Cation exchange interaction between antibiotic ciprofloxacin and montmorillonite

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ABSTRACT

Exploring the interactions between antibiotics and soils/minerals is of great importance in resolving their fate, transport, and elimination in the environment due to their frequent detection in wastewater, river water, sewage sludge and soils. This study focused on determining the adsorption properties and mechanisms of interaction between antibiotic ciprofloxacin and montmorillonite (SAz-1), a swelling dioctahedral mineral with Ca^{2+} as the main interlayer cation. In acidic and neutral aqueous solutions, a stoichiometric exchange between ciprofloxacin and interlayer cations yielded an adsorption capacity as high as 330 mg/g, corresponding to 1.0 mmol/g. When solution pH was above its pK_{a2} (8.7), adsorption of ciprofloxacin was greatly reduced due to the net repulsion between the negatively charged clay surfaces and the ciprofloxacin anion. The uptake of ciprofloxacin expanded the basal spacing (d_{001}) of montmorillonite from 15.04 to 17.23 Å near its adsorption capacity, confirming cation exchange within the interlayers in addition to surface adsorption. Fourier transform infrared results further suggested that the protonated amine group of ciprofloxacin in its cationic form was electrostatically attracted to negatively charged sites of clay surfaces, and that the carboxylic acid group was hydrogen bonded to the basal oxygen atoms of the silicate layers. The results indicate that montmorillonite is an effective sorbent to remove ciprofloxacin from water.

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1. Introduction

Ciprofloxacin (CIP) is a synthetic antibiotic categorized as the second generation of fluoroquinolones (FQs). It has been found in the wastewater and surface water with concentrations of several hundred ng/L [1–5]. Higher concentrations (up to 150 μg/L) were even reported in the effluents from hospitals [6,7]. In addition, CIP can be adsorbed by sewage sludge with the concentrations up to 2.42 and 0.37 mg/kg, respectively [8,9]. CIP could accumulate in soils after fertilizers made from sewage sludge containing CIP were applied [10]. From a risk assessment point of view, the calculated risk quotient of predicted environmental concentration/predicted no-effect environmental concentration suggested that CIP might be an environmental hazard [11].

Antibiotics can be eliminated effectively from the environment via adsorption on sludge, sediments, soils and pure minerals.

Detailed related investigations have been extensively reviewed in some literatures [12–14]; however, only a few studies focused on CIP. The distribution coefficient K_d for CIP adsorption was presented with a wide range from several hundred to 50,000 L/kg on different soils [15–20]. The large variation in K_d is often related to different constituents in soils from different geographic areas, which may yield multiple adsorption mechanisms simultaneously and even induce competitions between various mechanisms, and thus obscure the adsorption efficiency of each constituent. Pure minerals, such as hydrous oxides of aluminum and iron [21] and goethite [18,22], have also been studied for their CIP adsorption because they are important components of environmental particles or soils. Their adsorption capacities were suggested to be in the range of 15–50 mg/g, slightly higher than those reported for soils [18].

Montmorillonite is one type of clay minerals that has been shown to have a high adsorption capacity for tetracycline [23,24] and oxytetracycline [25]. The mechanism was attributed to intercalation of these molecules into the interlayer space of montmorillonite. Among FQs, enrofloxacin which has a molecular structure similar to that of ciprofloxacin, can be adsorbed into Mg-saturated montmorillonite with a K_d of 6310 L/kg and adsorption of 100 mg/g [15].

