Adsorption of Enrofloxacin on montmorillonite: Two-dimensional correlation ATR/FTIR spectroscopy study

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ABSTRACT

Adsorption of Enrofloxacin (ENR) on minerals dominates the fate and transport of ENR in the environment. In this study, the sorption process of ENR on montmorillonite and the impact of dissolved organic matters (DOMs) on ENR-montmorillonite interactions were investigated using *in situ* ATR-FTIR spectroscopy and two-dimensional correlation analysis (2D-COS). Negative peaks were observed in the 3400–2900 cm⁻¹ region due to the loss of hydrated protons at montmorillonite surfaces. The primary characteristic peaks of adsorbed ENR molecules were resolved in the 1800–1100 cm⁻¹ range. The results of 2D-COS suggested the sorption process was initiated by the interaction of hydrated protons on montmorillonite surfaces with diverse moieties of ENR molecules depending on pH. The sorption mechanism of ENR was mainly cation exchange at acidic condition, charge neutralization at neutral condition, and proton transfer at alkaline condition. DOM could interact with piperazinyl amine groups of dissolved ENR, which changed the interaction sequence of ENR molecule with montmorillonite surfaces. Electrostatic interaction was the predominant driving force for the interaction between DOM and dissolved ENR. H-donor–acceptor interaction and π – π interaction may also be responsible to this interaction. Insights gained from this study improve our understandings on sorption mechanism of ENR and similar ionic organic pollutants in soil systems.

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1. Introduction

Enrofloxacin (ENR) is a class of fluoroquinolone (FQ) antibiotics extensively used in veterinary pharmaceuticals [1,2]. Continuous ENR discharge to the environment results in the pseudo-persistent occurrence of ENR at ng L⁻¹ to low μ g L⁻¹ levels [3–5]. Prolonged exposure to ENR can promote antibiotic-resistance of bacteria and ultimately pose potential threats to ecological and human health [6–8]. Therefore, the need to predict its environmental risks motivates the research in the environmental behaviors of ENR.

Clay minerals are widely considered as an active component of soils for the adsorption of polar xenobiotics [9]. Sorption of ENR and ENR-like FQ compounds by clay minerals such as montmorillonite [2,10–12], kaolinite [10], metal (hydrated) oxides [6,13–15], and silica [15] has been widely investigated. Several interaction mechanisms between ENR and clay minerals have been proposed including electrostatic attraction [16], cation bridging [2,15], cation exchange [17], and surface complexation or ligand exchange [6,13]. Our previous study has demonstrated that multiple interactions simultaneously occurred [18]: cation exchange is the

dominant interaction between the protonated piperazinyl amine groups of ENR and the exchangeable cations on mineral surface; a small fraction of ENR molecules are adsorbed due to ligand exchange between carboxyl groups of ENR and hydroxyl groups on the mineral edge surface. These studies, however, under appreciate the polar characteristics of H₂O in sorbate–water and sorbent–water interactions, which may hinder the comprehensive understanding of the dynamic sorption process of polar organic pollutants.

Dissolved organic matter (DOM) plays an important role in the adsorption of ionizable organic compounds (IOCs) on clay minerals [19,20]. DOM can form complexes on clay minerals and subsequently change their surface properties [21,22]. The interactions among DOM, geosorbents, and IOCs are complicated because of the heterogeneity of DOM, diverse surface structures of clay minerals, and different molecular configurations of IOCs. The complexity of IOCs behaviors in this three-phase system should be taken into consideration to accurately simulate the interfacial processes in the environment.

Two-dimensional correlation spectroscopy (2D-COS) has been successfully applied to investigate the dynamics of adsorption, diffusion, and biological processes [23,24]. Based on the dynamic fluctuations of spectral intensity, 2D-COS is especially suitable in

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the study of external perturbations such as the change in pH and concentration using *in situ* flow-cell attenuated total reflectance Fourier transform infrared (ATR–FTIR) analysis. Two major advantages of 2D-COS are remarkable: One is its simplification in resolving overlapped peaks and enhancing spectral resolution. More importantly, 2D-COS can probe the specific sequence of spectral intensity changes corresponding to external perturbations [25]. To the best of our knowledge, no study has documented using 2D-COS to investigate the mineral–aqueous solution interfacial behaviors of organic contaminants in the presence of DOM.

