

# Effects of three additives on the removal of perfluorooctane sulfonate (PFOS) by coagulation using ferric chloride or aluminum sulfate

Naoyuki Kishimoto and Masanori Kobayashi

## ABSTRACT

Perfluorooctanesulfonic acid and its salts (PFOS) are emerging contaminants with long half-lives in water and human bodies. Accordingly, PFOS removal from water streams is required for controlling the PFOS pollution. To provide a simple PFOS separation technology, effects of three additives, powdered activated carbon (PAC), gelatin, and cetyltrimethylammonium bromide (CTAB), on the PFOS removal by coagulation with ferric chloride or aluminum sulfate were investigated in this study. As a result, coagulation with PAC or CTAB addition was effective in the PFOS removal, though the conventional coagulation and coagulation with gelatin addition were ineffective. A PFOS removal efficiency of over 90% was observed for the CTAB dose of over 1.6  $\mu\text{M}$  (0.58 mg/L) and for the PAC dose of over 40 mg/L, and that of over 95% was achieved by the CTAB dose of over 2.4  $\mu\text{M}$  (0.87 mg/L), when the initial PFOS concentration was 1.84  $\mu\text{M}$ . The positive effect of CTAB would be caused by micelle formation, which was enhanced by both the association of hydrophobic tails and the electrostatic attraction of hydrophilic heads of PFOS and CTAB. Thus, a linear cationic surfactant of CTAB was concluded to be an effective additive for the PFOS removal by coagulation.

**Key words** | cetyltrimethylammonium bromide, enhanced coagulation, gelatin, hexadecyltrimethylammonium bromide, perfluorooctane sulfonate, powdered activated carbon

**Naoyuki Kishimoto** (corresponding author)  
Faculty of Science and Technology,  
Ryukoku University,  
1-5 Yokotani, Setaoe-cho,  
Otsu 520-2194,  
Japan  
E-mail: [naoyuki@rins.ryukoku.ac.jp](mailto:naoyuki@rins.ryukoku.ac.jp)

**Masanori Kobayashi**  
Graduate School of Science and Technology,  
Ryukoku University,  
1-5 Yokotani, Setaoe-cho,  
Otsu 520-2194,  
Japan

## INTRODUCTION

Perfluorinated compounds are emerging contaminants detected in blood samples of both wildlife and humans (Corsini *et al.* 2014), the air (Kongpran *et al.* 2014), and the water environment (Fujii *et al.* 2007). Among them perfluorooctanesulfonic acid and its salts (PFOS) have attracted much attention, because PFOS are extremely persistent and have environmental accumulation and bioaccumulation properties (Fujii *et al.* 2007). Furthermore, they bind to serum proteins of birds, fishes and humans, and cause non-selective toxicity to rats, rabbits, and rhesus and cynomolgus monkeys (Lehmler 2005). Immunotoxicity of PFOS in humans has been also suggested (Corsini *et al.* 2014). As a result, PFOS were added to Annex B of the Stockholm Convention on Persistent Organic Pollutants in 2009 for restricting its production and use. PFOS are human-made compounds with long half-lives in water ( $\geq 41$  years (Beach *et al.* 2006)) and in human-bodies (4.8–5.4 years (Olsen *et al.* 2007)). Accordingly, PFOS removal from

industrial and municipal wastewater is strongly required for preventing its environmental contamination. However, industrial wastewater treatment plants are conventionally composed of coagulation–sedimentation and biological processes like the activated sludge process, which are not effective in removing PFOS (Sinclair & Kannan 2006; Xiao *et al.* 2013).

Many researches have tried to remove PFOS from water streams using various destruction techniques. Although it is well-known that advanced oxidation processes at the ambient pressure and temperature, in which hydroxyl radicals ( $\cdot\text{OH}$ ) act as main oxidants, can successfully degrade various persistent compounds (Ikehata *et al.* 2008), they are not effective in removing PFOS (Schröder & Meesters 2005), because  $\cdot\text{OH}$  are less reactive with perhalogenated aliphatic compounds (von Sonntag 2008). Therefore, some researchers discussed the applicability of treatment technologies under high temperature and pressure for PFOS removal.

