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SPECIAL FEATURE: ORIGINAL ARTICLE

Residual organic fluorinated compounds from thermal treatment of PFOA, PFHxA and PFOS adsorbed onto granular activated carbon (GAC)

Nobuhisa Watanabe[1] · Shusuke Takemine[2] · Katsuya Yamamoto[3] ·
Yuki Haga[3] · Mitsuyasu Takata[4]

Abstract Perfluorooctanoic acid (PFOA), perfluorohexanoic acid (PFHxA) and perfluorooctane sulfonate (PFOS) adsorbed onto granular activated carbon (GAC) were thermally treated in N_2 gas stream. The purpose was to assess the fate of perfluoroalkyl and polyfluoroalkyl substances (PFASs) during thermal regeneration of GAC, which had been used for water treatment. Mineralized F, residual PFASs including short-chained species, and volatile organic fluorine (VOF) were determined. In a temperature condition of 700 °C, VOF were 13.2, 4.8, and 5.9 % as for PFOA, PFHxA, and PFOS. However, the VOF decreased to 0.1 %, if the GAC and off-gas were kept at 1000 °C. No PFASs remained in GAC at 700–1000 °C; at the same time, short-chained PFASs were slightly detected in the aqueous trapping of off-gas at 800 and 900 °C conditions. The destruction of PFASs on GAC could be perfect if the temperature is higher than 700 °C; however, the process is competitive against volatile escape from GAC. Destruction in gaseous phase needs a temperature as high as 1000 °C. Destruction of PFASs on the surface of GAC, volatile escape from the site, and thermolysis in gas phase should be considered, as to thermal regeneration of GAC.

✉ Nobuhisa Watanabe
  nobuhisa.watanabe@oit.ac.jp

1 Osaka Institute of Technology, Ohmiya 5-16-1, Asahi-ku, Osaka 535-8585, Japan

2 Center for Environmental Science in Saitama, Kamitanadare 914, Kazo, Saitama 347-0115, Japan

3 Hyogo Prefectural Institute of Environmental Sciences, Yukihira-cho 3-1-18, Suma-ku, Kobe, Hyogo 654-0037, Japan

4 Towa Technology Co., Hirose-kitamachi 3-11, Naka-ku, Hiroshima 730-0803, Japan

Introduction

Environmental occurrence of perfluoroalkyl and polyfluoroalkyl substances (PFASs) [1] is widely reported in aquatic environments [2, 3]. PFASs have been used as water and oil repellents, fire-fighting foam, etc., since the 1950s; however, the environmental pollution by them was evidenced as late as the twenty-first century. Representative PFASs found as pollutants on the first stage are perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), which are thought to be stable forms originated from various PFASs. Currently, PFOS has been listed in the table of POPs treaty, and PFOA has been nominated there. After that short-chained PFASs, such as a perfluorohexanoic acid (PFHxA), are now prevailing [4].

Used PFASs may enter waste and sewage treatment system. The residue of those treatments gets together at a landfill site, which in turn can be important secondary sources of pollutants [5–8]. Neither biological water treatment nor sand-filtration could remove PFASs from landfill effluent water, whereas adsorption technique using granular activated carbon (GAC) was effective [9]. However, a breakthrough of GAC occurs after long usage; subsequently, the exhausted GAC are to be regenerated by a thermal treatment. Mineralization of PFASs through thermal process has been predicted [10–12] and evidenced [13]; however, partial missing of organic F may be possible [4, 12], since the mass balance of mineralized F was not perfect [13].

Destruction of PFOA and PFOS has been studied through sonolytic [14], mechanochemical [15], photolysis

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[16], and thermal processes [13, 17]. A recent study about mineralization of PFOA by radical attack induced by radioactivity revealed that PFOA is susceptible to alkaline condition to show stepwise degradation [18]. It has been viewed that PFOS is more persistent than PFOA in chemical attacks [10, 14, 15].

The question then arises whether PFASs are completely destructed or not during GAC regeneration. A real GAC regeneration facility which we have visited was a thermal treatment in a rotary kiln. GAC was gradually heated by O_2-poor combustion in the kiln, where the final temperature was ca 900 °C. The off-gas was washed with water; therefore, insoluble organic F would be released to the atmosphere.

