

## (21) APPLICABILITY OF CATIONIC ORGANIC COAGULANTS TO REMOVE PERFLUORINATED COMPOUNDS

STMLD. SENEVIRATHNA<sup>1\*</sup>, Shuhei TANAKA<sup>2</sup>, Shigeo FUJII<sup>2</sup>, Chinagam KUNACHEVA<sup>2</sup>, Hidenori HARADA<sup>2</sup> and Tharaka ARIYADASA<sup>2</sup>

<sup>1</sup>Research Center for Environmental Quality Management, Kyoto University.  
(1-2 Yumihama, Otsu, Shiga, 520-0811, Japan)

<sup>2</sup>Graduate School of Global Environmental Studies, Kyoto University.  
(Yoshida-honmachi, Sakyo-ku, Kyoto, 606-8501, Japan)

\*E-mail: lalantha.s@kt3.ecs.kyoto-u.ac.jp

Perfluorooctated compounds (PFCs) are recently identified tracer level anionic organic pollutant in water environment. We examined the possibility of PFCs removal by a combined coagulation/filtration process. Three conventional inorganic coagulants and six cationic organic coagulants were tested by a series of jar tests. It was determined that relatively high coagulant dose of 200  $\mu\text{L/L}$  of organic coagulant is needed for the optimum removal of PFCs at 10  $\mu\text{g/L}$ . The jar test results with perfluorooctanoic acid showed that polymer type cationic organic coagulants were 40 % better than conventional inorganic coagulants. Jar test with mixture of PFCs showed that long chain PFCs can be easily coagulated than short chain PFCs. The optimum molecular weight of cationic organic polymer for PFCs removal was identified as 100,000 Da. Jar test results with PFCs spiked wastewater showed that the other organic matters in the water encourages PFCs coagulation by organic coagulants for long chain and medium chain PFCs. The results of the experiment suggested the possibility of PFCs coagulation by organic coagulants, but more studies to be carried out with actual PFCs related wastewaters to concrete the idea.

**Key Words :** cationic coagulants, coagulation, jar test, PFCs

### 1. INTRODUCTION

Perfluorinated compounds (PFCs) including perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are anthropogenic organic pollutants, which have been recognized as emerging problems in water environment. PFOS was categorized as a persistent organic pollutant (POPs) in the 4<sup>th</sup> meeting of the conference of the parties to the Stockholm Convention in May 2009<sup>1)</sup>. Many researchers<sup>2-6)</sup> have identified wastewater discharged by the industries as the main PFCs polluter of water environment. Quinones and Snyder<sup>7)</sup> identified the adverse impacts from treated wastewater on PFC concentrations at downstream drinking water treatment plants in United State. Osaka tap water is also highly affected by treated industrial wastewaters<sup>8)</sup>. According to the PFCs monitoring researchers<sup>2,4)</sup>,

conventional water and wastewater treatment facilities can not remove PFCs. Several techniques have been suggested for PFCs treatment such as adsorption<sup>9)</sup>, direct UV-visible light irradiation<sup>10)</sup>, photochemical decomposition with persulfate ions ( $\text{S}_2\text{O}_8^{2-}$ )<sup>11)</sup>, photodegradation with vacuum ultraviolet (VUV) light<sup>12)</sup>, sonochemical degradations<sup>13)</sup> and reverse osmosis<sup>14)</sup>.

Some researchers<sup>15)</sup> have showed the possibility of POPs removal by inorganic coagulants, but previous studies on PFCs coagulation are limited. Water-soluble cationic polymers are mainly used for treatment of wastewater and more complete dehydration. Positively charged macromolecules of organic coagulants interact with negatively charged pollutant particles in water, causing their destabilization and rapid flocculation to form coarser aggregates<sup>16)</sup>.

The primary goal of this study was to determine the

degree of anionic PFCs coagulation by polymer type cationic coagulants. In addition, we determined the optimum dose of organic coagulant and compared the PFCs coagulation results by organic coagulants and conventional inorganic coagulants.

## 2. MATERIALS AND METHOD

All cationic organic coagulants (FL2250, FL2749, FL3050, FL4440, FL4620, FL4820) were received from *SNS, Inc* (Japanese agent). Inorganic coagulants (iron(III) chloride, sodium aluminate and Aluminium sulfate) were purchased from *Wako Chemicals* (Japan) as described in Tables 1 and 2.

