Adsorption of Chlortetracycline from Water by Rectories*

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Abstract The removal of antibiotics from water by clay minerals has become the focus of research due to their strong adsorptive ability. In this study, adsorption of chlortetracycline (CTC) onto rectories was conducted and the effects of time, concentration, temperature and pH were investigated. Experimental results showed that adsorption equilibrium was reached in 8 h. Based on the Langmuir model, the maximum adsorption capacity of CTC on rectories was 177.7 mg·g\(^{-1}\) at room temperature. By the study on adsorption dynamics, it is found that the kinetic date fit the pseudo-second-order model well. The adsorption of CTC by rectories is endothermic and the free energy is in the range of \(-10\) to \(-30\) kJ·mol\(^{-1}\). The pH value of solution has significant effects on adsorption and the optimal pH is at acidity (pH = 2 – 6). At concentration of 2500 mg·L\(^{-1}\), the intercalated CTC produces an interlayer space with a height of 1.38 nm, which is 1.12 nm in raw rectories, suggesting that the adsorption occurs between layers of rectories.

Keywords adsorption, rectory, chlortetracycline

1 INTRODUCTION

Antibiotics have become new pollutants in eco-environment due to their abuse of feed and aquaculture. When antibiotics are fed to animals, most of them will be discharged in the stool and only a little stays in the animal body. The discharged antibiotics will maintain active and cause serious pollution to soil and water [1]. To remove hydrophobic organic compounds from water, the adsorbent with higher total organic carbon content will achieve a better effect. However, for ionizable compounds, which are quite hydrophilic, their affinity to solid surface is strongly affected by the solution pH and their hydrophilicity, lowering the adsorption to activated carbon [2]. Antibiotics have different charges on different sites depending on solution pH. For example, for chlortetracycline (CTC), a widely used antibiotics additives, when solution pH is below 3.30, the dimethyl group will be protonated and CTC is present as a cation. At pH between 3.30 and 7.44, phenolic-pentanedione will lose protons and CTC exists as a zwitterion. At pH higher than 7.44, both carbonyl and phenolic-pentanedione will lose protons, so CTC presents a monovalent anion or a divalent anion (Fig. 1) [3].

The study of antibiotics adsorption on soils and clays began in the 1950s [4] but are still limited [5, 6]. Due to the hydrophilicity and surface electricity, antibiotic molecules could be adsorbed by minerals and fixed in mineral voids [7]. Recent studies on antibiotic removal used some montmorillonite, such as bentonite, on which the adsorption capacity of diphenhydramine is as high as 192 mg·g\(^{-1}\) at pH 5–7 [8–10], while kaolinite, rectories, and other soil components are used less often. Rectory is a regular interstratified mineral consisting of dioctahedral mica-unit and montmorillonite-unit layer in a ratio of 1 : 1. It contains exchangeable cations and interlayer water. The special structure determines its expansibility, ion exchange properties and...
good adsorption performance [11]. It is widely used in removing humic acid, toxic organic compounds or heavy metal cations from urban sewage [12, 13].

In view of the excellent wastewater treatment performance of rectories and the urgency of treating the pollution of antibiotics, we explore the mechanism about adsorption of CTC on rectories in this study. The effects of adsorption time, concentration of CTC solution, temperature and pH on the adsorption rate are investigated. The results are characterized with X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR).

2 EXPERIMENTAL

2.1 Materials

The rectories used is the clay obtained from Zhongxiang City, Hubei Province, China, and was used as received. Its rectories content is 70%-80%, and its chemical constituents are mainly SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, K₂O, Na₂O, P₂O₅, S, C and loss on ignition (LOI). CTC obtained from Tianjin Dongpeng Co., Ltd., China, is also called “chlortetracycline”, which is a kind of tetracyclines, with formula mass of 515.34 g·mol⁻¹, pKₐ₁, pKₐ₂, and pKₐ₃ values of 9.27, 7.44, and 3.30, respectively.

