

Detection and treatment methods for perfluorinated compounds in Wastewater Treatment Plants

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Abstract

This study surveyed the variation in Perfluorinated Compounds (PFCs) concentration entering urban wastewater treatment plants and proposed an optimal PFCS treatment method. The PFCS concentration in influent was shown to be affected by the types of industries and operating rate. The concentration of PFCs in the wastewater treatment effluent was slightly lower than that of influent. Thus, PFCs were considered to have barely been removed by the existing biological treatments. The pilot test result showed that about 10% of PFCs were removed by coagulation and precipitation, and the ozone and chlorine test also showed that few PFCs were removed regardless of the amount of injection. The activated carbon adsorption test showed that the removal was significantly increased by the empty bed contact time, with about a 60% removal in five minutes and over a 90% removal in 15 minutes. Therefore it is determined that a more stable and higher PFCs removal would result from the continuous oxidation processes such as ozone and adsorption processes such as activated carbon rather than a single biological treatment.

Keywords: Perfluorinated Compounds, Coagulation, Ozone, Chlorination, activated carbon

1. Introduction

Perfluorinated Compounds (PFCs) are very difficult to degrade biologically in natural environment due to their extremely stable covalent bond. Artificially synthesized and produced, PFCs are used in manufacturing various household goods and are detected consistently in water. There has been much research interest in PFCs as they have been reported to affect the natural water system, causing disturbance to the ecosystem [1,2].

Accordingly, PFCs are compounds with high persistence in the environment, and since the early 2000s, there has been much research on the bio-persistence, hazard, and toxicity of PFCs [2,3]. Since the mid-2000s, the EU, Canada, and USA among others have started regulating PFCs, and at the fourth Stockholm Treat Conference of the Parties in May, 2009, it was agreed that some of these PFCs would be included in the target compounds of the treaty [3-5]. The most well-known PFCs used in the industry and broader daily life are waterproof materials, lubricants, paint, ink, paper, fiber, carpet, oven, cooking equipment, electronic products, packaging materials, metal coating, cleaning products, semi-conductors, and firefighting products among others [2]. However, since many household products use PFCs as additives, it is very difficult to calculate the amount of usage and the amount released into the environment. Furthermore, the residual concentration of PFCs in the

environment is very small at ng/L(ppt) or below, but the effect on the ecosystem cannot be disregarded if the ecosystem is exposed to PFCs for a long time [6-8].

The pathways of PFCs to the environment are numerous; most of them enter wastewater treatment plants. However, little has been known about the mechanisms through which these PFCs with persistence and toxicity are removed; therefore, it is difficult to improve the removal of the small amount of PFCs with existing wastewater treatment methods [9-10].

PFCs concentration in the influent and effluent were investigated for the actual wastewater treatment plant, which is the source of perfluorocarbons in large industrial complexes and highly populated areas. Furthermore, this study investigate the distribution properties of PFCs from the influent wastewater treatment plant and proposed an optimal treatment plan through pilot test which may eventually serve the data for the possible direction for future surface water management plans.

2. Research Content and Method

2.1 The current status of the wastewater treatment plant

(A) Survey area

The major business types in the survey area are fabric manufacturing, metal, coating, and rubber, and the fabric manufacturers have the largest amount of the PFCs emissions. The public wastewater treatment plant implements the A2/O (i.e., anaerobic-anoxic-oxic) method, and the reaction tank consists of the anaerobic tank, the anoxic tank, and aerobic tank, as well as the internal and external returners. The treatment efficiency for organic compounds like BOD and SS is over 90%, that for T-N is between 40 and 70%, and that for T-P is 60%. Shown in Fig. 1 is the process flowchart of the pilot test.

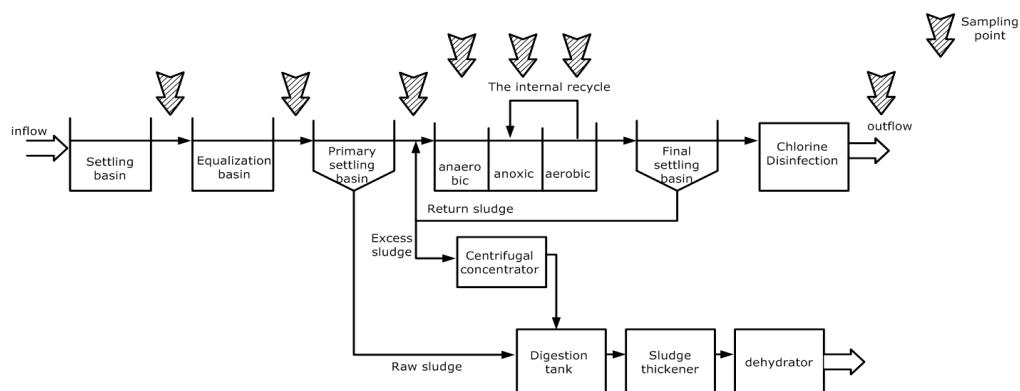


Fig.1 Sampling points of wastewater treatment plants in K city.

