Integrated investigations on the adsorption mechanisms of fulvic and humic acids on three clay minerals

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HIGHLIGHTS

- ▶ More HA is adsorbed on kaolinite and smectite than FA via hydrophobic interaction.
- ▶ More FA is adsorbed on vermiculite than HA due to an electron transfer mechanism.
- ▶ Ligand exchange is an important mechanism for FA and HA adsorption on clay minerals.
- ▶ Iron cation plays an important role in the adsorption of FA and HA on vermiculite.

GRAPHICAL ABSTRACT

FA and HA have different adsorption behaviors on the clay minerals of kaolinite, smectite and vermiculite.

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ABSTRACT

Adsorption behaviors of fulvic acid (FA) and humic acid (HA) on kaolinite, smectite and vermiculite were investigated. To explore the adsorption mechanism, characterization of both the adsorption FA/HA-clay complexes and suspensions was conducted by utilizing multiple analytical techniques including liquid-state ^1H nuclear magnetic resonance spectroscopy, high performance size exclusion chromatography, UV-vis spectroscopy, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. Both FA and HA underwent fractionation during the adsorption due to different affinity for the functional moieties of FA/HA on the minerals. More HA was adsorbed than FA on kaolinite and smectite mainly via hydrophobic interaction. Electron transfer from aromatic units of FA to iron cation induced more FA than HA adsorbed onto vermiculite at higher FA/HA concentrations ($>20\text{ mg C/L}$). Specific surface area and pore volume analyses indicated HA with larger particle size was prone to accumulate on the external mineral surfaces, while FA was easier than HA to block pores of the minerals. The increased pH in clay suspensions after FA/HA adsorption suggested that ligand exchange occurred and FA/HA-clay complexes formed, particularly for the 2:1 type minerals of smectite and vermiculite with the increase of pH at 0.41 and 0.62 units, respectively. Furthermore, the increase of the equilibrium pH or the decrease of the ionic strength led to the reduction of FA/HA adsorption on all the three minerals. Due to rich in iron cation, more carboxyl and hydroxyl functional groups were facilitated for the ligand exchange and cation-bridging on vermiculite, and thus improved the adsorption capacity. The results of this study will improve our understanding of the roles of mineral interfacial properties, characteristics of FA and HA in the adsorption of FA/HA on clay minerals.

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1. Introduction

Natural organic matter (NOM) is present throughout the ecosystem [1,2], and clay minerals are the important components of soils and sediments which are commonly coated with NOM as organic-clay complexes in the soil and sedimentary environments

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[3–5]. Interactions between NOM and clay minerals are expected to modify surface properties and reactivity of clay minerals [6,7], and change the mobility of pollutants bound to them [8,9]. Therefore, investigation of the interactions between NOM and clay minerals is the basis not only for understanding the interfacial properties of soils and sediments, but also for elucidating behaviors of contaminants in the natural environments [10,11].

Due to the heterogeneities and complexity of NOM in its composition and conformation, various adsorption behaviors have been observed for NOM with different minerals. Namjesnik-Dejanovic et al. [12] studied the adsorption of a muck fulvic acid (FA) on kaolinite and suggested that aromatic fractions were preferentially adsorbed. Similarly, Balcke et al. [13] reported that the adsorption affinity of humic substances (HS) onto kaolin clay was directly correlated with their aromaticity. Contrary to these conclusions, Wang and Xing [9] reported that aliphatic fractions of humic acid (HA) were preferentially adsorbed on both montmorillonite and kaolinite while aromatic fractions were left in the solution. Feng et al. [14] also observed that polymethylene groups of peat HA tended to be adsorbed on kaolinite, whereas montmorillonite adsorbed more aromatic compounds. It has also been suggested that large hydrophobic molecules of NOM have the strongest affinity toward kaolinite and montmorillonite surfaces [15]. However, research by Chorover and Amistadi [16] showed that lower molecular-weight NOM was preferentially retained on montmorillonite. Although there have been many studies to characterize the interactions between NOM and clay minerals, it is still difficult to reach a consensus on the adsorption behaviors and mechanisms of NOM on minerals.

