



Title	Stray particles as the source of residuals in sand filtrate : Behavior of superfine powdered activated carbon particles in water treatment processes
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1 **Stray particles as the source of residuals in sand filtrate: Behavior of**  
2 **superfine powdered activated carbon particles in water treatment processes**

3

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14

15

16 **Abstract**

17 Although superfine powdered activated carbon has excellent adsorption properties, it is not  
18 used in conventional water treatment processes comprising coagulation–flocculation,  
19 sedimentation, and sand filtration (CSF) due to concerns about its residual in treated water.  
20 Here, we examined the production and fate of very fine carbon particles with lacking in  
21 charge neutralization as a source of the residual in sand filtrate after CSF treatment. Almost  
22 all of the carbon particles in the water were charge-neutralized by coagulation treatment with  
23 rapid mixing, but a very small amount ( $\leq 0.4\%$  of the initial concentration) of very fine carbon  
24 particles with a lesser degree of charge neutralization were left behind in coagulation process.  
25 Such carbon particles, defined as stray carbon particles, were hardly removed by subsequent  
26 flocculation and sedimentation processes, and some of them remained in the sand filtrate. The  
27 concentration of residual carbon particles in the sand filtrate varied similarly with that of the  
28 stray carbon particles. The stray and residual carbon particles were similarly smaller than the  
29 particles before coagulation treatment, but the residual carbon particles had less charge  
30 neutralization than the stray carbon particles. The turbidity of water samples collected after  
31 sedimentation was not correlated with the residual carbon concentration in the sand filtrate,  
32 even though it is often used as an indicator of treatment performance with respect to the  
33 removal of suspended matter. Based on these findings, we suggest that reduction of the  
34 amount of stray particles should be a performance goal of the CSF treatment. Examining this  
35 concept further, we confirmed that the residence time distributions in the coagulation and  
36 flocculation reactors influenced the concentration of stray carbon particles and then the  
37 residual carbon particle concentration in sand filtrate, but found that the effect was dependent  
38 on coagulant type. A multi-chambered-reactor configuration lowered both the stray carbon  
39 particle concentration after coagulation treatment and the residual carbon particle  
40 concentration in sand filtrate compared with a single-chambered reactor configuration. When  
41 a normal basicity PACl that consisted mainly of monomeric Al species was used, the stray  
42 carbon particle concentration was decreased during coagulation process and then gradually  
43 decreased during subsequent flocculation process because the monomeric Al species were  
44 transformed to colloidal Al species via polymeric Al species. In contrast, when a high-basicity  
45 PACl that consisted mostly of colloidal Al species was used, coagulation treatment largely  
46 decreased the stray carbon particle concentration, which did not decrease further during  
47 subsequent flocculation process. These findings will be valuable for controlling residual  
48 carbon particles after the CSF treatment.

49  
50

51 **Keywords**

52 SPAC; PACl; aluminum species; filtration; turbidity

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54

## **Research highlights**

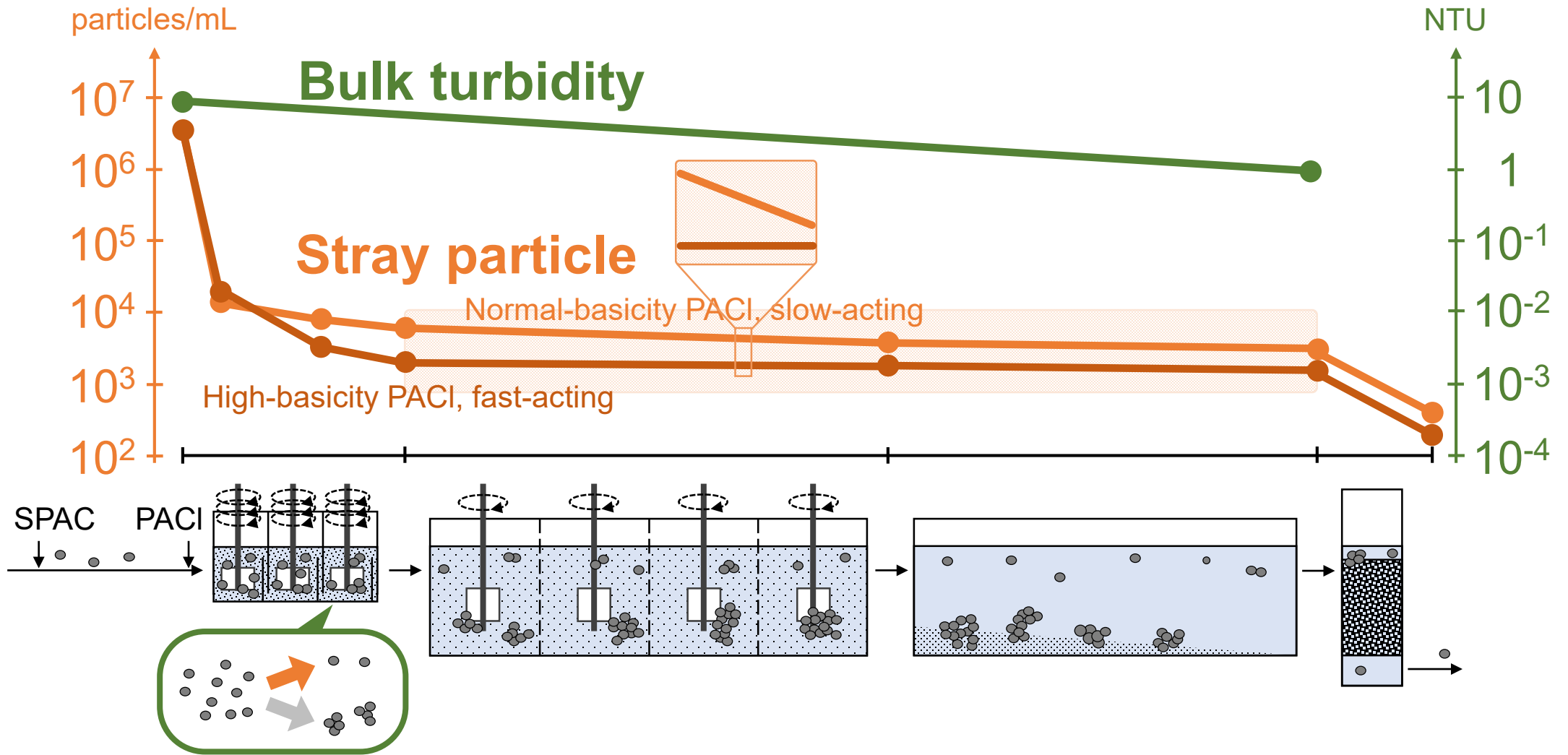
A very small portion ( $\leq 0.4\%$ ) of influent SPAC were left behind in coagulation

These stray particles drastically decreased only during early stage of coagulation

They barely decrease during flocculation to sedimentation and reside in sand filtrate

Stray particles had smaller size and less charge neutralization

Measures to effectively reduces stray particles were discussed



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53

54 **1. Introduction**

55 Superfine powdered activated carbon (SPAC; median diameter, approx. 1  $\mu\text{m}$ ) shows  
56 excellent adsorption performance for organic molecules and is drawing attention from  
57 researchers and practitioners as a very effective adsorbent for use in water and wastewater  
58 treatment processes (Amaral *et al.* 2016, Apul *et al.* 2017, Ateia *et al.* 2019, Bonvin *et al.*  
59 2016, Decrey *et al.* 2020, Matsui *et al.* 2013, Murray *et al.* 2019, Partlan *et al.* 2020). Some  
60 full-scale water purification plants that use membrane filtration processes are already using  
61 SPAC as an adsorbent (Kanaya *et al.* 2015); however, it is not yet used at plants that use  
62 conventional coagulation–flocculation, sedimentation, and sand filtration (CSF) processes.  
63 This is because there are concerns that the use of SPAC may result in the finished water’s  
64 containing a larger concentration of residual carbon particles than the concentration that  
65 would result from use of conventionally sized powdered activated carbon (PAC; median  
66 diameter, approx. 15  $\mu\text{m}$ ) had been used (Nakazawa *et al.* 2018a).

67  
68 Several studies have been conducted on the removal of activated carbon particles during CSF  
69 processes. These studies have focused mainly on particle charge neutralization, the size and  
70 growth of floc particles, and the reduction of turbidity after sedimentation and filtration with  
71 respect to the use of PAC. For example, it has been reported that the addition of PAC  
72 followed by alum coagulation increases turbidity after sedimentation and increases the size  
73 and growth rate of floc particles compared to use of only alum coagulation (Huang *et al.*  
74 2020). Similarly, it has been reported that the addition of PAC followed by  $\text{FeCl}_3$  coagulation  
75 decreases floc particle size but leaves the turbidity after sedimentation relatively unchanged  
76 compared with treatment with  $\text{FeCl}_3$  alone (Younker and Walsh 2016). Furthermore, the use  
77 of SPAC induces the formation of larger floc particles than use of PAC (Matsui *et al.* 2009).  
78 Thus, these studies have demonstrated how floc particles are formed by coagulation and  
79 flocculation, and how the coagulation and flocculation processes proceed, so that particles in  
80 raw water can be easily removed by sedimentation after coagulation and flocculation.

81  
82 However, few studies have focused on the residual particles remaining in treated water after  
83 sedimentation and filtration. If we examine the size distribution of floc particles (Hu *et al.*  
84 2013, Sun *et al.* 2016, Zhang *et al.* 2008), it may be possible to determine the amount of  
85 residual particles. However, such residual particles are present in only very small  
86 concentrations at the very extreme ends of the size distribution, making them difficult to be  
87 determined using particle distribution data (Lee *et al.* 2009, Yu *et al.* 2015). Indeed, it has  
88 been reported that under optimized CSF conditions, very few SPAC particles remain in sand  
89 filtrate (only  $10^{-5}$  to  $10^{-6}$  of the particles before treatment) (Nakazawa *et al.* 2018b). In this  
90 context, some studies on residual particles have been carried out using microscopy. Aguilar *et al.*  
91 (2003) report that the elimination efficiency of particulate matter is increased if PAC is  
92 dosed before coagulation process compared to without the use of PAC; however, they also  
93 reported that some carbon particles in the size range of 5.5–8.5  $\mu\text{m}$  remained in the treated  
94 water (Aguilar *et al.* 2003).

95



96 If coagulation and flocculation are performed well, there should be few residual particles in  
97 the treated water. That is because proper coagulation and flocculation results in the formation  
98 of large floc particles with good settling properties and water with low turbidity after settling  
99 and filtration. However, recent studies have shown that although carbon particles in raw water  
100 are effectively charge neutralized by coagulation treatment, resulting in good floc formation,  
101 some carbon particles still persist in the sand filtrate and that these particles lack charge  
102 neutralization (Nakazawa et al. 2018a, Nakazawa et al. 2018b). This suggests that although  
103 the size and settleability of floc particles and the persistence of residual particles in sand  
104 filtrate are determined by the performance of the coagulation–flocculation process, they  
105 reflect the results of different aspects of the process and are not necessarily interrelated.

106

107 Here, we assumed that two types of particles are formed after coagulation: those that can  
108 grow into floc particles due to adequate charge neutralization during the coagulation process,  
109 and those that cannot grow into floc particles due to insufficient charge neutralization. We  
110 then examined the behavior of the latter particles, which were referred as stray particles in this  
111 paper, during the CSF process with respect to the amount of residual carbon particles in sand  
112 filtrate at the end of the treatment process. The effects of coagulation and flocculation reactor  
113 configuration, as well as the type and dose of coagulant used, on the removal of SPAC  
114 particles were also investigated.

115

## 116 **2. Materials and methods**

117

### 118 *2.1. Coagulants and activated carbon particles*

119 Two kinds of commercially available poly-aluminum chloride (PACl), provided by Taki  
120 Chemical Co., Ltd. (Hyogo, Japan), were used as coagulants: PACl-70 (basicity,  
121 2.1; %basicity, 70%; sulfate ion, 2.2 wt%) and PACl-50 (basicity, 1.5; %basicity, 50%;  
122 sulfate ion, 2.9 wt%). The Al speciation (Ala, monomeric Al species; Alb, polymeric Al  
123 species; and Alc, colloidal species) distributions of the PACls were determined by the Ferron  
124 method (Wang *et al.* 2004), which uses the difference in reaction time with Ferron reagent (8-  
125 hydroxy-7-iodoquinoline-5-sulfonic acid; Fujifilm Wako Pure Chemical Corporation, Osaka,  
126 Japan) to distinguish between the different Al species. The procedure of Kimura *et al.* (2013)  
127 was applied, as described in the Supplementary Information (SI).

128

129 SPAC was prepared in our laboratory by wet ball milling (Nikkato, Osaka, Japan) for 6 h  
130 followed by wet bead milling for 30 min (LMZ015; Ashizawa Finetech, Ltd., Chiba, Japan),  
131 as summarized in the SI and described in detail elsewhere (Pan *et al.* 2017). The  
132 concentrations and particle sizes of carbon particles in water samples obtained from the CSF  
133 experiment were determined by membrane filtration (nominal pore diameter, 0.1  $\mu\text{m}$ ;  $\Phi$ 25  
134 mm; polytetrafluoroethylene; Merck KGaA, Darmstadt, Germany) and microscopic image  
135 analysis (1000 $\times$  magnification; VHX-2000; Keyence Corporation, Osaka, Japan), as  
136 summarized in the SI and described in detail elsewhere (Nakazawa et al. 2018a).

137

138 2.2. *Flow-through reactor tests of coagulation–flocculation, sedimentation, and rapid sand*  
139 *filtration*

140 A series of flow-through mode CSF tests were performed using a bench-scale CSF plant  
141 comprising five components: preparation unit, rapid mixing unit for coagulation, slow mixing  
142 unit for flocculation, sedimentation unit, and sand filter (Fig. 1 and Table S1). The rapid  
143 mixing unit constituted a single-chambered reactor or a 3-chambered-reactor with three  
144 equally-sized chambers; the two reactors had the same total hydraulic retention time (HRT) of  
145 100 s. The slow mixing unit constituted a single-chambered reactor or a 4-chambered reactor,  
146 both with four mixing impellers and the same total HRT of 2400 s. Regardless of reactor  
147 configuration, rapid mixing for coagulation was conducted at a fixed mixing intensity (G  
148 value: velocity gradient) of  $600\text{ s}^{-1}$  for 100 s, and slow mixing for flocculation was conducted  
149 at a fixed G value of  $12.5\text{ s}^{-1}$  for 2400 s. Residence time distributions of the reactors were  
150 measured via a step tracer test using NaCl as the tracer and conductivity detection (Crittenden  
151 *et al.* 2012). To prevent the effects of wind and temperature-induced density current, the  
152 bench-scale CSF plant was installed in a constant-temperature room with no wind, and the  
153 water temperature was kept at the same as the room temperature.

