



Title	Precoating membranes with submicron super-fine powdered activated carbon after coagulation prevents transmembrane pressure rise: Straining and high adsorption capacity effects
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2 **Research highlights**

3 • Submicron superfine PAC (SSPAC, median diameter 200 nm) adsorbed biopolymer well.

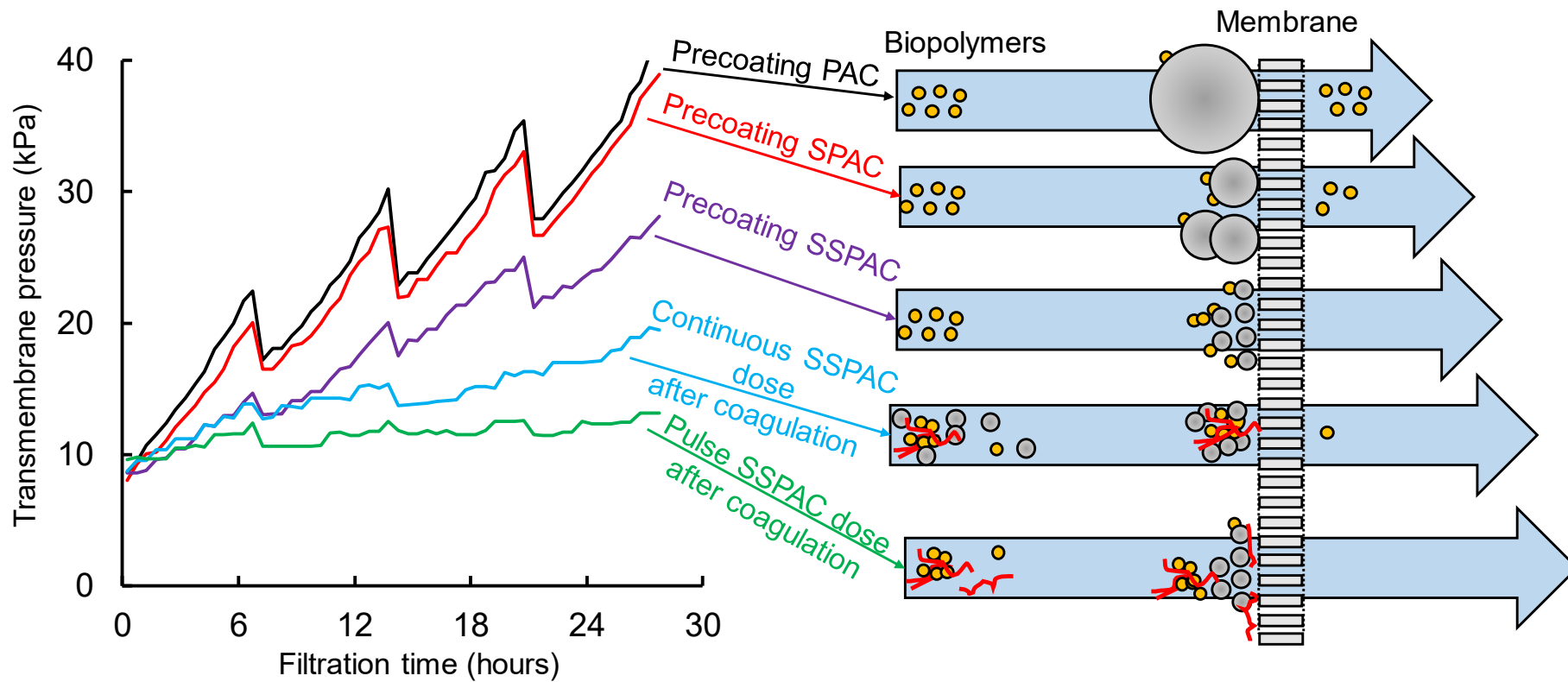
4 • SSPAC removed biopolymer best due to straining effect and high adsorption capacity.

5 • Precoating SSPAC on a membrane reduced the rise of transmembrane pressure (TMP).

6 • Precoating SSPAC after coagulation prevented the rise of TMP almost completely.

7 • Pulse dosing for precoating prevented the rise of TMP better than continuous dosing.

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**Precoating membranes with submicron super-fine powdered activated carbon after coagulation prevents transmembrane pressure rise: Straining and high adsorption capacity effects**

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19 **Abstract**

20

21 Commercially available powdered activated carbon (PAC) with a median diameter of 12–42  
22  $\mu\text{m}$  was ground into 1  $\mu\text{m}$  sized superfine PAC (SPAC) and 200 nm sized submicron SPAC  
23 (SSPAC) and investigated as a pretreatment material for the prevention of hydraulically  
24 irreversible membrane fouling during a submerged microfiltration (MF) process. Compared  
25 with PAC and SPAC, SSPAC has a high capacity for selective biopolymer adsorption, which is  
26 a characteristic found in natural organic matter and is commonly considered to be a major  
27 contributor to membrane fouling. Precoating the membrane surface with SSPAC during batch  
28 filtration further removes the biopolymers by straining them out. In lab-scale membrane  
29 filtration experiments, an increase in the transmembrane pressure (TMP) was almost  
30 completely prevented through a precoating with SSPAC based on its pulse dose after  
31 coagulation pretreatment. The precoated SSPAC formed a dense layer on the membrane  
32 preventing biopolymers from attaching to the membrane. Coagulation pretreatment enabled the  
33 precoated activated carbon to be rinsed off during hydraulic backwashing. The functionality of  
34 the membrane was thereby retained for a long-term operation. Precoating the membranes with  
35 SSPAC after coagulation is a promising way to control membrane fouling, and efficiently  
36 prevents an increase in the TMP because of the straining effect of the SSPAC and the high  
37 capacity of the SSPAC to adsorb any existing biopolymers.

38

39 *Keywords:*

40 SSPAC

41 SPAC

42 Membrane fouling

43 TMP

44 Filtration

45

## 46 **1. Introduction**

47

48 Although low-pressure membrane technology (e.g., microfiltration and ultrafiltration) is used  
49 worldwide in drinking water treatments, the practical application of this technology is  
50 constrained through membrane fouling (Filloux et al., 2016, 2012; Luo et al., 2018; Yu et al.,  
51 2018). An increase in the transmembrane pressure (TMP) caused by membrane fouling,  
52 particularly hydraulically irreversible membrane fouling, leads to high rates of energy  
53 consumption and a long-term degradation of the system performance.

54 Natural organic matter (NOM) is present in all bodies of water and plays an important role  
55 in membrane fouling. The chemical structure of NOM, however, is not well understood because  
56 its composition is variable and the chemical constituents that make up NOM have a wide range  
57 of molecular weights (Adusei-Gyamfi et al., 2019; Amy, 2008; Lee et al., 2004). The  
58 introduction of liquid chromatography-organic carbon detection (LC-OCD) used to separate  
59 NOM into various fractions (Huber et al., 2011) has revealed that a hydrophilic fraction that  
60 includes compounds with high molecular weights (also known as biopolymers) is the main  
61 cause of hydraulically irreversible membrane fouling (Ayache et al., 2013; Chen et al., 2016;  
62 Huang et al., 2017; Kimura et al., 2014; Tian et al., 2013; Wang and Li, 2008; Zheng et al.,  
63 2010).

64 Activated carbon (AC) adsorption, coagulation, and other pretreatment methods have been  
65 widely investigated to remove NOM (particularly biopolymers) prior to membrane filtration  
66 and to thus retard the long-term buildup of TMP (Cheng et al., 2017; Ding et al., 2018; Fabris  
67 et al., 2007; Jarvis et al., 2012; Kimura and Oki, 2017; Lee et al., 2006; Ma et al., 2014; Su et  
68 al., 2017; Umar et al., 2016; Wang et al., 2013; Xing et al., 2019). AC adsorption, coagulation,

69 and the combination of both have been studied for NOM removal in pilot plants (Keeley et al.,  
70 2016; Kweon et al., 2009; Wang et al., 2014). Although pretreatment using only powdered  
71 activated carbon (PAC) in an ultrafiltration system has produced a high removal of NOM, the  
72 PAC itself has caused severe membrane fouling (Lin et al., 2001, 1999). Recent studies,  
73 however, have produced more satisfactory results; when PAC is dosed at the very beginning of  
74 the filtration or is pre-deposited (referred to as a precoating) on the surface of the membrane,  
75 membrane fouling is prevented to a certain extent (Campinas, 2010; Kim et al., 2008; Ye et al.,  
76 2006). The reasons for these inconsistent results may be the hydrophobicity of the membrane  
77 and the diverse characteristics of raw waters. PAC causes less fouling with hydrophilic  
78 membranes (Crozes et al., 1993), and helps reduce fouling when its use is combined with  
79 coagulation pretreatment, although such a combination does not completely eliminate fouling.  
80 As a result, TMP increases gradually during long-term operation (Kweon et al., 2009).

81 Furthermore, superfine PAC (SPAC, median diameter of  $\sim 1 \mu\text{m}$ ), which is produced through  
82 the milling of ordinary PAC, has been found to more rapidly adsorb NOM than PAC and to  
83 have a higher NOM adsorption capacity; in addition, the required dosages are smaller (Amaral  
84 et al., 2016; Bonvin et al., 2016; Matsui et al., 2007, 2006, 2005, 2004). Dosing with SPAC as  
85 a membrane pretreatment method in combination with coagulation has resulted in high rates of  
86 NOM removal and the ability to mitigate the buildup of TMP (Matsui et al., 2009). Although  
87 biopolymers are efficiently removed through a precoating with SPAC, the SPAC layer itself  
88 reduces the permeability of the membrane (Heijman et al., 2009). However, the efficacy of the  
89 SPAC precoating combined with coagulation pretreatment remains unexplored. Recent studies  
90 on submicron SPAC (SSPAC) with a median diameter of  $\sim 200 \text{ nm}$  have revealed that when the  
91 size of the PAC decreases from  $30 \mu\text{m}$  to  $140 \text{ nm}$ , its capacity to adsorb NOM increases over  
92 the entire range of SSPAC particle sizes (Pan et al., 2017).

93 To determine the biopolymer adsorption capacity of SSPAC, we conducted adsorption

94 isotherm experiments using PAC/SPAC/SSPAC and biopolymers in natural river water.  
95 Furthermore, we conducted batch-scale submerged membrane filtration experiments to  
96 elucidate the mechanism of the biopolymer removal. Laboratory-scale membrane filtration  
97 experiments with treatments combining PAC/SPAC/SSPAC and coagulation under different  
98 dosing regimes were further investigated to compare the ability of the treatments to prevent a  
99 long-term increase in TMP during filtration with periodic backwashes.

100

## 101 **2. Materials and methods**

102

### 103 *2.1. ACs*

104

105 In this study, we used wood-based PAC (Taiko-W, Futamura Chemical Co., Ltd., Nagoya,  
106 Japan), SPAC, and SSPAC. A PAC slurry was made by dosing PAC into pure water (Milli-Q  
107 water, Merck KGaA, Darmstadt, Germany). The PAC concentration was consistently within  
108 the range of 10–15% (w/w). The PAC slurry was then milled in a closed chamber with alumina  
109 balls (diameters of 5 and 10 mm) at 45 rpm for 5 h to obtain AC with a median diameter (D50)  
110 of ~4  $\mu\text{m}$ . The milled slurry was then further milled using a bead mill (LMZ015, Ashizawa  
111 Finetech, Ltd., Chiba, Japan) with zirconium dioxide beads (diameter of 0.3 mm) in  
112 recirculation mode at 2,590 rpm for 30 min to produce SPAC with a D50 of ~1  $\mu\text{m}$ . SSPAC  
113 was produced from the same AC slurry using a bead (diameter of 0.1 mm) mill at 3,884 rpm  
114 for 2 h to achieve a D50 of ~200 nm.

115 We measured the size distribution of the AC particles using a laser-light-scattering  
116 instrument (Microtrac MT3300EXII, Nikkiso Co., Inc., Tokyo, Japan). A dispersant (Triton X-  
117 100, Kanto Chemical Co., Inc., Tokyo, Japan) was dosed into the samples, which were then  
118 sonicated (150 W, 19.5 kHz) for approximately 1 min in the case of PAC/SPAC and for 6 min



119 for SSPAC to break up the particle aggregates and determine the true particle sizes (Pan et al.,  
120 2016). The particle size distributions of the ACs are shown in Fig. 1S of the supplementary  
121 information (SI).

122

## 123 *2.2. Water*

124

125 The water of the Wanigawa River (Ibaraki, Japan) was sampled in May and November of 2017.

126 The samples were shipped to the authors' laboratory and designated as raw water-1 and raw

127 water-2, respectively. The water qualities of the two waters were not significantly different

128 (Table 1S, SI). The samples were then filtered through mixed cellulose ester (MCE) membrane

129 filters with a pore size of 0.1  $\mu\text{m}$  ( $\phi$ 142 mm, Merck KGaA, Darmstadt, Germany) to obtain a

130 working solution for the adsorption isotherm experiments (Section 2.3) and batch precoat

131 filtration experiments (Sections 2.4 and 2.5). A coated cellulose acetate membrane filter with a

132 pore size of 10  $\mu\text{m}$  ( $\phi$ 142 mm, Toyo Roshi Kaisha, Ltd., Tokyo, Japan) was used to produce 7

133 L of raw water for the experiments involving the AC addition and submerged membrane

134 filtration with a backwash (Section 2.6). Ultraviolet absorbance at 260 nm (UV260) and the

135 concentrations of biopolymer, humic substances, and total organic carbon (TOC) were used as

136 metrics of the concentrations. TOC concentration was determined using a TOC analyzer (Model

137 900, Sievers Instruments, Boulder, CO, USA). In addition, the UV260 was analyzed using a

138 UV spectrophotometer (UV-1800 with a 5 cm cell, Shimadzu, Kyoto, Japan). The biopolymer

139 and HS concentrations were analyzed using an HPLC system (1100 series, Agilent Tech, Tokyo,

140 Japan) consisting of a single column (Toyopearl HW-50S, 250 mm  $\times$  20 mm, Tosoh Inc., Tokyo,

141 Japan), an injection system (injection rate of 1.2 mL/min), a UV detector, and a TOC analyzer

142 (M9e, Central Kagaku Corp., Tokyo, Japan). The use of this system to measure the biopolymer

143 and HS concentrations corresponds to the application of the size-exclusion chromatography  
144 method developed by Huber et al. (2011).

145

### 146 *2.3. Adsorption isotherm experiments*

147

148 The PAC/SPAC/SSPAC particles were injected into shaking flasks containing 100 mL of raw  
149 water-2 at fixed carbon dosages of 0, 5, 10, 20, 30, and 40 mg/L. The sealed flasks were then  
150 shaken at room temperature (20 °C) for 1 week. The water in the flasks was taken out and then  
151 centrifuged. The supernatant was filtered through two stacked membrane filters, namely,  
152 polyvinylidene fluoride (PVDF), with a pore size of 0.2 µm (Dismic-25CS, Advantec Toyo  
153 Kaisha, Ltd., Tokyo, Japan) to remove residual AC that may interfere with further water quality  
154 analyses.

155

### 156 *2.4. Batch precoat single filtration*

157

158 The PAC, SPAC, and SSPAC particles and two sizes of polystyrene latex spheres (D50 values  
159 of 100 and 200 nm, henceforth referred to as PSL100 and PSL200, Micromod  
160 Partikeltechnologie GmbH, Rostock, Germany) were separately dosed into 50 mL of raw water-  
161 1. Each suspension was poured into a membrane filter funnel with a flat sheet MCE membrane  
162 (pore size of 0.1 µm, φ47 mm, and an effective membrane filtration area of 9.6 cm<sup>2</sup>, Merck  
163 KGaA). Next, 40 mL of the suspension was then filtered through the membrane by a vacuum  
164 (−80 kPa) to obtain an initial AC deposition mass of 0.17, 0.35, or 0.53 mg/cm<sup>2</sup> on the surface  
165 of the membrane. Ten milliliters of the suspension remained in the funnel. Another 50 mL of  
166 raw water-1 was then poured carefully into the funnel without breaking the precoating, and the  
167 filtration was resumed. The filtration was continued until 50 mL of the filtrate was collected for

168 the biopolymer analysis. The increase in the AC deposition mass during the 50-mL filtration  
169 was small (10%).

170

### 171 *2.5. Batch precoat repeat filtration*

172

173 Fifty milliliters of raw water-1 containing 84 mg/L of an AC suspension was poured into a  
174 membrane filter funnel, and 40 mL was filtered through the membrane to form an AC  
175 precoating. Then, 50 mL of raw water-1 was added to the funnel and allowed to pass through  
176 the filter. This process (the addition of 50 mL of raw water-1 + filtration) was repeated until the  
177 total filtrate volume reached 2,090 mL per filter. The filtrates were then sampled to determine  
178 the biopolymer concentrations. In some of the experiments, an AC precoating was applied after  
179 the AC suspension was sonicated (150 W, 19.5 kHz) for 3 min.