For instance, Hori *et al.* (2006) reported the rapid degradation of PFOS by subcritical water treatment with iron powders, and Liu *et al.* (2012) used heat-activated permanganate oxidation for PFOS degradation. The sonochemical degradation of PFOS was also reported by Cheng *et al.* (2008). These techniques can successfully decompose PFOS, but they require much energy for operation. Accordingly, PFOS in wastewater should be separated and concentrated prior to these treatments for energy-saving. Although nanofiltration, reverse osmosis, and activated carbon adsorption are effective separation technologies for PFOS (Ochoa-Herrera & Sierra-Alvarez 2008; Chen *et al.* 2012), these techniques require additional unit processes to the conventional wastewater treatment plants.

Enhanced coagulation may be an alternative technology for PFOS separation. Since coagulation is a very popular operation for wastewater treatment, PFOS separation by coagulation–flocculation is expected to be easily applicable to practical processes, especially in the case where a unit operation of coagulation has been already installed. Xiao *et al.* (2013) and Bao *et al.* (2014) studied the PFOS removal by coagulation. As a result, PFOS removal was caused by the adsorption onto fresh aluminum hydroxides surface (Xiao *et al.* 2013), but the PFOS removal efficiencies remained  $\leq 20\%$  (Xiao *et al.* 2013) and 32% (Bao *et al.* 2014) at the conventional pH condition. Although acidic condition enhanced the PFOS removal by coagulation, natural organic matter (NOM) did not enhance the PFOS removal (Xiao *et al.* 2013) or decreased the PFOS removal efficiency by the competitive adsorption (Bao *et al.* 2014). Accordingly, an enhanced coagulation will be required for effective application of coagulation to the PFOS removal.

In this study we focus on the addition of a PFOS removal function to a unit operation of coagulation. Widely used coagulants of ferric chloride ( $\text{FeCl}_3$ ) and aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ) were used for all experiments, and effects of three additives, namely, powdered activated carbon (PAC), gelatin, and cetyltrimethylammonium bromide (CTAB) on PFOS separation by coagulation were investigated. Activated carbon is an effective adsorbent for PFOS (Hansen *et al.* 2010), because PFOS have a hydrophobic perfluoroalkyl group. Accordingly, the simultaneous dosing of coagulant and PAC is expected to be effective in PFOS removal, similar to, for example, the successful removal of NOM (Szlachta & Adamski 2009). Gelatin is a natural protein polymer and has been used as a flocculation aid for water treatment (Suzuki & Maruyama 2000; Saranya *et al.* 2013). Since gelatin has a relatively high hydrophobic property of the four natural proteins, namely, casein, gelatin, hemoglobin, and albumin (Suzuki &

Maruyama 2000), it is also expected to effectuate PFOS removal. CTAB is a popular cationic surfactant, which easily associates with anionic surfactants like sodium lauryl sulfate and forms aggregates (Kishimoto & Kimura 2012). Accordingly, it is expected that CTAB-added coagulation would be effective in removing PFOS by coprecipitation of the CTAB-PFOS aggregates with hydroxide flocs.

## MATERIAL AND METHODS

### Chemicals used

A potassium salt of PFOS was purchased from Tokyo Chemical Industries (Japan), and a stock solution of 186  $\mu\text{M}$  was prepared by dissolution of the PFOS reagent into ultrapure water for coagulation tests. Another stock solution of 18.6 mM was prepared by dissolution of the PFOS reagent into methanol (high-performance liquid chromatography grade, Nacalai Tesque, Japan) as a standard for chemical analysis. The PAC was prepared by grinding particulate activated carbon (GW-HS2, Kuraray Chemical, Japan) with a mortar and a pestle. The effective particle size and the coefficient of uniformity of PAC measured with a laser diffraction particle size analyzer (SALD-300 V, Shimadzu, Japan) were 11.4  $\mu\text{m}$  and 2.1, respectively. Gelatin, CTAB,  $\text{Al}_2(\text{SO}_4)_3$ , and other chemicals except  $\text{FeCl}_3$  solution were analytical grade reagents purchased from Nacalai Tesque, Japan. The  $\text{FeCl}_3$  solution (ca. 38%) was obtained from Nacalai Tesque, Japan, and the exact concentration was checked by phenanthroline method (Rice *et al.* 2012).