2.2 Instruments

CTC was quantified by HPLC method. UV-Vis spectrophotometer (UV-751) at a wavelength of 290 nm was used for CTC detection. The standards were adjusted to the same pH as that in the experiments. Calibration was made with 6 standards between 0 and 100 mg·L⁻¹ with the value of r² no less than 0.99.

Powder XRD analysis was performed at 40 kV and 100 mA. Samples were scanned from 3° to 70° 2θ at 8(°)·min⁻¹ with a scanning step of 0.02° per step. The FTIR spectra were obtained by accumulating 256 scans at a resolution 4 cm⁻¹ in the range of 4000-400 cm⁻¹.

2.3 Batch experiment

For all batch experiments (each repeated twice), the amount of rectories used was 0.10 g, while the volume of solution was 25 ml. They were mixed in 100 ml conical flasks on the oscillator at 150 r·min⁻¹ with constant temperature and separated in 50 ml centrifuge tubes at 2500 r·min⁻¹. The supernatant was taken to a UV-Vis spectrophotometer (UV-751) at a wavelength of 290 nm [14]. The removal rate or adsorption was calculated to evaluate the effects of adsorption time, CTC solution concentration, temperature and pH. For batch kinetic study, the initial CTC concentration was 500 mg·L⁻¹ while the pH value was maintained at 1.98, 4, 6, 7.9, 10 and 11.5 at room temperature (298 K).

\[
\text{Removal ratio} = \frac{c_0 - c_e}{c_0} \times 100\% \quad (1)
\]

\[
q_e = \frac{(c_0 - c_e)}{M} \quad (2)
\]

where c₀ (mg·L⁻¹) is the initial concentration of solute, cₑ (mg·L⁻¹) is the equilibrium concentration, qₑ (mg·g⁻¹) is the amount of CTC adsorbed at equilibrium, V (L) is the volume of solution, and M (g) is the quality of adsorbent.

3 RESULTS AND DISCUSSION

3.1 CTC adsorption kinetics

The results showed that the adsorption reached equilibrium in 8 h (Fig. 2). The maximum removal ratio was about 90% and the equilibrium adsorption was 113.1 mg/g. In subsequent experiments the equilibration time was set for 8 h.

![Figure 2 The effect of time on removal efficiency and adsorption](image)

The pseudo-second-order kinetic model fits the experimental data well (Table 1). Its integrated form is [15]

\[
\frac{t}{q_t} = \frac{1}{k_e q_e^2} + \frac{1}{q_e} \quad (3)
\]

\[
q_t = \frac{(c_0 - c_t)}{M} \quad (4)
\]

where q₀ (mg·g⁻¹) is the amount of CTC adsorbed on the surface of adsorbent at time t (h), kₑ (g·mg⁻¹·h⁻¹) is the pseudo-second-order kinetic constant, and cᵣ (mg·L⁻¹)
is the solute concentration at time $t$. The pseudo-second-order kinetic model is plotted in Fig. 3. Based on the equation for the straight line ($R^2 = 0.999$), we obtain that the theoretical equilibrium adsorption of CTC is 113.6 mg·g$^{-1}$, which is close to the experimental value of 113.1 mg·g$^{-1}$.

3.2 CTC sorption isotherm

Figure 4 shows the adsorption of CTC on rectories at different temperatures. The adsorption capacity is 177.7, 206.5 and 239.8 mg·g$^{-1}$ at 298, 308 and 318 K, respectively, which is higher than that of ciprofloxacin (CIP) on rectories (135.9 mg·g$^{-1}$) [16]. The experimental data fit the Langmuir type isotherm [17] well (Table 2)

$$q_e = \frac{q_m c_e b}{1 + c_e b}$$

where $q_m (\text{mg·g}^{-1})$ is the maximum adsorption, and $b$ (L·mg$^{-1}$) is the Langmuir type isotherm constant. The Langmuir type isotherm is plotted in Fig. 5. Based on the equation of the straight line, we obtain that the theoretical maximum adsorption of CTC on rectories is 181.8 mg·g$^{-1}$ at room temperature (298 K), which is close to the experimental value of 177.7 mg·g$^{-1}$ (298 K). The Langmuir type isotherm constant $b = 0.015$ L·mg$^{-1}$ with $R^2 > 0.99$. The interlayer surface of rectories is relatively homogeneous and the adsorption obeys the Langmuir monolayer adsorption.

