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**Minimizing residual black particles in sand filtrate when applying super-
fine powdered activated carbon: coagulants and coagulation conditions**

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18 **Abstract**

19 Because of the eminent adsorptive capacity and rate for dissolved organic molecules
20 compared to conventionally-sized powdered activated carbon (PAC), super-fine powdered
21 activated carbon (SPAC) is gathering momentum for use in not only the pretreatment for
22 membrane filtration for drinking water purification but also the conventional water
23 purification process consisting of coagulation-flocculation, sedimentation, and rapid sand-
24 filtration (CSF). However, the probability of SPAC particles to leak through a sand bed is
25 higher than that of PAC, and their strict leakage control is an issue to be challenged when
26 applying SPAC to CSF. However, study focusing on very high particle removal, which yield
27 residual concentrations down to around 100 particles/mL, has been very limited. A previous
28 study mentioned that the tendency of SPAC leakage is related to its low destabilization. In
29 response to this, the present study focused on the two key components of coagulation (mixing
30 intensity and coagulants) and investigated how to effectively reduce the residual SPAC after
31 CSF.

32 Astonishingly, the flash mixing (the first process of CSF), especially its G (velocity gradient)
33 value, played the most important role in determining the residual SPAC in the filtrate of sand
34 filter (the fourth process). Even if the slow mixing time was short, a sufficiently large G value
35 but short T (mixing time) value in flash mixing effectively reduced the residual SPAC. When
36 the total GT value of flash and slow mixing was fixed at a constant, priority should be given
37 to flash mixing to reduce the residual SPAC.

38 Among 23 PACl (poly-aluminum chloride) coagulants, PACl with a high-basicity (basicity
39 70%) and with sulfate ion (0.14 of sulfate/aluminum in molar ratio), produced by $\text{Al}(\text{OH})_3$ -
40 dissolution, were the most effective to reduce the residual SPAC after CSF. PACls produced
41 by base-titration, which have been intensively investigated in previous researches, were not
42 effective due to lack of floc-formation ability. However, their Al species composition

determined by the ferron method were almost the same as those of PACl by $\text{Al}(\text{OH})_3$ -dissolution, and their charge-neutralization capacities were higher. PACls produced by $\text{Al}(\text{OH})_3$ -dissolution possessed both charge-neutralization and floc-formation abilities, but the former ability was more important to minimize the residual of SPAC.

Keywords

SPAC; filtration; mixing; floc; basicity

1. Introduction

When removing dissolved organic compounds, in particular those of low molecular size, in water treatment processes, adsorption by activated carbon (AC) has been a common practice for many years. Activated carbon is used as an adsorbent either in powdered or granular form. While granular activated carbon is used in a bed adsorber, powdered activated carbon (PAC) can be applied at any point in the treatment process if PAC is sufficiently removed before the treated water enters the distribution system. The main concern for the adsorption processes is the removal efficiencies of target adsorbate compounds to be treated, but plant operators also pay attention to avoid fine black carbon particles from remaining in treated water and entering the distribution system. It is actually not uncommon that PAC, which is applied upstream of a separation process such as rapid sand filtration, sometimes passes through the filters and enters the distribution system, provoking black or grey water complaints from consumers (American Society of Civil Engineers and American Water Works Association 1998). Black water is usually caused by inadequate coagulation and sedimentation or high doses of PAC (American Water Works Association and American Society of Civil Engineers 2012). Even trace concentrations of black carbon particles remaining in treated water, which do not make the water black or grey and do not violate drinking water quality standards for turbidity, could deteriorate the quality of food, such as tofu, that is produced from the water, etc., which causes complaints from food manufacturers. Plant operators pay closer attention to the turbidity or particle count in treated water when PAC is dosed than when PAC is not dosed (Bureau of Waterworks Tokyo Metropolitan Government 2014). Control of fine, black carbon remaining in treated water should be a critical issue, in particular, under the situation in which the application of super-fine PAC (SPAC), carbon particles with a size smaller than

the conventional size, attracts attention (Amaral et al. 2016, Ando et al. 2010, Bonvin et al. 2016, Ellerie et al. 2013, Matsui et al. 2004, Matsui et al. 2012, Partlan et al. 2016).

Plenty of studies have been conducted for the effect of coagulants and coagulation conditions on floc formation and turbidity removal (Letterman and Yiacoumi 2011). Some studies have been conducted for the effect of PAC on coagulation-sedimentation; however, studies regarding the control of carbon particles at trace concentration levels are very limited. Aguilar et al. (2003) reported that the use of PAC considerably increased the elimination efficiency of particulate matters by coagulation and sedimentation, but there was a diminution in the elimination efficiency for particles with diameters in the range 5.5–8.5 μm . They attributed this diminution to the carbon particles remaining in the treated water. In contrast, Younker and Walsh (2016) reported that the addition of PAC into FeCl_3 flocs reduced floc size but had little impact on final turbidity after sedimentation. Therefore, the researches of the two reports are not completely consistent with regard to the effect of PAC, but several reasons can be considered for this apparent discrepancy: raw water characteristics, coagulation conditions employed, etc. The effects of SPAC and PAC on floc formation were investigated in a membrane filtration study (Matsui et al. 2009). The authors reported that the floc particles that formed during coagulation preceded by SPAC pretreatment were larger and more porous than the floc particles formed during coagulation preceded by PAC pretreatment and those formed during coagulation without any pretreatment. The authors explained this result due to increased particle–particle collision frequency and better removal of natural organic matter, which inhibits coagulation by consuming coagulant, before the coagulation reaction. These previous researches focused on the effect of adsorbent on the formation of floc properties, settling velocity, permeability etc., and carbon particles have been investigated as

a ballasting agent for settling, nuclei for coagulation, or a pretreatment agent of coagulation-hindering compounds.

However, researches to investigate the effect of coagulation conditions and coagulants on the remaining carbon particles in finished water have, to the best of our knowledge, never been conducted except for that of our research group, although their control at a trace concentration level is an important issue in terms of customer satisfaction. Our research group recently revealed that at equivalent carbon doses to achieve the same adsorptive removal performance (30 mg/L for PAC and 7.5 mg/L for SPAC), the residual particle number concentrations after coagulation-flocculation, sedimentation, and sand filtration (CSF) were similarly low (100–200 particles/mL) between SPAC and PAC and the particle sizes were similarly small (Nakazawa et al. 2018). There is no drinking water quality standard or guideline in the world for black carbon particles, to the best of our knowledge. When applying SPAC instead of PAC, however, a criterion from plant operator sites, in particular those with a safety orientation, would be that the level of carbon particles remaining in treated water when SPAC is applied should be at a similar or lower level than when PAC is applied.

On the basis of these consideration, this study set its objectives to find better coagulation conditions and find a better coagulant (poly-aluminum chloride: PACl) for the removal of SPAC. In actual water treatments, SPAC/PAC is applied for the removal of dissolved organic compounds, and the removal of SPAC/PAC by CSF occurs in the presence of other substances, such as clay particles and natural organic matter, which may influence the removal of SPAC/PAC. Moreover, coagulation conditions better for SPAC removal may necessarily not bring a good performance for natural organic matter removal. However, the

CSF experiments in this study were conducted mainly with water made from filtered tap water supplemented with carbon slurry in order to gain basic information for carbon particle removal without any influence of other substances.