### Jar tests

A series of coagulation tests was performed using a jar tester (WT-6P, Sugiyama-gen, Japan). The test procedure was as follows: 500 mL of 100-times diluted PFOS stock solution was poured into a 1-L glass beaker. Then, 1.0 M of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) solution was added into the beaker at the final concentration of 2.5 to 9.0 mM for the pH control and alkalinity addition. Finally, an adequate portion of coagulant solution (2.53 M  $\text{FeCl}_3$  solution or 1.01 M  $\text{Al}_2(\text{SO}_4)_3$  solution) was put into the beaker at the final concentration of 2.0 mM Fe or 2.0 mM Al, and a rapid mixing was started at the G-value of 200  $\text{s}^{-1}$ . After rapid mixing for 3 minutes, a slow mixing at the G-value of 46  $\text{s}^{-1}$  was applied for 30 minutes, and flocs were settled for 5 minutes. Delphos & Letterman (2012) reported that typical G-values

for rapid mixing and slow mixing (flocculation) were 150–300 and 10–60  $s^{-1}$ , respectively. Thus, the G-values used were in the range of typical values. The supernatant after settling was sampled and filtered using a membrane filter with 0.2  $\mu m$  pores. The PFOS concentration in the filtrate was then analyzed by liquid chromatography coupled with mass spectroscopy. In addition, zeta-potentials of the flocs were measured with a zeta-potential analyzer (ZEEMOM ZC-2000, Microtec, Japan). The pretreatment and analytical conditions of the zeta-potential analyzer were the same as those used in a previous study (Hamamoto *et al.* 2015).

When an additive was used, the additive was put into the beaker just before the coagulant addition at the dose of 4–55 mg/L for PAC, 0.2–2.4 mg/L for gelatin, and 0.4–9.6  $\mu M$  for CTAB. The  $Na_2CO_3$  dose was set at 7.0 mM for  $FeCl_3$  coagulation and 4.0 mM for  $Al_2(SO_4)_3$  coagulation. As a result, the mixture solution pH was kept in the range of 7.2–7.3 for  $FeCl_3$  coagulation and 6.8–6.9 for  $Al_2(SO_4)_3$  coagulation, which were in the range of pH for sweep coagulation (Amirtharajah & Mills 1982; Johnson & Amirtharajah 1983).

### Chemical analysis

The concentration of PFOS was determined using a liquid chromatography system (1100, Agilent Technologies Japan) coupled with a quadrupole mass spectrometer (G1956B, Agilent Technologies, Japan). Analytical conditions were as follows: column: Cosmosil 5C18-MS-II (4.6  $\times$  150 mm); mobile phase A: 10 mM ammonium acetate; mobile phase B: acetonitrile; flow rate: 0.25 mL/min, gradient program: mobile phase A 60%, B 40% from 0 to 10 min, A 10%, B 90% from 10 to 20 min, and A 60%, B

40% from 20 to 30 min; sample injection volume: 5  $\mu L$ ; oven temperature: 40  $^{\circ}C$ ; ionization: electro-spray; fragmentor voltage: 75 V from 0 to 7 min, 200 V from 7 to 30 min. The solution pH was measured with a pH meter (B-212, Horiba, Japan).