The objective of this work was to investigate the impact of DOM on the ENR sorption on montmorillonite. The ATR–FTIR and 2D-COS analysis were employed to gain important insights during the ENR adsorption in the presence of humic acid (HA) and fulvic acid (FA) under various pH conditions.

2. Materials and methods

2.1. Materials

Montmorillonite (SWy-2) was obtained from the Source Clays Repository of the Clay Minerals Society (West Lafayette, Indiana, USA). The surface area of SWy-2 is ca. 32 m² g^{−1} and its cation exchange capacity is 76 cmol_c kg^{−1} [26]. The fraction with less than 2-μm size was separated by wet sedimentation and repeatedly washed with 0.1 M KCl solution. Then, the saturated clay sample was washed with deionized water to remove the excess electrolyte until the absence of chloride. The pretreated clay was then lyophilized and ready for use.

ENR (purity ≥ 98%, HPLC grade) was used as received from Fluka (Biochemica, distributed by Sigma–Aldrich, St. Louis, Missouri, USA). Suwannee River HA (catalog no. 2S101H) and Suwannee River FA (catalog no. 2S101F) were obtained from International Humic Substances Society (IHSS). HA solution was prepared by dissolving 100 mg of HA in 100 mL Milli-Q water. The pH was adjusted to 10 with NaOH, and the solution was then passed through a 0.45-μm cellulose nitrate filter. Inorganic chemicals, including KCl, AgNO₃, NaOH (≥98%) of analytical grade or higher, were purchased from Shanghai Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. FTIR measurements

In situ flow cell ATR–FTIR measurements were performed using a Thermo–Nicolet Nexus 6700 FTIR spectrometer equipped with a liquid–nitrogen cooled MCT detector. The IR spectra were collected using a horizontal attenuated total reflectance (HATR) cell (PIKE Tech) with a 45° ZnSe ATR crystal. A total of 512 scans were recorded over 600–4000 cm^{−1} at a resolution of 4 cm^{−1} for each spectrum.

ATR–FTIR measurements of ENR sorption on clay were similar to a previous publication with minor modifications [6]. Briefly, a 500 μL suspension containing 2 mg of montmorillonite (K-SWy-2) was evenly spread on the ZnSe crystal and air-dried overnight to form a uniform clay film. The flow cell with the coated film was washed with 0.01 M KCl solution using a LC pump (LC 10A, Shimadzu Corp.) at a flow rate of 0.6 mL min^{−1} for 40 min to flush out the uncoated particles and other impurities. The background IR spectrum was collected and saved. The electrolyte solution was then changed to a 10 mg L^{−1} ENR solution (27.8 μM) at the same pH value as that of electrolyte solution. Spectra were recorded as a function of time until the sorption reached equilibrium. HA/FA sorption and its cosorption with ENR on montmorillonite were measured using the same process.

2.3. 2D–COS

After essential smooth and baseline correction performed using the Omnic 8.0 software, FTIR spectra collected with an increment of 15 min during adsorption process were selected for 2D correlation analysis using the 2Dshige software (Shigeaki Morita, Kwansei–Gakuin University, 2004–2005). The sequential order of intensity change between band ν_1 and ν_2 could be obtained from the sign of synchronous correlation peak $\Phi(\nu_1, \nu_2)$ and asynchronous correlation peak $\Psi(\nu_1, \nu_2)$ under the well-established principles [24,27]. In brief, the change in the spectral intensity at ν_1 band occurs prior to that at ν_2 if $\Phi(\nu_1, \nu_2)$ and $\Psi(\nu_1, \nu_2)$ have the same sign, while the order is reversed if $\Phi(\nu_1, \nu_2)$ and $\Psi(\nu_1, \nu_2)$ have the opposite sign. The changes at ν_1 and ν_2 occur simultaneously if $\Psi(\nu_1, \nu_2)$ is zero.

3. Results and discussion

3.1. FTIR analysis of ENR sorption

The FTIR spectra of ENR on K-SWy-2 montmorillonite at pH 4.5 as a function of sorption time are present in Fig. 1a. The striking spectral changes mainly occurred at 3400–2900 cm^{−1} and 1800–1100 cm^{−1} regions that were the focus in this study (Fig. 1b and c).