2. Materials and Methods

2.1. *Activated carbon particles*

A commercially available wood-based PAC (Taiko W; Futamura Chemical Co., Ltd., Nagoya, Japan) was prepared as a slurry in pure water (Milli-Q water; Merck KGaA, Darmstadt, Germany) at a concentration of ~15% (w/w). The PAC in the slurry were milled in a closed-chamber ball mill (Nikkato, Osaka, Japan) with 5- and 10-mm-diameter Al_2O_3 balls at 45-50 rpm for 4–5 h to afford the particles with D_{95} (the diameter larger than 95% of the entire distribution) < 30 μm (Pan et al. 2017). The slurry was taken out from the chamber of the ball mill and then milled with a bead mill (LMZ015, Ashizawa Finetech, Ltd., Chiba, Japan) with 0.3-mm-diameter ZrO_2 beads at a rotational speed of 8 m/s (2590 rpm) in recirculation mode for 20 min to produce a SPAC slurry (Table 1).

The true particle size distributions of the carbons were determined using a laser light diffraction and scattering method (Microtrac MT3300EXII, Nikkiso Co., Inc., Tokyo, Japan), which followed addition of a dispersant (Triton X-100; Kanto Chemical Co., Inc., Tokyo, Japan; final concentration, 0.08% w/v) and ultrasonic dispersion with 150 W for 1 min (Fig. 1S, Supplementary Information of SI).

2.2. Coagulants

Twenty-three kinds of PACls were used as coagulants in the present study. Among them, PACl-70 (basicity 2.1; the number, 70, in the name indicates the % basicity; sulfate ion 2% w/w) and PACl-50 (basicity 1.5, sulfate ion 3% w/w) are commercial products provided by Taki Chemical Co., Ltd. (Hyogo, Japan), which are produced by dissolving $\text{Al}(\text{OH})_3$ into HCl and H_2SO_4 [as described by, e.g., Itoh and Sato (1995) and Sato and Matsuda (2009)]. On the other hand, B70ns, B70s0.11, B70s0.12, B70s0.13, B70s0.14, B70s0.15, and B70s0.17 (the numbers after “B” and “s” represent the “% basicity” and “mole ratio of sulfate ion to aluminum: SO_4/Al ” respectively, and “ns” stands for “non-sulfated”) were produced in the authors’ laboratory by the following method named $\text{Al}(\text{OH})_3$ -dissolution.

Predetermined amounts of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) and $\text{Al}_2(\text{SO}_4)_3 \cdot 14\sim 18\text{H}_2\text{O}$ (FUJIFILM Wako Pure Chemical Corporation) were dissolved into pure water (Milli-Q water) to get aluminum aqueous solution. This solution was mixed with $\text{Al}(\text{OH})_3$ powder (FUJIFILM Wako Pure Chemical Corporation) to form a milk-like slurry and then heated with microwaves (ETHOS TC, Milestone S.r.l., Sorisole (BG), Italy) at 150°C for 3 h. After that, the slurry was centrifuged by a centrifugal separator (H-9R, Kokusan Co., Ltd., Tokyo, Japan) at a rotation speed of 3,000 rpm (6,000 g) for 10 min at 20°C , and then the clear top of the liquid was filtered by a membrane filter (pore size $0.45\ \mu\text{m}$, PTFE, Toyo Roshi Kaisha, Ltd., Tokyo, Japan) to obtain a solution of PACl with basicity of 40~50%. The solution was poured into a beaker, stirred with a rotation speed of $>600\ \text{rpm}$, and heated at 50°C using a hot plate/magnetic stirrer, and then a predetermined amount of aqueous solution of sodium carbonate (FUJIFILM Wako Pure

Chemical Corporation) was dripped into the solution to adjust the basicity up to 70%. The basicity was calculated by the following formula.

$$\text{Basicity (\%)} = \frac{[\text{OH}^-]}{3[\text{Al}_t]} \times 100$$

where $[\text{Al}_t]$ is the total aluminum concentration determined by an inductively coupled plasma mass spectrometer (ICPMS, 7700x, Agilent Technologies, Inc., Santa Clara, CA, USA), $[\text{OH}^-]$ is the concentration of hydroxyl groups from the ingredients $\text{Al}(\text{OH})_3$ and sodium carbonate. The total mass of OH^- introduced to the final product was calculated by taking a mass balance.

PACls produced by the method named base-titration were used in the CSF experiments described in supplementary experiments. The method is described in SI.

The distributions of aluminum species in the coagulants were analyzed by the ferron method. On the basis of their reaction rates with ferron reagent (8-hydroxy-7-iodo-5-quinoline sulfonic acid, FUJIFILM Wako Pure Chemical Corporation), the aluminum species were divided into three categories: Ala, Alb, and Alc. Ala denotes aluminum species that reacted with ferron instantaneously (within 30 s). Alb denotes species that reacted with ferron within 120 min. Alc denotes species that did not react with ferron. These species were assumed to be monomeric, polymeric, and colloidal aluminum species, respectively (Wang et al. 2004). Ferron analyses of the PACls were conducted immediately after dilution with Milli-Q water to 2.7 g-Al/L (0.1 mol-Al/L) (Jia et al. 2004, Wang et al. 2004). Dilution reportedly has little effect on the ferron speciation distribution of PACl (Kimura et al. 2013, Wang et al. 2002).

2.3. Coagulation–flocculation, sedimentation, and rapid sand filtration

Tap water in Sapporo city was filtered through a membrane filter (nominal pore diameter, 0.1 μm ; Toyo Roshi Kaisha, Ltd.) to remove suspended matter, and then the water was adjusted for M alkalinity to 30 mg/L as CaCO_3 by adding NaHCO_3 (FUJIFILM Wako Pure Chemical Corporation). The water was supplemented with an activated carbon slurry to make a raw water for CSF experiments: activated carbon concentrations were 30 mg/L for PAC; 6 mg/L, 7.5 mg/L, 10 mg/L, or 30 mg/L for SPAC. Most CSF experiments were conducted with these waters, but some CSF experiments were additionally conducted with water from the Toyohira River (Sapporo, Japan) after supplementing it with SPAC at 10 mg/L. The river water was sampled at the location where it becomes the raw water source for the Moiwa Water Purification Plant (Sapporo).