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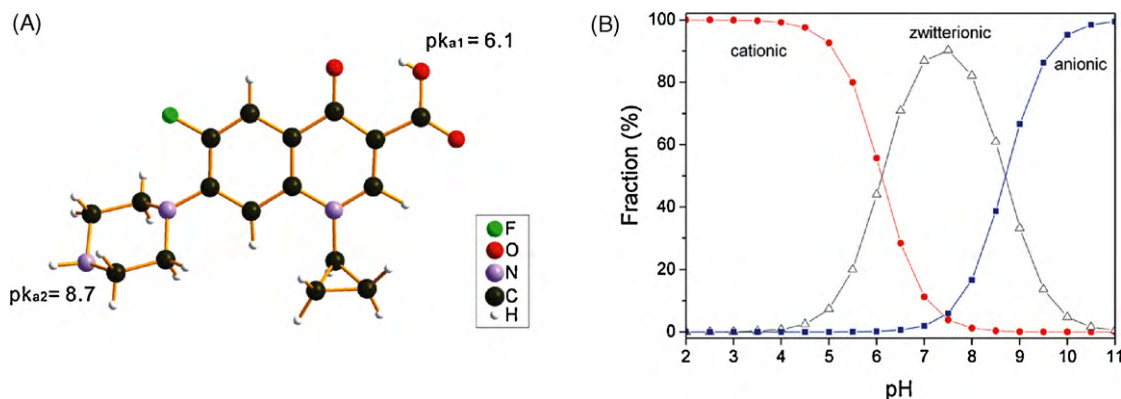E-mail addresses: li@uwp.edu (Z. Li), atwtj@mail.ncku.edu.tw (W.-T. Jiang).

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(B)

Fig. 1. Molecular structure of CIP from Cambridge Structure Database (A) and its speciation at different pHs (B).

Possible mechanisms of CIP-like compounds adsorbed on minerals have been previously proposed. Formation of surface complexes between zwitterionic/anionic CIP and aluminum/iron hydrous oxides was attributed to adsorption [21]. This interaction may also occur between CIP and the positively charged layer edges of montmorillonite. Because the fraction of edge to surface area is commonly rather low in clay minerals, such a mechanism would make a minor contribution to adsorption by montmorillonite, especially in acidic aqueous solution. A second mechanism involving cation bridging, a bonding between the carboxylate group of CIP and the interlayer cations of clay minerals was pointed out in a study of enrofloxacin adsorption on Mg-saturated montmorillonite in an aqueous solution with pH 6 [15]. By comparing the adsorption properties of CIP with a protonated amine group and phenylpiperazine (i.e., a structurally related probe compound possessing an amine group only) on Na-saturated kaolinite and montmorillonite, a cation-exchange mechanism was suggested [18]. Although the detection of CIP compounds in soils and their potential impacts on the ecosystems and human and animal health are obvious, the dominant interaction in the adsorption processes of the CIP-montmorillonite system remains uncertain.

In this study, a Ca-montmorillonite was tested for its CIP adsorption properties under ambient and controlled pH conditions. Cation desorption from the montmorillonite during CIP uptake was quantified to confirm the contribution of cation exchange interaction on adsorption, which has been rarely reported in the literature. In addition, the bonding between CIP and montmorillonite and the effect of cation exchange interaction on the structure of montmorillonite were examined through Fourier transform infrared (FTIR) and X-ray diffraction (XRD) analyses, respectively. A possible model for the conformation of the exchanged CIP in montmorillonite was thus proposed.

2. Experimental

2.1. Materials

Source clay SAz-1 from the Clay Minerals Society was used as the sorbent. The fraction of montmorillonite was higher than 98% [26] assuring that adsorption and interaction were restricted to one pharmaceutical compound and one clay phase. Montmorillonite has an expandable layer structure consisting of a gibbsite-like octahedral sheet sandwiched by two silicate tetrahedral sheets, commonly with variable amounts of exchangeable cations and water molecules located within the interlayer space. The structure formula of montmorillonite SAz-1 was reported as $(Ca_{0.88}Na_{0.01}K_{0.05})[Al_{2.96}Mg_{1.32}Fe^{3+}_{0.18}Ti_{0.02}][Si_{7.86}Al_{0.14}]O_{20}(OH)_4$ [27]. Its external specific surface area determined by the BET

method was $65.2 \, m^2/g$ [28] and the cation exchange capacity (CEC) measured by the ammonia-electrode method was $123 \, meq/100 \, g$ [29]. Ciprofloxacin hydrochloride with a purity higher than 99.6% was purchased from Hangzhou Minsheng Pharmaceutical Group Co. Ltd (China). Fig. 1(A) shows its molecular structure and acid dissociation constants (pK_{a1}, pK_{a2}) [21] and Fig. 1(B) presents its speciation at different pH conditions. In an acidic solution with pH below 6.1, CIP molecules exist in a cationic form mainly due to the protonation of the amine group in the piperazine moiety. When its pH is higher than 8.7, it exists as an anion due to the loss of a proton from the carboxylic group. Between pH 6.1 and 8.7, a zwitterion is dominant as a result of charge balance between the two groups mentioned above.