**Table 1** Inorganic coagulants tested in the experiment

Coagulant	Molecular Wt (Da)	Molecular structure
Ferric Chloride	162.20	$\text{Fe}(\text{Cl})_3$
Sodium Aluminate	163.936	$\text{Na}_2\text{Al}_2\text{O}_4$
Aluminium Sulfate	342.15	$\text{Al}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ ( $n=14-18$ )

**Table 2** Organic coagulants tested in the experiment

Name	Viscosity	Molecular Wt (Da)
FL2250	25-35	10,000
FL2749	200-400	120,000
FL3050	1000- 4000	500,000
FL4440	1000- 3000	300,000
FL4620	600- 1000	1,400,000
FL4820	1000- 3000	1,800,000

### (1) Jar test

Coagulation and flocculation experiments were performed in a jar test apparatus (JMD6E-Osaka Miyamoto Riken Ind, Japan). Each sample (1.0 L) was rapidly mixed at 80 rpm for 3 min, and then slowly mixed at 25 rpm for 30 min and settled (0 rpm) for 60 min. Glass beakers were used in the jar test and PP (polypropylene) lab wares used in all the other processes. In the beginning of rapid mixing, inorganic and organic coagulants were added using a mechanism provided with the jar test apparatus. In this mechanism, coagulant tubes mounted in a horizontal lever along the jars were able to be simultaneously tilted to coagulants to the jars placed in the bottom plate. Two duplicate jars were used for each condition and ensured that the deviation is within 5%. At the end of each jar test, the samples were filtered (GF/F; pore size: 0.45 $\mu\text{m}$ ) and analyzed for re-

maining PFCs in the filtrate.

Four series of jar tests were carried out in this experiment. The aim of the first jar test was to determine the minimum effective organic coagulant dose to remove PFCs. PFOA and FL2250 were selected as a PFC and a coagulant of FL2250 in the jar tests. PFOA stock solution was added to pure water to yield the initial PFOA concentration of 10  $\mu\text{g/L}$ , while five doses of coagulants ranging from 0  $\mu\text{L/L}$  to 1000  $\mu\text{L/L}$  (0 dose for the control) were added to five jars with a stock solution.

The second was designed to study the PFOA coagulation efficiencies by organic and inorganic coagulants. Three inorganic coagulants and six organic coagulants were tested with PFOA by a series of jar tests to determine the degree of coagulation. The applied dose was what gave the optimum coagulation in the first experiment. The initial concentration of PFOA solution was 10  $\mu\text{g/L}$ .

The third was carried out to investigate the PFCs coagulation as a mixture. A mixture of six PFCs, which consisted of long chain, medium chain, and short chain PFCs, and also different functional groups of acid and sulfonate was spiked into pure water to prepare an initial sample solution for the jar test. Studied PFCs were perfluorohexanesulfonate (PFHS), perfluorooctanesulfonate (PFOS), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA) and perfluorodecanoic acid (PFDA).

The forth was designed to observe the effects of coexisting organic matters on PFCs coagulation. Wastewater collected at a discharge point of a WWTP was spiked with the same mixture of PFCs stock solution applied in the previous experiment to prepare the initial solution for the jar test.

### (2) Sample pre-treatment

When pure water samples were used for the jar test, filterates were directly analyzed with liquid chromatography tandem mass spectrometry (LC/MS/MS) after dilution with acetonitrile (ACN) to ensure 40% ACN content in the analyzing samples. In case of the other jar tests, other than PFCs were removed by the following process. Fifty mL of filtrate after the jar test was sent through a Precip-C Agri cartridge by using the concentrator (flow rate 5mL/min). The cartridge was air-dried for 1 h using a vacuum manifold, and then it was eluted with organic solvents (methanol 3 mL + ACN 3 mL). Eluted solution was completely dried by a flow of nitrogen gas at 60°C and the dried tube was reconstituted with 40% ACN solution. Final solution was used for analysis by LC/MS/MS.

