekawa, H. (2015)
490 Drinking Water Treatment Using Superfine PAC (SPAC): Design and Successful
491 Operation History in Full-Scale Plant, Salt Lake City, Utah, USA.

492 Kaneko, Y., Abe, M. and Ogino, K. (1989) Adsorption characteristics of organic compounds
493 dissolved in water on surface-improved activated carbon fibres. *Colloids and Surfaces* 37,
494 211-222.

495 Letterman, R.D., Quon, J. and Gemell, R.S. (1974) Film transport coefficient in agitated
496 suspensions of activated carbon. *Journal (Water Pollution Control Federation)*, 2536-2546.

497 Li, L., Quinlivan, P.A. and Knappe, D.R.U. (2002) Effects of activated carbon surface
498 chemistry and pore structure on the adsorption of organic contaminants from aqueous
499 solution. *Carbon* 40(12), 2085-2100.

500 Li, M. (2014) Effects of Natural Organic Matter on Contaminant Removal by Superfine
501 Powdered Activated Carbon Coupled with Microfiltration Membranes. Thesis of Clemson
502 University.

503 Matsui, Y., Aizawa, T., Kanda, F., Nigorikawa, N., Mima, S. and Kawase, Y. (2007)
504 Adsorptive removal of geosmin by ceramic membrane filtration with super-powdered
505 activated carbon. *Journal of Water Supply: Research & Technology-AQUA* 56.

506 Matsui, Y., Ando, N., Sasaki, H., Matsushita, T. and Ohno, K. (2009a) Branched pore
507 kinetic model analysis of geosmin adsorption on super-powdered activated carbon. *Water*
508 *Research* 43(12), 3095-3103.

509 Matsui, Y., Ando, N., Yoshida, T., Kurotobi, R., Matsushita, T. and Ohno, K. (2011)
510 Modeling high adsorption capacity and kinetics of organic macromolecules on super-
511 powdered activated carbon. *Water Research* 45(4), 1720-1728.

512 Matsui, Y., Hasegawa, H., Ohno, K., Matsushita, T., Mima, S., Kawase, Y. and Aizawa, T.
513 (2009b) Effects of super-powdered activated carbon pretreatment on coagulation and
514 trans-membrane pressure buildup during microfiltration. *Water Research* 43(20), 5160-
515 5170.

516 Matsui, Y., Murase, R., Sanogawa, T., Aoki, N., Mima, S., Inoue, T. and Matsushita, T.
517 (2004) Micro-ground powdered activated carbon for effective removal of natural organic
518 matter during water treatment. *Water Science & Technology: Water Supply* 4(4).

519 Matsui, Y., Murase, R., Sanogawa, T., Aoki, N., Mima, S., Inoue, T. and Matsushita, T.
520 (2005) <Rapid adsorption pretreatment with submicrometre powdered activated carbon
521 particles before microfiltration.pdf>. *Water Science & Technology* 51(6-7), 7.

522 Matsui, Y., Nakano, Y., Hiroshi, H., Ando, N., Matsushita, T. and Ohno, K. (2010) Geosmin
523 and 2-methylisoborneol adsorption on super-powdered activated carbon in the presence
524 of natural organic matter. *Water Science & Technology* 62(11).

525 Matsui, Y., Nakao, S., Sakamoto, A., Taniguchi, T., Pan, L., Matsushita, T. and Shirasaki,
526 N. (2015) Adsorption capacities of activated carbons for geosmin and 2-methylisoborneol
527 vary with activated carbon particle size: Effects of adsorbent and adsorbate characteristics.
528 *Water Research* 85, 95-102.

529 Matsui, Y., Nakao, S., Taniguchi, T. and Matsushita, T. (2013) Geosmin and 2-
530 methylisoborneol removal using superfine powdered activated carbon: Shell adsorption
531 and branched-pore kinetic model analysis and optimal particle size. *Water Research* 47(8),
532 2873-2880.

533 Matsui, Y., Sakamoto, A., Nakao, S., Taniguchi, T., Matsushita, T., Shirasaki, N.,
534 Sakamoto, N. and Yurimoto, H. (2014) Isotope Microscopy Visualization of the Adsorption
535 Profile of 2-Methylisoborneol and Geosmin in Powdered Activated Carbon. *Environmental*
536 *Science & Technology* 48(18), 10897-10903.

537 Matsui, Y., Yoshida, T., Nakao, S., Knappe, D.R.U. and Matsushita, T. (2012)
538 Characteristics of competitive adsorption between 2-methylisoborneol and natural organic
539 matter on superfine and conventionally sized powdered activated carbons. *Water*
540 *Research* 46(15), 4741-4749.

541 Mende, S., Stenger, F., Peukert, W. and Schwedes, J. (2003) Mechanical production and
542 stabilization of submicron particles in stirred media mills. *Powder Technology* 132(1), 64-
543 73.

544 Mende, S., Stenger, F., Peukert, W. and Schwedes, J. (2004) Production of sub-micron
545 particles by wet comminution in stirred media mills. *Journal of Materials Science* 39(16),
546 5223-5226.

547 Moreno-Castilla, C. (2004) Adsorption of organic molecules from aqueous solutions on
548 carbon materials. *Carbon* 42(1), 83-94.

549 Najm, I.N., Snoeyink, V.L., Suidan, M.T., Lee, C.H. and Richard, Y. (1990) Effect of Particle
550 Size and Background Natural Organics on the Adsorption Efficiency of PAC. *Journal*
551 *(American Water Works Association)* 82(1), 65-72.

552 Pan, L., Matsui, Y., Matsushita, T. and Shirasaki, N. (2015) Effect of activated carbon
553 particle size on equilibrium adsorption capacity in the range of 200 nm to 2 mm. The 6th
554 IWA-ASPIRE Conference, Beijing, China. 20-24, September, 2017.

555 Pan, L., Matsui, Y., Matsushita, T. and Shirasaki, N. (2016) Superiority of wet-milled over
556 dry-milled superfine powdered activated carbon for adsorptive 2-methylisoborneol removal.
557 *Water Research* 102, 516-523.

558 Pan, L., Takagi, Y., Matsui, Y., Matsushita, T. and Shirasaki, N. (2017) Micro-milling of
559 spent granular activated carbon for its possible reuse as an adsorbent: Remaining capacity
560 and characteristics. *Water Research* 114, 50-58.

561 Partlan, E., Davis, K., Ren, Y., Apul, O.G., Mefford, O.T., Karanfil, T. and Ladner, D.A.
562 (2016) Effect of bead milling on chemical and physical characteristics of activated carbons
563 pulverized to superfine sizes. *Water Research* 89, 161-170.

564 Patel, C.M., Chakraborty, M. and Murthy, Z.V.P. (2014) Study on the stability and
565 microstructural properties of barium sulfate nanoparticles produced by nanomilling.
566 *Advanced Powder Technology* 25(1), 226-235.

567 Patel, C.M., Chakraborty, M. and Murthy, Z.V.P. (2015) Influence of pH on the Stability of
568 Alumina and Silica Nanosuspension Produced by Wet Grinding. *Particulate Science and*
569 *Technology* 33(3), 240-245.

570 Peel, R.G. and Benedek, A. (1980) Attainment of equilibrium in activated carbon isotherm
571 studies. *Environmental Science & Technology* 14(1), 66-71.

572 Pendleton, P., Wong, S.H., Schumann, R., Levay, G., Denoyel, R. and Rouquero, J. (1997)
573 Properties of activated carbon controlling 2-Methylisoborneol adsorption. *Carbon* 35(8),
574 1141-1149.

575 Qiu, J.-Y., Hotta, Y., Watari, K., Mitsuishi, K. and Yamazaki, M. (2006) Low-temperature
576 sintering behavior of the nano-sized AlN powder achieved by super-fine grinding mill with
577 Y2O3 and CaO additives. *Journal of the European Ceramic Society* 26(4–5), 385-390.

578 Quinlivan, P.A., Li, L. and Knappe, D.R.U. (2005) Effects of activated carbon
579 characteristics on the simultaneous adsorption of aqueous organic micropollutants and
580 natural organic matter. *Water Research* 39(8), 1663-1673.

581 Song, X., Liu, H., Cheng, L. and Qu, Y. (2010) Surface modification of coconut-based
582 activated carbon by liquid-phase oxidation and its effects on lead ion adsorption.
583 *Desalination* 255(1), 78-83.

584 Stenger, F., Mende, S., Schwedes, J. and Peukert, W. (2005) Nanomilling in stirred media
585 mills. *Chemical Engineering Science* 60(16), 4557-4565.

586 Wang, Y., Rao, G.Y. and Hu, J.Y. (2011) Adsorption of EDCs/PPCPs from drinking water
587 by submicron-sized powdered activated carbon. *Water Science and Technology: Water*
588 *Supply* 11(6), 711-718.

589

Table 1 – Commercial PACs used in this study.