FA and HA as the principal fractions of HS are the major components of NOM. Both FA and HA consist of heterogeneous components and have some similar properties, but still a general distinction can be observed between them. Compared to FA, HA molecules are larger in size (higher molar mass), contain more carbon, and are less soluble [8]. Although a number of studies have been performed on the adsorption of FA/HA on clays [6,12–14], how the differences in characteristics of FA and HA such as composition and particle size result in their different adsorption behaviors on clays has not been well elucidated. Furthermore, adsorption of FA/HA on minerals was dependent on the surface properties of the minerals [16]. As a result, the differences in type of clay minerals would lead to different reaction mechanisms and therefore to a different adsorption phenomenon. Consequently, it is necessary to identify the differences in FA/HA adsorption on various clays. Most of the current studies were conducted with one kind of clay, while few studies investigated the different adsorption phenomena and mechanisms between FA and HA adsorption onto different clay minerals.

Accurately exploring the adsorption mechanisms for FA/HA on clay minerals is still challenging due to the extreme complexity of FA/HA and limitation of analytical techniques. Comprehensive characterization of both the adsorption FA/HA-clay complexes and suspensions is a prerequisite to reveal the adsorption processes and further explore the adsorption mechanism of FA/HA on clays. Therefore, a combination of multiple analytical techniques is essential to provide comprehensive information on both FA/HA-clay complexes and suspensions. In the present study, the adsorption of FA and HA on three clay minerals of kaolinite, smectite and vermiculite with distinct crystal structures (Fig. S1 in the Supplementary material, SM) was investigated. Adsorption mechanisms were studied by comprehensively analyzing the physicochemical properties of the clays, adsorption FA/HA-clay complexes and suspensions using a combination of multiple analytical techniques including liquid-state ^1H nuclear magnetic resonance (NMR) spectroscopy, high performance size exclusion chromatography (HPSEC), UV-vis spectroscopy, Fourier

transform infrared (FT-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS).

2. Materials and methods

2.1. Clay mineral, FA and HA preparation

Kaolinite, smectite and vermiculite were obtained from Beijing Ruizhx Tech Co., Ltd. (Beijing, China). The $<2\ \mu\text{m}$ fraction of each clay mineral was separated by sedimentation, and then was respectively made homoionic by resuspension in a 0.01 mol/L NaCl to remove exchangeable cations prior to adsorption experiments. The excess salts were removed by washing with deionized water with repeated centrifugation and resuspension until a negative chloride test was obtained with AgNO_3 . The homoionic clay minerals were freeze-dried and kept in a desiccator for later use. Homoionic Fe^{3+} -vermiculite was prepared by sequential washing of the original vermiculite with 1 mol/L FeCl_3 [17], and partially de-iron-vermiculite was prepared by washing of the original vermiculite with 2 mol/L HCl to remove iron oxide from the vermiculite surface [18]. Then the excess FeCl_3 and HCl were removed in the same way as described above. The researches have shown that these treatments only slightly affect the crystal structures of clay minerals [17,18].

FA and HA were extracted from a Denmark peat sample according to the standard protocol of the International Humic Substances Society [19]. Purified FA and HA were freeze-dried and kept in a desiccator. Stock solutions of FA and HA were prepared by dissolving an appropriate amount of FA or HA in a base solution, followed by dilution with electrolyte solution (0.01 mol/L NaCl) into the required concentration. The pH was adjusted to 7.0 with NaOH or HCl (0.1 mol/L) before use.

2.2. Preparation of FA/HA-clay complexes

FA/HA-clay complexes were prepared by mixing 1 L of 200 mg C/L FA or HA solution with 30 g of homoionic clay (kaolinite, smectite or vermiculite) according to the solid/liquid ratio in the batch adsorption experiments. The mixture was adjusted to neutral pH with NaOH and HCl (0.1 mol/L) and then under vigorous magnetic stirring for 48 h (sufficient to reach the equilibrium state) at room temperature. The samples were centrifuged for 30 min at $4000 \times g$ and the supernatants were decanted and collected. The clay pastes were washed with deionized water to remove any unbound FA and HA by repeated centrifugation and resuspension until no significant desorption was observed by total organic carbon (TOC) analysis. The solid residue isolated after centrifugation is defined as the FA/HA-clay complex. Controls without clays were prepared in the same way. The collected samples and controls were then freeze-dried for further FTIR and ^1H NMR analyses as described below.