3.3 Effect of temperature on CTC adsorption

Figure 6 shows the adsorption of CTC on rectories at different concentrations and temperatures. The thermodynamic parameters of adsorption are expressed as

$$K_d = \frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

where $K_d$ (L·g$^{-1}$) is the ratio of the amount of CTC adsorbed at the equilibrium CTC concentration, $\Delta H$ (kJ·mol$^{-1}$) is the change in enthalpy, $\Delta S$ (kJ·mol$^{-1}$·K$^{-1}$) is the change in entropy, $R = 8.314$ J·mol$^{-1}$·K$^{-1}$ is the gas constant, and $T$ (K) is the reaction temperature. The free energy of adsorption can be determined by

$$\Delta G = \Delta H - T\Delta S$$

The calculated theoretical parameters are listed in Table 3. The negative value of $\Delta G$ indicates attractive adsorption.

| Table 1 Parameters in the pseudo-second-order kinetic model |
|------------------|------------------|------------------|------------------|
| $c_0$/mg·L$^{-1}$ | $q_e$ (exp)/mg·g$^{-1}$ | $q_i$ (cal)/mg·g$^{-1}$ | $R^2$ | RE/% |
| 500              | 113.1            | 113.6            | 0.9998 | -0.44 |

| Table 2 Parameters in Langmuir type isotherm model |
|------------------|------------------|------------------|---------------|------------|
| $T$/K            | $q_m$ (exp)/mg·g$^{-1}$ | $q_m$ (cal)/mg·g$^{-1}$ | $b$/L·mg$^{-1}$ | $R^2$ | RE/% |
| 289              | 177.7            | 185.2            | 0.0015        | 0.9977 | -4.05 |
| 308              | 206.5            | 212.8            | 0.0014        | 0.9979 | -2.96 |
| 318              | 239.8            | 250.6            | 0.0013        | 0.9962 | -4.08 |

The free energy of adsorption can be determined by

$$\Delta G = \Delta H - T\Delta S$$

The calculated theoretical parameters are listed in Table 3. The negative value of $\Delta G$ indicates attractive adsorption.

interaction between CTC and rectories, so the adsorption of CTC on rectories is spontaneous. Positive value of $\Delta H$ indicates an endothermic reaction and higher temperature is good for the reaction. According to the value of $K_d$ and $\Delta H$, we obtain a small positive value of $\Delta S$, so the adsorption is spontaneous. It suggests that the adsorbed CTC molecules may adopt a randomly oriented manner instead of arranging themselves in an orderly pattern on the external surface of rectories. It is different from the adsorption of ciprofloxacin on rectories [16].

### 3.4 Effect of pH on CTC adsorption

The amount of CTC adsorbed ranged from 114.2 to 124.8 mg·g$^{-1}$ or 91% to 99% at initial concentration of 500 mg·L$^{-1}$ and reached the maximum at acidity (2–6) at room temperature (298K) (Fig. 7), so the adsorption capacity of rectories depends on the pH environment. This is closely related to the surface electricity of CTC and rectories. When pH <3.30, CTC is in the cationic state (CTC$^+$) and exchanges the interlayer cations at 1 : 1. When pH = 3.30–7.44, CTC is in the neutral state (CTC$^0$), which reduces the cation exchange capacity, while the molecular adsorption remains similar. When pH>7.44, CTC is in the anion state (CTC$^-$, CTC$^{2-}$), which hinders the cation exchange capacity. Besides, under alkaline condition, the surface of rectories is electronegative [18] and creates a repulsive energy against CTC$^-$ and CTC$^{2-}$. Thus the adsorption decreases rapidly under alkaline condition.