The present study concerns residual organic F including short-chained PFASs and volatile organic F(VOF). The determination of VOF was carried out with adsorptive collection-thermal desorption followed by emission spectroscopy, which has been devised for determination of F, Cl, and Br in gaseous samples [19, 20], and has been employed for the monitoring of surrogates for dioxins [21, 22] in municipal solid waste incinerators. Granular activated carbon which adsorbed PFOA, PFHxA, and PFOS in advance was thermally treated in a stream of N_2 gas. Determination of mineralized F, short-chained PFASs, and VOF could suggest preferable destruction condition for PFASs.

Experimental

Reagent

Three PFASs reagents: PFOA (Wako pure chemical, >95 %), PFHxA (Fluka, >97 %), and PFOS potassium salt (Fluka, >98 %) were used as samples for thermal treatment experiment. The residue was analyzed referring mixed

PFASs standard (PFAC-MXB, Wellington). Granular activated carbon was identical with one used in a real effluent treatment system (Filtrasorb 300, Calgon Carbon).

### Adsorption of PFASs onto GAC

Every PFAS was separately adsorbed to GAC prior to the thermal treatment experiment. The procedure was same with our previous work [23]. Briefly, GAC was gently contacted to an aqueous solution of PFASs; afterward, complete adsorption was checked by analyses of remaining water and the inner surface of the container. The concentration of PFASs in GAC was 10 mgPFASs g^{-1}: this corresponds to 6.9 mgF g^{-1} for PFOA, 6.7 mgF g^{-1} for PFHxA, and 6.0 mgF g^{-1} for PFOS.

Thermal treatment of PFASs adsorbed on GAC

The instrumentation of thermal treatment and gas collection is described in Fig. 1. The quartz tube (id of 20 mm, length of 1200 mm) was inserted into a furnace whose heated span was 300 mm. Nitrogen gas was provided from gas bag connected to the inlet. The off-gas from the quartz tube was introduced to aqueous trapping (deionized water of 50 mL), ice-cooled dehumidifier and the collection of VOF. The gas was suctioned by a pump set after the VOF collection, which consisted of a column of Tenax TA (0.3 g, coverage of boiling point was 100–250 °C) and Carboxen 569 (0.3 g, 50–100 °C). The definition and range of boiling point of VOF are identical with that of volatile organic compounds (VOC) by World Health Organization (WHO) [24].

Fifty mg of GAC involving PFASs (ca 330 µgF) mounted on a ceramic boat was inserted in a quartz tube at the region of room temperature. Providing N_2 gas at a rate of 1.5 L min^{-1} for 2 min, the atmosphere in the quartz tube was replaced by N_2; afterward, the boat was inserted

Fig. 1 Sample PFASs adsorbed onto GAC was mounted on a ceramic boat, which was heated in a stream of N_2 gas. Off-gas was introduced to aqueous trapping, ice-cooled dehumidifier and adsorptive collection of volatile organic fluorine (VOF)
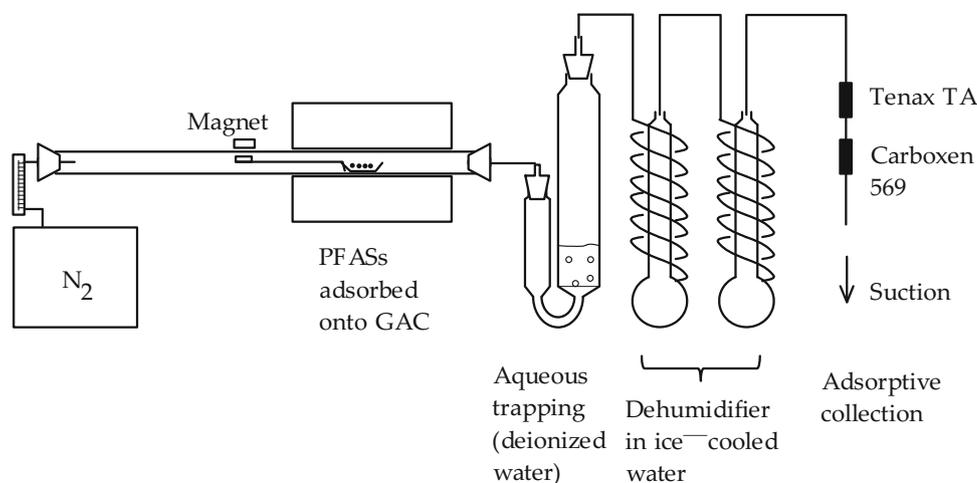
into the center of the furnace and kept there for 10 min. The experiment was conducted in triplicate for a temperature condition.