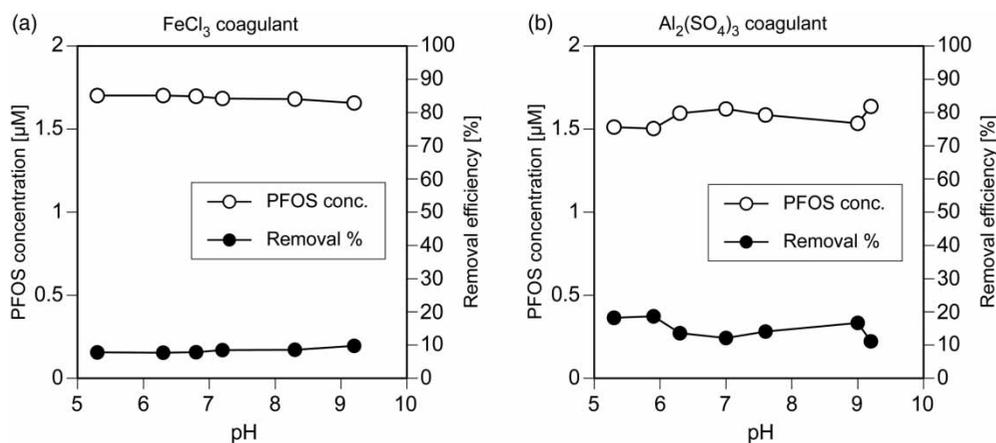
## RESULTS AND DISCUSSION

### PFOS removal by normal coagulation under different pH

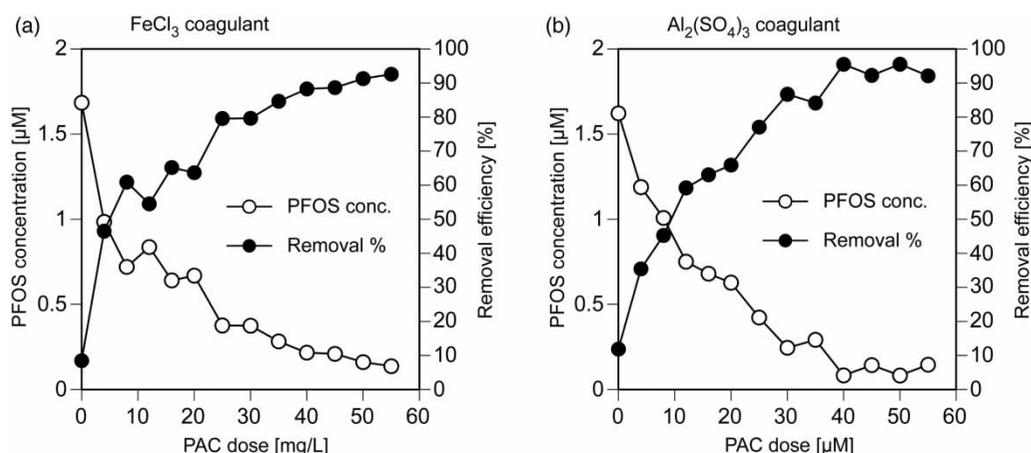
The observed PFOS concentrations in treated water and removal efficiencies are depicted in Figure 1. The initial PFOS concentration was in the range of 1.84–1.85  $\mu M$  due to the dilution effect of the coagulant and  $Na_2CO_3$  solution in the preparation step. Figure 1 clearly shows that the normal coagulation was ineffective in PFOS removal at all tested pHs, though the  $Al_2(SO_4)_3$  coagulant had slightly higher performance than the  $FeCl_3$  coagulant ( $p = 0.0009$  by two-sample *t*-test assuming unequal variances). The removal efficiency remained  $8.4 \pm 0.8\%$  (average  $\pm$  sample standard deviation) for the  $FeCl_3$  coagulation and  $15.0 \pm 2.8\%$  for the  $Al_2(SO_4)_3$  coagulation.

### PFOS removal by coagulation with PAC

The effect of simultaneous dosing of coagulant and PAC on PFOS removal was investigated under neutral pH. Figure 2 depicts PFOS concentrations after coagulation and removal efficiencies at various PAC doses. The PFOS removal efficiency increased with the increase in the PAC dose. Although the PFOS removal efficiency by  $Al_2(SO_4)_3$  coagulation at the PAC dose of over 40 mg/L ( $93.9 \pm 1.9\%$ ) seems



**Figure 1** | PFOS concentrations after coagulation and removal efficiencies by coagulation without any additive substance under different pH. The coagulant dose was 2.0 mM Fe (a) or 2.0 mM Al (b).