Designation	Series	Production year	Raw material	Brand name	Manufacture specifications				Manufacture
					Phenol number	Iodine number (mg/g)	Methylene blue number (mL/g)	ABS number	
PAC-A	Carbon-A	2008	wood	Taiko W	< 25	> 900	> 150	< 50	Futamura Chemical Co., Tokyo, Japan
PAC-B	Carbon-B	2015							
PAC-C	Carbon-C	2016							
PAC-D	Carbon-D	2016	wood	Shirasagi	< 25	> 900	> 150	< 50	Osaka Chemical Co., Osaka, Japan
PAC-E	Carbon-E	2016	coal	6MD	< 25	> 900	> 150	< 50	Calgon Carbon Japan KK

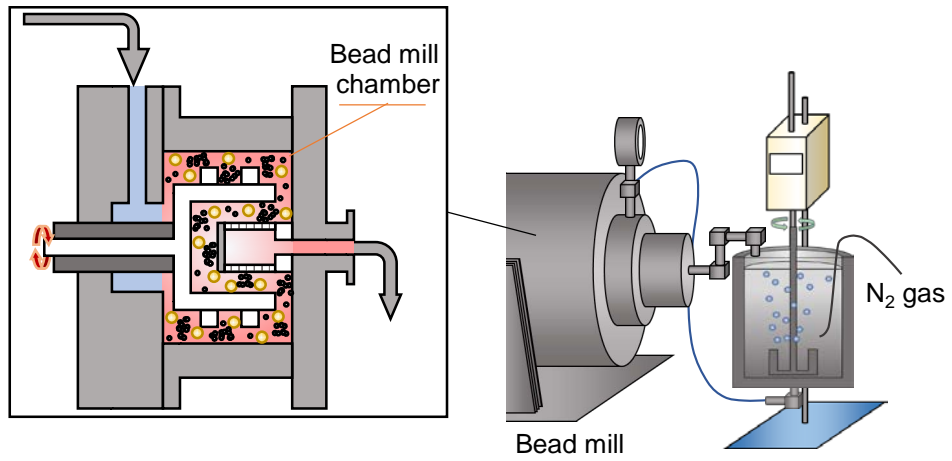


Fig. 1 – Schematic diagram of apparatus for bead milling under N₂.

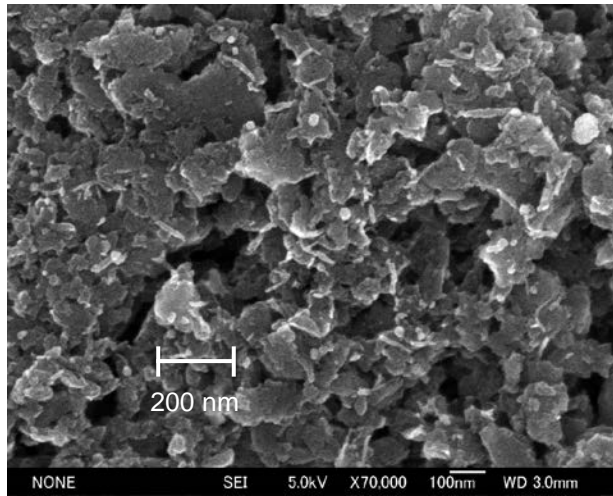
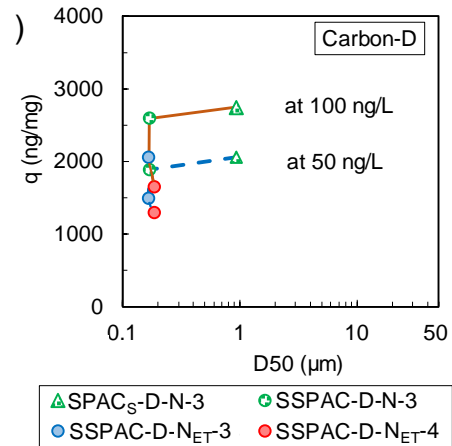
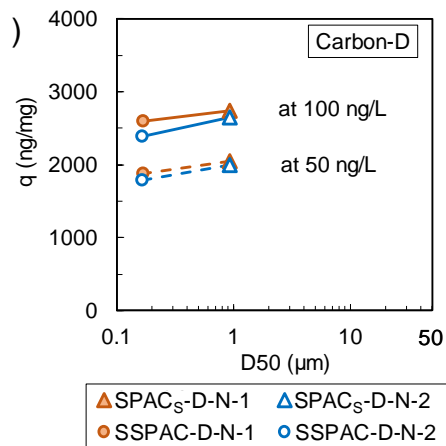
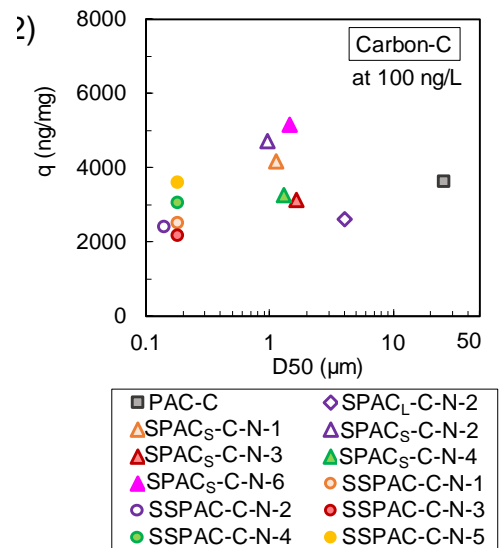
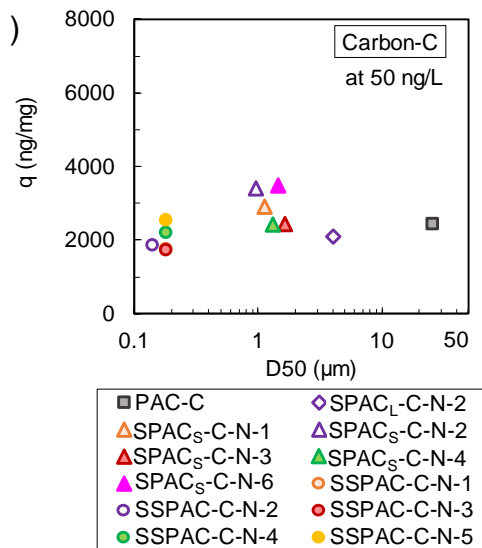
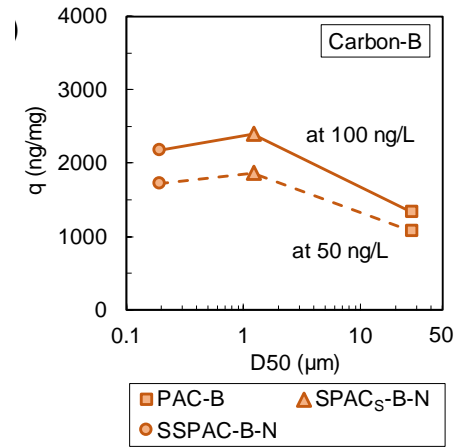
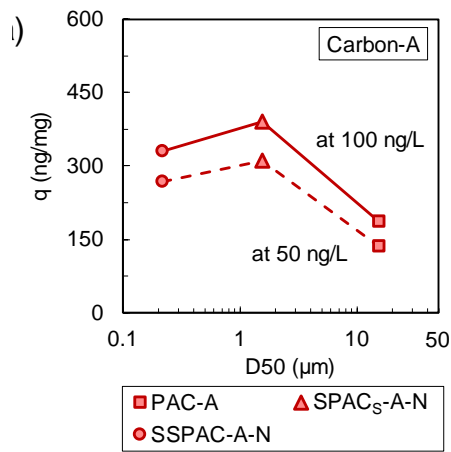


Fig. 2 – Scanning electron micrograph of SSPAC-B-N.



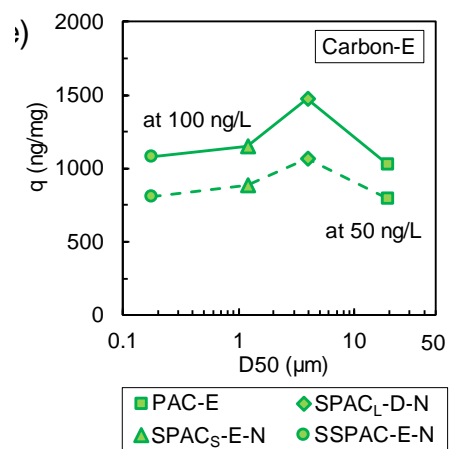


Fig. 3 – Plots of equilibrium MIB adsorption capacity versus AC particle size. Squares indicate PAC, diamonds indicate SPAC_L , triangles indicate SPAC_S , and circles indicate SSPAC. The adsorption capacities are given as solid-phase concentrations (q) at the equilibrium liquid-phase concentrations of 50 or 100 ng/L.

