

REMOVAL CHARACTERISTICS OF PFOS AND PFOA BY GRANULAR AND POWDER ACTIVATED CARBONS IN COMPOSITE SAMPLES

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Abstract

This paper focuses on a removal characteristics of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) by granular and powder activated carbons in composite samples. 100 mL PFOS and PFOA solution (50 mg/L, 100 µg/L, and 100 ng/L) was added into a bottle with phosphate buffer and activated carbons suspension. Bottles were set in a thermo shaker with constant temperature (25 °C), pH 7.0, and the shakeing speed of 120 rpm. The main conclusions obtained in this study are as follows: 1) Experimental results were described by a Freundlich-model equation. Adsorption capacity of PFOS was bigger than it of PFOA. 2) Adsorption on powder activated carbons (PAC) was from 20 to 100 µg/mg for PFOS, and from 10 to 200 µg/mg for PFOA, respectively. 3) DOM prevented PAC of adsorbing PFOS and PFOA.

Introduction

PFOS and PFOA are fully fluorinated organic compounds and synthetic surfactants used in a variety of industrial applications. They are able to enter into water environment and might cause diverse toxic effects on wild organisms as well as human being. Some researchers^{1,2} focus on removal methods of PFOS, PFOA and their related compounds in the laboratory. Main objective of this study is to understand a removal capacity of PFOS and PFOA by granular activated carbons (GAC) and powder activated carbons in environmental composite water samples.

Materials and Methods

Impurities were removed from activated carbons by a procedure (shown in Fig. 1). First, activated carbons were washed by *Mili-Q* water, then they were washed by heated water for two hours in a water bath in order to remove impurities in fine pores. After they had been kept in a dry oven for two days, they were crushed by a mortar and were screened. After activated carbons by screened with optional particle sizes were washed about ten times by *Mili-Q* water, they had been kept with 105 °C in a dry oven for two days. Finally, after they were weighed, they were kept in *Mili-Q* water in order to remove air in fine pores by a vacuum pump.

Filtrisorb 400 (© Calgon Mitsubishi Chemical) was used in this research work. Activated carbons (which particle sizes were from 1.0 mm to 1.4 mm) were defined as GAC, and activated carbons (which particle size were smaller than 0.075 mm) were defined as PAC. A particle size distribution of PAC was

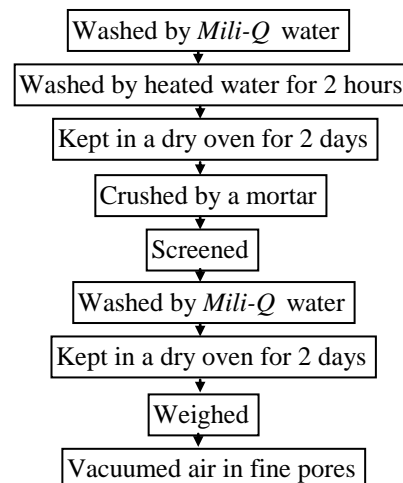


Fig.1 A procedure of impurities removal from activated carbons

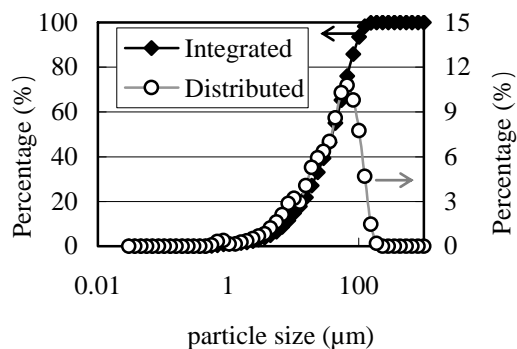


Fig.2 A particle size distribution of PAC

Table 1 Surface area of activated carbons

Type	GAC	PAC
Surface area (by Multipoint BET method)	1122	1099
Volume of fine pores (less than 777)	0.585	0.556

(m²/g)

Table 2 Primary Concentrations in batch experiments

	High	Middle	Low	
Primary PFOS, PFOA	50 mg/L	100 µg/L	100 ng/L	
Activated Carbons (GAC, PAC) (mg/L)	20 1,000	0.1 4.0	0.01 1.0	Lowest Highest
Phosphate Buffer (N)	0.02	0.001	0.00004	

measured by a laser diffraction particle size analyzer (SALD 2100 © Shimadzu) as shown in **Fig. 2**. There was a peak in a range from 50 µm to 70 µm, and the smallest size was 0.45 µm. Specific surface areas of GAC and PAC were measured by an accelerated surface area and porosimetry system (ASAP 2020 © Shimadzu) as shown in **Table 1**. GAC and PAC in this research had similar specific surface area.

