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**Differences in removal rates of virgin/decayed microplastics, viruses,
activated carbon, and kaolin/montmorillonite clay particles by coagulation,
flocculation, sedimentation, and rapid sand filtration during water treatment**

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Abstract

One of the main purposes of drinking water treatment is to reduce turbidity originating from clay particles. Relatively little is known about the removal of other types of particles, including conventionally sized powdered activated carbon (PAC) and superfine PAC (SPAC), which are intentionally added during the treatment process; microplastic particles; and viruses. To address this knowledge gap, we conducted a preliminary investigation in full-scale water treatment plants and then studied the removal of these particles during coagulation-flocculation, sedimentation, and rapid sand filtration (CSF) in bench-scale experiments in which these particles were present together. Numbers of all target particles were greatly decreased by coagulation-flocculation and sedimentation (CS). Subsequent rapid sand filtration greatly reduced the concentrations of PAC and SPAC but not the concentrations of viruses, microplastic particles, and clay particles. Overall removal rates by CSF were 4.6 logs for PAC and SPAC, 3.5 logs for viruses, 2.9 logs for microplastics, and 2.8 logs for clay. The differences in removals were not explained by particle sizes or zeta potentials. However, for clays, PAC and SPAC, for which the particle size distributions were wide, smaller particles were less efficiently removed. The ratios of both clay to PAC and clay to SPAC particles increased greatly after rapid sand filtration because removal rates of PAC and SPAC particles were about 2 logs higher than removal rates of clay particles. The trend of greater reduction of PAC concentrations than turbidity was confirmed by measurements made in 14 full-scale water purification plants in which residual concentrations of PAC in treated water were very low, 40–200 particles/mL. Clay particles therefore accounted for most of the turbidity in sand filtrate, even though PAC was employed. The removal rate of microplastic particles was comparable to that of clays. Sufficient turbidity removal would therefore provide comparable removal of microplastics. We investigated the effect of mechanical/photochemical weathering on the removal of microplastics via CSF. Photochemical weathering caused a small increment in the removal rate

of microplastics during CS but a small reduction in the removal rate of microplastics during rapid sand filtration; mechanical weathering decreased the removal rate via CS but increased the removal rate via rapid sand filtration. The changes of removal of microplastics might have been caused by changes of their zeta potential.

Keywords: Log-removal, Number concentrations, MS2, PMMoV, Weathering

53 Abbreviations

Shortened word	Meaning
AC	activated carbon
PAC	powdered activated carbon
SPAC	superfine powdered activated carbon
GAC	granular activated carbon
MP	microplastic
PA	polyamide
PA-pw	photochemically weathered PA
PA-md	mechanically damaged PA
PSi	polysilicone
PE	polyethylene
PMMoV	pepper mild mottle virus
PACl	poly-aluminum chloride
CSF	coagulation-flocculation, sedimentation, and rapid sand filtration
CS	coagulation-flocculation and sedimentation
PCR	polymerase chain reaction
ZP	zeta potential
D50	volume median diameter
FTIR	Fourier transform infrared spectroscopy
UV	ultraviolet
VUV	vacuum ultraviolet

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1. Introduction

The primary objective of drinking water treatment via coagulation-flocculation, sedimentation, and rapid sand filtration (CSF) is to reduce turbidity by removing suspended solids, which consist primarily of clay particles. Turbidity reduction via CSF has been thoroughly studied (Edzwald 2011). CSF has proven effective in removing clay particles (WHO 2019), but the behavior of particles in CSF and the residual of low concentrations of suspended solids in sand filtrate have not been adequately discussed. The sensitivity of turbidity measurements is insufficient to evaluate trace concentrations of particles and their high removal rates (log reduction) (Cho *et al.* 2020). In contrast, the removal of viruses (particle sizes: 30–100 nm) via CSF has been studied by quantifying their number concentrations with results using the real-time polymerase chain reaction (PCR), and removals of 0.8–2.5 log levels via normal CSF operations have been reported (Asami *et al.* 2016, Kato *et al.* 2018, Shirasaki *et al.* 2018). Activated carbon (AC) particles, which are usually dosed before coagulation and are expected to be removed by CSF, are black in color; however, if they remain in treated water, they tend to be conspicuous and cause consumer dissatisfaction. There is hence a need to reduce the concentrations of AC particles to extremely low levels that would have no detectable effect on turbidity. Our research group has also examined the removability of AC particles (particle sizes 1.0–14 μm) by counting the numbers of carbon particles under a microscope (Nakazawa *et al.* 2018).

Recently, microplastic (MP) particles have drawn attention throughout the world because they have been found to be widely distributed in the ocean, freshwater, air, and soil (Dris *et al.* 2016, Freeman *et al.* 2020, Iqbal *et al.* 2020, Iwasaki *et al.* 2017, Koelmans *et al.* 2019, Rodrigues *et al.* 2018, Uurasjärvi *et al.* 2020, Wang *et al.* 2021, Wong *et al.* 2020, Wu *et al.* 2019, Zhou *et al.* 2020). Because MPs $<10\ \mu\text{m}$ in size have been reported to adversely affect human health (Kögel *et al.* 2020, Revel *et al.* 2018), their fate in drinking water treatment should

81 be well understood (Syberg *et al.* 2015, WHO 2019). Among available drinking water treatment
82 processes, membrane filtration can separate MPs entirely (Ma *et al.* 2019). However, CSF is
83 still the major water treatment process in Japan and other countries, and there is concern that
84 MPs may pass through CSF treatment systems and enter the distribution system because
85 particles are probabilistically separated and removed in CSFs.

86 MPs have actually been detected in treated water as well as raw water of some full-scale
87 water treatment plants (Kosuth *et al.* 2018, Mintenig *et al.* 2019, Pivokonsky *et al.* 2018, Shen
88 *et al.* 2020, Wang *et al.* 2020b). Whereas MPs are present in treated groundwater in extremely
89 low concentrations (0–1 particles/m³) (Mintenig *et al.* 2019), the MP concentrations in treated
90 river water are much higher. When river water has been treated by coagulation, floatation, sand
91 filtration, and passage through granular activated carbon (GAC), the residual MP concentration
92 in the finished water has been 628 particles/L, which is slightly lower than the concentration
93 associated with ecological risks (Elizalde-Velázquez and Gómez-Oliván 2021), and the percent
94 removal of MPs has been 83% (Pivokonsky *et al.* 2018). The detected MPs had shapes like
95 fragments and fibers, and most of them were <10 µm in size. Wang *et al.* (2020b) have
96 investigated a water treatment plant (CSF and ozonation combined with GAC filtration) and
97 have reported a similar concentration and removal rate of MPs.

98 Quite recently, the effects of water treatment conditions on the treatability of MPs have been
99 investigated by using waters spiked with MPs (Ma *et al.* 2019, Rajala *et al.* 2020, Skaf *et al.*
100 2020, Wang *et al.* 2020c, Zhou *et al.* 2021). However, those studies have used water spiked
101 with MPs at unrealistically high concentrations. There is a need to evaluate removal
102 performances with trace MP concentrations that reflect actual levels of contamination. In
103 addition, some studies have used fluorescent MPs that have larger specific gravities than naked
104 MPs (Skaf *et al.* 2020), but the changes due to fluorescent marking of the physical properties of
105 the MPs (Zhou *et al.* 2021), including their specific gravities, may have affected the removal

efficiencies. Zhang *et al.* (2020) have used fluorescent particles at concentrations similar to those observed in river water (1800–9500 particles/L) and have reported removal rates of 86.9–99.9%. However, Zhang *et al.* (2020) used a filter that consisted of cheesecloth and anthracite, which is not widely used in water treatment compared with a sand filter composed of quartz sand. Moreover, it has been reported that industrially produced MPs are mechanically/photochemically weathered after being emitted to the environment (Sun *et al.* 2020), and the hydrophobicity and chemical composition of weathered MPs (WHO 2019) differ from those of MPs prior to weathering (Lin *et al.* 2020, Naik *et al.* 2020, Wang *et al.* 2020a, Zhu *et al.* 2020a, Zhu *et al.* 2020b). The changes related to weathering of MPs might affect the efficiency of their removal in water treatment.

Collectively, the above-mentioned studies suggest that the removal rates of particles that contaminate raw water to be treated for drinking purposes may differ greatly as a function of the type of particles: ~1 log removal for MPs 0.2–100 μm in size (Zhang *et al.* 2020), 0.8–2.5 log removal for viruses in the size range 30–100 nm (Asami *et al.* 2016, Kato *et al.* 2018, Shirasaki *et al.* 2018), and 5–6 log removal for AC particles 1.0–14 μm in size (Nakazawa *et al.* 2018).

However, these removal rates vary as a function of treatment conditions, and no studies have compared the removal rates of various types of particles in a mixture of particle types. Moreover, no information of log particle removal is available for clay causing turbidity, although the efficiency of removal of clay may be roughly inferred from changes of turbidity, and there have been no comparisons of the removal efficiencies of particles of all sizes by CSF under the same conditions and at concentrations representative of those encountered in the treatment of public water supplies. For example, even the basic question of whether MPs and viruses are more easily removed than clay particles has not been answered.

Accordingly, the objective of the present study was to determine the fates and removal efficiencies of MPs, clay, AC, and virus particles during CSF. Clay, AC, and viruses are conventional targets of CSF removal, and MPs are emerging targets of micropollutant removal. Our application of counting methods to identify and quantify clay and AC particles as well as MP particles enabled us to carry out the first comparative analysis of their removal by CSF based on the number concentrations of all particles, including viruses.

2. Materials and methods

2.1. Target particles

2.1.1. MPs

Microspheres of nylon composed of polyamides (NYLON 12, SP-500; D50 (volume median diameter), 4.8 μm ; density = 1.02 g cm^{-3} ; hereafter ‘PA’) were provided by Toray Industries, Inc. (Tokyo, Japan). Polysilicone microspheres (KMP-600; D50, 4.8 μm ; 0.99 g cm^{-3} ; hereafter ‘PSi’) were provided by Shin-Etsu Chemical Co., Ltd. (Tokyo, Japan). Polyethylene microspheres (LE-1080; D50, 6.5 μm ; 0.92 g cm^{-3} ; hereafter ‘PE’) were provided by Sumitomo Seika Chemicals Company, Ltd. (Osaka, Japan).

Before their use in experiments, these MPs were prepared as suspensions via the following procedure. First, each type of MP was added to pure water (Milli-Q water; Milli-Q Advantage A10 System; Merck KGaA, Darmstadt, Germany) at a concentration of 100 mg/L. To sufficiently disperse the MPs in the water, the MP suspension was exposed to ultrasonic treatment (FU-180C, Tokyo Garasu Kikai Co., Ltd., Tokyo, Japan) for 24 h and then stored at 4 °C before use. Before raw water was prepared for the CSF tests, the MP suspension was diluted with Milli-Q water to a concentration of 23.2 $\mu\text{g/L}$ and then exposed to ultrasonic

treatment (CPX8800h-J, Yamato Scientific Co., Ltd., Tokyo, Japan) for 30 min. Before measuring the and zeta potential (ZP) (see also Section 2.7), the MP suspension was exposed to ultrasonic sound waves (CPX8800h-J) for 30 min and diluted appropriately for the measurements.

Photochemical weathering was simulated on PA as follows. First, a PA suspension was prepared by addition of PA to Milli-Q water contained in a clear glass bottle at a concentration of 50 mg/L and then exposed to ultrasonic treatment (FU-180C, Tokyo Garasu Kikai Co., Ltd.) for 24 h. The bottle containing the PA suspension was then placed by a window and inverted each day to expose the PAs to sunlight for 68 days from 18 August to 24 October 2020. Henceforth, this photochemically weathered PA is denoted as PA-pw.

Mechanical weathering of PA was simulated as follows. First, PA (10 g) was transferred to a closed-chamber, ball-mill pot that contained 5- and 10-mm-diameter Al_2O_3 balls as the disintegrating medium. After the pot had been rotated at 94 rpm for 24 h, the PA was retrieved. This mechanically damaged PA is henceforth denoted as PA-md.

2.2.2. Activated carbon

Conventionally sized PAC (hereafter PAC; D50, 14 μm) and superfine PAC (SPAC; D50, 0.81 μm) were used as target ACs. The PAC was a commercially available, wood-based PAC (Taiko W; Futamura Chemical Co., Ltd., Nagoya, Japan). SPAC was prepared from the PAC by wet-mode ball milling (Nikkato, Osaka, Japan) followed by wet-mode bead milling (LMZ015; Ashizawa Finetech, Ltd., Chiba, Japan) in our laboratory. Details of the preparation procedure have been reported previously (Pan *et al.* 2017). Determination of the volume median diameter (D50) is described in Section 2.7.

2.2.3. Clay

Commercially available kaolin (D50, 5.6 μm ; FUJIFILM Wako Pure Chemical Corp., Osaka, Japan) and montmorillonite (D50, 12 μm ; Sigma-Aldrich Co., LLC., St. Louis, MO, USA) were used as the targets for clay removal. Kaolin and montmorillonite are the major clay minerals in most soils (Adamis and Williams 2005). These clay minerals were added to Milli-Q water at 10 g L⁻¹ to prepare stock suspensions. D50 determination is described in Section 2.7.

2.2.4. Viruses

F-specific RNA bacteriophage MS2 [diameter, 0.026 μm (Shirasaki *et al.* 2017); NBRC 102619, National Institute of Technology and Evaluation Biological Research Center, Kisarazu, Japan] and pepper mild mottle viruses [rod-shaped particles with diameter 0.018 $\times$ length 0.3 μm (Shirasaki *et al.* 2017); PMMoV pepIwateHachiman1 strain, MAFF 104099, National Institute of Agrobiological Sciences Genebank, Tsukuba, Japan] were used as the targets for virus removal after being propagated in *Escherichia coli* bacterial hosts (NBRC 13965) and *Nicotiana benthamiana*, respectively, followed by purification. The concentrations were quantified by the real-time polymerase chain reaction (PCR). Details of the procedures for the propagation, purification, and quantification of the viruses have been described previously (Shirasaki *et al.* 2016, Shirasaki *et al.* 2018).