**Figure 2** | PFOS concentration after coagulation and removal efficiencies by coagulation with the addition of PAC at different doses. The initial concentration of PFOS was 1.84 μM. The coagulant dose was 2.0 mM Fe (a) or 2.0 mM Al (b).

to be higher than that by FeCl<sub>3</sub> coagulation (90.2 ± 2.1%) at the same PAC doses, the paired *t*-test with a significance level of 0.05 revealed that the difference in PFOS removal efficiencies between FeCl<sub>3</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> coagulation was not significant. Consequently, the coagulation with PAC addition was demonstrated to be effective in the PFOS removal. Bao *et al.* (2014) reported that the combination of coagulant and PAC enhanced the PFOS removal efficiency up to >90%, which accorded with our results.

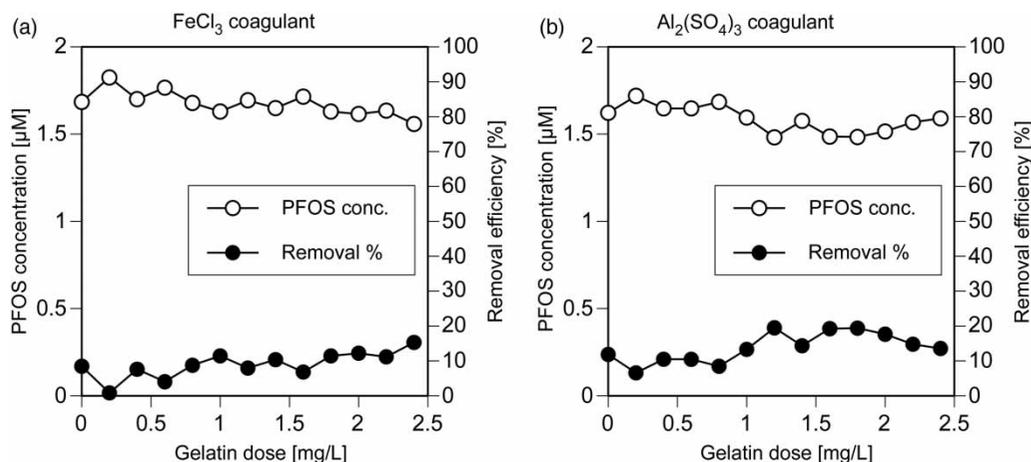
### PFOS removal by coagulation with gelatin

The simultaneous dosing of coagulant and gelatin is expected to enhance the PFOS removal due to its flocculation aid function and relatively hydrophobic property. Accordingly, the effect of gelatin addition on the PFOS

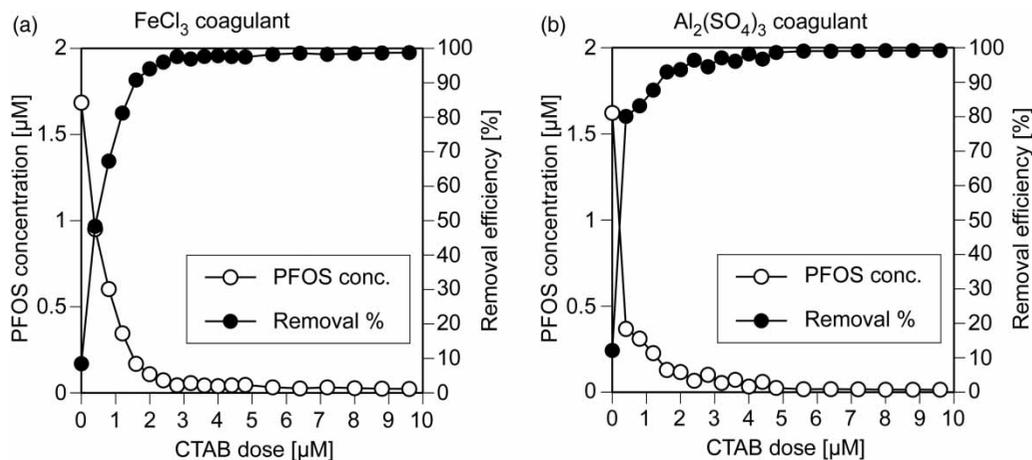
removal was studied. Figure 3 shows the PFOS concentrations after coagulation with the addition of gelatin at different doses. Figure 3 clearly shows that gelatin could not enhance the PFOS removal, probably due to its high solubility against water.

