

Influence of different types of humic substances on the adsorption behavior of PFOA in soils: Experimental insights and spectral characterization

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Abstract

The adsorption behavior of perfluorooctanoic acid (PFOA) in soils is critical for understanding its environmental transport. However, the effects and mechanisms of humic substances (HS) as an organic soil amendment on PFOA adsorption in soils are still unclear. This study investigated the interactions between HS, particularly humic acid (HA) and fulvic acid (FA), PFOA and soil during the PFOA adsorption process in soil environment. The adsorption capacities of PFOA followed the order: Soil > Soil + HA > Soil + FA > HA > FA. HS, with their negative charges, hindered PFOA adsorption by occupying surface adsorption sites. Fluorescence quenching experiments confirmed HS-PFOA complex formation. PFOA preferentially bound to humic acid-like and fulvic acid-like substances. The primary adsorption sites in both soil and HS were -OH and C-O-C groups. Although HS formed complexes with PFOA, they reduced the overall adsorption capacity in soil. HA provided more hydrophobic interaction sites for PFOA than FA, and FA, with a higher negative charge, exerted stronger electrostatic repulsion, leading to a more significant reduction in PFOA adsorption. This study highlights the role of different HS in PFOA soil adsorption and offers insights for soil remediation and risk assessment of PFOA.

1. Introduction

Per- and poly-fluoroalkyl substances (PFAS), with their excellent chemical stability, thermal stability, hydrophilicity and hydrophobicity, have been widely used as surfactants, emulsifiers, flame retardants, and in various industrial activities. However, due to their inherent high toxicity, persistence and bioaccumulation, PFAS pose significant risks to the environment and human health even at low concentrations [1, 2]. The maximum allowable concentrations of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) for drinking water were set at 100 ng/L in the EU in 2020 [3]. The United States Environmental Protection Agency even established a more stringent standard for 4 ng/L in drinking water in 2023 [4]. In the past decades, frequent detections of PFOA and PFOS have been reported in aquatic systems [5–6]. Therefore, it is an urgent need to clarify their transport patterns in different environmental media.

Soil serves as a significant reservoir for PFAS in various environmental media [7]. PFOA, one of a wide range of PFAS, exhibits high solubility in both polar and non-polar solvents due to its unique amphiphilic nature, which arises from the combination of a hydrophobic perfluorocarbon tail and hydrophilic functional groups [8]. The hydrophilic functional groups at the end of the long chain of PFOA facilitate its migration with soil pore water into groundwater [9]. Due to its high degree of stability, PFOA is persistent and non-biodegradable in soil, posing a significant risk as they enter the human body through the food chain and drinking water. Thus, the interactions between PFOA and soil, along with influencing factors of different perspectives such as soil texture, cation exchange capacity, anion exchange capacity, minerals, and organic carbon had been studied. Soil organic matter (SOM) is a critical factor influencing the adsorption between PFOA and soil colloids and its effect on the transport and retention of PFOA in soil has been reported [10–12]. However, the effect of SOM on PFOA adsorption in soil is often studied using organic carbon content as indicator, but SOM is mainly composed of humus (HS) with different

properties such as humic acid (HA) and fulvic acid (FA) [13–15]. The specific effect of different HS on PFOA adsorption in soils is a very important fundamental issue and remains to be studied.

Due to their distinctive properties and advantages, HA and FA have been extensively utilized in agriculture to enhance soil fertility, water retention, and enzyme activity, etc. HA consists of aliphatic and aromatic portions with various polar functional groups such as -OH and -COOH. Its complex functional group structure allows HA to exhibit both hydrophobic and electrostatic interactions, influencing its interaction with pollutants [16, 17]. Meanwhile, previous studies have reported that HA influences the adsorption of contaminants on soil or mineral surfaces through hydrophobic interactions, hydrogen bonding, and van der Waals forces [18, 19]. Additionally, HA also forms organic-inorganic complexes with multivalent metal cations through “crosslinking” and aggregation, affecting the adsorbent's ability to adsorb heavy metals [20]. In contrast, FA has a lower molecular weight and more functional groups than HA, and making it soluble in both acids and bases [13]. The abundance of functional groups in FA enhances its ability to remove contaminants from the soil. For instance, phenolic and carboxyl groups in FA decrease the bioavailability of heavy metals (e.g., Cu, Mn, and Ag) in water and soil through adsorption, complexation, and co-precipitation [14, 21, 22]. As reported in the literature, due to the differences in molecular weight and functional groups, various classes of HS interact differently with pollutants and exhibit varying effects on the adsorption and migration of these pollutants. For example, compared to other components of DOM, humic acid-like and fulvic acid-like substances dominated the binding of DOM and lead (Pb), and elucidated the potential complexation reactions that may occur between Pb and humic acid-like substances [23]. Although previous studies have demonstrated that different types of HS exhibit distinct influences on the adsorption of various pollutants in soils, the specific effects of different HS on the adsorption behavior of PFOA, which is characterized by its unique amphiphilic nature and charged functional groups, remain inadequately investigated..

This study investigated the impact of HA and FA on PFOA adsorption in soil. Specifically, the adsorption characteristics of PFOA on different soil and HS, as well as the effects of pH, ionic strength, and soil particle size on PFOA adsorption were investigated. In addition, due to the complex composition of HA and FA, three-dimensional excitation-emission matrix (3D-EEM) fluorescence spectroscopy and synchrotron fluorescence methods were conducted to clarify the interactions and complexation between various HS and PFOA. Meanwhile, Fourier transform infrared (FT-IR) spectroscopy and two-dimensional correlation spectroscopy (2D-COS) were employed to provide insights into the relative direction and order of the structural changes, along with potential adsorption mechanisms. Finally, the mechanism of PFOA adsorption in soils with HA and FA were elucidated using density functional theory (DFT). The present study is of practical significance as it enhances the understanding the role of different HS during the PFOA adsorption behavior in soil environment and enlightens PFOA soil remediation or risk assessment studies in the future.

2. Material and methods

2.1 Material

The original soil samples were sourced from the East China University of Science and Technology (depth of 0–20 cm), Shanghai, China. Detailed information regarding soil pretreatment procedures, fundamental soil parameters, as well as the PFOA standards (98% purity) and other chemical reagents utilized can be found in the Supporting Information (Text S1 and Table S1).

2.2 Batch sorption experiment

The adsorption experiments were divided into three groups: (A) 2.00 g of soil; (B) 2.00 g of soil + 0.002 g of HS (Soil + HA, Soil + FA); and (C) 2.00 g of HS (HA, FA). First, the corresponding soil or HS was added into 50 mL polypropylene tubes for each group. Then, the pH was adjusted to 7.0 using 0.5 M NaOH to facilitate the dissolution of the HS. Subsequently, 20 mL of deionized water was added to group A, while 20 mL of HS solution was added to groups B and C. Finally, 20 mL of a PFOA solution containing 0.01 M CaCl_2 was added to each centrifuge tube, ensuring a final PFOA concentration of 2 mg/L for the kinetic experiments. The pH was adjusted to 7.0 ± 0.1 with HCl or NaOH before adsorption. Afterward, the samples were shaken on a thermostatic oscillator ($25 \pm 1^\circ\text{C}$, 250 ± 5 rpm, ZD-85, Guohua Laboratory Instruments, China) [24]. Adsorption kinetics were performed at different time intervals of 1, 15, 30, 60, 120, 240, 480, 720, and 1440 min for sampling. Adsorption isotherm experiments were also performed to determine the adsorption capacities for PFOA in different soil and HS, with the initial PFOA concentrations from 0.2 to 20 mg/L, and shaking for 24 h at $25 \pm 1^\circ\text{C}$ to reach adsorption equilibrium [7]. Finally, the mixture was centrifuged at 4000 r/min for 5 min, and the supernatant was filtered using a $0.45\ \mu\text{m}$ filter tip (PTFE) and then analyzed for PFOA concentration by LC-MS (LC-MS 8050, Shimadzu, Japan).