Analyses

Collected analytical samples are summarized in Table 1. The aqueous trapping of off-gas and GAC was analyzed for mineralized F and PFASs [12, 23]. When the mounted sample was PFOA and PFHxA, analyzed PFASs were perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), PFHxA, perfluoroheptanoic acid (PFHpA), and PFOA, whose quantification limits were 0.05 µgF for each compound. For the experiment of PFOS, analyzed PFASs were perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate(PFHxS), and PFOS, the quantification limit of which was 0.1 µgF for each compound. The quartz tube, ceramic boat, and GAC were rinsed with deionized water of 30 mL, which was also analyzed for mineralized F and PFASs. The GAC was furthermore extracted with methanol and analyzed for PFASs.

The adsorbent tubes for VOF, i.e., Tenax TA and Carboxen 569, were thermally desorbed and determined separately. The instrumentation of the spectroscopy is described elsewhere [19–21, 25]. To enhance the sensitivity of F, a narrow aluminum SSA-S tube was used as the electric discharge tube [26]. The quantification limit was 0.3 µgF for each analysis.

Results and discussion

Mass balance

The overall mass balance including mineralized F, PFASs, and VOF after the thermal treatment of PFOA, PFHxA, and PFOS are depicted in Figs. 2, 3, and 4. Mineralized F found in the aqueous trapping of off-gas was predominant. The second majority was VOF in the low-temperature conditions. However, it became less than 0.1 % with 1000 °C. A slight amount of short-chained PFASs (less than 0.1 % in 800 and 900 °C conditions) was detected only in the off-gas. No PFASs was found in either quartz furnace rinse or GAC extract. The overall recovery rates increased with the temperature being 81.4, 82.6, and 88.2 % for PFOA, PFHxA, and PFOS at the highest.

The loss of F was supposedly due to adsorption and reaction of F compounds with the inner surface of the quartz tube. The amount of mineralized F in the aqueous trapping varied by 30 %. The fluctuation could be decreased using a new quartz furnace. In a preliminary study, overall recovery rate increased in accordance with gas flow rate. If the N_2 gas stream was set lower than 500 mL min^{-1} like the previous study [25], the overall recovery rate of F was very poor. Fluorine compounds react with quartz glass more intensively than Cl and Br. A higher N_2 stream rate was preferable to raise the recovery; however, entrained water from the aqueous trapping reached VOF collection tubes and interfered with VOF

Table 1 Analytical samples from thermal treatment of PFASs adsorbed onto GAC

|	Mineralized F	PFASs	Volatile organic fluorine (VOF)	
			Tenax TA	Carboxen 569
Aqueous trapping of off-gas	X	X		
Aqueous rinse of quartz tube and GAC	X	X		
Methanol extraction of GAC		X		
Adsorptive collection of off-gas			X	X