(B) Analysis of PFCs

The analysis of PFCs was conducted on five items: perfluorooctanoic acid (PFOA), perfluoro-n-pentanoic acid (PFPeA), perfluorohexane sulfonate (PFHxS), perfluorohexanoic acid(PFHxA), and perfluorononanoic acid (PFNA). The pre-treatment and analysis conditions are shown in Table 1. The pre-treatment for the analysis of PFCs uses SPE to conduct a four-stage solid phase extraction, and the conditioning stage used methanol as solvent., The loading and washing stages used 10.0 mL of deionized water, and the elution stage used 2.0 ml of methanol. After the solid phase extraction stage, the concentration stage used 40 °C nitrogen gas to concentrate the PFCs so that their final volume is reduced to 500µL. After the concentration stage, the analysis was conducted with LC-MS/MS [11].

Table 1 Analytical condition of PFCs

Parameters	Conditions		
LC	Waters	ACQUITY	UPLC
MS	AB	SCIEX	API-4000
Column	BEH C18, 2.1*50mm, 1.7 μ m (Waters)		
Mobile phase	A:10mM ammonium acetate in water		
	B:Acetonitrile		
Gradient	Time(min)		
	Solvent B(%)		
Flow rate	270 μ L/min		
Injection volume	5 μ L		
Column temp.	40°C		
Ionization mode	Negative		
Curtain Gas	40		
Collision Gas	8		
Ion Spray Voltage	-4500V		

(C) Pilot test

To determine the concentration change by coagulation • sedimentation, the study injected the coagulator using Alum at regular intervals from 10 to 20, 30, 40, and 50mg/L. After fixing the pH to 7, the study conducted the rapid spinning (67rpm) for one minute, slow spinning (31 rpm) for ten minutes, and after sedimentation for 30 minutes. The supernatant was then sampled and analyzed. The PFCs removal efficiency by ozone oxidation was conducted an ozone contact test. The ozone contact test was performed by determining the amount of ozone by KI titration and injecting ozone to the water in the Ozone Demand Flask by the concentration of 5, 10, 15, 20, 25, and 30mg O₃/L. The volume of the Demand Flask was 1.5L, and after injecting ozone, the Demand Flask was sufficiently shaken for 20 minutes to maximize the ozone contract efficiency before conducting the analysis. By measuring the effective chlorine of the hypochlorous acid sodium solution in the inflow water to the treatment plant, the corresponding amount of chlorine was calculated and injected. The amount of injected chlorine was 5, 10, 15, and 20mg/L at regular intervals, based on the guidelines for the sewage treatment facilities. To perform the activated carbon adsorption of PFCs, the study filled clearly washed and dried granular activated carbon to a column with an internal diameter of 20 mm and length of 350 mm. The influent wastewater was injected to this column using a controlled volume pump, and the treated sample was analyzed. For the test conditions, the empty bed contact time (EBCT) was varied from 5 to 10 and 15 minutes.

3. Results and Discussion

3.1 Variation in the amount of inflow water

Shown in Fig. 2 is the amount of influent flow to the treatment plant.

The daily average influent flow was $27,335\text{m}^3/\text{d}$, $40,948\text{m}^3/\text{d}$ at its maximum level, and $19,506\text{m}^3/\text{d}$ at its minimum level. Due to the precipitation in August 2017, the inflow water between the 13th and the 17th of August was the highest.

It is considered that the amount of influent flow partially changes due to the business operational rate.