In order to investigate the desorption performance of PFOA in different soil/HS samples after reaching the adsorption equilibrium, the desorption experiments were performed by adding 0.1 M CaCl_2 to the adsorbed samples [25]. Triplicate samples were set up for all experiments with negligible loss of PFOA during adsorption and filtration. In addition, the effects of pH, ion concentration, and soil particle size on PFOA adsorption were investigated under identical conditions. Detailed results are provided in the Supporting Information (Text S2).

2.3 Spectrum analysis

3D-EEM spectra and synchrotron fluorescence were employed to elucidate the binding behaviors between different HS and PFOA. Solutions of HA and FA were separately mixed into PFOA solutions at varying concentrations. The final solution consistently contained 10 mg/L of HS, while the PFOA concentration was adjusted from 0 to 30 mg/L [7]. Moreover, all solutions were shaken for 8 h to ensure adsorption equilibrium prior to spectral analysis [26]. The fluorescence spectra, including synchronous fluorescence spectra (SFS) and 3D-EEM, of HS adsorbed PFOA were recorded using the F-7000 fluorescence spectrometer from Hitachi, Japan. The experimental conditions and parameter settings are also described in the Supporting Information (Text S2).

2.4 Analytical methods

The soil and HS samples were characterized using elemental analysis, FT-IR, CP-MAS to investigate their composition and conformation. Basic sample parameters were analyzed using TOC-L, ICP-OES, conductivity meter, etc. More detailed information is presented in the Support Information (Text S3).

2.5 Quantum chemical calculation

The structures of HA, FA and PFOA were optimized using Gaussian 16, and their electrostatic potentials were further simulated using DFT. The theoretical calculations were performed via the Gaussian 16 suite of programs. The structures of the studied molecules (denoted by M1 ~ M3) were fully optimized at the B3LYP-D3BJ/def2-SVP level of theory. The vibrational frequencies of the optimized structures were carried out at the same level. The structures were characterized as a local energy minimum on the potential energy surface by verifying that all the vibrational frequencies were real. The Visual Molecular Dynamics (VMD) program was used to plot the color-filled iso-surface graphs to visualize the electrostatic potential (ESP). The ESP surface minima and maxima of the molecule are depicted as blue and yellow points, which were calculated based on the optimized structure.

2.6 Data process

SFS of HS under the influence of different concentrations of PFOA was performed using 2D-COS. Synchronous and asynchronous maps were plotted with MatlabR 2018b and Origin 2021. The degree and order of quenching of PFOA with organic matter components were interpreted according to Noda and Ozaki's report [27]. Spectral integration of ^{13}C NMR measurements was performed using MestReNova software. SPSS 23.0 and origin 2021 software were used for computational statistical analysis, model regression of adsorption parameters, and correlation analysis.

3. Results and discussion

3.1 Characterization of HS and soil

The HA and FA used in this study were commercially obtained and exhibited distinct physicochemical properties. HA had a higher carbon content and a lower polarity index, indicating stronger hydrophobicity, whereas FA had higher nitrogen and sulfur contents, greater polarity, and stronger acidity (Table S2). ^{13}C -NMR analysis showed that HA was mainly composed of aliphatic carbon structures, suggesting a relatively high proportion of long-chain fatty acids. In contrast, FA contained more O-alkyl and aromatic carbons, indicating greater chemical complexity and stability. Detailed elemental compositions, CP-MAS ^{13}C -NMR analyses, and soil-related parameters are provided in the Text S4.

As shown in Table S3, the pH of Soil + FA was lower than that of Soil + HA, which was attributable to the more acidic nature of FA. The zeta potential values for the three soil fractions (Soil, Soil + HA, and Soil + FA) were -11.3 ± 0.2 , -13.0 ± 0.4 , and -14.7 ± 0.7 , respectively. These results demonstrated that adding negatively charged HS to the soil increased the electronegativity of the soil surface. Meanwhile, the content of SOM and DOC in the soil fractions also increased with the addition of HS.

3.2 Effect of HS on the adsorption of PFOA by soil

3.2.1 Adsorption kinetics

Adsorption kinetics was employed to evaluate the impact of contact time and to illustrate the significance of PFOA transport and transformation rates in the soil environment. The effect of reaction time on PFOA adsorption in different HS and Soil + HS was shown in Fig. 1a. The amount of PFOA adsorbed by soil and HS reached 70% of the total adsorption capacity within 1 h, after which the adsorption rates gradually became slow. Furthermore, PFOA adsorption approximately reached equilibrium after 12 h, with the adsorption capacities of Soil, Soil + HA, Soil + FA, HA, and FA were 16.17, 15.93, 15.60, 14.78 and 14.19 $\mu\text{g/g}$, respectively. The desorption experimental data showed that PFOA desorption was minimal in all five experiments, accounting less than 10% of the adsorption capacity for each sample (Fig. S1a). This might be due to the high hydrophobicity of PFOA, which resulted in low adsorption reversibility. The desorption rate of Soil, which exhibited the highest adsorption capacity of PFOA, was also higher than those of the other groups. Compared with Soil, Soil + HS groups exhibited lower adsorption capacities for PFOA, indicating that the mass transfer of PFOA in the soil might be promoted by the addition of HS [28].

To further analyze the adsorption process, the kinetic data were fitted using pseudo-first order (PFO), pseudo-second order (PSO) and Elovich models (Table S4). The PSO model ($R^2 > 0.99$) was found to be more suitable for describing the adsorption process of PFOA in soil and HS compared to the PFO and Elovich models. This suggested that PFOA molecules may interact strongly with the functional groups on the surface of soil and HS through electron transfer, covalent bonding, or hydrogen bonding. Additionally, the presence of HS led to partial occupation of adsorption sites on the soil surface, which reduced the adsorption rate of PFOA [29]. Moreover, PFOA ($\text{pK}_a = 2.5$) tended to dissociate into anionic forms in aqueous solutions with a pH higher than 5.0. The anionic characteristics of PFOA might have engaged in electrostatic interactions with the negatively charged surfaces of HS, which reduced the adsorption rate of PFOA on the soil surface. Despite this, the adsorption process might still involve physical adsorption components, but chemisorption was considered the main rate-controlling step. The adsorption of PFOA in soil colloids and HS was characterized as a “three-stage” process through fitting the intraparticle diffusion curves [30]. Since the intraparticle diffusion curve did not pass through the origin as shown in Fig. S1b, the adsorption of surface PFOA was mainly attributed to thin-film diffusion, and intraparticle diffusion serving as an important rate-limiting mechanism [31].

3.2.2 Adsorption isotherms

Figure 2 showed the adsorption isotherms of PFOA on different samples with adsorption equilibrium time for 24 h. Soil exhibited the highest adsorption capacity, following by the order: Soil > Soil + HA > Soil + FA > HA > FA.

In addition, Langmuir and Freundlich models were used to fit the experimental data, which were listed in Eqs. (1), (2):

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e}$$

1

$$q_e = K_F C_e^{1/n}$$

2

where q_e is the adsorption capacity of PFOA at equilibrium ($\mu\text{g/g}$), C_e is the equilibrium concentration of PFOA in solution (mg/L). q_m ($\mu\text{g/g}$) is the maximum adsorption capacity of PFOA, and K_L ($\text{L}/\mu\text{g}$) is Langmuir adsorption constant. K_F ($\text{L}^{1/n} \cdot \mu\text{g}^{1-1/n}/\text{g}$) is Freundlich adsorption constant and n is an empirical constant related to the heterogeneity of the adsorbent surface.