154  
155 Toyohira River water, collected at the Moiwa Water Purification Plant, Sapporo, Japan  
156 (hereafter ‘River water 1’), was used as the raw water. We also used dechlorinated Sapporo  
157 municipal water (Municipal waters 1–3 and 5–7; Table S2) because only a limited volume of  
158 River water was available. Raw water was pumped into the first mixing chamber of the  
159 preparation unit, and SPAC was added in the second mixing chamber at a concentration of 2  
160 mg/L ( $3\text{--}5 \times 10^6$  particles/mL), which is a typical dose when SPAC is used as an adsorbent  
161 (Matsui *et al.* 2007). After the addition of NaOH or HCl to adjust the pH to 7.0, a coagulant  
162 (PACl) was injected into the coagulation reactor at a dose of 1.5 mg-Al/L, unless otherwise  
163 noted; the dose was predetermined to bring the settling turbidity down to less than 2 NTU.  
164 After coagulation–flocculation, the water flowed through a sedimentation reactor, which had a  
165 HRT of 65 min. After sedimentation, the supernatant flowed to a sand filter. Sand filtration  
166 was conducted at a rate of 90 or 150  $\text{m d}^{-1}$  using a 4-cm diameter column filled with sand  
167 (effective diameter, 0.94 mm; uniformity, 1.24; Nihon Genryo Co., Ltd., Japan) to a depth of  
168 50 cm.

169  
170 2.3. *Batch tests of coagulation–flocculation*

171 Three series of batch tests were conducted to examine the removal of SPAC by coagulation–  
172 flocculation, measure the zeta potential of the carbon particles, and examine changes in the  
173 aluminum species distribution during coagulation–flocculation.

174  
175 To examine SPAC coagulation–flocculation, 1 L of dechlorinated municipal drinking water  
176 (Municipal water 1; Table S2) or Wanigawa River water (Ibaraki, Japan; hereafter ‘River  
177 water 2’; Table S2), was transferred to a rectangular beaker, supplemented with SPAC at a  
178 concentration of 2 mg/L, and used for the tests. After adding NaOH (0.05 N) to bring the pH  
179 to 7.0, one of the PACls (1.5 mg-Al/L) was injected, and the water was subjected to rapid

180 mixing ( $G = 600 \text{ s}^{-1}$ ) for coagulation; samples of the water were collected at predetermined  
181 times and used for analysis. In some tests, after the rapid mixing for 100 s, the water was  
182 subjected to slow mixing ( $G = 12.5 \text{ s}^{-1}$ ) to flocculation.

183  
184 To measure zeta potentials, raw water (Municipal water 4; Table S2) was treated as described  
185 above, but PACl doses of 1.5 and 2.0 mg-Al/L were used. At 100 s from the start of rapid  
186 mixing, a 55-mL sample of water was collected and used for the measurement of the zeta  
187 potential (Zetasizer Nano ZS; Malvern, United Kingdom) of the carbon particles; 10 mL was  
188 used immediately for the measurement of zeta potential, and the remaining 45 mL was used  
189 after being subjected to centrifugal separation (see Section 2.4).

190  
191 To examine the changes in the aluminum species distributions, raw water (Municipal water 1)  
192 was treated as described above, but after adding NaOH to bring the pH to 7.0, one of the  
193 PACls was injected at a concentration of 270 mg-Al/L. Rapid mixing ( $G = 381 \text{ s}^{-1}$ ) was then  
194 conducted without SPAC. Immediately after sampling at predetermined times, the water was  
195 used for Ferron analyses with a glass cell (optical path length, 10 cm). The municipal water  
196 itself had little effect on the absorbance determined by Ferron analysis (blank test, data not  
197 shown).

198  
199 *2.4. Collection of stray particles by centrifugation*

200 In the water samples collected during rapid and slow mixing processes in the flow-through  
201 reactor tests and batch tests, particles that had not settled after centrifugation were considered  
202 to be stray particles. The centrifuge procedure was as follows. Aliquots (45 mL) of a single  
203 water sample were dispensed into four 50-mL glass tubes. The tubes were centrifuged by  
204 using a centrifuge (CT6E; Koki Holdings Co., Ltd., Tokyo, Japan) equipped with a swing  
205 rotor (T5SS; Koki Holdings Co., Ltd.). Centrifugation was carried out at 4800 rpm (3990g)  
206 for 10 min, halted, and then re-started for 20, 35, or 50 min (total time, 30, 45, and 60 min,  
207 respectively). The reason for the double centrifugation is discussed in Section 3.2. Thereafter,  
208 the concentrations of carbon particles in the centrifugal supernatant were determined by  
209 membrane filtration and microscopic image analysis (SI).

## 210 211 **3. Results and Discussion**

212  
213 *3.1. Residual carbon particles after treatment with a bench-scale CSF plant*

214 First, we examined the residual carbon particle concentration in sand filtrate with increasing  
215 filtration time using a bench-scale CSF plant, a SPAC dose of 2 mg/L, and PACl-70 as the  
216 coagulant at 1.5 or 2.25 mg-Al/L (Fig. 2). At each time point examined, the residual carbon  
217 particle concentration was lower when the higher concentration of coagulant was used than  
218 when the lower concentration was used. Irrespective of coagulant dose, the residual carbon  
219 particle concentration started high and then decreased with increasing filtration time until a  
220 steady state was reached at less than 200 particles/mL; this particle concentration is similar to  
221 that reported for a full-scale CSF water purification plant using PAC (Kobayashi *et al.* 2019).

222 The high concentration of particles during the initial period of filtration was not due to  
223 residual backwash water remaining in the filter because the filter media was washed with pure  
224 water (Milli-Q Advantage A10 System; Merck KGaA) during the final washing process.  
225 Therefore, we concluded that the filter underwent a ‘ripening’ process, which is when clean  
226 sand media captures particles that cause the filter to become more efficient at capturing  
227 additional particles over time (Crittenden et al. 2012).

228  
229 Although a clear decrease in residual carbon particle concentration was observed as the filter  
230 ripened, no clear change in the particle size distribution of the residual particles was observed  
231 (range, 0.3–2  $\mu\text{m}$ ; Fig. S1). Therefore, the increased removal of carbon particles with  
232 increasing filtration time was not related to the particle size of the carbon particles. In  
233 conjunction with our previously reported finding that the carbon particles remaining in sand  
234 filtrate had a higher negative charge than the carbon particles entering the sand filter  
235 (Nakazawa et al. 2018a), we interpreted this increased removal efficacy as follows. The sand  
236 filter treats the sedimentation supernatant, which contains particles with varying degrees of  
237 charge neutralization. Clean sand media has a high negative charge (Edzwald 2011), so the  
238 charge-neutralized particles attach to the surface of the sand particles and remain in the sand  
239 filter. In contrast, the less-charge-neutralized particles are unable to attach to the sand  
240 particles due to repulsive forces and therefore exit the filter. However, as the filter ripens by  
241 the accumulation of charge-neutralized particles, the ability of the less-charge-neutralized  
242 particles to attach to the immobilized charge-neutralized particles results in increased removal  
243 efficacy over time. To examine the role of particle attachment in more detail, we conducted  
244 experiments at two different filtration rates (Fig. S2) under the assumption that the filtration  
245 mechanism comprises two steps: transport, where suspended particles are transported to the  
246 surface of sand grains, and attachment, where the particles attach to the sand grains (Edzwald  
247 2011). In our experiments, we observed that the higher filtration rate resulted in higher  
248 particle concentrations in the filtrate, suggesting that the higher filtration velocity resulted in  
249 decreased attachment efficiency [the number of particle sand-grain adhesions divided by the  
250 number of particle sand-grain collisions (Crittenden et al. 2012)] of the carbon particles to the  
251 filter.

### 252 253 *3.2. Stray particles as the source of the residual particles*

254 As discussed in the previous section, less-charge-neutralized carbon particles with a size of  
255 0.3–2  $\mu\text{m}$  remained in the sand filtrate. We assumed that such particles were particles that had  
256 not reacted with the coagulant during the coagulation–flocculation process (we named these  
257 particles ‘stray particles’) and then evaded being captured by the filter media. Based on this  
258 assumption, we next examined the relationship between residual carbon particle concentration  
259 and stray carbon particle concentration to see whether the stray carbon particle concentration  
260 could be used as an index of residual carbon particle concentration. In addition, we examined  
261 the effect of coagulant dose on the stray carbon particle concentration and the residual carbon  
262 particle concentration in sand filtrate. To do these, we determined the stray particle

263 concentration in the centrifuged supernatant of water samples collected after coagulation  
264 treatment.

265

266 First, however, we optimized the conditions used for centrifugal separation. In test trials, we  
267 found that preliminary centrifugation for 10 min was sufficient to allow large floc particles to  
268 settle. We also found that adhesion to the centrifuge tube wall could be minimized by  
269 conducting a second centrifugation after the preliminary centrifugation. In centrifugal  
270 separation, a brake is usually applied to stop the rotation of the centrifuge. However, we  
271 found that small amounts of the particles were re-suspended by this braking operation.  
272 Therefore, we minimized the re-suspension of particles by waiting for the rotation to stop  
273 naturally. We also examined how total centrifugation time (the total time for both  
274 centrifugation stages) affected residual carbon particle concentration in the supernatant (Fig.  
275 S3). We found that the residual carbon particle concentration after centrifugal separation  
276 markedly decreased when the centrifuge time was extended from 30 to 45 min, but that it did  
277 not further decrease when the time was extended to 60 min. We also found that the particle  
278 concentration after centrifugation for 45 min did not vary depending on coagulant dose (Fig.  
279 S3b), even though we found that the particle concentration in sand filtrate did vary (Fig. S4).  
280 Based on our findings, we used a centrifugal separation time of 30 min to determine stray  
281 particle concentrations in the subsequent experiments.

282

283 The stray carbon particles and the residual carbon particles were similarly smaller than the  
284 particles before the CSF treatment (Fig. S5). The concentrations were decreased with  
285 increasing PACl dosage (Fig. 3a). In addition, the stray particle concentration was found to be  
286 highly correlated with residual carbon particle concentration in the sand filtrate ( $R^2 = 0.89$ ,  
287 square of Pearson's correlation coefficient). Thus, the stray particle concentration of the  
288 supernatant, which was determined after centrifugation for 30 min, was considered an index  
289 of the residual particle concentration in the sand filtrate. Furthermore, we found that the  
290 concentration of stray particles decreased during coagulation with rapid mixing. After  
291 coagulation, the concentration of stray particles (maximum,  $1.5 \times 10^4$  particles/mL, Fig. 3a)  
292 was less than 0.4% that of the initial suspension before coagulation ( $3\text{--}5 \times 10^6$  particles/mL).  
293 We also examined the correlation between the residual carbon particle concentration in the  
294 sand filtrate and the turbidity of settled water, which is conventionally used as an indicator of  
295 treatment performance with respect to the removal of suspended matter, but we found a lower  
296 correlation ( $R^2 = 0.72$ ) than that found for stray particle concentration (Fig. 3). Thus, stray  
297 particle concentration obtained by centrifugation was considered a better index of residual  
298 particle concentration than was the turbidity of water. It is important to note here that stray  
299 particle concentration was measured at an early stage of the CSF process (after coagulation),  
300 whereas turbidity was measured later in the process (after coagulation–flocculation and  
301 sedimentation). This suggests that the performance of the coagulation treatment, but not of the  
302 flocculation and sedimentation treatment, is the major determinant of the concentration of  
303 residual particles remaining after sand filtration. This is discussed further in Section 3.3.

304

305 Next, we examined the zeta potentials of bulk particles and stray particles in water samples  
306 collected after coagulation (Fig. 4). The bulk particles were charged-neutralized and had zero  
307 or only a slightly positive/negative charge. In contrast, the stray particles, which were only a  
308 portion of these particles, had a negative charge. This finding that the stray particles had less  
309 charge neutralization was similar to the previous researches. Ding *et al.* (2016) report that  
310 meso-particles (20 nm–0.5  $\mu$ m) remained with less charge-neutralization in comparison with  
311 the larger floc particles when surface water was treated by coagulation. Yu *et al.* (2015) report  
312 that the zeta potential of the remaining flocs became more negative after sedimentation  
313 process. A similar phenomenon was also observed for the residual carbon particles in the sand  
314 filtrate, which had less charge neutralization compared with the bulk particles sampled after  
315 coagulation (Nakazawa *et al.* 2018a), although the zeta potentials of the stray particles showed  
316 that they had a less-negative charge than did the residual carbon particles. This is thought to  
317 be because most of the stray particles with less-negative charges are preferentially removed  
318 by the sand filter, as will be discussed in section 3.5.

319  
320 Together, these findings further support the idea that stray carbon particles are the main  
321 source of the residual carbon particles in sand filtrate. This suggests that coagulation–  
322 flocculation treatments should be optimized not only to decrease settling turbidity via the  
323 formation of large-size floc particles but also to reduce the number of stray particles.

### 324 325 *3.3. Effect of mixing reactor configuration on the concentrations of stray particles and* 326 *residual particles*

327 From the results presented in the previous section, it was found that the concentrations of  
328 stray particles and residual carbon particles varied depending on the coagulant dose. However,  
329 even if a sufficient amount of coagulant is used, if the mixing is inappropriate, a large number  
330 of stray particles may be generated due to a lack of opportunities for the particles and  
331 coagulant to come into contact. Indeed, Nakazawa *et al.* (2018b) have reported that the  
332 concentration of residual particles after filtration varied with the intensity and time of mixing  
333 during coagulation treatment, though the concentration of stray particles are not measured.  
334 Another important mixing condition is the distribution of residence time. The experiments of  
335 Nakazawa *et al.* (2018b) were conducted as batch tests, which results in a constant and  
336 uniform residence time. However, actual water treatment systems use a continuous flow  
337 reactor, which results in a residence time that varies. In other words, even if the average  
338 residence time is long enough, if the residence time has a wide variance over time, the fact  
339 that some particles may not have sufficient opportunity to come into contact with the  
340 coagulant can result in the formation of stray particles (Bratby 2006, Crittenden *et al.* 2012).