2.2. Adsorption experiment

For each adsorption experiment, a quantity of 0.2 g SAz-1 was mixed with 20 mL CIP solution in a 50 mL centrifugal tube and shaken at 150 rpm for 24 h. The centrifuge tube was wrapped with aluminum foils to prevent light-induced decomposition. For batch adsorption experiments, the initial concentrations of CIP solutions (C_0) were set in the range of 500–4000 mg/L. For pH adsorption edge experiments, the initial CIP concentration was invariably fixed at 3000 mg/L, while the pH values were adjusted to 2.5–11, with either 1 M HCl or 1 M NaOH. After mixing and adsorption, all suspensions were centrifuged at 5000 rpm for 10 min, and the supernatants were passed through a 0.45 μm filter for analyses. All experiments were performed in duplicate.

2.3. Methods of analysis

The equilibrium concentration of CIP in the filtered supernatant was determined using a UV/VIS spectrophotometer (SmartSpec 3000, Bio-Rad Corp.) at a wavelength of 275 nm. The calibration curve was established with 5 standards between 0 and 10 mg/L with the r^2 higher than 0.99. Adsorption amount of CIP was calculated from the difference between initial and equilibrium concentrations. The concentrations of Na^+, K^+, Mg^{2+}, and Ca^{2+} cations released from the montmorillonite after batch adsorption experiments were measured with an ion chromatograph (Dionex 100) using external calibration. The mobile phase was 20 mM methanesulfonic. At a flow rate of 1 mL/min, the retention time for Na^+, K^+, Mg^{2+}, and Ca^{2+} was 3.2, 4.4, 5.2, and 6.0 min, respectively.

XRD analysis of the raw and treated montmorillonite specimens was carried out with a CuKα radiation at 40 kV and 40 mA on a D8 ADVANCE diffractometer (Bruker Corp.). Oriented samples were scanned from $1°$ to $27°$ 2θ with a scanning speed of $0.01°/s$.
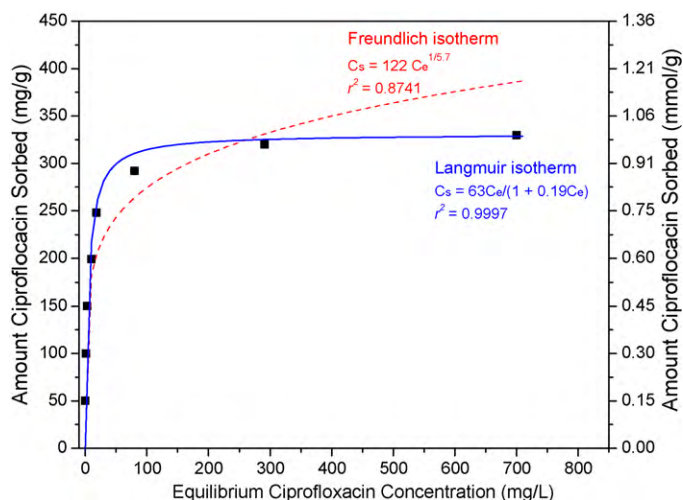
Fig. 2. Adsorption isotherms of CIP on montmorillonite. The solid and dashed curves are the Langmuir and Freundlich fits to the observed data, respectively. C_e is the equilibrium concentration of CIP in solution and C_s is the amount of CIP adsorbed on montmorillonite.

FTIR spectra were acquired by an Equinox 55 Spectrometer (Bruker Corp.) using the KBr pressing method. Absorbance data were collected by accumulating 256 scans at a resolution of $4\,cm^{-1}$ in the range of 4000–$400\,cm^{-1}$.

3. Results and discussion

In the following sections, the adsorption capacity of CIP on montmorillonite in neutral to acidic aqueous solutions was obtained through the construction of an adsorption isotherm. The effect of pH on the adsorption of CIP on montmorillonite is an important related issue and thus it was also evaluated. Cation exchange and layer expansion behaviors were shown by desorption measurements and XRD analyses, respectively. Additionally, the FTIR and XRD results helped establish a model for the adsorption site, and for the bonding and conformation of the CIP in the montmorillonite. Data collectively demonstrated a relatively high capacity with cation exchange as the principal mechanism for CIP adsorption on montmorillonite.