2.3. Characterizations

The freeze-dried FA and HA were analyzed for C, H, N and S contents with a Vario EL III Elemental analyzer (Elementar Co. Germany). Oxygen content was calculated by the mass difference. Ash content was determined by combustion of FA/HA at $800\ ^\circ\text{C}$ for 4 h. ^1H NMR spectra were recorded at 298 K on a Bruker Avance III spectrometer (Bruker, Germany) operating at 400 MHz. Briefly, the freeze-dried samples and controls without clay (10 mg) were dissolved in $\text{DMSO}-d_6$ (0.5 mL), and the chemical shifts (δ , ppm) were internally referenced to TMS.

Molecular weight distributions of the samples and controls without clays with an initial concentration of 4 mg C/L were assessed by high performance size exclusion chromatography

(HPSEC) using the method of Luo et al. [20]. The HPSEC data were collected by an Agilent 1200 HPLC system (Agilent Technologies, Inc., USA) equipped with an ultraviolet detector, a BioSep-SEC-S 2000 size-exclusion column (300 × 7.8 mm) and a guard column (35 × 7.8 mm) (Phenomenex, USA). The eluents were detected at a wavelength of 254 nm. UV–vis spectroscopy analysis of all samples and controls without clays in batch adsorption experiments was conducted with a UV759S spectrometer (Shanghai Precision & Scientific Instrument, China) equipped with a quartz cell of 1.0 cm path length. Specific UV absorbance (SUVA) at 254 nm ($SUVA_{254\text{ nm}} = UV_{254\text{ nm}}/TOC$) was used as an index of relative aromaticity of dissolved organic carbon (DOC) [21,22].

The clays, freeze-dried FA and HA and FA/HA-clay complexes were subjected to the following analyses. FTIR spectra were recorded in the range of 4000–600 cm^{-1} using a Nicolet iN10 MX Micro-infrared Spectrometer (Thermo Scientific, USA). Zeta potential analysis was performed with a Mastersizer 2000 particle size analyzer (Malvern Instruments, UK). All samples contained 0.1% solid in deionized water and were exposed to supersonic dispersion for 10 min before determination. Specific surface area (SSA) and pore volume were measured by applying the Brunauer–Emmett–Teller (BET) equation to multipoint isotherms of N_2 at 77 K with a Quadrasorb SI-MP analyzer (Quantachrome Instrument, USA) using the BET method. The morphological features of FA and HA were analyzed by a Hitachi S-3000N scanning electron microscope (SEM, Hitachi, Japan). The XRD patterns were recorded on an X'Pert Pro X-ray diffractometer (PANalytical Co., the Netherlands) equipped with a Cu source ($\text{Cu K}\alpha$). The scanning angle (2θ) ranged from 4° to 10° in step of 0.01. XPS measurements were carried out using a Kratos Axis Ultra spectrometer (Kratos Analytical, Manchester, U.K.) equipped with a monochromatized aluminum X-ray source. Iron contents in the clays were determined by inductively coupled plasma-optical emission spectrometer (ICP-OES, Optima 2000DV, Perkin-Elmer Co., USA) after microwave digestion with HNO_3 , HCl and HF in a ratio of 3:1:1 [23].

2.4. Adsorption experiments

Triplicate clay samples (0.6000 g) were placed into 30 mL glass centrifuge tubes with Teflon liners. A 20 mL aliquot of FA/HA solution (pH 7.0) with varying concentrations (5–160 mg C/L) or FA/HA solution at a constant concentration of 50 mg C/L with varying pH (7–11) at different ionic strengths (0.01 and 0.1 mol/L NaCl) was added. Controls without clay were prepared in the same way to account for possible loss of FA/HA other than adsorption by the clays. The samples and controls were equilibrated on a reciprocating shaker at 105 rpm at $25 \pm 1^\circ\text{C}$ for 48 h in the dark. Kinetic measurements showed that 48 h was sufficient for FA/HA to reach an equilibrium adsorption on all the minerals (data not shown). After equilibration, the samples and controls were centrifuged for 30 min at $4000 \times g$ and the supernatants were decanted for further analysis. The pH and concentration of organic carbon were determined in the filtered supernatants of the samples and controls with a FE20K pH meter (Mettler Toledo, Switzerland) and a TOC Analyzer (Phoenix 8000, Tekmar-Dohrmann Co., USA). The amount of FA/HA retained by the clay minerals was calculated by the difference between concentrations in the initial and equilibrium solutions.