As shown in Fig. 2 and Table S5 the adsorption isotherms for the five materials were better fitted by the Langmuir model than Freundlich model [32]. This indicated that PFOA adsorption onto soil and HS was likely monolayer adsorption. According to the Langmuir model, the maximum adsorption capacities of PFOA in Soil, Soil + HA, Soil + FA, HA, and FA were 55.17, 51.71, 45.28, 34.10, and 32.36 $\mu\text{g/g}$, respectively. The adsorption capacity of soil for PFOA was consistently higher than those of Soil + HS. This might be due to the larger specific surface area and more active sites for PFOA adsorption in soil colloids compared to HS [11, 28]. In addition, the adsorption of negatively charged PFOA on soil/HS was influenced by Coulombic interactions [33]. All three soil fractions had negatively charged surfaces, with zeta potential values of -11.3 ± 0.2 , -13.0 ± 0.4 , and -14.7 ± 0.7 for Soil, Soil + HA, and Soil + FA, respectively (Table S3), indicating that Soil + HA and Soil + FA had more negative surface charges. Although PFOA could also be adsorbed with the functional group ($-\text{COOH}$ and $-\text{OH}$) on the surface of HS, the electrostatic repulsion of PFOA was stronger on the surfaces of Soil + HA and Soil + FA, resulting in a lower adsorption capacity of Soil + HS for PFOA than Soil [34, 35].

3.3 Influence of different factors

PFOA adsorption is influenced by various soil properties, including environmental pH, cationic concentration, and soil particle size. Figure 3 showed the effect of different factors on the adsorption of PFOA in soils with different HS. The adsorption capacities of soil and soil + HS for PFOA decreased with increasing solution pH. The adsorption capacities of the three soils at all pH conditions followed order: Soil > Soil + HA > Soil + FA. This might be attributed to the increased electrostatic repulsion between PFOA and soil/HS [36]. The adsorption capacities of PFOA were reduced by the increase in solution pH which decreased the surface positive sites of soil and HS colloids. Furthermore, at low pH ($\text{pH} < 5$), the adsorption capacity of Soil + HA was still higher than that of Soil + FA, due to the lower electrostatic repulsion on the HA surface compared to FA. Additionally, HA molecules underwent significant structural

rearrangement under low pH conditions ($\text{pH} < 5$), resulting in a convoluted configuration with carboxyl and phenolic groups located within the matrix, which was more favorable for PFOA adsorption [37].

The effect of Ca^{2+} on PFOA adsorption was evident in Fig. 3b. The PFOA adsorption capacities of all three samples increased with the concentration of coexisting cations, and the trend of adsorption capacities remained consistent across all three samples. This might be due to the fact that Ca^{2+} neutralized the negative charge on the soil surface and increased the zeta potential of soil colloids and HS, enhancing the electrostatic attraction to the negatively charged PFOA molecules. Furthermore, the adsorption capacity of PFOA increased with higher Ca^{2+} concentrations, which might be due to the increased positive charge on the soil surface, leading to a stronger attraction of negative charges to the inner layer of the electric double layer, thereby causing compression of the diffusing double layer [38]. It has been reported that the interaction between Ca^{2+} and the functional groups on the BC surface neutralized some of the negative charges on the BC surface, thereby increasing attraction between the BC surface and the anionic PFOS [39]. The results demonstrated that the presence of Ca^{2+} in natural soils significantly affected PFOA transport.

Soil particle size is a key factor influencing pollutant adsorption due to variations in specific surface area and porosity among soils with different particle sizes. Smaller soil particles, having larger specific surface areas, generally exhibit higher adsorption capacities. The PFOA adsorption amounts for sand, coarse powder, and fine powder were 14.43, 16.17, and 17.39 $\mu\text{g/g}$ in Soil samples; 13.98, 15.93, and 16.56 $\mu\text{g/g}$ in Soil + HA; and 13.63, 15.60, and 16.32 $\mu\text{g/g}$ in Soil + FA (Fig. S2). According to BET results, the specific surface areas of sand, coarse powder, and fine powder soil colloids were 7.908, 15.525, and 21.228 m^2/g , respectively. HS occupied some adsorption sites on the soil colloid surfaces, thereby reducing the interaction between PFOA and soil colloids, which led to decreased adsorption capacities in Soil + HS. The adsorption capacity for PFOA was slightly lower in Soil + FA than in Soil + HA, which may be attributed to the relatively weaker hydrophobic interactions between FA and PFOA compared to HA. However, it should be noted that the differences in adsorption capacities between Soil + HA and Soil + FA were relatively small, and thus these differences should not be overemphasized. This finding contrasts with previous studies reporting that HA and FA enhanced adsorption of heavy metals and pesticides [25, 40]. Our results suggest that HS may have a different effect on PFOA adsorption, potentially promoting its transport in soil, which warrants further investigation.

3.4 HS complexation with PFOA

3.4.1 3D-EEM

To investigate the binding behavior between different HS and PFOA, 3D-EEM analysis was conducted. 3D-EEM analysis has gained wide popularity in characterizing DOM due to its advantages of low cost, high selectivity and high sensitivity [41]. Figure 4 showed the 3D-EEM spectra of HA and FA, indicating significant changes upon the addition of PFOA of different concentrations (0–30 mg/L).

The commercial HA exhibited a single prominent peak (Fig. 4a). HA-like peak A was located at $449 \text{ nm} < E_{\text{ex}} < 489 \text{ nm}$ (E_{ex} stands for excitation wavelength) and $513 \text{ nm} < E_{\text{em}} < 562 \text{ nm}$ (E_{em} represents the emission wavelength). Meanwhile, the commercial FA displayed two main peaks (Fig. 4g). FA-like peak B was located in $E_{\text{ex}} < 267 \text{ nm}$ and $418 \text{ nm} < E_{\text{em}} < 470 \text{ nm}$. Peak C was located in $317 \text{ nm} < E_{\text{ex}} < 360 \text{ nm}$ and $402 \text{ nm} < E_{\text{em}} < 448 \text{ nm}$. These peak ranges were consistent with the values reported in previous studies [42–44]. Following the addition of various concentrations of PFOA (0–30 mg/L), the fluorescence intensity of HA-like peak A decreased from 650 to 126. The fluorescence intensities of FA-like peaks B and C were reduced from 439 to 202 and 977 to 428, respectively. The significant attenuation of three peaks confirmed a strong interaction between PFOA and HS. This phenomenon suggested that the principal components of HS were substantially quenched as PFOA concentration increased [45], indicating that HS exhibited a strong binding capacity with PFOA, influencing PFOA migration in soil [15]. The results further demonstrated that HS played an important role in the migration performance of PFOA in soil phase.

To quantitatively compare the binding behavior of HA and FA with PFOA and to reveal the dynamic and static quenching mechanisms, the fluorescence quenching results for characteristic peaks (peak A of HA; peaks B and C of FA) were analyzed using the Stern-Volmer equation, as shown in Eq. (3) [46], and the corresponding quenching constants (K_{sv} and K_q) and number of binding sites (n) were calculated.

$$F/F_0 = 1 + K_{sv} [Q] = 1 + K_q \tau_0 [Q]$$

3

where F_0 and F represent the fluorescence intensities with and without contaminants, respectively. K_{sv} (L/mol) and K_q (L/mol·s) stand for the Stern-volmer fluorescence quenching constants and macromolecular fluorescence quenching constants, respectively. τ_0 represents the mean molecular lifetime without quencher (10^{-8} s). $[Q]$ indicates the concentration of PFOA (mol/L).

When the quenching type was static quenching, the intensity of the fluorescence data was analyzed and the number of binding sites of the complex (n) was obtained, which were listed in Eqs. (4) [23]:

$$\log \frac{F_0 - F}{F} = \log K_b + n \log [Q]$$

4

where K_b represent the binding site constant (L/mol).