3.1. Adsorption isotherm

Adsorption of CIP on montmorillonite was well fitted with the Langmuir sorption equation with a regression coefficient (r^2) of 0.9997 (Fig. 2). In contrast, fitting with the Freundlich equation resulted in a low r^2 of 0.8744. The adsorption capacity was $330\,mg/g$, corresponding to $1.0\,mmol/g$. With an initial concentration of $3000\,mg/L$, the equilibrium concentration of CIP was only $80\,mg/L$, suggesting higher than 97% of CIP removal from the solution. Using the specific surface area (SSA) of $65.2\,m^2/g$ of the montmorillonite [28], at the maximum adsorption capacity of $1.0\,mmol/g$, the adsorption area of each CIP molecule would be $11\,Å^2$, much less than $17\,Å^2$, the reported area of the cationic amine [19]. The ratio between the external and internal surface areas of the montmorillonite is about 1:10 [30]. Each CIP molecule could have an area of $110\,Å^2$ available for adsorption if both external and internal surface areas are considered available. Interlayer adsorption of CIP by montmorillonite is sustained by this estimation. The close agreement between the maximum CIP adsorption capacity and the CEC of the mineral suggests that it is the charge density, rather than the SSA, that is the limiting factor controlling the amount of CIP adsorbed on montmorillonite, a strong indication of adsorption dominated by a cation-exchange mechanism.
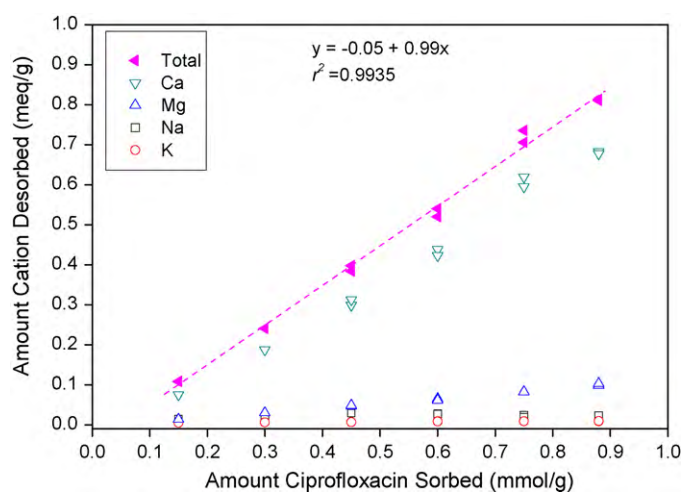

Fig. 3. Relations between cation desorption from montmorillonite and CIP adsorption on montmorillonite.

This confirms the validity of using the capacity-limited adsorption of a Langmuir isotherm to fit the experimental data.

Ion chromatography analyses revealed that Ca^{2+} is the major desorbed cation relative to the others (Fig. 3). Moreover, stoichiometric relation between the total cations desorbed and CIP adsorbed yielded a slope of ~1 with a negligibly small intercept, confirming cation exchange as the dominant mechanism for CIP adsorption. The equilibrium solution pH decreased from 6.5 to 5 as the initial CIP concentrations increased from 500 to $4000\,mg/L$. In the acidic aqueous solution, the CIP molecules are expected to be in the cationic and zwitterionic forms (Fig. 1). The positive charge of the amine group might be responsible for the exchange between CIP molecules and cations in the interlayer sites of montmorillonite. The stoichiometric correlation between CIP adsorption and cation desorption provides a direct evidence of cation exchange being the dominant adsorption mechanism on montmorillonite. It is noteworthy to mention that such an analysis has not received much attention that it deserved for studies of adsorption processes on swelling clays in the past.

