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Removal of short- and long-chain perfluorinated compounds from surface water by coagulation

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Abstract. Per- and poly-fluorinated compounds (PFCs) are persistently found during drinking water treatment processes, which can also be found in tap water. However, the mechanisms for removing PFCs during drinking water treatment processes have not been fully understood. In this study, we investigated the effect of coagulation on the removal of short- and long-chain PFCs. The PFCs mixture (C5–C10) resulted in a lower removal efficacy via coagulation treatment, and the average removals of selected PFCs were found to be below 5%. Only long-chain perfluorodecanoic acid (PFDA) (C10) and perfluorooctanesulfonic acid (PFOS) were significantly removed via coagulation. The removals of suspended particles and bacterial cells via coagulation were correlated with the reduction of PFDA and PFOS. However, higher turbidity, humic substances, and biopolymers in the source water were found to significantly reduce the removal efficiency of PFDA and PFOS, resulting in insignificant changes between the PFC species. We concluded that coagulation was not effective in removing selected PFCs, hence, a multiple-barrier treatment strategy is needed for PFC removal.

Keywords: chain length; coagulation; perfluorinated compounds

1. Introduction

Per- and poly-fluorinated compounds (PFCs) contaminants are widely found in surface water, groundwater, industrial wastewater, landfill leachate, and drinking water (Son *et al*. 2013, Pramanik 2015, Kim and Zoh 2016, Kim *et al*. 2020, 2021, Pierpaoli *et al*. 2021) and have been known to cause chronic and acute toxicity to humans. Recent studies have also reported PFCs in drinking water from source to tap (Jin *et al*. 2009, Li *et al*. 2019, Kim *et al*. 2020). PFCs are aliphatic carbon compounds with carbon-fluorine bonds, where hydrogen atoms are switched with fluorine. Due to their strong carbon-fluorine bonds, they often exhibit high thermal and chemical stabilities (Key *et al*. 1997, Bao *et al*. 2014), making them persistent not only in aquatic environments but also in drinking water treatment processes. Due to their high lipophilicity, PFCs can easily bio-accumulate in animals, including humans. PFCs are manufactured chemicals used in numerous industries to produce alkaline cleaners, paints, non-stick cookware coatings, textiles, soaps, shampoos, floor polishes, denture cleaners, fume suppressants, firefighting foams, semiconductors, packaging, and others (Xiao *et al*. 2013, Rahman *et al*. 2014, Pramanik *et al*. 2015).

Kunacheva *et al*. (2012) summarized the global distribution of PFCs and found significantly higher levels of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in industrialized areas. In Korea, one of the most industrialized countries, 2–19 and 1–89 ng L^{-1} of perfluorinated carboxylic and sulfonic acids (PFCAs and PFSAs) were detected in stream water, respectively (Rostkowski *et al*. 2006). However, there are no regulations on the concentration of PFOAs and PFOSs in Korea. PFCs in treated water have ranged below health advisory levels, but waterworks have recently started monitoring them to ensure safe water quality (Table 1). Due to health concerns, global industries have replaced long-chain PFCs with short-chain species, having relatively lower bioaccumulation potentials (Renner 2006, Ateia *et al*. 2019, Kim *et al*. 2021). Generally, long-chain PFCs have shown higher toxicity than short-chain PFCs (Gao *et al*. 2019), but a previous study reported higher toxicity for short-chain PFCs (Ateia *et al*. 2019), and mixture toxicity remains largely unknown (Brendel *et al*. 2018).

Coagulation treatment process possibly mitigates PFC levels for the following granular activated carbon filters, often used in advanced drinking water treatment processes. A recent study also confirmed the distribution of short- and long-chain PFCs in drinking water sources, possibly

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Table 1 Physicochemical properties of selected perfluorinated compounds

Compounds[1]	Formula	MW (g/mol)	Log K_{ow}[2]	Solubility (mg/L)	US EPA advisory (ng/L)	Guidance level in Korea (ng/L)	Removal via coagulation (%)	References
PFPeA	$C_5HF_9O_2$	264.1	2.81	196.5			n.a.[3]	
PFHxA	$C_6HF_{11}O_2$	314.1	3.48	27.12				
PFHpA	$C_7HF_{13}O_2$	364.1	4.14	3.65				
PFNA	$C_9HF_{17}O_2$	464.1	5.48	0.06				
PFDA	$C_{10}HF_{19}O_2$	514.1	6.15	0.008				
PFBS	$C_4F_9O_3S$	300.1	1.82	344				
PFHxS	$C_6HF_{13}O_3S$	400.1	3.16	6.174		480		
PFOS	$C_8HF_{17}O_3S$	500.1	4.49	0.104	70 (sum)	70 (sum)	35–54	Bao *et al.* 2014, Pramanik *et al.* 2015
PFOA	$C_8HF_{15}O_2$	414.1	4.81	0.481			24–27	

[1] perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), and perfluorooctanesulfonic acid (PFOS).

[2] Log K_{ow} and water solubility were calculated by EPI Suite software.

[3] n.a., non-applicable.