2.3. Coagulant

Commercially available, conventional poly-aluminum chloride [PACl; basicity of 1.5 (basicity of 50%), sulfate ion 2.9 wt%], provided by Taki Chemical Co., Ltd. (Hyogo, Japan), was used as a coagulant.

2.4. Bench-scale CSF tests

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206 Water taken from the Toyohira River (Table S1 for water quality) at the Moiwa Water
207 Purification Plant (Sapporo, Japan; sampled on 24 June 2020) was filtered through a membrane
208 filter (pore diameter 0.2 μm ; PTFE; Toyo Roshi Kaisha, Ltd., Tokyo, Japan) to remove
209 suspended matter. For the CSF tests, this filtered water was supplemented with stock
210 suspensions of PAC (10 mg/L, 7–8 NTU, 4.0×10^6 particles/mL), SPAC (2.0 mg/L, 7–8 NTU,
211 5.1×10^6 particles/mL), MP (1.0 $\mu\text{g/L}$, 11 particles/mL), viruses (10^7 copies/mL), and/or clay
212 particles (10 mg/L, 7–8 NTU, 8.7×10^5 particles/mL, for kaolin; 10 mg/L, 1.8 NTU, 2.2×10^4
213 particles/mL, for montmorillonite). The concentrations of clay and AC particles were
214 comparable to the concentrations that might be found in typical raw water. Because we assumed
215 that MPs and viruses were present at low concentrations in river water, their concentrations
216 were set to be as low as possible for measurement. The theoretical increase of dissolved organic
217 carbon (DOC) by the addition of the virus stock was 0.05 mg-C/L, which was much smaller
218 than the DOC of water from the Toyohira River (0.8 mg/L). We therefore assumed that the
219 addition of MPs and viruses had little effect on the removal of other particles. We prepared 17
220 kinds of water (Table S2), each of which contained either kaolin or montmorillonite, either PAC
221 or SPAC, and one kind of MP. Two of the 17 raw waters contained viruses in addition to PAC,
222 kaolin, and PE particles. The removal rates of the different kinds of particles were compared in
223 water subject to the same CSF.

224 The CSF test was conducted in a rectangular beaker containing 11 L of raw water (Fig. S1).
225 The dosage of the coagulant PACl was predetermined to be 3.0 mg-Al/L (unless otherwise
226 noted). Under these conditions, visible floc particles were formed, and the turbidity of the
227 supernatant after 60 min of sedimentation was < 0.2 NTU. The coagulant was injected into the
228 raw water after adding NaOH to bring the coagulation pH to 7.0. Rapid mixing for coagulation
229 was conducted at a G value of 600 s^{-1} for 100 s and was followed by slow mixing for

flocculation at a G value of 12.5 s^{-1} for 2400 s. After the slow mixing, the water was allowed to remain quiescent for 60 min to allow sedimentation to proceed. Virus concentrations in the supernatant were determined directly without further treatment. A portion of the supernatant was subjected to centrifugation pretreatment or ultrasonication pretreatment before determination of the concentrations of AC, MP, and clay particles (see Section 2.6). Ten liters of the sedimentation supernatant was transferred to another beaker, and the supernatant in the beaker was pumped to a sand filter (effective diameter and uniformity of sand grains: 0.94 mm and 1.24, sand depth 50 cm, column inner diameter 3.6 cm). Rapid sand filtration was performed in the down-flow direction at a rate of 90 m d^{-1} . The sand filtrate was collected from 0 to 50 min to determine the turbidity and concentration of each kind of particle. After each filtration run, the sand filter was backwashed with tap water and then forward washed with Milli-Q water. After each test, instruments that had contacted viruses were exposed to chlorine and washed with Milli-Q water to prevent viral contamination during the next run.

2.5. Centrifugation and ultrasonication pretreatments

A portion of the supernatant from the sedimentation was pretreated by centrifugation to determine the concentrations of stray, un-flocculated AC and clay particles that were not incorporated into floc particles. Aliquots (45 mL) of a supernatant sample collected after sedimentation were dispensed into four 50-mL glass tubes. The tubes were centrifuged (CT6E; Koki Holdings Co., Ltd., Tokyo, Japan) in a swing rotor (T5SS; Koki Holdings Co., Ltd.) at 3990 g for 10 min, halted for 2 min, and then re-centrifuged for 10 min (Nakazawa *et al.* 2021). The concentrations of particles in the centrifugal supernatant were then determined by membrane filtration and microscopic image analysis (see Section 2.6).

Ultrasonication pretreatment was used to disperse and determine the concentrations of AC, clay, and MP particles in the supernatant. The supernatant sample collected after sedimentation was transferred to a glass bottle, and HCl was added to bring the pH to < 3 . The resultant water was exposed to ultrasonic treatment (CPX8800h-J, Yamato Scientific Co., Ltd.) for 1 h to disperse particles suspended in the water. The concentrations of particles in the sonicated water were then determined by membrane filtration and microscopic image analysis (see Section 2.6).

2.6. Measurement of particle concentrations

MP, AC, and clay particles in each water sample were captured by filtering the water through a white membrane filter (nominal pore diameter, $0.1\ \mu\text{m}$; membrane diameter 25 mm; polytetrafluoroethylene; Merck KGaA, Darmstadt, Germany) and, separately, through a black membrane filter (nominal pore diameter, $0.45\ \mu\text{m}$; membrane diameter 25 mm; mixed cellulose esters; Merck KGaA). The filters were dried at room temperature.

AC particles were detected on color photomicrographs taken of the surface of the white membrane filter by a digital microscope (VHX-2000; Keyence Corp., Osaka, Japan) at $1000\times$ magnification by using the image analysis software associated with the microscope, and then their particle number concentration and particle size were calculated. MP particles were detected on the color photomicrographs taken of the surface of the white membrane filter at $500\times$ magnification and quantified. Clay particles were detected on the surface of the black membrane filter at $1000\times$ magnification and quantified. The minimum sizes of detectable particles were $0.23\ \mu\text{m}$ at $1000\times$ magnification and $0.47\ \mu\text{m}$ at $500\times$ magnification.

Virgin MP particles (spherical) and clay particles (non-spherical) in the same photomicrographs were identified and detected separately based on their shape. However,

because most PA-md particles were non-spherical, no CSF test using the mixture of PA-md and clay particles was conducted.

2.7. Other analysis of particles

Determination of the D50s of MP, AC, and clay particles in a completely dispersed form was carried out using a laser-light-diffraction and scattering method (Microtrac MT3300EXII; MicrotracBEL Corp., Osaka, Japan) after adding a dispersant (Triton X-100; Kanto Chemical Co., Inc., Tokyo, Japan; final concentration, 0.08% w/v) and exposing a 50-mL particle suspension to ultrasonication (US-300E; Nihonseiki Kaisha Ltd., Tokyo, Japan) for 1 min (Fig. S2 and Table 1).

The ZPs of AC, MP, and clay particles as functions of pH were determined as follows. Filtered water from the Toyohira River (Sapporo) was supplemented with a stock suspension of PAC (10 mg/L), SPAC (2.0 mg/L), MP (1.0 mg/L), or clay particles (10 mg/L). Either NaOH or HCl was added to the resulting water to adjust the pH to a value in the range 1.5–11.5, and the ZP was measured (Zetasizer Nano ZS; Malvern, United Kingdom).

Fourier transform infrared spectroscopy (FTIR) analysis of MPs was conducted with an FTIR spectrophotometer (IR-7500S, Shimadzu, Kyoto, Japan) at a resolution of 4 cm⁻¹ (Ninomiya *et al.* 2020) with KBr pellets containing PA or PA-pw particles at 0.25 wt%.

PA, PA-pw, and PA-md particles were collected on a membrane filter (nominal pore diameter, 0.45 µm; diameter 25 mm; mixed cellulose esters; Merck KGaA). The particles on the filter were observed using a field-emission scanning electron microscope (JSM-7400F, JEOL, Ltd., Tokyo, Japan).

Table 1

Diameters and zeta potentials of particles.

particle	Volume median diameter (D50)	ZP at pH 7
	μm	mV
PAC	14	-23
SPAC	0.81	-20
kaolin	5.6	-24
montmorillonite	12	-18
PA	4.8	-19
PA-pw	4.9	-16
PA-md	5.0	-22
PE	6.5	-15
PSi	4.8	-16
PMMoV	diameter 0.018, length 0.3 ^a (rod-shaped particle)	-26 ^b
MS2	diameter 0.026 ^a (spherical particle)	-51 ^c

^a Shirasaki et al. (2017).^b Calculated by using Henry equation with an electrophoretic mobility (Shirasaki et al. 2017).^c Calculated by using Henry equation with an electrophoretic mobility (Shirasaki et al. 2016).

2.8. Sampling of sand filtrates in full-scale water purification plants

Sampling of sand filtrates was conducted at 14 full-scale water-treatment plants in Japan that used the CSF process (Table S3) and were using PAC to treat the water. The samples were quantified for residual black-particle concentrations by using membrane filtration and microscopic image analysis as described in Section 2.6.

3. Results and Discussion

3.1. Residual carbon particles in full-scale CSF plants

Fig. 1 shows the residual concentrations of carbon particles in sand filtrates in the 14 full-scale water purification plants that treated their raw water by adding PAC followed by the CSF process. The residual concentrations of carbon particles were plotted against the PAC dosages, but there was little correlation ($R^2=0.13$, Fig. 1). This result was reasonable because plant configurations and operations differed. There was a weak correlation between the residual concentrations of carbon particle and the turbidities of the sedimentation supernatants ($R^2=0.44$, Fig. S3, Supplementary Information [SI]). The concentrations of residual carbon particles in sand filtrates were in the range 40–200 particles/mL (n.b., There were no reports of customer complaints about black particles in the waters supplied from these plants.). The highest concentration (200 particles/mL) with no customer complaints could be considered a rough indication for the goal of treatment with SPAC, which is not used in conventional water treatment consisting of CSF because of concern over its leakage. Turbidities of the sand filtrates were not different from those observed when the same plants were operated without PAC addition (data not shown).

There was no correlation between the turbidities and concentrations of PAC particles in sand filtrates (Fig. S4). The PAC particles were removed more efficiently than the usual turbidity components, most of which were probably clay particles. The turbidity of the raw water before the addition of PAC was 1.9–18 NTU; the turbidity removal rates were estimated to be in the range of 1–4 logs when calculated from the turbidity of the water after CSF treatment. PAC removals by the CSFs were 3.4–4.9 logs (4.2 ± 0.4 logs, average $\pm$ SD) in terms of particle number concentrations (Fig. S5). Consequently, the hypothetical turbidity originating from the PAC particles in sand filtrates, that was estimated to be 4.7×10^{-6} to 6.7×10^{-5} NTU (Kissa 1999, Nakazawa et al. 2018), was much smaller than the observed turbidity. Therefore, not only

do the concentrations of suspended particles vary greatly depending on the particle type, such as clay or PAC, but also their removal rates are likely to vary greatly. As a result, the observed turbidity could be unrelated to the concentrations of other type of particles, such as PAC particles.

On the other hand, the turbidity data could not be used to exactly compare the removals of turbidity components (clay particles) with AC particles because the principles associated with quantification of turbidity are quite different from those associated with quantification of particle counts. Also, the limit of quantification of turbidity is insufficient to accurately estimate log removals: e.g., a log removal > 3 is hard to estimate precisely when the initial turbidity is 10 NTU and the turbidity quantification limit is 0.01, which is a typical value. The bench-scale experimental testing in the subsequent sections attempted to elucidate different removal rates and behaviors of particles in the unit processes of CSF by applying particle counting methods.

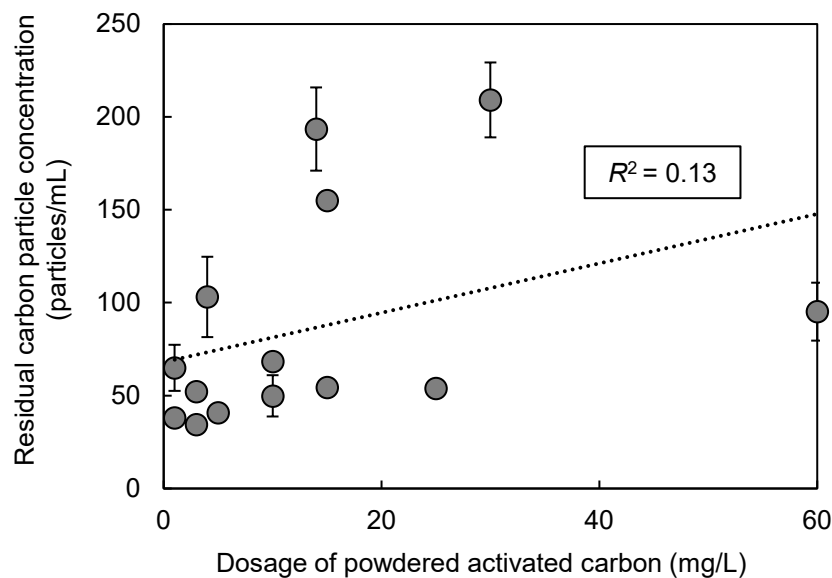


Fig. 1. Residual carbon particle concentration in sand filtrate vs. the dosage of powdered activated carbon. The sample waters were obtained from the 14 full-scale water purification plants employing the CSF process when powdered activated carbon was being injected for adsorption. The dotted line indicates the regression line. Error bars indicate standard deviations

of three measurements, but some of them are hidden behind the symbols.