341  
342 Thus, in the present study, we used flow-through reactors with different set-ups to investigate  
343 the effect of mixing reactor configuration on stray particle concentration. In these experiments,  
344 a single-chambered reactor or a 3-chambered reactor, with the same total HRT and same size  
345 impellers (one per chamber), was used for coagulation treatment with rapid mixing. In  
346 addition, a single-chambered reactor or a 4-chambered reactor, with the same total HRT and

347 same total number of impellers with the same size and rotational speed, was used for  
348 flocculation with slow mixing. According to the residence time distributions determined for  
349 the coagulation and flocculation reactors (Figs. S6 and S7), the proportion of the distributions  
350 indicating a short residence time (less than half of the HRT) was larger for the single-  
351 chambered reactor than for the 3- or 4-chambered reactors.

352  
353 First, we examined the effect of coagulation reactor (rapid mixing unit) configuration on  
354 residual carbon particle concentration in sand filtrate. Although the single-chambered reactor  
355 and the 3-chambered reactor had the same mixing intensity (G value) and HRT, a lower  
356 residual carbon particle concentration was obtained with the 3-chambered reactor than with  
357 the single-chamber reactor (Fig. 5a and Fig. S8). This suggests that the different residence  
358 time distributions of the two types of reactor influenced the residual carbon particle  
359 concentration in the sand filtrate. The same trend was observed for stray particle  
360 concentrations in water sampled at the end of flocculation: use of the single-chambered  
361 coagulation reactor resulted in a higher stray particle concentration (Fig. 5b). Thus, when a  
362 large proportion of the residence time distribution included short residence times, which was  
363 observed in the distribution for the single-chambered reactor (Fig. S6 and Fig. S7), the stray  
364 particle concentration was increased, which subsequently increased the residual carbon  
365 particle concentration in the sand filtrate.

366  
367 Next, we examined the effect of flocculation reactor (slow mixing unit) configuration on  
368 residual carbon particle concentration in sand filtrate (Fig. 6a and Fig. S9). The 4-chambered  
369 reactor resulted in a lower residual particle concentration in the sand filtrate than the single-  
370 chambered reactor when PACI-50 was used as the coagulant. The same trend was observed  
371 for stray particle concentration in water sampled at the end of flocculation treatment (Fig. 6b).  
372 However, when PAC-70 was used, this trend was not observed, because flocculation with  
373 slow mixing did not reduce the stray particle concentration, as discussed in the next section.

374  
375 When the residual carbon particle concentration in sand filtrate was plotted against the stray  
376 particle concentration in water sampled after flocculation treatment (slow mixing), a strong  
377 positive correlation was observed ( $R^2 = 0.96$ , Fig. 7a). This supports our finding that stray  
378 particle concentration can be used as an index of residual particle concentration in sand  
379 filtrate, and that such particles are the origin of the residual carbon particles. We also  
380 examined the correlation between the residual carbon particle concentration in sand filtrate  
381 and the stray particle concentration in water collected after coagulation treatment (rapid  
382 mixing), but a correlation was lower ( $R^2 = 0.70$ ; Fig. 7b). We concluded that this was because  
383 the stray particle concentration was changed slightly during the flocculation process after  
384 PACI-50 coagulation, as discussed in the next section. Similarly, we examined the correlation  
385 between the residual carbon particle concentration in sand filtrate and the turbidity of settled  
386 water sampled after sedimentation. The turbidity of settled water was not correlated with  
387 residual carbon particle concentration in sand filtrate ( $R^2 = 0.15$ ; Fig. 7c), although the  
388 turbidity of settled water was found to also be influenced by the residence time distribution of

389 the coagulation and flocculation reactors (Fig. S10). We concluded that turbidity was not an  
390 index of the residual carbon particle concentration in the sand filtrate.

391

### 392 *3.4. Effect of PACl type on stray particle concentration after coagulation and flocculation*

393 The stray particle concentration was markedly decreased during coagulation treatment but left  
394 unchanged or slightly decreased by flocculation treatment (Fig. 8). More specifically, stray  
395 particle concentration was decreased by flocculation treatment with a 4-chambered-reactor  
396 slow-mixing when PACl-50, but not clearly PACl-70, was used as the coagulant. To further  
397 examine why the behavior of the stray particles during the flocculation treatment differed  
398 depending on the coagulant used, we conducted a series of batch experiments. As shown in  
399 Fig. 9, the stray carbon particles behaved differently during coagulation and flocculation  
400 depending on which coagulant was used. When PACl-70 was used, the stray particle  
401 concentration was high during the initial 20 s of rapid mixing for coagulation and was  
402 markedly decreased at 100 s of rapid mixing. During the subsequent slow mixing for  
403 flocculation, the concentration remained unchanged. This trend was also held for raw water  
404 with high NOM (natural organic matter) concentration (DOC: 3.8 mg/L), though stray particle  
405 concentrations were generally high due to the consumption of coagulant by NOM (DOC after  
406 SPAC dose was 3.7 mg/L and DOC after SPAC and coagulant doses was 2.5 mg/L) (Bratby  
407 2006). In contrast, when PACl-50 was used, the stray particle concentration was lower at 20 s  
408 of rapid mixing compared with that when PACl-70 was used, and it then gradually decreased  
409 until the end of slow mixing.

410

411 We also examined the relationship between the behavior of the stray carbon particles and the  
412 distributions of the aluminum species derived from the coagulants. Fig. 10 shows the changes  
413 in the Al species distributions for PACl-70 and PACl-50 during rapid mixing ( $G = 381 \text{ s}^{-1}$ )  
414 and slow mixing ( $G = 8 \text{ s}^{-1}$ ). The stock solution of PACl-50 contained 42% Ala, 23% Alb,  
415 and 35% Alc. When PACl-50 was added to water and hydrolyzed, almost no Ala remained at  
416 20 s from the beginning of rapid mixing, and the amount of Alb increased to become the  
417 dominant species. Alb remained the dominant species until the second half of the slow mixing.  
418 In contrast, the stock solution of PACl-70 contained 25% Ala, 14% Alb, and Alc, 61%. When  
419 PACl-70 was added to water and hydrolyzed, as for PACl-50, almost no Ala remained at 20 s  
420 from the beginning of rapid mixing. However, unlike for PACl-50, Alc remained the  
421 dominant species throughout the rapid and slow mixing processes.

422

423 Considering that PACl-70 markedly decreased the concentration of stray particles within  
424 several tens of seconds from the beginning of rapid mixing, unlike PACl-50, the present data  
425 suggest that the reactive hydrolysis product formed from Alc contributed to the rapid decrease  
426 of stray particles after only a short period of mixing. However, the stray particle concentration  
427 was not decreased further after rapid mixing, probably because the reactive hydrolysis product  
428 was fast-acting but unstable, which could easily transform into unreactive products, although  
429 the unreactive product was still categorized as Alc. When using PACl-70, rapid dispersion of  
430 the short-lived reactive hydrolysis product formed from Alc may be key for reducing the



431 number of stray particles. This interpretation is consistent with our previously reported  
432 finding that PACI-70 needs rapid, intense mixing to reduce the concentration of residual  
433 particles after CSF (Nakazawa et al. 2018b).

434

435 In contrast to PACI-70, PACI-50 decreased stray particles less during rapid mixing because of  
436 lower Alc content. PACI-50 contained more Ala and Alb, the latter of which is reported to be  
437 effective for charge neutralization but have poor floc-forming ability (Yan *et al.* 2008).  
438 During slow mixing, the concentration of Alb decreased measurably by 15%, and the  
439 concentration of Alc increased in response. Therefore, this newly formed reactive Alc might  
440 contribute to the decrease of stray particles observed during slow mixing when PACI-50 was  
441 used. Therefore, it is expected that the stray particle concentration will be reduced even  
442 during slow mixing for flocculation if multiple stages of slow mixing are used. However, the  
443 formation of reactive Alc from Alb in slow mixing is slow, and then the decrease of stray  
444 particles is only slight.

445

### 446 *3.5. Fate and removal of stray particles by sand filtration*

447 As shown in Figs. 3 and 7, the concentrations of stray particles in water sampled after  
448 coagulation and flocculation were much higher than the residual particle concentrations in the  
449 sand filtrate. Furthermore, we found that stray particles are able to pass through the  
450 flocculation and sedimentation processes with only a slight decrease in their concentration  
451 (Fig. S11). Assuming that the source of the residual particles in the sand filtrate was stray  
452 particles (see the discussion in Section 3.2), most, but not all, of them are removed by sand  
453 filtration.

454

455 When we calculated the removal rate of particles by particle size using the stray particle  
456 concentration in water sampled after sedimentation and the residual carbon particle  
457 concentrations in sand filtrate, we found that the removal rate of stray particles was in the  
458 range of 60%–90% for particles with a diameter of 0.3 to 2.0  $\mu\text{m}$  (Fig. 11). There are many  
459 models that can be used to estimate the removal rate of fine particles by sand filtration. We  
460 used three representative models [RT model (Rajagopalan and Tien 1976), TE model  
461 (Tufenkji and Elimelech 2004), and Yao model (Yao *et al.* 1971)] presented by Crittenden et  
462 al. (2012) to estimate the removal rate of particles with a size of 0.3 to 2  $\mu\text{m}$ , which included  
463 both the stray particles and the residual particles in sand filtrate. The modeled removal rates,  
464 15%–55% for the particles with sizes of 0.3–2  $\mu\text{m}$  (Fig. S12), were much lower than the  
465 experimentally observed values of 60%–90%. Since the theoretical models assume a filtration  
466 media of spherical particles of uniform size, which is quite different from actual filters, it is  
467 not surprising that the experimental and calculated removal rates did not agree. Nevertheless,  
468 these findings suggest that a removal rate >60% would be achieved for particles with a  
469 diameter of 0.3 to 2  $\mu\text{m}$ . This suggests that some of the particles categorized as stray particles  
470 were easily removed by sand filtration. We imagine that such particles might be actually  
471 larger in size than the size of the particles observed under the microscope because the  
472 aluminum, which attaches to the particles and neutralizes their charge, is transparent and does

473 not appear in microphotographs. As already discussed in Section 3.2, zeta potential  
474 measurement revealed that the stray particles had less negative-charge than did the residual  
475 carbon particles in sand filtrate, which indicates that most of the stray particles were more  
476 charge-neutralized by the attachment of a larger amount of aluminum. This suggests that the  
477 true size of stray particles is likely to be larger than the apparent grain size observed under the  
478 microscope. Therefore, the removal efficiency of such particles would be higher than  
479 expected according to apparent particle size and filtration theory. In addition, we imagine that  
480 among the stray particles there are particles with much-less charge-neutralization and that  
481 these much-less-charge-neutralized, stray particles are able to easily pass through the sand  
482 filter and reach the filtrate. Thus, in future studies it will be important to evaluate not only  
483 particle size diversity but also charge diversity rather than rely only on average values. Such  
484 examinations will allow us to more efficiently control the carbon particle residual after CSF  
485 treatment.

486  
487

#### 488 **4. Conclusions**

489

490 Our conclusions from the present research are as follows:

491 1) In a CSF process using SPAC, the residual carbon concentration in the sand filtrate was  
492 dramatically decreased with time during the initial 2 h of filtration due to filter ripening, and a  
493 filtrate quality of <200 particles/mL was achieved. The size distribution of the residual carbon  
494 particles in the sand filtrate was not changed during the filter-ripening period, suggesting an  
495 increase in the efficiency of particle attachment rather than transport to the sand surface  
496 during this period. Therefore, charge-destabilization rather than particle size is likely key for  
497 minimizing residual particles.

498 2) Stray carbon particles, which were determined as the particles remaining in the centrifugal  
499 supernatant of the water sampled after rapid mixing for coagulation and slow mixing for  
500 flocculation, were less charge-neutralized than the bulk particles. The concentration of stray  
501 particles dropped markedly during rapid mixing process, and then it was unchanged or only  
502 slightly decreased during slow mixing and sedimentation processes. The concentrations of  
503 stray carbon particles in water sampled after rapid/slow mixing processes for  
504 coagulation/flocculation were well correlated with the residual carbon particle concentrations  
505 in sand filtrate, but the turbidity of water entering the sand filter water was not.

506 3) Among the bulk particles, stray particles, which account for less than 0.4% of the bulk  
507 particles, could be a major source of residual particles in sand filtrate due to their lower  
508 charge neutralization. Therefore, a goal of the coagulation treatment process should be to  
509 reduce the stray particle concentration.

510 4) Optimizing reactor configurations and the type and dose of coagulant were effective for  
511 reducing stray particle and residual carbon particle concentrations in sand filtrate. PACI-70  
512 performed better with a multi-chambered reactor than with a single-chambered reactor for  
513 coagulation with rapid mixing. In contrast, PACI-50 performed better with a multi-chambered  
514 reactor than with a single-chambered reactor for both coagulation with rapid mixing and

515 flocculation with slow mixing. The performance requirements of the reactors for coagulation  
516 and flocculation were related to the predominant aluminum species in the coagulant: Alc of  
517 PACl-70 is fast-acting, whereas Ala of PACl-50 is slow-acting.