Table 2 Surface water collected from drinking water treatment plants (DWTP) A and B. Coagulation, flocculation, and sedimentation processes were carried out to remove perfluorinated compounds (PFCs)

Raw water	Water quality	Coagulant type	Treatment processes	PFCs
DWTP A	3.0 NTU, Turbidity 3.6 mg L^{-1}, DOC 2.3 L mg^{-1} m^{-1}, SUVA 1.9 ×10^6 cell mL^{-1}, TCC	Each 10 mg L^{-1}, polyaluminum chloride, polyaluminum chloride sulfates, or polyaluminum chloride ferric	Coagulation/flocculation: 240 rpm (rapid mixing) for 1 min followed by 40 rpm (1 min)-30 rpm (1 min)-20 rpm (1 min) (slow mixing), and sedimentation:20 min.	Each 100 ng L^{-1} the final concentration of carboxylic (C5–C10) and sulfonic PFCs (C4, C6, C8)
DWTP B	3.7 NTU, Turbidity 2.3 mg L^{-1}, DOC 2.0 L mg^{-1} m^{-1}, SUVA 5.2 ×10^6 cell mL^{-1}, TCC	Each 10 mg L^{-1}, aluminum sulfate (alum), polyaluminum chloride sulfates, high polyaluminum chloride sulfates, or polyaluminum silicate sulfate		

contaminated by municipal and industrial wastewater effluents (Kim *et al.* 2020, 2021). However, the removal mechanisms for various PFC species in drinking water treatment processes have not been fully understood (Bao *et al.* 2014).

Molecular weight, solubility, and other physicochemical properties depend on the chain lengths of PFC species. In drinking water treatment plants (DWTPs), contaminants can be removed based on physicochemical properties, such as molecular weight, solubility, hydrophobicity, and ionic strength. In particular, coagulation treatment mechanisms rely on the properties of target pollutants (e.g., high molar, insoluble, and hydrophobic characteristics). Coagulation treatment has been shown to be cost-effective and has played an important role in the removal of contaminants. Furthermore, most DWTPs, where surface water is used, require a coagulation process to remove small colloids (McCleaf *et al.* 2017, Pramanik *et al.* 2017, Trojanowicz *et al.* 2018, Dixit *et al.* 2019). To the best of our knowledge, the removal of short- or long-chain PFCs has been recently understood only in adsorption mechanisms on media, such as granular activated carbon (GAC) and soils. However, as only some studies have been conducted on the removal of PFOSs and PFOAs (Xiao *et al.* 2013, Bao *et al.* 2014, Pramanik *et al.* 2015), no information is available on the coagulation treatment of a mixture of PFCs. It should be noted that the removal mechanism of different PFC species should be understood because of their potential impact on human health. In this study, nine PFCs were used for coagulation. We also examined the effect of model suspended particles (kaolin), model biopolymers (bovine serum albumin (BSA)), and model humic substances (humic acids (HAs)) on the removal of some selected PFCs.

2. Materials and methods

2.1 Water samples and jar tests

Surface water samples were collected from two full-scale DWTPs (i.e., A and B), with pH ranging from 6 to 7. Surface water from the DWTP A contained relatively fewer suspended particles and bacterial cells (Table 2). After the samples were collected, water temperature was maintained at 15 ± 5°C, and subsequently jar tests were performed. A working solution of PFCs was introduced into the water samples. Detailed PFC concentrations and chemical types are mentioned in section 2.3. First, raw water from the DWTPs (A and B) was used for the coagulation tests (PFC positive control test). Second, raw water from the DWTP A was used to perform jar tests with kaolin, BSA, and HA. To investigate the influences of kaolin, BSA, and HA on the removal of selected PFCs during coagulation, we prepared surface waters, which were supplemented with kaolin (5 and 10 NTU), HA (5 and 10 mg L^{-1} as dissolved organic carbon (DOC)), and BSA (5 and 10 mg L^{-1} as DOC).

Jar tests apparatus (acryl beaker and cubic) were used with 1 L samples, and we performed coagulation, flocculation, and sedimentation processes, sequentially (Table 2). As shown in Table 2, we have selected various coagulant types supplied for each DWTP (aluminum sulfate (alum), polyaluminum chloride, polyaluminum chloride sulfates, high polyaluminum chloride sulfates, polyaluminum ferric chloride, and polyaluminum silicate sulfate). Previous studies have been conducted with enhanced coagulant doses (1-100 mg L^{-1}) against PFOS and PFOA (0.3-1,000 µg L^{-1}) (Bao *et al*. 2014, Pramanik *et al*. 2015), but this study selected 10 mg L^{-1} for a realistic treatment option.

2.2 Dissolved organic matter and bacterial cell counts

DOC, ultraviolet 254 nm absorbance (UV 254), specific UV absorbance (SUVA), and excitation-emission matrix (EEM) fluorescence spectroscopy were used to characterize the changes in dissolved natural organic matter (NOM) of raw and treated waters. A total organic carbon analyzer (VCPH model, Shimadzu, Japan) was used to determine the DOC levels of the test water samples. To observe the differences in organic matter fluorescences, we analyzed tryptophan- (T1 and T2 peaks), fulvic- (A peak), and humic-like (C peak) using an RF-5301PC spectrophotometer (Shimadzu, Japan). All water samples were filtered with a 0.45 µm pore syringe filter (polypropylene, Whatman, UK) and were subsequently loaded into a quartz cuvette. Excitation light wavelength ranged between 220 and 400 nm at 10 nm intervals. Emission spectra were recorded at wavelengths from 280 to 600 nm at 1 nm intervals. The spectral areas of tryptophan- (T1 and T2), fulvic- (A), and humic-like (C) were as follows: T1 (ex: 220-240 nm, em: 330-360 nm), T2 (ex: 270-280 nm, em: 330-360 nm), A (ex: 230-260 nm, em: 400-450 nm), and C (ex: 300-340 nm, em: 400-450 nm) (Park *et al*. 2016, Noh *et al*. 2018).