A negative peak at 3148 cm^{−1} was progressively increased in intensity as a function of sorption time (Fig. 1b), indicating that a molecule originally adsorbed on montmorillonite was gradually released. The originally adsorbed molecule was expected to be water because the polarity of water molecule makes it easy to be adsorbed on the charged clay mineral. The OH stretching of bulk water, however, is usually observed at 3294 cm^{−1} [28]. A discrepancy of 146 cm^{−1} of the $\nu(\text{OH})$ band suggested that the structure and properties of interfacial water were significantly perturbed compared to those of bulk water.

Surface protonation effect may account for this perturbation. The montmorillonite contains negative structure charges on basal planes due to isomorphous cation substitutions. The negative charges can be compensated by protons (H_{aq}^+) and cations (e.g., K^+) from the electrolyte near the basal planes, leading to an increased proton activity in the vicinal solution near the surfaces ($\text{pH}_{\text{vicinal}} < \text{pH}_{\text{bulk}}$). In this vicinal solution with strong acid, concentrated protons can be associated with its nearest-neighbor water molecules to form a hydrated hydrogen ion, $\text{H}(\text{H}_2\text{O})_n^+$, and then adsorbed on the negatively charged surface. In agreement with our observation, Stoyanov et al. found that the $\nu(\text{OH})$ vibration of aqueous $\text{H}(\text{H}_2\text{O})_6^+$ was centered at 3146 cm^{−1} [29]. Similar solvation complex of exchangeable cation, such as $\text{Ca}(\text{H}_2\text{O})_6^{2+}$, has also been reported to be immobilized at the clay mineral interlayer [30]. Therefore, the absorbance loss in 3148 cm^{−1} was due to the release of adsorbed $\text{H}(\text{H}_2\text{O})_6^+$.

The spectra in the region of 1800–1100 cm^{−1} (Fig. 1c) exhibited main characteristic peaks of adsorbed ENR molecule. The peak position and assignment are shown in Table 1. A successive increase in intensity upon ENR sorption was observed with the increase in sorption time. However, the spectroscopic method alone is not sensitive enough to reveal the dynamics of the sorption process.

3.2. Two-dimensional correlation analysis

ENR sorption on montmorillonite is complicated due to its structure properties (Fig. S1). Depending on the solution pH, ENR can exist as three dominant species, namely cationic ENR (ENR^+), zwitterionic ENR ($\text{ENR}^\pm$), and anionic ENR (ENR^-) ($\text{pK}_{\text{a}1} = 6.27$, $\text{pK}_{\text{a}2} = 8.30$). The sorption of different ENR species may control by different mechanisms. In addition, montmorillonite contains two

Fig. 1. Adsorption-dependent FTIR spectra of ENR on K-SWy-2 with increasing sorption time at pH 4.5 in the region of 4000–650 cm^{-1} (a), 3400–2900 cm^{-1} (b), and 1800–1100 cm^{-1} (c).

Table 1
Vibrational frequencies (cm^{-1}) and assignments for adsorbed ENR on clay.

Position (cm^{-1})	Assignment
1706	Carboxylic acid C=O stretch ($\nu_{\text{C=O carboxy}}$)
1628	Ketone C=O stretch ($\nu_{\text{C=O ketone}}$)
1584	Carboxylate COO^- antisymmetric stretch (ν_{COOas})
1528	Aromatic C=C stretch ($\nu_{\text{C=C}}$)
1486	Aromatic C–H wag ($\omega_{\text{aromatic C-H}}$)
1456	C–H wag ($\omega_{\text{C-H}}$)
1394	Carboxylate COO^- symmetric stretch (ν_{COOs})
1302	NH^+ twisting (τ_{NH})
1264	C–O stretch (ν_{COOH}) + C–O–H deformation ($\delta_{\text{C-OH}}$)

types of surfaces. The basal planes carry permanent negative charge, and the edge surfaces contain pH-dependent charges with the amount of about 10% of the total charge. Both surfaces can interact with ENR, increasing the difficulty in the sorption process analysis [31].

To further discern the sorption sequence of each ENR functional groups during sorption at different pH, 2D-COS was employed and the results are shown in Fig. 2 and Table 2. Correlation peaks are indicated by the contour map where blue (red) regions were defined as negative (positive) correlation intensities. Because carboxyl group and piperazinyl amine group of ENR molecule are the main functional groups involved in sorption [18], these two function groups with vibrational peaks in the range of 1400–1200 cm^{-1} were investigated.