2.5. Data analysis

Adsorption isotherms of FA/HA were described by the Freundlich model, that is, $C_s = K_f C_e^n$, where C_s is mg C FA/HA sorbed per kg clay, C_e is equilibrium solution concentration (mg C/L) of FA/HA, K_f is the Freundlich coefficient $[(\text{mg C/kg})(\text{L/mg C})^n]$, and

Fig. 1. Adsorption of FA (blank symbols) and HA (solid symbols) on the clay minerals and Freundlich model fittings (lines).

n , an empirical constant, is an indicator of isotherm nonlinearity. The values of K_f and n for all adsorption isotherms were calculated by the Freundlich equation fitted using Origin 7.5 software at the 95% confidence level. Statistical analysis of the results was performed with SPSS for Windows (version 17.0, SPSS Inc.) using ANOVA (Tukey test, $p < 0.05$).

3. Results and discussion

3.1. Adsorption isotherms

Adsorption isotherms for FA and HA on the clay minerals are shown in Fig. 1 and the Freundlich model parameters are provided (Table S1 in the SM). The adsorption data were well fitted to the Freundlich model ($r > 0.99$). FA and HA exhibited distinct adsorption behaviors on the three clay minerals at the experimental conditions. Kaolinite and smectite had a higher adsorption capacity for HA than FA; however higher adsorption of HA than FA on vermiculite was only found when they were at lower levels ($< 20 \text{ mg C/L}$), and an opposite trend was obtained at higher levels. FA had the highest affinity toward vermiculite, followed by smectite and kaolinite. Vermiculite also showed a stronger affinity for HA than smectite and kaolinite at lower levels ($< 13 \text{ mg C/L}$). However, at higher HA levels, smectite exhibited the highest adsorption capacity for HA, followed by vermiculite and kaolinite. The increase of the equilibrium pH or the decrease of the ionic strength led to the reduction of FA/HA adsorption on all of the three clays (Fig. 2).

Fig. 2. Effects of pH and ionic strength on the adsorption of FA and HA on kaolinite (KFA, KHA), smectite (SFA, SHA) and vermiculite (VFA, VHA).

Fig. 3. ^1H NMR spectra of FA, HA and the relevant unbound FA/HA after their adsorption on kaolinite (KFA, KHA), smectite (SFA, SHA) and vermiculite (VFA, VHA).

3.2. Physicochemical characterization of FA, HA, clays and FA/HA-clay complexes

It is known that FA and HA belong to distinct groups and differ in elemental composition, molecular weight and functional group distributions. As explored by elemental analysis, HA had a lower (N+O)/C ratio than FA (Table S2 in the SM), indicating that HA was more hydrophobic than FA. The ^1H NMR results (Fig. 3) indicated that aliphatic moieties (0.8–2.2 ppm regions), aromatic moieties (6.5–8 ppm regions) [14,24] and a combination of amino acids, polysaccharides, aromatic methoxyl, or other moieties such as esters and ethers (3–5.5 ppm regions) [14,25] were the dominant fractions in the equilibrium solutions, while the strong signals at 2.50 ppm and 3.35 ppm were attributed to DMSO- d_6 and H $_2$ O [25,26], respectively. Fe was detected at 1.72 and 2.13 mg/L in the equilibrium solutions after FA and HA reacted with vermiculite, and the slightly broader peaks for unbound FA/HA after adsorption on vermiculite (Fig. 3) might be caused by the paramagnetic dissolved Fe. The HPSEC chromatograms indicated that the average molecular weight distribution of FA was significantly lower than that of HA (Fig. 4). These trends can be explained as a natural consequence of the extraction procedures.

Both FA and HA underwent significant fractionation during the adsorption process. As shown in Fig. 4, the larger-size molecules of FA/HA with higher molecular weight were preferentially adsorbed on the mineral surfaces, whereas the lower molecular weight

Fig. 4. HPSEC chromatograms of FA, HA and the unbound FA/HA after adsorption on kaolinite (KFA, KHA), smectite (SFA, SHA) and vermiculite (VFA, VHA).

fractions were left in the solutions, and this phenomenon was particularly obvious for their adsorption on vermiculite. Meanwhile, the HPSEC chromatograms also suggested that more FA/HA was adsorbed on vermiculite than on kaolinite and smectite with the initial concentration of 4 mg C/L based on the evidence that the measured absorbance is proportional to the concentrations of dissolved FA/HA [20].