180

### 181 *2.6. AC addition and submerged membrane filtration with backwash*

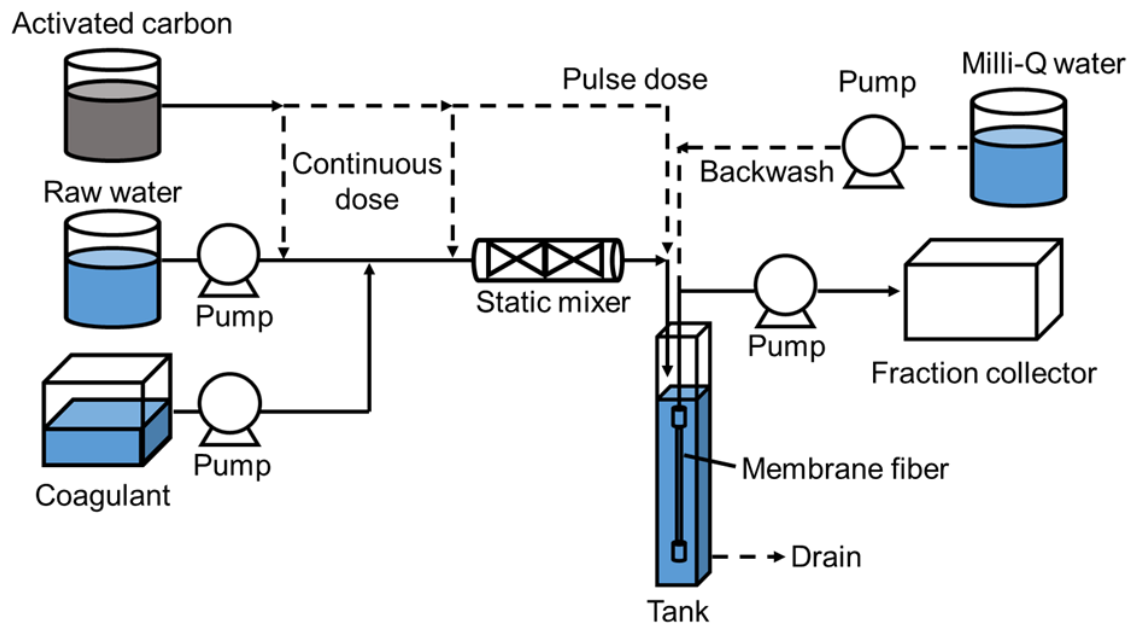
182

183 Fig. 1 shows a schematic diagram of the experimental setup. Raw water-2 was fed by means of  
184 a peristaltic pump with a constant flow rate of 0.64 mL/min into a rectangular tank (interior  
185 dimensions of 1.1 cm × 1.1 cm, water depth of 27.5 cm) in which a hollow fiber PVDF  
186 membrane fiber with a pore size of 0.1 μm (Asahi Kasei Corp., Tokyo, Japan) with its tip closed  
187 was submerged (the PVDF fiber had been purchased as a membrane module and cut to a length  
188 of 14 cm with an effective filtration area of 6 cm<sup>2</sup>). Prior to use in the experiments, every fiber  
189 was tested to ensure that the TMP was within the range of 46–48 kPa during filtration of Milli-  
190 Q water at a flow rate of 15 m/day (625 L/m<sup>2</sup> h). Filtration at a flow rate of 1.7 m/day (70.8  
191 L/m<sup>2</sup> h) was achieved by applying a vacuum to the inside of the membrane. The filtration lasted  
192 for 28 h with a periodic hydraulic backwash. The hydraulic backwash was conducted at 7 h

193 intervals by introducing pure water at 50 kPa from the filtrate side, and the suspension in the  
194 tank was then drained. Membrane filtrate was collected at 30 min intervals for analysis.

195

196



197

198 **Fig. 1 — Laboratory setup for additions of activated carbon and coagulant and for submerged**  
199 **membrane filtration with backwash.**

200

201

202 AC was added to the system in a pulse dose prior to the start of the filtration (referred to as  
203 Methods A, B, and C in Figs. 2S–4S, SI) after hydraulic backwash or added through a  
204 continuous dose (referred to as Methods D and E in Figs. 5S and 6S, SI) throughout the entire  
205 filtration process. In the pulse AC dose experiments, two methods of AC injection were used  
206 (Fig. 7S, SI). In the direct pulse dose methods (Methods A and B), AC was injected directly  
207 into the membrane tank followed by 3 min of bubbling with air at 3.2–5.2 L/min from the  
208 bottom of the tank. In the indirect pulse dose method (Method C), AC and raw water were  
209 mixed vigorously in a bottle, and the mixture was then injected into the membrane tank. In all  
210 experiments, AC dosages were fixed at 5 mg-C/L. The dosage in the case of a pulse dose was

211 expressed as the average dosage, which was equated to the mass of AC (milligram) divided by  
212 the volume (liter) of treated raw water.

213 In Methods B–E (Figs. 3S–6S, SI), a static mixer was placed in the feed line to the tank.  
214 Polyaluminum chloride coagulant (basicity 2.1; sulfate ion 2% (w/w), Taki Chemical Co.,  
215 Hyogo, Japan) was injected at 2 mg-Al/L and mixed with a static mixer. In Methods B and C  
216 (pulse AC dose), coagulant injection and mixing were applied before the AC dose (Figs. 3S and  
217 4S, SI). In Methods D and E (continuous AC dose), coagulant injection and mixing were  
218 conducted either before or after the AC dose (Figs. 5S and 6S, SI).

219 Raw water was supplemented with HCl or NaOH such that the filtrate pH became roughly  
220 constant at 7.5. The suction pressure was recorded based on the voltage using a digital pressure  
221 meter (GC61, Nagano Keiki Products, Tokyo, Japan) and converted into pressure using  
222 calibration curves determined during each experiment. The experiment was conducted in a  
223 room with a temperature of ~25 °C. During the experiment, the water temperature was  
224 measured using a digital thermometer (LR5011, Hioki E.E. Corp., Nagano, Japan), and TMP  
225 was normalized to 25 °C to avoid the influence of changes in the viscosity.

226

227

### 228 **3. Results and discussion**

229

#### 230 *3.1. Biopolymer and TOC adsorption capacities*

231

232 Adsorption isotherms of biopolymer, TOC, and UV260 were obtained on SSPAC, SPAC, and  
233 PAC (Fig. 8S–10S, SI). The adsorption capacities of the three ACs for biopolymer, TOC, and  
234 UV260 increased in order of PAC < SPAC < SSPAC. This order corresponds to the descending  
235 order of the AC particle size. The fact that the adsorption capacities were enhanced as the

236 particle size of the AC decreased is in accordance with the recent discovery that the adsorption  
237 capacity of AC toward adsorbates with a high molecular weight increases as the particle size of  
238 the AC decreases (D50 from 30  $\mu\text{m}$  to 140 nm) (Pan et al., 2017). This is because the molecules  
239 are mostly adsorbed on the exterior of the particles (Ando et al., 2011; Matsui et al., 2014, 2013,  
240 2011). The change in the AC particle size caused by the milling does not result in any substantial  
241 change in the internal pore area (Pan et al., 2017).

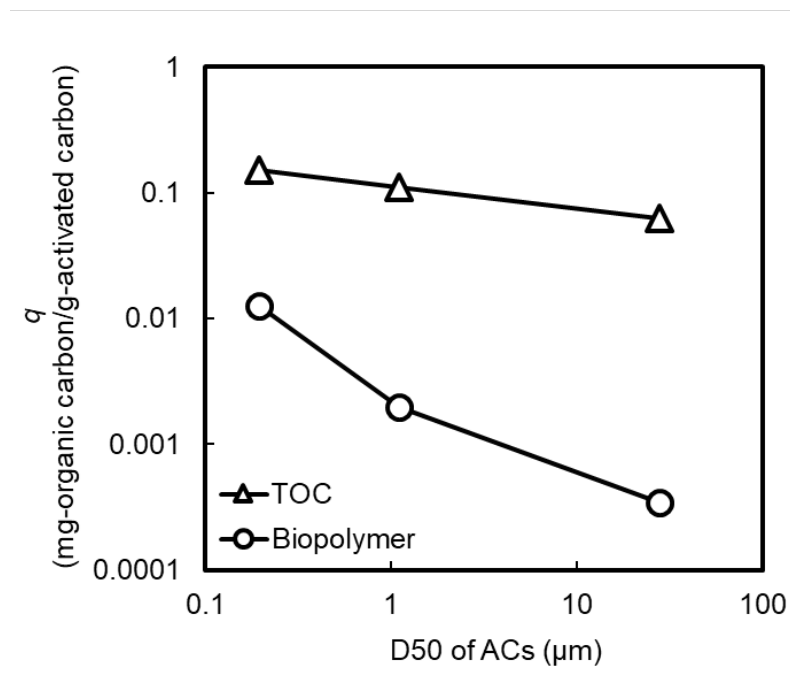
242 To further clarify the dependence of the adsorption capacity on the AC particle size, we  
243 plotted the solid-phase concentration at equilibrium with a liquid-phase concentration of 1.8  
244 mg/L (TOC) and 0.02 mg/L (biopolymer) against the D50 of the AC particles (Fig. 2). The  
245 adsorption capacity of the AC for the biopolymer was smaller than that for the TOC because  
246 biopolymers are constituents of NOM, and the biopolymer concentrations are therefore lower  
247 than the NOM concentrations (which are determined from the TOC). As the D50s of the ACs  
248 decreased, their capacities to adsorb both biopolymers and TOC increased. However, the  
249 adsorption capacity for the biopolymer depended more strongly on the AC particle size than  
250 did the adsorption capacity for the TOC. These trends held when the data were plotted for  
251 different equilibrium liquid-phase concentrations (Fig. 11S, SI). Of relevance to the capacity  
252 dependency on the AC particle size is the adsorption of high molecular-weight compounds  
253 mainly on the exterior of the AC particles owing to their limited intraparticle diffusion distances  
254 (Ando et al., 2011; Matsui et al., 2011). Ando et al. (2010) reported that the capacity  
255 dependency is large for large molecules. In our study, therefore, the strong dependence of the  
256 biopolymer adsorption capacity on the AC particle size was likely related to the large molecular  
257 size of the biopolymers in the NOM. Because of the different degrees of capacity dependency  
258 between the biopolymer and NOM, the biopolymer/TOC concentration ratio after AC contact  
259 decreased with the SSPAC and SPAC dosages, but increased with the PAC dosage (Fig. 12S,  
260 SI). Moreover, the biopolymer/TOC concentration ratio decreased more rapidly after the

261 SSPAC contact than after the SPAC contact. These results indicate that SSPAC selectively  
262 adsorbs the biopolymer from the NOM compared with SPAC and PAC.

263 Because biopolymers are commonly considered to be a major membrane foulant (Huber et  
264 al., 2011; Kimura et al., 2014; Myat et al., 2014; Tian et al., 2013; Zheng et al., 2010), these  
265 results suggest that adsorption pretreatment by SSPAC will mitigate the membrane fouling and  
266 attenuate the TMP buildup more efficiently than SPAC and PAC pretreatment. Heijman et al.  
267 (2009) have a higher biopolymer removal by SPAC than by PAC and suggest that if SPAC is  
268 evenly loaded on a membrane, it will remove the biopolymers and thereby decrease the  
269 membrane fouling. However, SSPAC is clearly superior to the SPAC.

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273

274 **Fig. 2** — Plots of solid-phase concentration ( $q$ ) at an equilibrium liquid-phase total organic carbon  
275 (TOC) concentration of 1.8 mg/L and a biopolymer concentration of 0.02 mg/L versus the median  
276 diameter (D50) of the activated carbons (ACs). The data are taken from Figs. 8S and 9S, SI. Raw  
277 water-2 was used in this experiment.

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### 282 3.2. Biopolymer removal by batch precoat single filtration

283

284 Fig. 3 shows the results of precoat experiments during which PAC, SPAC, SSPAC, PSL100,  
285 and PSL200 particles were each deposited on a 0.1  $\mu\text{m}$  MCE flat sheet membrane filter to  
286 produce a precoat layer, and a sample water containing biopolymers was then passed through  
287 the membrane with a precoat. As described in Section 2.4, the raw water in the experiments  
288 was filtered through a 0.1- $\mu\text{m}$  MCE membrane filter. Therefore, biopolymers were not removed  
289 simply by the water passing through the 0.1- $\mu\text{m}$  MCE membrane filters used for the precoat  
290 (Fig. 13S, SI). The fact that the biopolymers were not removed by the membrane filtration alone  
291 (Fig. 13S, SI) make it clear that the biopolymer removal was possible only when the membrane  
292 was precoat with polystyrene latex particles or AC particles.

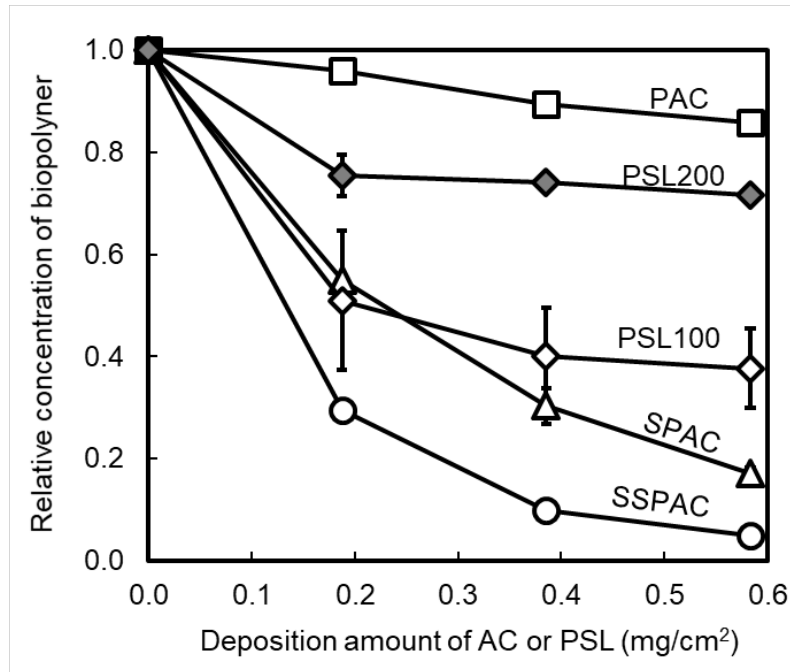
293 The biopolymer removal rates increased as the amount of particles precoat the membrane  
294 increased. However, the removal by the PSL-precoat membrane reached a plateau after a  
295 certain amount of PSL precoat. The plateau of the biopolymer removal rate was higher for  
296 the PSL100 particles than for the PSL200 particles. Biopolymer removal by the SPAC/SSPAC-  
297 precoat membranes was high and can be attributed to the adsorption of biopolymers onto the  
298 AC. However, the removal by a PSL precoat cannot be attributed to adsorption because no  
299 adsorption occurred (Fig. 14S, SI). Biopolymer removal from the PSL100 particles may have  
300 been due to a straining effect. If the ratio of particle diameter to media diameter is greater than  
301 0.15, the particle will be strained by the media (Crittenden et al., 2012). Therefore, the PSL100  
302 (100 nm) media could strain particles with the size  $> 15$  nm. On the other hand, biopolymer of  
303 extremely large molecular weights ( $> 1$  million Da) has high fouling potentials for MF (Kimura  
304 et al., 2018), and such molecular weights could be converted to molecular diameters  $> 17$  nm  
305 (Weiss et al., 2018). The estimation of the molecular diameters  $> 17$  nm is in accordance with  
306 the particle size distribution of the biopolymer determined by membrane filtration (Fig. 15S,



307 SI). Therefore, most of the biopolymer molecules would be greater than 15 nm in size. The  
308 biopolymer molecules are too large to pass through the interstitial spaces between the PSL  
309 particles and are captured as the flow of water moves them through the particles. The higher rate  
310 of biopolymer removal by the precoating of PSL100 versus the PSL200 particles is in  
311 accordance with this postulated straining mechanism. The difference in removal rates can be  
312 explained if there is variability in the sizes of the biopolymer molecules (Kimura et al., 2018).  
313 The interstitial spaces are smaller in a precoating by PSL100 particles versus that by PSL200  
314 particles, and the former can therefore filter the biopolymer molecules over a wider range of  
315 molecular sizes, including relatively small molecules. The fact that the straining effect can  
316 remove biopolymer molecules larger than a certain size but cannot filter biopolymers smaller  
317 than this size explains why the biopolymer removal plateaued as the amount of PSL precoating  
318 increased. The abilities of PAC, SPAC, and SSPAC to remove biopolymers were also consistent  
319 with the particle sizes of the ACs: SSPAC achieved the highest removal, followed by SPAC  
320 and then PAC. This result reflects the higher adsorption capacity as well as the higher straining  
321 effect of SSPAC.