518

519

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524

525

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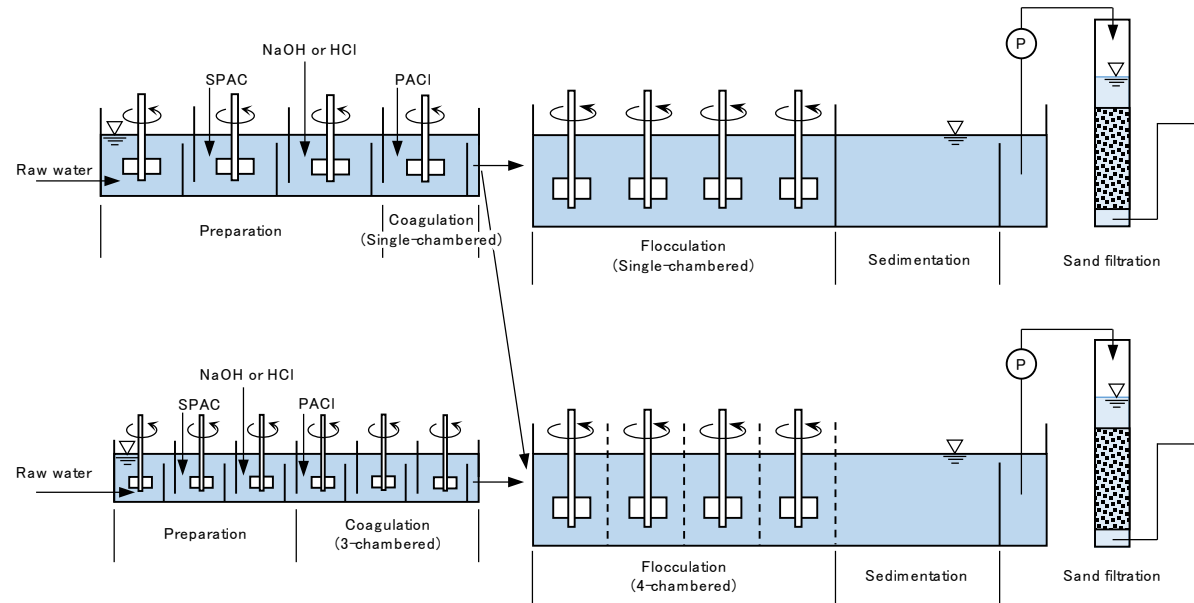
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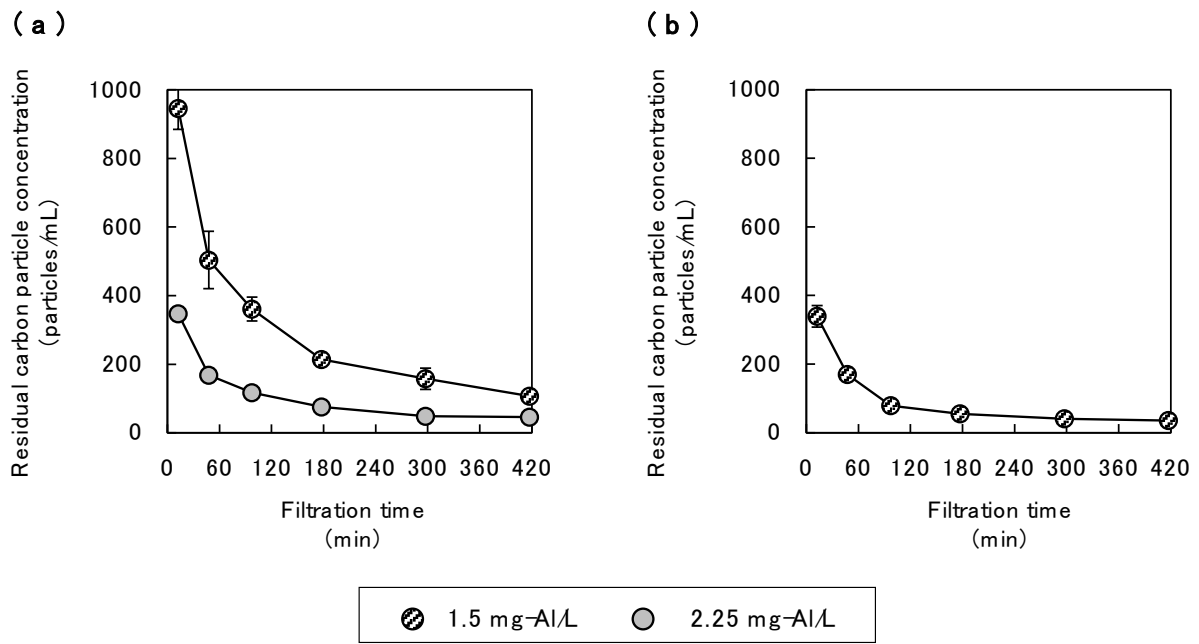
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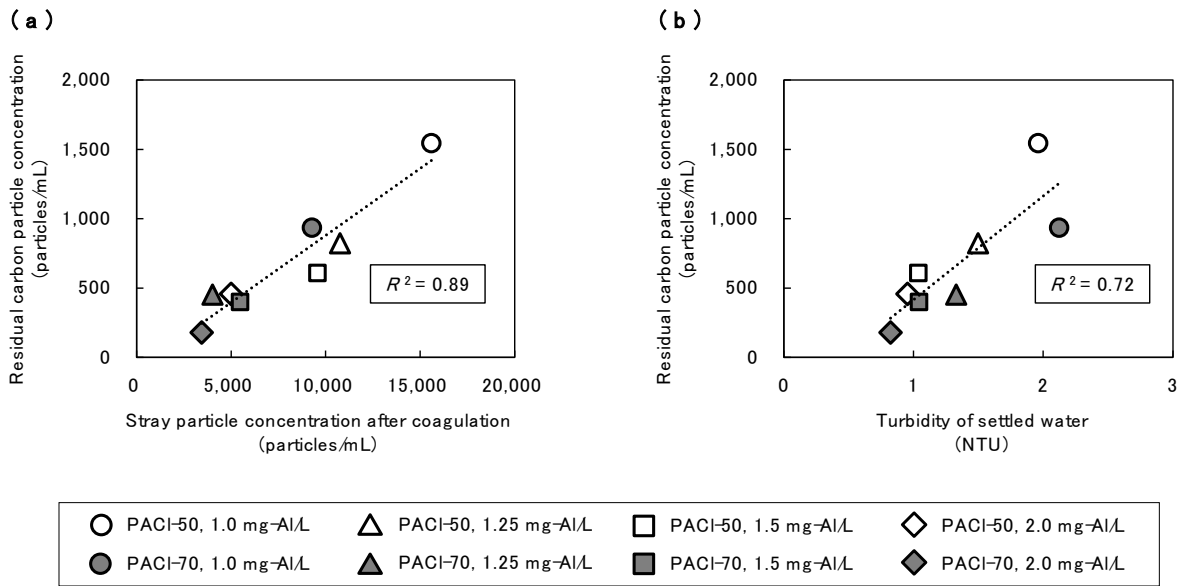
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**Fig. 1.** Schematic diagram of the bench-scale CSF plant.

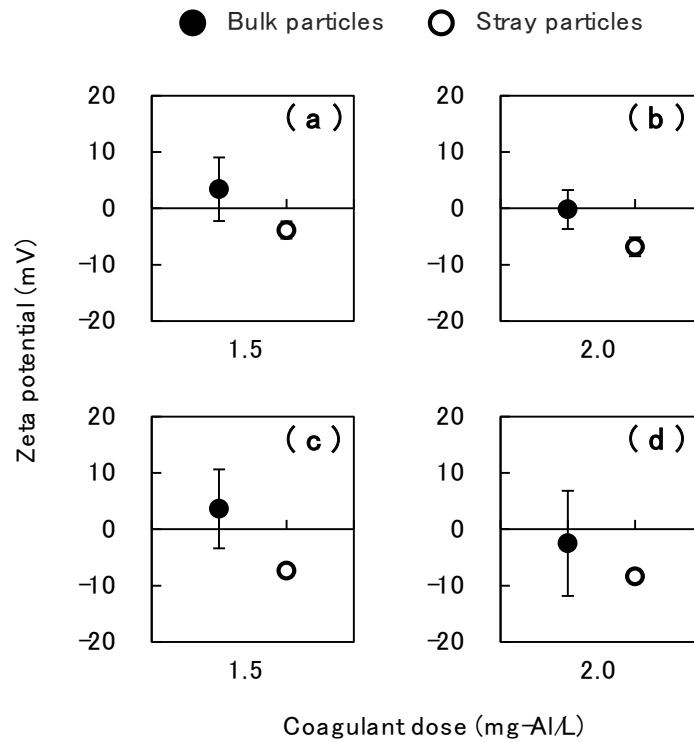


**Fig. 2.** Residual carbon particle concentration in sand filtrate after treatment of river water (a, River water 1) or municipal water (b, Municipal water 1) with a bench-scale CSF plant. Coagulation: single-chambered reactor,  $G = 600 \text{ s}^{-1}$ ; flocculation: 4-chambered reactor,  $G = 12.5 \text{ s}^{-1}$ ; filtration rate,  $90 \text{ m d}^{-1}$ . SPAC initial concentration,  $2.0 \text{ mg/L}$ ; coagulant (PACl-70),  $1.5$  or  $2.25 \text{ mg-Al/L}$ . Error bars indicate standard deviations of 3 measurements, but some of them are hidden behind the symbols.

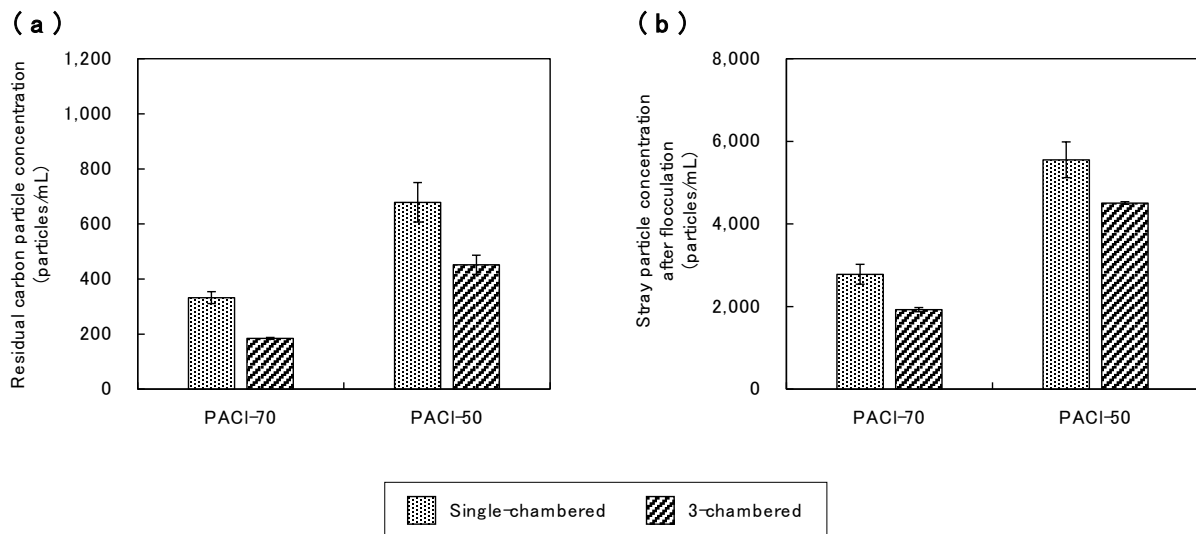


**Fig. 3.** Correlation between residual carbon particle concentration in sand filtrate and stray carbon particle concentration after coagulation with rapid mixing (a), and between residual carbon particle concentration of sand filtrate and turbidity of settled water (b). Municipal water 2 (PACI-70) or Municipal water 3 (PACI-50) was used as the raw water. SPAC initial concentration, 2.0 mg/L. Coagulant (PACI-50 or PACI-70), 1.0, 1.25, 1.5, or 2.0 mg-Al/L. Coagulation, single-chambered reactor,  $G = 600 \text{ s}^{-1}$ ; flocculation, 4-chambered reactor,  $G = 12.5 \text{ s}^{-1}$ ; filtration rate,  $90 \text{ m d}^{-1}$ .