Flow cytometry was used to measure the removal of suspended bacterial cells. The detailed protocols for total cell count enumeration can be found in Berney *et al*. (2008). In brief, a 100 × diluted SYBR Green I gel stain (Invitrogen, US) was used to stain the bacterial cells. One milliliter of an aliquot of raw and treated water samples were prepared and stained with SYBR Green I working solution (1%, v/v) and incubated for 10 min at 30 °C. Subsequently, the stained cells were enumerated using a flow cytometer (Cube 6, Partec, Germany) (ex 480/em 530 nm) and electronic gating.

2.3 Perfluorinated compounds

First, we analyzed the negative and positive control levels of PFCs before and after PFC addition in raw water (Table S1). In this study, six types of PFCA and three PFSA species were introduced into surface waters (100 ng L^{-1} per species and 900 ng L^{-1} for a total sum of PFCs). A native PFCA and PFSA mixture solution (PFAC-MXA, Wellington Laboratories, Canada) was used to prepare a PFC working solution. The analyzed compounds and their carbon chain lengths (in parentheses) were as follows: perfluoropentanoic acid (PFPeA) (C5), perfluorohexanoic acid (PFHxA) (C6), perfluoroheptanoic acid (PFHpA) (C7), PFOA (C8), perfluorononanoic acid (PFNA) (C9), perfluorodecanoic acid (PFDA) (C10), perfluorobutanesulfonic acid (PFBS) (C4), perfluorohexanesulfonic acid (PFHxS) (C6), and PFOS (C8).

We used solid phase extraction (SPE) and liquid chromatography-tandem mass spectroscopy techniques, based on the United States Environmental Protection Agency (US EPA) method 537.1.1 (2009) for PFC analysis. In brief, all water samples were filtered using a 0.2 µm pore polypropylene membrane filter. A manual vacuum manifold was used for cartridge extraction. After cleaning and conditioning the SPE cartridges (Oasis HLB, 6 cc Vac Cartridge, Waters, USA), an aliquot (250 mL) of water samples was introduced to the activated SPE cartridge (flow rate of 10-15 mL min^{-1}). The cartridges were dried for 60 min using a vacuum pump, and subsequently 5 mL methanol was added twice to elute the target analytes. The eluted solvent (10 mL) was concentrated in an evaporator using nitrogen gas at 40-50°C. Finally, the concentrate volumes were moderated by methanol (0.5 mL). To analyze PFC concentration, we introduced a 20 µL aliquot of the prepared concentrates into the Agilent 6460 triple quadrupole LC/MS with a 1260 infinity high-performance LC system (Agilent, USA). Chromatographic separation was performed using a binary pump equipped with a vacuum degasser, a thermostatted column oven set to 40°C, and an Agilent Poroshell 120 StableBond SB-C18 2.1 × 100 mm, packed with 2.7 µm particles. Eluents for the pumps were 5 mM ammonium acetate in water (A) and 100% methanol (B). The pump was run in a linear gradient from 10% (B) to 100% (B) over 16 min. The eluent composition was held at 10% (B) for 1 min before being returned to the initial conditions over the next 0.1 min and was equilibrated for 3 min. Nitrogen (99.9999%) and argon (99.999%) were used as dry, sheath, nebulizer, and collision gases. Dry and sheath gases were held at 11 L min^{-1} and heated at 320°C. The nebulizer pressure was set to 40 psi. Capillary and nozzle voltages of 3,500 and 500 V, respectively, were applied. All compounds were run in negative ionization mode. Individual PFC concentrations were calculated based on calibration curves, with the method detection limit being below 0.5 ng L^{-1}.

2.4 Statistics

To understand the different behaviors of PFC species via coagulation, we interpreted mean comparison using analysis of variance (ANOVA) and Pearson correlations between the removal rates of analyte parameters. For ANOVA, the removal rates of all analytes were used for the dataset, equal variances were assumed, and Tukey’s by data reduction using PASW statistics 18 (IBM, USA).