Compared with the adsorption capacity of 0.06–$0.15\,mmol/g$ for goethite at pH 5 [21,22], $0.041\,mmol/g$ for aluminum hydrous oxide at pH 7 [21], and $0.024\,mmol/g$ for kaolinite at pH 5 [18], the SAz-1 montmorillonite exhibits a much higher adsorption capacity of $1.0\,mmol/g$ for CIP at similar pH environments. The high adsorption amount and cation exchange phenomenon indicate that the CIP molecules were not only adsorbed on the external surfaces but also into the interlayer of montmorillonite. A relatively low adsorption capacity of $0.18\,mmol/g$ was previously reported for another montmorillonite material (STx-1) at pH 6.5 [19]. The difference may be due to the employment of a much lower initial CIP concentration of $33\,mg/L$ and a lower montmorillonite content (~68%) in the sorbent material in that particular study. However, as cation exchange is the major mechanism of CIP uptake by montmorillonite, using a lower initial CIP loading to assess the solute adsorption capacity due to cation exchange would provide much lower values.

3.2. Effect of pH on cation exchange interaction

CIP adsorption was maintained at 290–$300\,mg/g$ in the pH range of 2.8–8.8, but it decreased abruptly to $247\,mg/g$ as pH reached 11 (Fig. 4). The surface charge of montmorillonite remains negative over the entire range of pH in this study [31]; thus, the pH influence on the adsorption level is expected to be mainly controlled by the speciation of CIP molecules. In acidic to neutral conditions, although the ratio of zwitterion/cation form increases gradually
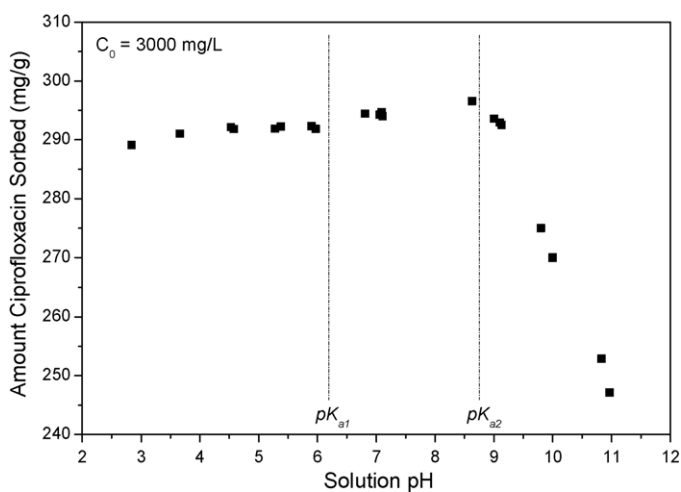
Fig. 4. Adsorption of CIP on montmorillonite as affected by solution pH.

with pH, the positive charge of the amine group of zwitterionic CIP may still contribute to the adsorption interaction. Under basic conditions, especially when the pH is higher than the pK_{a2} of the CIP, the anionic form would dominate and thus induce evident repulsion to negatively charged clay surfaces. Such behaviors would result in a significant diminution of CIP adsorption on montmorillonite, similar to the observations of CIP adsorption to soils, goethite, and kaolinite [18,20]. However, the onset pH corresponding to a decrease in CIP adsorption was close to the pK_{a1} of CIP in those cases. Such a difference is probably related to the dissimilarities in the charge and surface properties of the sorbents.

3.3. XRD analyses

Effects of cation exchange on the montmorillonite structure can be further verified by measuring the changes of its basal spacing d_{001}, the sum of one unit of layer thickness and gallery height, at different exchange levels (Fig. 5). For raw SAz-1, the d_{001} spacing was 15.04 Å, typical of a Ca^{2+}-dominated montmorillonite saturated with two layers of interlayer water molecules. At adsorption levels (C_s) below 150 mg/g, the diffraction peak shifted to a higher angle, corresponding to a reduction of d_{001} spacing to 14.62 Å. This reduction in d spacing implies that the interlayer water molecules were partially removed during the course of cation exchange between interlayer cations and CIP molecules. Furthermore, significant broadening and intensity reduction of the 0 0 1 reflection became evident after the adsorption, indicating that the interlayer compounds (i.e., adsorbed CIP molecules and residual Ca^{2+} and water molecules) are distributed in a somewhat disordered manner at low to intermediate levels of adsorption.