3.2. Comparison of AC and clay particles during the CSF process

After finding that the removal rate of AC particles was very different from that of turbidities in full-scale plants, we conducted bench-scale CSF experiments with water containing either kaolin or montmorillonite and either PAC or SPAC, to compare the fates and efficiencies of removal of AC and clay particles (Fig. 2 and Fig. 3). Initial concentrations of kaolin, montmorillonite, and PAC were set at 10 mg/L, and the initial concentration of SPAC was set at 2 mg/L. These concentrations corresponded to 1.2×10^6 , 2.3×10^4 , 4.0×10^6 , and 4.0×10^6 particles/mL, respectively. The reason for the low concentration of SPAC was the low concentration required for its adsorption and the low removability of SPAC itself (Bonvin *et al.* 2016, Nakazawa *et al.* 2018).

PAC particles were removed largely by coagulation-flocculation and sedimentation (CS). The concentration of PAC particles in the sedimentation supernatant was 2.2 logs lower than the initial PAC concentration (Fig. 2). The fact that the concentration of stray, un-flocculated PAC particles in the supernatant, which was determined after centrifuging the supernatant, was 1.8 logs lower than the total PAC in the supernatant indicated that most of particles in the supernatant were coagulated to some extent, though the degree of coagulation was low. Such PAC particles in the supernatant were therefore adequately removed via rapid sand filtration. The total removal rate of PAC by CSF was 4.7 logs, which was within the range observed for the full-scale water treatment plants (Section 3.1); therefore, the conditions under which our laboratory bench-scale experiments were carried out were realistic. The overall removal rate by

CSF was therefore similar for SPAC and PAC, but removal of SPAC versus PAC was slightly higher via CS and slightly lower via rapid sand filtration (Fig. 2).

Most kaolin particles were removed by CS (Fig. 2). The fact that kaolin particles in the sedimentation supernatant were not as efficiently removed by centrifugation as PAC and SPAC particles, however, indicated that the proportion of stray, un-flocculated kaolin particles among the kaolin particles in the sedimentation supernatant was high. The removal rate via rapid sand filtration of kaolin particles versus PAC and SPAC particles in the sedimentation supernatant was not high because the stray, un-flocculated kaolin particles in the supernatant were not likely to be removed efficiently (Nakazawa et al. 2021). The total removal rate of kaolin particles by CSF was consequently 2.8 logs, which was much lower than those of PAC and SPAC (4.6 ± 0.2 logs; from comparison of numbers [CNs] 1, 2, and 3 in Table 2). The total removal rate of montmorillonite clay particles by CSF in the presence of SPAC was 2.9 logs, which was also lower than that of the SPAC in the same water (4.5 logs) (Fig. 3). The total removal rate of montmorillonite was higher than that of kaolin because of its higher removal rate via rapid sand filtration. The removal rates by CS were consequently about the same for PAC, SPAC, kaolin, and montmorillonite, but the removal rates by rapid sand filtration were higher for PAC and SPAC than for montmorillonite, and the removal by rapid sand filtration was the lowest for kaolin. This trend was consistently observed in the 17 experimental runs that were conducted in duplicate with water containing either PAC or SPAC, either kaolin or montmorillonite, one kind of MP, and viruses (Fig. S6 and Table 2, where the removal rates are summarized).

The removal efficiency of suspended particles has conventionally been evaluated based on turbidity. Because turbidity is proportional to the surface-area concentration of a given material (Kissa 1999, Nakazawa et al. 2018), we calculated turbidity-equivalent removal rates based on surface-area concentrations. The results were consistent with the trend of lower removal of

kaolin and montmorillonite (3.2 ± 0.3 logs) versus PAC and SPAC (5.0 ± 0.1 logs) when concentrations were evaluated in terms of turbidity equivalents (Figs. S7 and S8 of SI).

The size and ZP of particles are widely recognized to be related to their removal by coagulation. We also measured particle sizes and ZPs (Table 1). The particle sizes of PAC and SPAC are different, but their removal by CSF followed almost similar trends. The particle sizes of PAC and montmorillonite were similar (Fig. S2 and Table 1), but the trends of their removal via CSF differed. The sizes of the residual particles of PAC, SPAC, and kaolin after CSF treatment all fell in the range $0.2\text{--}5\text{ }\mu\text{m}$, though the associated particle size distributions differed (Fig. S9). Therefore, differences of particle sizes are unlikely to account for the lower removal rates of kaolin and montmorillonite versus PAC and SPAC particles. The ZPs were all in the range of -18 to -24 mV, and the ZP of kaolin, which was removed with the lowest efficiency, was in the middle in this range. The ZP results therefore did not explain the lower removal rates of kaolin and montmorillonite versus PAC and SPAC (Table 2 and Fig. S10). The smaller sizes of particles of PAC, SPAC, kaolin, and montmorillonite after versus before CSF treatment indicated the preferential removal of large particles (Fig. S9). This preferential removal of large particles was consistent with our previous observations of PAC and SPAC removal (Nakazawa et al. 2021, Nakazawa et al. 2018).

The results in Section 3.1 showed that the concentrations of AC particles in sand filtrate were very low compared to the turbidities of the same water, and turbidity removal was not correlated with AC removal. These patterns were caused by the low removal rates of clay particles by rapid sand filtration (2.8 ± 0.2 logs; from CNs 4, 5, and 6 in Table 2) versus AC particles (4.6 ± 0.2 logs; from CNs 1, 2, and 3 in Table 2). Fig. 4 shows the calculated ratios of clay particles to AC particles in raw water before treatment, sedimentation supernatant, and sand filtrate in terms of turbidity equivalents (surface area concentrations). In raw water and

sedimentation supernatant, clay particles and AC particles were present in similar ratios, but in sand filtrate, the very high ratio of clay particles to AC particles indicated that clay particles accounted for the turbidity of the sand filtrate.

In the practice of water treatment, AC are added with great care to ensure that there is no leakage. However, this study showed that AC particles were two orders of magnitude more removable than clay particles; most of the particles remaining after filtration were probably clay particles, and only a small portion (on the order of 1%) could have been AC particles (Fig. 4). The apparent problem of leakage of AC particles is not their leakage rate but rather the fact that AC particles are black and conspicuous. As a result of the *Cryptosporidium* problem (Medema *et al.* 2009), the turbidity of water after CSF treatment is now strictly controlled, and the number of particles is monitored besides the turbidity. The concentration of particles after CSF treatment has been reported to be 1000 to 10,000 particles/mL (Watanabe and Ogino 2006). One percent of these concentrations (i.e., 10–100 particles/mL) is the same order of magnitude as the measured concentrations of AC particles (Section 3.1). If the particle concentration is maintained at less than 10,000 particles/mL, the concentration of residual AC particles when AC is injected will be less than 100 particles/mL, a level that will not cause any problem associated with leakage of carbon particles based on the plant data reported in Section 3.1.

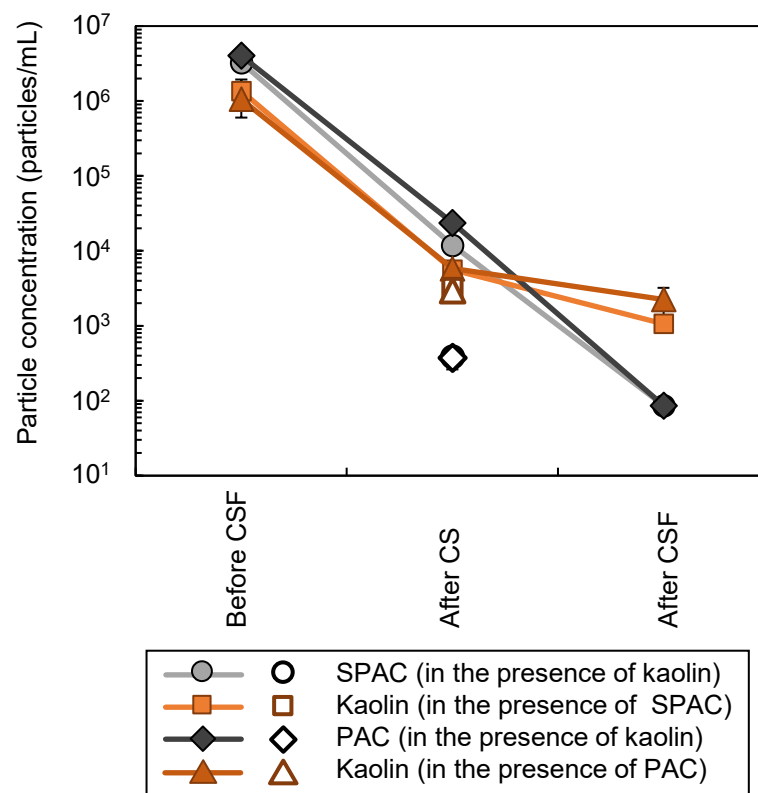


Fig. 2. Behaviors of PAC, SPAC, and kaolin during the CSF process. Kaolin and either PAC or SPAC were added simultaneously. The open symbols indicate the data measured after centrifugation. Data from Run 1 and Run 2. Details of the experimental condition are presented in Table S2. Error bars indicate standard deviations of measurements, but some of them are hidden behind the symbols.

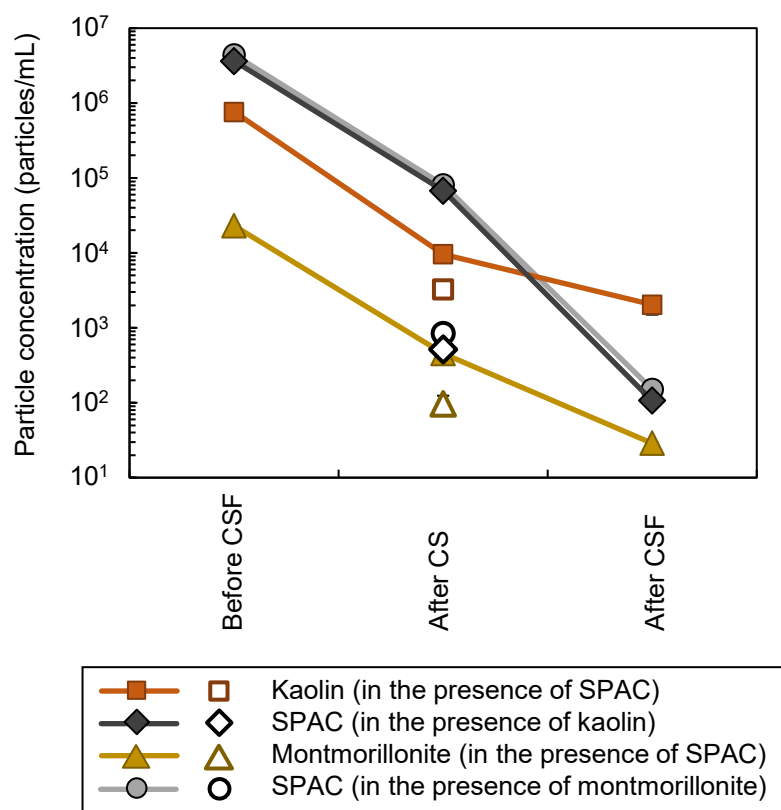


Fig. 3. Behaviors of kaolin, montmorillonite, and SPAC during the CSF process. Either kaolin or montmorillonite and SPAC were added simultaneously. The open symbols indicate the data measured after centrifugation. Data from Runs 3, 4, 5, and 6. Details of the experimental conditions are presented in Table S2. Error bars indicate standard deviations of experiments, but some of them are hidden behind the symbols.

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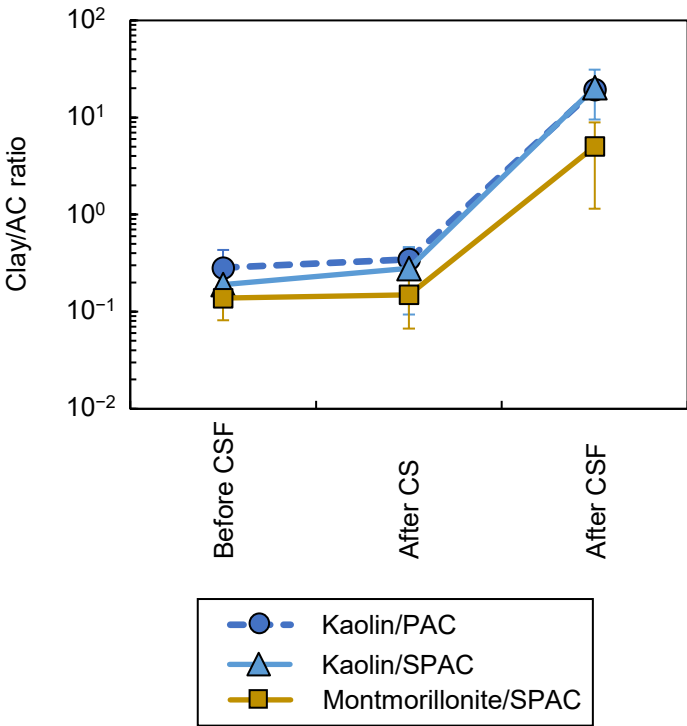
Table 2

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Removal rates of particles and experimental conditions.