Fluorescence quenching includes static and dynamic quenching. Static quenching refers to the formation of a complex between the quencher and the fluorophore, which results in a decrease in fluorescence intensity. In contrast, dynamic quenching occurs due to the collisions between the quencher agent and the fluorophore, leading to a decrease in intensity [47]. According to the Stern-

Volmer equation, the quenching rate constants (K_q) for peaks A, B, and C were 3.254×10^{12} L/mol·s, 1.341×10^{12} L/mol·s, and 1.203×10^{12} L/mol·s, respectively (Table S6). The upper limit of the collision-quenching constant, which represented the maximum quenching efficiency of the quencher on macromolecules, was 2.0×10^{10} L/mol·s [48]. Thus, the quenching process of HS by PFOA could be attributed to static quenching, indicating possible complexation between PFOA and HA or FA. In addition, the binding sites of the quencher and fluorophore were analyzed by plotting $\log [(F_0 - F) / F]$ against $\log PFOA$. The analysis showed that the binding sites (n) for HA were 1.42, while the binding sites for peak B and peak C were 0.52 and 0.53 (< 1), respectively, indicating that PFOA had only one class of fluorophore binding site in FA.

3.4.2 Synchronous fluorescence and quenching mechanism

SFS can also reflect the effect of PFOA adsorption on the components of organic matter. In addition, unlike one-dimensional spectra, two-dimensional SFS can differentiate overlapping and hidden peaks allowing for the analysis of the interactions between fluorophores and quenchers through variations in signal peaks.

The common components of DOM, including protein-like materials (i.e., tyrosine-like (250–265 nm) and tryptophan-like materials (265–300 nm), fulvic acid-like (300–380 nm), and humic acid-like (380–550 nm) materials, could be identified based on their SFS characteristics [49]. The characteristic peak A of HA and the characteristic peaks B and C of FA were located at 482 nm, 285 nm and 365 nm, respectively (Fig. 5). The results indicated that at pH 5.6, humic acid-like material dominated in HA, while tryptophan-like and fulvic acid-like materials were the main fluorescent substances in FA. With increasing concentrations of PFOA, the fluorescence intensity of peak B (from 235 to 115) diminished slightly, whereas the fluorescence intensities of peaks A (from 299 to 90) and C (from 484 to 250) decreased substantially. The results indicated differing binding behaviors (e.g., binding affinity, binding sequence) between HA and FA with PFOA. In addition, slight blue shifts were observed for peak A (from 482 nm to 480 nm), peak B (from 285 nm to 280 nm) and peak C (from 365 nm to 360 nm). The observed slight blue shifts in the emission maxima of all peaks upon PFOA addition further suggest that PFOA binding alters the electronic environment of HS, potentially changing their molecular conformation [50].

3.4.3 2D-COS

2D-COS enhances spectral resolution and enables a clearer analysis of fluorescent component peaks by extending the spectrum into two dimensions. There was one positive autopeak for HA and two positive autopeaks for FA along the diagonal line of the synchronous maps (Fig. 6a, 6c). Specifically, the positive autopeak of HA was centered at 482 nm, while the positive autopeaks for FA were centered at 285 nm and 365 nm, with the peak at 365 nm being more intense than that at 285 nm. This indicated that the fluorescence of humic acid-like components (482 nm) in HA and fulvic acid-like components (365 nm) in FA were more susceptible to PFOA addition.

The asynchronous 2D correlation maps further revealed the sequential order of the fluorescent components' responses to PFOA perturbation. (Fig. 6b, 6d). According to Noda's rule, in HA, the 482 nm peak (humic acid-like) responds to PFOA before the 499 nm peak (humic acid-like), indicating the contribution order of these two humic acid-like fluorescent components to PFOA binding. [27]. For FA, the asynchronous response sequence of multiple peaks was 365 nm (fulvic acid-like) first, followed by 340 nm (fulvic acid-like), and then 285 nm (tryptophan-like), demonstrating that different components bind with PFOA in a time-dependent manner, with fulvic acid-like components preferentially involved.

Overall, these results elucidate the binding mechanisms and dynamics between PFOA and different fluorescent components in HS. Due to their structural and chemical characteristics, humic acid-like and fulvic acid-like substances play dominant roles in interacting with PFOA, being preferentially bound and causing changes in fluorescence intensity. This not only reflects the selective adsorption of PFOA by HS components but also provides a molecular-level understanding of PFOA migration and distribution in soil environments, aiding in predicting its environmental behavior and associated risks.

3.5 FT-IR

Figure S3 showed the FTIR spectroscopy of soil and HS before and after PFOA adsorption. The peak intensities in the fingerprint region of soil and HS changed only slightly compared to the pre-adsorption period. The characteristic peaks observed at 3421–3428, 2851–2924, 1636 – 1582, 1400–1403, 1240–1383, 1087 – 1031 and 604–777 cm^{-1} were attributed to -OH (H-bonds), -CH₂ (aliphatic group), C = C (aromatic group) or N-H (amide groups), O-H (alcohols or carboxylic acids), C-O (carboxylic acids) or -OH (phenolic or alcohol), C-O-C, and carbonate substances, respectively [29, 51].

After PFOA adsorption, the most significant reductions occurred in the bands around 1240 cm^{-1} (C-O or -OH) and 1031 cm^{-1} (C-O-C), especially in HA and soil, suggesting involvement of oxygen-containing functional groups in the binding process. The broad -OH stretching bands (3421–3428 cm^{-1}) also showed intensity changes, implying hydrogen bonding or hydrophobic interactions. The results of ¹³C NMR confirmed the findings from FTIR analysis (Table. S2). HA was primarily composed of alkyl carbon (76.17%), with very low contents of O-alkyl carbon (17.92%) and carboxyl/carbonyl carbon (0.50%), indicating that its structure is mainly characterized by hydrophobic alkyl chains. In contrast, FA exhibited significantly higher proportions of O-alkyl carbon (65.63%), aromatic carbon (19.01%), and carboxyl/carbonyl carbon (5.67%), suggesting a more polar structure with a richer variety of functional groups.

The results suggested soil and HS may have formed carbon-hydrogen bonds with PFOA functional groups and produced carboxylic acids and carboxylic acids, and ester bound to PFOA through in situ chemical reactions involving carboxyl and phenolic hydroxyl groups [52]. Meanwhile, the limited changes in FA correlate with its highly oxygenated and polar nature, which may sterically hinder such interactions. A combined FTIR and ¹³C NMR analysis revealed that the primary interaction mechanisms between PFOA and HS involved hydrophobic interactions and the formation of hydrogen bonds or possible esterification reactions between the carboxyl groups of PFOA and functional groups such as hydroxyls

and ether linkages present in HA and soil. These structural distinctions, along with the differential accessibility of reactive functional groups, account for the enhanced adsorption capacity of the Soil + HA system for PFOA.

3.6 Adsorption mechanism

The surface electrostatic potential (ESP) is used to assess the propensity for electron acceptance and donation. The surface potential distribution of HA and FA molecules was heterogeneous, while PFOA exhibited a relatively uniform surface charge distribution (Fig. 7). The maximum positive and negative charges of HA were 61.04 and -40.25 kcal/mol, respectively, while those for FA were 51.96 and -46.44 kcal/mol, respectively. The negative charge of HA and FA was primarily localized on the carbonyl oxygen atom and the oxygen atom in the carboxyl group, while high positive potentials were observed around the carboxyl, alcohol hydroxyl, and phenol hydroxyl groups. Overall, the electrostatic potentials of both HA and FA surfaces were predominantly negative potential values, suggesting that HA and FA are more nucleophilic and more likely to interact with positively charged particles (Fig. 7d, 7e) [53]. In contrast, PFOA exhibited a relatively uniform surface charge distribution, with the overall negative electrostatic potential values (Fig. 7f). PFOA displayed negative charges around the carbonyl oxygen atom and the F atom, with a positive potential indicated around the carboxyl group in red. The results indicated that negatively charged PFOA may encounter electrostatic repulsion from negatively charged HS. Additionally, the ESP values indicated that FA has a higher negative potential than HA, suggesting there is a stronger electrostatic repulsive effect between FA and PFOA. Consequently, the HS adsorbed on the soil surface may generate electrostatic repulsion with PFOA, and Soil + FA shows a stronger electrostatic repulsion towards PFOA than Soil + HA.