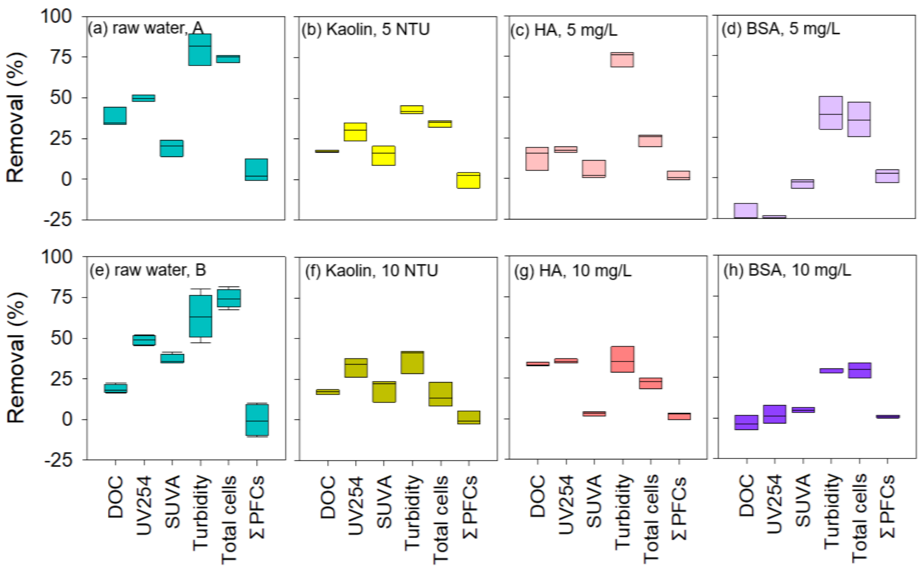

Fig. 1 Removal rates of dissolved organic carbon, UV 254 nm absorbance, specific UV absorbance (SUVA), turbidity, total bacterial cells, and bulk PFCs via coagulation in surface water collected from drinking water treatment plants A and B: raw water (a) and (e), Kaolin (b) and (f), humic acids (HA) (c) and (g), and bovine serum albumin (BSA) (d) and (h)

PCs 1 and 2 were extracted, and the varimax rotation method was used for a loading plot in the rotated space.

3. Results and discussion

3.1 Water quality

Turbidity, DOC, SUVA, and total bacterial cells are shown in Table 2. Turbidity of DWTP A (3.0 NTU) was reduced by 70-89% (0.3-0.9 NTU) after coagulation treatment (Fig. 1(a)), whereas the turbidity in the DWTP B sample (3.7 NTU) was attenuated by 47-80% (0.7-1.9 NTU) (Fig. 1(e)). We also observed that planktonic bacterial cell counts reduced by 59-76% (0.5-0.8 $\times 10^6$ cell mL^{-1}) and 68-82% (0.9-1.7 $\times 10^6$ cell mL^{-1}) for DWTP ‘A’ and ‘B’, respectively. Although bacterial cells were relatively abundant in the DWTP B sample (5.2×10^6 cells mL^{-1}) compared to that of the DWTP A (1.9×10^6 cells mL^{-1}), and coagulation was found to be effective for suspended particles.

The removals of DOC, UV 254, and SUVA were also found to be significant (16-44%, 48-52%, and 14-42%, respectively) (Figs. 1(a) and 1(e)). It was consistent with the fact that HA was preferentially removed via full-scale coagulation (Sharp *et al*. 2006 Park *et al*. 2016). EEM results also supported selective removal mechanisms via coagulation based on dissolved organic matter characteristics. Humic- and fulvic-like fluorescent components (A and C peaks) were found to be significantly reduced (44 ± 6%) after coagulation, whereas the mean reduction of protein-like components (T1 and T2 peak) was only 22 ± 8%.

3.2 Removal of perfluorinated compounds

The background levels of selected PFCs in surface water ranged from 0 to 7 ng L^{-1} in source water (without PFC stock solution), and the sum of PFOA and PFOS was found to be 13 ng L^{-1} (data not shown). In accordance with the US EPA and Korean advisory (Table 1), the detected PFC levels in raw water were found to be significantly lower than the guidance levels (e.g., 70 ng L^{-1} for the sum of PFOA and PFOS). Coagulation performance for surface waters of the DWTP A and B was found to be negligible for selected PFCs (4.6 ± 7.0% and - 0.4 ± 9.6% for the DWTP A and the DWTP B, respectively), which was found to be consistent with previous results (Xiao *et al*. 2013, Kim *et al*. 2020). However, coagulation was effective for long-chain PFCA and PFSA, such as PFDA (C10) (49.7 ± 17.6%) and PFOS (C8) (34.2 ± 18.8%) (Fig. 2). The average removal rates for other species fluctuated as follows: PFPeA (C5) (- 22.1 ± 50.0%), PFHxA (C6) (6.8 ± 4.8%), PFHpA (C7) (4.7 ± 4.6%), PFOA (C8) (- 3.3 ± 7.8%), PFNA (C9) (- 0.1 ± 17.6%), PFBS (C4) (- 14.9 ± 35.3%), and PFHxS (C6) (6.5 ± 12.7%). The shortest carbon chain length (C4) species were not found to be removed and were slightly increased via coagulation (Fig. 2). It was consistent with a previous study carried out in the full-scale DWTP with conventional and advanced treatment processes (Kim *et al*. 2020). Understanding why short-chain PFCs increase through water treatment processes is very limited. We cannot guarantee that coagulants and jar test apparatus were PFC-free. In the full-scale, water-repellent paints, plumbing materials, filtration media, and chemicals in contact with water are not guaranteed to be PFCs-free, thus, it requires further validations.

Comparison between the DWTPs showed that the removal of selected PFCs from DWTP A was not significant (4.1-14.9%, except PFDA [33.8%] and PFOS [15.8%]), whereas no removals were found in the DWTP B (- 49.5-3.9%), except for PFDA (61.6%) and PFOS (48.0%). A relatively lower DOC removal was found in the DWTP B, possibly resulting in the negligible removal of shorter-chain PFCs.