The experimental setup and procedure were basically the same as those of Nakazawa et al. (2018) but are shown in Fig. 2S (SI). The coagulation–flocculation and sedimentation steps were conducted in a 4-L rectangular beaker. After a predetermined volume of HCl or NaOH (0.1 N) was added to adjust the coagulation pH to 7.0, the coagulant (PACl) was injected into the beaker to a final concentration of 4 mg-Al/L, unless otherwise noted. Then the water was mixed rapidly followed by slow mixing with a three-stage mixing intensity. The mixing intensities (G value: velocity gradient, see Fig. 3S and Table 1S of SI for the G value calculation) and times (T value: mixing time) of the flash (indicated by subscript F) and slow mixing (indicated by subscript S, with the order: 1, 2, and 3) were varied depending on each experiment, and these values are described in each case in the Results and Discussion section

(see also Table 2S, SI). The water was then left at rest for 1 h. Next, the top three liters of the water (supernatant) were transferred to another beaker for determination of the turbidity (2100Q portable turbidimeter; Hach Company, Loveland, CO, USA) and for rapid sand filtration. Sand filtration was conducted for 40 min at a rate of 90 m d^{-1} in the down-flow direction using a column ($\Phi 4 \text{ cm}$) filled to a depth of 50 cm with sand (effective diameter, 0.6 mm; uniformity, 1.3). The sand filtrate was collected from 13 to 40 min after the start of filtration, and the turbidity and carbon particle count of the filtrate were determined. After each filtration run, the sand filter was backwashed with tap water, then washed forward with pure water (Milli-Q water) and membrane-filtered tap water.

2.4. Membrane filtration and microscopic image analysis

To sample the carbon particles in the water, the water was filtered through a PTFE membrane filter (nominal pore diameter, $0.1 \text{ }\mu\text{m}$; $\Phi 25 \text{ mm}$; Merck KGaA) supported by a glass filter holder (KG-25; Toyo Roshi Kaisha, Ltd.) (Fig. 4S, SI). After drying the filter, color digital photomicrographs were captured for nine or eighteen predetermined observation zones (microscope view area, $247 \times 330 \text{ }\mu\text{m}$) per filter (Fig. 5S, SI) with a digital microscope (VHX-2000; Keyence corporation, Osaka, Japan) at $1000\times$ magnification. The photomicrographs were analyzed using the image analysis software supplied with the microscope. Details of the analytical procedures are reported elsewhere (Nakazawa et al. 2018).

3. Results and Discussion

3.1. Comparison of commercially-available PACI-50 and PACI-70

Fig. 1 shows the number concentrations of residual carbon particles in sand filtrate after CSF when water containing SPAC or PAC of various mass concentrations was coagulated using PACI-70 (a high-basicity PACI) or PACI-50 (a conventional PACI having normal basicity). When PAC at the initial concentration 30 mg/L was treated with PACI-70, the residual concentrations were around 200 particles/mL, and PACI-70 resulted in a slightly higher residual concentration than PACI-50, but the difference was small.

When SPAC of the same initial concentration (30 mg/L) was treated using conventional PACI-50, the residual concentration was much higher (800 particles/mL). When PACI-70 was used to treat the SPAC, the residual concentration was reduced to 400 particles/mL. The lower the initial concentration of SPAC was, the lower the residual concentration, both for PACI-50 and PACI-70; and at the initial concentration of 7.5 mg/L or less, the difference of residual concentrations between the two cases of using PACI-50 or PACI-70 became smaller. Overall, high-basicity PACI-70 was superior to PACI-50 to remove SPAC. With PACI-70, the removal rates in terms of particle number concentrations depended on the concentration of SPAC: 5.3 log removal was lowest at an SPAC concentration of 10 mg/L. Nevertheless, the removal rates with PACI-70 were slightly higher than with PACI-50 (Fig. 6S, SI). In contrast, the turbidity of the supernatant after sedimentation following coagulation by PACI-50 was slightly lower than that by PACI-70, and the result was opposite to the residual number concentration mentioned above (Fig. 7S, SI).

Higher-basicity PACIs (e.g. PACI-70) are known to neutralize negative charges more according to the results of colloid titration (Fig. 8S, SI) (Matsui et al. 2017). Accordingly,

although PACl-70 is not superior compared with PACl-50 in terms of forming large flocs bringing a lower turbidity of supernatant water, PACl-70 is inferred to neutralize the negative charges of carbon particles efficiently due to its high capacity in charge neutralization. The high capacity in charge neutralization seemed to contribute to the removal of carbon particles.

We previously reported that the particles remaining after CSF were smaller in size than the particles before CSF (Nakazawa et al. 2018). Although the tendency of small carbon particles to remain after CSF is overall attributable to their size, the size effect is comprised of the following three reasons: 1) low destabilization rate during the coagulation process, 2) low frequency of particle–particle collisions during flocculation, and 3) low probability of the particles coming into contact with sand grains during the sand filtration process. Therefore, particle destabilization is a key to reduce remaining carbon particles after CSF. When comparing the zeta potentials of residual carbon particles after CSF treatments with PACl-70 and PACl-50, they were not different (Fig. 2). Therefore, particles with a certain zeta potential value or lower regardless of PACl-70 or 50 passed through the filter. Accordingly, the merit of PACl-70 in reducing carbon particle concentration after CSF was due to its high capacity to minimize the number of non-neutralized carbon particles (with a certain zeta potential value or lower) rather than due to its high positive charge to neutralize the negative charge of particles to nearly zero level.

When the SPAC suspension was coagulated using PACl-70, the formation of micro floc particles was not confirmed in the photograph taken soon after flash mixing (Fig. 3). When the PAC suspension was coagulated with PACl-70, the formation of micro floc particles was confirmed marginally. In contrast, when PACl-50 was used in the coagulation process, the formation of micro floc particles was clearly observed in the experiments of all experimental

conditions. However, floc size at the end of slow mixing was not different between each pair of experiments using PACl-50 and PACl-70.

Therefore, it can be said that the rapid formation of large-size floc particles and the lowered turbidity of supernatant water, although such information can be obtained by a conventional jar test, are not indicators for a lower residual carbon particle concentration after CSF. PACls are rich in diversity in terms of two different aspects: charge-neutralization capacity to destabilize particles and the bridge-formation ability to form large floc particles, but the charge-neutralization capacity is not related to the bridge-formation ability (Zhao et al. 2010). Consequently our study revealed that PACls having a feature of the charge-neutralization capacity to destabilize particles rather than the bridge-formation ability to form large-size floc particles are beneficial for lowering residual carbon particle concentration after CSF.

3.2. Effect of mixing intensity in coagulation and flocculation

As mentioned in the preceding paragraph, the high-basicity PACl (PACl-70) formed flocs slowly, but it had a high charge neutralizing capacity. Hence, it was hypothesized that optimizing the mixing intensity and time would lead to further reduction of residual carbon particle concentration in sand filtrate, and experiments were conducted. Fig. 4 illustrates the residual SPAC concentrations in sand filtrates when coagulation-flocculation were conducted with three different $G_T T_T$ values ranging from 19,500 to 78,000 by adjusting T_T . (The $G_T T_T$ value means total GT, which is the sum of flash-mixing GT ($G_F T_F$) and slow-mixing GT ($G_S T_S$.) In the case with the small $G_T T_T$ value of 19,500, the residual carbon particle concentration was 800-particles/mL after CSF using PACl-50, whereas a much higher residual concentration of 2,200 particles/mL was observed using PACl-70. In such a low

mixing intensity, large floc particles were seen in the photographs at the end of slow mixing, but many small floc particles were also observed in the same photographs, in both cases of PACI-50 and PACI-70 (Fig. 5); the mixing intensity was obviously insufficient. In contrast, as the $G_T T_T$ value increased from 39,000 to 78,000, small floc particles diminished, seen in the photographs taken at the end of slow mixing (Fig. 5). At the same time, the turbidity of supernatant water (Fig. 9S, SI) and the residual carbon particle concentration of sand filtrate also decreased substantially. As shown in Fig. 4 and Fig. 9S (SI), furthermore, the effect of $G_T T_T$ on the turbidity of supernatant water and the residual carbon particle concentration of sand filtrate was more pronounced for PACI-70, which had a higher capacity for charge neutralization, than PACI-50.

