Adsorption of Tetracycline by Wuhan Lake Sediments

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Abstract. The antibiotic contamination in the environment has attracted people’s attention now. The adsorption characteristics of tetracycline (TC) by lake sediments in east lake and south lake of Wuhan city were investigated in this paper. The results showed that the adsorption reactions could reach balance after 13 hours. The effects of pH and calcium ion intensity on the adsorption were significant, and the adsorption capacities decreased with the increase of the pH as well as calcium ion concentration. The increase of initial TC concentration was beneficial to adsorption of TC until reaching 200mg/L. The adsorption process conformed to the pseudo second-order kinetics model and had three steps according to Weber-Morris model. The Langmuir adsorption isotherm could better fit adsorption than Freundlich model. The maximum adsorption quantities were 62.74 and 75.41 mg/L respectively for east lake and south lake at the temperature of 25°C.

1. Introduction
Tetracycline (TC) is widely used in the production and treatment of livestock and poultry due to its low price and wide spectrum. However, with the abuse of TC, the problems like high detection rates, drug resistance and aquatic toxicity gradually arouse people's attention. As the widespread use of wastewater treatment technologies cannot completely remove antibiotics from water, the degradation of TC has become a hot area of researches in recent years. Adsorption is an effective method to remove pollutants from wastewater by adsorbing substances onto adsorbent. Materials for instance bentonite, montmorillonite, modified zeolite and carbon nanotube have been applied to adsorb antibiotics in several studies. How to choose efficient and cheap adsorbent is still a big challenge.

In this paper, the adsorption properties of TC were studied by using common lake sediments as adsorbents. The effects of time, temperature, pH, TC initial concentration and cationic intensity on adsorption were investigated. The kinetics and isotherms studies were carried out to explore the mechanisms of adsorption.

2. Materials and methods

2.1. Adsorbents
The surface sediments were sampled from the middle of the east lake and south lake in Wuhan city using grab sampler. The sediments were pretreated as deslagging, air drying, grinding and sieving before adsorption studies.
2.2. Analytical Methods
The experiment showed that TC had ultraviolet absorption, and the concentration had linear relationship with solution absorbance. A UV-vis spectrophotometer was used to measure TC concentration in 356 or 384nm wavelength when pH of solution was respectively less than 7 or greater than 7. Hydrolysis of TC in alkalies caused red shift of the adsorption spectra.

![Figure 1. The TC UV-vis spectrum of different pH.](image)

2.3. Adsorption
When adsorption experiment carried out, a certain amount of sediments and tetracycline were added into the 500mL Erlenmeyer flasks, which were sealed and placed in a thermostatic shaker (25℃, 200r/min). In addition to the adsorption time effect test, 5mL solution was sampled using syringes after 15h. The residual tetracycline concentration in the solution was determined by the UV-vis spectrophotometer after filtered. Samples were taken according to the gradient time in adsorption time effect experiment.

3. Results and Discussion

3.1. The effects of adsorption time
The adsorption capacities of TC increased with time for both two sediments (Fig.2(a)). At the beginning, the amount of TC adsorbed on sediments increased rapidly as sufficient binding sites in the sediments for combining with TC. With the increase of adsorption time, the binding sites on surface layer were gradually occupied, and then the adsorption efficiency decreased. When saturation reached, adsorption tended to equilibrium. The balance time for adsorption of TC on two sediments was 13 hours, the maximum adsorbance was 7.87mg/g for sediments from the East lake and was 8.90mg/g for sediments from the South lake.

3.2. The effects of TC initial concentration
With the increase of the initial concentration of TC, the adsorption capacity of the two sediments increased until concentration of TC reached 200mg/L (Fig.2 (b)). With low concentration, the TC molecules could quickly disperse to the surface of the adsorbents and occupy the binding sites. With the binding sites gradually taken up, the increase of adsorption tended towards stabilization. Superabundant TC molecules in solution exceeded the adsorption capacity of the sediments resulting in saturation of adsorption capacity.
Figure 2. Effects of adsorption time (a) and initial concentration (b) of TC adsorption on sediments (25°C, pH 7).