Figure 3 shows a procedure of PFOS and PFOA removal experiment by activated carbons. First, PFOS (CF₃(CF₂)₇SO₃⁻, Wako 508-53921) and PFOA (CF₃(CF₂)₆COO⁻, Wako 163-09542) were solved in Methanol (PFOS, 5 mL, PFOA, 5 mL). **Table 2** indicates a summary of batch experiments. After 100 mL PFOS and PFOA solution which concentration was set in three levels (50 mg/L, 100 µg/L, and 100 ng/L) was added into a bottle (which volume was 125 mL, 125 mL, and 1,000 mL) made from polypropylene, phosphate buffer (0.02 N, 0.001 N, and 0.00004 N) and activated carbons suspension (which concentration was in the range from 20 to 1,000 mg/L, from 0.1 to 4.0 mg/L, and from 0.01 to 1.0 mg/L) were added in this bottle. Bottles were set in a thermo shaker (NTS-1300s) with constant temperature (25 °C), pH 7.0, and the shaking speed of 120 rpm as shown in **Fig. 4**. Batch experiments were carried out in this condition.

In case of 50 mg/L solutions (high concentration), a sample was diluted by *Mili-Q* water in order to be in the range from 1 to 100 µg PFOS and PFOA/L. In case of 100 µg/L solutions (middle concentration), a sample was measured. In case of 100 ng/L solutions (low concentration), a sample (about 1 L) was filtered with a glass fiber filter, and was loaded at a flow rate of 10 mL/min right onto a cartridge (*Presep-C Agri*, Wako, Japan), which was conditioned with methanol followed by *Mili-Q* water rinsing right before the loading. The cartridge was then eluted with methanol. Finally, exact 1 mL of extract was collected for HPLC measurement.

A 10 µL sample of each extract was applied to an Agilent Zorbax XDB C-18 column at a flow rate of 0.1 mL/min. The mobile phase consisted of 10 mM ammonium acetate and acetonitrile. The HPLC system was interfaced to TSQ

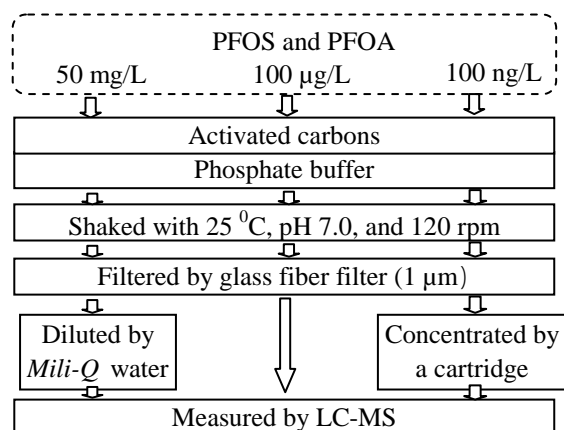


Fig. 3 A procedure of PFOS and PFOA removal experiments by activated carbons

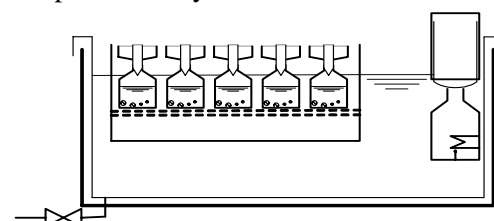


Fig. 4 Configuration of batch experiments

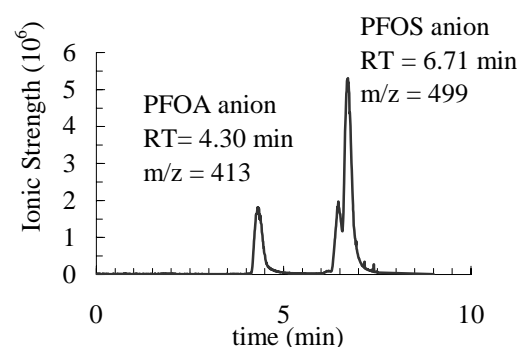


Fig. 5 Mass chromatograph of 100 µg/L PFOS and PFOA standard solution

7000 (ThermoQuest, USA), atmospheric pressure ionization tandem mass spectrometer, operating in the electrospray negative mode. **Figure 5** shows a chromatographic identification of PFOS and PFOA. Quantification was based on selected ion monitoring mode detecting single product ions: $C_8F_{17}SO_3^-$ (m/z 499) for PFOS and $C_7F_{15}CO_2^-$ (m/z 413) for PFOA.