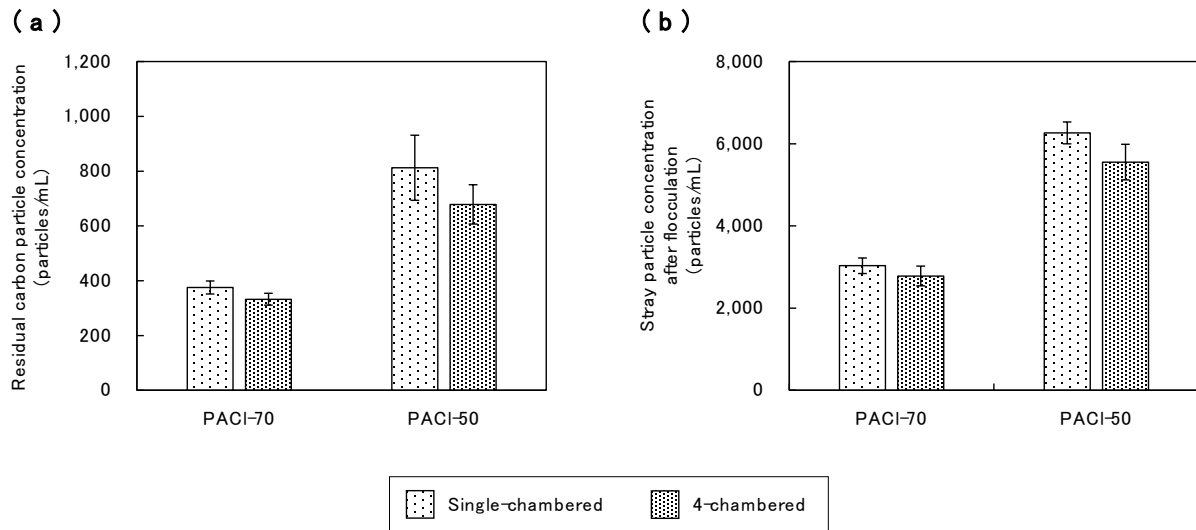




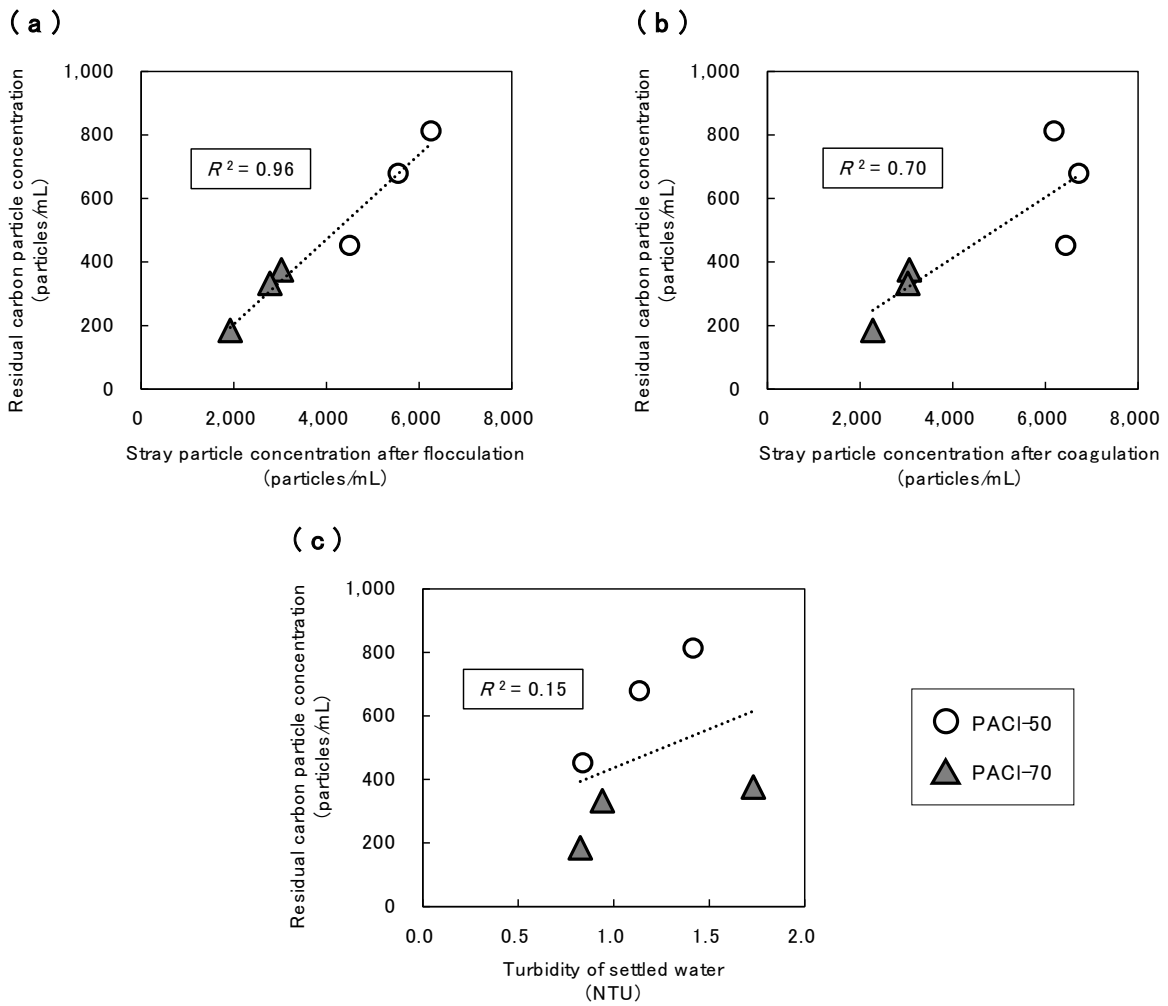
**Fig. 4.** Comparison of the zeta potentials of bulk particles and stray carbon particles after coagulation. Water samples were collected after coagulation with rapid mixing. The zeta potentials of bulk particles were determined for each sample without further processing. The zeta potentials of the stray particles were determined after the samples were subjected to centrifugal separation. Municipal water 4 was used as the raw water. SPAC initial concentration, 2.0 mg/L; coagulant, PACl-70 (a, b) or PACl-50 (c, d), 1.5 or 2.0 mg-Al/L. This was a batch-type coagulation test using a 1-L rectangular beaker and a mixing velocity of  $G = 600 \text{ s}^{-1}$ . The error bars represent standard deviations of 7–11 measurements, but some of them are hidden behind the symbols.



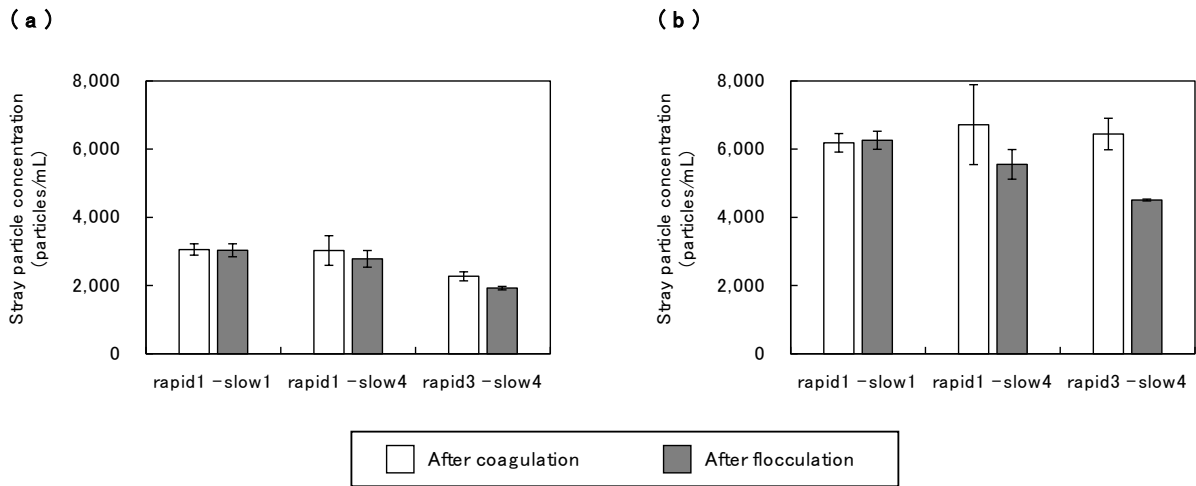
**Fig. 5.** Effect of rapid mixing reactor configuration (a single-chambered or 3-chambered coagulation reactor) on (a) residual particle concentration in sand filtrate and (b) stray particle concentration in water sampled after flocculation. Both reactors used the same mixing intensity ( $G = 600 \text{ s}^{-1}$ ) and same total HRT (100 s), and were followed by a 4-chambered flocculation reactor ( $G = 12.5 \text{ s}^{-1}$ ) and a sand filter. Municipal water 5 was used as the raw water. SPAC initial concentration, 2.0 mg/L; coagulant (PACI-50 or PACI-70), 1.5 mg-Al/L; filtration rate, 90 m d<sup>-1</sup>. Error bars indicate standard deviations of 3 measurements.



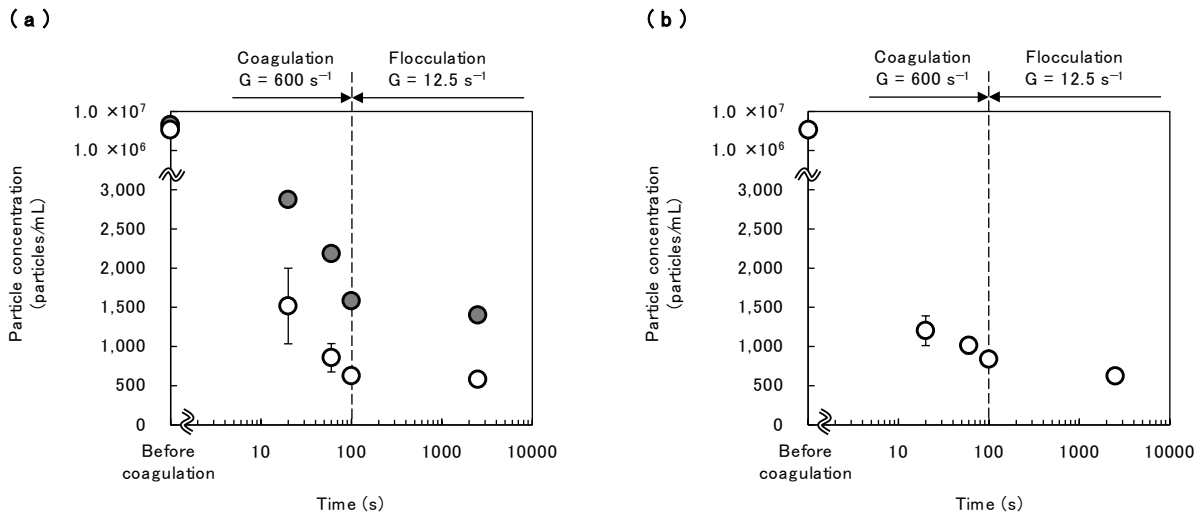
**Fig. 6.** Effect of slow mixing reactor configuration (a single-chambered or 4-chambered flocculation reactor) on (a) residual particle concentration in sand filtrate and (b) stray carbon particle concentration in water sampled after flocculation. Both reactors used the same mixing intensity ( $G = 12.5 \text{ s}^{-1}$ ) and same total HRT (2400 s) and were preceded by a single-chambered coagulation reactor ( $G = 600 \text{ s}^{-1}$ ). The experimental conditions were the same as described in the caption to Fig. 5. Error bars indicate standard deviations of 3 measurements.



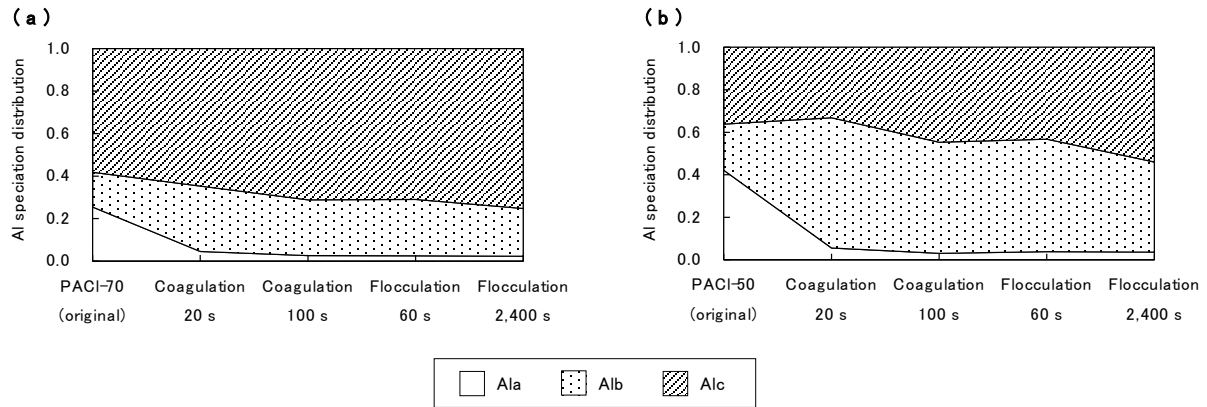
**Fig. 7.** Correlations between residual carbon particle concentration in sand filtrate and stray particle concentration in water sampled after flocculation with slow mixing (a), stray particle concentration in water after coagulation with rapid mixing (b), and turbidity of settled water (c). The experimental conditions were the same as described in the captions to Figs. 5, 6, and S10, respectively.



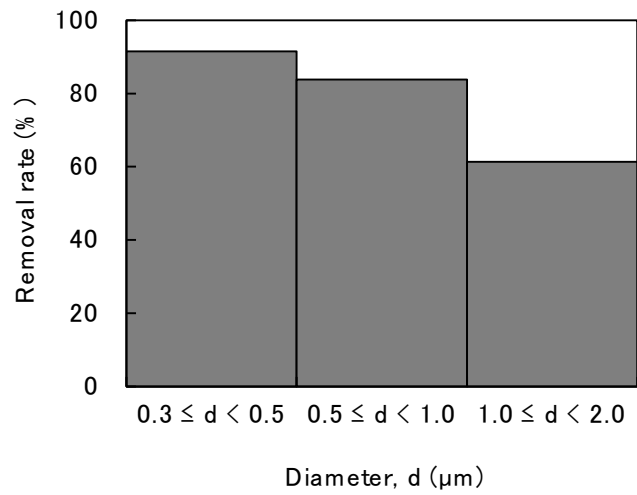
**Fig. 8.** Change in stray particle concentration after coagulation and flocculation. On the horizontal axis, the numbers after “rapid” and “slow” indicate the number of chambers in the coagulation and flocculation reactors, respectively. Coagulation was conducted with rapid mixing ( $G = 600 \text{ s}^{-1}$ , 100 s). Flocculation was conducted with slow mixing ( $G = 12.5 \text{ s}^{-1}$ , 2400 s). SPAC initial concentration, 2 mg/L. PACI-70 (a) or PACI-50 (b) was used as the coagulant. The experimental conditions were the same as described in the caption to Figs. 5 and 6.



**Fig. 9.** Change of particle concentration against mixing time during coagulation and flocculation. Batch experiments were conducted using a 1-L rectangular beaker, Municipal water 1 (white plots) or River water 2 (grey plots) as the raw water, and PACI-70 (a) or PACI-50 (b) at 1.5 mg-Al/L as the coagulant. SPAC initial concentration, 2.0 mg/L. Water samples were collected during coagulation and flocculation treatments and then subjected to centrifugal separation treatment (see Section 2.4). Centrifugal supernatants were examined for carbon particle concentration. Water sampled before coagulation was also examined. Two runs were conducted for Municipal water 1, and one run for River water 2. Error bars represent the standard deviations for experiments, but some of them are hidden behind the symbols.



**Fig. 10.** Change in Al species distribution of PACl by coagulation and flocculation. PACl-70 (a) and PACl-50 (b) were hydrolyzed at 270 mg-Al/L in Municipal water 1 without carbon particles. Batch-type coagulation tests were conducted using a 1-L rectangular beaker. “original” means the Al speciation distribution of the PACl stock solution. “Coagulation” refers to coagulation with rapid mixing ( $G = 381 \text{ s}^{-1}$ ); “Flocculation” refers to flocculation with slow mixing ( $G = 8 \text{ s}^{-1}$ ). Ala, Alb, and Alc are monomeric, polymeric, and colloidal species, respectively.



**Fig. 11.** Removal rate of carbon particles in three size classes by sand filtration. Removal rate was calculated between the stray particle concentration in water sampled after sedimentation and the residual carbon particle concentration in sand filtrate. River water 1 was used as the raw water. Coagulant (PAC1-70) dose, 2.25 mg-Al/L. The experimental conditions were the same as described in the caption to Fig. 2.