Comparison number (CN)	Number of experimental runs	Target particle	Average Log-removal rate $\pm$ Log-SD of target particle by CS	Average Log-removal rate $\pm$ Log-SD of target particle by CSF			Initial concentration of target particle		Major coexisting substance with concentration > 1 mg/L	Coagulant dose	Run No.
							mg/L	particles/mL or copies/mL		mg-Al/L	
1	4	PAC	2.2 $\pm$ 0.1	4.7 $\pm$ 0.1		4.6 $\pm$ 0.2	10	4.0 $\times$ 10 ⁶	Kaolin 10 mg/L	3	2, 8, 11, and 12
2	7	SPAC	2.1 $\pm$ 0.3	4.7 $\pm$ 0.2			2	4.9 $\times$ 10 ⁶	Kaolin 10 mg/L	3	1, 3, 4, 7, 9, 10, and 13
3	2	SPAC	1.7 $\pm$ 0.1	4.5 $\pm$ 0.0			2	4.4 $\times$ 10 ⁶	Montmorillonite 10 mg/L	3	5 and 6
4	4	kaolin	2.1 $\pm$ 0.1	2.7 $\pm$ 0.0		2.8 $\pm$ 0.2	10	8.1 $\times$ 10 ⁵	PAC 10 mg/L	3	2, 8, 11, and 12
5	7	kaolin	2.2 $\pm$ 0.2	2.8 $\pm$ 0.2			10	9.5 $\times$ 10 ⁵	SPAC 2 mg/L	3	1, 3, 4, 7, 9, 10, and 13
6	2	Montmorillonite	1.7 $\pm$ 0.0	2.9 $\pm$ 0.0			10	2.3 $\times$ 10 ⁴	SPAC 2 mg/L	3	5 and 6
7	1	PA	ND	2.9		2.9 $\pm$ 0.3	0.001	6	PAC 10 mg/L, Kaolin 10 mg/L	3	8
8	3	PA	1.4 $\pm$ 0.1	2.7 $\pm$ 0.2			0.001	7	SPAC 2mg/L, Kaolin 10 mg/L	3	3, 4, and 7
9	2	PA	2.0 $\pm$ 0.0	3.1 $\pm$ 0.0			0.001	17	SPAC 2mg/L, Montmorillonite 10 mg/L	3	5 and 6
10	2	PE	2.4 $\pm$ 0.1	3.2 $\pm$ 0.0			0.001	11	PAC 10 mg/L, Kaolin 10 mg/L	3	11 and 12
11	1	PE	2.5	3.3			0.001	10	SPAC 2mg/L, Kaolin 10 mg/L	3	13
12	1	PSi	ND	2.6			0.001	5	PAC 10 mg/L, Kaolin 10 mg/L	3	1
13	1	PSi	ND	2.5			0.001	5	SPAC 2mg/L, Kaolin 10 mg/L	3	2
14	2	PMMoV	3.3 $\pm$ 0.1	3.6 $\pm$ 0.1		3.5 $\pm$ 0.3	Not applicable	10 ⁷ –10 ⁸	PAC 10 mg/L, Kaolin 10 mg/L	3	11 and 12
15	2	MS2	2.6 $\pm$ 0.3	3.4 $\pm$ 0.4			Not applicable	10 ⁷ –10 ⁸	PAC 10 mg/L, Kaolin 10 mg/L	3	11 and 12
16	2	PA	1.7 $\pm$ 0.1	2.6 $\pm$ 0.0			0.001	14	SPAC 2 mg/L	1.5	14 and 15
17	2	PA-pw	1.7 $\pm$ 0.1	2.2 $\pm$ 0.2			0.001	16	SPAC 2 mg/L, Kaolin 10 mg/L	3	9 and 10
18	2	PA-md	1.1 $\pm$ 0.0	2.6 $\pm$ 0.1			0.001	12	SPAC 2 mg/L	1.5	16 and 17

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Fig. 4. Ratio of clay particles to activated carbon particles quantified by surface-area concentrations. Either kaolin or montmorillonite and either PAC or SPAC were added simultaneously. Data from Runs 1, 2, 3, 4, 5, 6, 7, 8, 9 10, 11, 12 and 13. Details of the experimental condition are presented in Table S2. Error bars indicate standard deviations of experiments, but some of them are hidden behind the symbols.

3.3. Comparing MP versus clay/AC particles during the CSF process

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This section focuses on the concentrations of MPs. Total removal rates of PE, PA, and PSi by CSF were almost the same— 2.9 ± 0.3 logs (from CNs 7, 8, 9, 10, 11, 12, and 13 in Table 2)—a rate that was much lower than those of SPAC and PAC particles but similar to that of kaolin particles (Fig. 5 and Fig. S11). PA removal was lower than PE removal by CS, but PA removal by rapid sand filtration was higher. As a result, the total removals of PA and PE by CSF were similar. These trends were almost unchanged by conversion to turbidity equivalents

using surface-area concentrations (Fig. S12). Zhou et al. (2021) have reported that MPs with relatively high densities are removed more efficiently by CS. However, we did not observe such a trend: in our experiments, PE particles, which have a lower density than PA particles, were removed with higher efficiency than the latter. Zhou et al. (2021) used waters containing only extremely high concentration of MPs (100–1000 mg/L). Floc particles should therefore have been formed mainly by MPs, and the density of the floc particles would have been largely determined by the density of the MPs. In contrast, we mimicked a normal water treatment situation wherein MPs were present in trace amounts compared to clay and ACs. Under these conditions, the density of floc particles was determined by clay and AC particles rather than by MP particles. The density of the MPs would consequently not have influenced their removal by CS. We feel that the less negative ZP of PA compared to PE was related to its higher removal by CS because the same trend was observed before/after PA weathering (detailed in Section 3.5). It should be noted, however, that ZP could not explain the differences in removal rates between very different types of particles (clay versus AC, see section 3.2).

The observed removal rate of PE, PA, and PSi by CSF, 2.9 ± 0.3 logs, exceeded rates reported previously (~ 1 log) (Pivokonsky et al. 2018, Wang et al. 2020b, Zhang et al. 2020), but direct quantitative comparisons between our data and previous data are inappropriate because particle removal rates by CSF are highly dependent on the design of the CSF and operating conditions such as coagulant dose and filtration speed. This study showed that a rate of removal of MPs as high as ~ 3 logs (99.9%) can be achieved. More importantly, the fact that the removal rate of MP particles was comparable to that of clay particles (kaolin and montmorillonite) means that if satisfactory removal of turbidity—the principal metric of the adequacy of drinking water purification—is consistently achieved, a similar level of removal can be expected for MP particles. In other words, MP particles are not unusually difficult to

remove. Of course, the removability of particles depends on the properties of the particles, but this trend of removal was also observed for MPs after weathering, as described in Section 3.5.

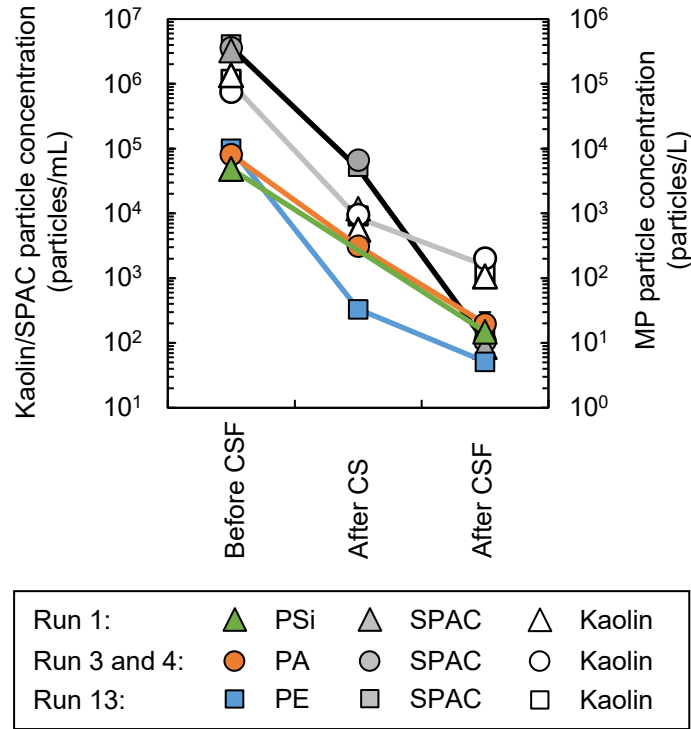


Fig. 5. Behavior of PE, PA, and PSi during the CSF process. PA, Psi, and PE were each treated by CSF in the presence of SPAC and kaolin. Data from Runs 1, 3, 4, and 13. Details of the experimental condition are presented in Table S2. Error bars indicate standard deviations of experiments, but some of them are hidden behind the symbols.

3.4. Comparison of viruses versus clay/AC particles during CSF processes

Overall removal rates of viruses by CSF were 3.6 logs for the PMMoV strain and 3.4 logs for the MS2 strain (Fig. 6). These rates were higher than those for kaolin and montmorillonite particles but lower than those for PAC and SPAC particles (Fig. 6 and Table 2). The fact that the abundances of both PMMoV and MS2 decreased greatly after CS (3.3 logs and 2.6 logs,

respectively) compared with the other types of particles (clay, AC, and MPs) resulted in high total removals of viruses by CSF, though the removal by rapid sand filtration was not high (<0.8 log) (Fig. 6).

The relationship between the size of particles and their removal by a sand filter has been studied theoretically, and it is commonly understood that the removal rate of particles around 1 μm in size is the lowest. The removal of smaller particles as well as larger particles is higher because of Brownian transport (Edzwald 2011). The particle sizes of the MS2 and PMMoV strains are diameter 26 nm (spherical particle) and diameter $18\times$ length 300 nm (rod-shaped particle), respectively, and according to this filtration theory, these viruses should have been removed with higher efficiency than SPAC, which has a particle diameter of ~ 1 μm (Figs. S2 and S9). However, the removal rate of viruses by rapid sand filtration was clearly lower than that of SPAC (Figs. 2 and 6). We feel that most of the viruses remaining after CS were single-strand, un-flocculated particles with insufficient charge neutralization and consequently a small probability of attachment onto sand grains, as described in Section 3.2 in the case of kaolin particles.

The observed virus removal rates (3.5 ± 0.3 logs; from CN 14 and 15 in Table 2) were high compared to those previously reported (Asami et al. 2016, Kato et al. 2018, Shirasaki et al. 2018) and could be related to the CSF operating conditions. For example, it is very reasonable that CS removal of particulate matter, including virus particles, would be highly dependent on coagulant dosage (Shirasaki *et al.* 2009, Zhou et al. 2021). Shirasaki et al. (2018) have reported 1.5–2.0 log removal of the PMMoV and MS2 strains by CSF, but their filter depth was only 20 cm, and their filtration velocity was 120 m d^{-1} , which was higher than ours (90 m d^{-1}). The coagulant dosages in the CSF experiments of Kato et al. (2018) were 0.8–2 mg/L and therefore lower than our dosage of 3 mg/L, though the DOC of their raw water was higher than that of ours. Asami et al. (2016) have reported a PMMoV removal of 2.4 logs by a full-scale water

purification plant employing CSF. The fact that the turbidity of treated waters in that plant after
 CSF was not low, 1–3 formazin attenuation units, suggests that clay particle removal by the
 plant was not as high as the removal by our CSF plant. Nonetheless, our data were in accordance
 with the previous data in two respects. First, the removal of PMMoV was somewhat higher than
 removal of turbidity. In the study of Asami et al. (2016), PMMoV removal was 2.4 logs, and
 turbidity removal was 1.5–2 logs. In our data, PMMoV removal was 3.6 logs (Fig. 6), and the
 turbidity-equivalent removal of kaolin particles was 3.4 logs (Fig. S8). Second, the virus
 removal by CSF was accomplished largely by CS, and the contribution of rapid sand filtration
 was marginal (Kato et al. 2018). We also feel that the presence of AC may have accelerated the
 removal of viruses by coagulation in an synergetic way because AC can to some extent adsorb
 and remove viruses (Matsushita *et al.* 2013). In our data, however, the viruses were not removed
 by PAC alone (Fig. 6).

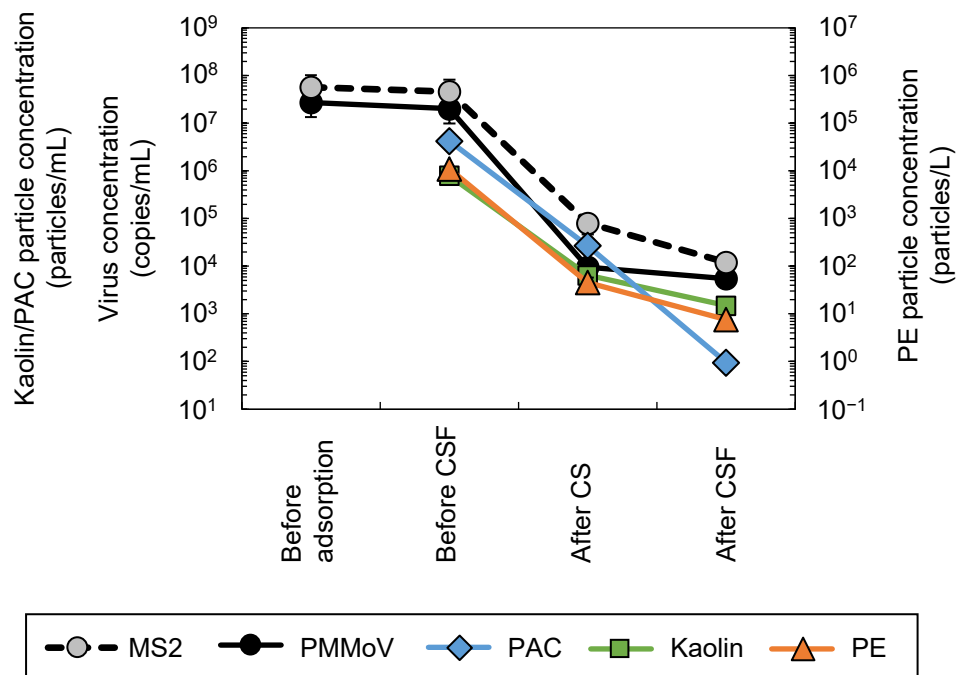


Fig. 6. Behavior of PMMoV and MS2 during the CSF process. Vertical axis on left side is for PMMoV, MS2, Kaolin, and PAC concentrations, whereas vertical axis on right side is for PE concentration. PMMoV, MS2, kaolin, PAC, and PE were added simultaneously. Data from Runs 11 and 12. Details of the experimental condition are presented in Table S2. Error bars indicate standard deviations of experiments, but some of them are hidden behind the symbols.

