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Effect of soil organic matter on the plant uptake of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in lettuce on granular activated carbon applied soil

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Abstract

The presence of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in crops is an important consideration for food safety. The soil organic matter (SOM) content may affect the adsorption potential of PFOA and PFOS in water and soil and their subsequent uptake in crops. To better understand these dynamics, the adsorption and uptake of PFOA and PFOS in lettuce was investigated using granular activated carbon (GAC)-treated soils with varying SOM content. The adsorption potential of GAC was investigated, with maximum adsorption capacities for PFOA and PFOS calculated to be 9.091 mg g^{-1} and 27.778 mg g^{-1}, respectively. These values decreased to 5.208 mg g^{-1} and 17.241 mg g^{-1}, respectively, after the addition of 0.04 wt.% humic acid. The average plant uptake factor (PUF) in low and high perfluoroalkyl and polyfluoroalkyl acid (PFAA)-contaminated soils with 4.0 wt.% SOM was restricted to 0.353 for PFOA and 0.108 for PFOS. The PUFs were approximately two times lower than those for soil with 2.6 wt% SOM. Addition of 1 wt% GAC to the soil successfully reduced the PUF by up to 99.4%, with values of 0.006 (PFOA) and 0.005 (PFOS) in 2.6 wt% SOM treated soil and 0.079 (PFOA) and 0.023 (PFOS) in 4.0 wt% SOM treated soil. Although the PUF in the GAC-treated soil was drastically decreased, the PUF of the soil with 4.0 wt% SOM was at least four times higher than that with 2.6 wt% SOM. Therefore, SOM content is an important consideration in the remediation of PFOA and PFOS contaminated farmland soil using carbonaceous adsorbent.

Key words: Soil organic matter (SOM), carbonaceous adsorbent, perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), lettuce, plant uptake

Introduction

Perfluoroalkyl and polyfluoroalkyl acids (PFAAs) are widely used in industrial and consumer products, as they are anti-static, flame retardant, and waterproof (Jian et al., 2017; Mahinroosta and Senevirathna, 2020). Long-chained PFAAs such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) have reportedly demonstrated high physicochemical stability and bioaccumulation rates with potent toxicity. PFOA, PFOS, and their precursors were listed as persistent organic pollutants (POPs) by the Stockholm Convention; hence, their use is being phased out globally (Ghisi et al., 2019; Kim et al., 2015; Seong et al., 2019; Weber et al., 2019; Stockholm Convention, 2019). However, being highly persistent, PFAAs are frequently detected even in remote regions (Guo et al., 2016; Jian et al., 2017; Perez et al., 2014; Sungur, 2018). Recent research has indicated that PFAAs are present in sub part-per-billion (ppb) concentrations of 88.7% in farmland soil in Korea (Choi et al., 2017). Furthermore, for humans, the major sources of exposure to PFAAs are the PFOA and PFOS residues present in food, particularly protein-rich foods, such as meat, dairy, and fish (Brambilla et al., 2015; Ghisi et al., 2019; Heo et al., 2014; Xiang et al., 2020). In addition, the uptake and accumulation of PFAAs in crops could be an important pathway for their accumulation in animal feed and food (Choi et al., 2018; Eun et al., 2020; Ghisi et al., 2019; Liu et al., 2017; Luo et al. 2019; Sungur, 2018; Wen et al., 2018; Xiang et al., 2020). Bioaccumulation factors (BAFs) of PFAAs in crops have been widely reported. Reported BAFs for PFOA in different crops are: 0.004-0.006 in $\text{rice}_{\text{grain}}$, 0.435 in $\text{rice}_{\text{whole}}$, 0.02 in $\text{corn}_{\text{fruit}}$, 0.111-2.821 in spinach, 0.12 in wheat, 0.154 in parsley, 0.252-6.6 in lettuce, 0.26-1.349 in carrot, 0.256-0.962 in Welsh onion, 0.355 in plum, and 0.592 in white cabbage. Similar BAFs have been reported for PFOS: 0.002-0.003 in $\text{rice}_{\text{grain}}$, 0.057 in $\text{rice}_{\text{whole}}$, 0.017-0.181 in Welsh onion, 0.048-3.175 in spinach, 0.067 in parsley, 0.086 in white cabbage, 0.181-1.071 in carrot, 0.286-0.65 in lettuce, and 0.96 in corn

(Bizkarguenaga et al. 2016; Choi et al. 2018; Choi et al. 2020; Lee et al. 2020; Ghisi et al. 2019; Liu 2017; Navarro et al. 2017; Xiang et al. 2018). Although BAFs in crops are generally lower than those in animals, the dietary exposure of PFAAs from crops was high enough to almost reach the revised reference doses (RfD) for PFOA and PFOS as stipulated by European Food Safety Authority (EFSA) (Choi et al. 2020). Therefore, PFAA residues in crops should be strictly controlled and monitored to reduce human health risks from translocation and bioaccumulation of PFAAs in animal feed and food.