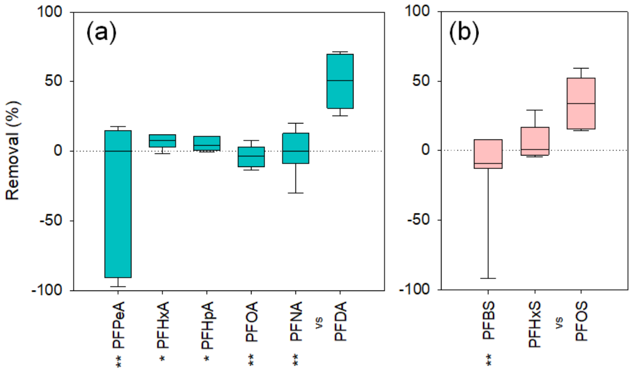

Fig. 2 Perfluorinated compounds removals from the raw waters of drinking water treatment plants A and B via coagulation: (a) perfluorodecanoic acid (PFDA) versus carboxylic species and (b) perfluorooctanesulfonic acid (PFOS) versus sulfonic species. Asterisks represent the significant difference of removal rates (* and ** for p values < 0.05 and < 0.01, respectively).

3.3 Influence of suspended particles

Kaolin is often used as a model suspended particle to determine coagulation performance using different coagulant chemicals and aiding agents (Li *et al*. 2013). Coagulation performance was retarded by adding kaolin (5 and 10 NTU), which suppressed the removal of bacterial cells (32-35% and 9-23% removed, respectively). Interestingly, kaolin also suppressed coagulation performance against HA, and the removal of DOC, UV 254, and SUVA was found to be reduced to 17-19%, 24-38%, and 9-24%, respectively (Fig. 1b and f). The relatively low removal rates of HA due to the addition of kaolin were found to be compatible with the EEM results, the reduction of humic- and fulvic-like fluorescence ranged from 19 to 22%, indicating the effect of kaolin.

The removal of selected PFCs was also significantly influenced by suspended particles in water. Removal efficacy of bulk PFCs was reduced from 4.6 ± 7.0% (raw water ‘A’) to 0.4 ± 5.0% in surface water (5 NTU). Except for PFDA and PFOS (13 ± 19% and 12 ± 11% removed, respectively), the average removal rates for PFC species ranged from - 6 to 4%. Interestingly, higher turbidity was observed to significantly reduce the PFOS removal (from 17 ± 10% to 6 ± 10%). ANOVA results also revealed that higher turbidity in surface water for 10 NTU led to insignificant differences between PFC species removal ($p > 0.05$), which changed from 0.026 to 0.349, indicating that turbidity suppressed PFDA and PFOS removal. Thus, higher turbidity in source water can be considered as one of the factors obstructing the coagulation performances against PFCs, and this hypothesis was inconsistent with Bao *et al*. (2014).

3.4 Influences of humic acids and bovine serum albumin

HA and BSA are often used as model humic substances and biopolymers in drinking water treatment processes, including coagulation and membrane filtration processes (Xiao *et al*. 2013, Yu *et al*. 2016, Pramanik *et al*. 2017, Xu *et al*. 2019). HA has been regarded as the most popular NOM surrogate in environmental science studies, exhibiting relatively higher hydrophobicity and electronegativity in water (Yu *et al*. 2016, Xu *et al*. 2019). Higher HA concentration was observed to reduce the removal of turbidity (28-78%) and bacterial cells (9-36%) compared to raw test water. EEM results also suggested that HA addition retarded the removal of fluorescent NOM moieties via coagulation (data not shown). The removal of bulk PFCs was found to reduce to 1.4 ± 2.7% and 2.0 ± 2.2% in HA -added water with the initial DOCs of 5 and 10 mg L^{-1}, respectively. Only the removal of PFDA was found to be significant between the PFC species ($p < 0.05$). Pramanik *et al*. (2015) reported that higher DOC levels in raw water (5-25 mg L^{-1}) decreased the adsorption capacities of activated carbon media versus PFOS and PFOA. Coagulants also consist of limited active sites interacting with target micropollutants (Sillanpää *et al*. 2018), hence, PFCs might behave as competitive pollutants with other organic matters.

BSA often exhibits relatively hydrophilic and easily soluble characteristics in water. Notably, hydrophilic BSA interrupted the removal of water quality parameters. DOC, UV 254, and SUVA were found to be not removed (Fig. 1d and h), whereas turbidity and bacterial cells decreased slightly (34-41% and 24-25%, respectively). Along with BSA, the removals of selected PFCs were found to be 1.4 ± 4.1% and 0.9 ± 0.9% in water with 5 and 10 mg L^{-1} DOC, respectively. Interestingly, we observed the lowest removal of PFNA and PFDA (- 1.87% and - 1.72%, respectively) in water with 10 mg L^{-1} BSA. Pramanik *et al*. (2017) also reported that protein led to a lower rejection of PFOA and PFOS than other model pollutants. This result putatively explained that model biopolymers in surface water significantly interrupt the removal of PFCs.

3.5 ANOVA and principal component analysis

To better understand the removal of long- and short-chain PFCs, we ANOVA and principal component analysis (PCA) in this study. We confirmed that individual removal rates for PFC species were significantly different in raw water coagulation ($p < 0.01$, between PFC species groups). Post-hoc results showed that PFDA removal rates were significantly higher than PFPeA, PFHxA, PFOA, and PFNA (Fig. 2(a)). PFOS removal was higher but statistically significant compared to only PFBS (Fig. 2(b)). Therefore, we concluded that coagulation was only valid for removing the longest chain carboxylic and sulfonic species, i.e., PFDA and PFOS, respectively. Under the model pollutant loadings, we found no significant differences in the removals of the PFCs ($p > 0.05$), which indicated the importance of source water quality monitoring and watershed protection scheme. Hence, the relationships between PFCs, nonpoint pollution, and seasonal quality changes in watersheds require further studies (Zhang *et al*. 2016). In addition, PCA was performed to reduce the data dimensions in the multi-variable dataset. Furthermore, the Pearson correlation matrix (Fig. 3) was used to show the