3.5. Effects of weathering on MP removal

It has been reported that MPs can be mechanically/photochemically weathered after being released to the environment (Sun et al. 2020), but the effect of weathering on the rate of their removal by CSF has been unclear. We began the experiments with photochemical weathering and examined the effects of the weathering by comparing weathered PA particles that had been exposed to the sun for 68 days (PA-pw) with virgin ones. The removal rate of the PA-pw by CS was 1.7 logs, which was slightly higher than that of the virgin PA (1.4 logs) (Fig. 7). However, its removal rate by rapid sand filtration was slightly lower (0.5 log) than that of virgin PA (1.3 logs). The result was a higher residual concentration of PA-pw particles than virgin PA particles in sand filtrate. Prior to carrying out these experiments, we thought that the hydrophilicity of PA might be changed by exposure to the ultraviolet (UV) radiation in sunlight, as reported for the UV in artificial light (Lin et al. 2020). With this mind, we compared the physical properties of PA and PA-pw. However, there was no difference in the FTIR spectrum before and after exposure to sunlight (Fig. S13). Exposure of the PA to sunlight for 68 days may not have been sufficient to cause a change of the FTIR spectrum. Lin et al. (2020) used UV and vacuum ultraviolet (VUV) lamps and irradiated polyvinylchloride and polystyrene MPs at 1.8 (UV) or 36 (VUV) kJ/m². In contrast, we estimated the UV irradiation intensity associated with the 68

598 days of our experiment to be 0.21 kJ/m² based on the global horizontal intensity of irradiance
599 and glass transmittance. This intensity was merely ~10% of the intensity used by Lin et al.
600 (2020). Particle shape (Fig. 8) and size (Fig. S2 and Table 1) were not changed by the 68-day
601 exposure, but the ZP decreased somewhat after sunlight exposure (Fig. S14). Although it seems
602 unlikely that this change of ZP would have caused a great change in the particle removal rate,
603 it is possible that reducing the magnitude of the negative charge caused a small increase in the
604 removal rate of the PA particles via CS and a small decrease via sand filtration. This
605 interpretation is consistent with the result described in Section 3.3 that the removal rates of the
606 PE particles, which had a less negative ZP than the PA particles, were higher via CS but lower
607 via rapid sand filtration than the removal rates of the PA particles (Table 2).

608 We also examined the effect of mechanical damage on PA removal by placing the PA in a
609 ball-milling. The size of the PA particles was not changed much (Fig. S2 and Table 1). Instead,
610 the particles were abraded or deformed rather than crushed by the ball milling (Fig. 8). The
611 FTIR spectrum was not changed (Fig. S13), but the observed ZP became slightly more negative
612 (Fig. S14). The fate of PA during the CSF process was clearly changed by the mechanical
613 damage (Fig. 7). The removal rate by CS was decreased from 1.7 logs (PA) to 1.1 logs (PA-
614 md). However, the removal rate by rapid sand filtration increased from 0.9 log (virgin PA) to
615 1.5 logs. The overall removal of PA by CSF was unchanged by mechanical damage. This effect
616 of mechanical weathering on the removal rate and ZP of PA was opposite to the effect of
617 photochemical weathering. The negative shift of the ZP of PA caused by mechanical weathering
618 might enhance its removability via rapid sand filtration.

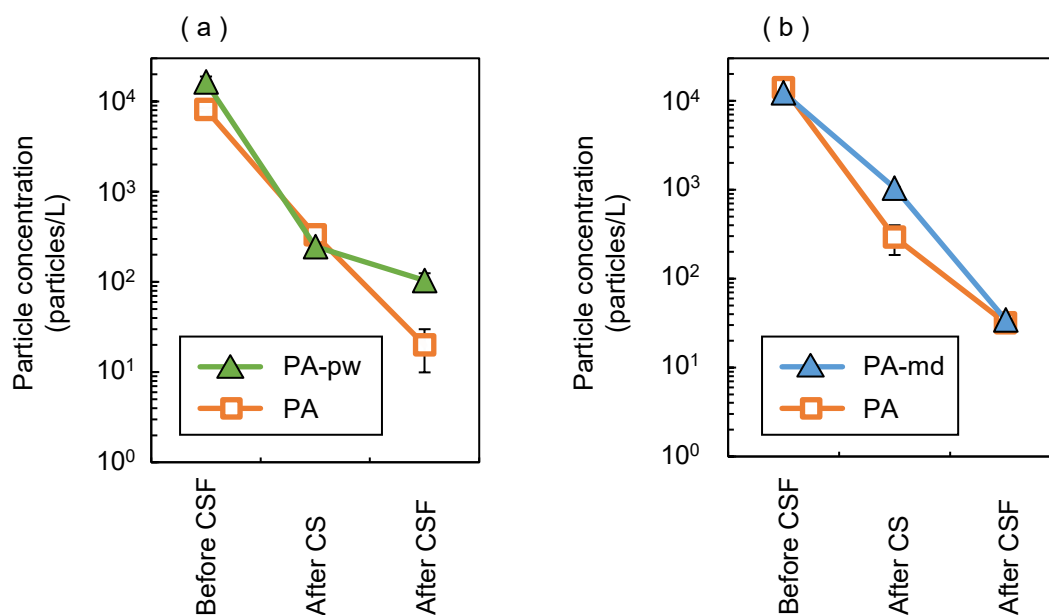


Fig. 7. Effect of photochemical/mechanical weathering on the removal of MP particles during CSF process. Panel a: PA and PA-pw were each added in the presence of kaolin and SPAC simultaneously (Run 3, 4, 9, and 10). Panel b: PA or PA-md was each added in the presence of SPAC simultaneously (Run 14, 15, 16, and 17). Details of the experimental conditions are presented in Table S2. Error bars indicate standard deviations of experiments, but some of them are hidden behind the symbols.

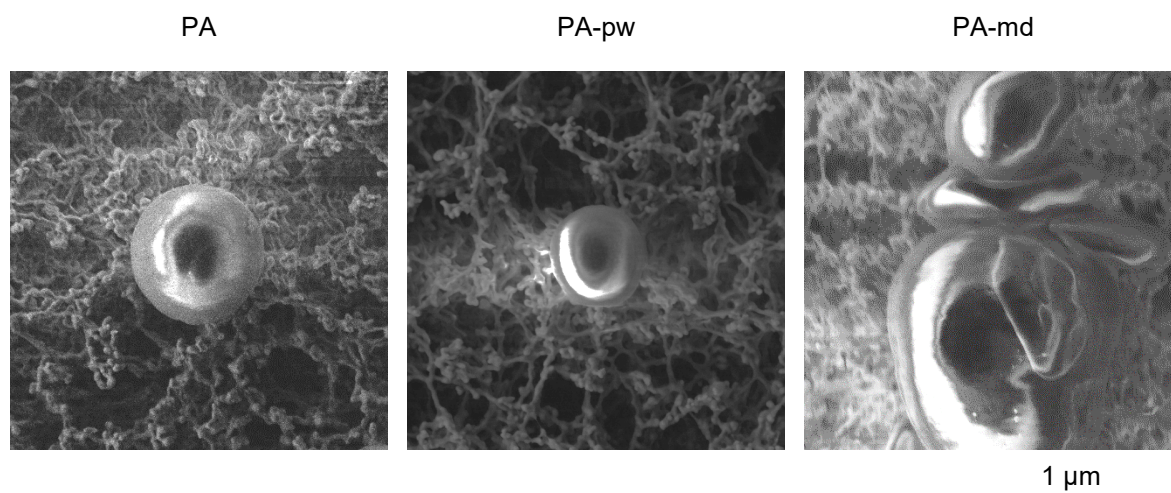


Fig. 8. Field-emission scanning electron microscope images of PA particles before and after weathering.

4. Conclusions

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634 The results of this research led to the following conclusions:

635 1) The present study determined, for the first time, the residual concentrations of carbon
636 particles remaining in sand filtrate in actual, full-scale water purification plants
637 employing a CSF process when PAC was used for the adsorption treatment; the range
638 of the concentrations was < 200 particles/mL. Since no customer complaints, this
639 concentration with could be considered a rough indication for the goal of treatment with
640 SPAC.

641 2) CS greatly decreased the concentrations of all target particles tested (kaolin,
642 montmorillonite, PAC, SPAC, PA, PE, PSi, MS2, and PMMoV). Rapid sand filtration
643 greatly decreased the concentrations of PAC and SPAC, but the decreases in the
644 concentrations of the other particles by rapid sand filtration were not large. In particular,
645 viruses (strains PMMoV and MS2) were greatly removed by CS, but they were removed
646 only a little by rapid sand filtration. In the case of kaolin, the high proportion of stray,
647 un-flocculated particles in the sedimentation supernatant led to low removal by rapid
648 sand filtration of particles in the supernatant.

649 3) The particle removal rates by CSF were 4.6 ± 0.2 logs for PAC and SPAC, 3.5 ± 0.3
650 logs for PMMoV and MS2, 2.9 ± 0.3 logs for PA, PE, and PSi MPs, and 2.8 ± 0.2 logs
651 for kaolin and montmorillonite. The PA, PE, and PSi (particle sizes: $4.8\text{--}6.5\text{ }\mu\text{m}$) could
652 be removed by CSF at a rate similar to the rate of removal of clay particles (kaolin: $5.6\text{ }\mu\text{m}$,
653 montmorillonite: $12\text{ }\mu\text{m}$). The removal rates of the MPs (2.9 ± 0.3 logs) were
654 slightly lower than that of turbidity caused by clays (3.2 ± 0.3 logs). The removal rate
655 of the viruses by CSF was higher than that of clay particles. The turbidity-equivalent
656 removal rates were 5.0 ± 0.1 logs for PAC and SPAC and 3.2 ± 0.3 logs for kaolin and

montmorillonite. These differences in removal rates between particles were not explained by particle size or ZP. However, for kaolin, montmorillonite, PAC, and SPAC, which have wide particle-size distributions, smaller particles of each remained after treatment.

4) The ratio of clay/AC particles became very high after CSF treatment because AC particles were removed at rates about 2 orders of magnitude higher than the rates of removal of clay particles. Consequently, clay particles contributed predominantly to the turbidity in sand filtrate, even when PAC was added to the raw water.

5) Mechanical/photochemical weathering of PA affected the removal of PA in CS and rapid sand filtration to some extent. PA-pw was removed by CS slightly higher than virgin PA. During rapid sand filtration, PA-pw was removed at a somewhat lower rate than virgin PA. The removal rate of PA-md by CS and rapid sand filtration decreased and increased, respectively, relative to the removal rates of virgin PA. The change of ZP by the mechanical/photochemical weathering may have caused these changes of PA removals by CS and rapid sand filtration. However, no clear difference was apparent in the FTIR spectra of PA, PA-pw, and PA-md.