Target substances are obtained from the samples denoted by symbol X
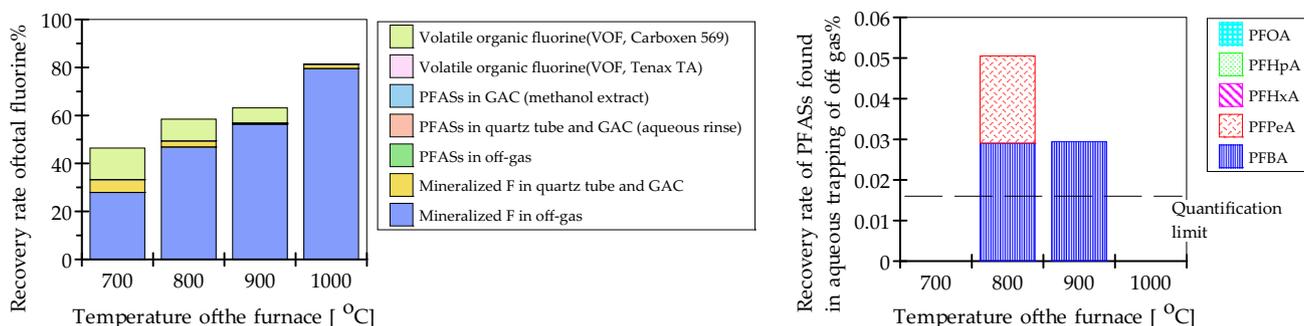
Fig. 2 Mineralized F, PFASs and VOF after the thermal treatment of PFOA in a N_2 stream. Residual PFASs were detected only in aqueous trapping of off-gas, whereas no PFASs remained either quartz tube or GAC
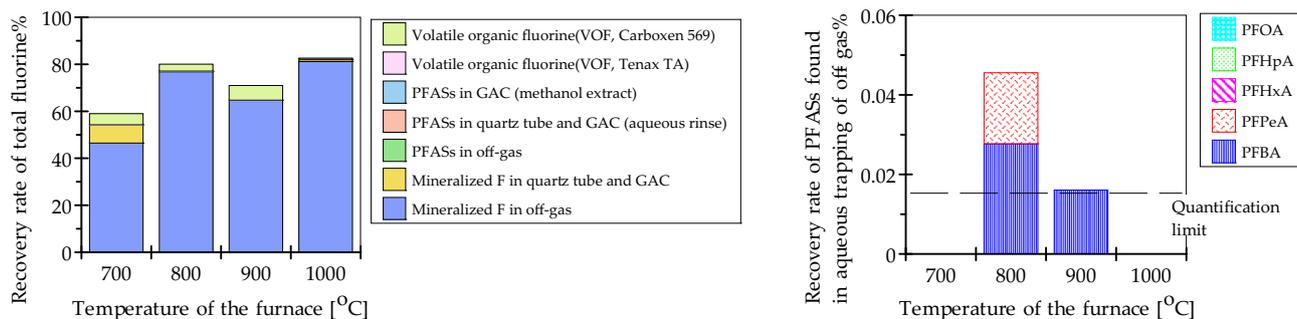
Fig. 3 Mineralized F, PFASs and VOF after the thermal treatment of PFHxA in a N_2 stream. Residual PFASs were detected only in aqueous trapping of off-gas, whereas no PFASs remained either quartz tube or GAC
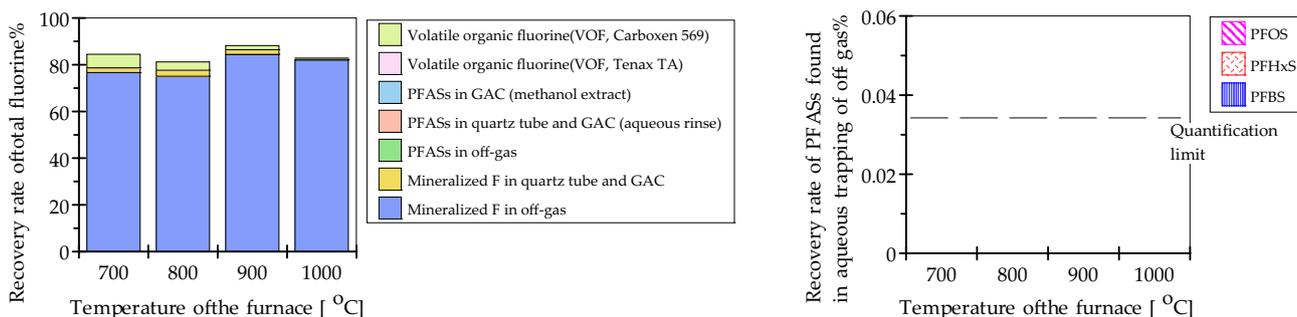
Fig. 4 Mineralized F, PFASs and VOF after the thermal treatment of PFOS in a N_2 stream. No residual PFASs had remained

determination. The employed flow rate of 1.5 L min^{-1} was set to compromise the overall recovery rate and VOF determination. To minimize the adverse effect of entrained water on VOF determination, double-dried condensation traps in an ice-cooled bath were used as the dehumidifier. The obtained VOF values were within 20 % error in the experiments with 700–900 °C conditions. Trace levels found in 1000 °C varied more.

Formation of unidentified organic F should be remarked from the low recovery rate, which was significant in the experiment of PFOA at relatively lower temperature. Those compounds were expected to be collected in the aqueous trapping. As stated before, real GAC regeneration facilities is equipped with off-gas washing device; hence, such soluble organic F will not be released to the atmosphere. However, analytical efforts to identify those organic F should be furthered; at the same time, searching for an optimum condition to raise mineralization efficiency is also in progress.

Volatile organic fluorine (VOF) and PFASs

The rate of VOF from PFOA and PFOS was the highest at 700 °C; they were 13.2 and 5.9 %, respectively. The rate decreased in accordance with temperature, namely they resulted in 0.1 % at 1000 °C.