Remediation techniques including conventional thermal and physicochemical treatments, have been successfully applied to remove PFOA and PFOS residues from farmland soils. However, incineration, sonication with water-extraction, and chemical treatments (oxidation/reduction), are difficult to apply cost-effectively on large agricultural scales (Mahinroosta and Senevirathna, 2020; Santos et al., 2016). Recently, carbonaceous adsorbents such as activated carbon (AC) and biochar have been considered as alternative physicochemical treatment agents. They have helped to immobilise organic pollutants with AC shown to adsorb over 90% of the leaching PFAAs in soil (Choi et al., 2018; Hale et al., 2017; Kupryianchyk et al., 2016; Silvani et al., 2019; Zhang et al. 2019). Carbonaceous adsorbents can also bring added benefits such as carbon sequestration and improvement of physicochemical soil properties (Jakob et al. 2012; Mahinroosta and Senevirathna, 2020; Xia et al. 2020). While adsorption properties of carbonaceous adsorbents for PFAAs in water and soil have been investigated, studies regarding the relationship between adsorption of carbonaceous adsorbents and crop-uptake of PFAAs are limited (Askeland et al., 2020; Hale et al., 2017; Kupryianchyk et al., 2016; Xiao et al., 2017; Zhang et al., 2019).

The plant uptake of PFOA/PFOS depends on crop cultivars, soil properties, and environment parameters such as humidity, light-conditions, and temperature (Blaine et al., 2013; Eun et al., 2020; Ghisi et al., 2019; Navarro et al. 2017; Xiang et al., 2018; Xiang et al., 2020). Among them, soil organic matter (SOM) and humic acid (HA) content both affect the adsorption on soil, and the crop-uptake of PFAAs (Blaine et al., 2014; Ghisi et al., 2019; Wang et al., 2015). Organic matter helps adsorb PFAAs in soil and reduce their uptake in crops; similarly, carbonaceous adsorbents in soils with high natural SOM content may inhibit the mobilisation of PFAAs (Hale et al. 2017; Yu et al., 2012). However, to the best of our knowledge, studies demonstrating the effect of varying SOM content on plant uptake upon the application of a carbonaceous adsorbent to farmland soils have not been reported so far. Hence, to better understand the effect of SOM and carbonaceous adsorbents on the PFOA and PFOS uptake by plants, we performed three experiments. The adsorption and immobilisation of PFAAs by granular activated carbon (GAC) was analysed to understand the effect of powdered AC on crop-growth (Jakob et al., 2012). First, the adsorption kinetics of PFOA and PFOS on GAC (with and without 0.04 wt.% HA) were investigated to understand the inhibitive effects of organic matter on the adsorption of PFAAs on GAC. Second, the effect of SOM on the uptake of PFAAs in lettuce was investigated by comparing the uptake in soils with two different SOM concentrations (2.6 and 4.0 wt.%). Finally, the role of SOM was further investigated by analysing the plant uptake factor (PUF) in GAC-treated soils with different SOM concentrations (2.6 and 4.0 wt.%).

Materials and Methods

Chemicals and standards

Technical grades of PFOA and PFOS were purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). Analytical standards of PFOA and PFOS including the isotope labelled standards were obtained from Wellington Laboratories Inc. (ON, Canada). Humic acid (HA) was obtained from Sigma Aldrich (Buchs, Switzerland). ENVI-Carb^{TM} (Supelco, Bellefonte, PA, USA), hydrophilic lipophilic balance (HLB) solid phase extraction (SPE) cartridges (0.5 g, 6 mL, Waters Co., Ireland), and nylon filter for solvent and sample (0.20 μm, Silicycle Inc. Quebec, Canada) were purchased. Acetic acid, acetone, acetonitrile, methanol, tetrahydrofuran, and water were HPLC grade and obtained from Merck KGaA (Darmstadt, Germany). Polypropylene (PP) bags were used for soil and lettuce sampling.