### (3) Analysis of PFCs

Separation of PFCs was performed with Agilent 1200SL high-performance liquid chromatography (HPLC). 10  $\mu$ L of prepared sample was injected to a 2.1x100 mm (5  $\mu$ m) Agilent Eclipse XDB-C18 column. Mobile phase consisted of (A) 5mM ammonium acetate in ultrapure water (LC/MS grade) and (B) 100% ACN (LC/MS grade). At a flow rate of 0.25 mL/min, the separation process started with an initial condition of 30% (B), increased to 50% (B) at 16.5 min, then to 70% (B) at 16.6, held at 70% (B) for 3.4 min, went up to 90% (B) at 21 min, kept at 90% (B) for 1 min, and then ramped down to 30% (B). The total running time was 34 min for each sample. For quantitative determination, the HPLC was interfaced with an Agilent 6400 Triple Quadrupole (Agilent, Japan) mass spectrometer (MS/MS). Mass spectrometer was operated with the electrospray ionization (ESI) negative mode. Analyte ions were monitored using multiple reaction monitoring (MRM) mode. Table 3 shows the analytical parameters.

**Table 3** Conditions of HPLC/MS/MS analysis

PFCs	Parent ion (m/z)	Daughter ion (m/z)	Retention time (min)	LOQ (ng/L)
PFHxA	313	269	3.2	0.4
PFHpA	363	319	5.4	0.3
PFOA	413	369	8.1	0.5
PFDA	513	469	13.8	0.2
PFHS	399	80	8.9	0.4
PFOS	499	80	15	0.2

## 3. RESULTS AND DISCUSSION

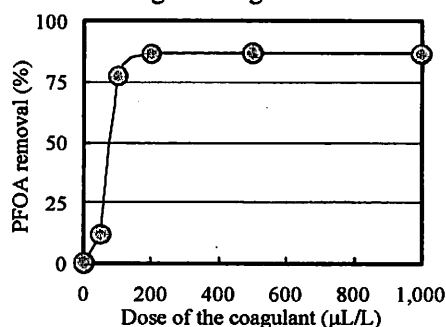
### (1) Optimum dosage of organic coagulants

Figure 1 shows the PFOA removal percentage by coagulation with different organic coagulant doses. 200  $\mu$ L/L was the minimum dose of coagulant among optimum results. Even though this concentration may essentially vary according to the characteristics of target wastewaters and applied organic coagulants, it was always used in this comparative study.

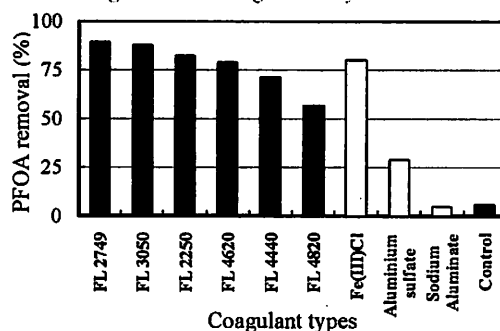
### (2) PFOA coagulation by organic and inorganic coagulants

Figure 2 shows the PFOA removal percentage by each organic and inorganic coagulant. The coagulant dosage of this experiment was 200  $\mu$ L/L for liquid coagulant and 200 mg/L for solid coagulants. The average efficiency of coagulation for organic coagulants was 78%, which is 40% higher than that of inorganic coagulants. Among the organic polymers,

FL2749, FL3050 and FL2250 showed more than 80% coagulation efficiencies. In the experiment with inorganic coagulants, high dose of 200 mg/L was applied, which was comparable with the dosage of organic coagulants. It was noticed that Ferric Chloride showed almost 80% PFOA removal, which dominated all inorganic coagulants.



**Fig. 1** PFOA coagulation by FL2250



**Fig. 2** PFOA coagulation by different coagulants

### (3) Coagulation of a PFCs mixture

Coagulation of PFCs as a mixture was studied by spiking a mixture of PFCs in to pure water and treated wastewater. Figure 3 shows the percentage removal of each PFCs by various organic and inorganic coagulants in deionized water and wastewater. There was a reduction of PFCs in the control experiment, may be due to the interference of glass beakers in the jar test. The results of the experiment with pure water confirmed the previous results showing better performances from organic coagulants than conventional inorganic coagulants. It was noticed for both organic and inorganic coagulants that there is no single coagulant to get the maximum performance for all PFCs. In the first glance it can be concluded that the PFCs coagulation by organic coagulants is double than that of inorganic coagulants for PFCs spiked to deionized water. Among the tested coagulants with deionized water, FL 2749 was identified as the best organic coagulant with 86% average overall PFCs removal. For the inorganic coagulants, aluminum sulfate was the best candidate in overall PFCs removal of 54% followed by ferric chloride with 36% removal.