Acknowledgments

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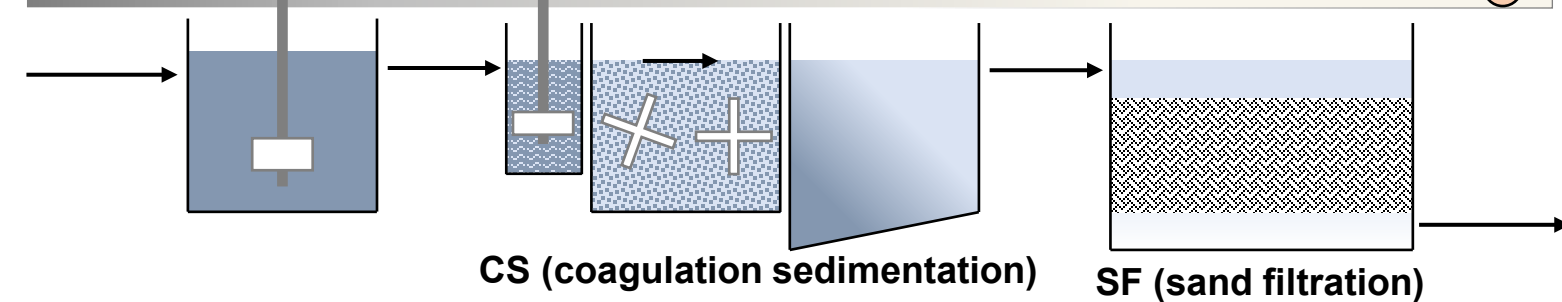
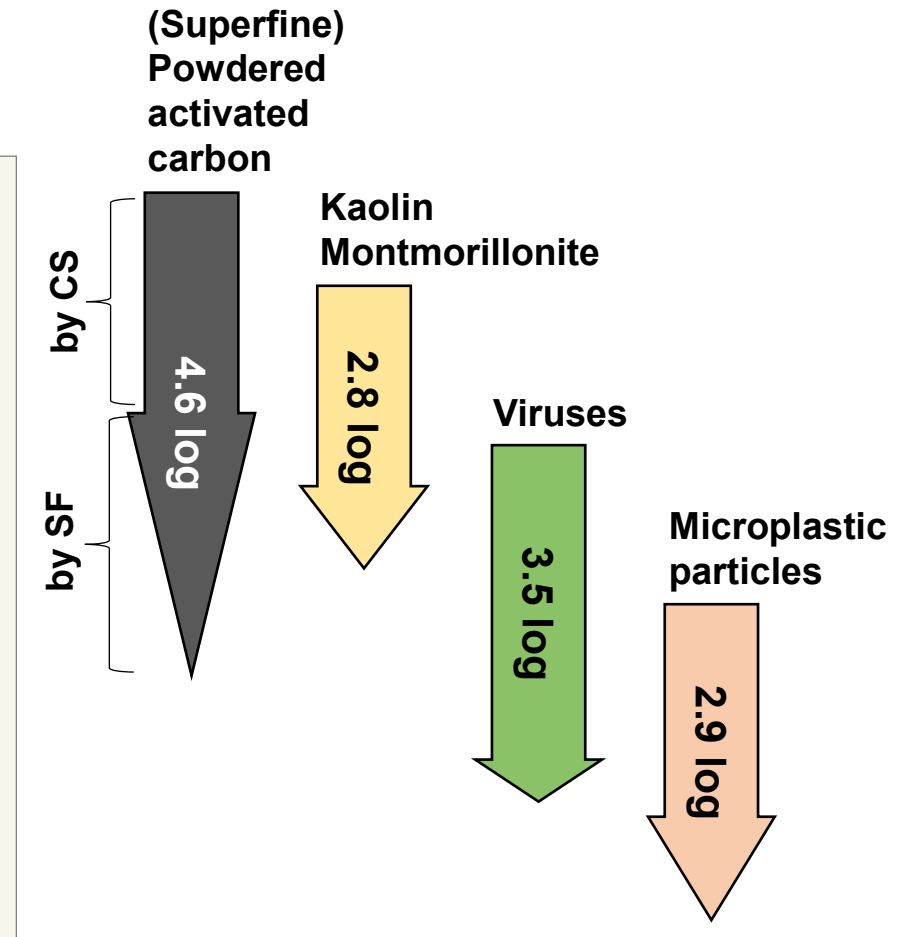
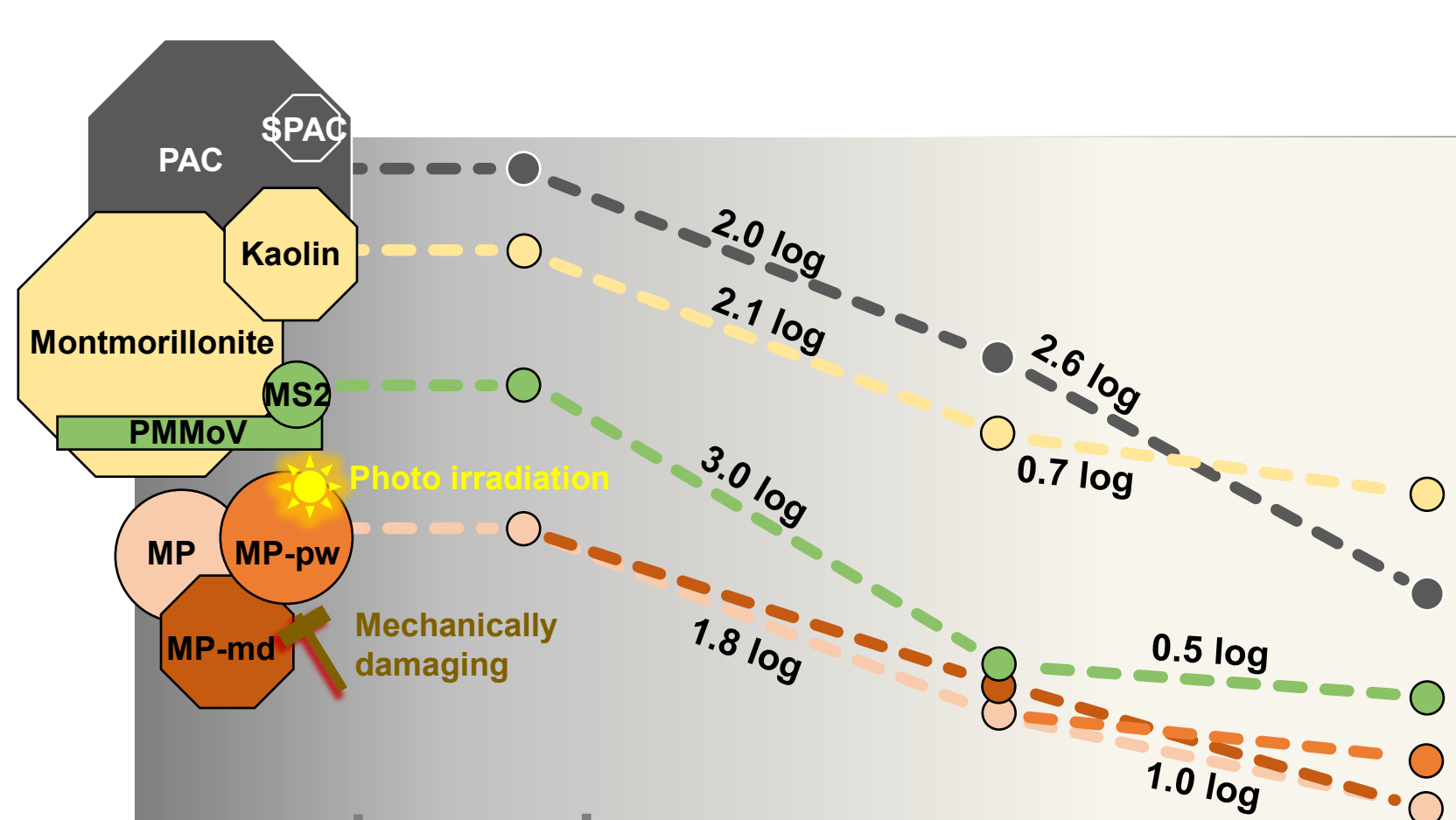
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Highlights

- Activated carbon in water treatment plant sand filtrate was 40–200 particles/mL
- The order of removal rates were activated carbon >> viruses >> clay $\approx$ microplastics
- Coagulation-sedimentation accounted for most virus, clay, and microplastic removal
- These particles were removed by rapid sand filtration less than by activated carbon
- Weathering changed the zeta potential and removal of microplastics a little



Supplementary Information

Differences in removal rates of virgin/decayed microplastics, viruses, activated carbon, and kaolin/montmorillonite clay particles by coagulation, flocculation, sedimentation, and rapid sand filtration during water treatment

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Table S1

Characteristics of raw water used in CSF tests.

Turbidity	DOC	Alkalinity	Na ⁺	K ⁺	Mg ⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
NTU	mg/L	mg/L as CaCO ₃	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
2.7	0.8	16	12	2.1	1.8	9.7	22	1.5	20

Table S2

Experimental conditions. PA-pw indicates PA exposed to sunlight for 68 days. PA-md indicates PA mechanically damaged by ball milling. All MP particle initial concentrations were 1 µg/L, clay initial concentrations were 10 mg/L and virus initial concentrations were $10^7 - 10^8$ copies/mL.

Exp. Run No.	AC		MP	Clay	Virus	Coagulant	Figures
	type	Initial concentration (mg/L)	type	type	type	dose (mg-Al/L)	
1	SPAC	2.0	PSi	kaolin		3.0	Fig. 2, Fig. 4, Fig. 5, Fig. S6, Fig. S12
2	PAC	10	PSi	kaolin		3.0	Fig. 2, Fig. 4, Fig. S6, Fig. S8, Fig. S11
3	SPAC	2.0	PA	kaolin		3.0	Fig. 3, Fig. 4, Fig. 5, Fig. 7, Fig. S6, Fig. S7, Fig. S12
4	SPAC	2.0	PA	kaolin		3.0	Fig. 3, Fig. 4, Fig. 5, Fig. 7, Fig. S6, Fig. S7, Fig. S12
5	SPAC	2.0	PA	montmorillonite		3.0	Fig. 3, Fig. 4, Fig. S6, Fig. S7, Fig. S9
6	SPAC	2.0	PA	montmorillonite		3.0	Fig. 3, Fig. 4, Fig. S6, Fig. S7
7	SPAC	2.0	PA	kaolin		3.0	Fig. 4, Fig. S6
8	PAC	10	PA	kaolin		3.0	Fig. 4, Fig. S6, Fig. S11
9	SPAC	2.0	PA-pw	kaolin		3.0	Fig. 4, Fig. 7, Fig. S6
10	SPAC	2.0	PA-pw	kaolin		3.0	Fig. 4, Fig. 7, Fig. S6
11	PAC	10	PE	kaolin	PMMoV, MS2	3.0	Fig. 4, Fig. 6, Fig. S6, Fig. S8, Fig. S9, Fig. S11
12	PAC	10	PE	kaolin	PMMoV, MS2	3.0	Fig. 4, Fig. 6, Fig. S6, Fig. S8, Fig. S11
13	SPAC	2.0	PE	kaolin		3.0	Fig. 4, Fig. 5, Fig. S6, Fig. S12
14	SPAC	2.0	PA			1.5	Fig. 7
15	SPAC	2.0	PA			1.5	Fig. 7
16	SPAC	2.0	PA-md			1.5	Fig. 7
17	SPAC	2.0	PA-md			1.5	Fig. 7

Table S3

List of full-scale water treatment plants where sand filtrates were sampled.

Plant No	Sampling date	Raw water		PAC		
		Turbidity	DOC	Material	D50	Dosage
		(NTU)	(mg/L)		(μm)	(mg-dry/L)
1	2018/8/20	4	1.2	Wood	19	5
2	2018/8/21	2	0.6	Wood	33	3
3	2018/8/22	2	1.2	Coconut shell	17	1
4	2018/8/28	5	1.2	Wood	22	4
5	2018/8/27	7	2.2	Wood	21	14
6	2018/8/28	8	1.5	Wood	21	15
7	2018/8/24	9	2.2	Wood	22	30
8	2018/8/27	5	1.3	Wood	23	10
9	2018/9/5	14	1.4	Wood	19	10
10	2018/11/8	2	0.5	no data	5.4	1
11-1	2018/7/27	no data	0.1	Wood	21	25
11-2	2018/8/30	no data	no data	Wood	21	3
12-1	2018/8/27	4	2.5	Wood	17	15
12-2	2018/8/28	18	2.8	Wood	17	60

Plant No	Coagulant			Coagulation	Sedimentation	Filtration			
	Type	Basicity	Dosage	pH	Time	Rate	Anthracite	Sand	Time from the last backwash
		%	(mg-Al/L)		(min)	(m/d)	(cm)	(cm)	(min)
1	PACl	67–75	1.2	7.3	374	72	30	40	90
2	PACl	52.8	1.0	6.8	164	67	25	45	213
3	PACl	no data	1.5	6.9	85	71	no data	60	92
4	PACl	59.2	1.3	7.1	240	69	10	60	300
5	PACl	52.2	1.2	7.0	105	120	0	70	no data
6	PACl	51	2.1	6.9	170	120	0	65	540
7	PACl	49	2.9	7.0	240	120	0	80	270
8	PACl	53.1	1.4	7.0	342	120	3	60	243
9	PACl	51-55	2.1	6.9	169	83	0	65	70
10	PACl	54.7	1.1	7.3	209	no data	no data	60	360
11-1	PACl	54	1.1	7.2	47	81	7	53	no data
11-2	PACl	54	1.4	no data	47	no data	7	53	no data
12-1	PACl	51.5	1.3	7.0	139	54	0	60	35.5
12-2	PACl	51.5	2.6	7.1	156	47	0	60	24.4

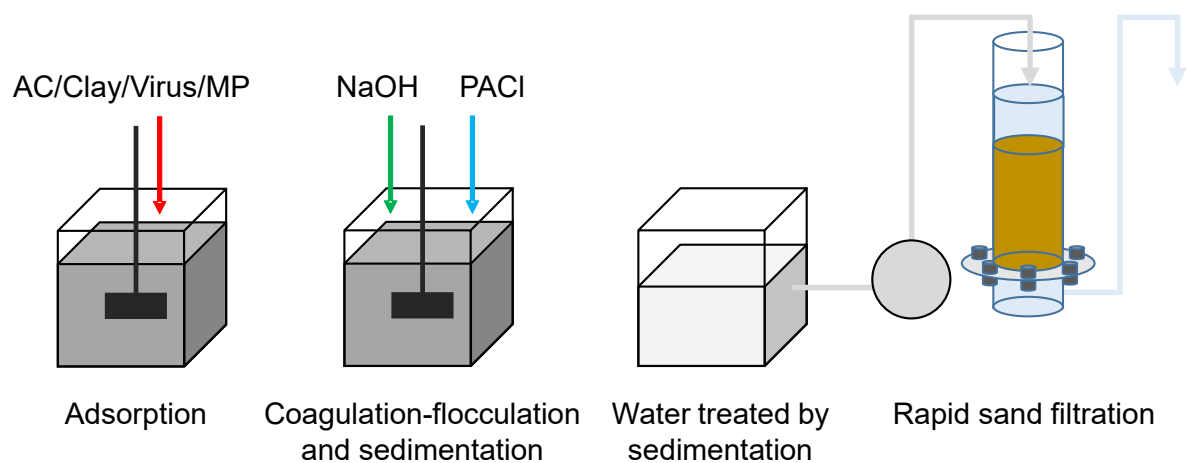


Fig. S1. Schematic diagram of the experimental setup for the coagulation-flocculation, sedimentation, and sand filtration experiment.