3.3. Effect of flash mixing intensity in coagulation

Because charge neutralization occurs mostly during the flash mixing stage, we hypothesized that the residual carbon particle concentration of sand filtrate is influenced more by the flash mixing conditions than by the slow mixing conditions, so we conducted other series of CSF experiments. In the first series of experiments, the $G_T T_T$ was fixed at 39,000, but its allocation to flash mixing was changed; i.e. the larger the $G_F T_F$ value of flash-mixing was, the smaller the $G_S T_S$ value of slow-mixing. The results are shown in Fig. 6. When the flash-mixing $G_F T_F$ was small (6,000), the residual carbon particle concentration was high at 900 particles/mL. The residual concentration, however, decreased as the flash-mixing $G_F T_F$ increased. The effect of the flash-mixing $G_F T_F$ was more prominent with PACI-70 than with PACI-50. At the largest flash-mixing $G_F T_F$ (24,000), the residual carbon particle concentration was reduced to <200 particles/mL.

In a series of experiments for which flash-mixing $G_F T_F$ was changed by adjusting T_F but slow mixing intensity was fixed at a constant value ($G_S T_S = 15,100$), a $G_F T_F > 24,000$ resulted in a low residual carbon particle concentration (Fig. 7), indicating that there is a certain minimal value for $G_F T_F$ required for lowering the carbon particle concentration in sand filtrate. Next, the effect of G_F value on residual carbon particles was examined in the condition where G_T values of both flash and slow mixing intensities were fixed ($G_F T_F = 24,000$ and $G_S T_S = 15,100$). Residual carbon particle concentration became smaller with a larger G_F value (smaller T_F value) (Fig. 8). It was minimal at $G_F = 600 \text{ s}^{-1}$ (experiments at G value $> 600 \text{ s}^{-1}$ could not be conducted because the mixing caused the water to splash out of the container. Kan et al. (2002) conducted jar tests by using alum and commercially-available PACl to investigate the effect of flash-mixing time on the removal of clay particle. They report that the residual turbidity decreased sharply with increasing duration of flash-mixing. Lin et al. (2013) also conducted jar tests by using turbid surface-water and commercially-available PACl to investigate the effect of flash-mixing intensity on the turbidity and DOC removal. They reported that the removal performances of turbidity and DOC were improved as flash-mixing intensity increased. We used fine carbon particles as the target matter in the present study, but the tendency that the turbidity after settling and residual carbon particles remaining in sand filtrate reduced as flash-mixing intensity or time increased was much the same as those previous studies.

It is of great interest that the trace residual-carbon-particle concentration as an outcome after the fourth step of sand-filtration in the CSF was largely affected by the mixing intensity of the first step of coagulation in the CSF, although the flocculation and sedimentation processes occurred in between the coagulation and the sand-filtration. The flocculation and sedimentation processes had long detention time, and most of the carbon particles were

removed by the sedimentation process. During the flash mixing process for coagulation, the PACls hydrolyzed in water and formed a hydrolyzing aluminum polymer, which efficiently neutralized the negative charge of carbon particles. Thus, providing both rapid dispersion of dosed PACls and high-frequent contact between the hydrolyzing aluminum polymer and the carbon particles, in particular very fine carbon particles, was necessary to decrease charge-un-neutralized particles. Finally, achieving these conditions produced low residual carbon particles, which penetrated through the sand bed situated in the last stage in the CSF. A high G_F value created such conditions of the rapid dispersion and the high-frequent contact.

3.4. Effect of coagulant dosage

It is generally known that turbidity removal by coagulation-sedimentation improves as the dosage of coagulant increases when the coagulation processes are mainly due to sweep flocculation mechanism, which operates at near neutral pH, but not due to charge-neutralization mechanism, which operates at $pH < 6$ (Amirtharaja and O'Melia 1990, Hendricks 2010, Letterman and Yiacoumi 2011). The present study of CSF, which was conducted at pH 7, also confirmed the relationship between the dosage of coagulant and the residual concentration of SPAC or the turbidity of supernatant water in CSF (Fig. 10S and Fig. 11S, SI); increasing coagulant dosage resulted in an increase in the removal of carbon particles both after sedimentation and sand filtration. Additionally, the superiority of PACI-70 to PACI-50 was held in the entire range of coagulant dosages tested in terms of residual carbon particle concentration. The very low residual concentration of 6 particles/mL was attained with the highest coagulant dosage of PACI-70.

3.5. Development and performance of coagulants by base-titration

386

387 The above described investigation suggests the importance of decreasing the number of
388 charge-un-neutralized particles in order to enhance the separation of SPAC particles and
389 lower the number of residual SPAC particles after CSF. Available techniques for decreasing
390 the number of charge-un-neutralized particles were enumerated using a coagulant with high
391 a charge-neutralization capacity, such as high-basicity PACl with the optimized flash mixing
392 intensity, as well as increasing the dosage of coagulant. We further searched for a better PACl
393 that lowered the number of residual SPAC particles. We produced a series of PACls with
394 high basicity (Table 3S, SI) and conducted jar tests (Table 4S, SI).

395

396 It is widely known that the Al_{13} species in PACl have a high charge-neutralizing ability (Gao
397 et al. 2005, Lin et al. 2008, Parthasarathy and Buffle 1985, Wu et al. 2007, Zhao et al. 2009),
398 and Alb analyzed by the ferron method corresponds to the Al_{13} species (Parker and Bertsch
399 1992, Parthasarathy and Buffle 1985). In the present study, some PACls with a high content
400 of Alb (Alb-type PACl) were produced by base-titration (Fig. 12S, SI), and experiments of
401 coagulation-flocculation and sedimentation were conducted. The zeta potential of carbon
402 particles became zero at a lower dosage of Alb-type PACl (B80ns-1) than of PACl-70 (Fig.
403 13S, SI), and Alb-type PACls (B65ns, B80ns-1, B80ns-2) supplied a higher positive charge
404 to carbon particles than PACl-70 at the same coagulant dosage (Fig. 14S, SI). These results
405 indicate that Alb-type PACls actually had a higher charge-neutralizing ability than PACl-70.
406 However, these Alb-type PACls could not flocculate carbon particles, and consequently
407 resulted in a high turbidity after sedimentation, even given large mixing intensity (Fig. 14S,
408 SI). Even at the coagulant dose, which brought the zeta potentials of carbon particles to
409 around zero, the turbidities after sedimentation were still high, compared with those obtained
410 by PACl-70 (Fig. 13S, SI).