Two-dimensional synchronous spectra (Fig. 2a, c, e) could reflect simultaneous change between the correlated peaks. For all investigated pHs, three prominent auto-peaks on the diagonal were observed at 1394, 1302, and 1264 cm^{-1} in synchronous spectra, suggesting that the spectral intensities in these peaks have distinctly changed during the adsorption process. Three positive cross peaks off the diagonal at 1302/1394, 1264/1394, and 1264/1302 cm^{-1} were also exhibited in the synchronous spectra. The positive sign of the cross peaks indicated that the peaks at 1264, 1302, and 1394 cm^{-1} were of the same origin and resulted in the same responses of spectral intensities to the adsorption perturbation. These cross peaks were derived from vibrations of adsorbed ENR (Table 1), and the adsorption capacity was increased with the increase in sorption time.

Two-dimensional asynchronous spectra could identify the specific order in surface interactions taking place under external perturbations. In this study, the sequences of vibrational response toward the perturbation of surface sorption were different at pH 4.5, 7, and 9 (Fig. 2b, d, f). At pH 4.5 (Fig. 2b), a strong positive cross

peak at 1302/1264 cm^{-1} and a weak negative cross peak at 1394/1302 cm^{-1} were observed. The asynchronous correlation analysis based on the Noda's rule [24] led to the sequence of the spectral change (“→” means prior to): 1302 → 1264 cm^{-1} , 1302 → 1394 cm^{-1} . Similarly, the sequence of the spectral change at pH 7 (Fig. 2d) was 1264 → 1302 cm^{-1} , 1264 → 1394 cm^{-1} , 1394 → 1302 cm^{-1} . At pH 9 (Fig. 2f), the cross peak at 1302/1264 cm^{-1} was too weak to be clearly resolved. Instead, strong negative cross peaks at 1394/1302 cm^{-1} and 1394/1264 cm^{-1} were observed and the sequence of the spectral change was 1302 → 1394 cm^{-1} , 1264 → 1394 cm^{-1} . The results of 2D-COS are summarized in Table 2. The spectral analysis resulted in a pH-dependent ENR sorption process on clay surfaces (Fig. 3). The dynamic processes at pH 4.5, 7, and 9 are discussed in detail as follows.

At pH 4.5, clusters of hydrated protons (e.g., $\text{H}(\text{H}_2\text{O})_6^+$) were attracted to the negatively charged clay surfaces and the electrical double layer (EDL) was formed. Because the siloxane group (Si_2O) at the basal surface of clay is chemically inert with an intrinsic protonation constant at -16.9 [32], the specifically adsorbing ions are unable to exist at the basal surface. Thus, the classic Basic Stern (BS) model can describe the adsorption behaviors in the EDL in our study [33]. In addition, the ζ potential of montmorillonite is negative (-30 to -50 mV) within a broad pH domain from 2 to 12 [34]. At pH 4.5 with the ionic strength of 0.01 M KCl, the ζ potential of montmorillonite in this study was -35.6 mV (Fig. S2), indicating that the negative surface charge cannot be totally neutralized by the adsorbed counter ions (H^+ , K^+), even at low pH. Meanwhile, 98.3% ENR was in cationic form due to the protonation of piperazinyl amine group at pH 4.5 (Fig. S1). This positive group was initially attracted to the solution side near the head end of the EDL by electrostatic forces, resulting in a subsequent cation exchange with the adsorbed $\text{H}(\text{H}_2\text{O})_6^+$. Moreover, the edge surface of phyllosilicate contains aluminum and silica sites with broken bonds [35]. These sites could interact with ENR to form surface complexes by ligand exchange. However, the contribution of ligand exchange may be negligible at pH 4.5 because only less than 2% of carboxyl groups of ENR are in deprotonated form. Therefore, the sequence for the ENR sorption on the montmorillonite surface should be $\text{NH}^+ \rightarrow \text{COOH}$. The possible ENR sorption processes at pH 4.5 can be summarized as the following equation.

On basal planes,

where $\equiv \text{X}^-$ represents the structure charge sites.

At pH 7, ENR^+ became predominant and the negative ζ potential of montmorillonite surface was increased to -41.3 mV (Fig. S2).

Fig. 2. Synchronous (a, pH 4.5; c, pH 7; e, pH 9) and asynchronous (b, pH 4.5; d, pH 7; f, pH 9) 2D FTIR correlation spectra of ENR adsorbed on K-SWy-2 in the region of 1400–1200 cm^{-1} .