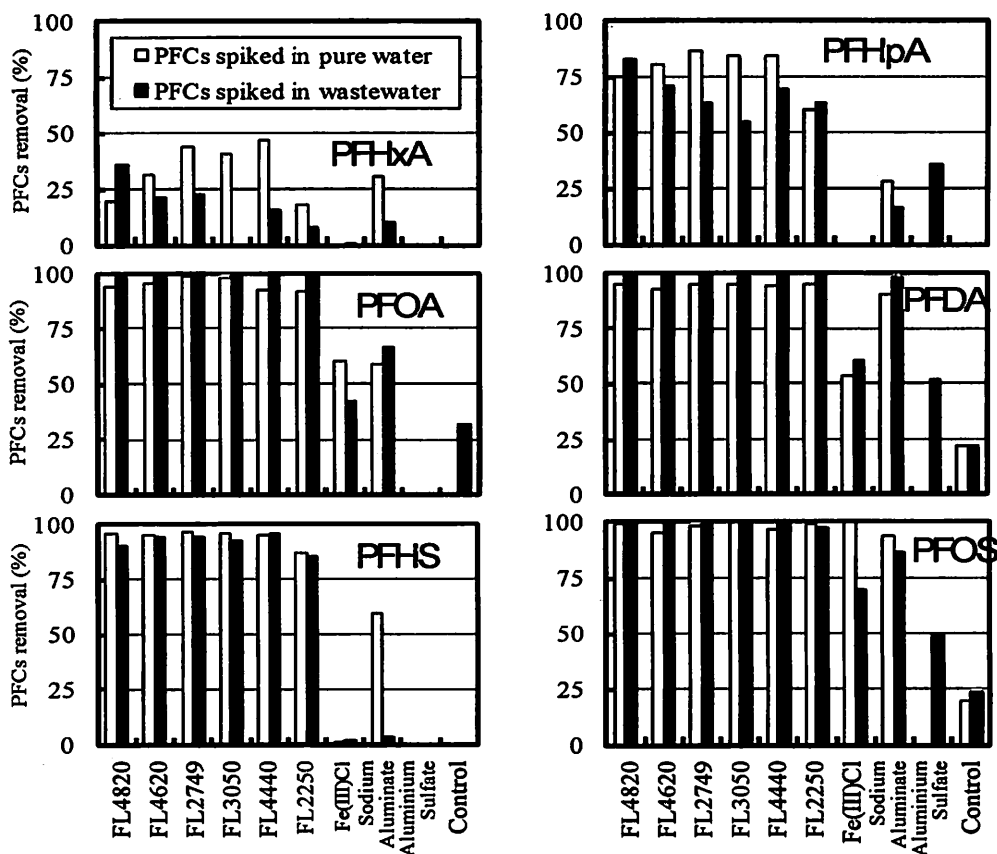


Fig. 3 PFCs coagulation by various organic and inorganic coagulant

Figure 3 also shows the results of the jar test with PFCs spiked wastewater. Initial TOC was 10.5 mg/L and pH was 7.0 in the effluent wastewater used in this experiment. It was clearly observed in most of the organic coagulants that the pure water spiked with PFCs gave better removal percentage than wastewater spiked with PFCs did in case of short chain PFCs (PFHxA, PFHpA and PFHS). In the case of medium chain and long chain PFCs, it was observed that a slight improvement of PFCs removal with the presence of other organics. These observations can be explained with the charges in molecules. Short chain PFCs with less charge (negative) cannot compete with other organics to attach with coagulant polymers, so their removal efficiencies were affected adversely. Long chain and medium chain PFCs (PFOS, PFOA and PFDA) with higher molecular charges can compete with other organic matter and attach with the coagulant polymer. Long-chain polymers adsorbed on particles can have loops and tails extending some way into the solution<sup>17)</sup> and this seems to accelerate the process of coagulation for long chain PFCs.