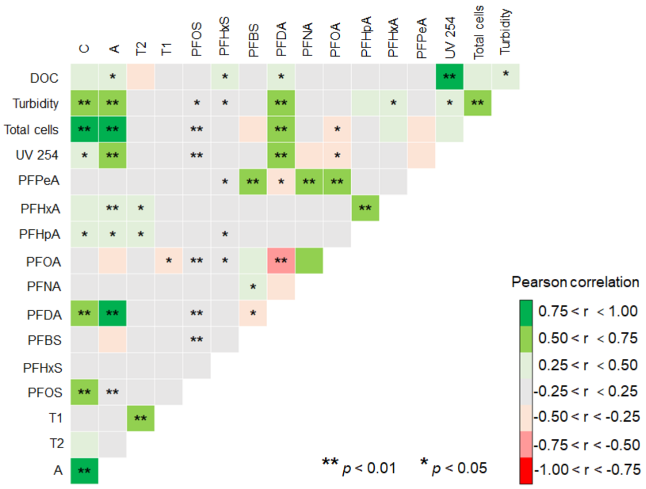

Fig. 3 Pearson correlation heatmap for the changes in water quality parameters

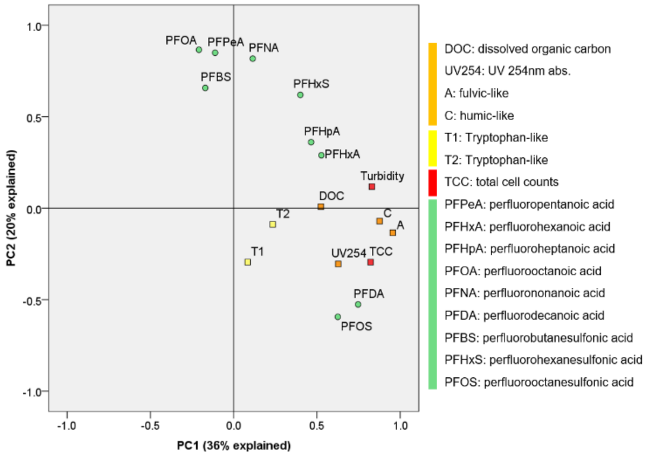

Fig. 4 Principal component analysis in a rotated space. PC1 axis putatively explains the removal mechanisms based on the hydrophobicity and insolubility of pollutants

relationships between the removal of PFC species and water quality parameters. PFDA removal was found to be highly correlated with the removals of suspended particles, bacterial cells, EEM A and C peaks, and UV 254 (Fig. 3). For PCA loading plots, two principal components (PCs) were extracted (Fig. 4), PC1 axis explained 32% variance, whereas PC2 axis explained 20%. PC1 axis was observed to be positively related to humic- and fulvic-like organic matters (relatively hydrophobic) and suspended particles (e.g., turbidity and bacterial cells), whereas PC2 could not be specified. Notably, long-chain PFDA and PFOS exhibited higher molecular weight (514.1 and 500.1 Da, respectively), low solubility (0.008 and 0.104 mg L^{-1}, respectively), and relatively higher log K_{ow} values (6.15 and 4.49, respectively) (Table 1). Parameter cluster with low removal (PFOA, PFPeA, PFNA, and PFBS) was found to be independent from other pollutant groups.

In chain-length comparison, PFSAs behaved differently than the same chain-length PFCAs. For instance, we found better removal of PFOS (C8) (34 ± 19%) than PFOA (C8) (- 3 ± 8%). Applying the removal model based on the chain length, we confirmed that the zero-chain length fitting parameters of PFCAs were lower than those of PFSAs in PFC removal regression models throughout the drinking water treatment processes (coagulation, GAC filtration, and anion exchange) (McCleaf *et al*. 2017, Kim *et al*. 2020), demonstrating that PFCAs were more persistent than PFSAs. This phenomenon can be explained by the higher adsorption strengths of PFSAs against cations (Ateia *et al*. 2019). In our experiment, the removals of long-chain PFCAs (C7-C10) and PFSAs (C4, C6, and C8) were slightly correlated with the chain length (R^2 = 0.39 and 0.44, respectively).

4. Conclusions

In this study, we found that chain-length was slightly correlated with the removal rates of PFCs through coagulation, but only long-chain PFCs (e.g., PFDA and PFOS) were found to be significantly removed. The present study also demonstrated that removal of bulk mixture PFCs was significantly lower than those reported in the studies that performed coagulation against only PFOA and PFOS, relatively long-chain compounds. Considering that long-chain PFCs often exhibit higher toxicity potential than short-chain species, the removal of long-chain PFCs via coagulation requires further study and optimization. Coagulation treatment process possibly mitigates the concentrations of PFCs for subsequent water treatments, such as GAC filters; thus, it is still important to enhance the coagulation efficiency as a multiple-barrier treatment strategy. Under pollutant loadings, source water quality may influence the removal of PFCs through DWTPs. Thus, monitoring PFC levels and bulk organic matters in watersheds will be needed to manage safe drinking water. The following conclusions were drawn from this research:

- The physicochemical properties of chemicals are important for the removal of selected PFCs via the coagulation process.
- Coagulation resulted in the removal of some long-chain PFDAs (C10) and PFOSs (C8) in surface water.
- Suspended particles, BSA, and HA may deteriorate the removal of PFCs via coagulation.