322

323



324

325

326 **Fig. 3** — Fractions of biopolymers that remained after passing through a precoat membrane  
 327 versus amounts of activated carbon (AC) or polystyrene latex spheres (PSLs) precoat the  
 328 membrane. Biopolymer concentration was determined for 50-mL filtrate samples taken after  
 329 precoat by filtering a 40-mL sample. Error bars indicate ranges of two measurements by liquid  
 330 chromatography-organic carbon detection methodology. Raw water-1 was used in this experiment.  
 331

332 *3.3. Biopolymer removal by batch precoat repeated filtration*

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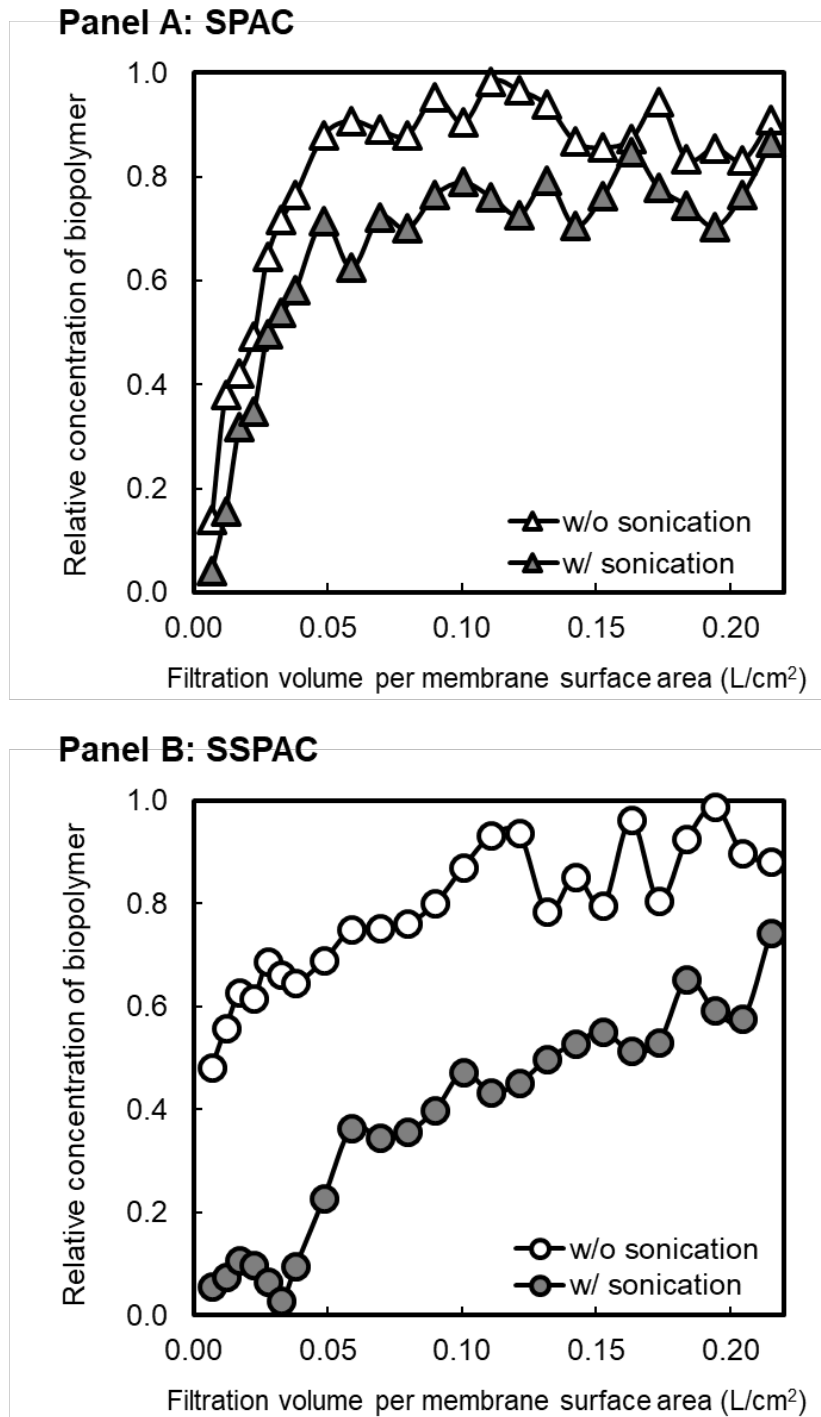
334 We conducted batch precoat repeated filtration experiments to further clarify the straining effect  
 335 of SPAC and SSPAC particles on the biopolymer removal. Fig. 4 shows the percentage of  
 336 biopolymers remaining in the filtrates versus the filtration volume per membrane surface area.  
 337 The fact that the biopolymer concentration in the filtrate was low at the beginning of the  
 338 filtration (i.e., the biopolymer removal was high) was probably due to the fact that the AC was  
 339 fresh and had a high adsorption capacity. The biopolymer concentration in the filtrate increased  
 340 as the filtration progressed but did not reach the influent concentration level. The biopolymer  
 341 concentration plateaued at a level of less than the inflow concentration. This result indicates  
 342 that there was a certain degree of removal maintained by the straining effect even after the  
 343 adsorption capacity had been fully saturated. This stable level of removal was higher with the

344 SSPAC precoating than with the SPAC precoating, and was higher when AC particles were  
345 sonicated before precoating than when they were not (compare the white and gray symbols in  
346 Fig. 4). SSPAC and SPAC particles mildly agglomerate when produced by milling (Pan et al.,  
347 2016). AC particles sufficiently dispersed by sonication can therefore deposit densely on a  
348 membrane and thereby strengthen the straining effect.

349 A biopolymer is known to be a membrane-fouling substance. The high biopolymer removal  
350 by SSPAC owing to its high adsorption capacity and straining effect strongly suggests that  
351 precoating a membrane with SSPAC can mitigate the increase in TMP during the operation of  
352 a membrane filtration system.

353

354



355

356 **Fig. 4 — Relative concentration of biopolymer versus filtration volume per membrane surface**  
 357 **area of water samples. The amount of powdered activated carbon (PAC) deposited on the**  
 358 **membrane for precoating was 0.38 mg/cm<sup>2</sup>. Panel A: SPAC. Panel B: SSPAC. Raw water-1 was**  
 359 **used in this experiment.**

360

361

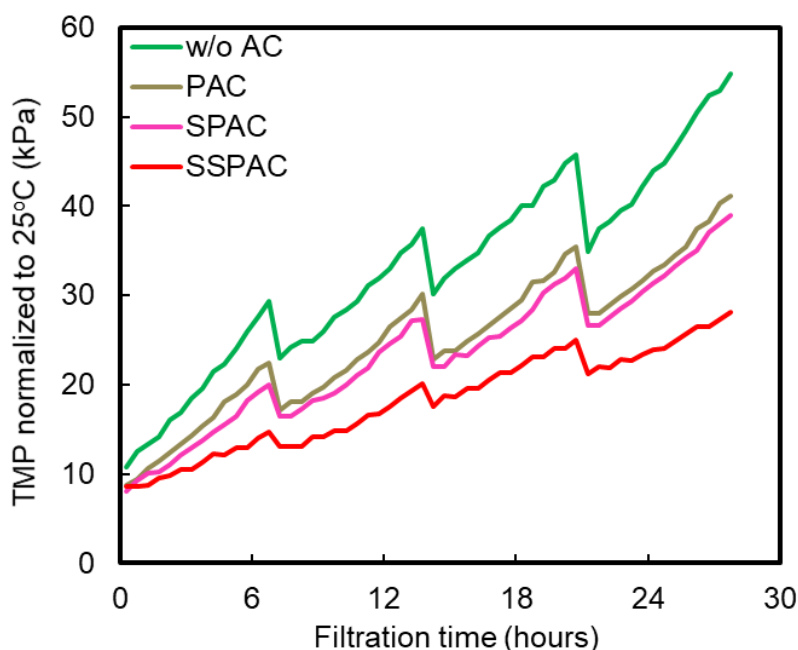
362

363 *3.4. Changes in TMP during AC addition and membrane filtration with backwash*

364

365 Fig. 5 shows the changes in the TMP during filtration with periodic backwashes. During the  
366 experiments (Method A), AC was dosed just after every backwash using a direct pulse dose to  
367 make a precoat on the membrane. Among the three ACs, SSPAC alleviated the increase in the  
368 TMP the most, followed by SPAC and PAC. TMP increased rapidly without an AC  
369 pretreatment. However, even with SSPAC pretreatment, TMP increased with time. Hydraulic  
370 backwashes, which were conducted every 7 h, canceled the increase in the TMP to only a certain  
371 extent. The implication here is that hydraulically irreversible membrane fouling cannot be  
372 stopped simply by precoating with SSPAC.

373



374 **Fig. 5 — TMP versus filtration time for powdered activated carbon (PAC), superfine PAC (SPAC),**  
375 **and submicron SPAC (SSPAC). The experiments were conducted by Method A, where direct**  
376 **pulse dosing (explained in Figs. 2S and 7S, SI) was used. Backwash interval was 7 hours. Filtration**  
377 **rate was 1.7 m/day (70.8 L/m<sup>2</sup>h). Raw water-2 was used in this experiment.**  
378

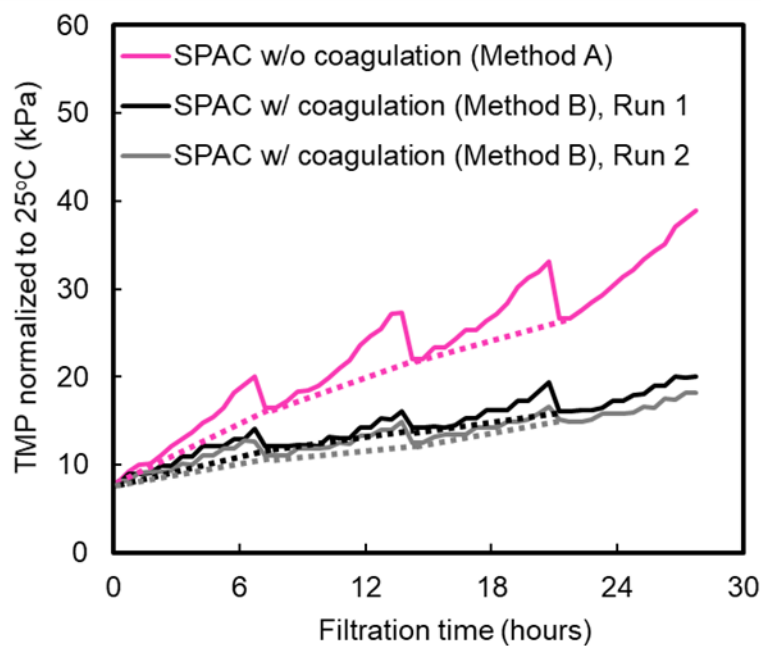
379

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381

382 The addition of SPAC during membrane filtration is already being used in full-scale water  
383 treatments (Kanaya et al., 2015). SPAC has not been added intermittently to form a precoating,  
384 but instead has been added continuously prior to coagulation pretreatment. A continuous SPAC  
385 addition followed by coagulation pretreatment has successfully mitigated an increase in the  
386 TMP better than coagulation pretreatment alone, and the efficacy of adding SPAC followed by  
387 coagulation pretreatment (Matsui et al., 2009) implies the important role of coagulation in  
388 controlling the membrane fouling. We therefore conducted experiments using both coagulation  
389 and AC pretreatment. Fig. 6 shows a comparison of the changes in the TMP in systems with  
390 and without coagulation pretreatment. The fact that TMP increases at a much lower rate with  
391 coagulation than without coagulation indicates that coagulation pretreatment before AC dosing  
392 is necessary to mitigate membrane fouling.

393



394

395 **Fig. 6 — TMP versus filtration time with/without coagulation. The experiments were conducted**  
396 **by Methods A and B, where direct pulse dosing (explained in Figs. 2S, 3S and 7S, SI) of superfine**  
397 **powdered activated carbon (SPAC) was used. Dotted lines show TMP rise due to hydraulically**  
398 **irreversible fouling. Backwash interval was 7 hours. Filtration rate was 1.7 m/day (70.8 L/m<sup>2</sup> h).**  
399 **Raw water-2 was used in this experiment.**

400

401

402 It is widely known that coagulation can remove biopolymers to a certain extent and mitigate  
403 an increase in the TMP (Jung et al., 2006; Kimura et al., 2018; Wray and Andrews, 2014).  
404 During coagulation treatment, NOMs (including biopolymers) are coagulated to form large  
405 flocs. This process increases the permeability of the gel cake layer formed on the membrane  
406 surface and thereby mitigates an increase in the TMP. Experiments with and without  
407 coagulation pretreatment (Fig. 6) were conducted using the same water and the same AC dose.  
408 The depositions on the membrane will therefore be similar, although the fact that the rate of  
409 increase in the TMP during each filtration cycle was lower with coagulation than without  
410 coagulation suggests that the material deposited on the filters was more permeable in the former  
411 case.

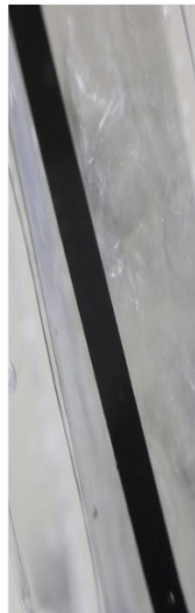
412 Membrane fouling, which causes an increase in the TMP, is divided into hydraulically  
413 reversible and irreversible fouling. On the one hand, hydraulically reversible fouling can be  
414 physically removed (e.g., using a backwash). On the other hand, hydraulically irreversible  
415 fouling can be removed only through chemical cleaning methods, which require more time and  
416 effort than a backwash (Kimura et al., 2008; Peiris et al., 2013). The control of hydraulically  
417 irreversible fouling is therefore extremely important for a reduction in the operational cost  
418 during the membrane filtration process. The dotted lines in Fig. 6 show the changes in the  
419 increase in TMP through hydraulically irreversible fouling. SPAC dosing through direct pulses  
420 mitigates irreversible fouling better with coagulation pretreatment than without such a  
421 pretreatment. Fig. 7 shows photographs of a membrane-submerged tank during a hydraulic  
422 backwash (Fig. 16S shows similar results in the case of SSPAC). The membrane remained  
423 black because of AC accumulation in the system without coagulation pretreatment, whereas the  
424 membrane became white because of a detachment of the floc particles during a backwash in the  
425 system with coagulation pretreatment. A more severe hydraulically irreversible fouling that  
426 occurs without coagulation pretreatment may therefore be due to the attachment of AC particles

427 on the membrane along with the NOM, including biopolymers. Coagulation alleviates the  
428 attachment of AC particles on the membrane. Hydrolysis of the aluminum polymer formed  
429 from the polyaluminum chloride coagulant will impede the strong attachment of AC to the  
430 membrane and can thereby facilitate the release of the AC attached to the membrane during a  
431 backwash.

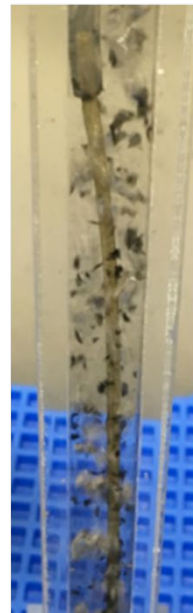
432

433

**Panel A: SPAC direct pulse dose  
w/o coagulation (Method A)**



**Panel B: SPAC direct pulse dose  
w/ coagulation (Method B)**



434

435 **Fig. 7 — Photographs of a membrane tank during backwash. Panel A is a picture of the system**  
436 **without coagulation pretreatment (Method A). Panel B is a picture of the system with coagulation**  
437 **pretreatment (Method B). Direct pulse dosing (explained in Figs. 2S, 3S, and 7S, SI) was used in**  
438 **the experiments. Backwash pressure was 50 kPa. Filtration rate was 1.7 m/day (70.8 L/m<sup>2</sup> h). Raw**  
439 **water-2 was used in this experiment.**

440

441

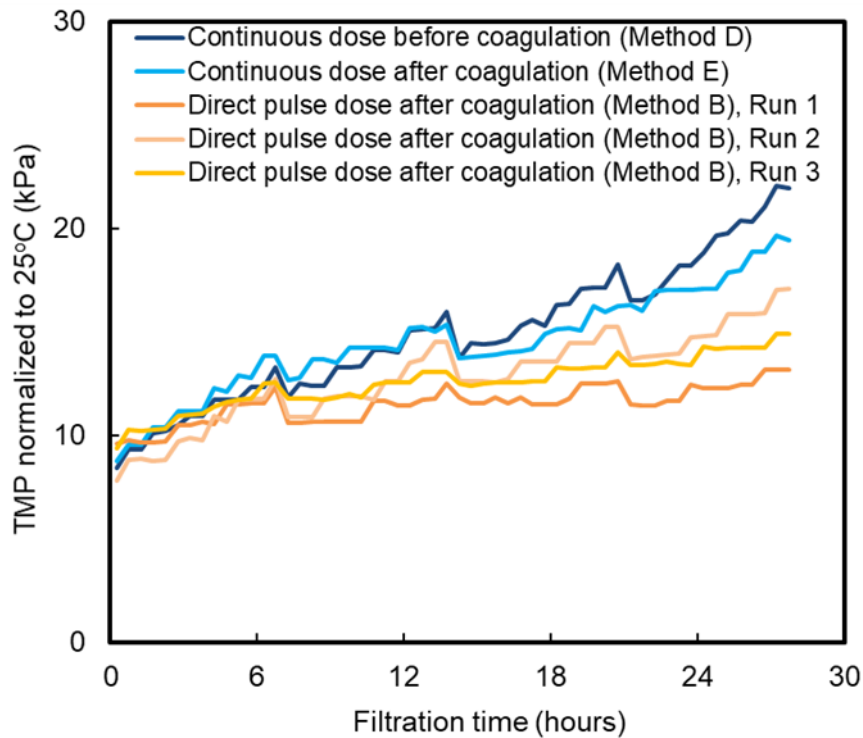
442 Membrane filtration experiments with continuous and pulse AC dosing were conducted to  
443 compare the effectiveness of a precoating as a means of controlling the membrane fouling. In  
444 the pulse AC dose experiments, AC was dosed only after the hydraulic backwash was applied  
445 to re-form the precoating. Two methods were used to continuously apply an AC dose. The



446 method for dosing the AC before coagulation (Method D) was taken from the methodology in  
447 use at full-scale water treatment plants (Kanaya et al., 2015); to facilitate a comparison with the  
448 pulse AC results, the method for dosing the AC continuously after coagulation (Method E) was  
449 identical to that used in the pulse dose experiments (Method B) in terms of the sequence applied.