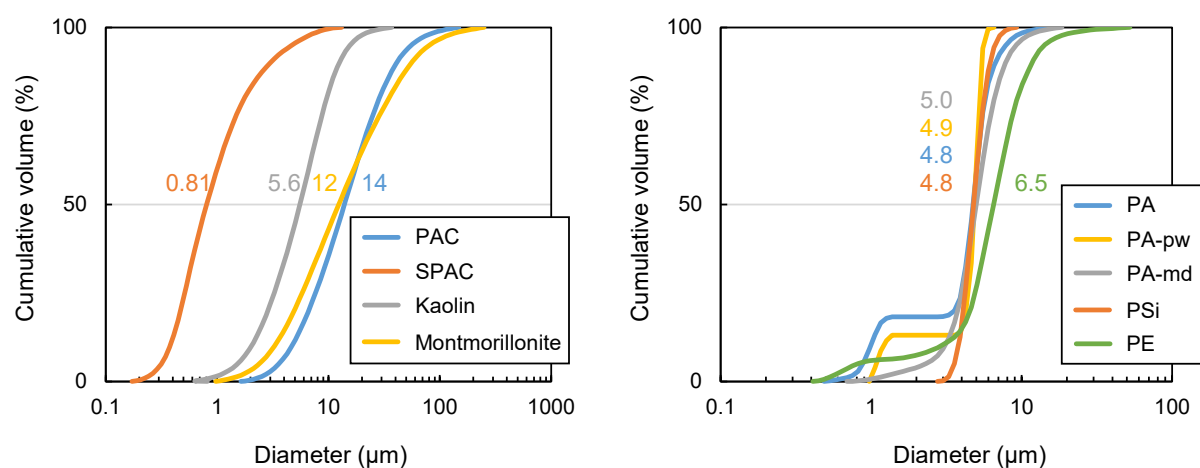


Fig. S2. Particles size distribution of PAC, SPAC, kaolin, montmorillonite, PA, PA-pw, PA-md, PSi, and PE. The numbers indicate D50 (volume median diameter) of particles associated with lines of the same color.

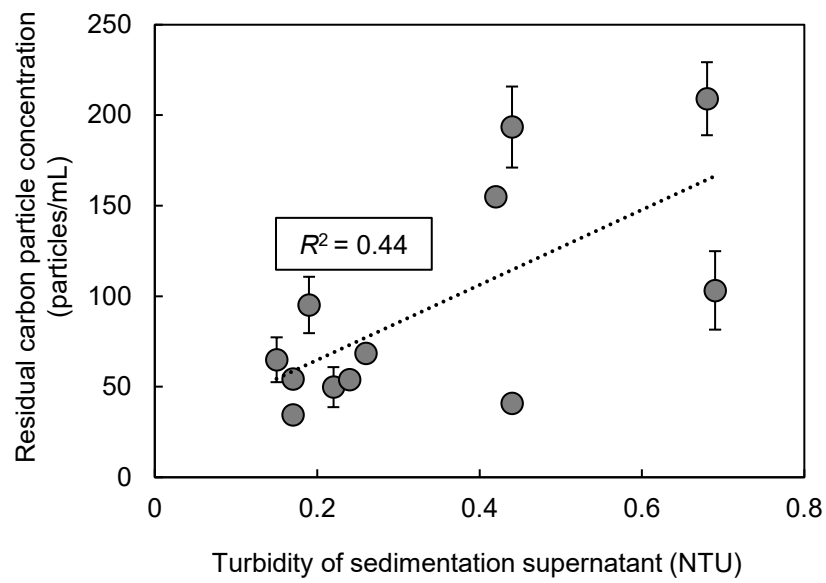


Fig. S3. Regression between the residual carbon particle concentrations and the turbidities of settled waters. The data were obtained from all of the 14 full-scale water purification plants using CSF processes. The dotted line indicates the regression line. Error bars indicate standard deviations of three measurements, but some of them are hidden behind the symbols.

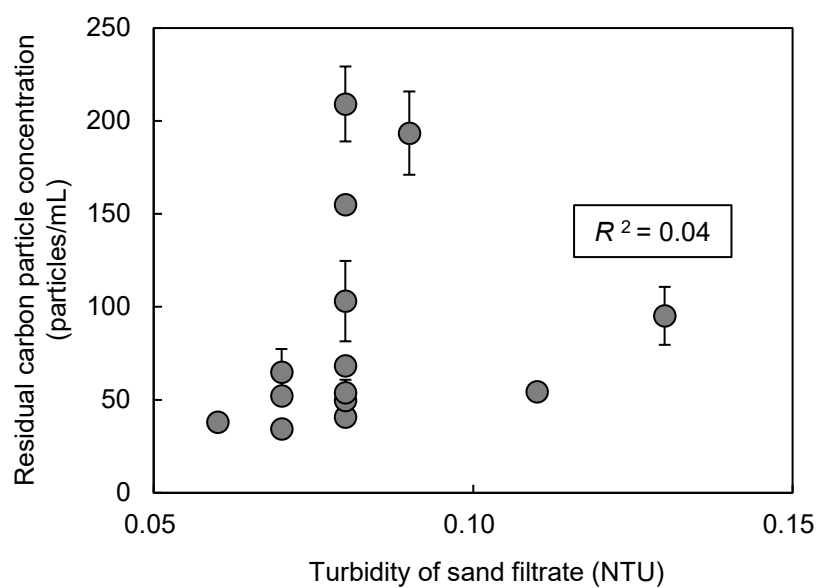


Fig. S4. Correlation between the residual carbon particle concentrations and turbidities of sand filtrate. The data were obtained from all of the 14 full-scale water purification plants using CSF processes. Error bars indicate standard deviations of three measurements, but some of them are hidden behind the symbols.

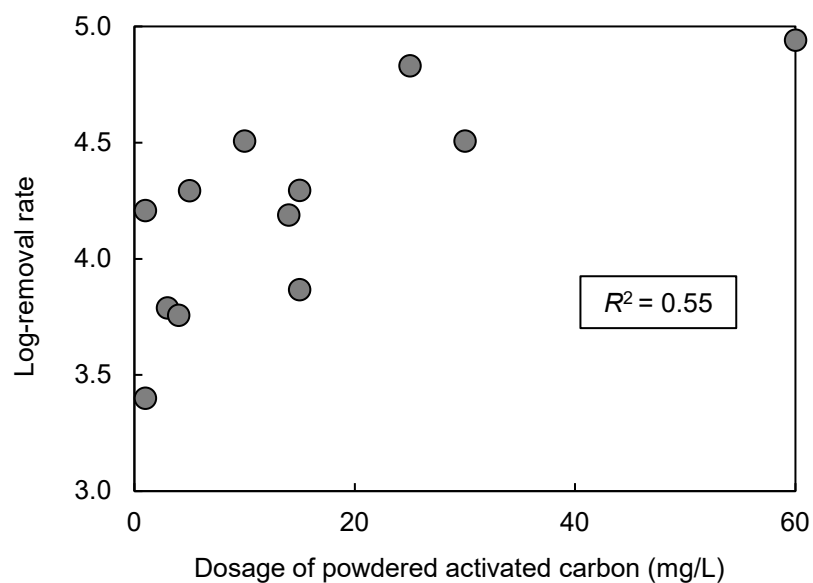


Fig. S5. Correlation between the log-removal rate of carbon particles and the dosage of powdered activated carbon. The data were obtained from the 12 full-scale water purification plants using CSF processes. Two initial carbon particle concentrations of the plants could not obtain and so are excepted.

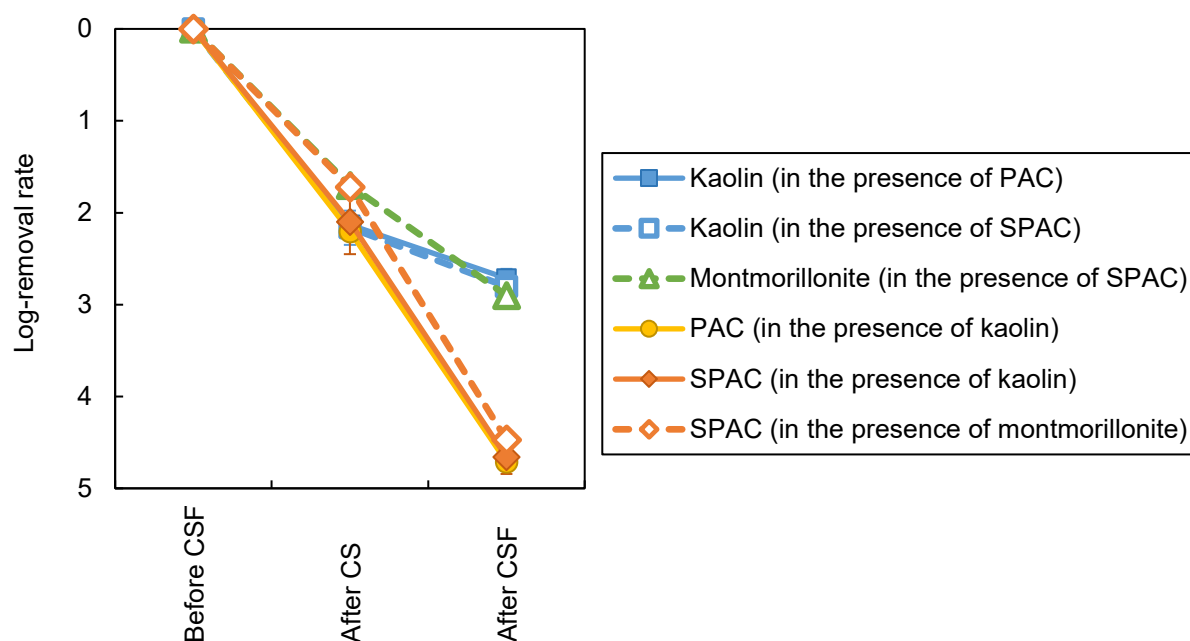


Fig. S6. Log-removal rate comparison between kaolin, montmorillonite, PAC, and SPAC during the CSF process. The data are also listed in Table 1. Data from Runs 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, and 13. Details of the experimental conditions are presented in Table S2. Error bars indicate standard deviations of experiments, but some of them are hidden behind the symbols.

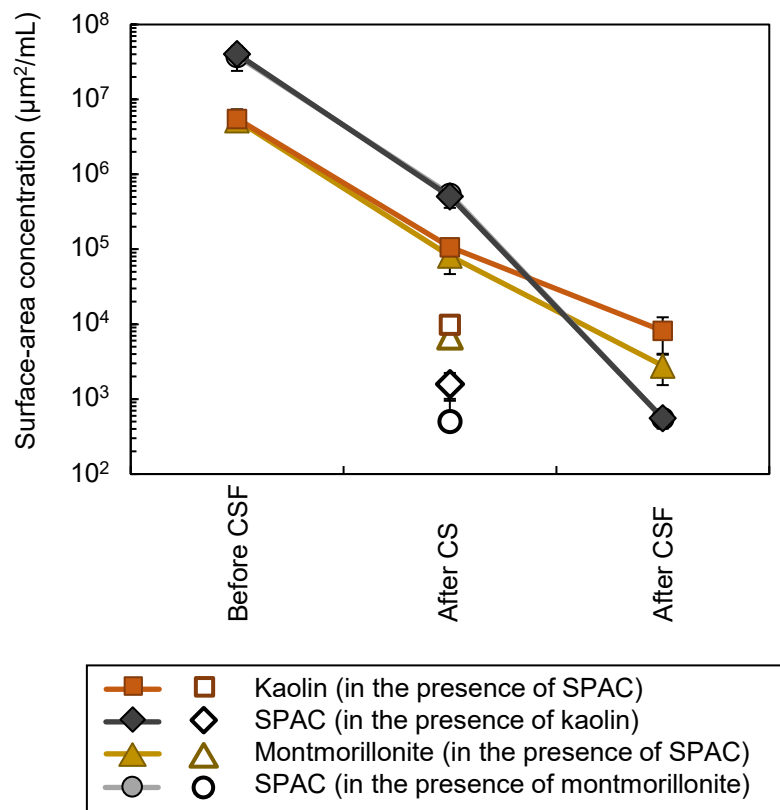


Fig. S7. Comparison of removal rates by CSF between kaolin, montmorillonite, and SPAC quantified in terms of surface-area concentrations. Either kaolin or montmorillonite and SPAC were added simultaneously. The open symbols indicate the data measured after centrifugation. Data from Runs 3, 4, 5, and 6. Details of the experimental conditions are presented in Table S2. Error bars indicate standard deviations of experiments, but some of them are hidden behind the symbols.

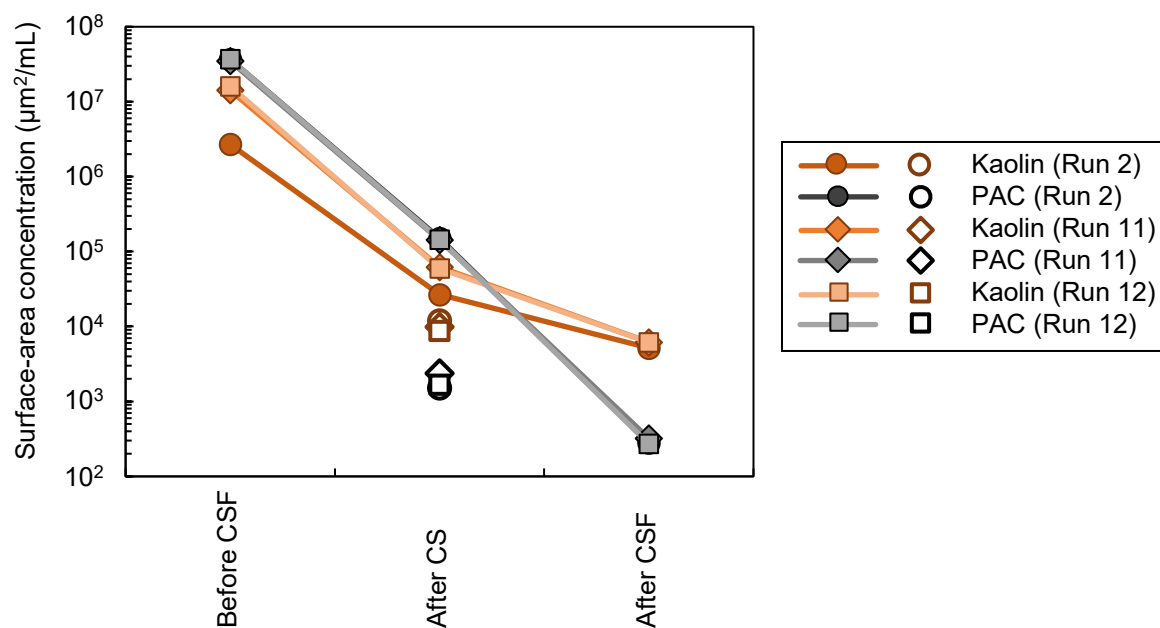


Fig. S8. Comparison of removal rates by CSF between kaolin and PAC quantified in terms of surface-area concentrations. Kaolin and PAC were added simultaneously. The open symbols indicate the data measured after centrifugation. Data from Runs 2, 11, and 12. Details of the experimental conditions are presented in Table S2.