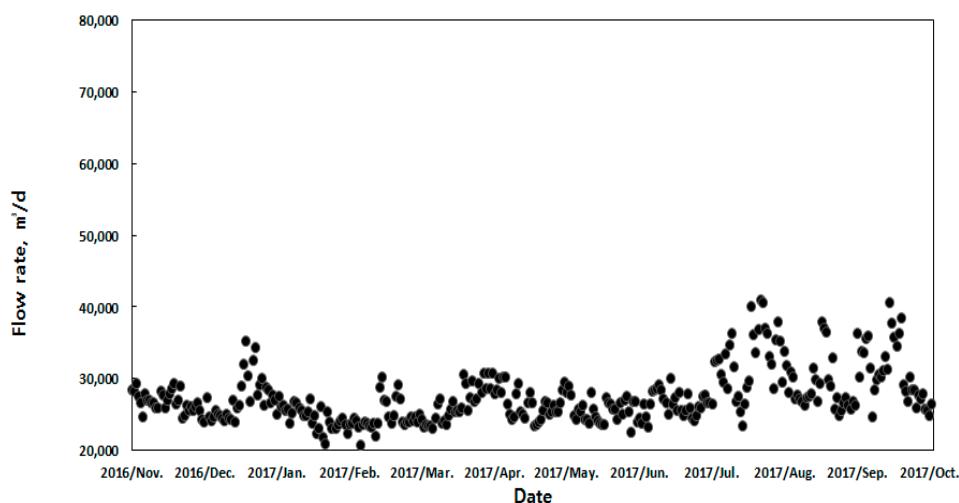


Fig.2 Flow variations of Wastewater Treatment Plant in K city

3.2 Monthly PFCs concentration change

The average PFOA in the influent was 11.7ng/L , and that in the effluent was 11.0ng/L , and the PFOA removal was very low. The average PFHxA in the influent was 11.9ng/L , and that in the effluent was 11.1ng/L , showing little removal. The average PFNA in the influent was 4.1ng/L , but that in the effluent was 2.9ng/L , showing an average PFNA removal of 27.2%. The average PFPeA in the influent was 3.2ng/L , and the effluent 2.7ng/L with the removal at 7.8%. The average PFHxS in the influent was 1.0ng/L , and that in the effluent 0.8ng/L .

The concentration distribution of these substances tended to be somewhat higher in the dry winter season. More specifically, PFHxS is frequently used as a fire extinguisher material and so its concentration tended to be higher in the fall and winter when there is a lot of fire. In addition, PFCs are shown to be largely affected by the business operational ratio, and for the efficient management, it is determined that a detailed and continuous emissions survey would be required in industry-concentrated regions. Finally, while some items were removed by the existing treatments, most of the items were shown to not be well treated.

3.3 Correlation of PFCs between cities

Shown in Table 2 are the correlations of PFCs of the survey city to those of another city whose wastewater properties are similar. The correlational coefficient between 0.000 and 0.200 was considered to have no relation and was marked as xx, while the one between 0.210 and 0.400 was considered to be low and marked as x. The correlational coefficient between 0.410 and 0.600 was considered to have some relation and marked as Δ .

The correlation coefficient between PFOA and PFHxS was 0.486, showing some correlation. That between PFHxA and PFNA or PFPeA was 0.516 or 0.583, respectively, showing some correlation.

All the other items had low or little correlation. The correlation among PFCs showed that PFOA, PFHxA, and PFNA had the -COOH group so that they were highly correlational with PFCs with the same reaction group [3], Ahrens et al. also showed that the correlation coefficient between PFO and PFNA was highest at 0.752 [12]. However, So et al. reported that while PFCs in the -COOH group had relatively higher correlation, the correlation coefficient between PFOA and PFNA was low at 0.375 [13]. This is because there are various emission sources for PFCs, and the outflow water from the wastewater treatment plants are known to be key point pollution sources. Therefore, effluent flow to the water system reflects regional characteristics and determines the correlation of the substances in actual streams, producing such regional differences [3].

The correlational study among PFCs in this study was significant in determining the concentration level of PFCs through the concentration of some PFCs among those with high correlation, but such data are still lacking in representability and therefore, further research is necessary.

Table 2 Comparison of Correlation Coefficients of PFCs with other city with similar population and industry

R ²	Other city									
	PFOA		PFHxA		PFNA		PFPeA		PFHxS	
Item	1	-	0.050	xx	0.013	xx	0.141	xx	0.486	△
PFOA	-	-	1	-	0.516	△	0.583	△	0.090	xx
PFHxA	-	-	-	-	1	-	0.160	xx	0.019	xx
PFNA	-	-	-	-	-	-	1	-	0.098	xx
PFPeA	-	-	-	-	-	-	-	-	1	-
PFHxS	-	-	-	-	-	-	-	-	-	-

3.4 PFCs Removal efficiency through pilot test

The study conducted pilot test on the influent to the treatment plant to determine the removal efficiency. In particular, it examined the change in the removal by coagulation • sedimentation, ozone oxidization, chlorine injection, and activated carbon adsorption.