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References

Ateia, M., Arifuzzaman, M., Pellizzeri, S., Attia, M.F., Tharayil, N., Anker, J.N. and Karanfil, T. (2019), “Cationic polymer for selective removal of GenX and short-chain PFAS from surface waters and wastewaters at ng/L levels”, *Water Res*., **163**. https://doi.org/10.1016/j.watres.2019.114874.

Bao, Y., Niu, J., Xu, Z., Gao, D., Shi, J., Sun, X. and Huang, Q.

(2014), "Removal of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) from water by coagulation: Mechanisms and influencing factors", *J. Colloid Interf. Sci.*, **434**, 59-64. https://doi.org/10.1016/j.jcis.2014.07.041.

Berney, M., Vital, M., Hülshoff, I., Weilenmann, H.-U., Egli, T. and Hammes, F. (2008), "Rapid, cultivation-independent assessment of microbial viability in drinking water", *Water Res.*, **42**(14), 4010-4018. https://doi.org/10.1016/j.watres.2008.07.017.

Brendel, S., Fetter, E., Staude, C., Vierke, L. and Biegel-Engler, A. (2018), "Short-chain perfluoroalkyl acids: Environmental concerns and a regulatory strategy under REACH", *Environ. Sci. Eur.*, **30**. https://doi.org/10.1186/s12302-018-0134-4.

Dixit, F., Barbeau, B., Mostafavi, S.G. and Mohseni, M. (2019), "PFOA and PFOS removal by ion exchange for water reuse and drinking applications: Role of organic matter characteristics", *Environ. Sci. Water Res.*, **5**(10), 1782-1795. https://doi.org/10.1039/C9EW00409B.

Gao, S.C., Cao, Z.Z., Niu, Q.G., Zong, W.S. and Liu, R.T. (2019), "Probing the toxicity of long-chain fluorinated surfactants: Interaction mechanism between perfluorodecanoic acid and lysozyme", *J. Mol. Liq.*, **285**, 607-615. https://doi.org/10.1016/j.molliq.2019.04.134.

Jin, Y.H., Liu, W., Sato, I., Nakayama, S.F., Sasaki, K., Saito, N. and Tsuda, S. (2009), "PFOS and PFOA in environmental and tap water in China", *Chemosphere*, **77**(5), 605-611. https://doi.org/10.1016/j.chemosphere.2009.08.058.

Key, B.D., Howell, R.D. and Criddle, C.S. (1997), "Fluorinated organics in the biosphere", *Environ. Sci. Technol.*, **31**(9), 2445-2454. https://doi.org/10.1021/es961007c.

Kim, K.Y., Ekpe, O.D., Lee, H.J. and Oh, J.E. (2020), "Perfluoroalkyl substances and pharmaceuticals removal in full-scale drinking water treatment plants", *J. Hazard. Mater.*, **400**, 123235. https://doi.org/10.1016/j.jhazmat.2020.123235.

Kim, K.Y., Ndabambi, M., Choi, S. and Oh, J.E. (2021), "Legacy and novel perfluoroalkyl and polyfluoroalkyl substances in industrial wastewater and the receiving river water: Temporal changes in relative abundances of regulated compounds and alternatives", *Water Res.*, **191**, 116830. https://doi.org/10.1016/j.watres.2021.116830.

Kim, M.K. and Zoh, K.D. (2016), "Occurrence and removals of micropollutants in water environment", *Environ. Eng. Res.*, **21**(4), 319-332. https://doi.org/10.4491/eer.2016.115.

Kunacheva, C., Fujii, S., Tanaka, S., Seneviratne, S.T., Lien, N.P., Nozoe, M., Kimura, K., Shivakoti, B.R. and Harada, H. (2012), "Worldwide surveys of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in water environment in recent years", *Water Sci. Technol.*, **66**(12), 2764-2771. https://doi.org/10.2166/wst.2012.518.

Li, J., Jiao, S.F., Zhong, L., Pan, J.F. and Ma, Q.M. (2013), "Optimizing coagulation and flocculation process for kaolinite suspension with chitosan", *Colloid Surface A*, **428**, 100-110. https://doi.org/10.1016/j.colsurfa.2013.03.034.

Li, Y.N., Li, J.F., Zhang, L.F., Huang, Z.P., Liu, Y.Q., Wu, N., He, J.H., Zhang, Z.Z., Zhang, Y. and Niu, Z.G. (2019), "Perfluoroalkyl acids in drinking water of China in 2017: Distribution characteristics, influencing factors and potential risks", *Environ. Int.*, **123**, 87-95. https://doi.org/10.1016/j.envint.2018.11.036.

McCleaf, P., Englund, S., Ostlund, A., Lindegren, K., Wiberg, K. and Ahrens, L. (2017), "Removal efficiency of multiple poly- and perfluoroalkyl substances (PFASs) in drinking water using granular activated carbon (GAC) and anion exchange (AE) column tests", *Water Res.*, **120**, 77-87. https://doi.org/10.1016/j.watres.2017.04.057.

Noh, J.H., Lee, S.H., Choi, J.W. and Maeng, S.K. (2018), "Dissolved organic matter characteristics and bacteriological changes during phosphorus removal using ladle furnace slag", *Membr. Water Treat.*, **9**(3), 181-188. https://doi.org/10.12989/mwt.2018.9.3.181.