Figure 4 shows the removal of perfluorocarboxylates (PFCAs) (with different chain lengths) by organic and inorganic coagulants. The removal percentages are averages of those in organic (6 coagulants) and inorganic (2 coagulants, sodium aluminate was not considered because its removal is almost zero) coagulants. In this experiment, PFCAs were

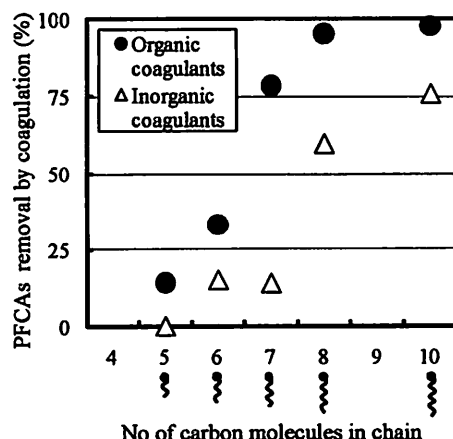


Fig. 4 Different PFCAs removal by coagulation

spiked into pure water and it can be assumed that the competition to attach with sites in the coagulant chain is only among PFCAs molecules. In this attachment process, long chain PFCAs seems to be more effective than short chain PFCAs.

Longer carbon chain and higher number of fluorine

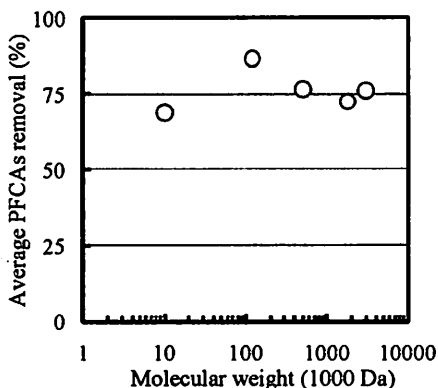


Fig. 5 PFCAs coagulation by organic coagulants with different molecular weights

attached ultimately may increase the negative charge in the molecule, which can beat weakly charged short chain PFCAs at the competition to attach with cationic coagulants. This comparative study clearly showed that the organic coagulants are much more effective than conventional inorganic coagulants to remove PFCAs. In PFOA, some organic coagulants showed more than 98% removal efficiencies. Figure 5 shows the average PFCAs removal for different molecular weights of organic coagulants.

Cationic organic coagulant with molecular weight around 100,000 Da seems to be ideal to remove PFCAs with all chain lengths by coagulation /filtration process.

#### (4) Possible removal mechanism of cationic organic coagulants

Once a polymeric coagulant was added to a solution, the first expected process is mixing. In the mixing process the polymer becomes distributed evenly throughout the solution. The mixing was achieved in this experiment using rapid mixing at 80 rpm for 3 min. Comparatively low mixing speed was

selected as there is a possibility to break some long chain polymers with a high degree of turbulence<sup>18</sup>. Since concentrated polymer solutions are quite viscous, mixing usually becomes easier, and flocculation more effective, with more dilute dosing solutions<sup>19</sup>. Mixing effects are generally more important for more concentrated suspensions. Figure 6(a) schematically shows the mixing process.

The second possible process is the attachment of positively charged active sites of the polymers with the anionic PFCs in the solution. The rate of attachment mainly depends on their concentrations and it follows the Smoluchowski kinetics<sup>20</sup>. This process is schematically shown in Fig. 6(b). According to the literature data, the dose of optimum polymeric coagulant and adsorption rate are proportional to particle concentration<sup>21</sup>. The PFCs concentration was 10 µg/L in the experiment. We also noticed that the optimum dose of polymeric coagulant for the removal of PFCs at tracer level concentration was comparatively higher (200 µL/L).

The third identified process is rearrangement of adsorbed chains (Fig. 6(c)). The polymer chain reaches its equilibrium in adsorbed configuration with a characteristic distribution of loops, trains and tails. According to the literature data, high MW polymers take several seconds to reach equilibrium concentration<sup>22</sup>, when the adsorbed polymers have more extended configuration and form bridging contacts. The coagulant dose applied in this experiment was 200 µL/L, TOC level in wastewater was less than 10 mg/L, and PFCs concentration was 10 µg/L, so that there was an unbalance concentrations of opposite charges in the solution and total charge neutralization in polymer coagulants could not be achieved. There is also a possibility for charge pockets or patch mechanism; it occurs when high charge density cationic polymers adsorb negative surfaces with a fairly low density of charged sites<sup>23, 24</sup>. There is a possibility for some polymers to remain without attaching to a surface or a PFCs.