A progressive increase of d_{001} spacing occurred at adsorption levels greater than 199 mg/g while peak broadening was still prominent. A maximal value of 17.23 Å was reached when the amount of CIP adsorption was above 290 mg/g, approaching the prime CIP adsorption capacity demonstrated in the adsorption isotherm experiment. Meanwhile, the peak profile of the 0 0 1 reflection was restored to a smaller peak width and a more symmetric shape compared to those with low adsorption levels. These changes imply a transition from a relatively disordered to an ordered sequence of adsorbed CIP molecules as the amount of adsorption increases to a certain level. A similar trend was also observed for tetracycline adsorption on rectorite [32]. However, in reality, the fully adsorbed specimen still showed a weaker 0 0 1 peak intensity and poorer crystallinity relative to the raw montmorillonite. This is a common phenomenon for montmorillonite
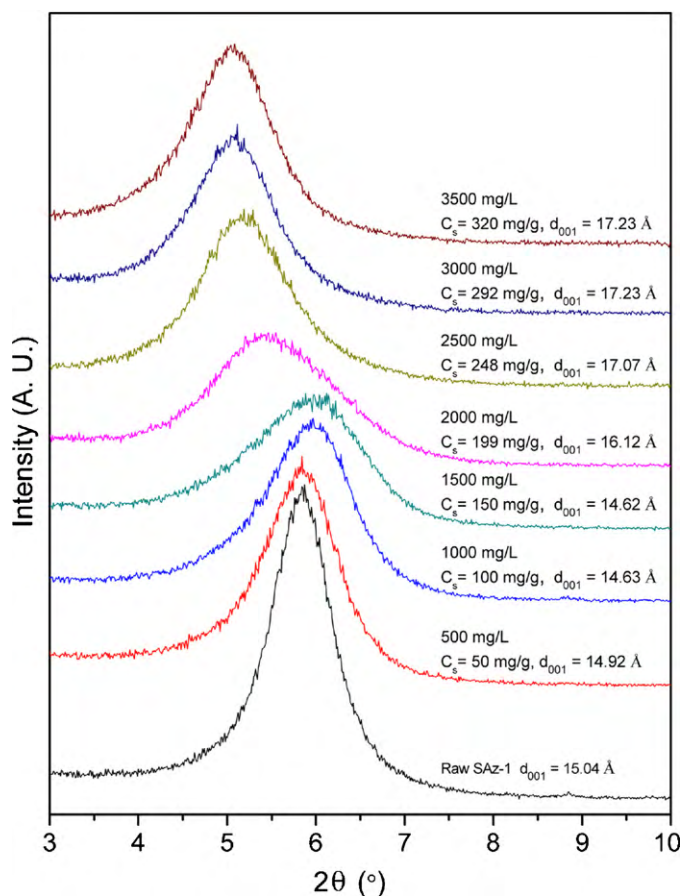

Fig. 5. XRD patterns of montmorillonite at various adsorption levels of CIP.

intercalated with various types of organic substances [23,32–35] and was attributed to heterogeneous intercalation and/or delamination of silicate layers.

3.4. FTIR analyses

The FTIR spectra of pure ciprofloxacin hydrochloride, raw SAz-1 montmorillonite powder, and SAz-1 with a CIP adsorption level of 292 mg/g (C_0 = 3000 mg/L) are shown in Fig. 6. Only the wave numbers that include the main characteristic peaks of CIP molecules in the range of 1250–1850 cm^{-1} are presented because the adsorption interaction did not influence the vibration bands of montmorillonite in the whole scanning range. The band positions and their corresponding band assignments for the CIP and CIP-adsorbed samples are listed in Table 1.

The peak at 1707 cm^{-1} can be assigned to the C=O stretching of carboxylic acid, 1624 cm^{-1} to ketone C=O stretching, and 1274 cm^{-1} to the coupling of carboxylic acid C–O stretching and O–H deformation [36]. The vibration peak at 1385 cm^{-1} was interpreted as being due to the protonation of the amine group in the piperazine moiety [21].