Physico-chemical property analysis of granular activated carbon (GAC)

The GAC was purchased from Samchully Activated Carbon Co. Ltd. (Seoul, Korea). 1 - 2 mm of GAC was used for these adsorption and plant uptake experiments. The chars were dried at 140 °C for 72 h before the application to soil. The pH and EC were measured using a pH meter (Jenway 3540, Bibby Scientific Ltd., UK) and EC meter (WalkLAB, Trans Instrument, Singapore) with a suspended GAC (5 g) solution in 100 mL dH_2O. The total pore volume and surface areas of the GAC were analyzed by ASAP2020 (Micromeritics Instrument Co., GA, USA). The elemental analysis of chars was performed by dry combustion (CHN628, Leco Co., MI, USA). The physico-chemical properties of the GAC are described in Table 1.

Table 1 Physico-chemical properties of GAC

pH (1:20)	EC (1:20, dS m^{-1})	H/C	O/C	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore size (nm)
10.2	7.47	0.42	0.14	1230.0	0.452	24.29

PFCs adsorption kinetics of GAC

The adsorption experiments were performed in 250 mL PP bottles. Twenty milligrams of GAC was added to 100 mL PFOA and PFOS aqueous solutions (0.1-100 mg L^{-1}) w/wo 0.04 wt% HA in a PP bottle. The mixed solution was shaken at 150 rpm in room temperature for 6 days to reach an equilibrium condition. The solution was filtered and diluted with methanol to fit within the calibration range for instrumental analysis. The residual concentrations of PFOA and PFOS were determined by HPLC-MS/MS. A zero adsorption property of HA was confirmed on the experimental condition without GAC before the GAC adsorption experiment. Matrix effect of HA was calculated from the following equation (Eq. 1):

$$Matrix\ effect\ (\%) = [1 - (\frac{Slope\ of\ matrix\text{-}included\ adsorption\ curve}{Slope\ of\ non\text{-}matrix\ included\ adsorption\ curve})] \times 100 \quad \text{(Eq. 1)}$$

The slope of adsorption curve was calculated with C_0 and C_e in Figure 1. The adsorption isotherm for PFOA and PFOS of GAC was calculated using the Freundlich equation and Langmiur equation. The Freundlich equation can be expressed as follows equation (Eq. 2):

$$Q_e = K_F C_e^{n^{-1}} \quad \text{(Eq. 2)}$$

Linearizing equation (Eq. 2), It can be expressed as follows equation (Eq. 3):

$$\log Q_e = \frac{1}{n} \log C_e + \log K_F \quad \text{(Eq. 3)}$$

Q_e (µg g^{-1}) is amount of PFOA and PFOS adsorbed per unit weight of adsorbent at equilibrium, C_e (µg L^{-1}) is equilibrium concentration, K_F [(ng g^{-1}) (µg $L^{-1})^{-n}$] is the Freundlich isotherm constant related to adsorption capacity, n^{-1} is adsorption intensity.

The Langmiur equation can be expressed as follows equation (Eq. 4):

$$Q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad \text{(Eq. 4)}$$

Linearizing equation (Eq. 4), It can be expressed as follows equation (Eq. 5):

$$\frac{1}{Q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max} K_L C_e} \qquad \text{(Eq. 5)}$$

q_{max} is maximum sorption capacity (μg g^{-1}), K_L is the constant related to the energy of adsorption (L μg^{-1}).

Soil preparation for plant uptake experiment

Soils with SOM contents of 2.6 wt% and 4.0 wt% were collected form the top soil of agricultural field in Gyeongsang National University and dried for 14 days under fume hood. This soil was analysed and identified to have a background PFOA and PFOS concentration of 0.601 and 0.343 μg kg^{-1} in 2.6 wt% SOM of the soil, and 4.802 and 3.701 μg kg^{-1} in 4.0 wt% SOM of the soil, respectively. The soil was divided into two subsamples with and without PFOA and PFOS standard solutions spiked to give a resultant concentration of 1000 μg kg^{-1}. All the soil samples were homogenized for 10 days and aged for six months in a green house. Then each of the PFAAs non-spiked and spiked soils were prepared with and without 1 wt% GAC treatment. The lettuce was cultivated with 10-replication in Wagner pots (0.02 m^2) that allowed no leaching of irrigated water, each pot containing 2.5 kg of soil. The analysis of SOM, dissolved organic carbon (DOC), pH, EC, and available P_2O_5 was performed using the methods reported by Choi et al. (2019). Briefly, SOM was measured by the Walkley-Black chromic acid wet oxidation method and DOC determined by a TOC analyzer (TOC-L, Shimadzu). The pH and EC for the soil were measured a 50 mL of the five-fold diluted suspended aqueous solution. Available P_2O_5, and exchangeable cations for K, Ca, Mg were analyzed by Lancaster methods and ICP-OES (OPTIMA 5300, PerkinElmer), respectively. The soil properties are described in Table 2.