### PFOS removal by coagulation with CTAB

Figure 4 shows the PFOS concentrations after coagulation and removal efficiencies by coagulation with the CTAB addition. The PFOS concentration decreased with the increase in the CTAB dose, and finally the PFOS removal efficiency reached around 99% for both coagulants. When the CTAB was added into the PFOS-contaminated water, the mixture became slightly cloudy. This indicated that some colloidal particles like micelles were formed in the



**Figure 3** | PFOS concentration after coagulation and removal efficiencies by coagulation with the addition of gelatin at different doses. The initial concentration of PFOS was 1.84 μM. The coagulation dose was 2.0 mM Fe (a) or 2.0 mM Al (b).

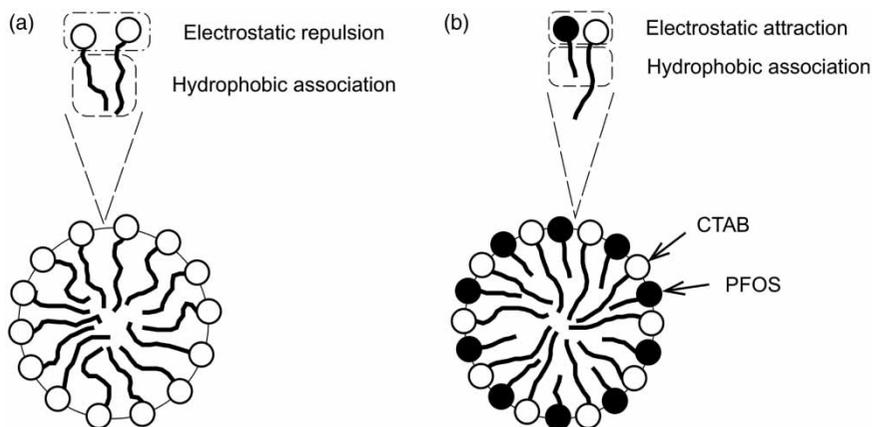


**Figure 4** | PFOS concentrations after coagulation and removal efficiencies by coagulation with the addition of CTAB at different doses. The initial concentration of PFOS was 1.84 μM. The coagulation dose was 2.0 mM Fe (a) or 2.0 mM Al (b).

mixture. CTAB is a quaternary ammonium cation with a hydrophobic linear alkyl group. Accordingly, the CTAB acts as a cationic surfactant, whereas the PFOS are an anionic surfactant with a linear fluorinated alkyl group. Surfactants usually form micelles if the surfactant concentration is over the critical micelle concentration (CMC). The CMCs of PFOS and CTAB were reported to be 8.1 mM at 17 °C (Takagi & Shukuro 2003) and 0.97 mM at 25 °C (Modaressi *et al.* 2007), respectively, which were much higher than the PFOS and CTAB concentration in this research. Accordingly, micelle formation by the single surfactant of PFOS or CTAB did not occur, and micelles containing both PFOS and CTAB were inferred to form in the mixture. In normal micelle formation, hydrophobic tails of surfactants are associated with each other as shown in Figure 5(a). However, the hydrophilic groups of PFOS and

CTAB are inversely charged. Therefore, hydrophilic groups of PFOS and CTAB will be also associated with each other as shown in Figure 5(b), which will enhance the association of PFOS with CTAB. The FeCl<sub>3</sub> or Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> coagulants then help the coagulation of micelles and remove them by coprecipitation. If this hypothesis is true, the molar dose of CTAB required for PFOS removal is inferred to be equal to or higher than the molar concentration of PFOS. Figure 4 demonstrates that the PFOS removal efficiency of over 95% was observed at the molar dose ratio of CTAB to PFOS of over 1.3, and supports the aforementioned hypothesis.