The CIP molecules would be ionized into 80% cationic and 20% zwitterionic forms at pH of 5.5 according to the theoretical calculation (Fig. 1). After adsorption under such a condition, there was a shift of the ketone stretching band to a higher frequency of 1628 cm^{-1} which could be attributed to the release of intra-molecular hydrogen bonding between the carboxylic acid and ketone groups in the cationic form, strengthening the ketone C=O bond. This result is similar to that of the CIP adsorption on goethite [36] and implies a possible formation of hydrogen bonding between released carboxylic acid groups and basal oxygen atoms of

Table 1
FTIR band positions (cm^{-1}) and suggested assignment for ciprofloxacin hydrochloride and montmorillonite cation exchanged with ciprofloxacin.

Ciprofloxacin hydrochloride	Montmorillonite cation exchanged with ciprofloxacin (C_s = 292 mg/g)	Band assignment
1707	1707	ν (carboxylic acid C=O) [36]
1624	1628	ν (ketone C=O) [36]
–	1582	ν_{as} (carboxylate group COO$^-$) [36]
1385	1390	Protonation of amine group in the piperazine moiety [21]
–	1379	ν_s (carboxylate group COO$^-$) [36]
1274	1274	ν (carboxylic acid C–O)/δ (carboxylic acid C–OH) [36]

ν: stretching, δ: bending, C_s: adsorbed CIP weight per gram montmorillonite.
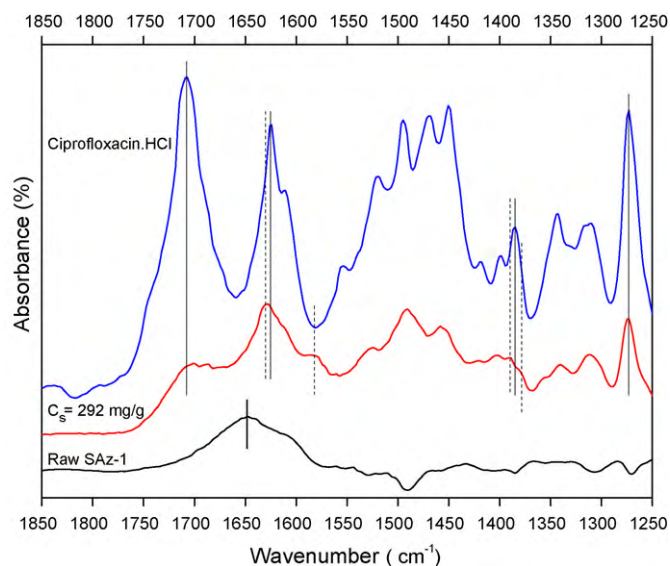

Fig. 6. FTIR spectra of raw montmorillonite, pure CIP, and CIP-adsorbed montmorillonite at 292 mg/g. The characteristic band positions of pure CIP are marked by gray lines and that of raw montmorillonite by a black line. The distinctive band positions of CIP as a result of adsorption on montmorillonite are denoted by dashed lines.

montmorillonite. Two additional peaks are presented at 1582 cm^{-1} and 1379 cm^{-1} corresponding to the asymmetric and symmetric stretching of the carboxylate group in zwitterionic CIP, respectively, which were well illustrated in previous studies for the CIP solution systems at different pH conditions [21,36]. The intensities of those peaks are rather weak because the fraction of the zwitterionic form is small in this study. The peak shift from 1385 cm^{-1} to 1390 cm^{-1} suggests the establishment of a bonding or electrostatic attraction between the protonated amine group and the negatively charged montmorillonite surface.