Table 2 Physico-chemical properties of the plantation soil for pot experiment

SOM (wt%)	Texture	DOC (g kg^{-1})	pH (1:5)	EC (dS m^{-1})	Available P_2O_5 (mg kg^{-1})	Exchangeable cations ($c$mol$_c$ kg^{-1})		
						K	Ca	Mg
2.6	Sandy clay loam	0.192	6.57	2.26	324	0.45	14.9	4.34
4.0	Sandy clay loam	0.442	5.97	2.95	300	0.09	0.1	1.68

Cultivation of lettuce

Lettuce seeds were purchased from Asia Seed Co. Ltd. (Seoul, Korea) and seeds sown in an individual pot that had been treated with 2.5 g of NPK complex fertilizer (21%-8%-10%). The lettuce was cultivated for two months in green house, at which point the aerial part of the lettuce was harvested. The sampled lettuce was chopped and homogenized with dry ice and stored in a freezer at -20 °C until extraction.

Sample preparation for the analysis of PFOA and PFOS in soil and crops

The sample preparation for the extraction of soil was followed the reported method by Choi et al. (2017). Briefly, the soil samples were dried at the room temperature under fume hood and passed through 2 mm sieve. 1.0 g of dried soil was extracted with 1.0% aqueous acetic acid (10.0 mL) by mechanical shaking for an hour and sonication at 30 °C for 15 min. The extract was centrifuged for 10 min then the supernatants were collected in a new PP tube. A mixture of 90:10 (*v/v*) methanol and 1.0 % aqueous acetic acid was added to the extracted soil, then the re-extraction was performed three times. The collected extracts were concentrated to 15 mL then diluted with dH_2O. The HLB cartridges were conditioned using 10 mL of methanol and 10 mL of dH_2O and the diluted extract was loaded to the cartridge with a rate of 1.3-1.6 mL min^{-1}, then washed with 5 mL of 30% methanol. The cartridge was eluted with 10 mL of methanol, then the eluent was concentrated to incipient dryness using nitrogen evaporation, before being re-constituted with 1 mL of methanol. The solution was cleaned up with 20 mg of ENVI-Carb^{TM} then filtered with nylon syringe filter. Before the instrumental analysis, isotope labelled injection standards were spiked with 0.010 mg L^{-1} of $^{13}C_4$-PFOA and of $^{13}C_4$-PFOS.

The sample preparation method reported method by Choi et al. (2018) was followed for the extraction of crops. Briefly, 10.0 g of crop sample was extracted with 10 mL of 90% aqueous methanol (10 mL x 2) and with 75% tetrahydrofuran in DW (10 mL x 2) by shaking (1 h) and sonication (20 min). The extracts were centrifuged at 3500 rpm and supernatants were collected in a new PP tube. The combined extracts were concentrated to 10 mL under nitrogen then diluted with dH_2O to a 50 mL. The extracts were concentrated under nitrogen, before being reconstituted with 1 mL of methanol. The diluted sample was extracted with HLB SPE cartridges as described for soil and the rest of the process was followed with the same as the soil treatment.

Instrumental analysis and quality assurance

The concentration of PFOA and PFOS were determined using HPLC-MS/MS. The HPLC system was an Agilent HP1100 (Agilent Technologies, CA, USA) coupled to a triple quadruple mass spectrometer API3200^{TM} system (AB SCIEX, ON, Canada) operated using ESI in negative ionization mode. Separation was performed using a Siliachrom C18 column (3 μm, 100 mm x 2.1 mm; Silicycle Co. Ltd, Canada). The optimized analytical conditions are described in supporting information (Table S1). The accuracy of the method was evaluated by determining recoveries associated with relative standard deviation (% RSD) of PFOA and PFOS fortified at 0.05 μg kg^{-1} in lettuce and soil. The recoveries of PFOA and PFOS were 70.4-78.7% and the interday precision ranged from 5.6-8.3%, respectively. The linearity of PFOA and PFOS was acceptable for quantitation across the range of 0.010 to 1.000 ng mL^{-1} (R^2 >0.997). The method limit of quantitation (mLOQ) of PFOA and PFOS were determined at 0.001 and 0.010 μg kg^{-1} for lettuce and soil, respectively. More detailed information is described in Table S2.