### 3.5 XRD analysis

Figure 8 shows the XRD patterns of raw rectories and those after adsorbing CTC at different initial concentrations. The XRD patterns are similar, indicating similar structure of rectories with and without the adsorption. However, for 1000 and 2500 mg·L$^{-1}$ concentration of CTC, the important peak located at $5^\circ$–$10^\circ$($2\theta$) shifts compared with that of raw material. After adsorbed a certain amount of CTC, two weak peaks $d_{002}$ and $d_{003}$ appear instead of one strong peak $d_{002}$ of raw rectories. The $d$-spacing of rectories increases. The $d$-spacing of raw rectories is 1.12 nm, and

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<th>$c_0$/mg·g$^{-1}$</th>
<th>ln$K_d$ 298 K</th>
<th>ln$K_d$ 308 K</th>
<th>ln$K_d$ 318 K</th>
<th>$\Delta H$ /kJ·mol$^{-1}$</th>
<th>$\Delta S$ /kJ·mol$^{-1}$·K$^{-1}$</th>
<th>$\Delta G$ /kJ·mol$^{-1}$ 298 K</th>
<th>$\Delta G$ /kJ·mol$^{-1}$ 308 K</th>
<th>$\Delta G$ /kJ·mol$^{-1}$ 318 K</th>
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<td>5.09</td>
<td>5.28</td>
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<td>−13.9</td>
</tr>
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<td>4.80</td>
<td>5.04</td>
<td>16.6</td>
<td>0.09</td>
<td>−11.4</td>
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that of adsorbed one at the 2500 mg·L⁻¹ initial concentration of CTC increases to 1.38 nm. Thus CTC intercalates into the interlayer of rectories and adsorption occurs between the layers.

3.6 FTIR analyses

Figure 9 shows the FTIR spectra of raw rectories and rectories with absorbed CTC at different initial concentrations. There is no significant change in the vibration of the backbone of the silicate structure of rectories before and after CTC adsorption, which indicates that the adsorbed CTC does not alter the structure, consistent with XRD observation. The FTIR spectrum shows Si–O and C–O stretching vibration near 1030 cm⁻¹, C=O stretching vibration near 1500–1650 cm⁻¹, –COOH and –OH stretching vibration near 3600 cm⁻¹. The most obvious changes are those in 1500–1650 cm⁻¹ and 3300–3600 cm⁻¹. At wave number 1529 cm⁻¹, the rectories after CTC adsorption show a strong peak compared with the raw material, characterizing the reaction between rectories and CTC. Besides, the bands at 3581 cm⁻¹ shift to higher frequencies, indicating a strong interaction between rectoriy surface and the intercalated CTC molecules [18].

![FTIR spectra of rectories in equilibrium with CTC solutions](image)

Figure 9 FTIR spectra of rectories in equilibrium with CTC solutions

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4 CONCLUSIONS

The adsorption of CTC on rectories follows the pseudo-second-order kinetics and the Langmuir adsorption isotherm well. The adsorption equilibrium is reached in 8 h and the maximum adsorption is 177.7 mg·g⁻¹ at room temperature. The optimal adsorption pH is 2–6 and the adsorption decreases rapidly over pH > 7.

The adsorption of CTC on rectories is a spontaneous and endothermic reaction. ΔG is in the range of –10 to –30 kJ·mol⁻¹ and ΔH is 10–30 kJ·mol⁻¹. Thus, higher temperature will enhance the uptake of CTC by rectories. The small value of ΔS suggests that the adsorbed CTC molecules may adopt a randomly oriented manner instead of arranging themselves in order on the external surface of rectories.

XRD analyses show that the intercalated CTC produces an interlayer space with a height of 1.38 nm, which is 1.12 nm in the raw rectories. The FTIR analyses show a stronger peak after adsorption of CTC compared with that without adsorption, characterizing the reaction between rectories and CTC. The mechanism is the interlayer adsorption and the adsorbed CTC does not alter the structure based on the characterization of XRD and FTIR analysis.

REFERENCES