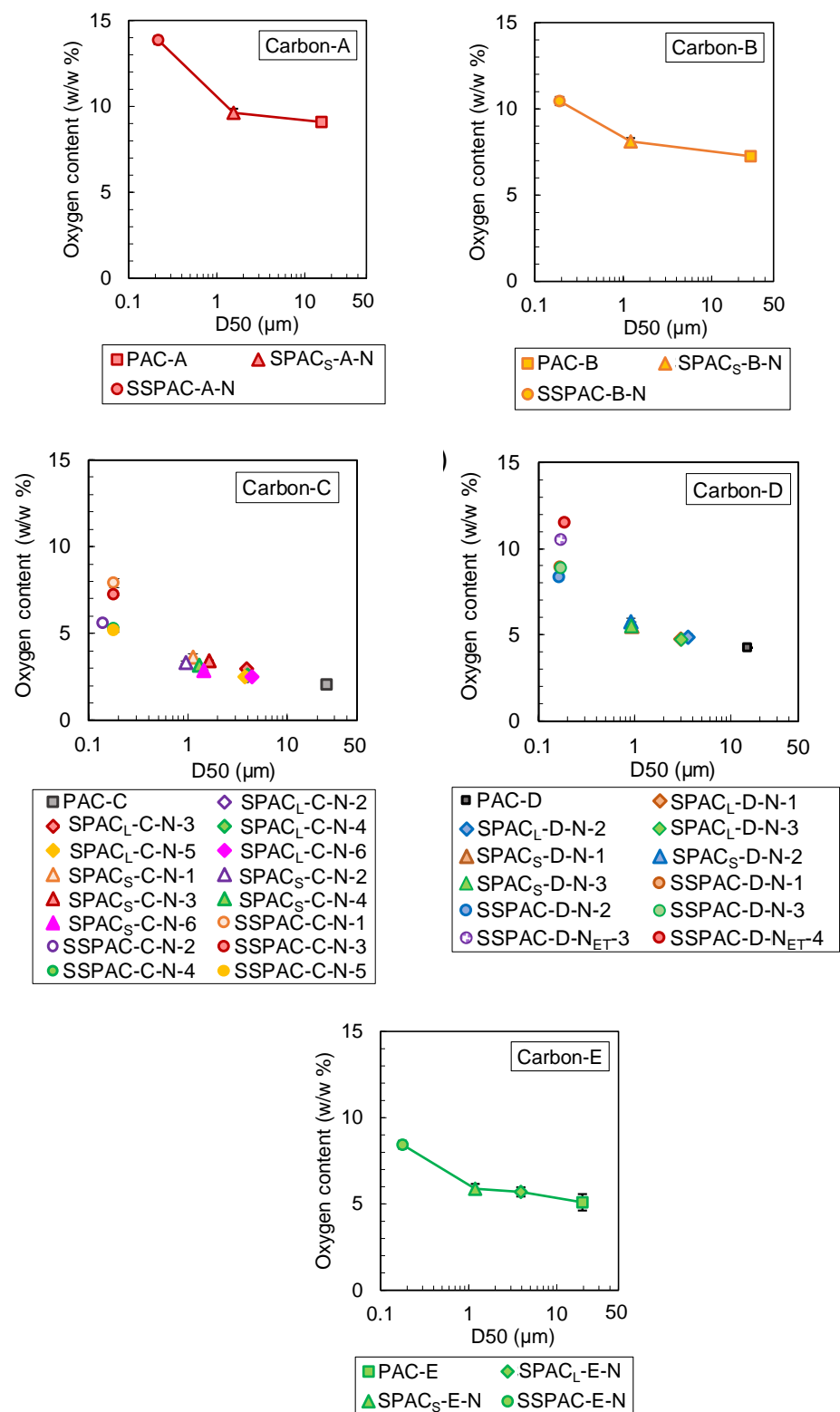


Fig. 4 – Plots of oxygen contents of Carbons A–E produced by normal milling versus AC particle size. Squares indicate PAC, diamonds indicate SPAC_L, triangles indicate SPAC_S, and circles indicate SSPAC. Error bars, which indicate standard deviation, are obscured by the symbols.

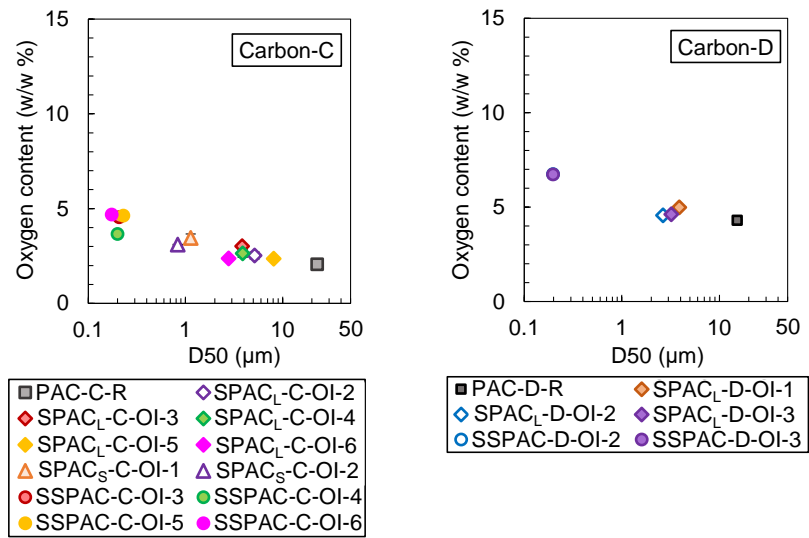


Fig. 5 – Plots of oxygen contents of Carbons C and D produced by oxidation-inhibiting milling versus AC particle size. Squares indicate PAC, diamonds indicate SPAC_L, triangles indicate SPAC_S, and circles indicate SSPAC. Error bars, which indicate standard deviation, are obscured by the symbols.

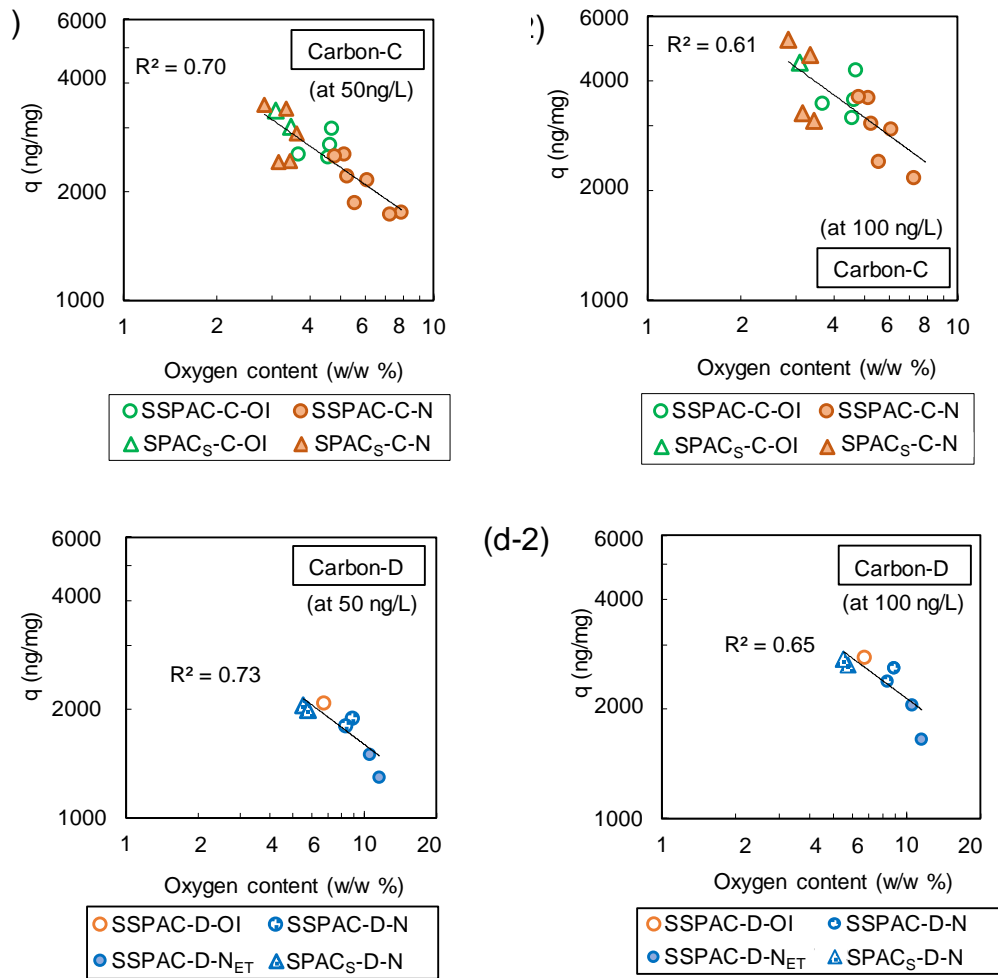


Fig. 6 – Correlation between MIB adsorption capacity and oxygen content. Triangles indicate SPAC_S, and circles indicate SSPAC.