(1) Removal variation by coagulation • sedimentation

As shown in Fig. 3, the PFCs in the coagulation • sedimentation test showed a phased concentration decrease. However, overall, the removal did not increase in spite of additional injection of the coagulator more than 40~50mg/L. When 40~50mg/L of coagulator was injected, the removal of PFPeA was highest at 12.3%, followed by PFHxS at 11.5%, PFNA at 10.9%, PFHxA at 8.9%, and PFOA at 6.4%.

The overall removal of PFCs was about 10%, thus demonstrating that they were somewhat removed by the coagulation • sedimentation treatment. However, its effect was shown to be negligible and that it would be limited in removing non-degradable PFCs.

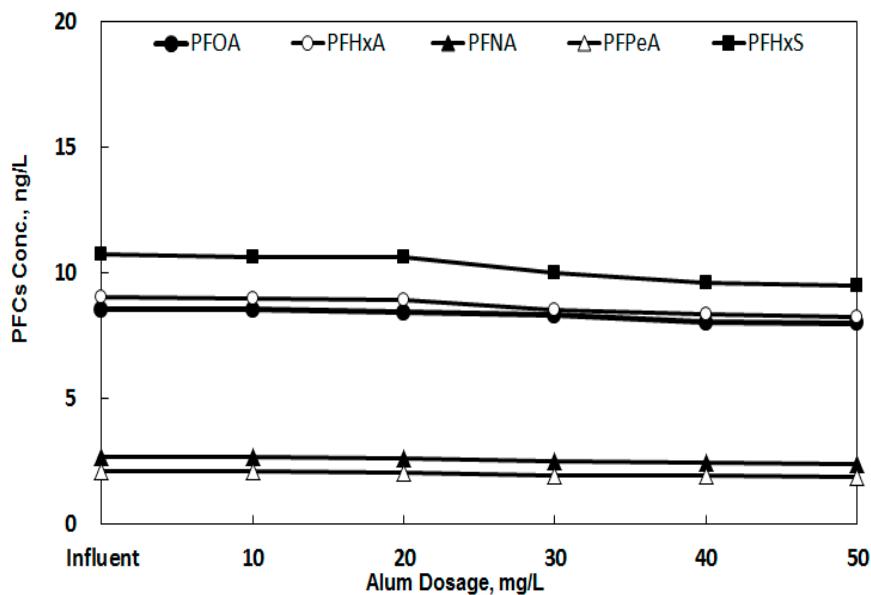


Fig.3 Variations of PFCs concentration by Alum dosages

(2) Removal variation by ozone oxidation

The ozone contact test result in Fig.4 shows that in all items from PFOA to PFHxA, PFNA, PFPeA, and PFHxS, the removal was 5% or below, and regardless of the change in the amount of the injected ozone, the removal was negligible. Additionally, other research showed that the PFOA removal was between 10 and 20%, but the removal by ozone oxidization was shown to be difficult [9].

It has been reported that due to the highly stable structure, PFCs are difficult to remove through existing biochemical or oxidation processes, and this study also determined that PFCs removal by ozone oxidization would be difficult. Therefore, to remove them effectively, it is determined that other additional treatment methods are required.

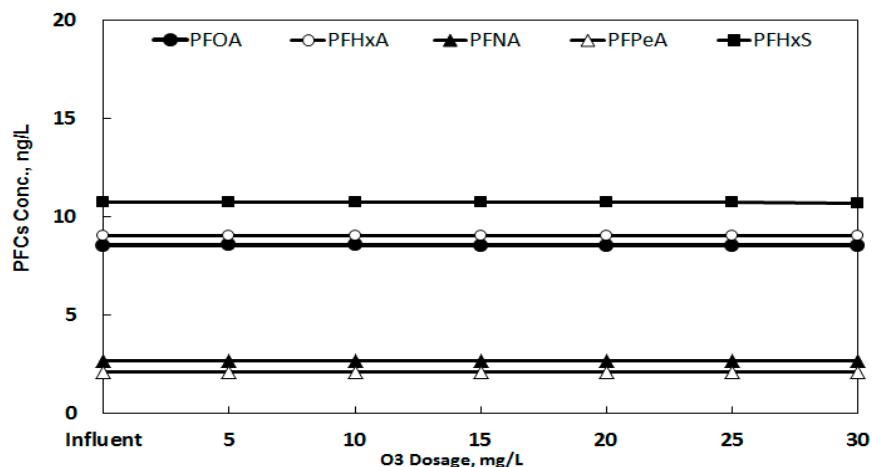


Fig.4 Variations of PFCs concentration by O₃ dosages

(3) Removal change by chlorine injection

As shown in Fig. 5, PFOA showed the highest removal of 9.7% with 20mg/L of the injection,