During the $\text{ENR}^{\pm}$ adsorption due to electrostatic forces, some $\text{ENR}^{\pm}$ may change their molecular direction toward the surface because of increased repulsive forces (toward NH^+) and attractive forces (toward COO^-) of hydrated protons on the surface. Subsequently, $\text{ENR}^{\pm}$ could enter the Stern layer by charge neutralization between deprotonated carboxyl groups of ENR and hydrated protons. This sorption process may dissociate $\text{H}(\text{H}_2\text{O})_n^+$ and release water molecules, where the value of n depends on $\text{pH}_{\text{vicinal}}$ [29]. Thus, the sequence for the ENR sorption on the montmorillonite surface at pH 7 was $-\text{COOH} \rightarrow -\text{NH}^+$.

In addition, ligand exchange could occur between hydroxyl groups on the edge surface of montmorillonite and ENR COO^- groups. The possible ENR sorption process at pH 7 can be summarized as follows.

On basal planes,

At edge surfaces,

At pH 9, montmorillonite surfaces contained a stronger negative ζ potential (42.2 mV, Fig. S2) and adsorbed less hydrated protons compared to that at pH 7. Meanwhile, about 38.6% $\text{ENR}^{\pm}$ and

61.2% ENR^- existed in bulk solution (Fig. S1). The decreased amount of protonated piperazinyl amine group led to a weak ENR sorption at alkaline condition. The sequence for the ENR sorption at pH 9 was $-\text{NH}^+ \rightarrow -\text{COO}^-$. The presence of a negative peak at around 3280 cm^{-1} (Fig. 4) may be explained by the following two reasons: (a) proton transfer occurred between piperazinyl amine group of ENR^- and hydrated proton which released adsorbed water molecules; and (b) neutralization occurred between deprotonated carboxyl group of $\text{ENR}^{\pm}$ and hydrated proton. The 2D-COS analysis favored the former interpretation. The possible ENR sorption process at pH 9 can be summarized as follows.

On basal planes,

At edge surfaces,

The proposed ENR sorption process at different pH was supported by 1D FTIR spectra in Fig. 4. With the increase in pH, the number of “ n ” in $\text{H}(\text{H}_2\text{O})_n^+$ changes, resulting in the shift of $\nu(\text{OH})$ band of $\text{H}(\text{H}_2\text{O})_n^+$ from 3146 cm^{-1} to 3166 cm^{-1} . In addition, a distinct shoulder exhibited at around 3280 cm^{-1} , which was probably due to the stretch of H-bonding of adsorbed water [36]. The con-

Table 2

Results of 2D-COS on the sign of each cross peak in synchronous and asynchronous spectra.

pH	Signs of synchronous cross peaks (Φ)			Signs of asynchronous cross peaks (Ψ)			The sequences of spectral change	Main reaction
	1394	1302	1264	1394	1302	1264		
4.5	1394	+	+	+	—	+	$-\text{NH}^+ \rightarrow \text{COOH}$; $-\text{NH}^+ \rightarrow \text{COO}^-$	Cation exchange
	1302	+	+	+	—	+		
	1264	+	+	+	—	+		
7.0	1394	+	+	+	+	—	$\text{COOH} \rightarrow \text{COO}^-$; $\text{COO}^- \rightarrow -\text{NH}^+$; $\text{COOH} \rightarrow -\text{NH}^+$	Charge neutralization
	1302	+	+	+	—	—		
	1264	+	+	+	+	—		
9.0	1394	+	+	+	—	—	$-\text{NH}^+ \rightarrow \text{COO}^-$; $\text{COOH} \rightarrow \text{COO}^-$	Proton transfer
	1302	+	+	+	—	—		
	1264	+	+	+	—	—

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Fig. 3. Schematic illustration of the sorption process of ENR on K-SWy-2 at pH 4.5, pH 7, and pH 9. The red circles highlight the piperazinyl amine group with N atom (blue) and carboxyl group with O atom (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.) **Fig. 4.** FTIR spectra of ENR adsorbed on K-SWy-2 in the region of 4000–2200 cm^{-1} at pH 4.5, 7, and 9.

currence of the absorbance loss at 3146 and 3280 cm^{-1} implied the multiple sorption mechanisms of ENR on the montmorillonite surfaces.