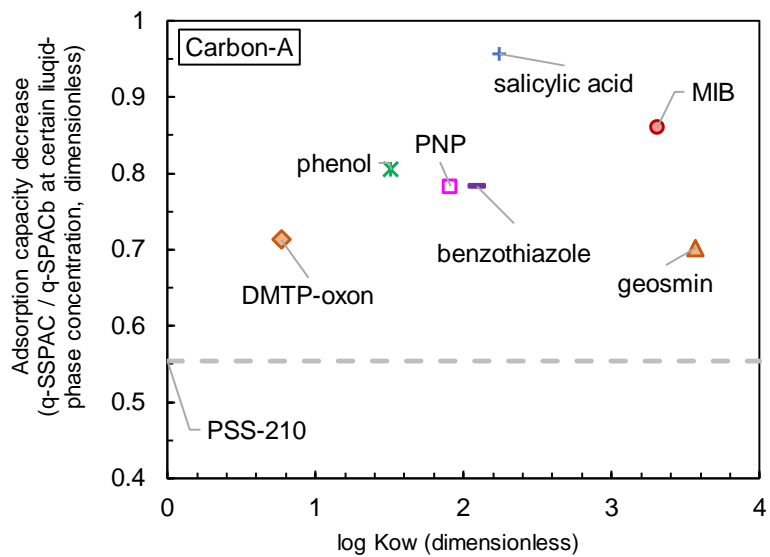


Fig. 7 – Plot of ratios of SPAC_s and SSPAC adsorption capacities versus adsorbate log Kow.

The adsorption capacities were quantified in terms of the solid-phase adsorbate concentrations at equilibrium liquid-phase concentrations: MIB and geosmin, 50 ng/L; DMTP-oxon, 5 µg/L; benzothiazole, phenol, *para*-nitrophenol (PNP), and salicylic acid, 0.5 mg/L; PSS-210, 2 mg/L. The ratio for PSS-210 is indicated by a dashed line because the log Kow is unavailable.

Supplementary Information

Effects of Decreasing Activated Carbon Particle Diameter from 30 μm to 140 nm on Equilibrium Adsorption Capacity

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Table S1 – Characteristics of normally milled PACs, SPACs, and SSPACs.

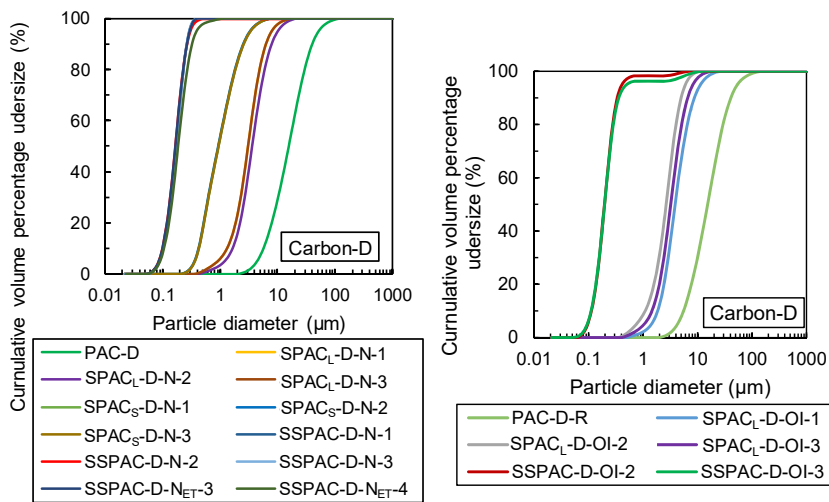
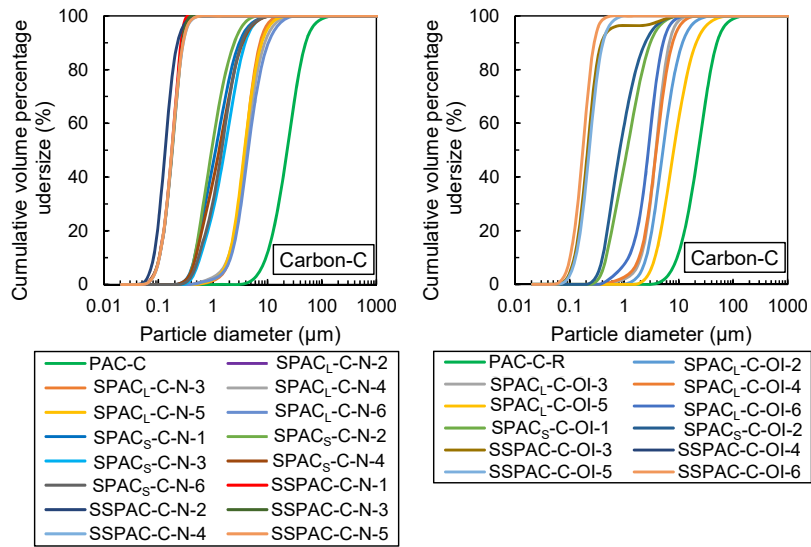
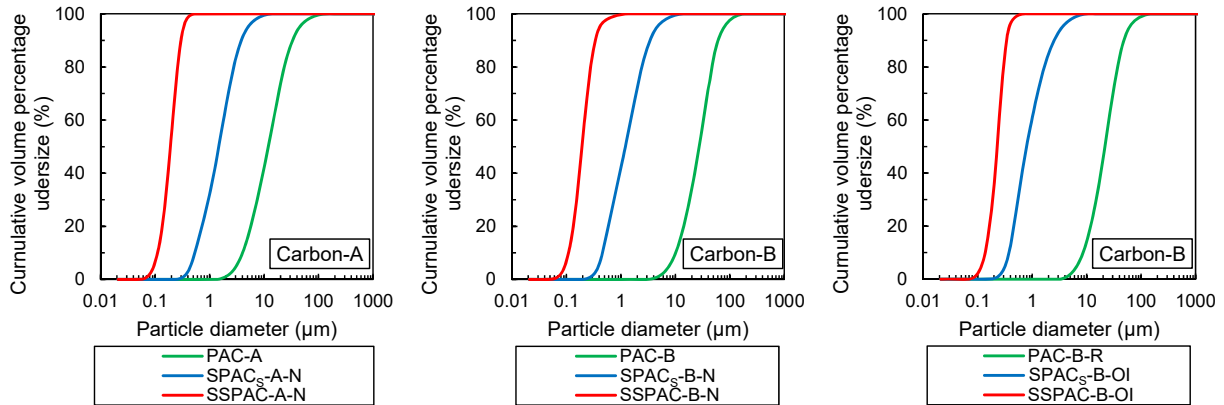
Designation	Median diameter D ₅₀ (µm)	Mill	Source carbon	Median diameter D ₅₀ (µm)	
SPAC _L -A-N	not measured	Ball mill	PAC-A	12.0	
SPAC _S -A-N	1.47	Bead mill	SPAC _L -A-N	not measured	
SSPAC-A-N	0.198		SPAC _S -A-N	1.47	
SPAC _L -B-N	3.85	Ball mill	PAC-B	27.5	
SPAC _S -B-N	1.21	Bead mill	SPAC _L -B-N	3.85	
SSPAC-B-N	0.194		SPAC _S -B-N	1.21	
SPAC _L -C-N-1	not measured	Ball mill	PAC-C	23.1	
SPAC _L -C-N-2	4.00				
SPAC _L -C-N-3	3.87				
SPAC _L -C-N-4	4.04				
SPAC _L -C-N-5	3.79				
SPAC _S -C-N-1	1.12	Bead mill	SPAC _L -C-N-1	not measured	
SPAC _S -C-N-2	0.949		SPAC _L -C-N-2	4.00	
SPAC _S -C-N-3	1.64		SPAC _L -C-N-3	3.87	
SPAC _S -C-N-4	1.30		SPAC _L -C-N-4	4.04	
SPAC _S -C-N-5	not measured		SPAC _L -C-N-5	3.79	
SPAC _S -C-N-6	1.45		SPAC _L -C-N-6	4.44	
SSPAC-C-N-1	0.176		SPAC _L -C-N-1	not measured	
SSPAC-C-N-2	0.137		SPAC _L -C-N-2	4.00	
SSPAC-C-N-3	0.179		SPAC _L -C-N-3	3.87	
SSPAC-C-N-4	0.177		SPAC _L -C-N-4	4.04	
SSPAC-C-N-5	0.177		SPAC _L -C-N-5	3.79	
SPAC _L -D-N-1	3.03		Ball mill	PAC-D	15.5
SPAC _L -D-N-2	3.57				
SPAC _L -D-N-3	3.00				
SPAC _S -D-N-1	0.927		Bead mill	SPAC _L -D-N-1	3.03
SPAC _S -D-N-2	0.915	SPAC _L -D-N-2		3.57	
SPAC _S -D-N-3	0.927	SPAC _S -D-N-3		3.00	
SSPAC-D-N-1	0.169	SPAC _L -D-N-1		3.03	
SSPAC-D-N-2	0.164	SPAC _L -D-N-2		3.57	
SSPAC-D-N-3	0.169	SPAC _S -D-N-3		3.00	
SSPAC-D-N _{ET} -3	0.168	SPAC _S -D-N-3		3.00	
SSPAC-D-N _{ET} -4	0.170	SPAC _S -D-N-3		3.00	
SPAC _L -E-N	3.90	Ball mill	PAC-E	19.5	
SPAC _S -E-N	1.19	Bead mill	SPAC _L -E-N	3.90	
SSPAC-E-N	0.177		SPAC _L -E-N	3.90	

Table S2 – Characteristics of PACs, SPACs, and SSPACs produced by rinsing with pure water (R) and by oxidation-inhibiting milling (OI).