The interlayer conformation of CIP molecules in montmorillonite can be schemed by combining the XRD and FTIR results. The d_{001} spacing of montmorillonite was expanded to 17.23 Å when the exchanged CIP reached its saturation level. Subtracting 10 Å for the d_{001} spacing of dehydrated montmorillonite, the gallery height could be considered as 7.23 Å. Taking the molecular length along its long dimension as 12 Å, the exchanged CIP would thus exhibit a tilt orientation relative to the silicate layer with an angle of about 35° (Fig. 7). For cationic CIP, the main species in the studied pH range, two ends of the molecule would adopt electrostatic attraction and hydrogen bonding to the clay surface through its specifically protonated amine group and carboxylic acid, respectively. The molecular orientation in this study is different from that in the study of Carrasquillo et al. [19] in which a vertical arrangement of zwitterionic CIP adsorbed on montmorillonite surface was
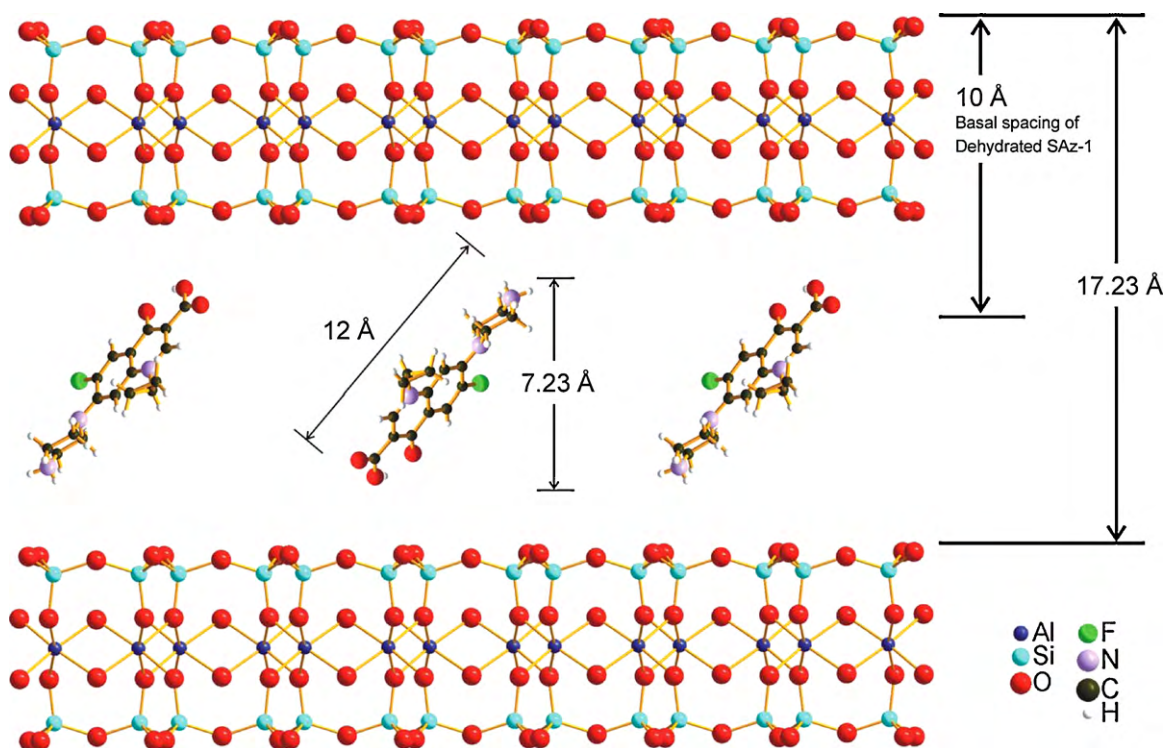

Fig. 7. Schematic conformation of CIP adsorption in the interlayer of montmorillonite.

hypothesized for maximizing the attraction between the cationic amine and the clay surface, and minimizing the repulsion between anionic moiety and clay surface. The model for the CIP conformation in the present study is supported by considering the results of several experiments collectively.

4. Conclusions

The following conclusions can be made from the experimental results of ciprofloxacin on montmorillonite:

1. Montmorillonite SAz-1 had a maximal adsorption capacity of 330 mg/g (1.0 mmol/g) for CIP, close to its CEC of 1.23 meq/g, suggesting site-limited adsorption. The nearly 1:1 replacement relationship between the amounts of adsorbed CIP and those of desorbed interlayer cations from montmorillonite demonstrated that the process was highly dominated by a cation exchange interaction mechanism.
2. As the equilibrium pH value was greater than the pK_{a2} of CIP, the increased abundance of anionic CIP induced strong repulsion to the negatively charged layers of montmorillonite, thus reducing its adsorption level below 250 mg/g.
3. A conformation model involving a tilted orientation of exchanged CIP molecules with their protonated amine group and carboxylic acid group having electrostatic attraction and hydrogen bonding to the clay layers was proposed based on interlayer expansion of the montmorillonite from XRD analyses and shifts in FTIR band positions after CIP adsorption.

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