Park, J.W., Kim, H.C., Meyer, A.S., Kim, S. and Maeng, S.K. (2016), "Influences of NOM composition and bacteriological characteristics on biological stability in a full-scale drinking water treatment plant", *Chemosphere*, **160**, 189-198. https://doi.org/10.1016/j.chemosphere.2016.06.079.

Pierpaoli, M., Szopinska, M., Wilk, B.K., Sobaszek, M., Luczkiewicz, A., Bogdanowicz, R. and Fudala-Ksiazek, S. (2021), "Electrochemical oxidation of PFOA and PFOS in landfill leachates at low and highly boron-doped diamond electrodes", *J. Hazard. Mater.*, **403**. https://doi.org/10.1016/j.jhazmat.2020.123606.

Pramanik, B.K. (2015), "Occurrence of perfluoroalkyl and polyfluoroalkyl substances in the water environment and their removal in a water treatment process", *J. Water Reuse Desal.*, **5**(2), 196-210. https://doi.org/10.2166/wrd.2014.068.

Pramanik, B.K., Pramanik, S.K., Sarker, D.C. and Suja, F. (2017), "Removal of emerging perfluorooctanoic acid and perfluorooctane sulfonate contaminants from lake water", *Environ. Technol.*, **38**(15), 1937-1942. https://doi.org/10.1080/09593330.2016.1240716.

Pramanik, B.K., Pramanik, S.K. and Suja, F. (2015), "A comparative study of coagulation, granular- and powdered-activated carbon for the removal of perfluorooctane sulfonate and perfluorooctanoate in drinking water treatment", *Environ. Technol.*, **36**(20), 2610-2617. https://doi.org/10.1080/09593330.2015.1040079.

Rahman, M.F., Peldszus, S. and Anderson, W.B. (2014), "Behaviour and fate of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in drinking water treatment: A review", *Water Res.*, **50**, 318-340. https://doi.org/10.1016/j.watres.2013.10.045.

Renner, R. (2006), "The long and the short of perfluorinated replacements", *Environ. Sci. Technol.*, **40**(1), 12-13.

Rostkowski, P., Yamashita, N., So, I.M., Taniyasu, S., Lam, P.K., Falandysz, J., Lee, K.T., Kim, S.K., Khim, J.S., Im, S.H., Newsted, J.L., Jones, P.D., Kannan, K. and Giesy, J.P. (2006), "Perfluorinated compounds in streams of the Shihwa Industrial Zone and Lake Shihwa, South Korea", *Environ. Toxicol. Chem.*, **25**(9), 2374-2380. https://doi.org/10.1897/05-627R.1.

Sharp, E.L., Parsons, S.A. and Jefferson, B. (2006), "Seasonal variations in natural organic matter and its impact on coagulation in water treatment", *Sci. Total Environ.*, **363**(1-3), 183-194. https://doi.org/10.1016/j.scitotenv.2005.05.032.

Sillanpaa, M., Ncibi, M.C., Matilainen, A. and Vepsalainen, M. (2018), "Removal of natural organic matter in drinking water treatment by coagulation: A comprehensive review", *Chemosphere*, **190**, 54-71. https://doi.org/10.1016/j.chemosphere.2017.09.113.

Son, H.J., Hwang, Y.D., Yoom, H.S., Choi, J.T. and Kwon, K.W. (2013), "Detection of perfluorinated compounds (PFCs) in Nakdong River basin", *J. Korean Soc. Environ. Eng.*, **35**(2), 84. https://doi.org/10.4491/KSEE.2013.35.2.084.

Trojanowicz, M., Bojanowska-Czajka, A., Bartosiewicz, I. and Kulisa, K. (2018), "Advanced Oxidation/Reduction Processes treatment for aqueous perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS) - A review of recent advances", *Chem. Eng. J.*, **336**, 170-199. https://doi.org/10.1016/j.cej.2017.10.153.

US EPA. (2009), Method 537.1: Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, Washington, DC, U.S.A.

Xiao, F., Simcik, M.F. and Gulliver, J.S. (2013), “Mechanisms for removal of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) from drinking water by conventional and enhanced coagulation”, *Water Res*., **47**(1), 49-56. https://doi.org/10.1016/j.watres.2012.09.024.

Xu, W.Y., Chen, Y.Y., Liang, H.K., Sang, G.Q., Wei, D., Wang, D.S. and Du, B. (2019), “A comparison study of in-situ coagulation and magnetic ion exchange (MIEX) as pre-treatments for ultrafiltration: Evaluating effectiveness of organic matters removals and fouling mitigation”, *Chemosphere*, **214**, 633-641. https://doi.org/10.1016/j.chemosphere.2018.09.136.

Yu, Y., Zhao, C.W., Yu, L., Li, P., Wang, T. and Xu, Y. (2016), “Removal of perfluorooctane sulfonates from water by a hybrid coagulation-nanofiltration process”, *Chem*. *Eng*. *J*., **289**, 7-16. https://doi.org/10.1016/j.cej.2015.12.048.

Zhang, Y.Z., Wang, B., Wang, W., Li, W.C., Huang, J., Deng, S.B., Wang, Y.J. and Yu, G. (2016), “Occurrence and source apportionment of Per- and poly-fluorinated compounds (PFCs) in North Canal Basin, Beijing”, *Sci*. *Rep*, **6**, 36683. https://doi.org/10.1038/srep36683.

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