3.3. FTIR study of DOM sorption on clay film

Understanding the DOM sorption on montmorillonite is a prerequisite to explore the ENR sorption in the presence of DOM. ATR–FTIR spectra of adsorbed HA and FA on clay are shown as a

function of adsorption time in Fig. 5. In the 3600–2800 cm^{-1} region (Fig. 5b and d), both HA and FA exhibited progressive absorbance loss. For HA, the position of the main negative peak was initially at around 3223 cm^{-1} and gradually shifted to 3164 cm^{-1} after 150 min. This absorbance loss was probably due to the release of adsorbed hydrated protons. Besides, the growth of the negative peak at 3223 cm^{-1} was coincident with the emergence of a negative shoulder peak at around 3340 cm^{-1} , indicating the concurrent removal of surface water. This observation indicated that HA can interact with clay surface through multiple mechanisms because of its diverse functional moieties. In contrast, adsorbed FA only exhibited a broad negative peak around 3332 cm^{-1} (Fig. 5d). This difference in HA and FA adsorption spectra might be attributed to their different physical conformation, especially the contents of amino groups. HA contains about 2.1% N, which was higher than FA (0.7% N in FA) [37,38]. The amino groups in HA could facilitate the release of both hydrated hydrogen protons and water molecules originally adsorbed on the mineral surfaces, while the FA sorption could mainly replace adsorbed water.

The spectrum of HA in the region 1850–650 cm^{-1} (Fig. 5a) showed the absence of peak at 1720 cm^{-1} , which is probably caused by the ligand exchange between HA carboxyl functional groups and hydroxyl groups on edge surface of clay [22]. The extremely broadened peak at around 1630 cm^{-1} , assigned as C=O stretching vibrations, can be attributed to the heterogeneous nature of HA, which has a wide distribution of chemical environments for ketone groups. Compared to the C=O stretching vibration, the peak intensity of aromatic C=C stretching at around 1600 cm^{-1} was relatively weak and in discriminable. A huge negative peak at around 1075 cm^{-1} could be due to the release of adsorbed carbon-

ate in the presence of HA [22]. Besides, the relative high content of amino groups in HA exhibited a prominent τ_{NH} at 1305 cm^{-1} .

In comparison with adsorbed HA, a similar FTIR spectrum of adsorbed FA in the region $1850\text{--}650\text{ cm}^{-1}$ was obtained except the presence of $\text{C}=\text{O}$ stretching vibrations and relative weak τ_{NH} (Fig. 5c). Two peaks at 749 and 835 cm^{-1} were observed in FA (Fig. 5c) that were assigned to OH deformation of the non-H-bonded surface OH group and the bulk OH group, respectively [28]. Because these two peaks were unique for FA in our investigated system, they can be used as an index of FA sorption sequence in the following 2D-COS analysis.

3.4. Bi-solute sorption on clay film

DOM can greatly affect the sorption of organic compounds on clay minerals. Generally, the influence was explained by the pore blockage and direct site competition. In our previous study [18], however, negligible impact was found at acidic condition in the presence of HA at low concentration (5 mg L^{-1}). One reason for this marginal impact was that the bulky volume of HA molecules ($0.43\text{--}0.63\text{ cm}^3\text{ g}^{-1}$) is too large to fit on the nanometer-scale surface charged sites on montmorillonite (0.26 nm) [18]. Another reason, which may be more important, was that soluble HA and FA are negatively charged in a broad pH range ($\text{pH}_{\text{PZC}} < 3$ [39]). The electrostatic repulsion between negative HA/FA and basal plane of montmorillonite weakens their interaction.

In contrast, when the bi-solute sorption experiments were conducted containing ENR (10 mg L^{-1}) and FA (100 mg L^{-1}) as co-solutes at pH 4.5, strong affinity between FA and free ENR was found. As shown in Fig. 6a, the peak intensity at 1302 cm^{-1} (τ_{NH}) and