Apart from different adsorption capacity for FA/HA, the three minerals also exhibited distinct affinity for the functional moieties of the FA and HA. Aliphatic moieties of FA/HA were preferentially adsorbed on kaolinite and smectite while aromatic moieties were preferentially adsorbed on vermiculite as indicated by the integration results of ^1H NMR spectra in Table 1. The different affinity of the three minerals for different functional moieties of FA/HA was also

Table 1

Integration results of ^1H NMR spectra and ratios of the sum of aliphatic to aromatic peak area.

Sample	Aliphatic C (0.8–2.2 ppm)	Aromatic C (6.5–8 ppm)	Ratio (aliphatic C/aromatic C)
FA	7.87 ^a	0.39	20.2
KFA	6.47	0.38	17.0
SFA	5.89	0.35	16.8
VFA	5.86	0.23	25.5
HA	9.45	0.45	20.9
KHA	7.78	0.42	18.5
SHA	7.32	0.39	18.8
VHA	5.93	0.24	24.7

^a The integration value of TMS was set 1.

Fig. 5. $SUVA_{254}$ values of FA, HA and the relevant unbound FA/HA after their adsorption on kaolinite (KFA, KHA), smectite (SFA, SHA) and vermiculite (VFA, VHA).

confirmed by the $SUVA_{254}$ results (Fig. 5). After adsorbed on kaolinite and smectite, the $SUVA_{254}$ values of FA and HA in the equilibrium solutions tended to increase, indicating that aliphatic moieties were preferentially adsorbed from the solutions [22]. While the increase of $SUVA_{254}$ values for FA/HA after their adsorption on vermiculite was only evidenced with a low initial concentrations of FA (<20 mg C/L) and HA (<40 mg C/L), and an opposite decreasing trend was observed at higher concentrations of FA/HA. Once adsorbed on the minerals, the FA and HA formed stable FA/HA-clay complexes through their functional moieties as shown in the FTIR spectra (Fig. 6). After adsorbed on the minerals, the aliphatic groups (peaks at 2850 and 2926 cm^{-1}) were enriched on kaolinite and smectite, which was well consistent with the results of NMR and $SUVA_{254}$ analyses.

3.3. Mechanism analysis

A combination of the adsorption behaviors of FA/HA on the minerals and physicochemical analyses of the minerals, FA/HA-clay complexes and suspensions suggests there are several possible factors that may dominate the adsorption mechanisms. Firstly, the distinct differences in structures of the three minerals resulted in the different adsorption capacities of FA/HA on them. As a 1:1 type mineral (Fig. S1 in the SM), kaolinite had the smallest surface area (Table 2) and the relatively flat and smooth surface (Fig. S2 in the SM), therefore owning the weakest adsorption ability. As a 2:1 type mineral (Fig. S1 in the SM), smectite showed stratified structure with the largest SSA and thus had a strong adsorption

Fig. 6. FTIR spectra of (a) FA and HA, the unbound FA/HA after their adsorption on kaolinite (KFA, KHA), smectite (SFA, SHA) and vermiculite (VFA, VHA); (b) original clays (kaolinite, smectite and vermiculite), FA-clay complexes (KFAC, SFAC and VFAC) and HA-clay complexes (KHAC, SHAC and VHAC).

ability, particularly for HA (Fig. 1), while vermiculite had a loosely porous structure and also exhibited a strong adsorption ability for FA/HA [27].

Both FA and HA are a heterogeneous mixture with different molecular weight distributions and functional group compositions, and different functional moieties of FA and HA have distinct affinity for the mineral surfaces [28]. During the adsorption processes, both FA and HA were significantly fractionated on minerals. As shown in Fig. 4, the fractions with higher molecular weight were preferentially adsorbed on the mineral surfaces. It was believed

Table 2

Surface areas, pore volumes, carbon content and ζ potential of original clays and FA/HA-clay complexes.