## Supplementary Information

### **Stray particles as the source of residuals in sand filtrate: Behavior of superfine powdered activated carbon particles in water treatment processes**

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### **Ferron method for aluminum speciation in poly-aluminum chloride**

In the Ferron method, Ala denotes aluminum species that react with Ferron within 30 s, which are mainly monomeric Al species. Alb denotes Al species that react with Ferron from 30 s to 120 min, which are mainly polymeric Al species. Alc denotes Al species that do not react with Ferron, which are mainly colloidal Al species. The Ferron analyses of the poly-aluminum chlorides (PACl) were conducted immediately after diluting each PACl with pure water (Milli-Q water; Milli-Q Advantage A10 System; Merck KGaA, Darmstadt, Germany) to 0.27 g-Al/L (0.01 mol-Al/L). Absorbance at 366 nm was measured using a glass cell that had a 10-cm optical path length. Dilution is reported to have little effect on the Ferron assay for PACl (Kimura *et al.* 2013).

### **Wet ball and wet bead milling to produce superfine powdered activated carbon**

First, a powdered activated carbon (PAC) slurry (31% w/w) was prepared by admixing a commercially available wood-based PAC (Taiko W; Futamura Chemical Co., Ltd., Nagoya, Japan) with Milli-Q water. This slurry was transferred to a closed-chamber ball mill (Nikkato, Osaka, Japan) including 5- and 10-mm-diameter Al<sub>2</sub>O<sub>3</sub> balls as the disintegrating media, and the PAC was pulverized at 45–50 rpm for 6 h to reduce its D95 (the diameter where 95% of the entire distribution lies below) to less than 30 μm. After that, the slurry was moved to a bead mill system (LMZ015; Ashizawa Finetech, Ltd., Chiba, Japan). The bead mill system was operated in circulation mode with 0.3-mm-diameter ZrO<sub>2</sub> beads, and the carbon particles in the suspension were further pulverized at a rotational speed of 8 m s<sup>-1</sup> (2590 rpm) for 30 min to produce a superfine powdered activated carbon (SPAC) slurry.

The particle size distribution of the SPAC was determined as follows. A portion of SPAC slurry was added to a dispersant (Triton X-100; Kanto Chemical Co., Inc., Tokyo, Japan; final concentration, 0.08% w/v) and sonicated at 150 W for 1 min to thoroughly disperse the carbon particles. Then, the size distribution was measured by using a laser light diffraction and scattering method (Microtrac MT3300EXII; MicrotracBEL Corp., Osaka, Japan).

### **Membrane filtration and microscopic image analysis to determine carbon particle concentration and particle size**

The concentrations and particle sizes of carbon particles were determined by membrane filtration and microscopic image analysis. Carbon particles in water samples were captured on a membrane filter (nominal pore diameter, 0.1 μm; Φ25 mm; polytetrafluoroethylene; Merck KGaA). After the filter was left to dry naturally at room temperature, color digital photomicrographs of the filter surface were recorded under a digital microscope (VHX-2000; Keyence Corporation, Osaka, Japan) at 1000× magnification. The number of observation zones (9, 10, or 18 per

filter; microscope view area,  $247 \mu\text{m} \times 330 \mu\text{m}$ ) were predetermined depending on particle concentration (Nakazawa *et al.* 2018). Finally, the photomicrographs were analyzed by using the image analysis software associated with the microscope and the particle concentration, and the sizes calculated were represented by the surface-equivalent sphere diameter. The analytical procedures are reported in detail elsewhere (Nakazawa *et al.* 2018).

### **Flow-through coagulation–flocculation, sedimentation, and sand filtration experiment**

The plant comprised five components: preparation unit, coagulation reactor (rapid mixing), flocculation reactor (slow mixing), sedimentation reactor, and sand filter (Fig. 1 and Table S1). Coagulation was conducted using a single-chambered reactor or a 3-chambered-reactor with three equally-sized chambers; the two reactors had the same total hydraulic retention time (HRT) of 100 s. Flocculation was conducted using a single-chambered reactor or a 4-chambered reactor, both with four mixing impellers and the same total HRT of 2400 s. Regardless of reactor configuration, coagulation was conducted with rapid mixing at a fixed mixing intensity (G value: velocity gradient) of  $600 \text{ s}^{-1}$  for 100 s, and flocculation was conducted with slow mixing at a fixed G value of  $12.5 \text{ s}^{-1}$  for 2400 s. Residence time distributions of the reactors were measured by tracer test using NaCl as the tracer and conductivity detection (Crittenden *et al.* 2012). All chemicals and raw water were fed into the plant via peristaltic pumps at constant flow rates.

Toyohira River water, collected at Moiwa Water Purification Plant, Sapporo, Japan (hereafter ‘River water 1’) was used as the raw water. We also used dechlorinated Sapporo municipal water (Municipal waters 1–3 and 5–7) because only a limited volume of River water was available (Table S2). The raw waters were stored in a tank (130 or 500 L) and then pumped into the first mixing chamber of the preparation unit at 0.5 L/min. SPAC was added to the second mixing chamber of the preparation unit at a concentration of 2 mg/L, which is a typical dose when SPAC is used as an adsorbent (Nakayama *et al.* 2020).

After the addition of NaOH (0.05 N) or HCl (0.05 N) to adjust the final coagulation pH to 7.0 in the third chamber of the preparation unit, coagulant (PACl) was injected into the coagulation reactor; when the 3-chambered reactor was used for coagulation, the coagulant was injected into the first chamber. The coagulant dose was 1.5 mg-Al/L, unless otherwise noted, and it was predetermined to bring the settling turbidity to less than 1.0 NTU. Samples of water were collected from the outlet of the coagulation reactor and from the outlet of the flocculation reactor for the determination of non-coagulated carbon particle concentration, as described in Sections 2.1 and 2.4, respectively.

After flocculation, the water flowed through a sedimentation unit, which had a HRT of 60 min, and a portion of the supernatant was sampled for the determination of turbidity (2100Q portable turbidimeter; Hach Company, Loveland, CO, USA). In some cases, a portion of supernatant was sampled for the determination of stray carbon particle concentration.

After sedimentation, the supernatant was transferred to a sand filter. Sand filtration was conducted at a rate of 90 or 150 m d<sup>-1</sup> in the down-flow direction using a 4-cm diameter column filled with sand (effective diameter, 0.94 mm; uniformity, 1.24; Nihon Genryo Co., Ltd., Japan) to a depth of 50 cm. After the start of filtration, sand filtrates were collected from 0 to 25, from 35 to 60, from 85 to 110, from 165 to 190, from 285 to 310, and from 405 to 430 min, representing filtration times of 12.5, 47.5, 97.5, 178, 298, and 418 min, respectively, and used to determine turbidity and carbon particle concentration. After each filtration run, the sand filter was backwashed with municipal water and then washed forward with Milli-Q water before the next filtration run.

Table. S1. Specifications of the bench-scale coagulation–flocculation, sedimentation, and rapid sand filtration plant.

Component	Type	Number of chambers	Length × width × height per chamber	Water depth	Volume per chamber	Hydraulic retention time per chamber	G value
			cm	cm	L	s	s <sup>-1</sup>
Preparation unit	Connected to the single-chambered coagulation reactor	3	9.5 × 9.5 × 15	9.2	0.83	100	600
	Connected to the 3-chambered coagulation reactor	3	6.6 × 6.6 × 12	6.4	0.28	33	600
Coagulation reactor	Single-chambered reactor	1	9.5 × 9.5 × 15	9.2	0.83	100	600
	3-chambered reactor	3	6.6 × 6.6 × 12	6.4	0.28	33	600
Flocculation reactor	Single-chambered reactor	1	56 × 19 × 25	19	20	2400	12.5
	4-chambered reactor	4	14 × 19 × 25	19	5	600	12.5

Component	Length × width × height	Water depth	Volume	Hydraulic retention time	Overflow rate
	cm	cm	L	s	mm min <sup>-1</sup>
Sedimentation reactor	88 × 19 × 25	19	32	3900	3.0

Component	Outer diameter of column	Inner diameter of column	The column to particle diameter ratio	Length of column	Effective diameter of sand	Uniformity coefficient of sand	Sand depth	Filtration rate
	cm	cm		cm	mm		cm	m d <sup>-1</sup>
Sand filter	4.0	3.6	40	140 or 90	0.94	1.24	50	90 or 150

Table. S2. Raw waters used in the present study.

Raw water	Turbidity NTU	Black particle concentration particles/mL	DOC mg/L	Alkalinity mg/L as CaCO <sub>3</sub>	Na <sup>+</sup> mg/L	K <sup>+</sup> mg/L	Mg <sup>2+</sup> mg/L	Ca <sup>2+</sup> mg/L	Cl <sup>-</sup> mg/L	NO <sub>3</sub> <sup>-</sup> mg/L	SO <sub>4</sub> <sup>2-</sup> mg/L	
River water 1	2.3	no data	0.8	16	12	2.1	1.8	10	21	1.5	20	Fig. 2 (a), Fig. 11, Fig. S1 (a, b), Fig. S11
River water 2	13	16	3.8	76	44	6	9	19	19	<0.14	6	Fig. 9
Municipal water 1	0.1	15	0.6	18	15	2.3	2.4	11	23	0.8	21	Fig. 2 (b), Fig. 9, Fig. 10, Fig. S1 ( c )
Municipal water 2	0.1	no data	0.5	20	17	2.6	2.1	10	24	1	19	Fig. 3 (PACl-70), Fig. S3 (PACl-70), Fig. S4 (PACl-70), Fig. S5 (PACl-70)
Municipal water 3	0.1	no data	0.6	20	18	2.6	1.6	11	28	0.8	19	Fig. 3 (PACl-50), Fig. S3 (PACl-50), Fig. S4 (PACl-50), Fig. S5 (PACl-50)
Municipal water 4	no data	no data	0.4	20	12	0.8	2.4	7	11	0.9	18	Fig. 4
Municipal water 5	0.1	no data	no data	16	13	1.7	1.8	9	23	0.9	18	Fig. 5, Fig. 6, Fig. 7, Fig. 8, Fig. S2, Fig. S10
Municipal water 6	0.1	no data	0.4	20	11	0.8	3.1	8	14	1.3	19	Fig. S8
Municipal water 7	0.1	no data	0.5	20	12	1.6	2.4	11	18	1	19	Fig. S9

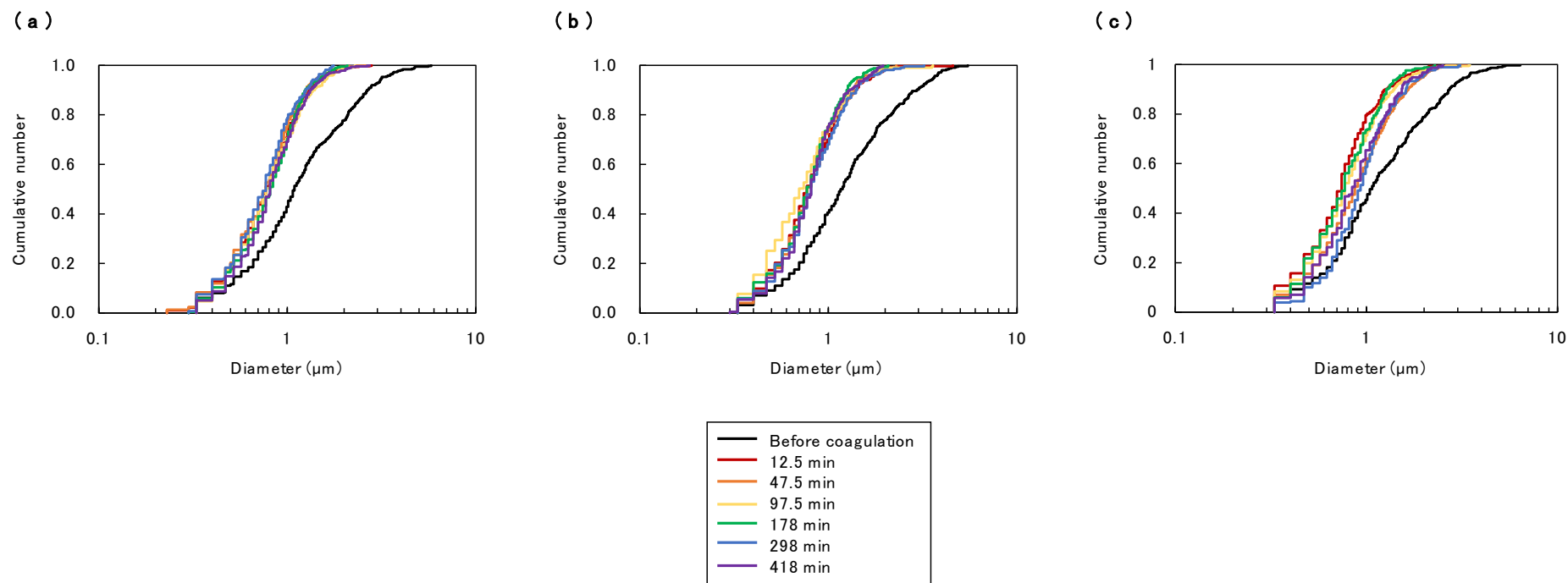


Fig. S1. Particle size distributions of carbon particles in water sampled from the preparation unit before coagulation or in sand filtrate. The numbers in the legend indicate the filtration time. Particle sizes were determined by using membrane filtration and microscopic image analysis. River water 1 (a, b) or Municipal water 1 (c) was used as the raw water. Coagulant (PACI-70) dose, 1.5 mg-Al/L (a, c) or 2.25 mg-Al/L (b). The experimental conditions were the same as those described in the caption to Fig. 2.