Results and Discussion

Figure 6 shows a removal ratio of PFOS and PFOA in high concentration level (50 mg/L) experiment by GAC and PAC. 1,000 mg/L PAC removed PFOS (more than 99 %) and PFOA (more than 98 %) within 30 minutes. In case of GAC, it took two hours to remove 99 % PFOS. More than 90 % PFOA was removed by shaking for 72 hours. Removal ratio of PFOS was higher than it of PFOA. Amount of activated carbons had effects on removal ratio.

Figure 7 shows a relationship between PAC concentration and PFOS and PFOA concentration after shaking for 72 hours in middle concentration level (100 µg/L) experiment. In *Mili-Q* water, PAC concentration was related to the equilibrium concentration. In case of 100 µg/L PFOS and PFOA solution, 2.0 mg/L PAC removed 87 % PFOS and 20 % PFOA, and 4.0 mg/L PAC removed 81 % PFOA. A similar experiment was carried out in lake water. After lake water was filtered by glass fiber filter, it was added to a bottle instead of *Mili-Q* water. As the result, removal ratio of PFOS and PFOA by PAC decreased significantly as shown in **Fig. 7 (b)**. 4.0 mg/L PAC removed 70 % PFOS and 34 % PFOA. PFOS and PFOA might be adsorbed on surface of dissolved natural organic matter (DOM) in lake water, and DOM might decrease an adsorption capacity of PAC. When we develop a removal equipment by activated carbons, DOM concentration should be focused.

Figure 8 shows a relationship between PAC concentration and PFOS and PFOA concentration after shaking for 72 hours in low concentration level (100 ng/L) experiment. Less than 0.25 mg/L PAC was not able to remove trace PFOS and PFOA.

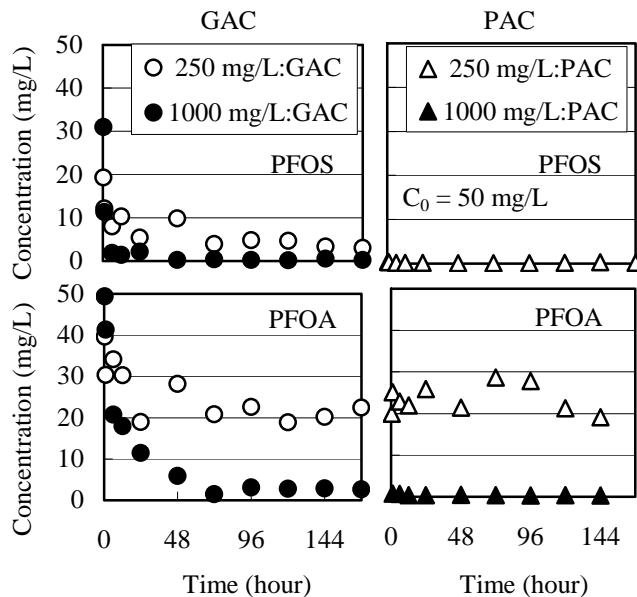


Fig. 6 Removal ratio of PFOS and PFOA on granular and powder activated carbons

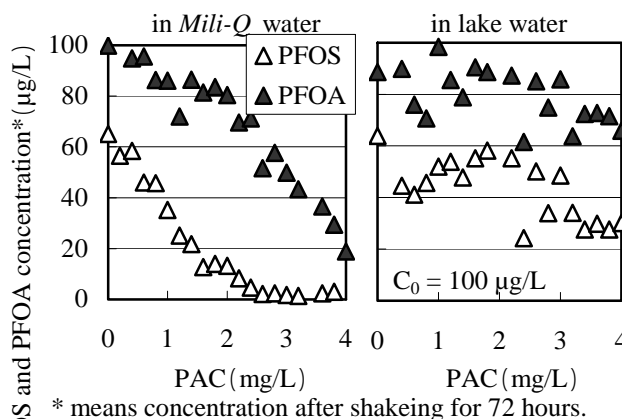


Fig. 7 A relationship between PAC concentration and PFOS and PFOA concentration after shaking for 72 hours

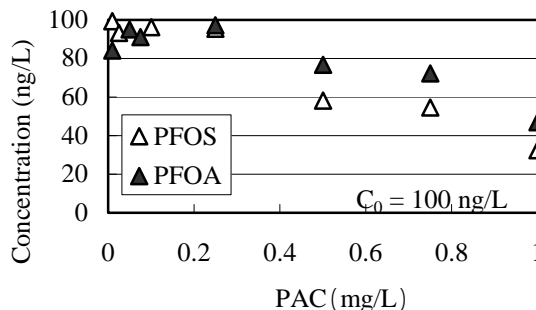


Fig. 8 A relationship between PAC concentration and PFOS and PFOA concentration after shaking for 72 hours in *Mili-Q* water

1.0 mg/L PAC removed 77 % PFOS and 53 % PFOA.