Soil is a multiphase system comprises various minerals, organic matter and microorganisms. The adsorption mechanisms of PFOA in soil are complex and include ion exchange, surface hydrophobic interactions, electrostatic interactions, partitioning, and other processes. Based on the experimental results of isothermal adsorption, the adsorption capacity of PFOA followed the order of Soil > Soil + HA > Soil + FA > HA > FA. The specific surface area of soil colloids provided crucial sites for ion exchange and hydrophobic interaction sites for the PFOA tail. HA and FA occupied some available adsorption sites on the surface of soil colloids, thereby inhibiting PFOA adsorption in soils. Additionally, the addition of HS increased the electronegativity of soil particle surfaces, reducing the adsorption capacities of soil for PFOA presented as the anionic form. On the other hand, the results of the fluorescence quenching experiment also indicated that the fluorescence of HS was gradually quenched as the PFOA concentration increased, confirming the complexation between HS and PFOA exist during the adsorption of PFOA in soil. Combining the above results, although HS formed some complexes with PFOA, it still interfered with the adsorption of PFOA in soil in general. Furthermore, different fractions of HS had varying effects on PFOA adsorption in soils. HA has the stronger hydrophobicity than FA, which means it could provide more hydrophobic interaction sites for the PFOA tails. Moreover, Compared to FA, HA was more effective at promoting the formation of soil aggregates by bridging soil particles. These aggregates not only increased the available adsorption surface area, but also enhanced hydrophobic

interactions with PFOA due to the enrichment of organic matter [54, 55]. Furthermore, the higher electronegativity of the FA also contributed to a greater negative effect on PFOA adsorption in soil. Based on the above discussion, a proposed mechanism for the effect of HS on soil PFOA adsorption was illustrated (Fig. 8).

4. Conclusion

This study systematically revealed the effects and mechanisms of HS on the adsorption behavior of PFOA in soil. The results showed that the addition of 0.1% HS significantly reduced the soil's adsorption capacity for PFOA, with adsorption capacities ranked as: soil > soil + HA > soil + FA > HA > FA. The negative charge of HS increased electrostatic repulsion between soil particles and PFOA while occupying some adsorption sites, leading to an overall decrease in adsorption. Different types of HS had distinct effects on PFOA adsorption by soil. FTIR and ^{13}C NMR analyses indicated that PFOA adsorption mainly involved hydrogen bonding and hydrophobic interactions through oxygen-containing functional groups such as -OH and C-O-C. HA, rich in hydrophobic alkyl carbon, exhibited significantly stronger adsorption of PFOA than FA, which contained more polar functional groups. DFT calculations further confirmed that the more negatively charged FA caused stronger electrostatic repulsion with PFOA. Overall, HA demonstrated stronger adsorption capacity due to hydrophobic interactions combined with weaker electrostatic repulsion. Additionally, fluorescence spectroscopy and 2D-COS analyses revealed that PFOA preferentially binds to humic acid- and fulvic acid-like substances, with static quenching as the main mechanism, confirming the formation of HS-PFOA complexes. Although both HA and FA increased PFOA mobility in soil by negatively affecting adsorption, their mechanisms of action differed. This study provides valuable insights for future soil remediation, particularly in the selection of appropriate HS, where their distinct properties can be used to optimize remediation strategies.

Declarations

CRedit authorship contribution statement

Mengwei Li: Investigation, Data curation and Writing-original draft. **Xinlin Wang:** Investigation and Writing-review & editing. **Xiaochong Wang:** Methodology, Investigation and Data curation. **Wei Zhang:** Conceptualization, Supervision, and Writing-review & editing. **Guangli Xiu:** Supervision and Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version.

Author Contribution

Mengwei Li: Investigation, Data curation and Writing-original draft. Xinlin Wang: Investigation and Writing-review & editing. Xiaochong Wang: Methodology, Investigation and Data curation. Wei Zhang: Conceptualization, Supervision, and Writing-review & editing. Guangli Xiu: Supervision and Funding acquisition.

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Figures

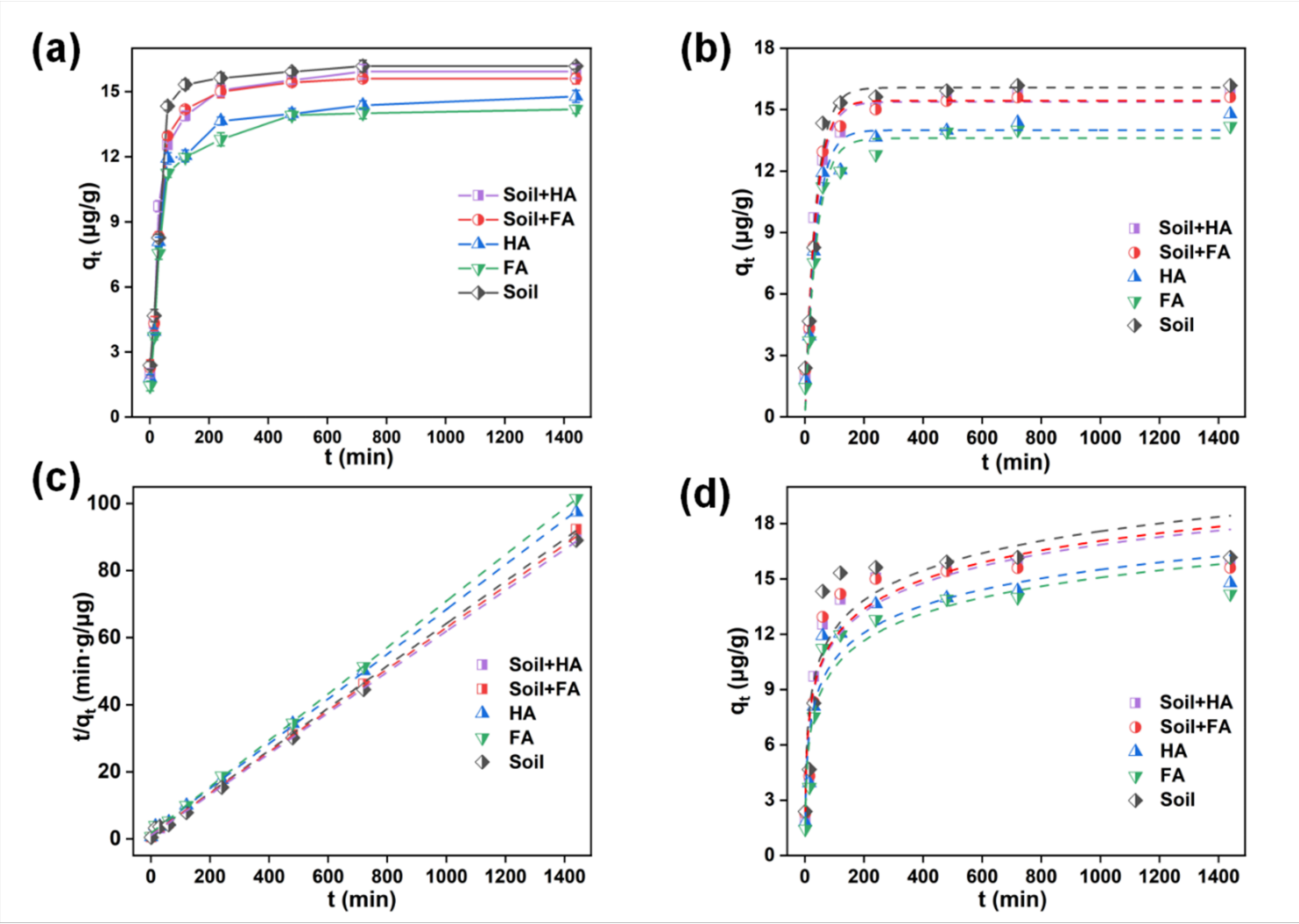


Figure 1

Effect of reaction time on adsorption (a) of PFOA, pseudo-first order model (b), pseudo-second order model (c) and Elovich model (d), $C_{\text{PFOA}} = 2 \text{ mg/L}$, $T = 298 \text{ K}$, $\text{pH} = 7.0$.