Designation	Median diameter D ₅₀ (µm)	Milling system	Detail Production method			Source carbon
			Rotational speed (rpm)	Bead/ball diameter (mm)	Slurry volume (mL)	
PAC-B-R	21.7	no			PAC-B	
SPAC _L -B-OI	not measured	Ball mill – N ₂ filled	45	5 & 10	100	PAC-B-R
SPAC _S -B-OI	0.794	Bead mill – N ₂ purging	2590	0.3	400 - 500	SPAC _L -B-OI
SSPAC-B-OI	0.230			0.1		SPAC _L -B-OI
PAC-C-R	22.7	no			PAC-C	
SPAC _L -C-OI-1	not measured	Ball mill – N ₂ filled	45	5 & 10	100	PAC-C-R
SPAC _L -C-OI-2	5.15					
SPAC _L -C-OI-3	3.82					
SPAC _L -C-OI-4	3.88					
SPAC _L -C-OI-5	8.11					
SPAC _L -C-OI-6	2.78					
SPAC _S -C-OI-1	1.13	Bead mill – N ₂ purging	2590	0.3	400 - 500	SPAC _L -C-OI-1
SPAC _S -C-OI-2	0.831			0.1		SPAC _L -C-OI-2
SSPAC-C-OI-3	0.213			0.3		SPAC _L -C-OI-3
SSPAC-C-OI-4	0.200					SPAC _L -C-OI-4
SSPAC-C-OI-5	0.229			0.1		SPAC _L -C-OI-5
SSPAC-C-OI-6	0.174					SPAC _L -C-OI-6
PAC-D-R	15.3	no			PAC-D	
SPAC _L -D-OI-1	3.87	Ball mill – N ₂ filled	45	5 & 10	100	PAC-D-R
SPAC _L -D-OI-2	2.65					
SPAC _L -D-OI-3	3.21					
SSPAC-D-OI-2	0.197	Bead mill – N ₂ purging	2590	0.1	400 - 500	SPAC _L -D-OI-2
SSPAC-D-OI-3	0.197					SPAC _L -D-OI-3

Table S3 – Composition of the working solution.

Ion	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ³⁻	SO ₄ ²⁻	Alkalinity
Concentration (mg/L)	19	3.1	24	18	31	6.9	14	50



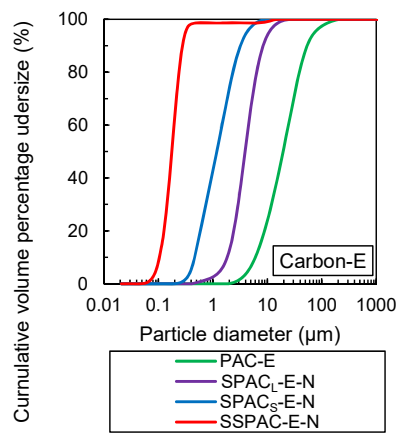
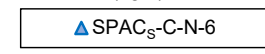
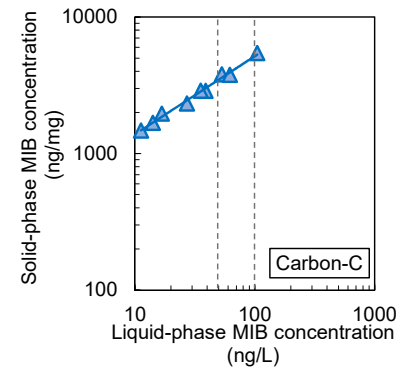
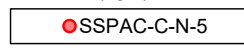
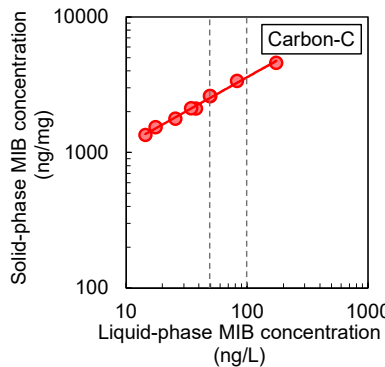
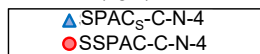
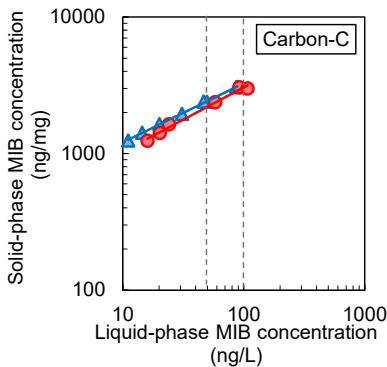
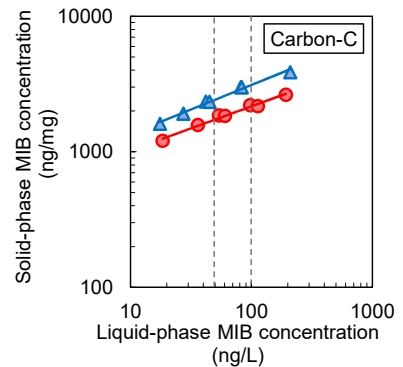
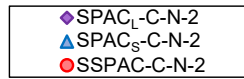
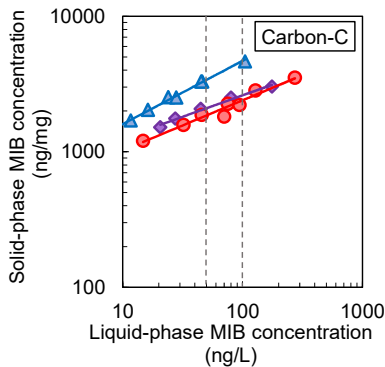
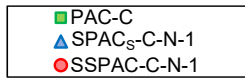
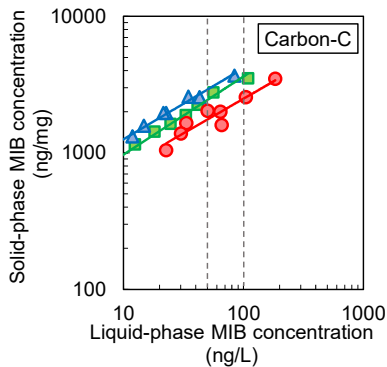
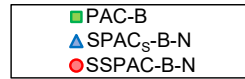
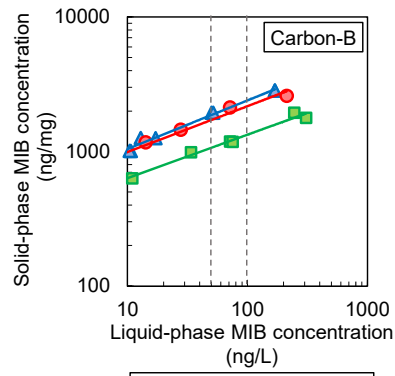
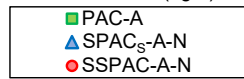
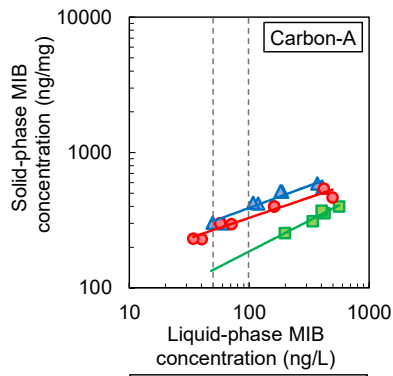


Fig. S1 – Particle size distributions of PACs, SPACs, and SSPACs.