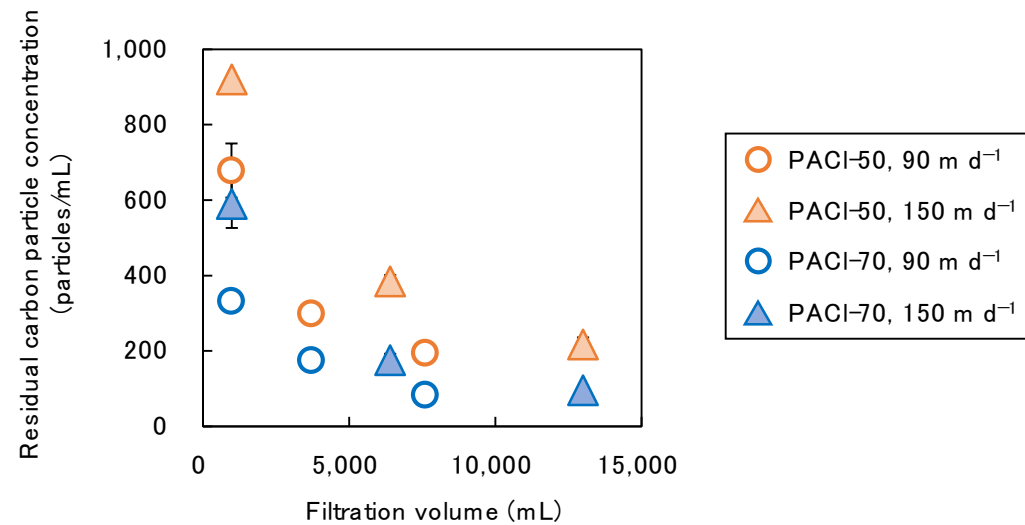


Fig. S2. Effect of filtration rate on residual particle concentration in sand filtrate. Filtration rate, 90 or 150 m d<sup>-1</sup>. Municipal water 5 was used as the raw water. SPAC initial concentration, 2.0 mg/L; coagulant (PACI-50 or PACI-70), 1.5 mg-Al/L. Coagulation, single-chambered reactor,  $G = 600 \text{ s}^{-1}$ ; flocculation, 4-chambered reactor,  $G = 12.5 \text{ s}^{-1}$ .



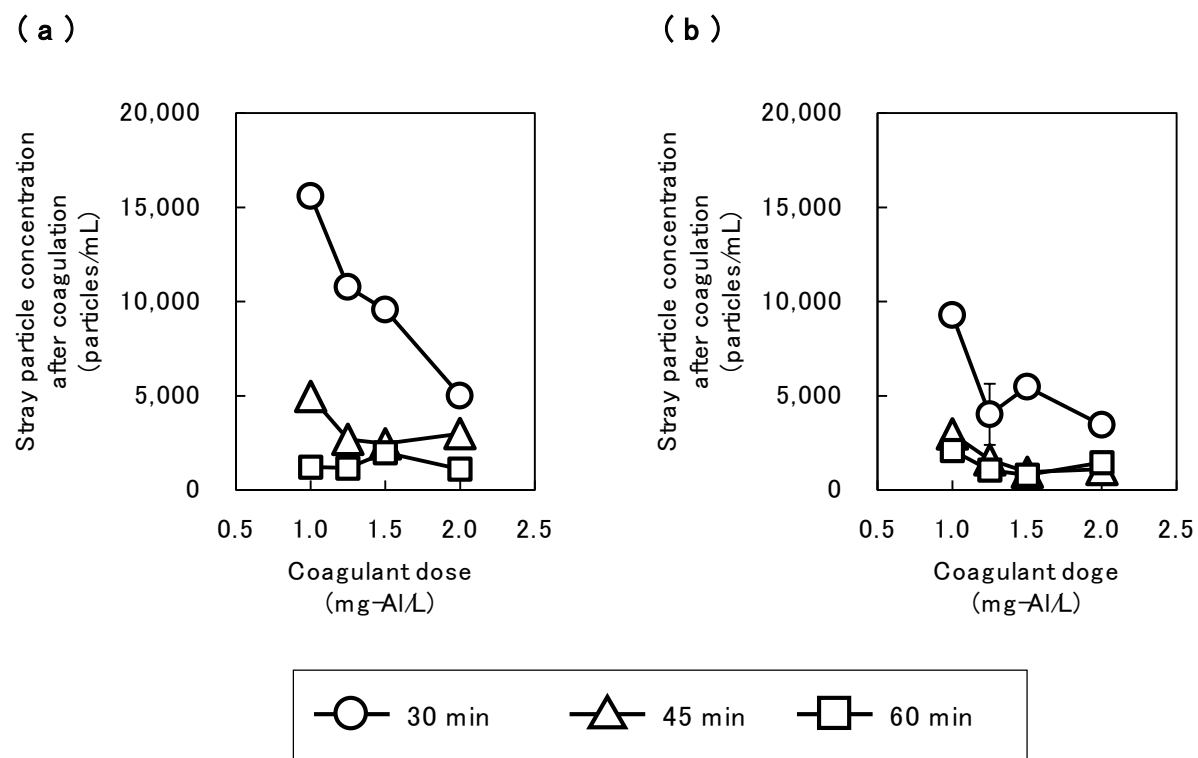


Fig. S3. Effect of coagulant dose on stray carbon particle concentration after coagulation with rapid mixing. PACI-50 (a) or PACI-70 (b) was used as the coagulant. Stray particles were collected from water sampled after coagulation by using a double-centrifugation method to remove floc particles. Total centrifugation times were 30 min (circles), 45 min (triangles), and 60 min (squares). Municipal water 2 (PACI-70) or Municipal water 3 (PACI-50) was used as the raw water. SPAC initial concentration, 2.0 mg/L. Coagulation, single-chambered reactor,  $G = 600 \text{ s}^{-1}$ .

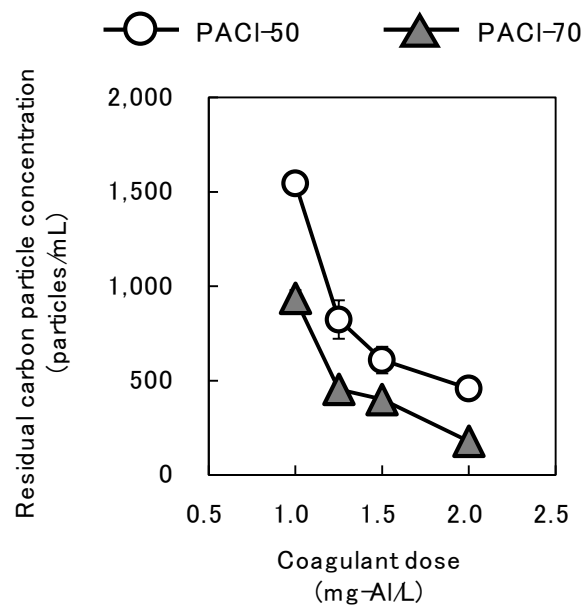


Fig. S4. Effect of coagulant dose on residual carbon particle concentration in sand filtrate. PACI-50 or PACI-70 was used as the coagulant at 1.0, 1.25, 1.5, or 2.0 mg-Al/L. Municipal water 2 (PACI-70) or Municipal water 3 (PACI-50) was used as the raw water. SPAC initial concentration, 2.0 mg/L. Coagulation, single-chambered reactor,  $G = 600 \text{ s}^{-1}$ ; flocculation, 4-chambered reactor,  $G = 12.5 \text{ s}^{-1}$ ; filtration rate,  $90 \text{ m d}^{-1}$ . The experimental conditions were the same as described in the caption to Fig. 3.

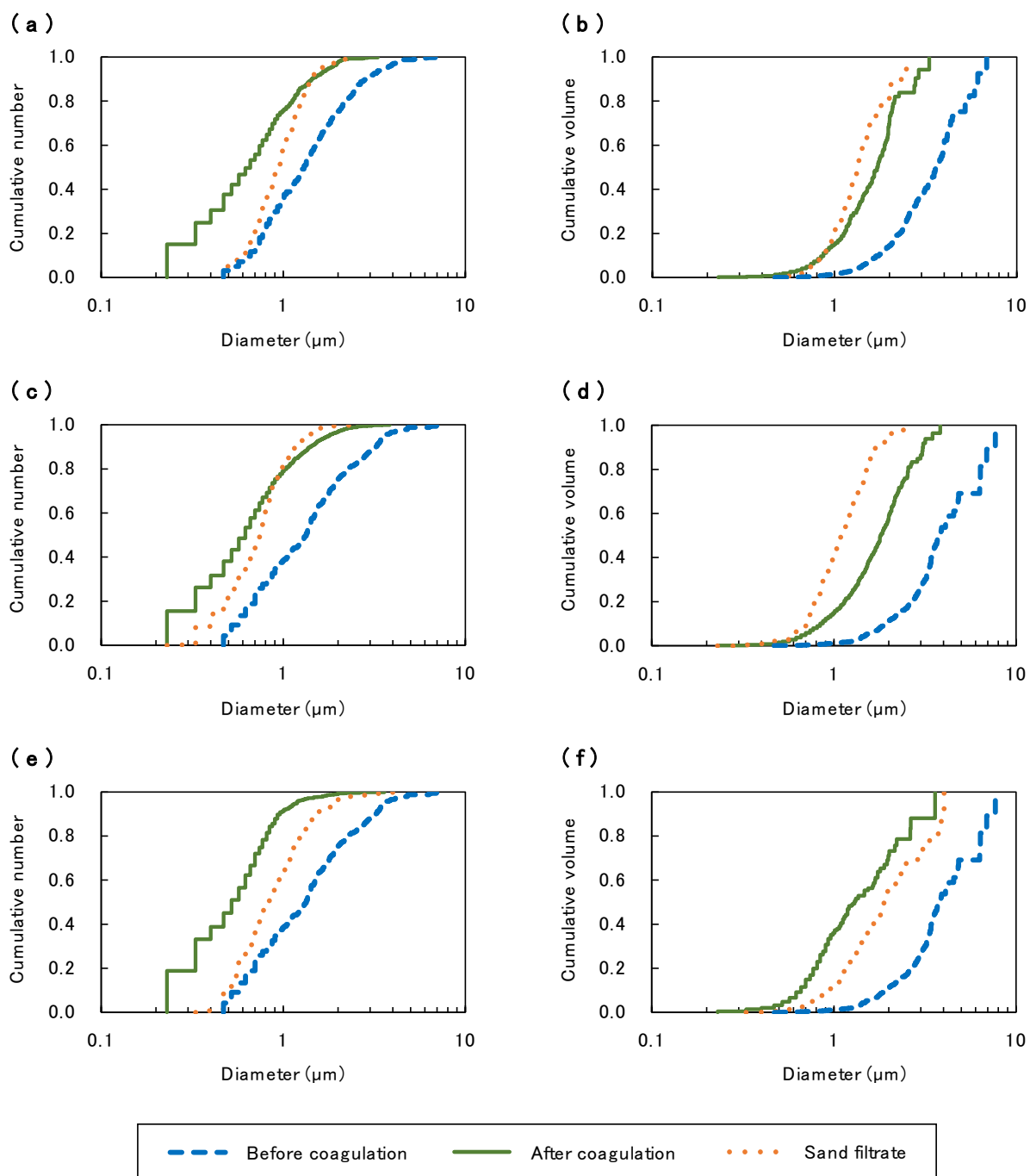
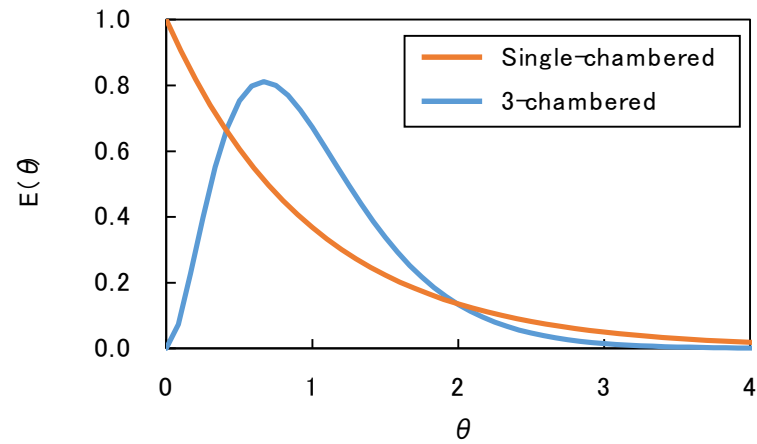


Fig. S5. Particle size distributions of carbon particles in water samples; cumulative number (a, c, e) or cumulative volume (b, d, f). Water samples were collected after coagulation, subjected to centrifugal separation treatment (see Section 2.4), and the supernatants were examined for particle size distribution. Water sampled before coagulation and sand filtrate were also examined. Particle sizes were determined by using membrane filtration and microscopic image analysis. Municipal water 2 (a, b) or Municipal water 3 (c, d, e, f) was used as the raw water. SPAC initial concentration, 2.0 mg/L. Coagulant, PACI-70 (a, b) or PACI-50 (c, d, e, f), 1.5 mg-Al/L (c, d) or 2.0 mg-Al/L (a, b, e, f). The experimental conditions were the same as described in the caption to Fig. 3.

(a)



(b)

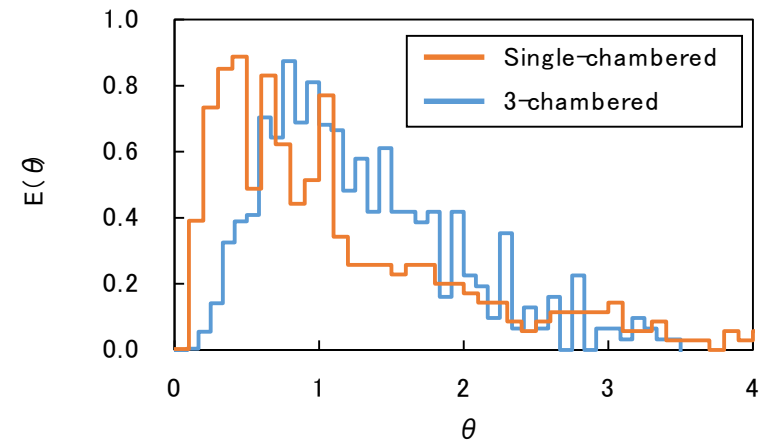
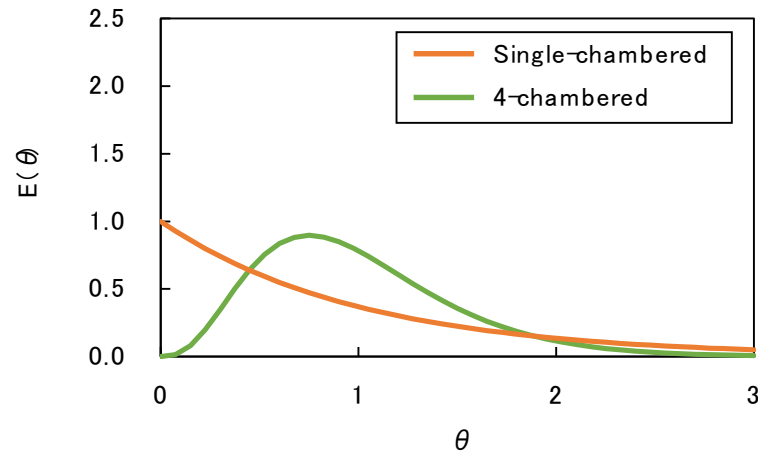


Fig. S6. Theoretical (a) and experimental (b) residence time distributions for the single-chambered or 3-chambered coagulation reactor with rapid mixing.  $\theta$  is normalized residence time divided by HRT, and  $E(\theta)$  is residence time distribution (Crittenden et al. 2012).