It was reported that sulfate ions in PACl play a role in enhancing floc formation (Wang et al. 2002). Actually, the commercial PACl products, PACl-50 and PACl-70, both of which produce larger floc particles than the Alb-type PACl, contain sulfate ion. Accordingly, we supplemented sulfate ion and prepared three Alb-type PACls (Fig. 15S, SI). One PACl (B82s0.11) among the sulfated Alb-type PACls slightly flocculated carbon particles at a large mixing intensity (as a GT value of 57,000). However, turbidity-removal performance was considerably inferior to PACl-50 and PACl-70.

Gao and Yue (2005) produced sulfated PACls of different SO_4/Al ratios by base-titration at ambient temperature and reported that a sulfated high-basicity PACl (basicity 67%) with $\text{SO}_4/\text{Al}=0.066$ in the range from 0 to 0.15 reduced residual turbidity the most when an experiment consisting of coagulation-flocculation and sedimentation was conducted with lake water. In our experiments, however, the production of sulfated high-basicity PACls at ambient temperature by base-titration was unsuccessful due to the occurrence of aluminum hydroxide precipitation during titration, and we were not able to apply the sulfated high-basicity PACl. Shi et al. (2007) also mentioned that room temperature was not suitable for preparation of PACl because a large amount of aluminum precipitate could form during titration.

Yan et al. (2008) investigated the relationship between Al species and their behavior in coagulation targeting NOM. They reported that Ala (monomeric species) combined with NOM but most of the flocs formed by Ala were small and difficult to settle. Alb (polymeric species) had high charge-neutralizing ability but flocs formed by Alb were not larger and did not settle faster than those formed by Alc (colloidal species), and Alc adsorbs and removes

the target matter most efficiently. In the present study, in addition, given that the major aluminum fraction in PACI-50 and PACI-70 was not Alb but Alc, Alc-type PACIs (rich in content of Alc fraction) were also produced (see SI for the preparation method). Those Alc-type PACIs showed high charge-neutralization ability, however their flocculation performances were almost the same as the Alb-type PACIs and had a low removal efficiency (Fig. 16S, SI). In summary, Alb or Alc in PACIs prepared by base-titration had a high capacity for charge-neutralization, but the bridge-formation ability to form floc particles was poor and resulted in high turbidity after sedimentation.

3.6. Development and performance of coagulants by $Al(OH)_3$ -dissolution

Subsequently, we applied another method to produce PACIs: $Al(OH)_3$ -dissolution (Table 2). Eleven PACIs with a basicity of 70% and with a variety of sulfate ion contents were produced (Table 2): it was impossible to produce PACIs with a basicity >70% because of the gelation of Al solution or the presence of too much undissolved residue. As shown in Fig. 9, the performance on reducing residual SPAC particles increased as sulfate content increased from $SO_4/Al=0$ to $SO_4/Al=0.14$ but decreased for $SO_4/Al>0.14$. The preparation of PACIs with $SO_4/Al>0.14$ required rising the temperature from 50°C to 80°C when adjusting the basicity. In terms of high temperature, this process was similar to the process of base-titration PACIs, which do not have sufficient bridge-formation ability. The loss of the bridge-formation ability might be related with a high temperature in production process.

Among the PACIs prepared by $Al(OH)_3$ -dissolution, B70s0.14 with the $SO_4/Al=0.14$ showed the highest performance on reducing residual SPAC particles after CSF. B70s0.14

outperformed commercially available PACI-70, which was used in the experiments of the paragraph 3.1, 3.2, and 3.3 and effectively removed SPAC. As shown in Fig. 10 (A), B70s0.14 highly reduced residual carbon particles at a higher mixing intensity, and was superior to PACI-70 for all mixing conditions tested. The superiority of B70s0.14 to PACI-70 was also confirmed in the experiments where natural water supplemented with SPAC was used (Fig. 10 (B)). Moreover, the trend that high $G_F T_F$ results in low concentration of residual carbon particles, which described in the section 3.3, was also observed in the data of natural water. In case of very high $G_F T_F$ (60,000) applied, very low concentrations of residual carbon particles were attained with both B70s0.14 and PACI-70 and their difference was small. Residual carbon particle concentrations obtained in the experiments using river water (Fig. 10 (B)) were somewhat lower than those using filtered tap water (Fig. 10 (A)). However the effect of organic matter concentrations and turbidity should not be inferred by the comparison of these two data because the two waters differed in ionic composition as well as organic matter concentrations and turbidity, all of which affect coagulation performance.

The PACIs produced by $Al(OH)_3$ -dissolution, including B70s0.14, which showed the high performance on the reduction of residual SPAC after CSF, contained Alc as the main component. However, the percentages of Ala, Alb, and Alc were almost the same as those of the Alc-type PACIs prepared by base-titration (Fig. 17S, SI), which were not effective coagulants. This means that the Al species distribution determined by the ferron method is not informative in evaluating the ability for coagulation treatment targeting SPAC, in particular the ability of floc formation. Base-titration required a high temperature when adjusting the basicity and resulted in a high salt (Na and Cl) content in comparison to $Al(OH)_3$ -dissolution. These differences were inferred to influence the ability of floc formation. Studies on PACI produced by $Al(OH)_3$ -dissolution are scarcely seen, and further

investigations are expected.

4. Conclusions

The addition of SPAC in water treatment is a promising technology to remove organic contaminants, but efficient removal of the loaded SPAC is needed. In this study, key control points to attain the high log removal rates of SPAC and to reduce residual SPAC particles at trace concentration levels of 100 to 1000 particles/mL in treated water were examined, and their background mechanisms were discussed, focusing on the process points of coagulation-flocculation and coagulants in CSF. The following conclusions were obtained.

1) A sufficiently large G value in flash mixing for the first step of coagulation was clearly a dominant factor for minimizing residual carbon particle concentration in the treated water after the fourth step of sand filtration. Adequate mixing for coagulation would enable complete dispersion of coagulant thereby reducing the number of particles that were not charge-neutralized. Such particles would pass through the sand filter into the treated water.

2) Commercially available PACls were compared with each other: high-basicity PACl (basicity 70%) was more effective in removing residual carbon particles. It was because the high-basicity PACl had a high charge neutralizing capacity to destabilize many particles, though it formed flocs slowly. However, this superiority of high-basicity PACl was provided by the sufficient flash mixing. Without sufficient flash mixing, not only the removal rate decreased but also the high-basicity PACl became inferior to conventional-basicity PACl.

3) High-basicity PACl with $\text{SO}_4/\text{Al}=0.14$ reduced residual carbon particles down to the minimum concentration. Such a high performance PACl coagulant was produced by using $\text{Al}(\text{OH})_3$ -dissolution, and the dominant Al species was Alc determined by the ferron method. In contrast, Alb and Alc type PACls produced by base-titration had a high positive charge capacity and were poor at forming floc particles due to lack of bridge-forming ability; this was true even if they were used at a large dosage or the optimal dosage in terms of charge neutralization.

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Table 1. Activated carbon particle size. The median diameters were determined by laser light diffraction and scattering.