3.3. The effects of pH and ionic strength

The effects of solution pH have been shown in figure 3(a). The adsorption capacity of TC on two sediments decreased greatly with the increase of pH, and the changes were less when the solution pH turned from neutral to weakly alkaline. Sediments were most composed of layered silicate, and isomorphous replacement effects can make the surface with a negative charge. In acid solution, TC was mainly in the form of cation, which can be adsorbed on the sediments’ surface under the electrostatic force. In weakly alkaline solution, TC was mainly comprised of neutrals and anion. With the increase of negative charge, TC can combine with cation such as Ca$^{2+}$ and Mg$^{2+}$ on the surface of the adsorbents, therefore the sediments still had strong adsorption of TC. Nevertheless, as the alkaline enhanced, more TC anion formed electrostatic repulsion with negative charge on adsorbent surface, thereby the adsorption quantity reduced.

Figure 3. Effects of pH (a) and ionic strength (b) of TC adsorption to sediments (25°C).

Figure 3 (b) expressed the effect of ionic strength (Ca$^{2+}$). The effects displayed similar patterns for both sediments from east lake and south lake, that the adsorption capacity decreased with the increase of Ca$^{2+}$ concentration. As pH of the solutions ranged from 7.1 to 7.8, the effect of pH on the adsorption was very small. Due to the negative charge on the sediment, the increase of Ca$^{2+}$ concentration could occupy binding sites and hinder the contact between TC and the sediments. Besides, the increase of cation decreased the activity of TC, with the result that the effective concentration of tetracycline reduced. The probability of TC contacting with adsorbents’ surface decreased, giving rise to reduction of adsorption capacity.
3.4. Adsorption kinetics

The adsorption rate and mechanism can be discussed by the simulation of adsorption kinetics. According to the pseudo-first-order and pseudo-second-order kinetic model equations [1], the linear fitting was performed by using the Origin software (OriginLab, 2016). The kinetic curves were shown in figure 4 (a) and (b) respectively, and the parameters were in table 1.

![Image](figure4.png)

**Figure 4.** Fitting curves of pseudo-first-order (a) and pseudo-second-order kinetic (b).

The R-squared for pseudo-first-order kinetic was both lower than 0.9 on two sediments, and the calculated equilibrium adsorption quantities were quite different from the experimental ones. On the contrary, the R² of pseudo-second-order kinetic both reached 0.9999 for two sediments, and the calculated quantities had little deviation from the experimental ones. The pseudo-second-order kinetic model could better fit the processes of adsorption TC on two sediment, which illustrated that the adsorption process was mainly controlled by chemical action.

![Image](table1.png)

**Table 1.** Parameters of pseudo-first-order kinetic and pseudo-second-order kinetic.

|           | Pseudo-first-order kinetic | Pseudo-second-order kinetic |
|-----------|---------------------------|-----------------------------|
|           | $Q_e$ mg/g                | $K_1 \times 10^{-2}$ min$^{-1}$ | $Q_{e,cal}$ mg/g | $\Delta Q$ % | $R^2$ | $K_2 \times 10^{-2}$ g/(mg·min) | $Q_{e,cal}$ mg/g | $\Delta Q$ % | $R^2$ |
| East lake | 7.87                      | 0.277                       | 1.99 | 74.71 | 0.8161 | 0.428 | 7.99                       | 1.52 | 0.9999 |
| South lake| 8.90                      | 0.251                       | 1.34 | 84.94 | 0.7852 | 0.678 | 8.96                       | 0.67 | 0.9999 |

In order to more clearly understand the adsorption processes, Weber-Morris model [1] was also applied to find out the control steps of adsorption rate. The results of model fitting have been displayed in figure 5. The Curves both had three linear processes, namely instantaneous adsorption, gradually adsorption and equilibrium adsorption process.