(a)



(b)

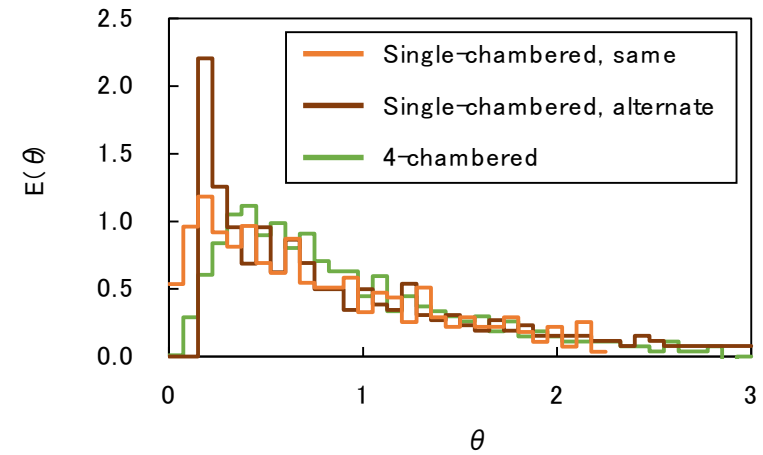


Fig. S7. Theoretical (a) and experimental (b) residence time distributions for the single-chambered or 4-chambered flocculation reactor with slow mixing. “alternate” means that the direction of rotation of the 4 mixers alternated; “same” means that the direction of rotation of the 4 mixers was the same.  $\theta$  is normalized residence time, time divided by HRT, and  $E(\theta)$  is residence time distribution (Crittenden et al. 2012).

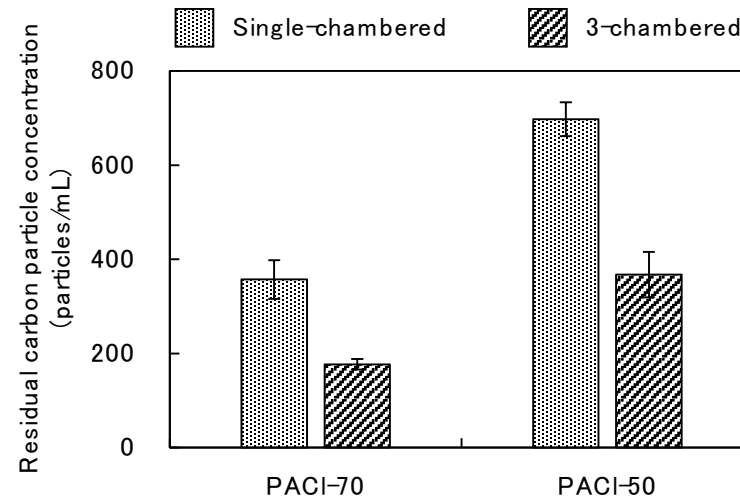


Fig. S8. Effect of coagulation reactor configuration on residual carbon particle concentration in sand filtrate. A single-chambered or 3-chambered coagulation reactor with the same mixing intensity ( $G = 600 \text{ s}^{-1}$ ) and same total HRT (100 s) was used. Both reactors were followed by a 4-chambered flocculation reactor ( $G = 12.5 \text{ s}^{-1}$ ) and a sand filter. Municipal water 6 was used as the raw water. SPAC initial concentration, 2.0 mg/L; coagulant (PACI-50 or PACI-70), 1.5 mg-Al/L; filtration rate,  $90 \text{ m d}^{-1}$ .

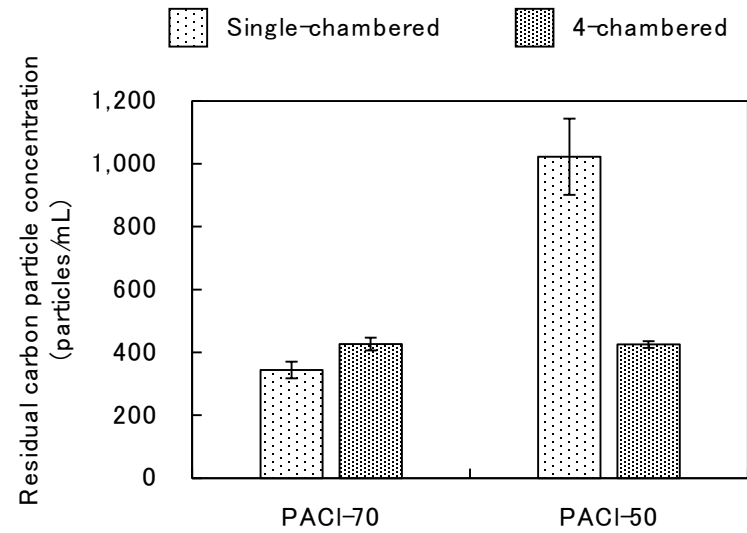


Fig. S9. Effect of flocculation reactor configuration on residual particle concentration in sand filtrate. A single-chambered coagulation reactor ( $G$  value of  $600 \text{ s}^{-1}$ ) followed by a single-chambered or 4-chambered flocculation reactor with the same mixing intensity ( $G = 12.5 \text{ s}^{-1}$ ) and same total HRT (2400 s) were used. Municipal water 7 was used as the raw water. SPAC initial concentration, 2.0 mg/L; coagulant (PACI-50 or PACI-70), 1.5 mg-Al/L; filtration rate,  $90 \text{ m d}^{-1}$ .

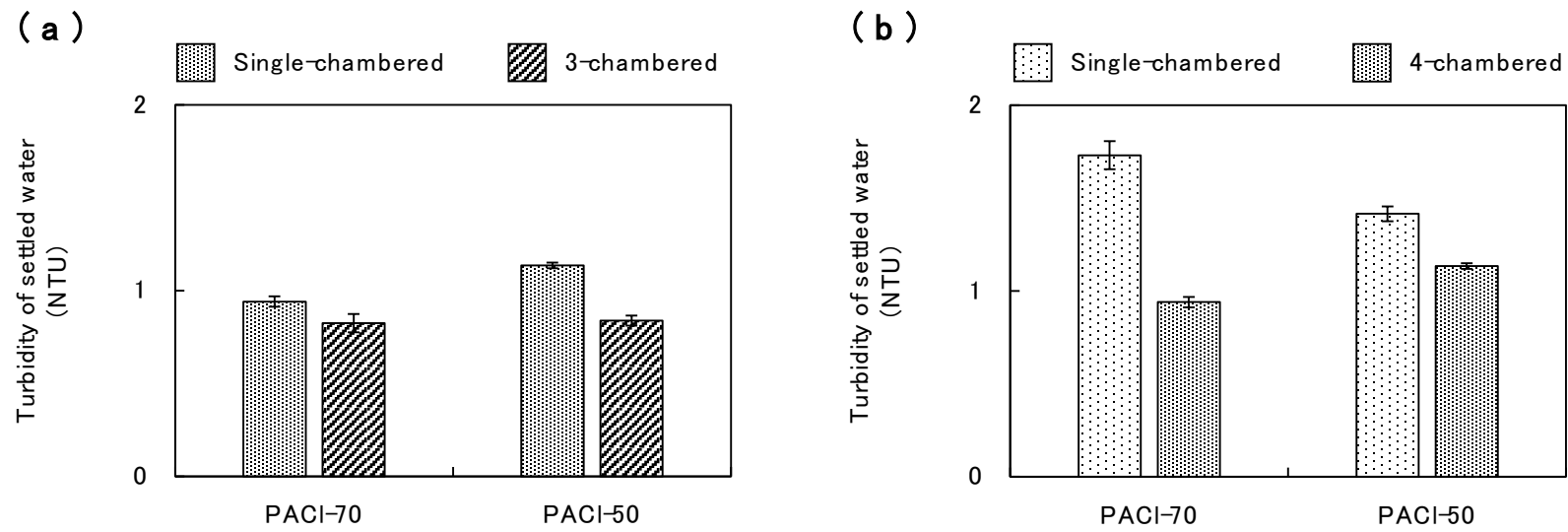


Fig. S10. Effect of mixing reactor configuration on the turbidity of settled water after sedimentation. (a) Effect of a single-chambered or 3-chambered coagulation reactor. Both reactors used the same mixing intensity ( $G = 600 \text{ s}^{-1}$ ) and the same total HRT (100 s) and were followed by a 4-chambered flocculation reactor ( $G = 12.5 \text{ s}^{-1}$ ). (b) Effect of a single-chambered or 4-chambered flocculation reactor. Both reactors used the same mixing intensity ( $G = 12.5 \text{ s}^{-1}$ ) and same total HRT (2400 s) and were preceded by a single-chambered coagulation reactor ( $G = 600 \text{ s}^{-1}$ ). Municipal water 5 was used as the raw water. SPAC initial concentration, 2.0 mg/L; coagulant (PACI-50 or PACI-70), 1.5 mg-Al/L; settling time, 65 min. The experimental conditions were the same as described in the caption to Figs. 5 and 6.



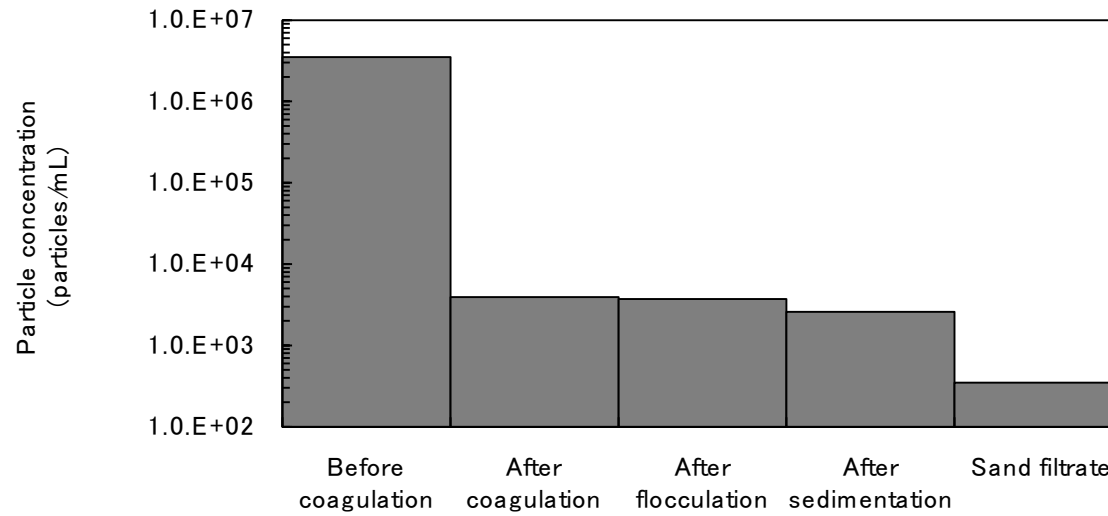


Fig. S11. Change in carbon particle concentration during the CSF process. Water samples were collected after coagulation, after flocculation, and after sedimentation, subjected to centrifugal separation treatment (see Section 2.4), and the supernatants were examined for carbon particle concentration. Water sampled before coagulation and sand filtrate were also examined. River water 1 was used as the raw water. Coagulant (PACl-70) dose, 2.25 mg-Al/L. The experimental conditions were the same as described in the caption to Fig. 2.

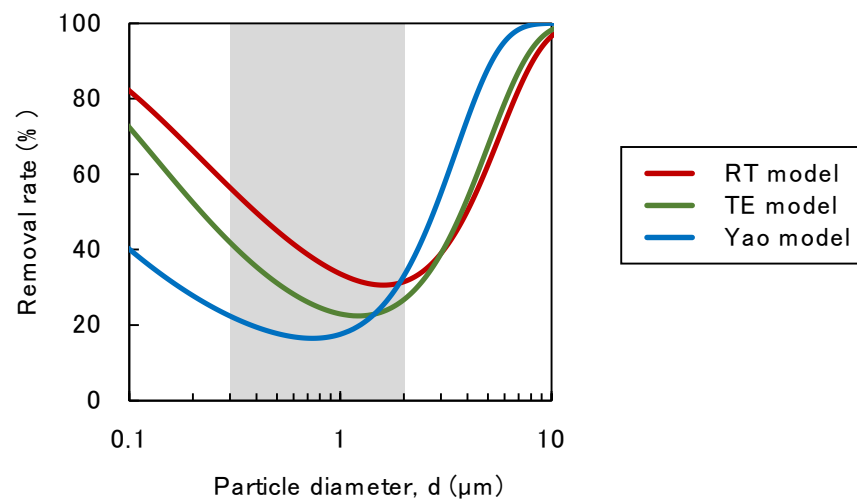


Fig. S12. Theoretical rates of particle removal by sand filtration, as determined by three different models. Removal rates were calculated by using the three models [RT model (Rajagopalan and Tien 1976), TE model (Tufenkji and Elimelech 2004), and Yao model (Yao *et al.* 1971)] and the following parameters: collector diameter (effective diameter of sand),  $d_c = 0.94$  mm; filtration rate,  $v = 3.75$  m/h; temperature,  $T = 20$  °C; particle density,  $\rho_P = 1,330$  kg/m<sup>3</sup>; depth of filter,  $L = 0.5$  m; bed porosity,  $\varepsilon = 0.40$ ; and Hamaker constant,  $Ha = 1.73 \times 10^{-20}$ , geometric mean of  $Ha$  values of activated carbon (Chen and Huang 2017) and quartz (Adamczyk 2017). In the figure, the grey band (particle diameter, 0.3–2 μm) shows the particle size range for the stray particles and residual carbon particles in sand filtrates in the present study.

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