Activated carbon		Median diameter (μm)
PAC		13.7
SPAC	SPAC ₁	0.96
	SPAC ₂	0.90

Figure 1. Particle number concentration of residual activated carbon vs. initial activated carbon concentration at a fixed mixing intensity (G_{TT} : 39,000, G_F : 600 s^{-1} , T_F : 20 s; G_{S1} : 50 s^{-1} , T_{S1} : 300 s, G_{S2} : 20 s^{-1} , T_{S2} : 300 s, G_{S3} : 10 s^{-1} , T_{S3} : 600 s). PAC and SPAC₁ were used. Error bars indicate standard deviations of measurements.

Figure 2. Zeta potentials of residual carbon particles in sand-filtrate vs. initial activated carbon concentration. Experimental conditions were the same as those described for Fig. 1. The number of measurements was described as follows: with PACI-70, two measurements for SPAC 6 mg/L and 30 mg/L, and one measurement for SPAC 10 mg/L; with PACI-50, three measurements for SPAC 30 mg/L, two measurements for SPAC 6 mg/L and 10 mg/L, and one measurement for PAC 30 mg/L. Error bars indicate standard deviations of measurements.

Figure 3. Photos of floc particles during the experiments of Fig. 1. The two columns of the left side are experiments using PACI-50. The two columns of the right side are experiments using PACI-70. The photos in the first column in each set of two rows were taken immediately after flash mixing was finished. The photos in the second column in each set of two rows were taken immediately after slow mixing was finished.

Figure 4. Effect of total mixing intensity ($G_T T_T$ value= $G_F T_F$ value of flash mixing+ $G_S T_S$ value of slow mixing) on the particle number concentration of residual carbon. SPAC₁ was used. Initial SPAC₁ concentration was 10 mg/L. Details of the mixing conditions are shown in Table 2S of SI. The number of experiments for each mixing condition was described as follows: with total GT 39,000, two experiments; with total GT 19,500 and 78,000, one experiment each. Error bars indicate standard deviations of measurements.

Figure 5. Photos of floc particles during the experiments of Fig. 4. The two columns of the left side are experiments using PACI-50. The two columns of the right side are experiments using PACI-70. The photos in the first column in each set of two rows were taken immediately after flash mixing was finished. The photos in the second columns in each set of two rows were taken immediately after slow mixing was finished.

Figure 6. Effect of mixing intensity in flash and slow mixing on the particle number concentration of residual carbon at a fixed total mixing intensity. SPAC₁ was used. Initial SPAC₁ concentration was 10 mg/L. $G_T T_T$ value ($=G_F T_F$ of flash mixing + $G_S T_S$ of slow mixing) was fixed at about 39,000. Details of the mixing conditions are shown in Table 2S of SI. The number of experiments for each mixing condition was described as follows: with $G_T T_T$ 39,000 ($G_F T_F=12,000$), two experiments; with $G_T T_T$ 39,000 ($G_F T_F=6,000$) and 39,100 ($G_F T_F=24,000$), one experiment. Error bars indicate standard deviations of measurements.

Figure 7. Effect of flash mixing time (T_F) on the particle number concentration of residual carbon. SPAC₂ was used. Initial SPAC₂ concentration was 10 mg/L. PACI-70 was used. G_F value was fixed at 600 s^{-1} . $G_S T_S$ of slow mixing=15,100. Details of the mixing conditions are shown in Table 2S of SI. Error bars indicate standard deviations of measurements.

Figure 8. Effect of mixing speed (G_F) and time (T_F) in flash mixing on the particle number concentration of residual carbon at a fixed flash mixing intensity ($G_F T_F = 24,000$) and a fixed slow mixing intensity ($G_S T_S = 15,100$). SPAC₂ was used. Initial SPAC₂ concentration was 10 mg/L. PACI-70 was used. Error bars indicate standard deviations of measurements.

Table 2. Coagulants made by $\text{Al}(\text{OH})_3$ -dissolution.

Name	Basicity	SO_4/Al	Cl/Al	Na/Al	Al content	Titrating process	
						Time	Temperature
	%	mole ratio	mole ratio	mole ratio	mol/L	h	$^{\circ}\text{C}$
B70ns	70	0.00	1.68	0.78	2.0	1.0	50
B70s0.11	70	0.11	1.46	0.79	2.0	1.0	50
B70s0.12	70	0.12	1.36	0.69	2.2	1.0	50
B70s0.13	70	0.13	1.36	0.72	2.0	1.3	50
B70s0.14-1	70	0.14	1.43	0.79	2.1	1.3	50
B70s0.14-2	70	0.14	1.44	0.81	2.1	1.4	50
B70s0.14-3	70	0.14	1.37	0.75	1.9	1.4	50
B70s0.14-4	70	0.14	1.37	0.75	1.9	1.4	50
B70s0.15-1	70	0.15	1.31	0.71	2.2	1.4	50~77
B70s0.15-2	70	0.15	1.29	0.68	2.1	1.3	50~77
B70s0.17	70	0.17	1.34	0.78	2.1	1.0	50~80

Figure 9. Particle number concentration of residual carbon after CSFs with various PACs. SPAC₁ was used. Initial SPAC₁ concentration was 10 mg/L. G_TT_T value was fixed at 39,000. Three runs were conducted for PACI-70, B70s0.12, B70s0.14 (B70s0.14-1 was used for all Runs), and B70s0.15 (B70s0.15-1 was used for Run 1, and B70s0.15-2 was used for Run 2 and 3). Two runs were for B70s0.13. One run was conducted for B70ns, B70s0.11, and B70s0.17. Error bars indicate standard deviations of three measurements.

Figure 10. Effect of flash mixing time on the particle number concentration of residual carbon. SPAC₂ was used. Initial SPAC₂ concentration was 10 mg/L. G_F value was fixed at 600 s⁻¹. $G_S T_S$ of slow mixing was 15,100. Details of the mixing conditions are shown in Table 2S of SI. Error bars indicate standard deviations of measurements. (A) Filtered tap water supplemented with SPAC₂ was used as raw water; PACI-70 and B70s0.14-2 were used as coagulant. (B) River water (turbidity 2.5 NTU and TOC 0.6 mg/L) supplemented with SPAC₂ was used as raw water; PACI-70, B70s0.14-3, and B70s0.14-4 were used.

Supplementary Information

Minimizing residual black particles in sand filtrate when applying super-fine powdered activated carbon: coagulants and coagulation conditions

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Figure 1S. Particle size distributions of PAC, SPAC₁, and SPAC₂.

Coagulation-flocculation
and sedimentation

Water treated by
sedimentation

Rapid sand filtration

Figure 2S. Schematic diagram of the experimental setup for the coagulation-flocculation, sedimentation, and sand filtration experiment.

Calculation of G (velocity gradient) value

The mean velocity gradient G (s^{-1}) is defined as a function of P , μ , and V as follows.

$$G = \sqrt{\frac{P}{\mu V}} \quad (1)$$

where P is power consumed by the agitating impeller in a mixing vessel (W), μ is the viscosity of water (Pa s), and V (m^3) is the volume of the water in the mixing vessel.