![Image](figure5.png)

**Figure 5.** Fitting curves of Weber-Morris model.
Table 2. Parameters of Weber-Morris model.

|                | first process | second process | third process |
|----------------|---------------|----------------|--------------|
| $K_{i1}$ mg/g min$^{-1/2}$ | $X_1$ | $R_2^2$ | $K_{i2}$ mg/g min$^{-1/2}$ | $X_2$ | $R_2^2$ | $K_{i3}$ mg/g min$^{-1/2}$ | $X_3$ | $R_2^2$ |
| East lake      | 0.4275        | 2.25           | 1            | 0.1300      | 4.83 | 0.9988 | 0.0105      | 7.42       | 0.9857 |
| South lake     | 0.65984       | 2.45           | 1            | 0.0582      | 7.30 | 0.9923 | 0.0068      | 8.59       | 0.9925 |

The results in table 2 demonstrated that the $X$ values were all greater than zero for three processes of two sediments, indicating that the adsorption rate was controlled by internal and external diffusion together. For two kinds of sediments, the $K_i$ values were diminishing from first step to the third. At the beginning, the rate for adsorption occurred on outer layer of the adsorbents was high. Then as the boundary layer was gradually formed, the adsorption turned to be internal particle diffusion, leading to the decrease of the adsorption rate until equilibrium.

3.5. Adsorption isotherm

The adsorption isotherm models were used to determine adsorption mechanisms. The Langmuir and Freundlich models were commonly applied. Results of fitting linear isothermal equations of Langmuir and Freundlich models were illustrated in figure 6 (a) and (b), and the parameters for two models were presented in table 3. Through the comparison of $R^2$ values, the Langmuir model was more suitable than Freundlich for describing adsorption characteristics of TC on sediments. As the Langmuir isotherm model assumed the adsorbent surface was uniform and the adsorption was monolayer, the adsorption quantities were associated with the surface characteristics of sediments. Researches indicated that large specific surface area could be conducive to the adsorption. The $R_L$ values for two sediments were both between 0 and 1, indicating that adsorption of TC was preferential. The $n$ values were both greater than 1, also suggesting that the adsorption easily came up.

Figure 6. Effects of pH (a) and ionic strength (b) of TC adsorption to sediments (25°C).

Table 3. Parameters of Langmuir adsorption isotherm and Freundlich adsorption isotherm.

|                | Langmuir adsorption isotherm | Freundlich adsorption isotherm |
|----------------|-----------------------------|--------------------------------|
|                | $Q_m$ mg/g                  | $K_L$ L/mg                     |
|                | $R_L$                        | $R^2$                          |
|                | $K_F$ (mg/g)(L/mg)$^{1/n}$   | $n$                            |
|                | $R^2$                       |                               |
| East lake      | 62.74                       | 0.0346                         |
|                | 0.0546—0.7429               | 0.9913                         |
|                | 5.2473                      | 2.2552                         |
|                | 0.9519                      |                               |
| South lake     | 75.41                       | 0.0446                         |
|                | 0.0429—0.6916               | 0.9977                         |
|                | 6.1265                      | 2.1245                         |
|                | 0.9421                      |                               |

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4. Conclusion
The adsorption of TC on sediments of the east lake and south lake in Wuhan city, as well as the effects of other factors were studied in this paper. The two kinds of sediments presented good adsorption properties of TC, and proved that they may have the potential to be used as adsorbent to eliminate TC pollution in water as its low-price and environment friendly. Since the environmental factors such as pH and cationic concentration could effect adsorption, so it is important to control these factors when sediments are applied as adsorbent.

References
[1] Y. Wu, Xi. B, G. Hu, Adsorption of tetracycline and sulfonamide antibiotics on amorphous nano-carbon, Desalin. Water Treat., 57 (2016) 1–13.