Calculation on plant uptake factor (PUF)

The plant uptake factor is represented as the ratio between concentrations of a chemical analyte determined in plant tissue and soil, it can be expressed as follows equation (Eq. 6) (Liu et al. 2019):

$$PUF = \frac{Concentration\ in\ crop}{Concentration\ in\ soil} \qquad \text{(Eq. 6)}$$

Results and discussion

PFOA and PFOS adsorption properties of GAC

The adsorption capacity of GAC was calculated using the equilibrium concentrations obtained from the various initial concentrations of aqueous solutions of PFOA and PFOS. Fig. 1 shows a plot of equilibrium concentrations of PFOA and PFOS against their initial concentrations in an aqueous solution containing GAC, with and without 0.04 wt.% HA. With an increase in the initial PFOA and PFOS concentration, the equilibrium concentration increased linearly, with higher values observed in the solution containing HA compared to that containing only GAC. It should be noted that 0.04 wt.% HA was initially tested separately and was found to have no impact on the adsorption of PFOA and PFOS.

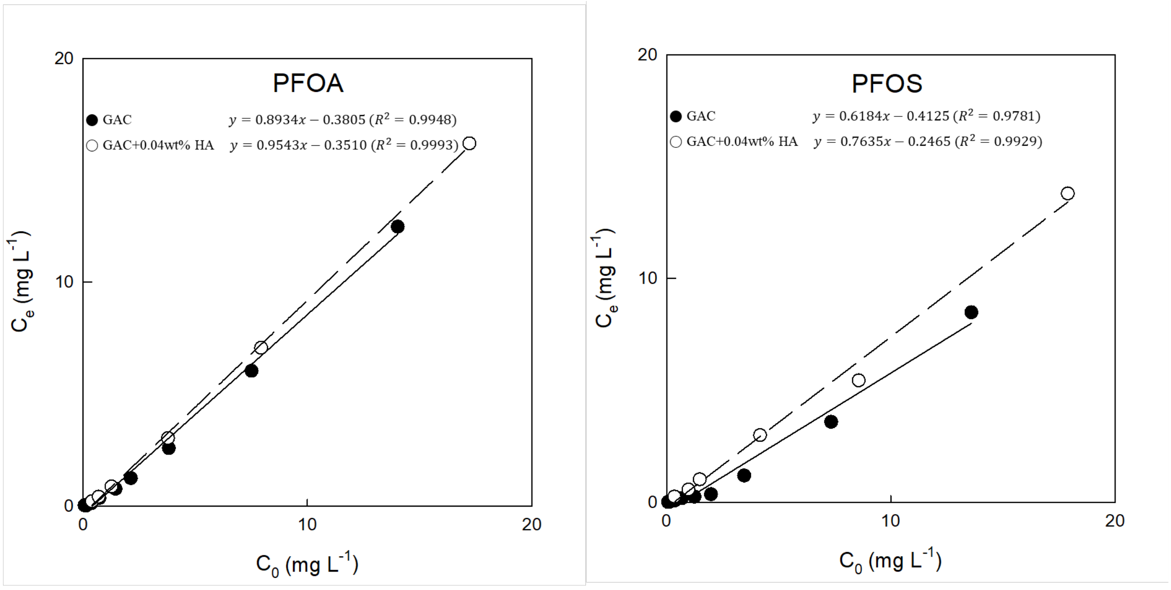

Fig. 1 Adsorption properties of GAC for PFOA and PFOS. C_0 (mg L^{-1}) was the initial concentration of PFOA and PFOS and C_e (mg L^{-1}) was the equilibrium concentration of PFOA and PFOS.

In Fig. 1, the slopes of the plots of PFOA and PFOS adsorption on GAC adsorption are higher for the solutions containing 0.04% HA. The slopes were used to calculate the matrix effects of 0.04 wt.% HA on the adsorption of PFOA (-6.8%) and PFOS (-23.5%), on GAC. Therefore, the presence of HA appeared to reduce the adsorption of both PFAAs on GAC, with the effect being more pronounced for PFOS than PFOA.