Power consumption is given by the product of force acting on an impeller blade and its moving velocity. Velocity and force acting on the blade of the impeller varies radially such that the tip of the blade moves fastest (tip speed) and the force acting on the tip is strongest, but the root end of the blade moves slowest and its force is smallest. Therefore, power consumed by a rotating impeller blade is given by:

$$P_B = \int v p dA \quad (2)$$

$$p = \frac{1}{2} \rho_w C_d v^2 \quad (3)$$

where, P_B is the power required to move a blade (W), v is the velocity of the moving blade (m/s), p is the pressure acting vertically on the blade (Pa), A is the area of blade (m^2), ρ_w is the density of fluid (kg/m^3), and C_d is drag coefficient (dimensionless).

For a flat rectangular blade shown in Fig. 3S,

$$v = 2\pi(1 - K_r)xN_s \quad (4)$$

$$dA = h dx \quad (5)$$

where, K_r is (dimensionless), x is the radial distance from the impeller center (m), N_s is rotational speed (rps), and h is the height of a impeller blade (m).

By substituting equations (3), (4) and (5) into (2):

$$P_B = \int_{r_1}^{r_2} \frac{1}{2} \rho_w C_d [2\pi(1 - K_r)xN_s]^3 h dx = \rho_w C_d [\pi(1 - K_r)N_s]^3 h (r_2^4 - r_1^4) \quad (6)$$

The total power input to the mixing tank having multiple impeller blades is given by:

$$P = nP_B = n\rho_w C_d [\pi N_s]^3 h (r_2^4 - r_1^4) \quad (7)$$

where, n is the number of impeller blades in a mixer.

Substituting Eq. (10) into Eq. (1) gives,

$$G = \sqrt{\frac{n\rho_w C_d \pi^3 (1 - K_r)^3 N_s^3 h (r_2^4 - r_1^4)}{\mu V}}. \quad (8)$$

The values used for the calculation of G values by equation (8) were summarized in Table 1S.

Figure 3S. Schematic diagram of mixing blade for the calculation of G value.

Table 1S. Parameter values used for G value calculation.

Parameter symbol	Unit	Value
V	m^3	0.004
μ	Pa s	1.005×10^{-3}
h	m	0.035
r_1	m	0.014
r_2	m	0.05
ρ_w	kg m^{-3}	9.982×10^2
C_d	dimensionless	1.5
K_r	dimensionless	0
n	dimensionless	4
N_s	rps	from 0.22 to 3.28

Table 2S. The experimental conditions of coagulation in CSF experiments.

	Activated carbon		Coagulant		Flash mixing		Slow mixing						Flash + slow mixing
	Name	Initial concentration (mg L ⁻¹)	Name	Dosage (mg-Al L ⁻¹)	G _F (s ⁻¹)	T _F (s)	G _{S1} (s ⁻¹)	T _{S1} (s)	G _{S2} (s ⁻¹)	T _{S2} (s)	G _{S3} (s ⁻¹)	T _{S3} (s)	G _T T _T (dimensionless)
Fig. 1 Fig. 6S Fig. 7S	PAC and SPAC ₁	30 (PAC) and 6~30 (SPAC ₁)	PACI-50 and PACI-70	4	600	20	50	300	20	300	10	600	39,000
Fig. 4 Fig. 9S	SPAC ₁	10	PACI-50 and PACI-70	4	600	10	50	150	20	150	10	300	19,500
					600	20	50	300	20	300	10	600	39,000
					600	40	50	600	20	600	10	1,200	78,000
Fig. 6	SPAC ₁	10	PACI-50 and PACI-70	4	600	10	50	375	20	375	10	675	39,000
					600	20	50	300	20	300	10	600	39,000
					600	40	50	170	20	170	10	320	39,100
Fig. 7	SPAC ₂	10	PACI-70	4	600	20	50	170	20	170	10	320	27,100
					600	40	50	170	20	170	10	320	39,100
					600	60	50	170	20	170	10	320	51,100
					600	100	50	170	20	170	10	320	75,100
Fig. 8	SPAC ₂	10	PACI-70	4	150	160	50	170	20	170	10	320	39,100
					300	80	50	170	20	170	10	320	39,100
					600	40	50	170	20	170	10	320	39,100
Fig. 9	SPAC ₁	10	PACI-70 and PACIs by Al(OH) ₃ -solution	4	600	20	50	300	20	300	10	600	39,000
Fig. 10	SPAC ₂	10	PACI-70 and B70s0.14	4	600	20	50	170	20	170	10	320	27,100
					600	40	50	170	20	170	10	320	39,100
					600	60	50	170	20	170	10	320	51,100
					600	100	50	170	20	170	10	320	75,100
Fig. 10S Fig. 11S	SPAC ₁	10	PACI-50 and PACI-70	1.5~8	600	40	50	600	20	600	10	1,200	78,000

G and T stand for velocity gradient and mixing time, respectively. Subscripts F, S, and the numbers after S mean flash mixing, slow mixing, and the order of the slow mixing part, respectively.

Figure 4S. Schematic diagram of the experimental setup for membrane filtration and microscopic image analysis.

Figure 5S. The position of observation zones on a membrane filter. The observation was conducted with 18 zones in the case that the particle number concentration was expected to be lower than 200 particles/mL. In the other case, the observation was conducted with 9 zones (zone numbers 1 and from 3 to 10).

Figure 6S. Removal rate in terms of particle number concentration after CSF in the experiments of Fig. 1. C_r and C_f indicate the particle number concentration of carbon in raw water and sand filtrate, respectively.

Figure 7S. Turbidity of supernatant after coagulation, flocculation, and sedimentation in the experiments of Fig. 1. Error bars indicate standard deviations of measurements.

Figure 8S. Colloid charge capacity of PACI-50 and PACI-70 (Matsui et al. 2017).

Figure 9S. Turbidity of supernatant after coagulation, flocculation, and sedimentation in the experiments of Fig. 4. Error bars indicate standard deviations of measurements.

Figure 10S. Effect of coagulant dosage on the particle number concentration of residual carbon in sand filtrate. SPAC₁ was used. Initial SPAC₁ concentration was 10 mg/L. G_{TT} value was fixed at 78,000 ($G_{FT_F}=24,000$, $G_{ST_S}=54,000$). Error bars indicate standard deviations of measurements.

Figure 11S. Turbidity of supernatant after coagulation, flocculation, and sedimentation in the experiments of Fig. 10S. Error bars indicate standard deviations of measurements.

Table 3S. Coagulants made by base-titration.