The final expected process is flocculation, mainly by bridging mechanism (Fig. 6(d)). Flocculation is a second order rate process, so that the rate depends on the square of the particle concentration. The

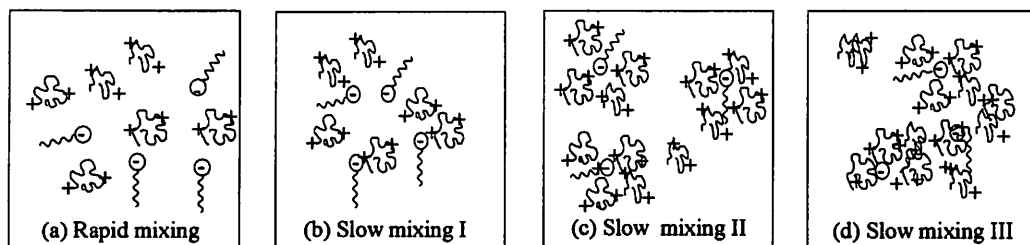


Fig. 6

Schematic diagram to explain possible PFCs coagulation mechanism.

mechanism of charge-neutralisation/precipitation has been proposed for the removal of humic substances by cationic polymers. In many cases<sup>24, 25, 26</sup>, it has been shown that molecular weight (MW) has little or no effect, indicating that polymer bridging is not a significant mechanism. The results of this experiment suggests that the polymer bridging is important than charge neutralization for PFCs coagulation and the optimum MW might be around 100,000 Da.

#### 4. CONCLUSION

We examined the possibility of PFCs removal by combined coagulation/filtration process. The experiment with pure water spiked with PFCs suggested that comparatively higher coagulant dose is required to get a good PFCs removal efficiency by organic coagulants. The results of the experiment with actual wastewater spiked with PFCs indicated that occurrence of other organic matters discourages coagulation of short chain PFCs, but it encourages the coagulation of long chain PFCs. It also showed that the efficiency of PFCs coagulation by organic coagulants is almost double than that of inorganic coagulants. Among the organic coagulants tested, FL 2749 was identified as the best candidate to remove any PFCs. Organic coagulation followed by microfiltration seems to be an effective combination to remove PFCs, but more studies to be done with different PFCs related wastewater to confirm this.