which, nonetheless, is determined to be negligible. The PFHxA removal was 3.33%, which means little to no removal, and the PFNA removal was 4.6% and its concentration some increased with 10mg/L of the injection and again decreased. The other items, PFPeA and PFHxS, showed a removal of 5% or below, which was negligible. Furthermore, other research result showed little to no effect of the chlorine injection on the PFCs removal regardless of the amount of the injection [9], which was similar to the results of this study.

Since PFCs are very stable and non-degradable, the use of a single chlorine disinfection process would not be able to effectively remove them.

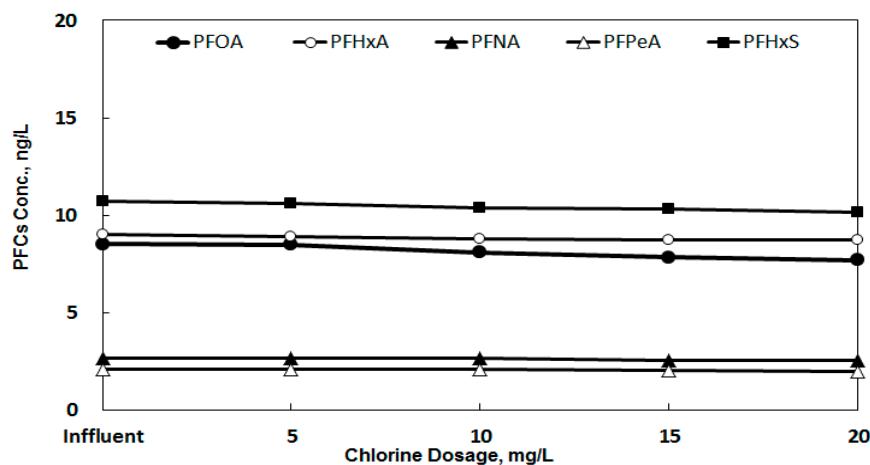


Fig.5 Variations of PFCs concentration by Chlorine dosages

(4) Removal variation by activated carbon adsorption

As shown in Fig. 6, the PFNA removal at 5 min was 69.55%, which rose to the highest of 98.55% at 15 min. The PFPeA removal at 5 min was 36.49%, which rose to the lowest 90.1% at 15 min. The PFHxS removal at 5 min was 61.8%, which rose to 93.6% at 15 min. PFOA and PFHxA showed a 64.8 and 42.73% removal at 5 min of EBCT, which increased to 95.43% and 92.12% at 15 min of EBCT, respectively.

It was shown that 50 to 60% of PFCs were removed by 5 min of EBCT, and over 90% of them were removed after 15 min. PFNA showed the highest removal at 98.5%, and PFPeA showed the lowest at 90.1%. Another research reported that the longer the length of the carbon ring in PFCs, the more the adsorption force to the activated carbon would increase, and when the length of the carbon ring is identical, the adsorption force of the activated carbon to sulfone substituent would be stronger than that to carboxyl substituent [14]. In this study, the removal of PFNA which has a large number of carbon was highest, and for PFHxA and PFHxS in which the number of carbon was identical, PFHxS, which has the sulfone substituent, would have a somewhat higher removal.

The activated carbon adsorption test showed relatively higher removal, and it is considered that since the surface of the activated carbon is hydrophobic, it is useful in removing hydrophobic PFCs.