450 Figs. 17S (SI) and Fig. 8 compare the changes in TMP between the systems with continuous  
451 AC dosing (Methods D and E) and pulse AC dosing (Method B, for precoat) for SPAC (Fig.  
452 17S) and SSPAC (Fig. 8). For SSPAC, the TMPs increase at slower rates in both the direct and  
453 the indirect pulse dose experiments than in the continuous dose experiments. The superiority of  
454 the pulse dose to the continuous dose methodology for preventing an increase in the TMP was  
455 confirmed during the experiments in which SSPAC was added as a pulse or continuously after  
456 coagulation treatment. The amount of SSPAC used to precoat the membrane was higher for the  
457 pulse dose method than for the continuous dose method from the beginning of the filtration.  
458 The precoat prevented biopolymers from attaching to the membrane through the adsorptive  
459 removal of the biopolymers and based on the straining effect described in Sections 3.1 and 3.2.  
460 The superiority of the pulse dose method over continuous dosing for precoat was clear for  
461 SSPAC (Fig. 8), but was less apparent for SPAC (Fig. 17S, SI). Precoat using AC to mitigate  
462 membrane fouling was therefore effective when the AC particles were within the submicron  
463 range. In other words, continuous dosing, which is simpler than pulse dosing, is a reasonable  
464 dosing method if the AC particles are within the micron range.

465



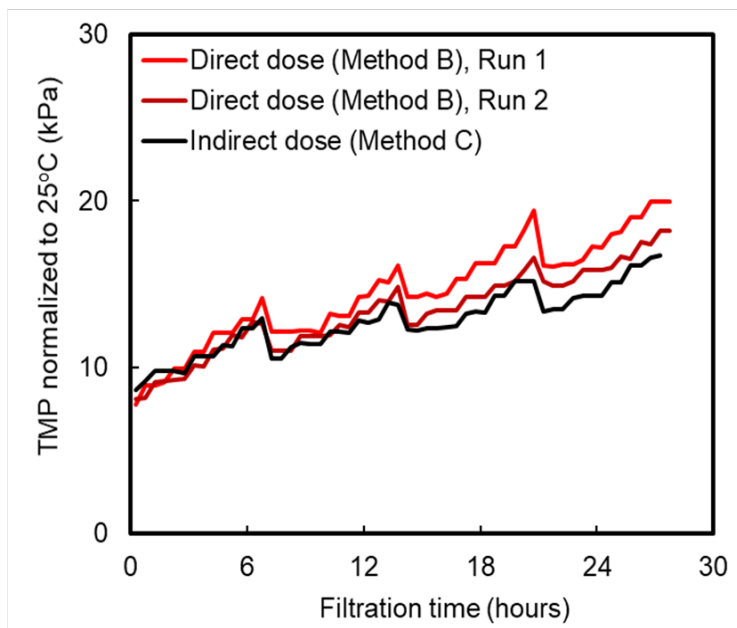
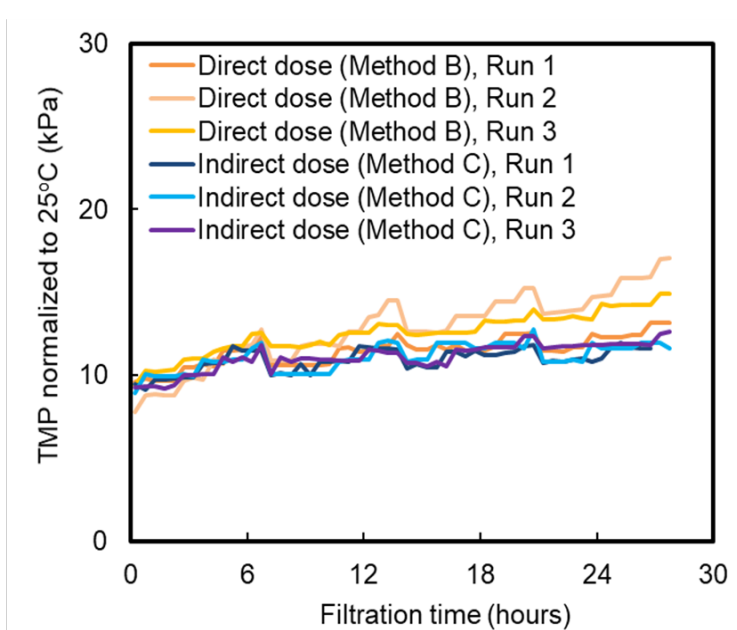
466

467 **Fig. 8** —TMP as a function of filtration time when membrane filtration was conducted after  
 468 SSPAC adsorption and coagulation pretreatment. The experiments were conducted by Methods  
 469 B, D, and E (explained in Figs. 3S, 5S, and 6S, respectively, SI) to compare direct pulse dose and  
 470 continues dose. Backwash interval was 7 hours. Filtration rate was 1.7 m/day (70.8 L/m<sup>2</sup>h). Raw  
 471 water-2 was used in this experiment.

472

473

474 Fig. 9 shows comparative plots of TMP versus the filtration time for direct and indirect  
 475 pulse dose methods (Fig. 7S, SI) combined with a coagulation treatment (Methods B and C  
 476 described in Figs. 3S and 4S, respectively). Analogous comparisons between SPAC and SSPAC  
 477 are shown in Fig. 18S (SI). The indirect pulse dose method resulted in a more stable and lower  
 478 TMP than the direct pulse dose method for both SPAC and SSPAC. With the indirect pulse  
 479 dose method, water was manually shaken vigorously after the injection of the AC. With the  
 480 direct pulse dose method, the AC was injected into the tank and mixed with raw water by  
 481 bubbling for 3 min. The TMP was therefore lower with indirect dosing than with direct dosing  
 482 because indirect pulse dosing produced a well-mixed AC suspension. The implication here is  
 483 that complete dispersion of the AC before being deposited on the membrane is a key for a better  
 484 precoating.

**Panel A: SPAC****Panel B: SSPAC**

486

487 **Fig. 9** —TMP as a function of filtration time when membrane filtration was conducted after  
 488 **SPAC/SSPAC** adsorption and coagulation pretreatment. **SPAC** (Panel A) and **SSPAC** (Panel B)  
 489 **with direct pulse dose and indirect pulse dose (Method B and C, respectively, as explained in**  
 490 **Figures 3S, 4S and 7S, SI) were used in this experiment. Backwash interval was 7 hours. Filtration**  
 491 **rate was 1.7 m/day (70.8 L/m<sup>2</sup> h). Raw water-2 was used in this experiment.**

492

493

494

495 *3.5. Biopolymer and HS removal during AC addition and membrane filtration with backwash*

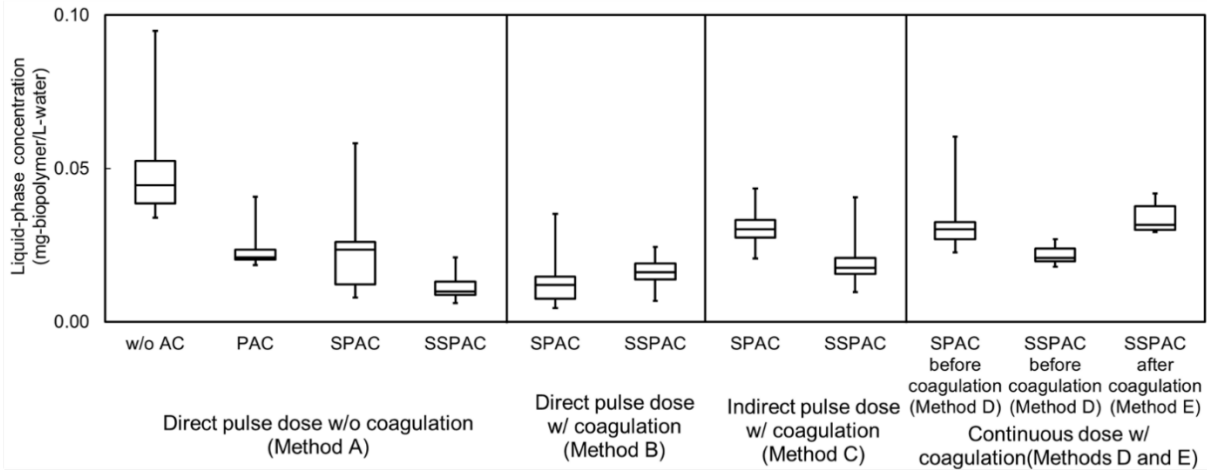
496

497 During the filtration process, filtrate samples were taken and analyzed regarding the biopolymer  
498 and HS concentrations (Fig. 10). During experiments with a direct pulse dose but without  
499 coagulation, the removal was mostly higher for biopolymers than for HS. Biopolymer removal  
500 was improved by reducing the AC particle size and through coagulation pretreatment. The  
501 improvement of the removal was more apparent for biopolymers than for HS. The biopolymer  
502 concentrations in the filtrate were reduced by precoating with SSPAC, followed by SPAC and  
503 PAC. This order was the same as that of the TMP reduction (Fig. 5). During experiments with  
504 direct pulse SSPAC dosing without coagulation, the high percentage of biopolymer removal  
505 (75%) indicated that the biopolymers were removed primarily by the thin cake layer formed  
506 with SSPAC on top of the membrane before the biopolymers could reach and foul the  
507 membrane. However, the quantitative contributions of the coagulation, adsorption, and  
508 straining effects on the biopolymer removal, as well as the mitigation of the increase TMP, have  
509 yet to be investigated.

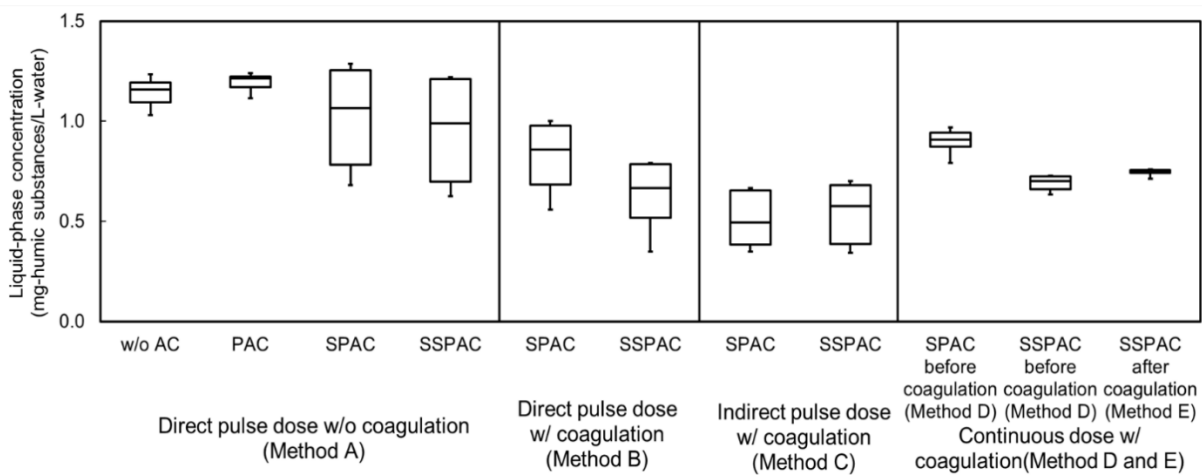
510 The fact that biopolymer removal was also higher with pulse SSPAC dosing than with  
511 continuous SSPAC dosing supports the merit of using a precoating to prevent membrane  
512 fouling. In the direct SSPAC pulse dosing experiments, biopolymer removal was higher without  
513 coagulation than with coagulation. This result was unexpected but can be explained if a denser  
514 deposition of SSPAC on the membrane without coagulation than with coagulation leads to a  
515 higher biopolymer removal. It should be noted, however, that without coagulation, the  
516 membrane was severely fouled by the AC itself (section 3.4).

517

Panel A: Biopolymer



Panel B: HS



518

519

520 **Fig. 10 — Box and whisker plots of biopolymers and humic substances (HS) concentrations in**  
 521 **filtrates for different combinations of coagulation and powdered activated carbon (PAC)**  
 522 **treatment. Horizontal lines within boxes represent median values, the upper and lower lines of the**  
 523 **boxes represent the 75th and 25th percentiles, respectively, and the upper and lower bars outside**  
 524 **the boxes indicate the maximum and minimum values, respectively.**

525

526

527

528 **4. Conclusions**

529

- 530 (1) The capacity of AC to adsorb a biopolymer increases with a decrease in the AC particle  
 531 size and hence follows the order PAC < SPAC < SSPAC. SSPAC selectively adsorbs a  
 532 biopolymer from NOM compared with SPAC and PAC. The superiority of SSPAC for

533 biopolymer adsorption suggests that it has potential application in the control of  
534 membrane fouling.

535 (2) Biopolymers are also physically removed by a SPAC/SSPAC layer which precoats the  
536 membrane. The SSPAC precoating removes biopolymers through a better straining than  
537 SPAC; sonication can disperse agglomerated SPAC/SSPAC to produce a denser precoat  
538 and thereby enhance the straining effect.

539 (3) Coagulation is indispensable in the AC precoat filtration. Coagulation not only removes  
540 biopolymers it also facilitates the detachment of AC particles from the membrane during  
541 hydraulic backwashing, and in this way prevents hydraulically irreversible membrane  
542 fouling by AC.

543 (4) The pulse dosing of SSPAC (for precoating a submerged membrane) shows superiority  
544 in alleviating the buildup of TMP owing to hydraulically irreversible membrane fouling  
545 versus continuous dosing. The fact that an indirect pulse dosing of SSPAC preceded by  
546 coagulation pretreatment achieves the best prevention of an overall increase in the TMP  
547 indicates that AC dispersion is important for a precoating.

