DISTRIBUTION CHARACTERISTICS OF PERFLUOROCARBOXYLATES (PFCAs) AND PERFLUOROALKLYSULFONATES (PFASs) IN INDUSTRIAL WASTEWATER TREATMENT PLANTS IN KOREA

Geum-Ju, SONG[1*], Young-Hoon MOON[1], Jong-Ho JOO[1], A-Yeoung LEE[1], Ki Ho Jeoung[2], Ki-Bong SONG[3], Kwang-Seol SEOK[3]

[1]Institute of Environmental and Energy Technology, POSTECH, Pohang, Kyoung-buk, South Korea; [2]Department of Chemistry, Pusan National University, Pusan, South Korea, [3]National Institute of Environmental Research, Incheon, South Korea

Introduction

Recently, the perfluorinated compounds (PFCs) including perfluorocarboxylates (PFCAs) and perfluoroalklysulfonates (PFASs) are recognized as an important emerging pollutant in the world. Especially, PFCs with long chain structure have a bad influenced on wildlife and humans. PFCs have been produced and used in the worldwide as consumer products for the past five decades but since 2000, their manufacturing and use are reduced and restricted due to the toxicity of PFCs. Therefore, in 2009, perfluorooctanesulfonate (PFOS) and its salts were listed in Annex B of the Stockholm Convention of POPs and their use is restricted. PFCs have properties of persistent organic pollutants (POPs) such as persistent, bioaccumulation and long range transport and distribute in everywhere. PFCAs and PFASs have very high solubility in water and high absorbability in soil or sediment/sludge with high content of organic carbon. Due to those chemical and physical properties, PFCAs and PFASs are normally detected in the industrial wastewater and in the sludge of the treatment plants and the detected compounds were very various according to the plants. The industrial wastewater treated in treatment plants are discharged into a river and the wastewater discharged into a river was one major source of PFCs in river. The treatment plants have no any process to reduce and remove PFCs and in the processes of the plant the high-molecular-weight PFCs could be changed to low-molecular-weight PFCs or reverse because of the chemical and physical properties such as the high solubility in water and high absorbability in soil or sediment/sludge with high content of organic carbon. Therefore, to observe the behavior of PFCAs and PFASs in the process of a plant the influent, effluent and sludge of the 15 industrial wastewater treatment plants in Korea were investigated in this study.

Materials and methods

(1) Plant

There are 46,860 industrial wastewater treatment plants in Korea (2009) and the plants are classified 5 groups based on the treatment capacity with above 2,000m^3/day (class 1), 700-2,000m^3/day (class 2), 200-700m^3/day (class 3), 50-200m^3/day (class 4) and below 50m^3/day (class 5). The plants of classes 4-5 are much more than plants of classes 1-3, but the industrial wastewater was treated above 80% from the plants of classes 1-3 in Korea.

Therefore, to investigate the plants of classes 1-3 were selected and classified industry. The classified industries were the paper and pulp manufacturing industry (plants 1-4), the electricity and electronic industry (plants 5-7), the chemical products manufacturing industry (plants 8-9) and metal products manufacturing industry (plant 10). And also the 5 industrial wastewater treatment plants (plants 11-15) flowing very various industrial wastewater in great industrial complex were investigated.

(2) Target compounds and samples

The target compounds were 8 PFCAs (perfluorohexanoic acid, perfluoroheptanoic acid, perfluorooctanoic acid, perfluorononanoic acid, perfluorodecanoic acid, perfluoroundecanoic acid, perfluorododecanoic acid and perfluorotridecanoic acid) and 3 PFASs (perfluorohexane sulfonate, perfluorooctane sulfonate and perfluorodecane sulfonate). The samples were first influent wastewater, final effluent wastewater and final discharged sludge of each plant.

(3) Sample collection and analysis

The sampling and analysis were based on the Korean Standard Testing Methods (KSTM) for PFCs (ES 10394.1 & ES 10454.1). ES 10394.1 is KSTM for PFCs in influent sewage/wastewater or effluent sewage/wastewater of treatment plant using LC/MS/MS and ES 10454.1 is KSTM for PFCs in soil/sludge/sediment using LC/MS/MS. The sample bottle with polypropylene (PP) was used and the sample was collected 3 times in a day. The samples were keeping in a freezer and analyzed in a week after sampling. To extract of PFCs in samples the solid phase extraction (SPE) and to analyze the isotopes of PFCs as internal standard were used. The analyzer was LC/MS/MS with electro-spray ionization (ESI) and multiple-reaction monitoring (MRM).