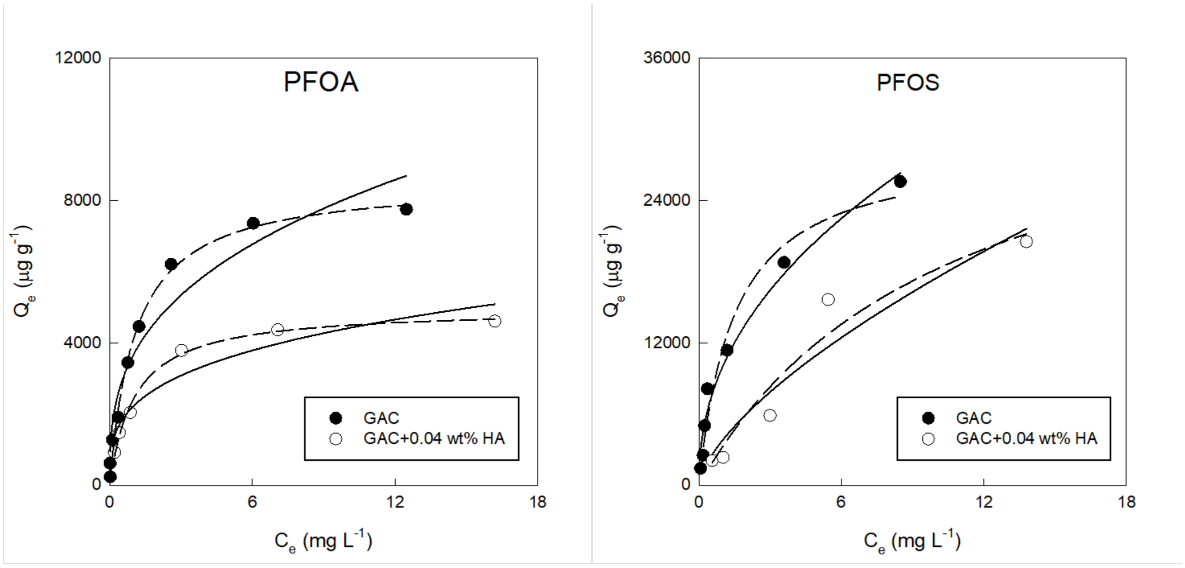

Fig. 2 Sorption isotherms of PFOA and PFOS on GAC. Q_e (μg g^{-1}) was amount of PFOA and PFOS adsorbed per unit weight of GAC equilibrium and C_e (mg L^{-1}) was equilibrium concentration in water. The solid lines are the fitted Freundlich isotherms and the dashed lines are the fitted Langmuir isotherms

The adsorption isotherms of PFOA and PFOS fit both the Langmuir and the Freundlich equations (Fig. 2). The maximum adsorption capacities (q_{max}) of GAC for PFOA and PFOS were 9.091 mg g^{-1} and 27.778 mg g^{-1}, respectively, in the solution without HA. The values decreased to 5.208 mg g^{-1} and 17.241 mg g^{-1} for PFOA and PFOS respectively, when tested in the solution containing 0.04 wt.% HA. Thus, the addition of 0.04 wt.% HA resulted in a decrease in q_{max} for both PFOA (43%) and PFOS (38%). The adsorption intensities (K_L) for PFOA and PFOS in the solution without HA were 0.76 mL µg^{-1} and 0.74 mL µg^{-1}, respectively. The K_L for PFOS in the solution with HA decreased to 0.21 mL µg^{-1} (Table 3). The adsorption capacity (K_F) and adsorption intensity (n^{-1}) values are presented in Table 3.

The respective log K_Fs [(μg kg^{-1}) (μg kg^{-1})$^{-n}$] values of PFOA and PFOS in the HA-free solution, were 5.41 and 5.21 and were similar to previously reported values (Silvani et al., 2019). For the solution containing 0.04 wt.% HA, the respective log K_Fs values decreased slightly to 5.36 and 4.05. Wang et al. (2015) reported that HA competes for the adsorption of PFAAs in soil, which explains the decrease in K_F values in the solution containing HA.