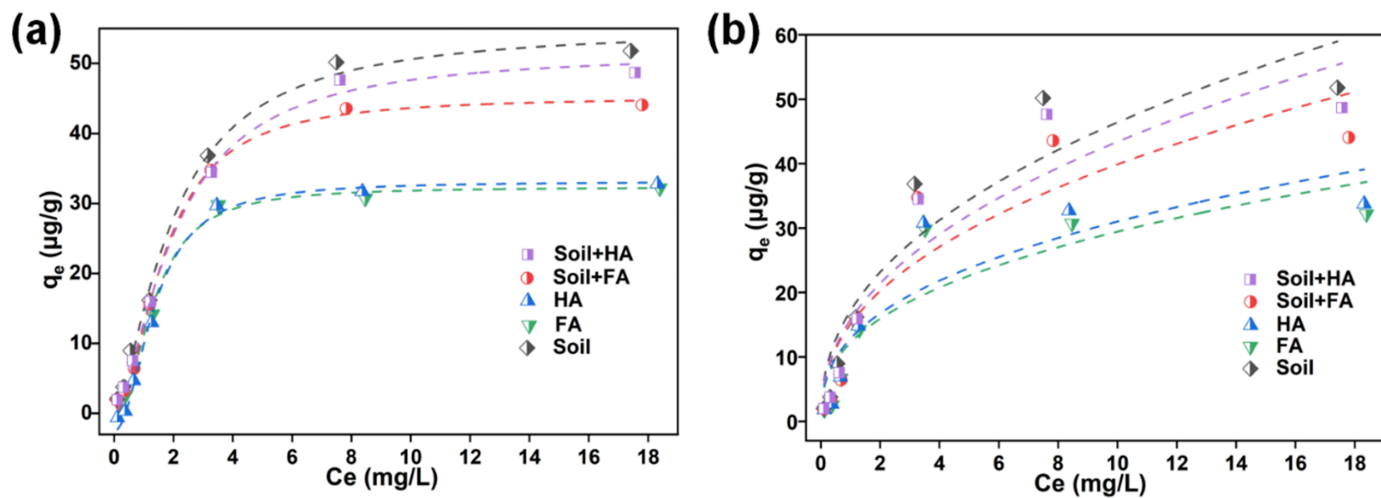


Figure 2

Adsorption isotherms of PFOA, (a) Langmuir isotherms, (b) Freundlich isotherms, $t=24$ h, $T=298$ K, $\text{pH}=7.0$.

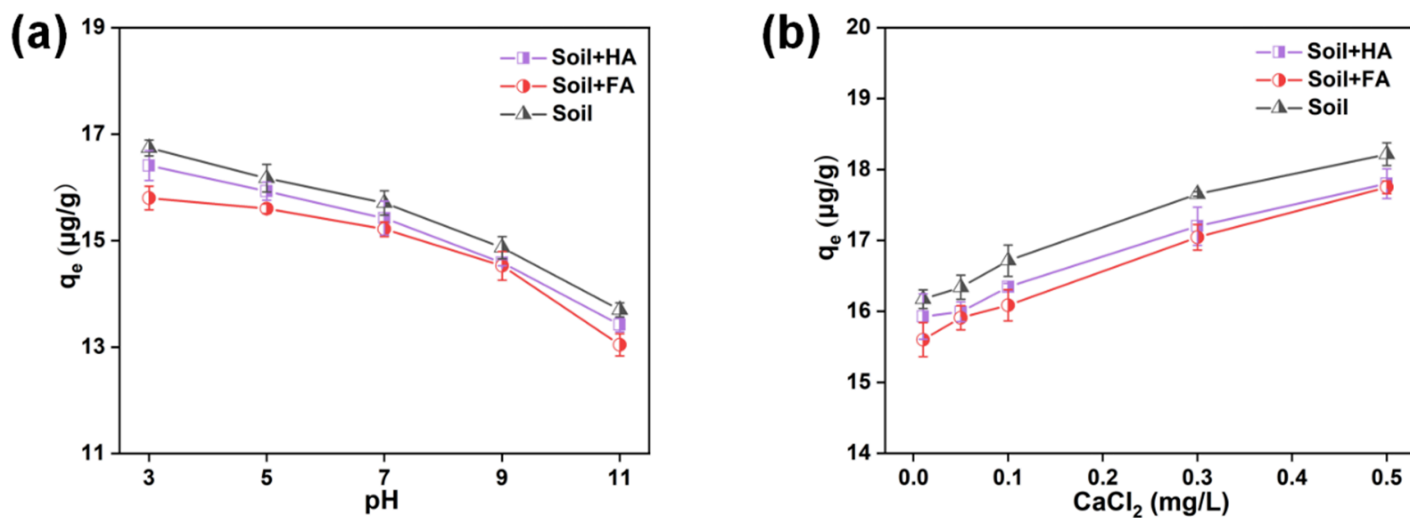


Figure 3

Effects of different factors on the adsorption of PFOA in three types of soils,

(a) pH, (b) Ca^{2+} concentration, $C_{\text{PFOA}} = 2$ mg/L, $t=24$ h, $T=298$ K, $\text{pH}=7.0$.