Clay mineral	N ₂ BET SA (m ² /g)	Pore volume (cm ³ /g)	Percent C (%)	ζ potential (mV)
Kaolinite	1.96 ^a	0.005	0.30	−22.5
FA complex	1.94	0.004	0.37	−26.3
HA complex	2.05	0.005	0.31	−26.2
Smectite	19.09	0.036	0.10	−24.8
FA complex	15.42	0.031	0.18	−29.8
HA complex	20.09	0.037	0.15	−26.1
Vermiculite	12.92	0.035	0.15	−27.7
FA complex	12.38	0.029	0.29	−40.5
HA complex	13.08	0.034	0.18	−28.7

^a N₂ BET SA is the cumulative surface area determined with N₂ at 77 K using the Brunauer–Emmett–Teller (BET) equation.

Table 3

Effect of FA and HA (50 mg C/L) adsorption on the final equilibrium pH of the clay suspensions.

Suspensions	Original	FA adsorption	HA adsorption
Kaolinite	7.10 ± 0.04	7.17 ± 0.05	7.19 ± 0.06
Smectite	7.18 ± 0.04	7.62 ± 0.07	7.59 ± 0.05
Vermiculite	7.26 ± 0.05	8.01 ± 0.07	7.88 ± 0.08

that larger molecular weight fractions of dissolved HS which occupied more aliphatic functional groups [29] had a stronger affinity with clay minerals [15]. Due to the larger molecular weight of HA than FA, more HA molecules were fractionated from the solutions and adsorbed on the mineral surfaces as evidenced by the HPSEC results (Fig. 4). In addition, elemental analysis (Table S2 in the SM) showed that HA was more hydrophobic than FA, and therefore had a stronger hydrophobic interaction with clays. As a result, more HA than FA was adsorbed on kaolinite and smectite (Fig. 1). Although the minerals showed a higher adsorption capacity for HA than FA, it is noteworthy that a larger amount of FA was retained on minerals when FA/HA-clay complexes were prepared (Table 2). Due to the smaller particle size, FA tended to enter into the pores formed by close-packing of clay particles as evidenced by the smaller pore volumes and SSAs of FA-clay complexes than those of the original clays (Table 2). Therefore FA was relatively stable in the water-desorbing process for the preparation of FA/HA-clay complexes. Whereas, HA with much bigger particle size (Fig. S3 in the SM) tended to attach on the externally planar surfaces of the minerals and thus was more likely to be removed than FA by washing during the preparation. Meanwhile, the d_{001} reflection for basal spacing of the minerals in the XRD pattern did not suffer a significant change (Fig. S4 in the SM), indicating that FA and HA molecules did not significantly intercalate the mineral layers even for the 2:1 type of smectite and vermiculite [30].

Ligand exchange-surface complexation might be another important mechanism for FA/HA adsorption on the minerals. FTIR spectra showed there was a significant decrease in the peaks assigned to hydroxyl and carboxyl groups in FA and HA after the formation of FA/HA-clay complexes (Fig. 6). Furthermore, the pH values increased consistently although at small level after the adsorption of FA/HA on all the three minerals (Table 3), suggesting that the negatively charged FA/HA groups formed stable FA/HA-clay complexes through ligand exchange with the surface hydroxyl groups of the minerals, which is consistent with the results of previous researches [17,31]. Ligand exchange-surface complexation was highly influenced by pH and ionic strength [31,32]. It was observed that the adsorption of FA/HA on the clays decreased gradually with increasing pH, implying that hydroxyl ions in the aqueous solution might suppress ligand exchange between negatively charged FA/HA groups and the surface hydroxyl groups of the clay minerals. Ionic strength independency was also evidenced for the adsorption with more FA/HA adsorbed on the minerals at higher ionic strength (Fig. 2). Electrolytes could reduce the electrostatic repulsion between the clays and FA/HA and therefore improved the adsorption of FA/HA on the minerals. The adsorption of FA/HA on smectite and vermiculite was more strongly dependent on ionic strength than on kaolinite, owing to the higher CEC values of smectite and vermiculite than kaolinite [27].

However, there existed differences in the adsorption controlled by the ligand exchange mechanism among the minerals. This mechanism is more reasonable for FA/HA adsorption on the 2:1 type minerals of smectite and vermiculite than on the 1:1 type mineral of kaolinite, likely attributing to the more negatively charged surfaces as evidenced by the lower zeta potentials of smectite and vermiculite than kaolinite (Table 2). As a result, the pH value did

Fig. 7. XPS spectra of the original vermiculite, FA-vermiculite complex (VFAC) and HA-vermiculite complex (VHAC).

not change significantly after the adsorption of FA and HA on kaolinite. Weak ligand exchange ability of kaolinite was also observed in comparing DOC adsorption on kaolinite and gibbsite [33], and enzymes adsorption on kaolinite and goethite [34].