Table 3 Constants of the Langmiur and Freundlich isotherm equations of GAC for PFOA and PFOS

	Chemicals	Langmiur constant			Freundlich constant		
		q_{max}[a]	K_L[b]	R^2	log K_F[c]	n^{-1} [d]	R^2
GAC	PFOA	9.091	0.76	0.999	5.41	0.383	0.897
	PFOS	27.778	0.74	0.968	5.21	0.585	0.921
GAC+0.04 wt% HA	PFOA	5.208	0.75	0.995	5.36	0.325	0.927
	PFOS	17.241	0.21	0.893	4.05	0.802	0.949

[a] q_{max} : maximum sorption capacity (mg g^{-1}); [b] K_L : energy of adsorption (mL μg^{-1}); [c] K_F : Freundlich isotherm constant, adsorption capacity [(ng g^{-1}) (μg L^{-1})$^{-n}$]; [d] n^{-1}: adsorption intensity.

The adsorption intensity/heterogeneity is represented by n^{-1}. If $n^{-1} > 1$, it indicates that chemical adsorption is the dominant process; if $n^{-1} < 1$, physical adsorption is the dominant process, which is most effective when the value is 0.1–0.5 (Bang and Kim, 2017). Here, all the values of n^{-1} for PFOA and PFOS ranged from 0.325–0.582, except for PFOS in the solution with 0.04% HA where the value was 0.802. These results indicate that in the absence of HA, GAC effectively adsorbed PFOA and PFOS through physical adsorption. However, the physical adsorption efficiency of GAC for PFOS decreased in the presence of 0.04 wt.% HA, suggesting that HA could interfere with the adsorption efficiency of GAC for PFOS, and with GAC treatment in soil with high SOM content. Thus, the immobilization ability of GAC for PFOS in high SOM containing environment would be lower than that for PFOA.

Effect of SOM on the uptake of PFOA and PFOS in lettuce

The uptake of PFOA and PFOS in lettuce was investigated under two conditions (2.6 wt.% and 4.0 wt.% of SOM) and two concentrations ('high' and 'low') of PFOA and PFOS (Table 4). No visible evidence of phytotoxicity due to PFOA/PFOS was observed in the lettuce during cultivation. In the soil with 2.6 wt.% SOM, the average PUFs for low and high concentrations of PFAAs were 0.629 and 0.252 for PFOA and PFOS respectively. In the soil with 4.0 wt.% SOM, the PUFs were approximately two times lower: 0.353 (PFOA) and 0.108 (PFOS). Plant uptake factors have been shown to vary by crop type, part of the crop, and crop growth rates (Ghisi et al. 2019; Xiang et al. 2018). They are also influenced by the leaching and adsorption potential of the soil which is influenced by soil properties such as pH, mineral content, anion exchange capacity and SOM (Li et al. 2019; Wei et al. 2017; Xiang et al. 2018). The log K_ds values of soil were reported in the range of -0.97-1.69, and -1.0-35.3, for PFOA and PFOS respectively, with higher K_ds values observed in soil with a greater SOM content (Kupryianchyk et al. 2015; Martz et al. 2019; Milinovic et al. 2015; Silvani et al. 2019; Zareitalabad et al. 2013). This explains why lower PUFs for PFOA and PFOS were observed in the soil containing 4.0% SOM compared to the soil with 2.6% SOM. In addition, the PUF for PFOA was consistently higher than that for PFOS. The low PFAA-contaminated soil showed similar PUFs for both PFOA and PFOS in the soil with 2.6 wt.% SOM (0.349 and 0.297, respectively) and with 4.0 wt.% SOM (0.127 and 0.115, respectively). However, the high PFAA-contaminated soil showed a much larger increase in the PUF for PFOA compared to that for PFOS in both the 2.6 wt.% SOM soil (0.908 and 0.207 respectively) and 4.0 wt.%

SOM soil (0.578 and 0.100 respectively). It could be because of the difference in leaching of PFOA and PFOS in the soil environment (Milinovic et al., 2015; McSachlan et al., 2019).