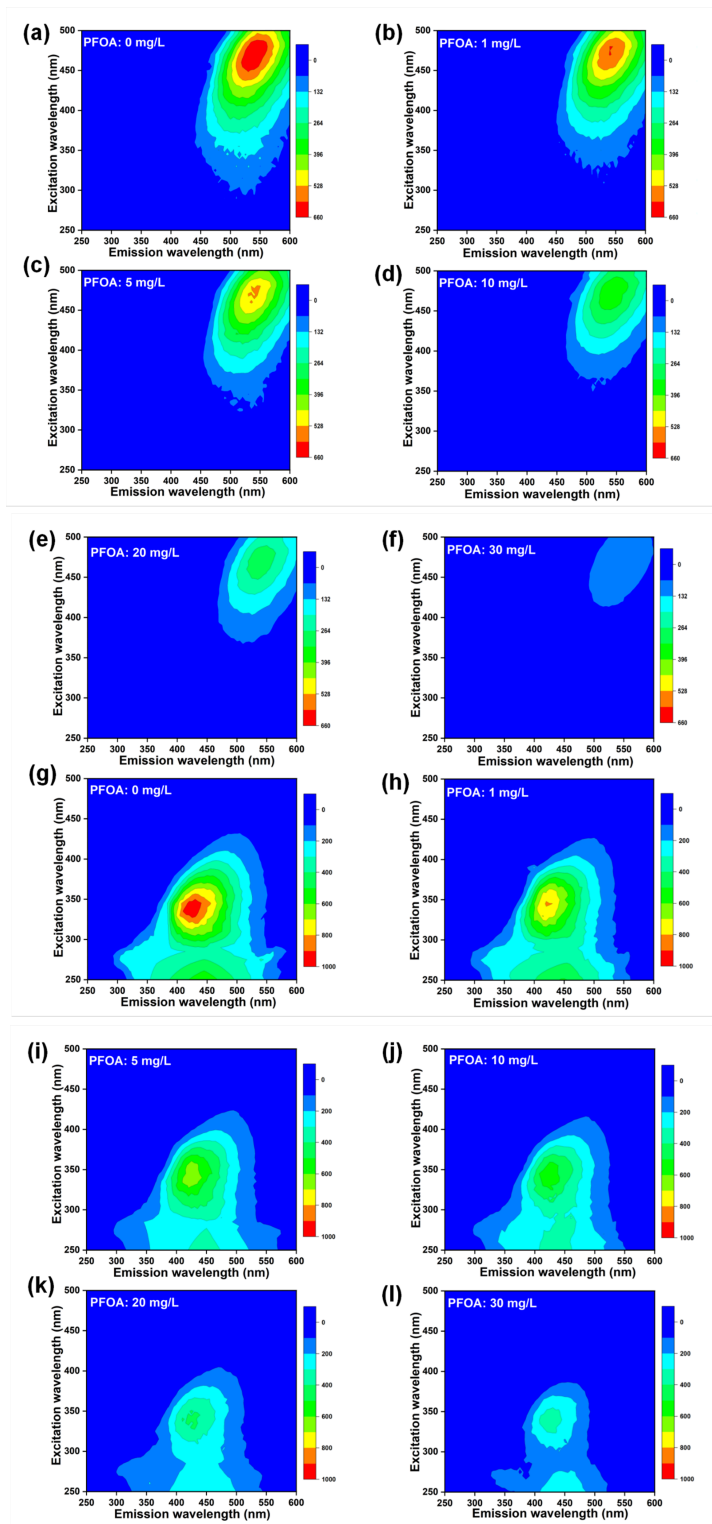


Figure 4

3D-EEM fluorescence spectra of HS (a-f: HA, g-l: FA) with increasing PFOA concentrations (0-30 mg/L), $t=8$ h, $T=298$ K, $pH=5.6$.

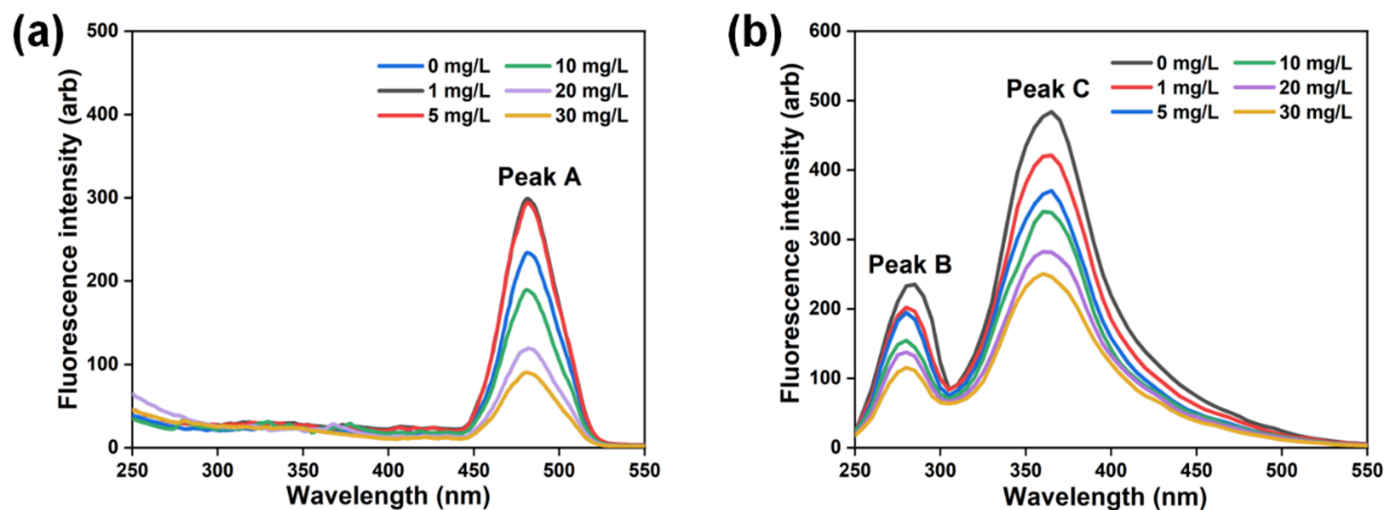


Figure 5

SFS of HS at different PFOA concentrations (a. HA, b. FA), $t=8$ h, $T=298$ K, $pH=5.6$.

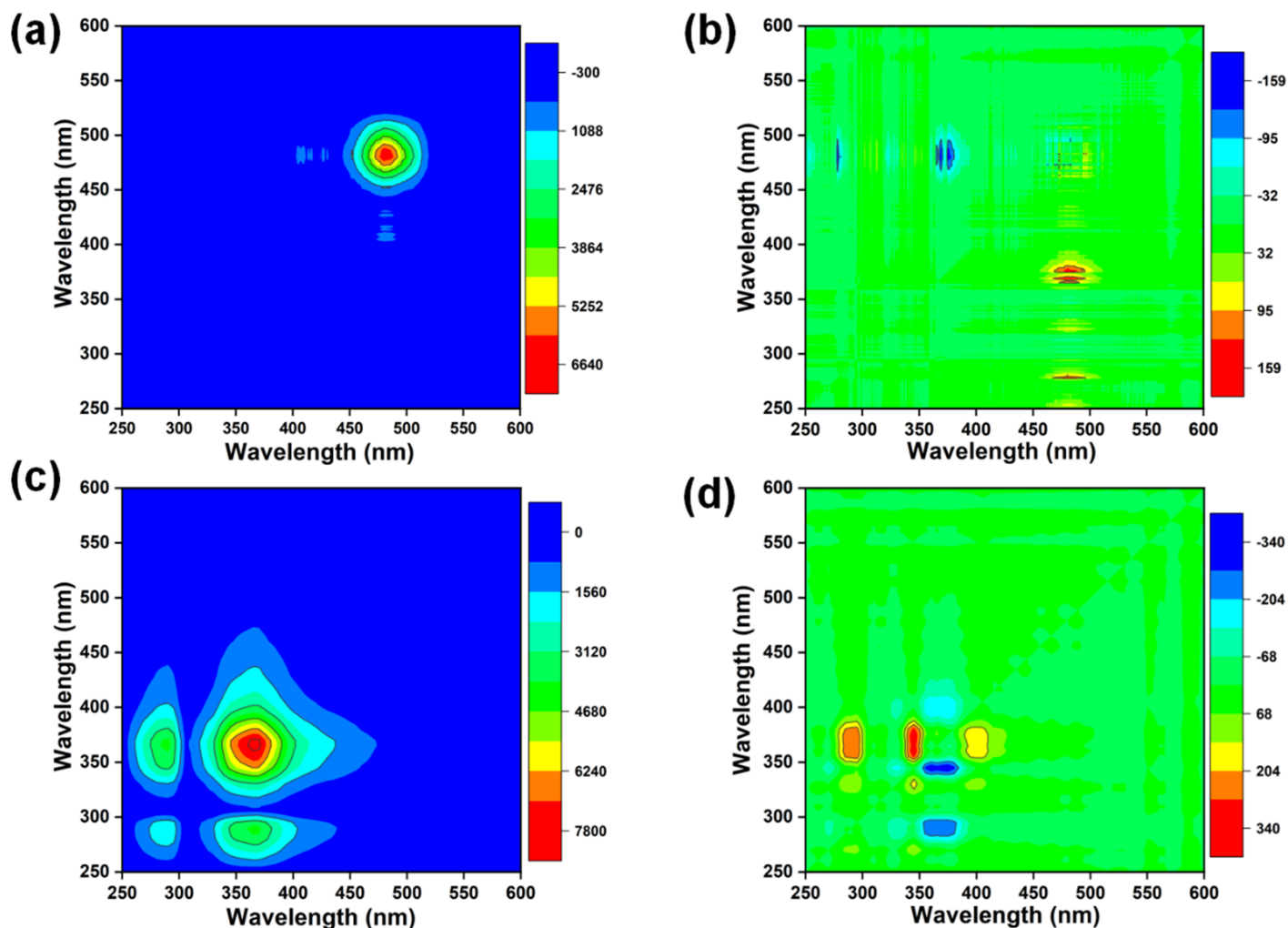


Figure 6

Synchronous and asynchronous 2D fluorescence correlation maps of the HS (a, b. HA, c, d. FA) with PFOA (0-30 mg/L), t=8 h, T=298 K, pH=5.6.