However, low-carbon organic F species can be more stable than larger ones. As much as 6.3 and 0.6 % of VOF has survived 900 and 1000 °C in the experiment with PFHxA; moreover, residual PFASs found in the aqueous trapping were short-chained species, namely 0.098 µgF of PFBA (C_4 compound) and 0.073 µgF of PFPeA (C_5 compound) were detected from 342 µgF of PFOA on GAC heated at 800 °C. It suggests a stepwise dissociation of the carbon chain. Considering all VOF distributed to Carboxen 569 (boiling point range is ca 50–100 °C) while no VOF was detected from Tenax TA (ibid. >100 °C), relatively larger organic F compounds could not survive the condition whereas smaller species could do.

It should be noted that most stable C–F compounds have high values of global warming potential (GWP). Complete destruction of PFASs and other C–F compounds is important in the viewpoint of climate change.

Degradability of organic F in thermal condition with or without oxygen

In a laboratory study, PFOA could be combusted to yield no remaining PFASs at 700 °C [27]. From an observation of a real facility incinerating PFASs-containing materials, sufficient destruction of PFASs was proven [14]. Besides, C–Cl–F compounds destruction in cement kiln [28] and

industrial waste incinerator [29] have been reported. Subsequently, the thermal oxidation processes have the higher ability to decompose those compounds than the non-oxidative process in N_2.

In the present study, generated VOF was several percents of initial PFASs at 800 and 900 °C, suggesting incomplete destruction. However, 1000 °C condition could decrease VOF significantly.

Comparison with organic Cl is also interesting. Duvall et al. [30] investigated degradability of 2, 2′, 4, 5, 5′-pentachlorobiphenyl with or without O_2. At 700 °C in air, half of pentachlorobiphenyl remained. In nitrogen, 40 % of the initial compound remained even at 900 °C, namely pentachlorobiphenyl is more stable than PFOA in thermal condition. Although C–F bond is stronger than C–Cl bond, the difference might not be so large as to thermal reactivity.

Suppression of volatile escape of PFASs from GAC

No PFASs remained in GAC in all temperatures conditions, while no PFASs were detected in off-gas at the temperature of 700 °C. It suggests that PFASs on the surface of GAC is completely destructed, at the temperature as low as 700 °C. However, on the other hand, short-chained PFASs were detected in off-gas aqueous trapping at 800 and 900 °C. The source of those PFASs in off-gas is expected to be any quick release of PFASs from GAC before they are destructed.

In thermal destruction, not only reaction on the site but also volatile release from there must be taken into account. In previous reports comparing the degradability of PFOA and PFOS under aqueous ultrasonic irradiation [14] and mechanochemical ball milling [15], PFOS was considered to be more persistent than PFOA. However, volatile missing of PFOA from heated zone may result in incomplete destruction. In other words, PFOS is easier to be destructed than PFOA by the thermal process. Destruction and volatile release are in competition on the surface of GAC. The same discussion is true of PFHxA. Destruction in gaseous phase can be completed at 1000 °C, because no PFASs were detected and VOF was near the quantification limit. Even if volatile PFOA and PFHxA are missed from GAC, thermal condition as high as 1000 °C could complete destruction in the gaseous phase. Hence, an ideal thermal destruction should have two stages: GAC is kept hold in 700 °C condition whose off-gas is introduced to high-temperature zone as high as 1000 °C. The condition in the real GAC regeneration plant which we have visited may resemble it. An optimum condition to destruct PFASs could be achieved by slow GAC heating to keep PFASs held on GAC until it is thermally destructed. Further investigation is in progress.

Conclusion

Thermal susceptibility of PFASs was evidenced; however, gaseous organic F can be emitted, if the temperature is lower than 900 °C. The potency of the gaseous organic F emission was in the rank order of PFOA > PFHxA > PFOS. No organic F was detected at 1000 °C. If PFASs is kept adsorbed onto GAC, the destruction on the site takes place at 700 °C. However, the reaction is in competition with volatile release from GAC; in other words, some fragmented organic F are released before they are mineralized. Non-volatile PFOS cannot escape from heated zone; thereby, PFOS is easier to be destructed than PFOA and PFHxA.

The results of the present study can suggest a practical treatment method for water contaminated with PFASs. They are adsorbed onto GAC, which is regenerated by a thermal process. A preferable regeneration process is to keep GAC at relatively low temperature, e.g., 700 °C; at the same time, the off-gas is introduced into a high-temperature zone as high as 1000 °C.

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