Results and discussion

(1) Concentration of PFCs in the influent wastewater

The total concentrations of PFCs (11 target compounds) in the influent wastewater of 15 treatment plants were 4.3-4188.0 ng/L (414.0 ng/L). According to the plant the total concentration of PFCs and the distribution of target compounds in the influent wastewater were very varied. In the influent wastewater of the plants 1-4, PFOA and PFOS were high detected compounds but the first dominant compound and second dominant compound were PFOS and PFOA in the plant 1, PFOA and PFOS in the plants 2 and 3 and PFHxA and PFOA in the plant 4, respectively. In the influent wastewater of the plants 5-7, PFHxA was the first dominant compound and PFHpA was the second dominant compound in the plants. Next followed compound was PFOA in the plants. PFOS was detected very low. In the influent wastewater of the plants 8-9, the total concentration in the influent wastewater of the plant 8 was the most highest and PFOS was above 98%, but the total concentration in the influent wastewater of the plant 9 was the lowest and PFOA was about 64%. In the influent wastewater of the plant 10, PFHxA was above 82% and next followed compound was PFOS (about 8%). In the influent waste

water of the plants 11-15, PFOA was first dominant compound. However, in the influent of the plant 13, PFOS was first dominant compound (about 70%). Therefore, it was estimated that the character of the wastewater flowing into a treatment plant was important factor to decide the total concentration of PFCs and the distribution of target compounds.

(2) Concentration of PFCs in the effluent wastewater

The total concentrations of PFCs (11 target compounds) in influent wastewater of 15 treatment plants were 16.9-7627.3 ng/L (611.4 ng/L). According to the plant the total concentration of PFCs and the distribution of target compounds in the effluent wastewater were very varied. The detected compounds in the effluent wastewater were similar from that in the influent wastewater, but the distribution of compounds in the influent wastewater and effluent wastewater was a little difference. In the effluent wastewater of the plants 1-4, PFOA and PFOS were high detected compounds but the first dominant compound and second dominant compound were PFOS and PFOA in the plant 1, PFOA and PFOS in the plant 2 and PFHxA and PFOA in the plants 3 and 4, respectively. In the effluent wastewater of the plants 5-7, PFHxA was first dominant compound and PFHpA was second dominant compound in the plants. Next followed compound was PFOA in the plants. In the effluent wastewater of the plants 8-9, the total concentration in the effluent wastewater of the plant 8 was the most highest and PFOS was above 99% but the total concentration in the effluent wastewater of the plant 9 was the most lowest and PFOA was first dominant compound and PFOS was second dominant compounds. In the influent wastewater of the plant 10, PFHxA was above 94% and next followed compound was PFOS (about 3%). In the influent wastewater of the plants 11-15, PFOA was first dominant compound in the effluent wastewater of the plants 11, 12, 14. But in the effluent wastewater of the plant 13 PFOS was about 93% and in the effluent wastewater of the plant 15 PFHxA was about 64%. Therefore, it was estimated that the character of the wastewater discharged from a treatment plant was based on the character of the wastewater flowing into a treatment plant. It means that by treatment process or time the PFCs could not be removed, but changed between compounds.

(3) Concentration of PFCs in the sludge

The total concentrations of PFCs (11 target compounds) in the sludge of 15 treatment plants were 0.000-2528.2 ng/g (220.2 ng/g). According to the plant the total concentration of PCFs and the distribution of target compounds in the sludge were very varied. In most plants PFOS was high detected compound and the high-molecular-weight compounds (C8-C11) were detected mainly in most plants. The detected compounds and distribution of compounds in the sludge were very dissimilar from that in the influent and effluent wastewater. Therefore, it was estimated that the character of the sludge discharged from a treatment plant was not based on the character of the wastewater flowing into a treatment plant, but the physical and chemical properties of PFCs. In other words, it was guessed that during the treatment of wastewater in a plant the PFCs were changed or

reacted in the solid-phase. It means that by treatment process or time the PFCs could not be removed, but changed between compounds.

References

1. Ministry of Environment of Korea. (2010) *The Korean Standard Testing Method of POPs.*
2. Ministry of Environment of Korea. (2010) *Statistical data of the industrial wastewater in Korea*.
3. OECD (2002) *Hazard Assessment of Perfluorooctane Sulphonate (PFOS) and Its Salts*.
4. OECD (2006) *OECD Workshop on Perfluorocarboxylic acids (PFCAs) and Precursors*.
5. Alexander G. P., Kevin C. J., Andrew J. S. (2009) *Environ Sci Technol*. 43: 386-392.
6. Armiatage J. M., Schenker U., Scheringer M., Martin J. W., Macleod M., Cousins I. T. (2009) *Environ Sci Technol*. 43: 9274-9280.
7. Alexander G. P., Kevin C. J., Andrew J. S. (2009) *Environ Sci Technol*. 43: 386-392.
8. Bossi R., Strand J., Sortkjar O., Larsen M. (2008) *Environ Int.* 34: 443-450.
9. Clara M., Scheffknecht C., Scharf S., Weiss S., Gans O. (2008) *Water Science Technology* 58: 59-66.
10. Ellis D. A., Cahill T.M., Mabury S. A., Cousins I. T., Mackay D. (2002) *In Handbook of environmental Chemistry* 63-83.
11. Higgins C. P., Jennifer A. F., Criddle C. S., Luthy R. G. (2005) *Environ Sci Technol*. 39: 3946-395.
12. Loganthan B. G., Sajwan K. S., Sinclair E., Kannan K. (2007) *Water Research* 41: 4611-4620.
13. Sinclar E., Kannan K. (2006) *Environ Sci Technol.* 40: 1408-1414.
14. Yu J., Hu J., Tanaka S., Fujii S. (2009) *Water Research* 43: 2399-2408.