548

549

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551

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555

556

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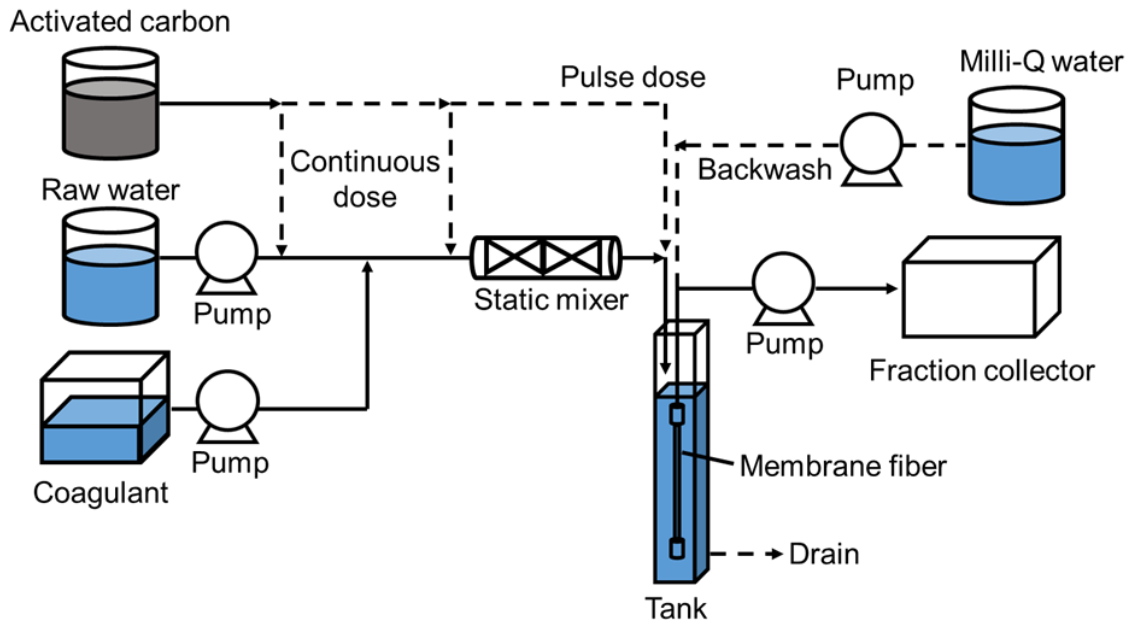
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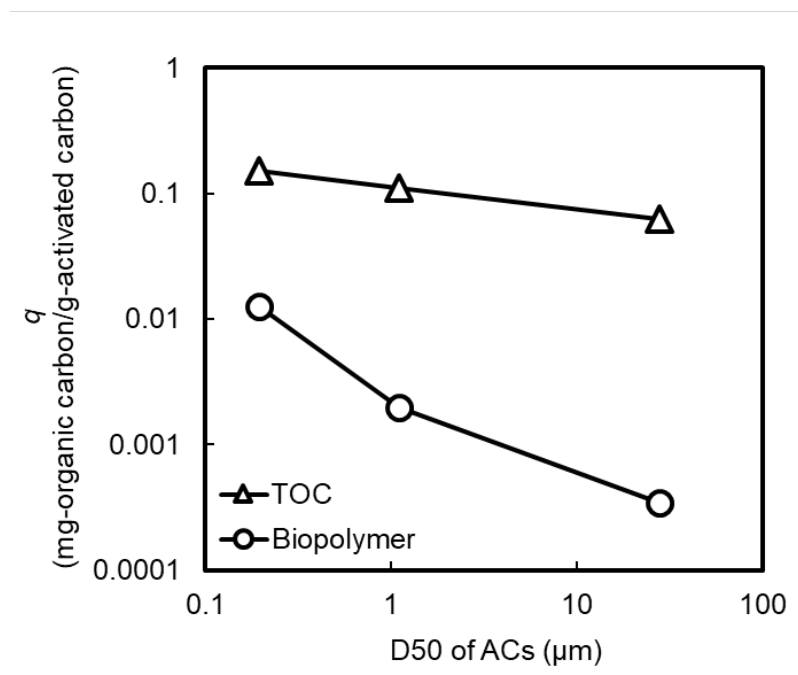
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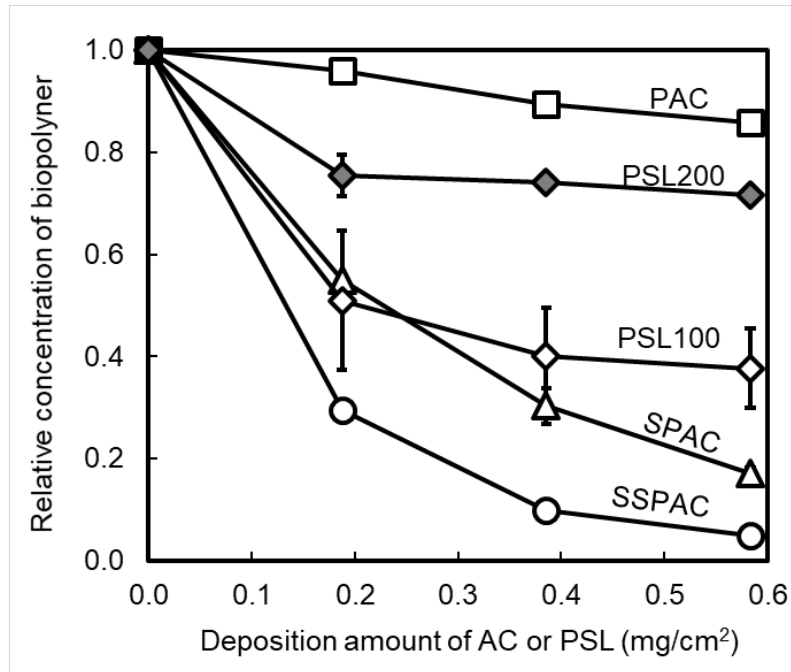
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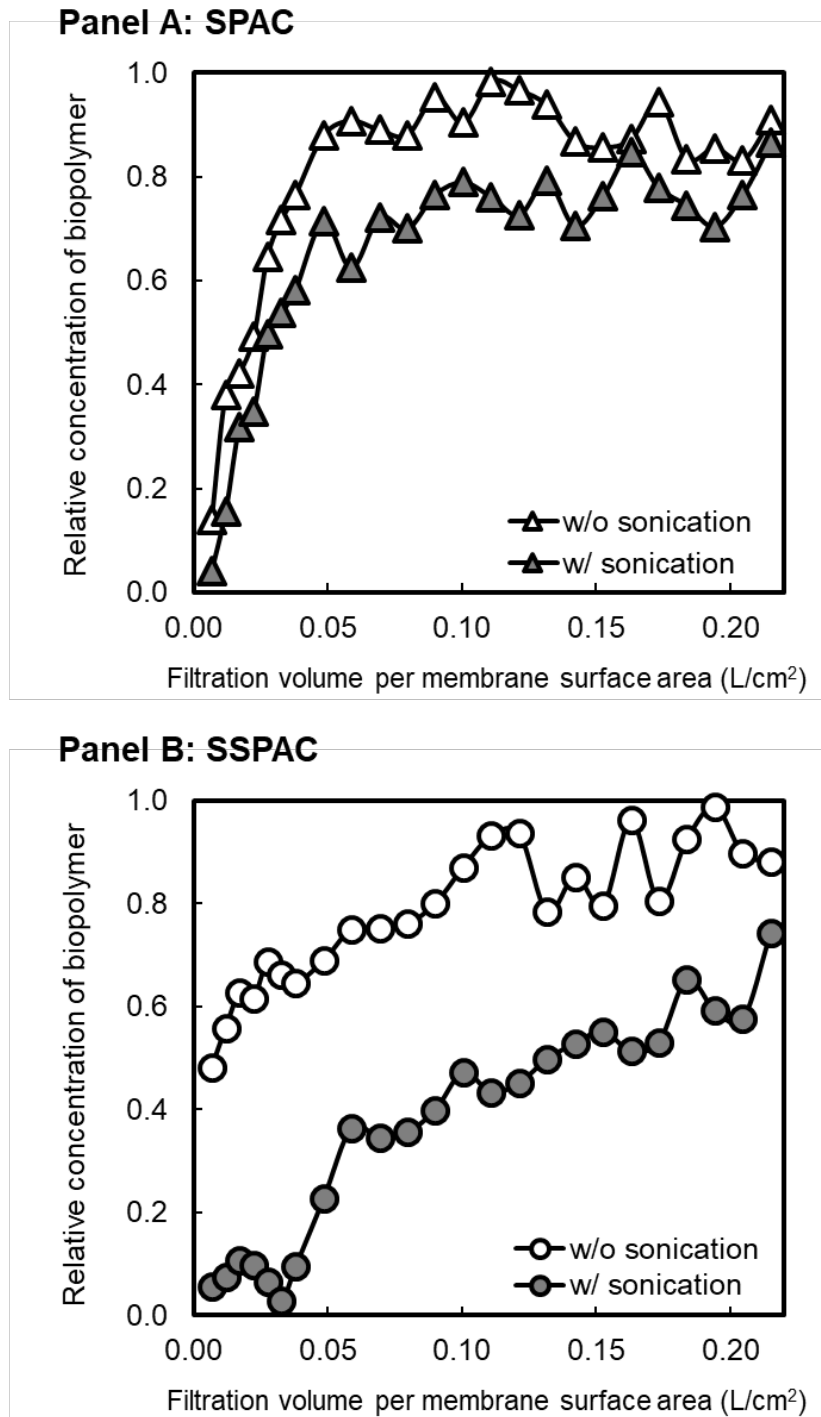
**Fig. 1 — Laboratory setup for additions of activated carbon and coagulant and for submerged membrane filtration with backwash.**



**Fig. 2** — Plots of solid-phase concentration ( $q$ ) at an equilibrium liquid-phase total organic carbon (TOC) concentration of 1.8 mg/L and a biopolymer concentration of 0.02 mg/L versus the median diameter (D50) of the activated carbons (ACs). The data are taken from Figs. 8S and 9S, SI. Raw water-2 was used in this experiment.

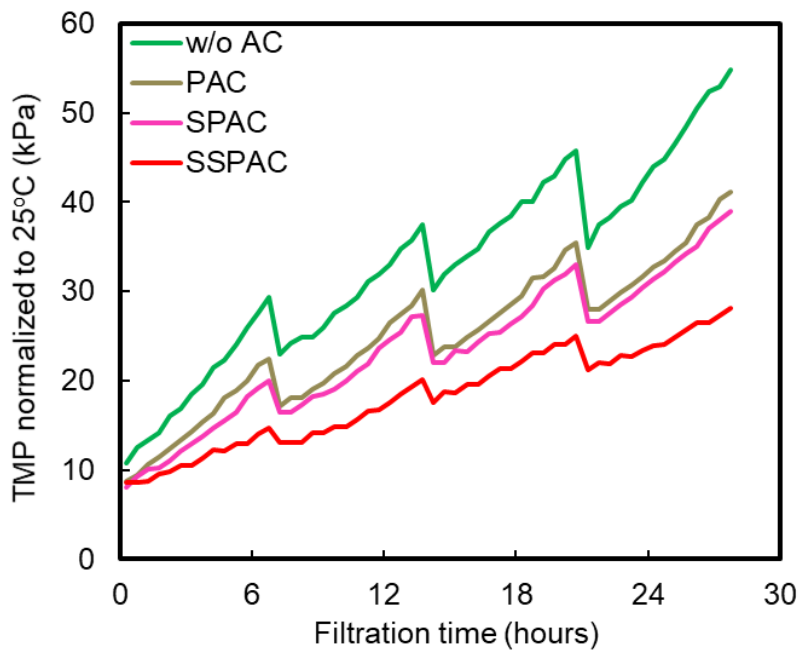


**Fig. 3** — Fractions of biopolymers that remained after passing through a precoated membrane versus amounts of activated carbon (AC) or polystyrene latex spheres (PSLs) precoating the membrane. Biopolymer concentration was determined for 50-mL filtrate samples taken after precoating by filtering a 40-mL sample. Error bars indicate ranges of two measurements by liquid chromatography-organic carbon detection methodology. Raw water-1 was used in this experiment.

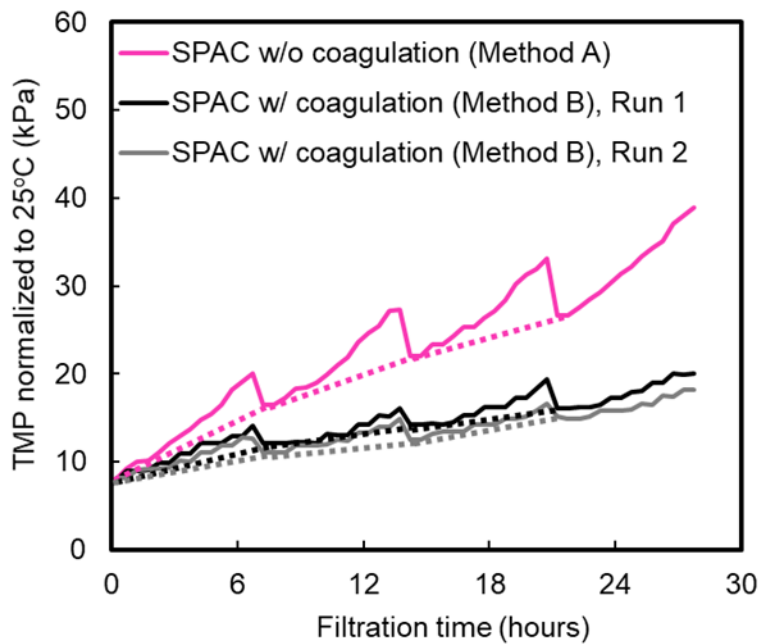


**Fig. 4** — Relative concentration of biopolymer versus filtration volume per membrane surface area of water samples. The amount of powdered activated carbon (PAC) deposited on the membrane for pre-coating was 0.38 mg/cm<sup>2</sup>. Panel A: SPAC. Panel B: SSPAC. Raw water-1 was used in this experiment.





**Fig. 5** — TMP versus filtration time for powdered activated carbon (PAC), superfine PAC (SPAC), and submicron SPAC (SSPAC). The experiments were conducted by Method A, where direct pulse dosing (explained in Figs. 2S and 7S, SI) was used. Backwash interval was 7 hours. Filtration rate was 1.7 m/day (70.8 L/m<sup>2</sup>h). Raw water-2 was used in this experiment.

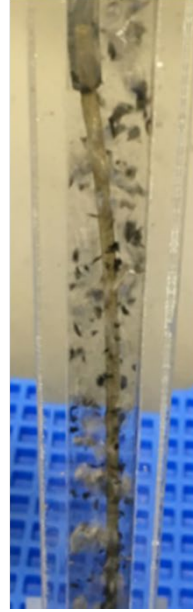


**Fig. 6 — TMP versus filtration time with/without coagulation. The experiments were conducted by Methods A and B, where direct pulse dosing (explained in Figs. 2S, 3S and 7S, SI) of superfine powdered activated carbon (SPAC) was used. Dotted lines show TMP rise due to hydraulically irreversible fouling. Backwash interval was 7 hours. Filtration rate was 1.7 m/day (70.8 L/m<sup>2</sup> h). Raw water-2 was used in this experiment.**

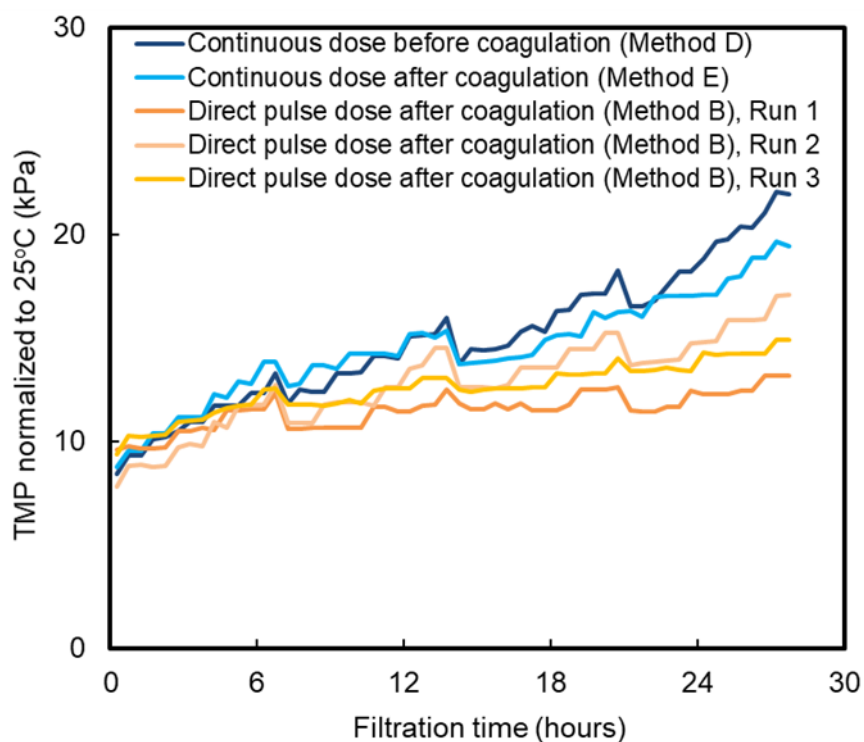
**Panel A: SPAC direct pulse dose  
w/o coagulation (Method A)**



**Panel B: SPAC direct pulse dose  
w/ coagulation (Method B)**

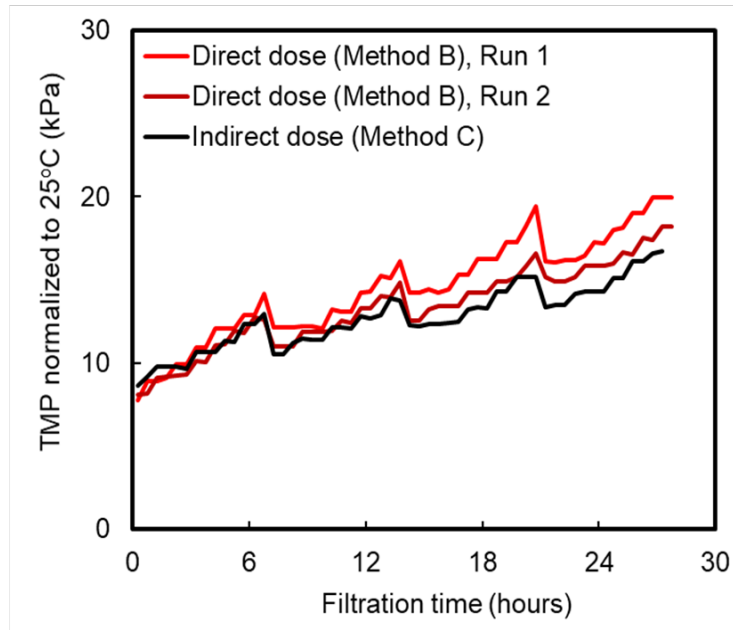


**Fig. 7 — Photographs of a membrane tank during backwash. Panel A is a picture of the system without coagulation pretreatment (Method A). Panel B is a picture of the system with coagulation pretreatment (Method B). Direct pulse dosing (explained in Figs. 2S, 3S, and 7S, SI) was used in the experiments. Backwash pressure was 50 kPa. Filtration rate was 1.7 m/day (70.8 L/m<sup>2</sup> h). Raw water-2 was used in this experiment.**

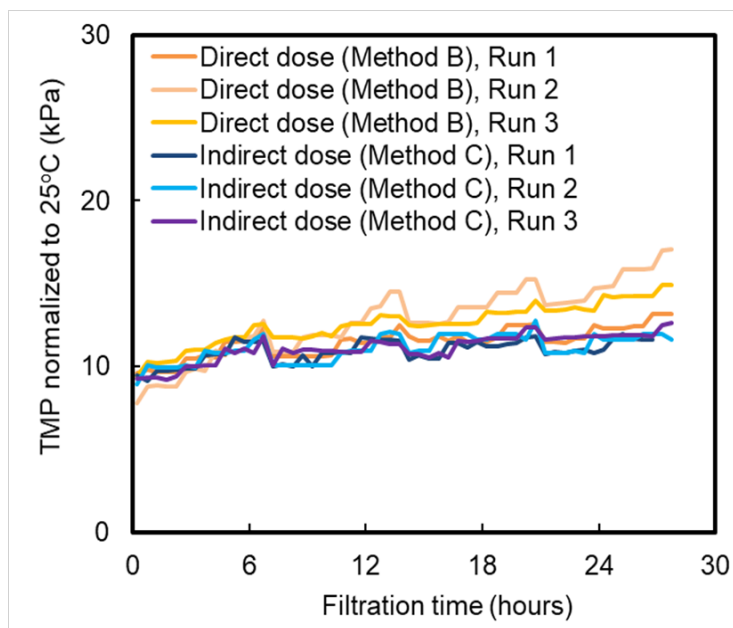


**Fig. 8** —TMP as a function of filtration time when membrane filtration was conducted after SSPAC adsorption and coagulation pretreatment. The experiments were conducted by Methods B, D, and E (explained in Figs. 3S, 5S, and 6S, respectively, SI) to compare direct pulse dose and continuous dose. Backwash interval was 7 hours. Filtration rate was 1.7 m/day (70.8 L/m<sup>2</sup>h). Raw water-2 was used in this experiment.