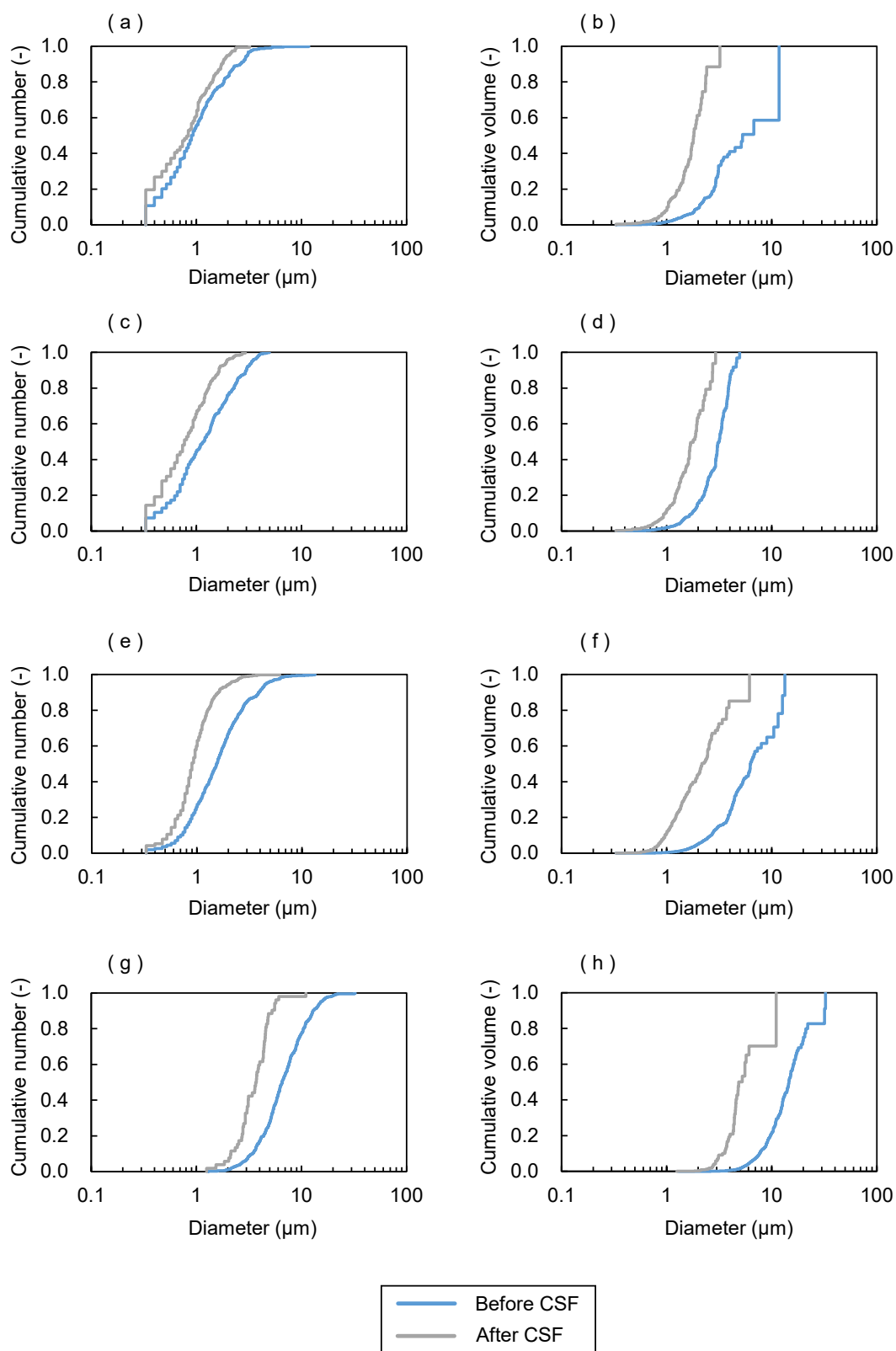


Fig. S9. Particles size distribution of PAC, SPAC, kaolin, and montmorillonite before and after the CSF process. Panels a and b: PAC. Panels c and d: SPAC. Panels e and f: kaolin. Panels g and h: montmorillonite. Panels a, c, e, and g: cumulative numbers. Panels b, d, f, and h: cumulative volumes. Data from Runs 5 and 11. Details of the experimental conditions are presented in Table S2.

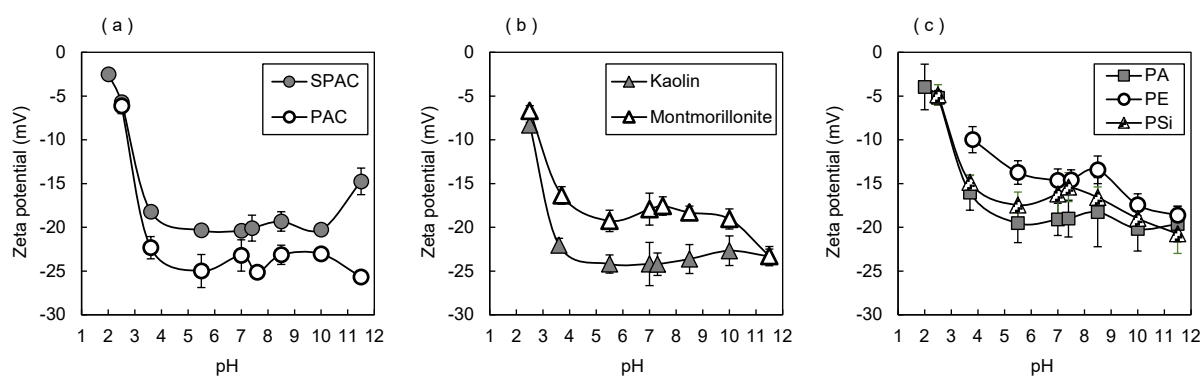


Fig. S10. Comparison of zeta potential between particles. Panel a: activated carbon particles. Panel b: clay particles. Panel c: MP particles. Error bars indicate standard deviations of measurements, but some of them are hidden behind the symbols.

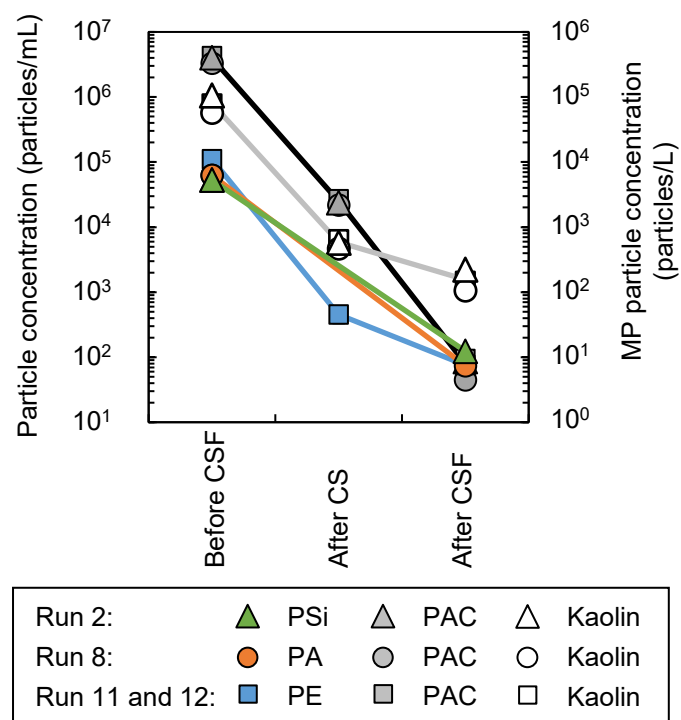


Fig. S11. Behavior of PE, PA, and PSi during the CSF process. PA, PSi, and PE were each treated by CSF in the presence of PAC and kaolin. Data from Runs 2, 8, 11, and 12. Details of the experimental conditions are presented in Table S2. Error bars indicate standard deviations of experiments, but some of them are hidden behind the symbols.

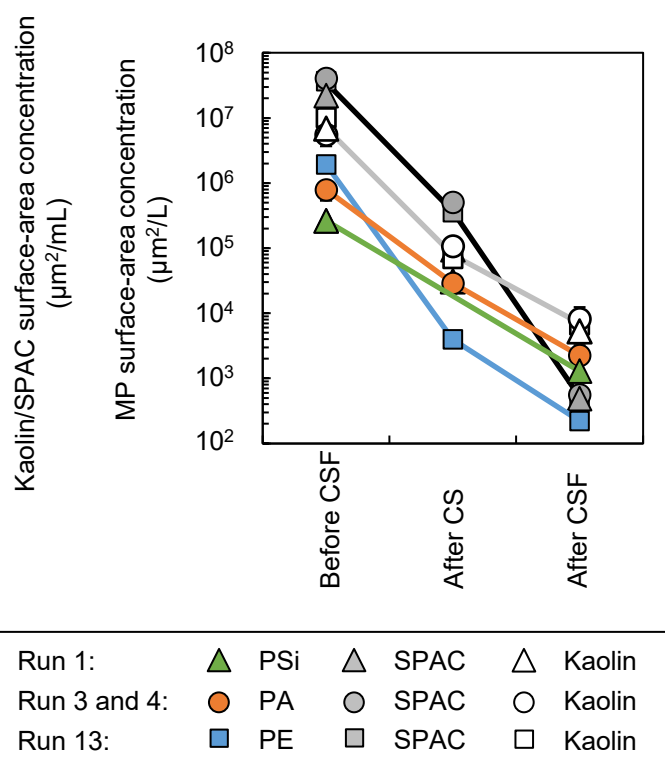


Fig. S12. Behavior of PE, PA, and PSi during the CSF process. PA, Psi, and PE were each treated by CSF in the presence of SPAC and kaolin. Data from Runs 1, 3, 4, and 13. Details of the experimental conditions are presented in Table S2. Error bars indicate standard deviations of experiments, but some of them are hidden behind the symbols.

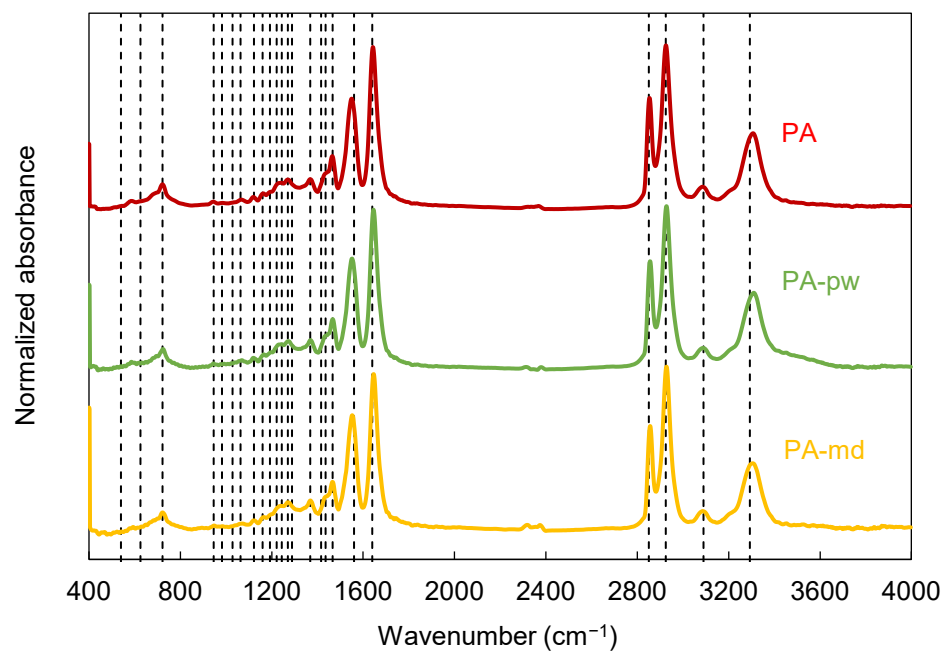


Fig. S13. FTIR of PA particles before and after weathering.

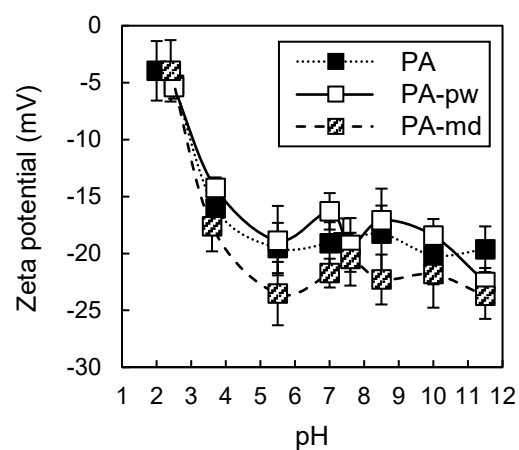


Fig. S14. Zeta potential of PA particles before and after weathering. PA-pw stands for PA exposed to sunlight for 68 days. PA-md stands for PA mechanically damaged by ball milling. Error bars indicate standard deviations of measurements, but some of them are hidden behind the symbols.