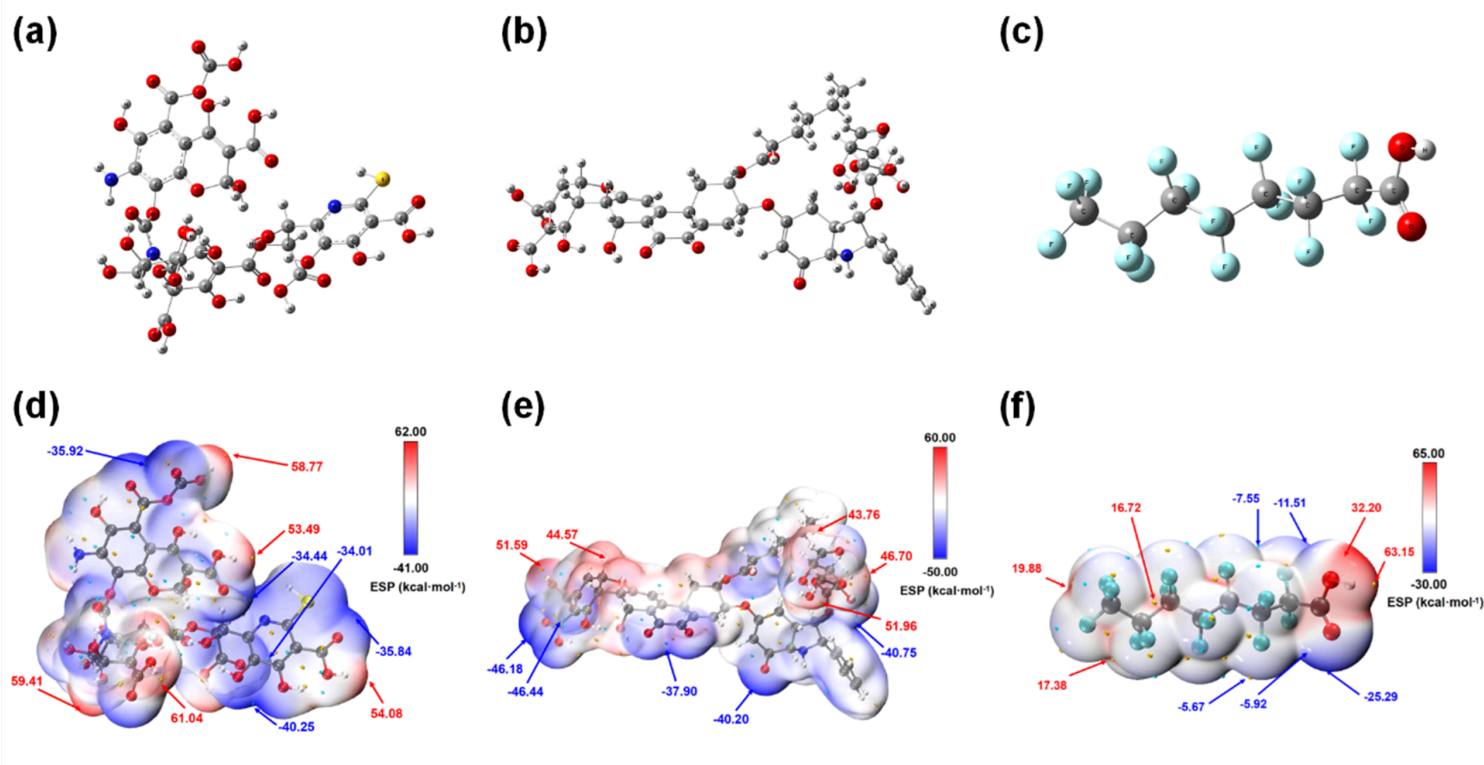


Figure 7

Optimization of the structure and electrostatic potential of adsorbent (HA, FA) and PFOA molecules (a, d. HA, b, e. FA, c, f. PFOA).

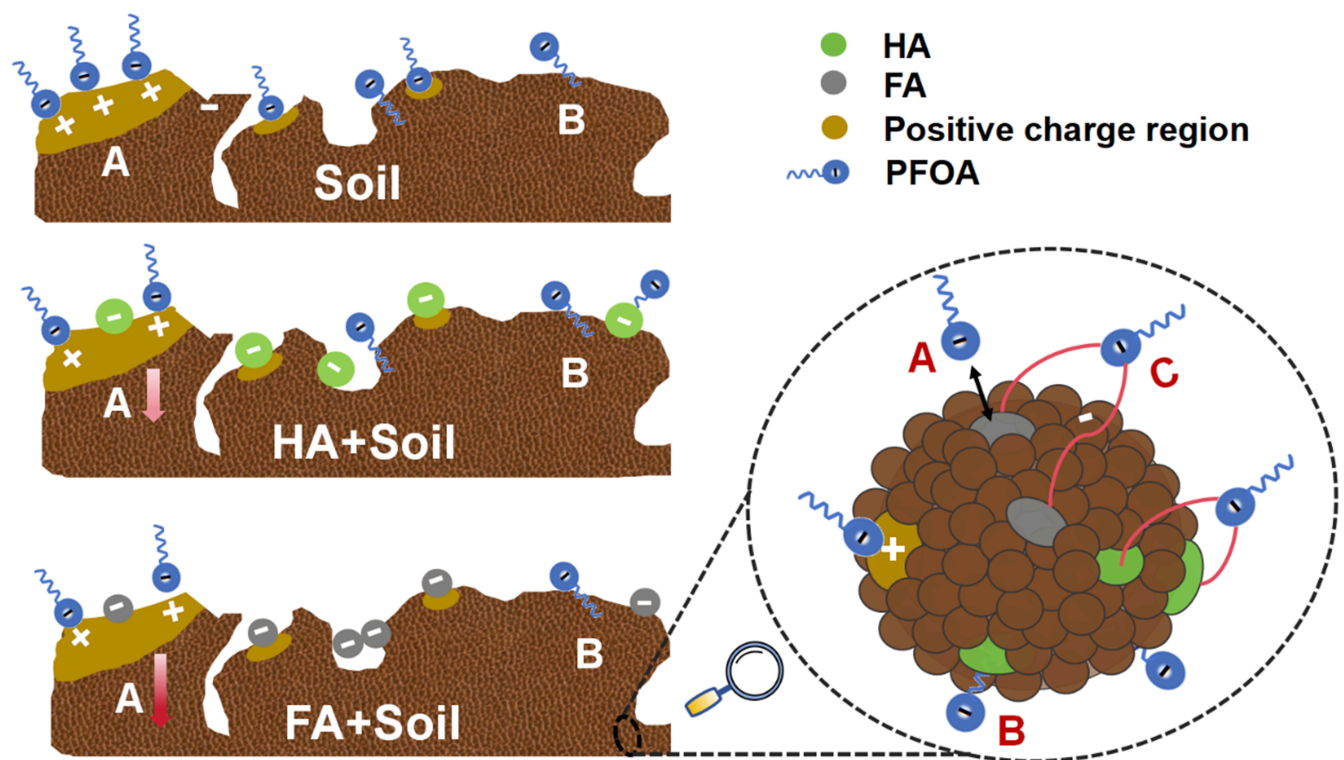


Figure 8

Adsorption mechanism of PFOA on soil with/without HS.

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