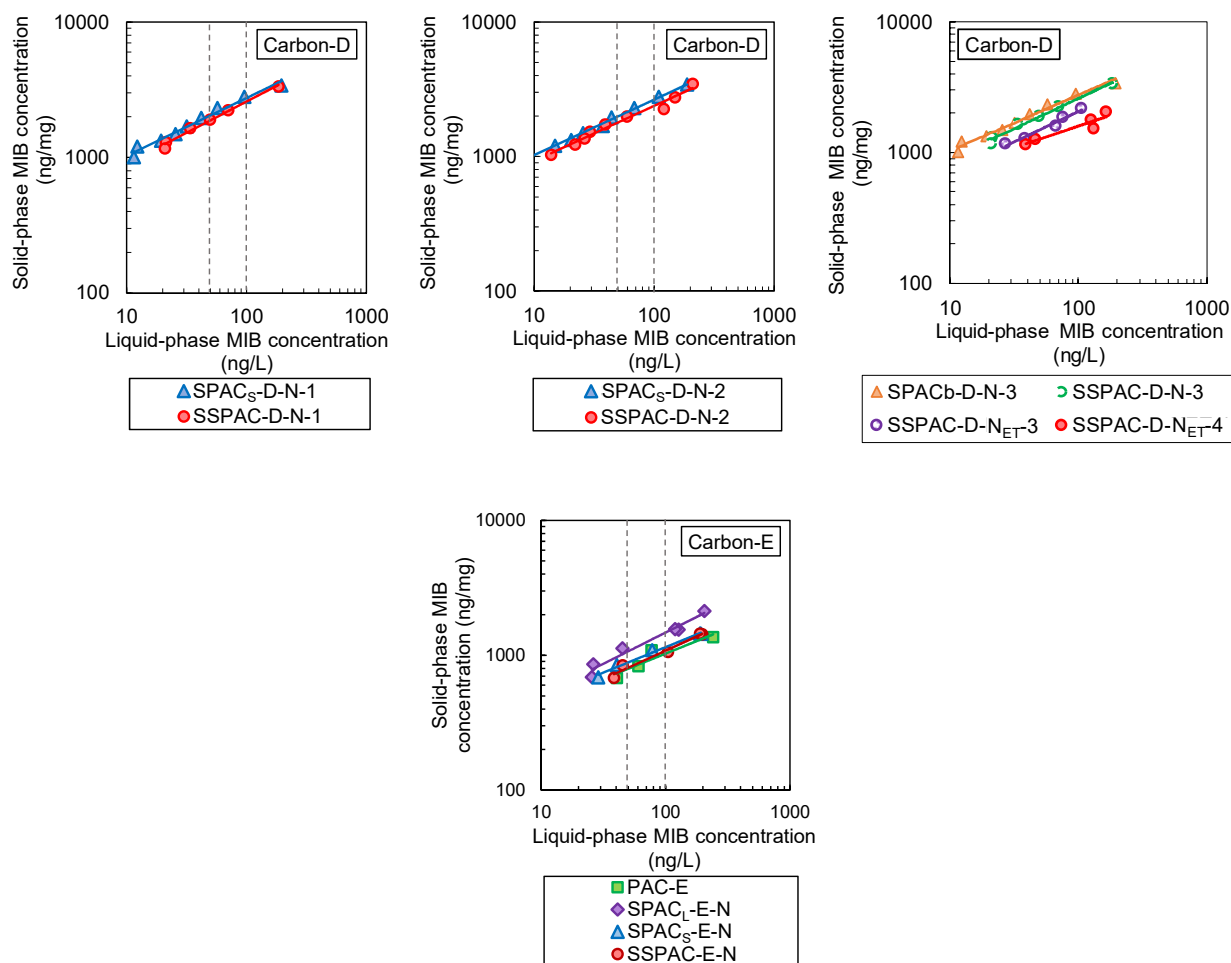


Fig. S2 – MIB adsorption isotherms for Carbons A–E. Squares indicate PAC, diamonds indicate SPAC_L, triangles indicate SPAC_s, and circles indicate SSPAC.

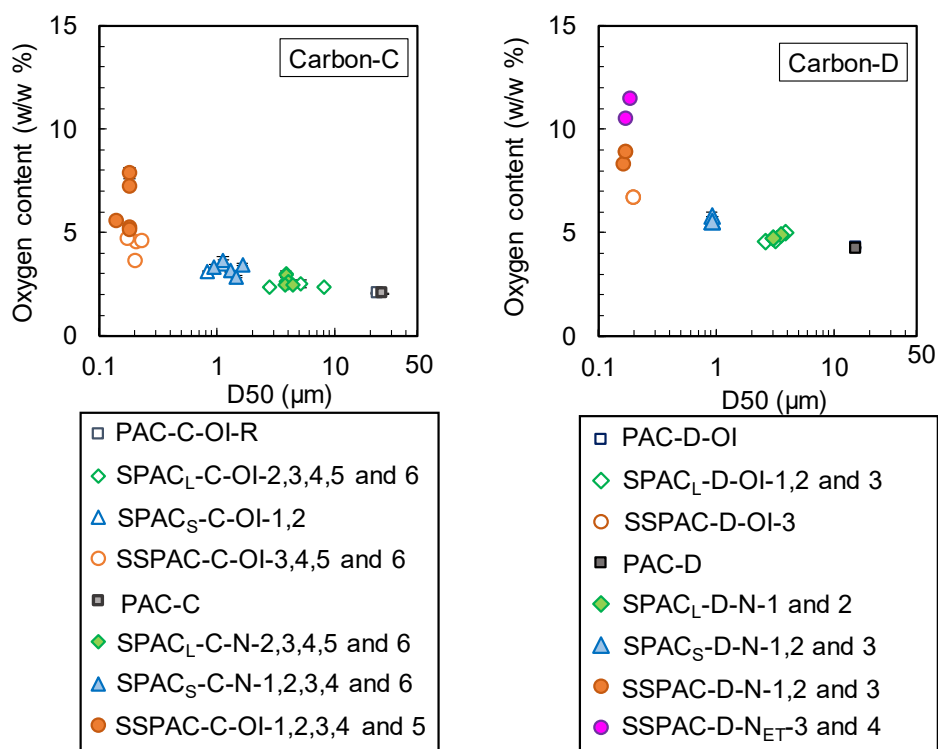


Fig. S3 –Plots of oxygen contents of Carbons C and D produced by normal and oxidation-inhibiting millings versus AC particle size. Squares indicate PAC, diamonds indicate SPACL, triangles indicate SPACS, and circles indicate SSPAC. Closed plots indicate carbons produced by normal milling and open plots indicate those by oxidation-inhibiting milling. Error bars, which indicate standard deviation, are obscured by the symbols.

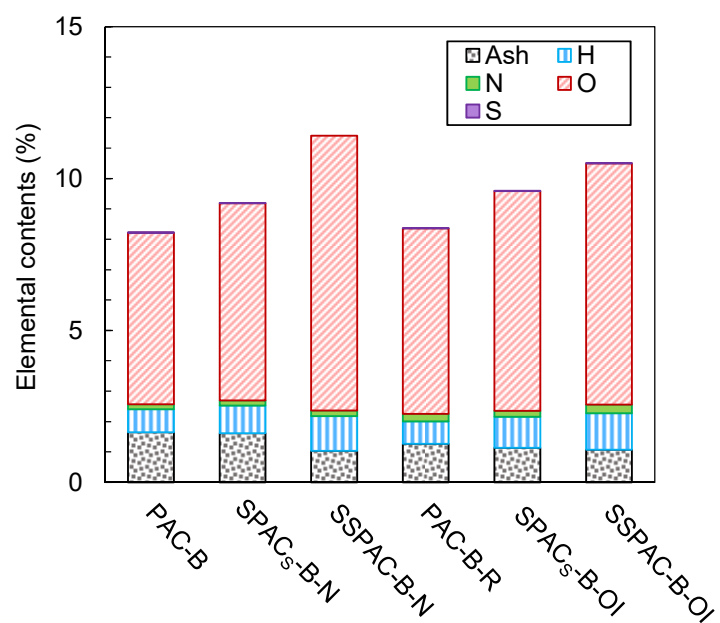


Fig. S4 – Hydrogen, nitrogen, sulfur, oxygen, and ash contents of Carbons-B produced by normal milling and oxygen-inhibiting milling.

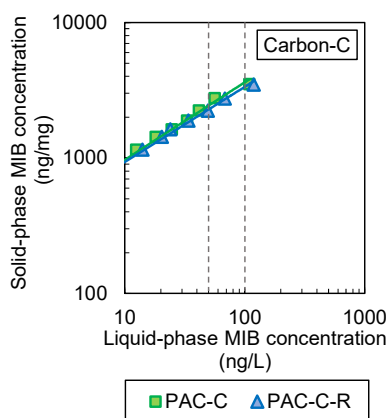


Fig. S5 – MIB adsorption isotherms of PAC-C-N and PAC-C-R (produced by rinsing PAC-C-N with pure water).