Israelachvili (2011) summarized that the shape of micelles depended on the structure of the surfactant. Since the PFOS used in this research have a linear hydrophobic tail, a cationic surfactant with a linear hydrophobic tail



**Figure 5** | Illustrations of (a) normal micelle structure and (b) proposed micelle structure formed by the association of PFOS and CTAB. The circles and tails depict the hydrophilic and hydrophobic groups, respectively.

like CTAB is thought to be comparable to PFOS for micelle formation.

In the comparison of  $\text{Al}_2(\text{SO}_4)_3$  coagulant with  $\text{FeCl}_3$  coagulant the simultaneous dosing of CTAB was more effective in the PFOS removal by  $\text{Al}_2(\text{SO}_4)_3$  coagulation than by  $\text{FeCl}_3$  coagulation, especially at the molar dose ratio of CTAB to PFOS of less than 1, where the micelles formed were expected to be negatively charged because of the lack of CTAB. The zeta-potentials of  $\text{FeCl}_3$  flocs at pH 7.2 and  $\text{Al}_2(\text{SO}_4)_3$  flocs at pH 6.8 were  $-27.0 \pm 5.4$  mV and  $0.9 \pm 4.8$  mV, respectively. Therefore, electrostatic repulsion between micelles and  $\text{FeCl}_3$  flocs was thought to inhibit the coprecipitation at the low CTAB dose, while  $\text{Al}_2(\text{SO}_4)_3$  flocs had no electrostatic repulsion toward micelles.

Since the molecular weight of CTAB is 364, the minimum dose required for over 90% PFOS removal was calculated to be 0.58 mg/L (1.6  $\mu\text{M}$ ) for CTAB (Figure 4), whereas that for PAC was 40 mg/L (Figure 2) in this study. The lower dose results in a smaller coagulation sludge production. Although the excess CTAB will remain in the treated water, the increase in chemical oxygen demand by the residual CTAB is not so high because the theoretical oxygen demand of CTAB is calculated to be 0.91 mg- $\text{O}_2/\mu\text{mol}$ . Furthermore, CTAB can be degraded by advanced oxidation processes (Hinkova *et al.* 2015), whereas PFOS cannot. Thus, a linear cationic surfactant of CTAB was concluded to be an effective additive in removing PFOS from water streams by coagulation.

## CONCLUSIONS

Effects of three additives, PAC, gelatin, and CTAB, on PFOS removal by coagulation with conventional  $\text{FeCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  coagulants at the dose of 2.0 mM Fe or 2.0 mM Al were studied, with the aim of providing a simple technology for PFOS separation from water streams. The obtained results are summarized as follows.

1. The coagulation with the addition of PAC was effective in PFOS removal. The PAC dose of over 40 mg/L resulted in a removal efficiency of over 90%. A significant difference in the removal efficiency between  $\text{FeCl}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  coagulation was not observed.
2. Gelatin had no enhancement effect on the PFOS removal by coagulation, probably due to its high solubility against water.
3. The coagulation with the addition of CTAB was the most effective of the three coagulants for PFOS removal. The PFOS removal efficiency of over 95% was observed for

the molar dose ratio of CTAB to PFOS of over 1.3, which was equal to the CTAB dose of only 2.4  $\mu\text{M}$  (0.87 mg/L) in this study. The effective removal of PFOS by CTAB addition would be caused by the formation of micelles of PFOS and CTAB, which was enhanced by both the association of the hydrophobic tails and the electrostatic attraction of hydrophilic heads of PFOS and CTAB. The micelles formed were then coprecipitated with the coagulants. Thus, a linear cationic surfactant of CTAB was concluded to be an effective additive in removing PFOS from water streams by coagulation.

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