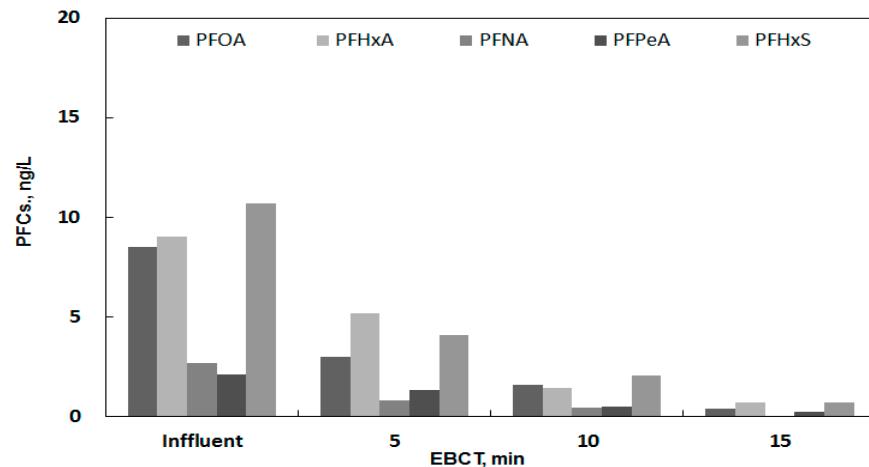


Fig.6 Variations of PFCs concentration by GAC EBCT

3.5 The proposal of an optimal PFCs treatment process

Based on the analysis results of each unit process and the pilot test effluent, the study reviewed an efficient treatment process for removing PFCs and showed the PFCs process efficiencies and cumulative removal efficiencies in Table 3.

Non-degradable, it is known that PFCs are difficult to degrade and remove through the existing biological treatment methods [9].

As for the activated carbon adsorption, it has been reported that the longer the length of the carbon ring of PFCs, the more the adsorption force of the activated carbon increases, and if the length of the carbon ring is identical, the adsorption force of the activated carbon is stronger with the sulfone substituent than with the carboxyl substituent [15]. As for the adsorption and removal of PFCs using zeolite, the higher the Si content in zeolite, the more the PFCs adsorption capacity increases. However, this treatment is reported to have a smaller adsorption capacity than the treatment with activated carbon [16].

Activated carbon adsorption showed a relatively higher PFCs removal than the other treatments. Therefore, it is determined that it would be effective in the PFC removal of the wastewater treatment process. Furthermore, the PFHxS removal in the single ozone process or the single activated carbon process was low, but it improved in the continuous treatment of the ozone process followed by the activated carbon process. Accordingly, the implementation of an oxidation process like the ozone process followed by an adsorption process using activated carbon, for example, is considered to be the most desirable process with a higher removal.

Table 3 Summary of PFCs applicability by various treatment

Process		PFCs										
		PFOA		PFHxA		PFNA		PFPeA		PFHxS		
Batch	Continuous	Bat	Conti*	Bat	Conti	Bat	Conti	Bat	Conti	Bat	Conti	
		*	*	*	*	*	*	*	*	*	*	
Bioreactor		X	X	△	△	X	X	△	△	X	X	
Coagulation-Sedimentation		X	△	X	△	△	△	△	△	△	△	
Ozonation		X	△	X	△	X	△	X	△	X	△	
Activated carbon treatment	EBCT 5min	◎	◎	O	O	◎	◎	O	O	O	◎	
	EBCT 15min	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	
Chlorination		X	◎	X	◎	X	◎	X	◎	X	◎	

X : removal efficiency: < 10%, △ : removal efficiency: 10~40%, O : removal efficiency: 40~70%, ◎ : removal efficiency: > 70%

* : Batch process

**: Continuous process

4. Conclusion

This study surveyed the PFCs pollution sources targeting the influent and effluent of wastewater treatment plants and conducted pilot test with influent to review whether PFCs could be removed by physiochemical methods. The study produced the following results.

1. The influent/effluent removal from the existing biological treatment process showed the removal of some amount of PFNA, PFPeA, and PFHxS, but most of the other items could not be removed through the biological treatment.
2. The correlational analysis results showed that there was a high correlation among PFOA, PFHxA, and PFNA with a carboxyl group in the wastewater. Since the PFCs correlational research did not produce data that could be representative, it was determined that further research would be required.
3. The pilot batch test with the influent to the treatment plant showed that about 10% of PFCs was removed by the injection of 40 to 50mg/L of Alum in the coagulation • sedimentation test. In case of the pilot continuous test, the removal in the ozone test and chlorine injection test was negligible regardless of the amount of injection. The activated carbon adsorption test showed that about 60 to 70% of PFCs were removed after EBCT 5 min, and it was shown to be possible to remove over 90% of PFCs after EBCT 15 min.
4. The pilot test results showed that the PFHxS removal in the single ozone or activated carbon process was low. However, it improved in the continuous process of the ozone process followed by the activated carbon process. This signified that the ozone oxidization would promote the removal of the next process. Therefore, it is determined that the continuous process of the oxidization process, such as the ozone process, followed by an adsorption process using activated carbon would be a desirable process with a high removal.

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