In order to examine a relationship between an adsorption capacity of activated carbons and PFOS and PFOA equilibrium concentration in liquid phase, adsorption isotherms in *Mili-Q* water were shown in Fig. 9. Adsorption on PAC was from 20 to 100 µg/mg for PFOS, and from 10 to 200 µg/mg for PFOA, respectively. The Freundlich model,

$$Q = k C_f^{(1/n)}$$

Where k and n are Freundlich constants, which correlated to the maximum adsorption capacity and adsorption intensity, respectively. This experimental results were described by a Freundlich-model equation. Adsorption capacity of PFOS was bigger than it of PFOA.

Figure 10 shows adsorption isotherms of PFOS and PFOA on powder activated carbons in PFOS and PFOA composite samples. Adsorption capacity of PFOS on PAC decreased a little compared with it in *Mili-Q* water. In case of PFOA, adsorption capacity was in the range from 7 to 25 µg/mg. It might be because an adsorption rate of PFOS was more rapidly than it of PFOA.

Adsorption isotherms of PFOS and PFOA on powder activated carbons was shown in Fig. 11 in PFOS and PFOA composite samples in lake water. These results indicates that PAC did not remove PFOS and PFOA very much in environmental water. Concentration of PFOS was from 30 to 60 µg/L after shakeing for 72 hours. In case of PFOA, it was from 70 to 90 µg/L. DOM might prevent PAC of adsorbing PFOS and PFOA. As a further study, continuous experiments will be required.

Acknowledgements

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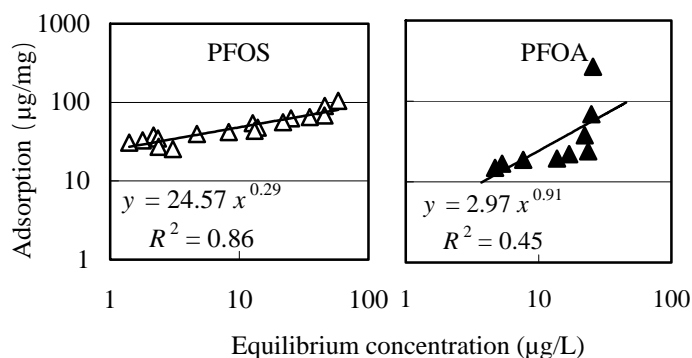


Fig. 9 Adsorption isotherms of PFOS and PFOA by powder activated carbons in *Mili-Q* water

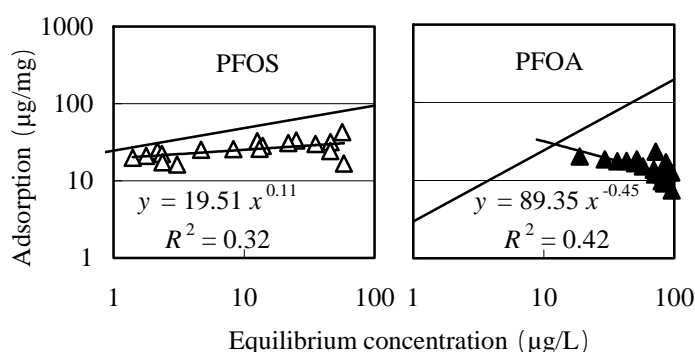


Fig. 10 Adsorption isotherms of PFOS and PFOA by powder activated carbons in PFOS and PFOA composite samples

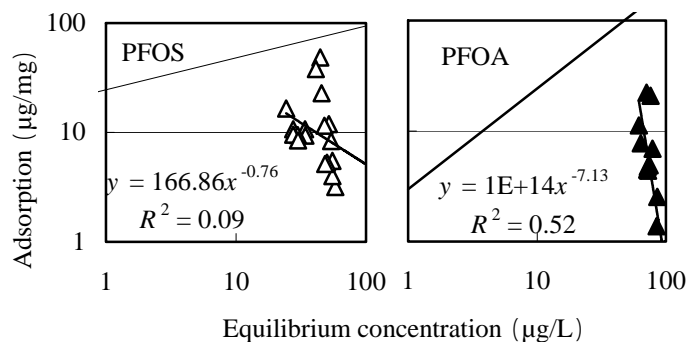


Fig. 11 Adsorption isotherms of PFOS and PFOA by powder activated carbons in PFOS and PFOA composite samples in lake water