Name	Basicity	SO ₄ /Al	Cl/Al	Na/Al	Al content	Heating process	
	%	molar ratio	molar ratio	molar ratio	mol/L	Time h	Temperature °C
B65ns	65	0	3.00	1.95	0.1		
B65ns-heat	65	0	3.00	1.95	0.1	5.0	121
B79s0.10-1	79	0.10	2.80	2.38	0.04		
B79s0.10-2-heat	79	0.10	2.80	2.38	0.09	(5.0)	(121)
B80ns-1	80	0	3.00	2.40	0.05		
B80ns-2	80	0	3.00	2.40	0.1		
B80ns-2-heat	80	0	3.00	2.40	0.1	0.33	120
B82s0.11	82	0.11	2.79	2.45	0.1		
B82s0.11-heat	82	0.11	2.79	2.45	0.1	72	90~95
B88s0.10	88	0.10	2.80	2.64	0.05		

Preparation of coagulants by base-titration

The 10 poly-aluminum chlorides (PACls) were produced by base-titration. These PACls are designated by the following rules: the number after “B” represents “% basicity”, “s” indicates “sulfated”, “ns” indicates “non-sulfate”, “heat” indicates “heated”, the number after “s” represents “mole ratio of sulfate ion to aluminum: SO₄/Al”, and the number after the hyphen indicates serial number. AlCl₃·6H₂O, Al₂(SO₄)₃ · 14~18H₂O, and Na₂CO₃ were provided by FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan), and NaOH was by Kanto Chemical Co., Inc., (Tokyo, Japan).

B65ns was prepared as follows: an AlCl₃ solution (0.5 M as Al, 80 mL) in a 500 mL Erlenmeyer flask was titrated with NaOH (0.24 M, 320 mL) by means of a peristaltic pump at a rate of 4 mL/min. During the titration, a combined hot plate/magnetic stirrer was used to agitate the solution in the flask and maintain the temperature at 85–90°C. B80ns-1 was prepared with the same materials and procedure for B65ns, except that the concentrations of AlCl₃ solution and NaOH were 0.25 M as Al and 0.15 M. The same materials and procedure were used to prepare B80ns-2, except that the concentration of AlCl₃ solution was 0.3 M. B82s0.11 was prepared as follows: an Al solution (0.49 M as Al, SO₄/Al=0.11 in mole ratio, 80 mL) was prepared with AlCl₃ and Al₂(SO₄)₃ in a 500 mL Erlenmeyer flask and titrated with NaOH (0.3 M, 320 mL) as the same procedure described above.

B65ns-heat was prepared by heating B65ns at 121°C for 5 h with an autoclave (MLS-3781, PHC Holdings Corporation, Tokyo, Japan). B80ns-2-heat was prepared by heating B80ns-2 at 120°C for 20 min with the same autoclave. B80s0.05-heat was prepared by heating B82s0.11 at 90~95°C for 72 h with a combined hot plate/magnetic stirrer.

B79s0.10-1 was prepared by adding a Na₂CO₃ solution and an Al₂(SO₄)₃ solution into B65ns at ambient temperature until the basicity became 79% (calculation of the basicity is described in paragraph 2.2 of the main paper) and SO₄/Al became 0.10. B79s0.10-2-heat was prepared by adding a Na₂CO₃ solution and an Al₂(SO₄)₃ solution into B65ns-heat at ambient temperature. B88s0.10 was also prepared by adding a Na₂CO₃ solution and an Al₂(SO₄)₃ solution into B80ns-2 at ambient temperature.

Table 4S. The mixing conditions of coagulation in the jar-test (Figures 13S to 16S).

SPAC	Coagulant	Flash		Slow						Total
Median diameter μm	Dosage mg-Al/L	G_F s^{-1}	T_F s	G_{S1} s^{-1}	T_{S1} s	G_{S2} s^{-1}	T_{S2} s	G_{S3} s^{-1}	T_{S3} s	$G_T T_T$ dimensionless
1.0	0~1.5	190	60	19	600					22,800
1.0	0~1.5	200	60	20	600	15	600	10	1,200	45,000
1.1	1.5	200	120	20	600	15	600	10	1,200	57,000

Jar-tests using the coagulants made by base-titration

Filtered tap water was obtained by the method described in the main text of this paper (paragraph 2.3) except that its alkalinity was not adjusted. The water was supplemented with an SPAC slurry (median diameter is described in Table 4S) at concentration 10 mg/L to make raw water for the experiment consisting of coagulation-flocculation and sedimentation (jar test). Jar-tests were conducted in a 1-L rectangular beaker. After a predetermined volume of HCl or NaOH (0.1 N) was added to order to achieve the coagulation pH at 7.0, the coagulant (PACl) was injected into the beaker to a final concentration between 0 and 1.5 mg-Al/L (see also Table 4S). Then, the water was mixed rapidly and slowly. The mixing speed (G value) and times (T value) of the flash and slow mixing were varied depending on each experiment (see also Table 4S). The water was then left at rest for 1 h. A supernatant of 50 mL was sampled and determined for turbidity (2100Q portable turbidimeter; Hach Company, Loveland, CO, USA).

Figure 12S. Proportions of Al species in PACl coagulants made by base-titration.

Figure 13S. Turbidity removal of and zeta potential of carbon particles. Initial SPAC concentration was 10 mg/L. Alb type base-titration PACIs (B80ns-1, B80ns-2) and PACI-70 were used as coagulant with a dosage of 0 to 1.5 mg-Al/L. Coagulation pH was 7.0. Settling time was 60 min. Error bars of turbidity and zeta potential indicate standard deviations of three measurements and five measurements, respectively. Details of the mixing conditions are shown in Table 4S.

Figure 14S. Turbidity removal of and zeta potential of carbon particles. Initial SPAC concentration was 10 mg/L. Alb type base-titration PACs (B65ns, B80ns-1 and B80ns-2), PACI-50, and PACI-70 were used as coagulant with a dosage of 1.5 mg-Al/L. Coagulation pH was 7.0. Settling time was 60 min. Error bars of turbidity and zeta potential indicate standard deviations of three measurements and five measurements, respectively. Details of the mixing conditions are shown in Table 4S.

Figure 15S. Turbidity removal and zeta potential of carbon particles. Initial SPAC concentration was 10 mg/L. Base-titration PACIs that contained sulfate ion (B79s0.10-1, B82s0.11, B88s0.10), PACI-50, and PACI-70 were used as coagulant with a dosage of 0 to 1.5 mg-Al/L. Coagulation pH was 7.0. Settling time was 60 min. Error bars of turbidity and zeta potential indicate standard deviations of three measurements and five measurements, respectively. Details of the mixing conditions are shown in Table 4S.

Figure 16S. Turbidity removal and zeta potential of carbon particles. Initial SPAC concentration was 10 mg/L. Alc-type base-titration PACIs (B82s0.11-heat, B80ns-2-heat, B65ns-heat, and B79s0.10-2-heat), PACI-50, and PACI-70 were used as coagulant with a dosage of 0 to 1.5 mg-Al/L. Coagulation pH was 7.0. Settling time was 60 min. Error bars indicate standard deviations of measurements. Details of the mixing conditions are shown in Table 4S.

Figure 17S. Proportions of Al species in PACl coagulants made by base-titration, Al(OH)_3 -dissolution, and commercial product.

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Matsui, Y., Shirasaki, N., Yamaguchi, T., Kondo, K., Machida, K., Fukuura, T. and Matsushita, T. (2017) Characteristics and components of poly-aluminum chloride coagulants that enhance arsenate removal by coagulation: Detailed analysis of aluminum species. *Water Research* 118, 177-186.