Table 4 The PUFs of PFOA and PFOS in lettuce cultivated on 2.6 wt% and 4.0 wt% SOM of soils with or without GAC

		PUF (Average±SE)		Lettuce (Average±SE, μg kg^{-1})		Soil (Average±SE, μg kg^{-1})	
		PFOA	PFOS	PFOA	PFOS	PFOA	PFOS
2.6 wt% SOM	Low	0.349 ±0.062	0.297 ±0.059	0.210 ±0.040	0.102 ±0.027	0.601 ±0.071	0.343 ±0.070
	High	0.908 ±0.135	0.207 ±0.048	873.3 ±130.0	226.6 ±41.1	961.4 ±104.5	1,093 ±195.0
	High+GAC[a]	0.006 ±0.002	0.005 ±0.002	5.617 ±2.155	5.936 ±2.185	-	-
PUF suppression by GAC		99.4%	97.4%				
4.0 wt% SOM	Low	0.127 ±0.035	0.115 ±0.039	0.609 ±0.128	0.426 ±0.278	4.802 ±0.970	3.701 ±0.649
	High	0.578 ±0.116	0.100 ±0.027	618.3 ±124.9	85.70 ±12.96	1,070 ±160.8	859.2 ±92.14
	High+GAC[a]	0.079 ±0.021	0.023 ±0.006	84.45 ±11.22	19.61 ±6.388	-	-
PUF suppression by GAC		86.3%	77.1%				

[a] GAC was treated to 1 wt% of dried soil

Effect of GAC treatment on the PUF for PFOA and PFOS in lettuce

When comparing the PUFs for PFOA and PFOS in soils treated with GAC, the results showed a significant reduction in PFAA uptake (Table 4). The PUFs in the soil with 2.6 wt.% SOM reduced to 0.006 (PFOA) and 0.005 (PFOS). These results were mirrored in the soil containing 4.0 wt.% SOM with PUFs of 0.079 (PFOA) and 0.023 (PFOS). These results highlight the effectiveness of GAC for active immobilisation of PFOA and PFOS in contaminated soils. When GAC was applied to the high PFAA-contaminated soils, the PUFs in the soil with 2.6% SOM were calculated to be below 0.01, and were reduced by 99.4% (PFOS) and 97.4% (PFOA); in the soil with 4.0% SOM, relatively higher PUFs were observed, reduced by 86.3% (PFOS) and 77.1% (PFOA). As concluded by Hale et al. (2017), GAC treatment in soil can significantly reduce leaching of PFAAs. This is considered to have contributed significantly to the reduction in PUF observed in the lettuce samples. In addition, the results show that the PUFs for PFOA and PFOS were more effectively suppressed in the soil with low SOM than in the soil with high SOM. This could be explained by the adsorption kinetics experiment of GAC with HA, as an increase in SOM resulted in decreased adsorption of PFAAs on GAC. Therefore, the adsorption of PFAAs by GAC in soil with high SOM was reduced, outweighing the benefits of having additional SOM. Although the PUFs were relatively higher in GAC-treated soil with high SOM than with low SOM, GAC treatment could effectively reduce approximately 4.3-155-fold of the PFAA residues in crops. Thus, GAC application could be considered to reduce the dietary exposure of PFAAs from crop consumption. Further studies are necessary on the appropriate GAC application procedures in farmland soil with varying SOM content.

Conclusion

Soil organic matter was shown to adsorb PFOA and PFOS, and its presence helped reduce the uptake of PFAAs from soil into crops. Similarly, the addition of GAC to soil helped reduce the uptake of PFAAs. It was demonstrated that GAC can effectively adsorb both PFOA and PFOS and therefore suppress the crop-uptake of PFAAs (up to 99.4% for PFOA in 2.6% SOM soil. However, a higher SOM content as well as the presence of HA reduced the effectiveness of GAC and ultimately its capacity to adsorb PFOA and PFOS. The PUF of lettuce grown in soil with higher SOM indicated a suppression in the ability of GAC to adsorb PFAAs. Hence, the existing SOM content of the soil should be considered when a carbonaceous adsorbent is applied to ensure effective immobilisation and successful reduction of crop-uptake of PFAAs. Further research is required to better understand the effectiveness of GAC to immobilise PFAAs in soils with various amounts of SOM. This could help establish a correlation factor for GAC immobilization of PFAAs based on the SOM content.

Appendix. Supplementary data

Supplementary data related to this article can be found at Supporting Information

Credit authorship statement

Lee DY performed the experiments and data collection; Choi GH analyzed the PFAAs in crop; Choi IW, Oh KY and Seo DC analyzed the data for the adsorbent; Megson D discussed the results; Kim JH wrote and revised the manuscript. All authors read and approved the final manuscript.

Conflicts of Interest

The authors declare no conflicts of interest

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