### Panel A: SPAC

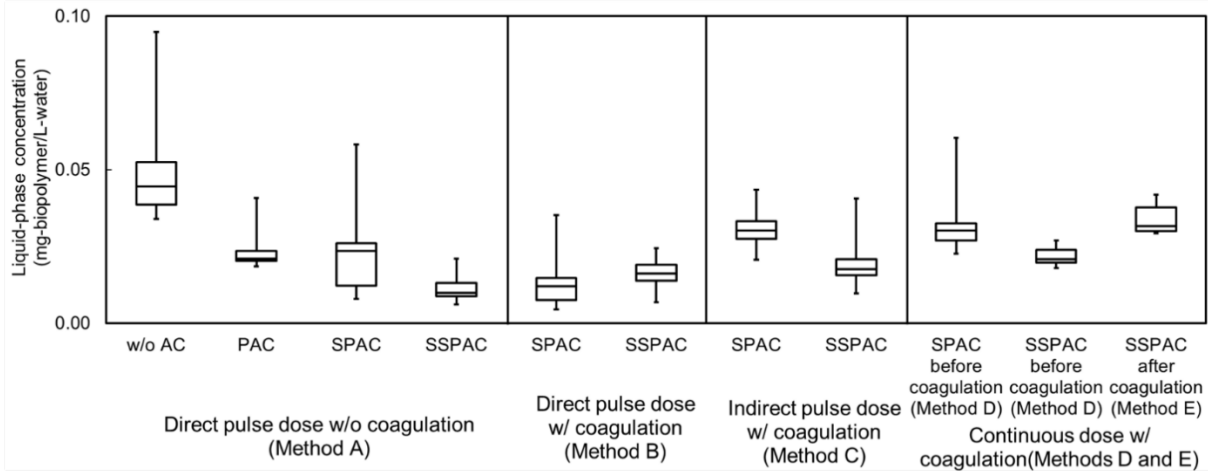


### Panel B: SSPAC

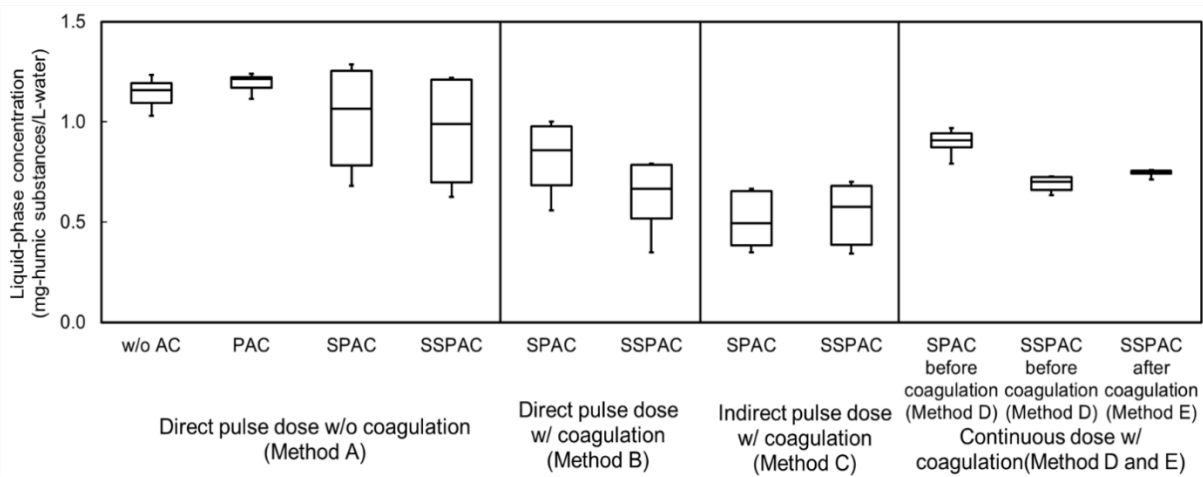


**Fig. 9** —TMP as a function of filtration time when membrane filtration was conducted after SPAC/SSPAC adsorption and coagulation pretreatment. SPAC (Panel A) and SSPAC (Panel B) with direct pulse dose and indirect pulse dose (Method B and C, respectively, as explained in Figures 3S, 4S and 7S, SI) were used in this experiment. Backwash interval was 7 hours. Filtration rate was 1.7 m/day (70.8 L/m<sup>2</sup> h). Raw water-2 was used in this experiment.

**Panel A: Biopolymer**



**Panel B: HS**



**Fig. 10 — Box and whisker plots of biopolymers and humic substances (HS) concentrations in filtrates for different combinations of coagulation and powdered activated carbon (PAC) treatment. Horizontal lines within boxes represent median values, the upper and lower lines of the boxes represent the 75th and 25th percentiles, respectively, and the upper and lower bars outside the boxes indicate the maximum and minimum values, respectively.**

## Supplementary Information

**Precoating membranes with submicron super-fine powdered activated carbon after coagulation prevents transmembrane pressure rise: Straining and high adsorption capacity effects**

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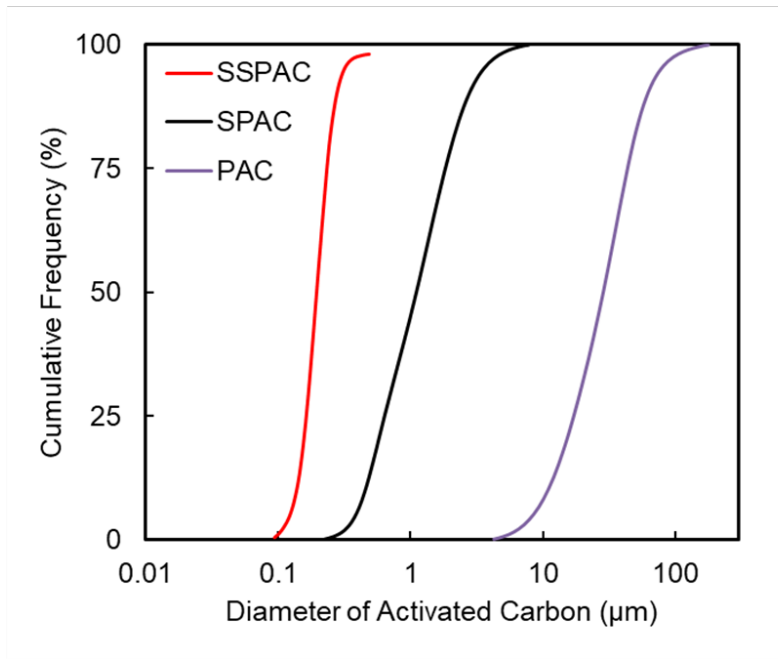
*\* Corresponding author. Tel./fax: +81-11-706-7280  
E-mail address: matsui@eng.hokudai.ac.jp (Y. Matsui)*

**Tab. 1S — Water quality of Raw water-1 and Raw water-2 (Raw water was pre-filtrated by 0.1- $\mu\text{m}$  MCE membrane).**

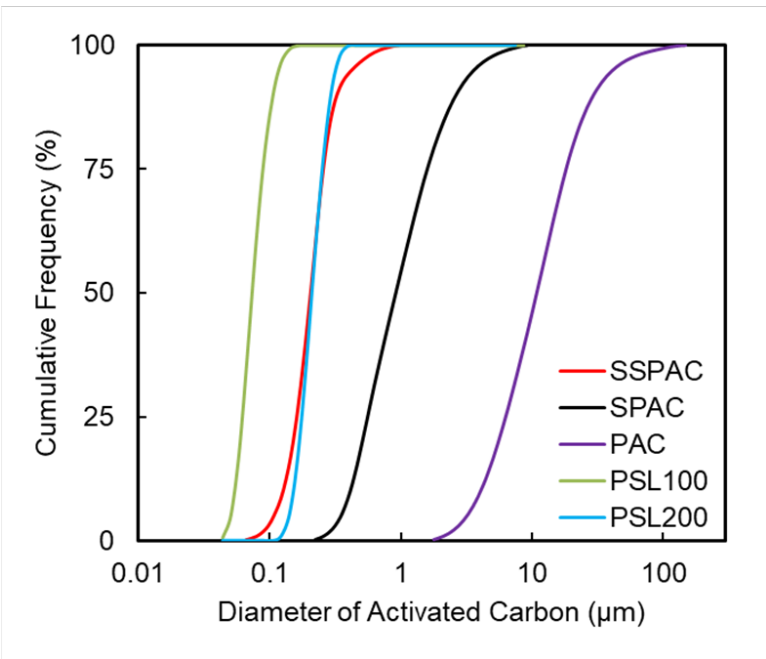
	pH	TOC (mg/L)	UV260 ( $\text{cm}^{-1}$ )	Biopolymer (mg/L)	Alkalinity (mg/L as $\text{CaCO}_3$ )	$\text{Na}^+$ (mg/L)	$\text{K}^+$ (mg/L)
Raw water-1	8.07	2.61	0.06	0.0725	71	52.7	6.03
Raw water-2	7.62	2.66	0.06	0.0770	72	43.7	5.84
	$\text{Mg}^{2+}$ (mg/L)	$\text{Ca}^{2+}$ (mg/L)	$\text{Cl}^-$ (mg/L)	$\text{NO}_3^-$ (mg/L)	$\text{SO}_4^{2-}$ (mg/L)		
Raw water-1	11.0	19.0	70.7	13.3	24.4		
Raw water-2	9.18	18.0	54.0	13.8	22.3		



**Panel A: AC used in Sections 2.3 and 2.6**

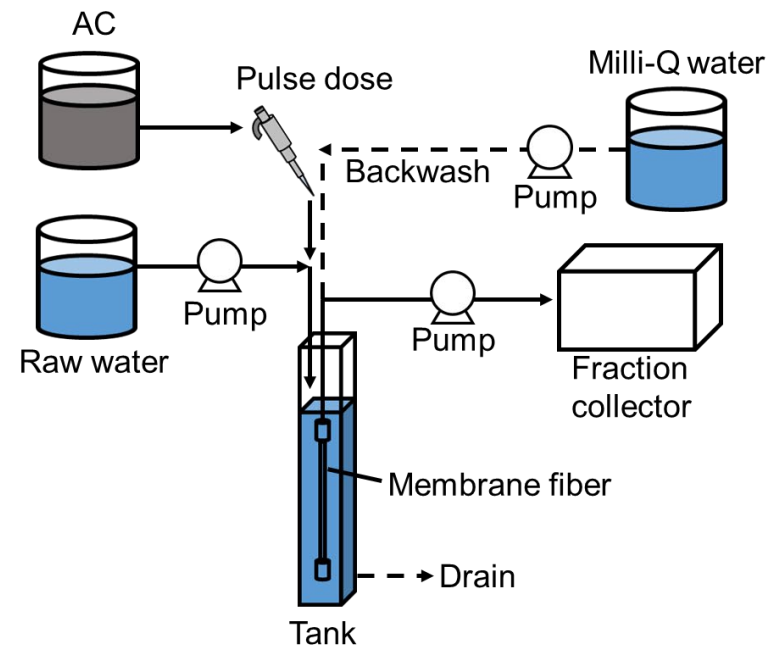
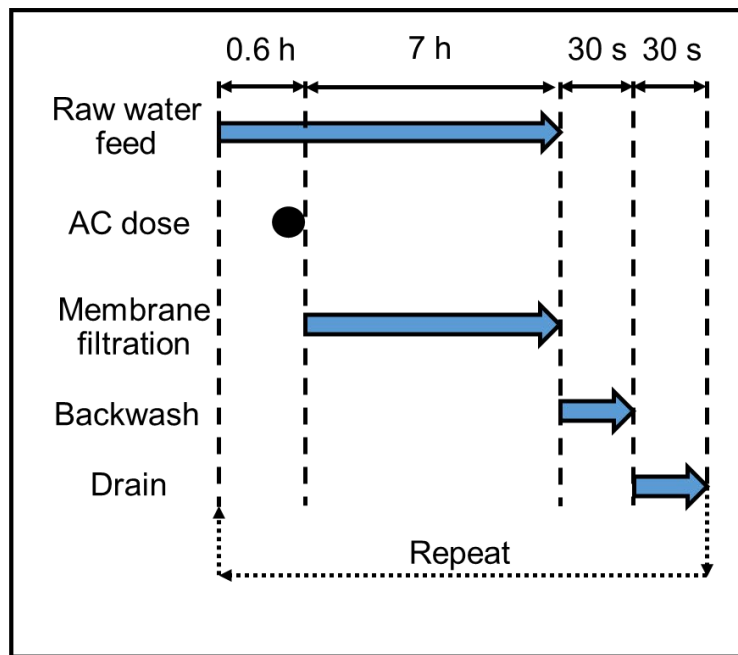


**Panel B: AC and PSL used in Sections 2.4 and 2.5**



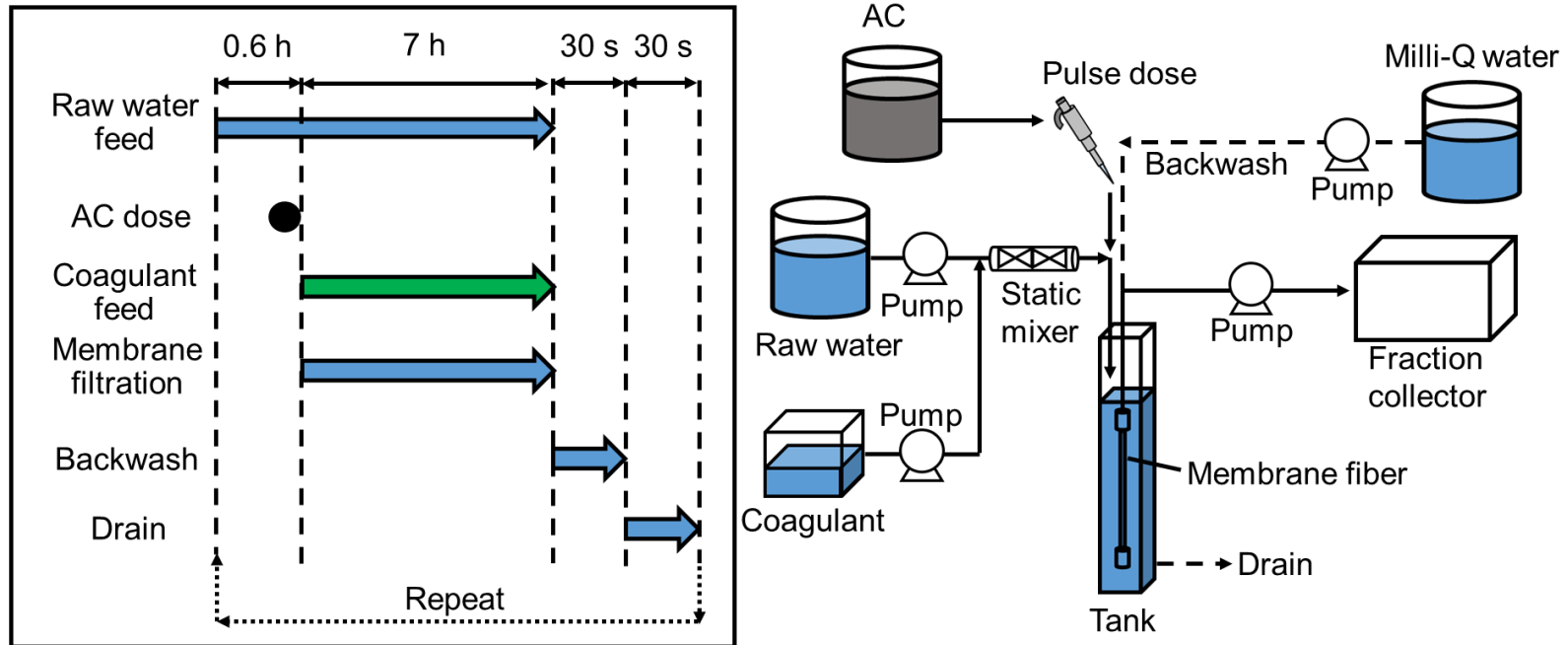
**Fig. 1S — Size distributions of PAC (powdered activated carbon) and PSL (polystyrene latex) particles.**

Method A:  
Direct pulse AC dose w/o coagulation



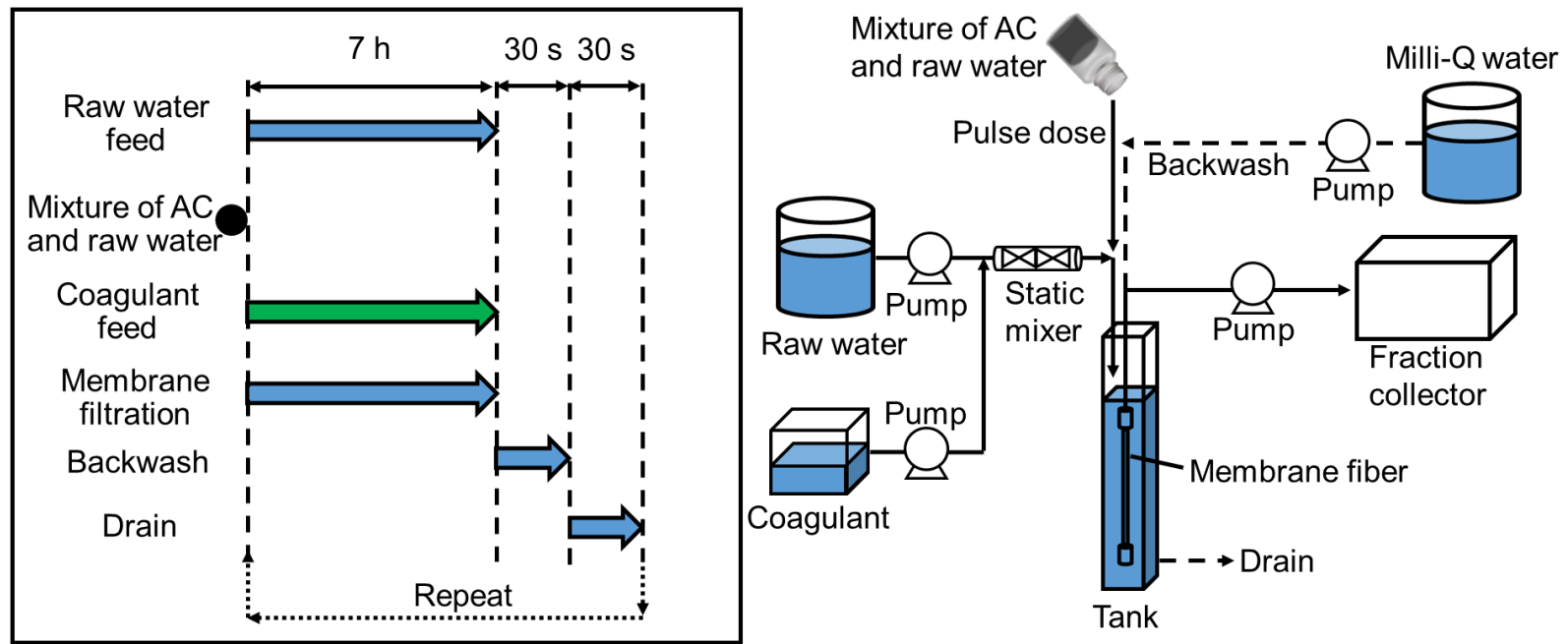
**Fig. 2S —Method A: Process flow and time flow of the direct pulse AC dose without coagulation. (The process was repeated four rounds in every experiment)**