#### REFERENCES

- 1) Earth Negotiations Bulletin, Published by the International Institute for Sustainable Development (IISD), Vol. 15, No. 174, 2009.
- 2) Fujii S., Polprasert C., Tanaka S., Lien P.H. and Qiu Y.: New POPs in the water environment: distribution, bioaccumulation and treatment of perfluorinated compounds- a review paper, *Water Sup. Res. and Technol. - AQUA*, Vol. 56, No. 5, pp. 313-326, 2007.
- 3) Jin Y.E., Liu W., Sato I., Nakayama S.F., Sasaki K., Saito N. and Tsuda S.: PFOS and PFOA in environmental and tap water in China, *Chemosphere*, Vol. 77, pp. 605-611, 2009.
- 4) Lien N.P.H., Fujii S., Tanaka S., Nozoe M. and Tanaka H.: Contamination of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in surface water of the Yodo river basin (Japan), *Desalination*, Vol. 226, pp. 338-347, 2008.
- 5) Quinete N., Wub Q., Zhang T., Yun H.S., Moreira I. and Kannan K.: Specific profiles of perfluorinated compounds in surface and drinking waters and accumulation in mussels, fish, and dolphins from southeastern Brazil, *Chemosphere*, Vol. 77, pp. 863-869, 2009.
- 6) Yu J., Hu J., Tanaka S. and Fujii S.: Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in sewage treatment plants, *Water Res.*, Vol. 43, pp. 2399 - 2408, 2009.
- 7) Quinones O. and Snyder S.A.: Occurrence of perfluoroalkyl carboxylates and sulfonates in drinking water utilities and related waters from the United States, *Environ. Sci. Technol.*, Vol. 43, pp. 9089-9095, 2009.
- 8) Saito N., Harada K., Inoue K., Sasaki K., Yoshinaga T. and Koizumi A.: Perfluorooctanoate and perfluorooctane sulfonate concentrations in surface water in Japan, *J. Occup. Health*, Vol. 46, pp. 49-59, 2004.
- 9) Qiang Y., Ruiqi Z., Shubo D., Jun H. and Gang Y.: Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated carbons and resin: kinetic and isotherm study, *Water Res.*, Vol. 43, pp. 1150-1158, 2009.
- 10) Hori H., Hayakawa E. and Einaga H.: Decomposition of environmentally persistent perfluorooctanoic acid in water by photochemical approaches, *Environ. Sci. Technol.*, Vol. 38, pp. 6118-6124, 2004.
- 11) Hori H., Yamamoto A. and Hayakawa E.: Efficient decomposition of environmentally persistent perfluorocarboxylic acids by use of persulfate as a photochemical oxidant, *Environ. Sci. Technol.*, Vol. 39, No. 7, pp. 2383-2388, 2005.
- 12) Jing C., Peng Z. and Jian L.: Photodegradation of perfluorooctanoic acid by 185 nm vacuum ultraviolet light, *J. Env. Sci.*, Vol. 19, No. 4, pp. 387-390, 2007.
- 13) Moriwaki H., Takagi Y., Tanaka M., Tsuruho K., Okitsu K. and Maeda Y.: Sonochemical decomposition of perfluorooctane sulfonate and perfluorooctanoic acid, *Environ. Sci. Technol.*, Vol. 39, No. 9, pp. 3388-3392, 2005.
- 14) Tang C.Y., Fu Q.S., Robertson A.P., Criddle C.S. and Leckie J.O.: Use of reverse osmosis membranes to remove perfluorooctane sulfonate (PFOS) from semiconductor wastewater, *Environ. Sci. Technol.*, Vol. 40, pp. 7342-7349, 2006.
- 15) Bolto B. and Gergory J.: Organic polyelectrolytes in water treatment, *Water Res.*, Vol. 41, pp. 2301-2324, 2007.
- 16) Kurenkov V. F., Gogolashvili E. L., Molgacheva I. V. and Gaisina A. I.: Cationic polymers as organic coagulants in water treatment at heat and electric power plants, *Russian J. App. Chem.*, Vol. 76, No. 12, pp. 1951-1954, 2003.
- 17) Ruehrwein R.A. and Ward D.W.: Mechanism of clay aggregation by polyelectrolytes, *Soil Sci.*, Vol. 73, No. 6, pp. 485-492, 1952.
- 18) Sikora M.D. and Stratton R.A.: The shear stability of flocculated colloids, *Tappi.*, Vol. 64, No. 11, pp. 97-101, 1981.
- 19) Gregory J. and Li G.B.: Effects of dosing and mixing conditions on polymer flocculation of concentrated suspensions, *Chem. Eng. Commun.*, Vol. 108, pp. 3-21, 1991.
- 20) Gregory J.: Polymer adsorption and flocculation in sheared suspensions, *Colloids Surf.*, Vol. 31, pp. 231-253, 1988.
- 21) Bolto B., Dixon D., Eldridge R. and King S.: Cationic polymer and clay or metal oxide combinations for natural organic matter removal, *Water Res.*, Vol. 35, No. 11, pp. 2669-2676, 2001.
- 22) Pelssers E.G.M., Stuart M.A.C. and Fleer G.J.: Kinetics of bridging flocculation—role of relaxations in the polymer layer, *J. Chem. Soc.—Faraday Trans.*, Vol. 86, No. 9, pp. 1355-1361, 1990.
- 23) Kasper D.R.: Theoretical and experimental investigation of the flocculation of charged particles in aqueous solution by polyelectrolytes of opposite charge, California Institute of Technology, Pasadena, 1971.

- 24) Gregory J.: Rates of flocculation of latex particles by cationic polymers, *J. Colloid Interface Sci.*, Vol. 42, No. 2, pp. 448-456, 1973.
- 25) Glaser H.T. and Edzwald J.K.: Coagulation and direct filtration of humic substances with polyethylenimine, *Environ. Sci. Technol.*, Vol. 13, No. 3, pp. 299-305, 1979.
- 26) Kam S.K. and Gregory J.: Charge determination of synthetic cationic polyelectrolytes by colloid titration, *Colloids Surf. A-Physicochem. Eng. Aspects.*, Vol. 159, No. 1, pp. 165-179, 1999.