1264 cm^{-1} (ν_{COOH} and $\delta_{\text{C-OH}}$) was increased with time. Moreover, the increase rate at 1302 cm^{-1} was much slower than that at 1264 cm^{-1} . It was quite different from the IR analysis for single-solute ENR sorption that these two peaks should increase simultaneously (Fig. 1c). The difference indicated that the piperazinyl amine group of ENR in bi-solute system could interact with soluble FA before the sorption on mineral surface. In addition, in the region $3600\text{--}2800\text{ cm}^{-1}$ at pH 4.5 (Fig. 6b), the position of negative peak was shifted from 3284 cm^{-1} to 3344 cm^{-1} with time, which was close to the peak position of single FA sorption (3332 cm^{-1} , Fig. 5d). The negative shoulder peak at 3280 cm^{-1} (Fig. 4) in the single-solute ENR sorption was also present in bi-solute system with a peak shift to 3220 cm^{-1} (Fig. 6b). The negative peak at 3148 cm^{-1} (Fig. 1b), which was attributed to the cation exchange between protonated piperazinyl amine group of ENR and hydrated hydrogen ion, was not observed in bi-solute system. The results also suggested that the piperazinyl amine groups of dissolved ENR interacted with soluble FA under acidic conditions.

Furthermore, consistent results are obtained from the 2D-COS analysis. Based on the signs of synchronous correlation peaks and asynchronous correlation peaks (Fig. 6c, d), the sequence of the spectral change was $-\text{COOH} \rightarrow -\text{NH}^+ \rightarrow \text{P}_{749} \sim \text{P}_{835}$ (“ $\sim$ ” means simultaneous to, “ P_{749} ” and “ P_{835} ” are two specific peaks for FA). Compared with the sorption consequence of single-solute system, the results of 2D-COS analysis of bi-solute sorption showed that the presence of FA changed the sorption sequence of ENR on montmorillonite surface.

The strong affinity between ENR and FA at pH 4.5 could be explained by several mechanisms. First, electrostatic interaction might be the predominant driving force for this strong interaction.

Fig. 5. FTIR spectra of HA (a, b) and FA (c, d) adsorbed on K-SWy-2 in the region of $1900\text{--}650\text{ cm}^{-1}$ and $3600\text{--}2800\text{ cm}^{-1}$, respectively, at pH 4.5.

Fig. 6. FTIR spectra of the cosorption of FA and ENR on K-SWY-2 in the region of 1900–650 cm^{-1} (a) and 3700–2800 cm^{-1} ; and (b) their 2D FTIR correlation spectra (c, synchronous spectrum; d, asynchronous spectrum) in the region of 1400–650 cm^{-1} at pH 4.5.

At pH 4.5, ENR^+ is the dominant species. The positively charged piperazinyl amine groups of ENR^+ can form strong ionic bonds with carboxylic groups of FA which is the second strongest binding type following covalent bond [19]. Second, H-donor–acceptor interaction could be responsible for this affinity. FA may act as hydrogen-bond donors because of their appreciable amount of carboxylic and phenolic moieties, and ENR^+ may act as hydrogen-bond acceptors by their carbonyl and carboxyl groups [39]. Conversely, the deprotonated carboxyl groups of FA could also act as hydrogen-bond acceptors and form H-bonds with positively charged piperazinyl amine groups of ENR^+ [19]. Third, the π – π interaction may also contribute to this affinity. Wang et al. [40] have reported that the norfloxacin, a FQ antibiotic with similar molecular structure to that of ENR, could function as a π -electron acceptor due to the strong electron withdrawing ability of the fluorine group on benzene ring, whereas benzene ring of carboxylated carbon nanotubes could function as a π -electron donor. Similarly, this π – π interaction between benzene ring of ENR and aromatic domain of FA may also exist.

4. Conclusions

ATR–FTIR and 2D-COS were used to explore the sorption process of ENR on montmorillonite in this study. The sorption mechanisms depended on pH: The sorption of ENR at mineral–water interface was predominantly initiated by cation exchange at acidic

condition, charge neutralization at neutral condition, and proton transfer at alkaline condition. The different sorption processes were due to various ENR species and surface potentials at different pH. Besides, ligand exchange between hydroxyl groups on the edge surface of montmorillonite and carboxyl groups of ENR would also be responsible for the interaction of ENR with clay. Water molecules at mineral surface can combine with proton to form hydrated hydrogen ions and then play an important role in the proton transfer for the sorption. In addition, the polar functional groups (e.g., $-\text{OH}$, $-\text{COOH}$) of DOM can interact with piperazinyl amine groups of ENR and subsequently influence the ENR sorption process at interfacial surfaces. The results of this study can improve our understanding of the fate and risk assessment of FQ antibiotics and, more generally, complex environmentally relevant IOCs in soils.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcis.2012.09.039>.

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