Method B:  
Direct pulse AC dose w/ coagulation



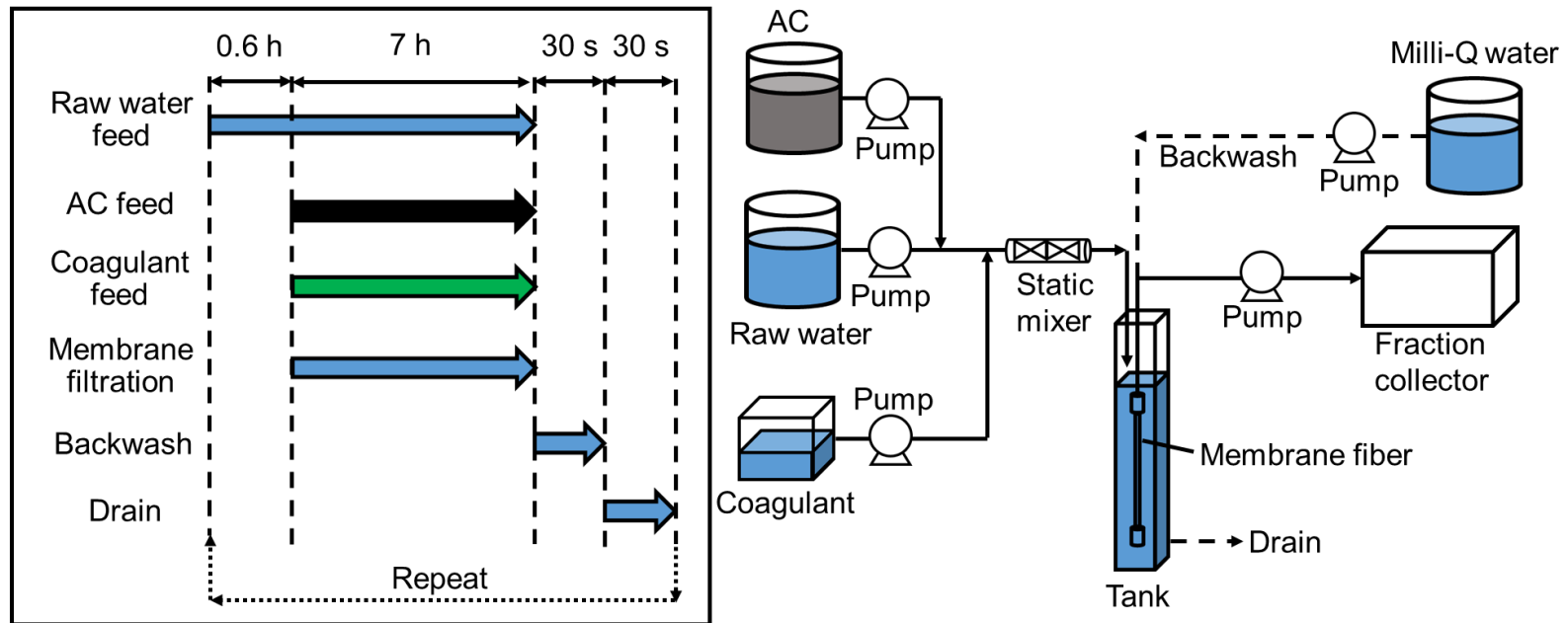
**Fig. 3S —Method B: Process flow and time flow of the direct pulse AC dose with coagulation. (The process was repeated four rounds in every experiment)**

Method C:  
Indirect pulse AC dose w/ coagulation



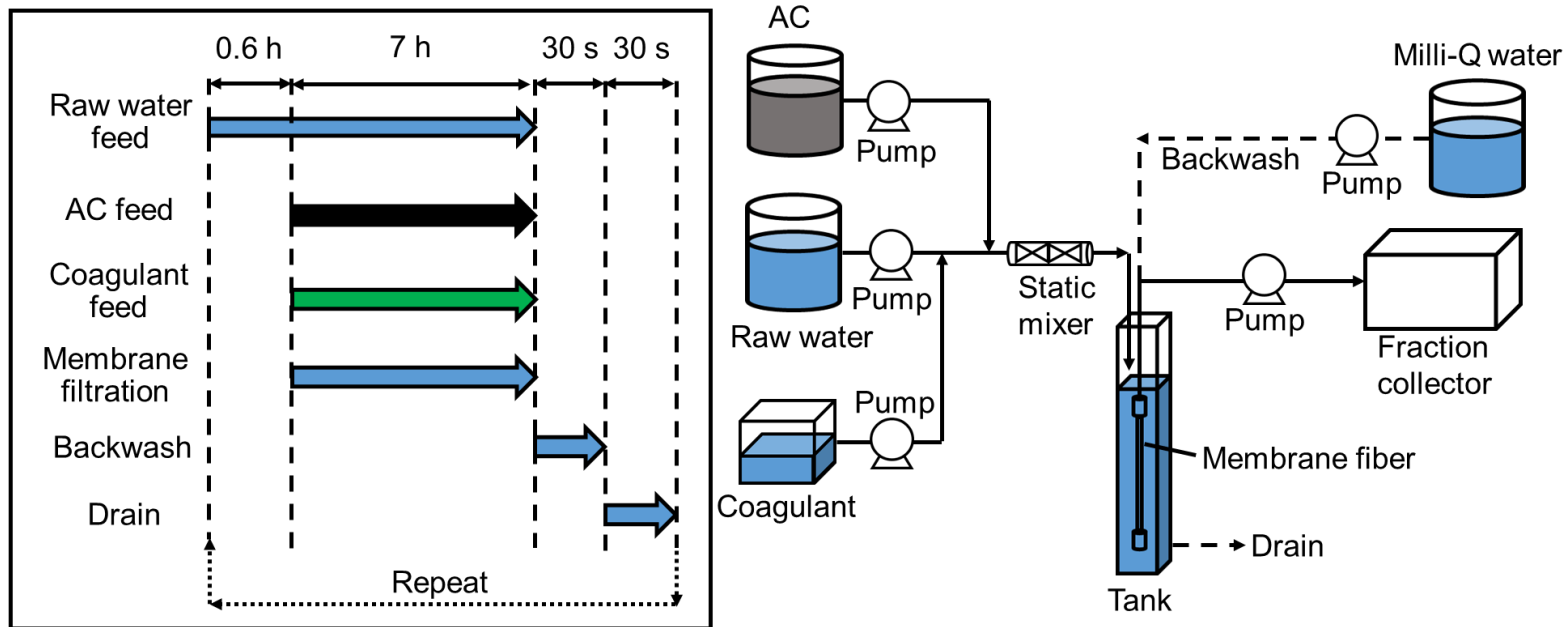
**Fig. 4S —Method C: Process flow and time flow of the indirect pulse AC dose with coagulation. (The process was repeated four rounds in every experiment)**

Method D:  
Continuous AC dose before coagulation



**Fig. 5S —Method D: Process flow and time flow of continuous AC dose before coagulation. (The process was repeated four rounds in every experiment)**

Method E:  
 Continuous AC dose after coagulation



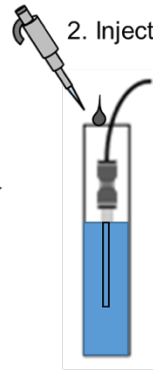
**Fig. 6S —Method E: Process flow and time flow of continuous AC dose after coagulation. (The process was repeated four rounds in every experiment)**

**Direct pulse dose:**

1. Inject raw water into tank



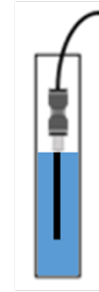
2. Inject AC



3. Three minutes bubbling



4. Start filtration



**Indirect pulse dose:**

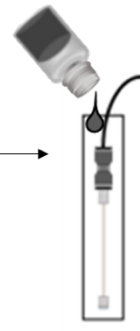
1. Inject AC and raw water into bottle



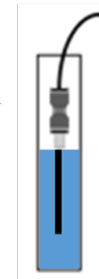
2. Shake suspension vigorously



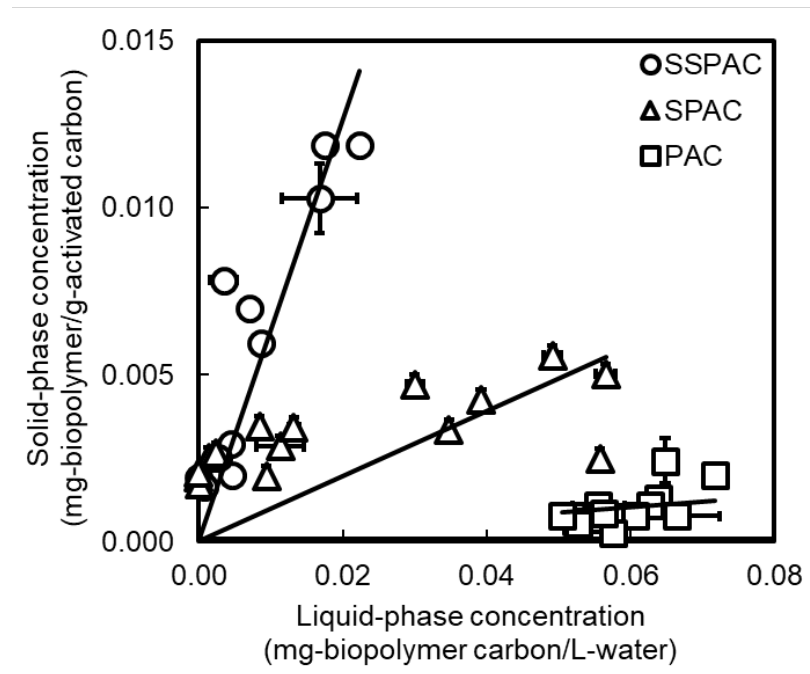
3. Inject suspension into tank



4. Start filtration

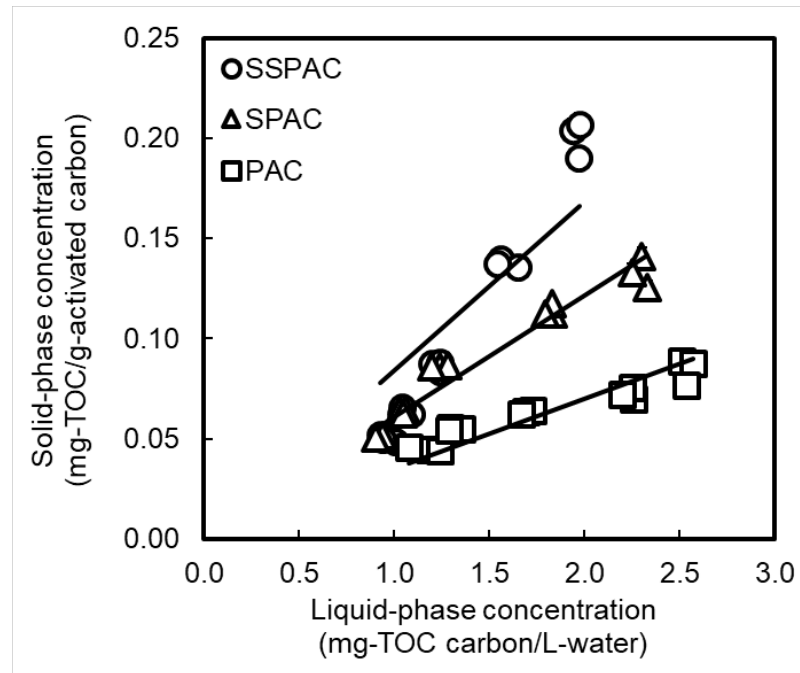


**Fig. 7S — Direct and indirect pulse dose method explanation.**

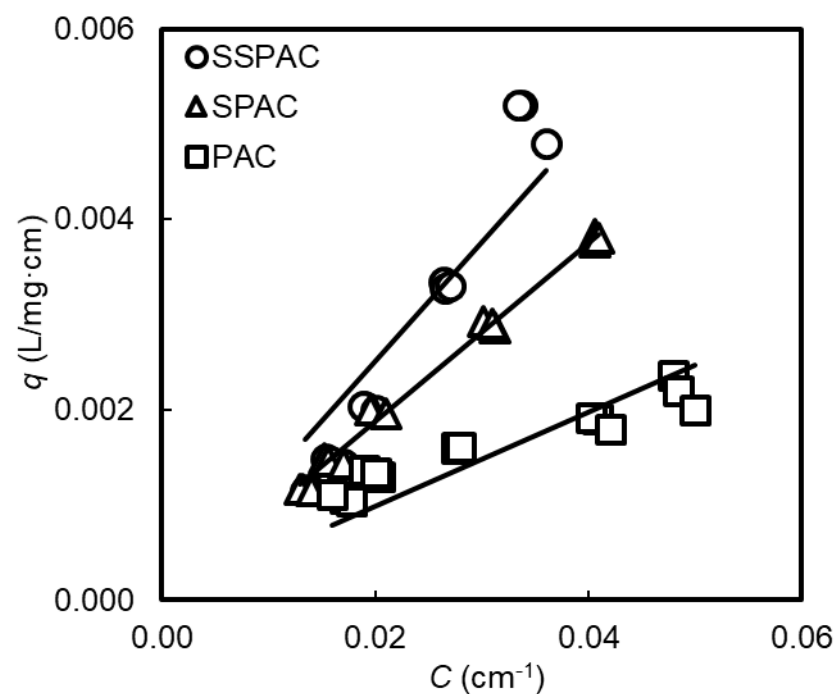


**Fig. 8S — Solid-phase concentration versus liquid-phase concentration of biopolymer for different forms of powdered activated carbon (PAC). Raw water-2 was used in this experiment. The symbols indicate the data points. The lines are regression lines with an intercept of 0. The error bars indicate ranges of two measurements by liquid chromatography–organic carbon detection methodology (for the x axis) and consequent changes of calculated concentrations (for the y axis). Error bars indicate standard deviations of measurements. Some error bars are hidden behind the symbols.**



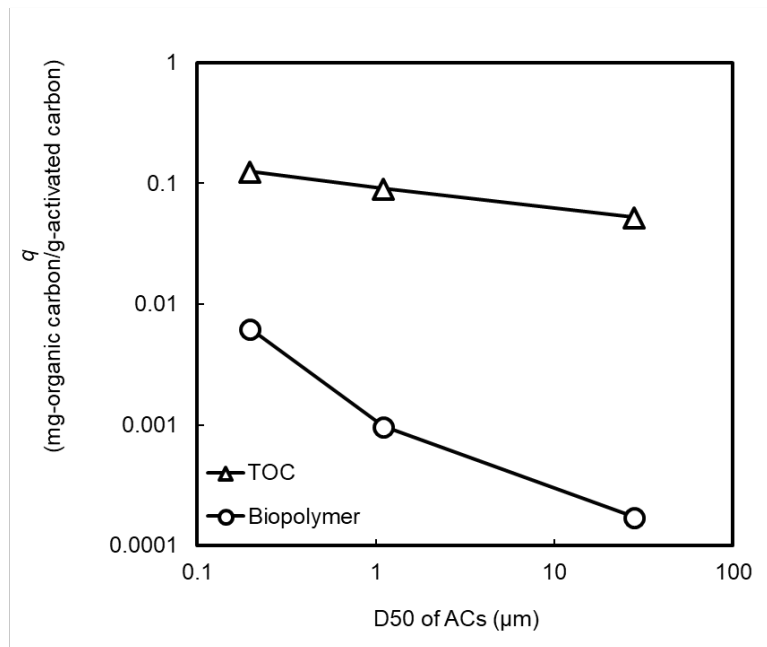


**Fig. 9S — Solid-phase concentration versus liquid-phase concentration of total organic carbon (TOC) for different forms of powdered activated carbon (PAC). Raw water-2 was used in this experiment. The lines are regression lines with an intercept of 0. Error bars, which indicate standard deviations of measurements, are hidden by the plots.**