Vermiculite had the highest adsorption coefficients (K_f) for both FA and HA (Table S1 in the SM), which can be attributed to its particular surface element composition. ICP-OES analysis indicated that Fe contents were 0.21, 0.30 and 4.29 wt% in kaolinite, smectite and vermiculite, respectively. It is generally believed that trivalent cations can form relatively strong complexes with DOC [17,35,36]. With the presence of Fe^{3+} in vermiculite, more carboxyl and hydroxyl functional groups were facilitated for the ligand exchange and cation-bridging on the vermiculite surface, thus improving the adsorption capacities of FA/HA on vermiculite. This assumption was further confirmed by the evidence of a higher amount of FA/HA adsorbed on Fe^{3+} -vermiculite (6.58 wt% Fe) and a lower amount of FA/HA adsorbed on the partially de-iron-vermiculite (2.77 wt% Fe) compared with the adsorption on the original vermiculite (4.29 wt% Fe) (Table S3 in the SM). The role of iron cation in the adsorption of HA would be also affected by stereo-hindrance [17] due to the larger particle size of HA than FA. With the adsorption sites of iron cation on vermiculite saturated gradually, the adsorbed macromolecular units of HA limited its further accessibility to react with iron cation, and thus the adsorbed amount was reduced (Fig. 1). Therefore it was observed that different from FA/HA adsorption on kaolinite and smectite, FA adsorption on vermiculite was much higher than HA at higher concentrations.

Contribution of iron cation to the complexation of FA/HA on vermiculite also induced more FA than HA to retain on vermiculite, different from the adsorption of FA/HA on kaolinite and smectite (Fig. 1). Iron cation had a strong affinity for the aromatic moieties; therefore, aromatic moieties were preferentially attached to the vermiculite surface and the aromatic fractions in the solutions after adsorption were significantly decreased as evidenced by the results of NMR and SUVA₂₅₄ analyses (Figs. 3 and 5, Table 1). Previous works suggested that the phenomenon in which Fe^{3+} induced selective adsorption of aromatic moieties of NOM was probably due to the electron transfer mechanism [37,38]. In this study electron transfer was directly evidenced by the XPS spectra of iron cation (Fig. 7). The Fe 2p photoelectron spectra showed that the binding energy shifted toward lower energy by 0.10 and 0.19 eV for HA- and FA-vermiculite complexes compared with that of the original vermiculite, indicative a transfer of the electronic density from FA/HA to iron cation [30]. FA with lower molecular weight was easier than HA to get into close contact with vermiculite surface [8] and acted

as a stronger π -donor role than HA. The stronger cation- π bonding between FA and iron cation resulted in more FA adsorption on vermiculite, which was also confirmed by the much greater increase of surface negative charge for FA-vermiculite complex than HA-vermiculite complex (Table 2). By using Fe^{3+} -exchanged montmorillonite, Polubesova et al. [17] also observed the preferential adsorption of aromatic moieties of FA on Fe^{3+} -montmorillonite.

4. Conclusions

This study used a combination of multiple analytical techniques to provide comprehensive information on both FA/HA-clay complexes and suspensions and to investigate the different adsorption phenomena and mechanisms between FA/HA and different clay minerals. Overall, differences in structural and surface properties of clay minerals result in their different affinity for FA/HA, and differences in characteristics of FA and HA such as molecular weight, functional group compositions and hydrophobicity lead the different adsorption of FA and HA on kaolinite and smectite, while the electron transfer mechanism is much more important in determining the different adsorption behaviors of FA and HA on vermiculite. The results of the present study will improve our understanding of the roles of mineral interfacial properties, composition and particle size of FA and HA in the adsorption processes, which will benefit elucidating the adsorption mechanisms of NOM on clay minerals. In addition, this study is also helpful in further understanding behaviors of contaminants in the natural environments since interactions between NOM and clay minerals will determine bioavailability, toxicity, and transport of the contaminants in the environment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2012.05.003>

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