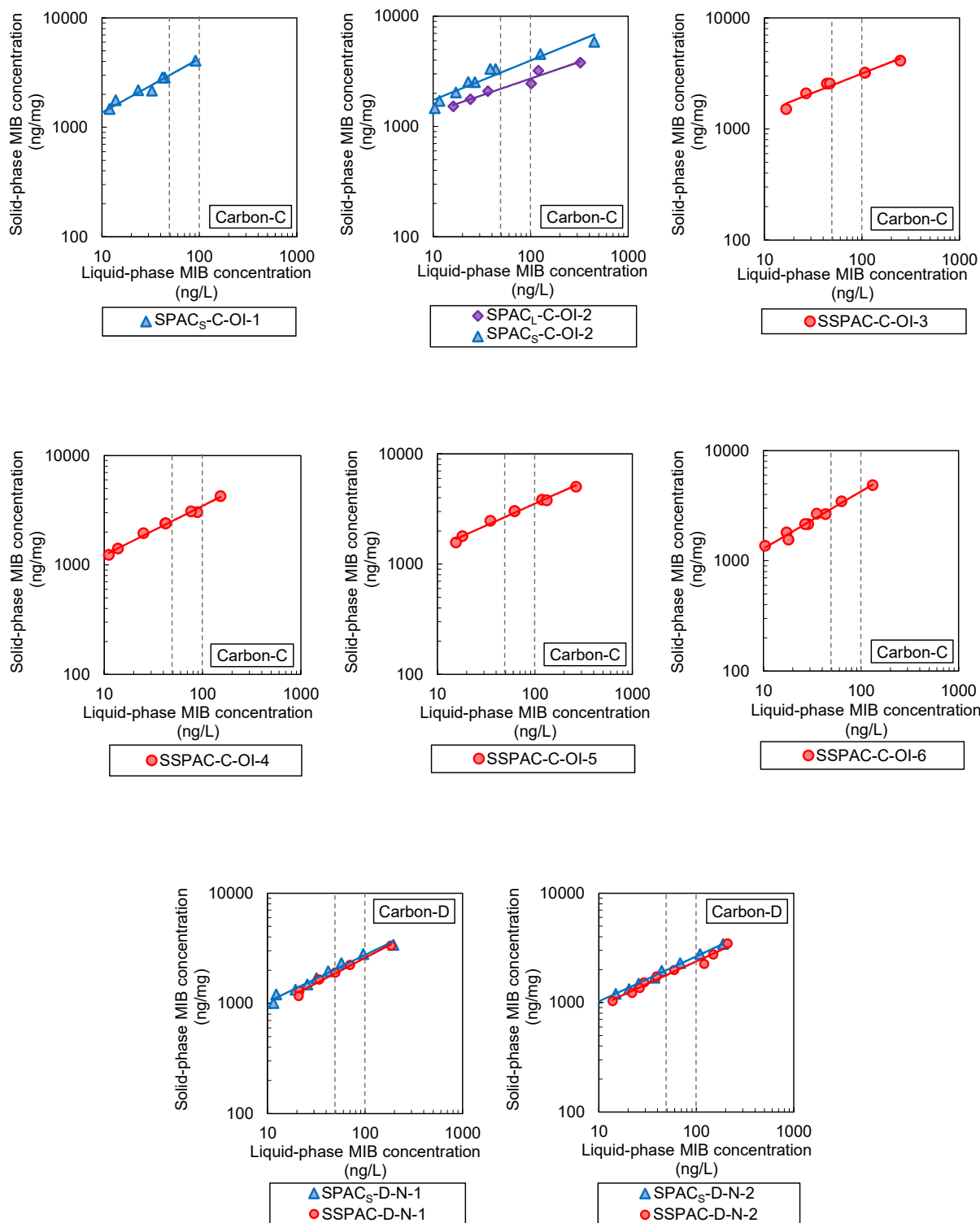
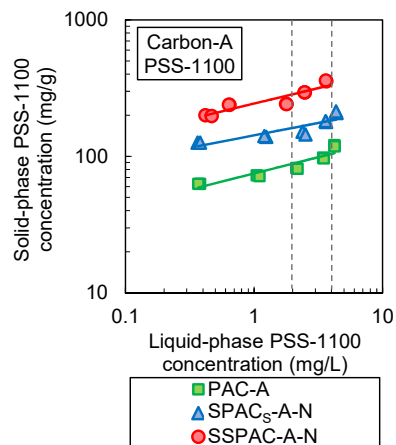
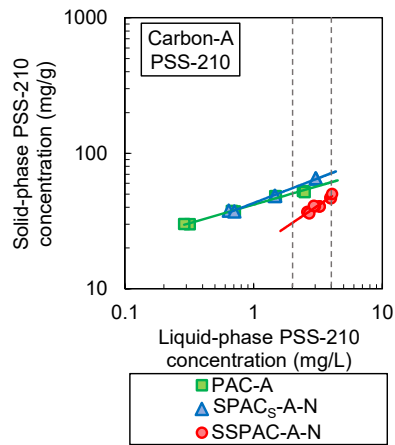
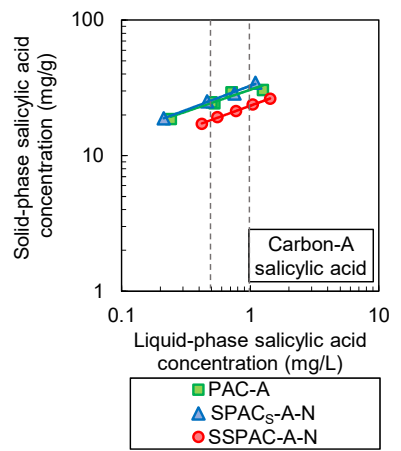
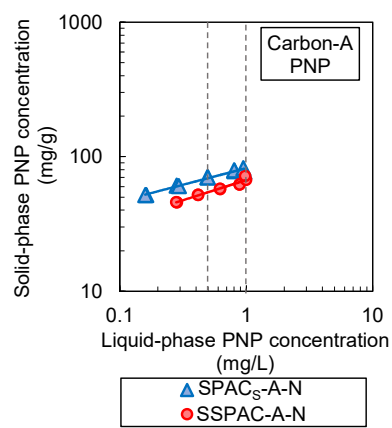
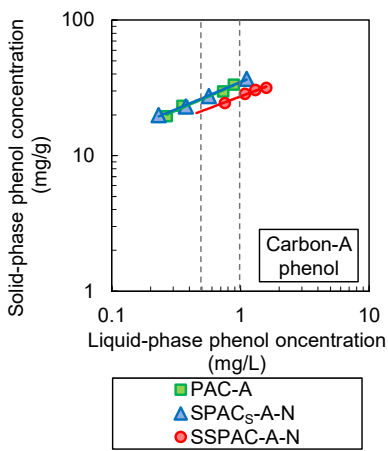
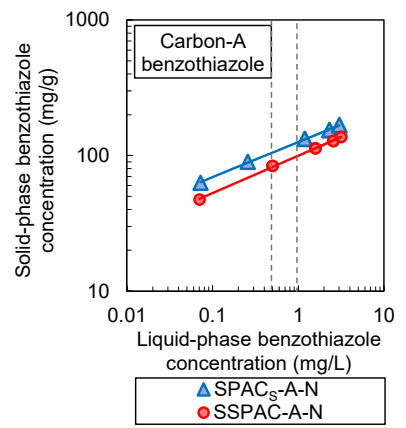
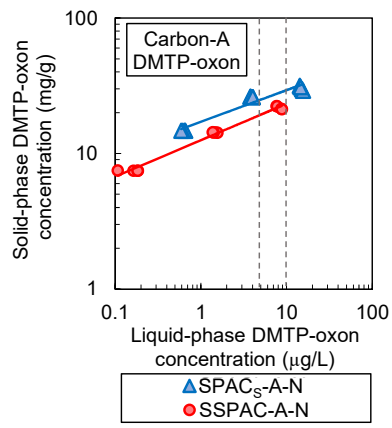
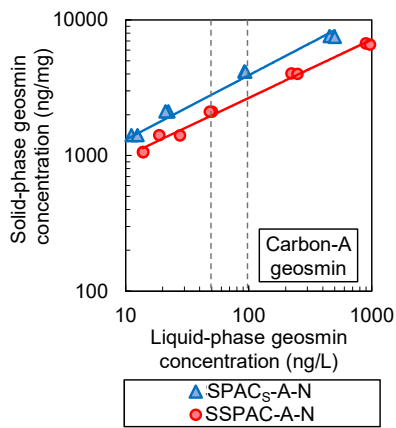


Fig. S6 – MIB adsorption isotherms for SPAC_L, SPAC_s, and SSPAC prepared from Carbons C and D by oxidation-inhibiting milling. Diamonds indicate SPAC_L, triangles indicate SPAC_s, and circles indicate SSPAC.