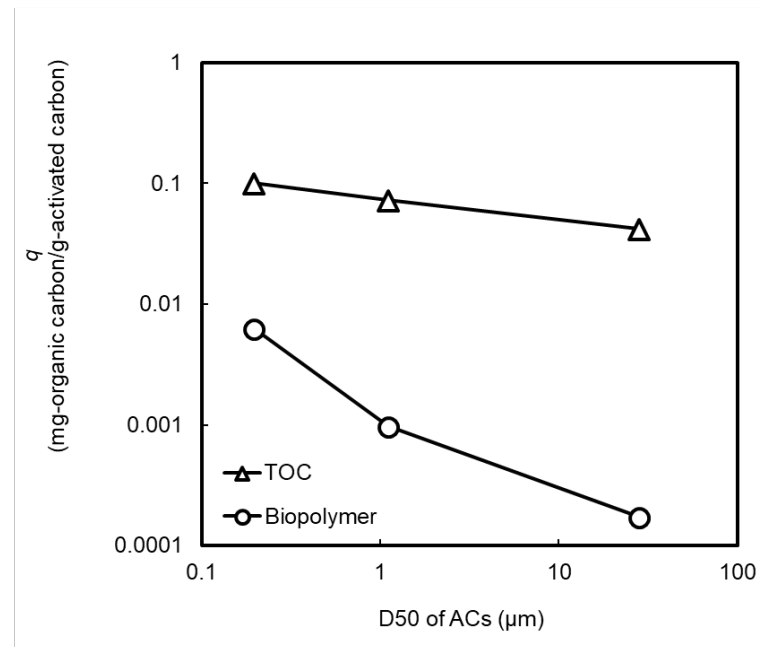


**Fig. 10S — Solid-phase concentration ( $q$ ) versus liquid-phase concentration ( $C$ ) of UV260 for different forms of powdered activated carbon (PAC). Raw water-2 was used in this experiment. The lines are regression lines with an intercept of 0.**

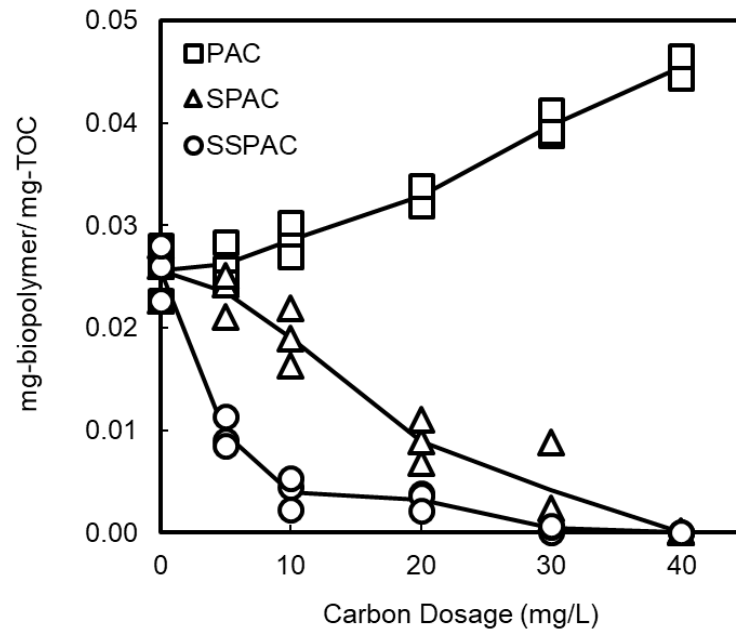
Panel A



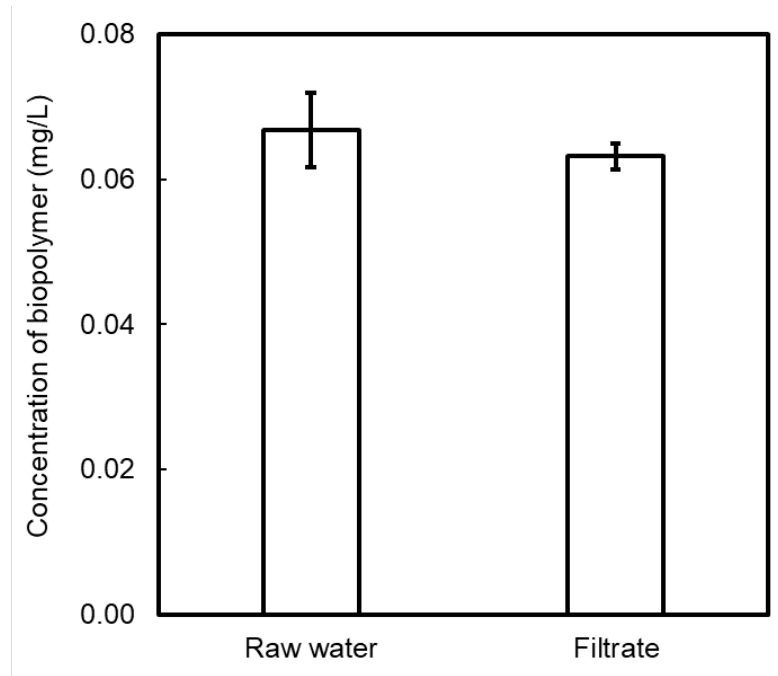
Panel B



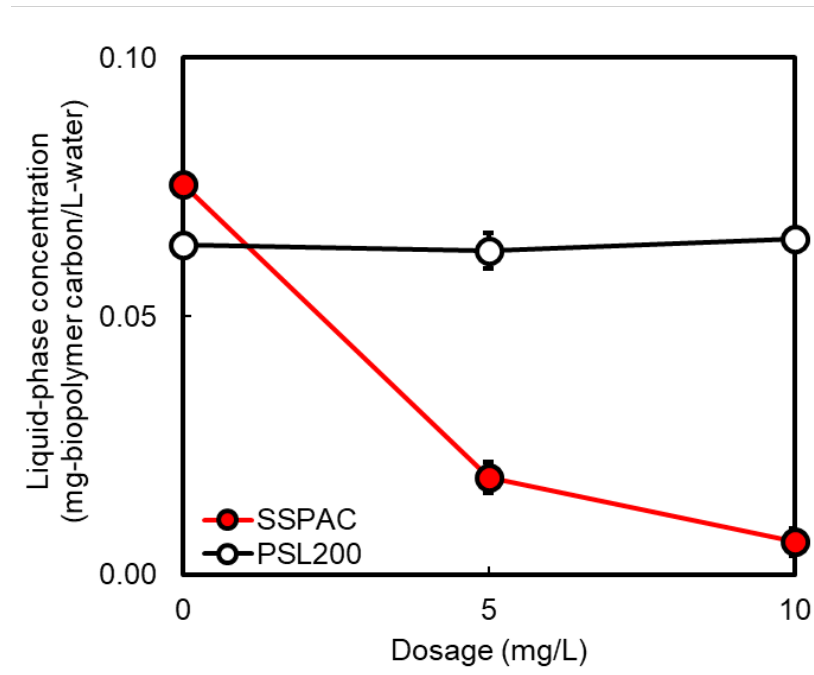
**Fig. 11S** — Plots of solid-phase concentration ( $q$ ) at equilibrium with liquid-phase concentration of 1.5 mg/L of total organic carbon (TOC) and 0.01 mg/L of biopolymer (Panel A) and 1.2 mg/L TOC and 0.01 mg/L biopolymer (Panel B) versus median diameter (D50) of ACs (PAC, SPAC, and SSPAC). The data are taken from Figs. 8S and 9S. Raw water-2 was used in this experiment.



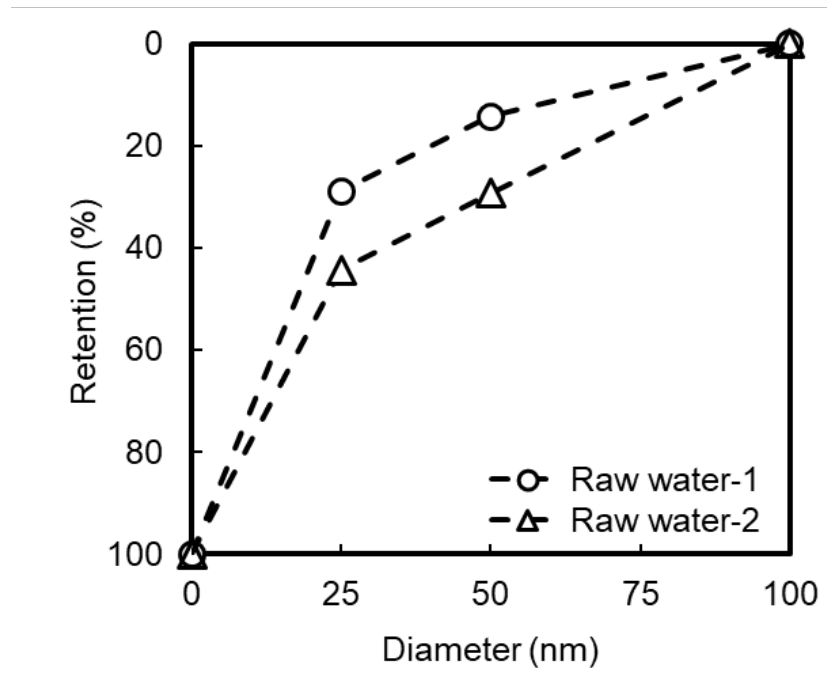
**Fig. 12S — Biopolymer/total organic carbon (TOC) mass ratio versus carbon dosage for different kinds of powdered activated carbon (PAC). Raw water-2 was used in this experiment.**



**Fig. 13S — Biopolymer concentrations of water samples before and after passing through a membrane with a pore size of 0.1  $\mu\text{m}$ . Raw water-2, which was prepared by filtration through a 0.1- $\mu\text{m}$  pore-size membrane, was used in this filtration experiment. Error bars indicate standard deviations of measurements.**

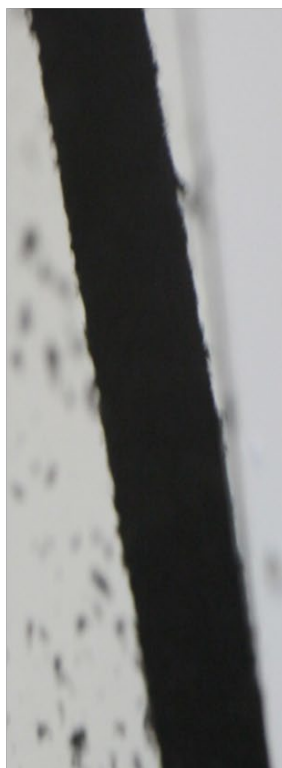


**Fig. 14S — Liquid-phase concentration of biopolymer versus SSPAC (submicron superfine powdered activated carbon) and PSL200 (polystyrene latex of diameter 200 nm) dosages. Raw water-2 was used in this experiment. Error bars indicate standard deviations of measurements.**

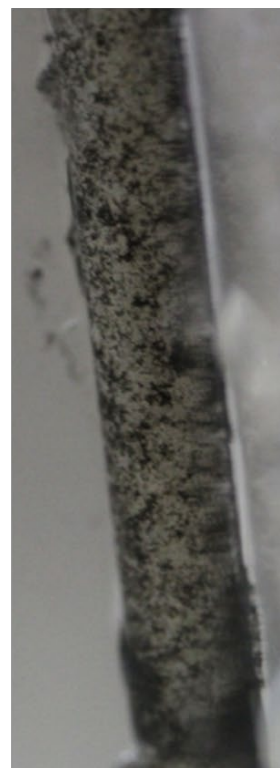


**Fig. 15S — Retention of biopolymer vs. membrane pore diameter. MCE membrane filters ( $\phi$ 47 mm, Merck KGaA, Darmstadt, Germany) were used.**

**Panel A: SSPAC direct pulse dose  
w/o coagulation (Method A)**

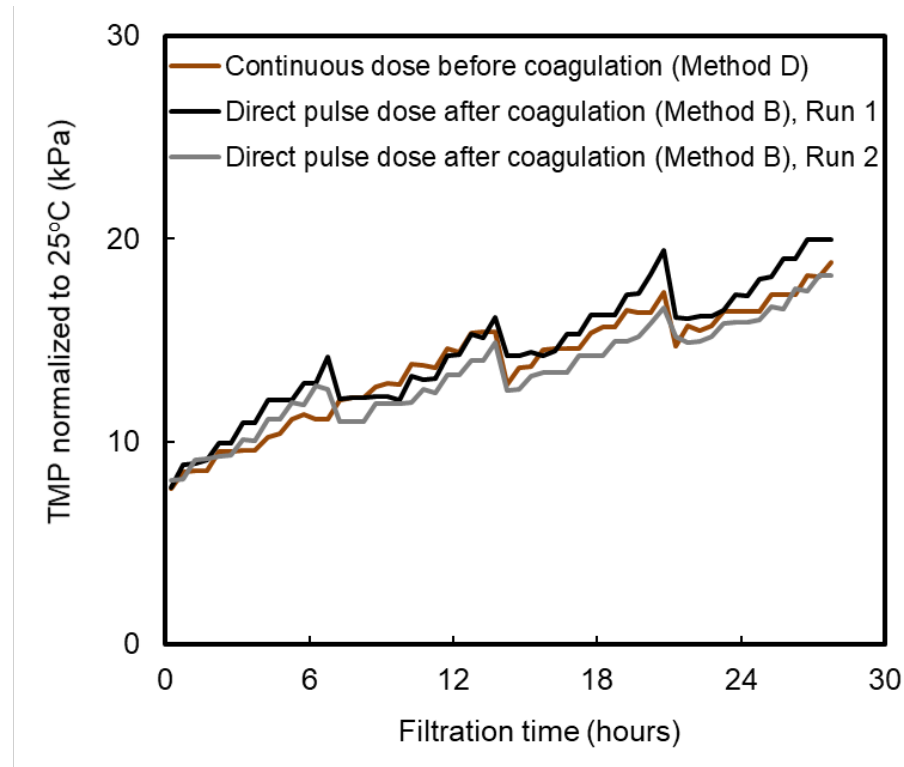


**Panel B: SSPAC direct pulse dose  
w/ coagulation (Method B)**



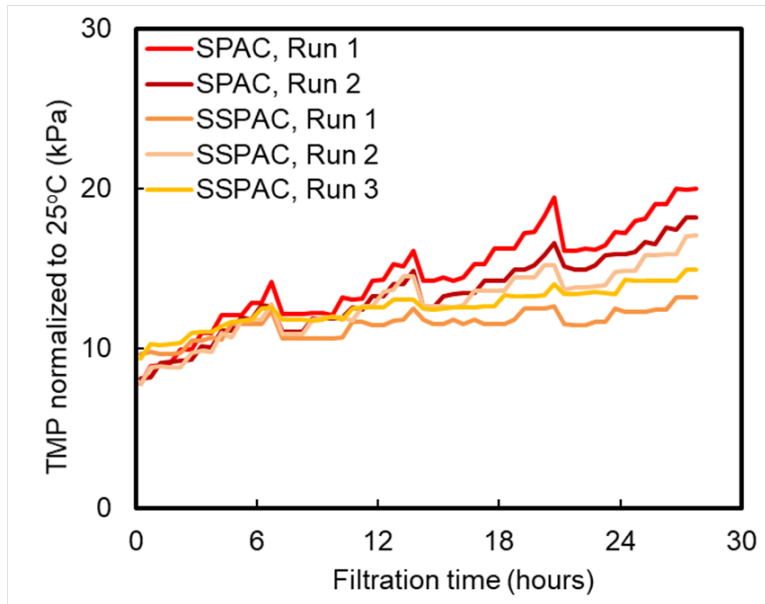
**Fig. 16S — Photographs of a membrane tank during backwash. Panel A is a picture of the system without coagulation pretreatment (Method A). Panel B is a picture of the system with coagulation pretreatment (Method B). Direct pulse dosing (explained in Figs. 2S, 3S, and 7S, SI) was used in the experiments. Backwash pressure was 50 kPa. Filtration rate was 1.7 m/day (70.8 L/m<sup>2</sup>h). Raw water-2 was used in this experiment.**



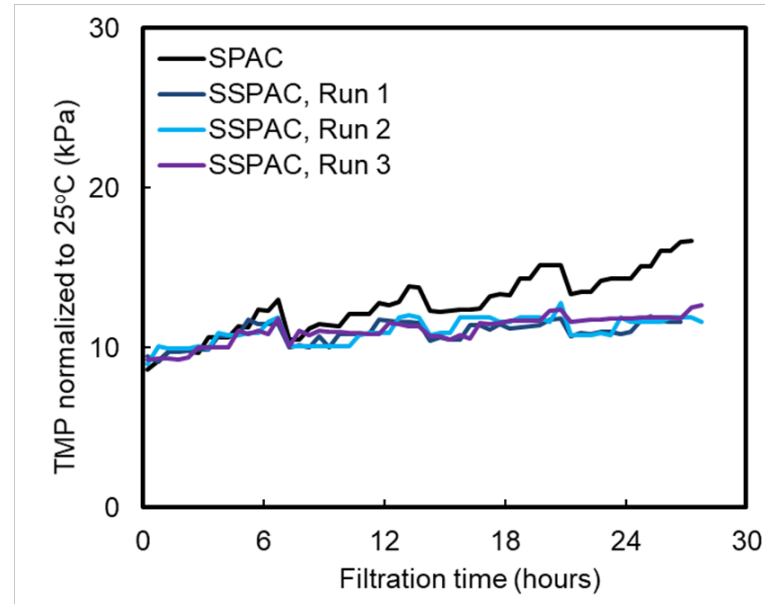


**Fig. 17S**—TMP as a function of filtration time when membrane filtration was conducted after SPAC (superfine powdered activated carbon) adsorption and coagulation pretreatment. The experiments were conducted by Methods B and D (explained in Figs. 3S and 5S, respectively, SI) to compare direct pulse dose and continues dose. Backwash interval was 7 hours. Filtration rate was 1.7 m/day (70.8 L/m<sup>2</sup>h). Raw water-2 was used in this experiment.

**Panel A: Direct pulse dose (Method B)**



**Panel B: Indirect pulse dose (Method C)**



**Fig. 18S** —TMP versus filtration time when membrane filtration was conducted after SPAC/SSPAC adsorption and coagulation pretreatment. Direct (Panel A) and indirect (Panel B) pulse dose (explained in Figs. 3S, 4S, and 7S, SI) were used in this experiment. Backwash interval was 7 hours. Filtration rate was 1.7 m/day (70.8 L/m<sup>2</sup>h). Raw water-2 was used in this experiment.