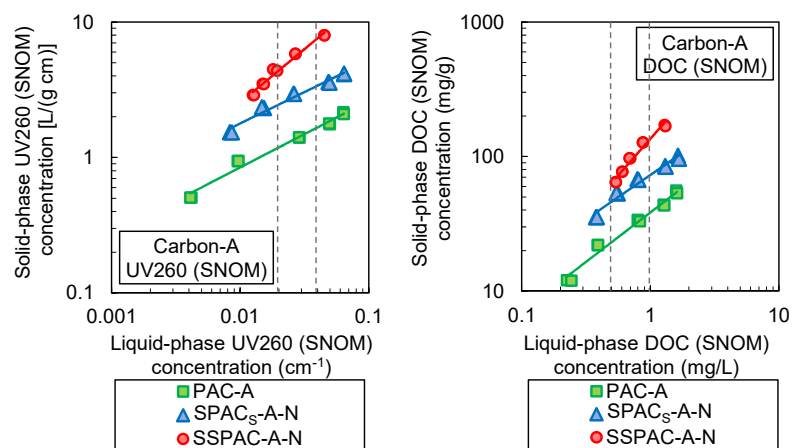
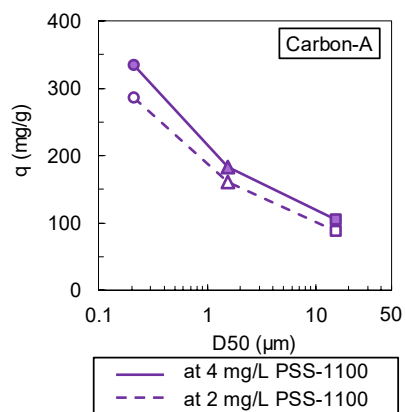
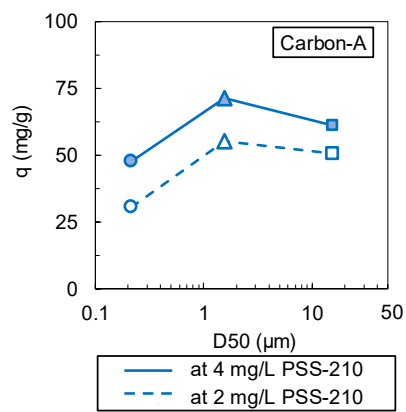
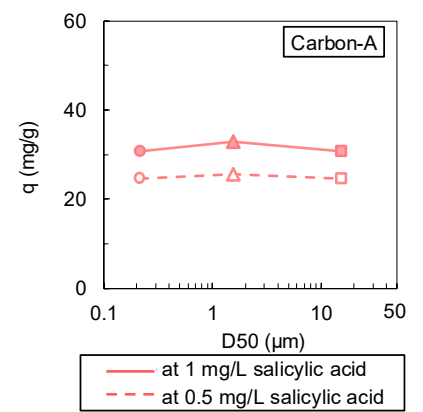
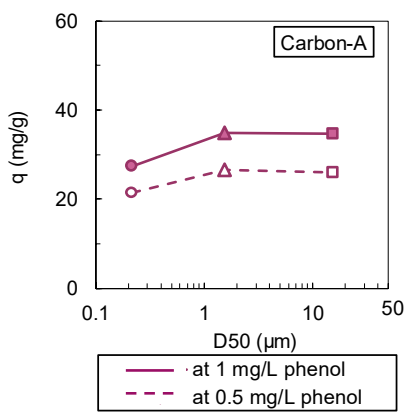
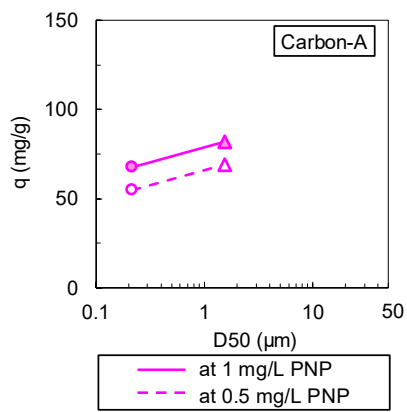
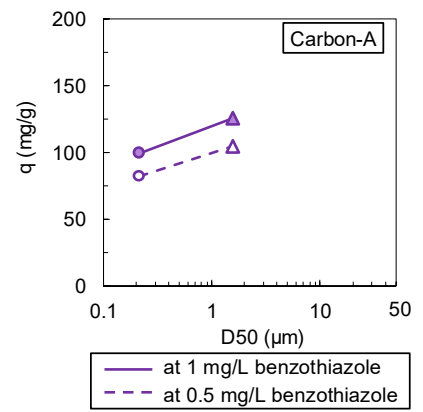
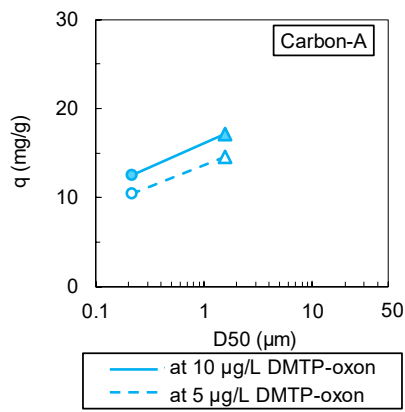
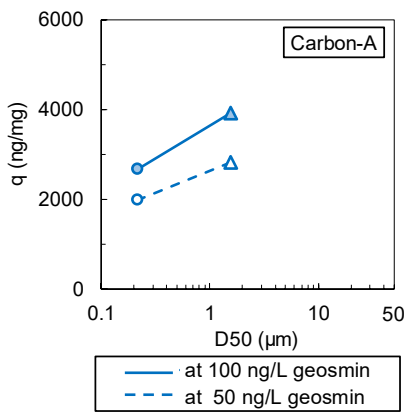


Fig. S7 – Isotherms for adsorption of 9 adsorbates on Carbons A. Squares indicate PAC, triangles indicate SPAC_s, and circles indicate SSPAC.



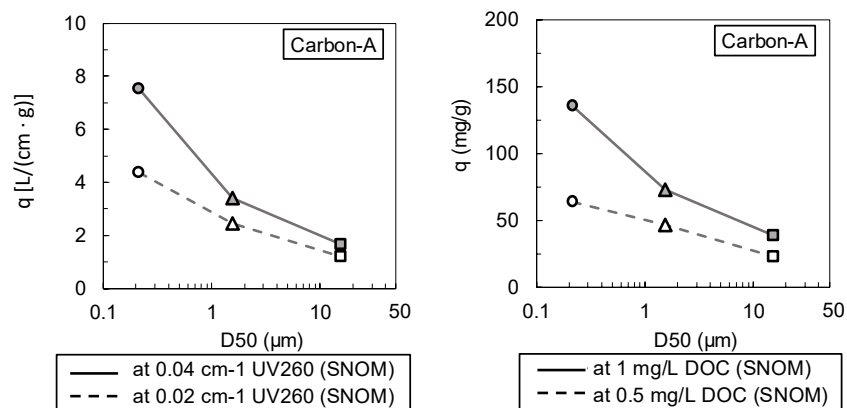
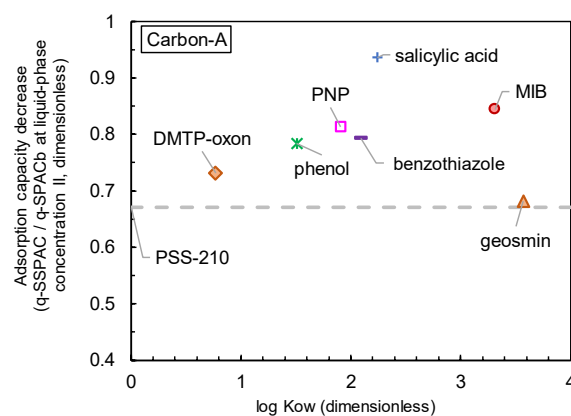
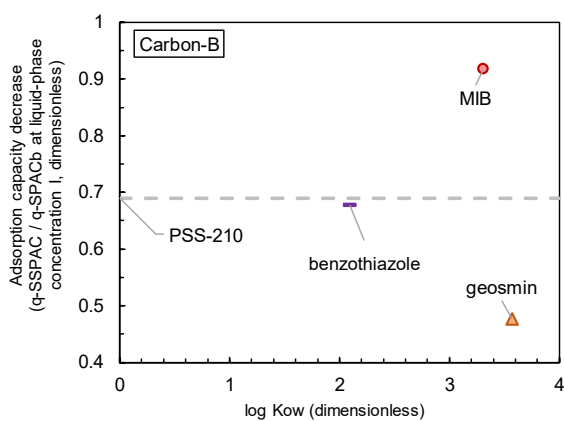


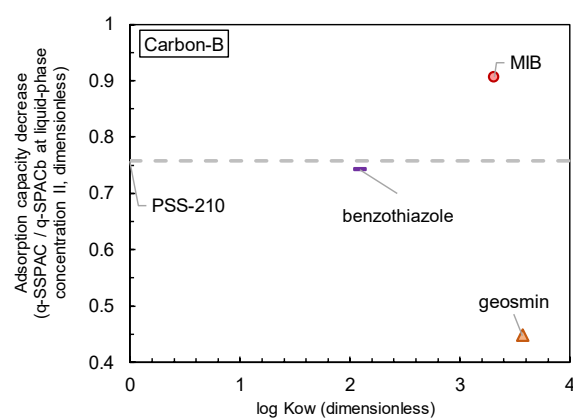
Fig. S8 – Plots of equilibrium adsorption capacity versus particle size (Carbon A) for 9 adsorbates. Squares indicate PAC, triangles indicate SPACs, and circles indicate SSPAC.



(a)



(b-1)



(b-2)

Fig. S9 – Plots of ratios of SPACs and SSPAC adsorption capacities versus adsorbate log Kow.

Adsorbate concentrations I and II (panels b-1 and b-2, respectively): MIB and geosmin, 50 and 100 ng/L; DMTP-oxon, 5 and 10 $\mu\text{g/L}$; benzothiazole, phenol, *para*-nitrophenol (PNP), and salicylic acid, 0.5 and 1 mg/L; PSS-210, 2 and 4 mg/L. The ratios for PSS-210 are indicated by the dashed lines because the log Kow value is unavailable.