Effect of pH value on adsorption of Levofloxacin in agricultural silty clay of North China

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Abstract: The entry of quinolone antibiotics into the soil will cause serious soil antibiotic contamination. The migration and whereabouts of antibiotics in soil are mainly affected by soil adsorption. The change of pH value will have a great impact on soil adsorption. In this paper, the adsorption characteristics of typical fluoroquinolones (levofloxacin) in the silty clay widely distributed in the farmland of North China and the effect of pH value change were studied. The results show that Langmuir adsorption isotherm model can well fit the isotherm adsorption process of levofloxacin on silty clay. The adsorption process of levofloxacin on silty clay was fast, and equilibrium was reached in about 16 hours. The adsorption amount decreases with the increase of pH value. After the pH value reaches 10.86, the adsorption amount rises.

1. Introduction
Antibiotics were a large class of chemicals used in the prevention and treatment of human and animal bacterial diseases, as well as the promotion of animal growth. It was estimated that 16,000 tons of antibacterial agents were used in the United States each year, of which 70% were antibiotics. About 5,000 tons of antibiotics were used in EU countries each year. China was also a big country in the use of antibiotics. According to statistics, 10 of the top 15 drugs used and sold in China were antibiotics. The spatial distribution of antibiotics in the soil was complex, and adsorption, degradation, and transformation of surface water, groundwater, vegetation, and soil components may be the ultimate trend.

A comprehensive and systematic understanding of the adsorption mechanism of antibiotics in soil and its combined mechanism was an important prerequisite for risk assessment. The pH value of the soil varies greatly with the type and composition of the soil, and it had a significant effect on the adsorption by changing the electrical properties of the antibiotic and the adsorption medium. Under different pH value conditions, ionized organic compounds with different charges could be formed due
to protonation or deprotonation. Wu [6] found that pH value could change the surface electric property of naphthenic acid when studying its adsorption behavior in soil under different pH value conditions. Some studies had pointed out that quinolones had a positive charge when the pH value is lower than its pK\textsubscript{a1} value; when the pH value is higher than its pK\textsubscript{a2} value, quinolones have a negative charge; when the pH value is between its pK\textsubscript{a1} value and pK\textsubscript{a2} value, quinolones have a positive charge and a negative charge at the same time [7].

The amount and electrical properties of the charge carried by antibiotics were important reasons affecting the adsorption of antibiotics in soil. Silty clay was widely distributed in the lower layer of the aeration zone in the North China Plain [8]. The permeability and dispersion of pollutants were weak, which determined whether the pollutants could penetrate the aeration zone to reach the underground water layer. Levofloxacin, with typical quinolone antibiotic structure [9], had been detected in different areas as a common antibiotic [10]. Based on the previous study on the adsorption of antibiotics in soil, this paper takes levofloxacin, a typical quinolone antibiotic pollutant, as the research object, analyzes the influence of pH value on the adsorption of quinolones in agricultural silty clay in North China, and further discusses the influence of pH value on the adsorption process according to its adsorption mechanism.

2. Materials and methods

2.1 Experimental materials

Levofloxacin (purity > 98.0%) were purchased from Aladdin, Shanghai. The remaining reagents were of analytical grade. The experimental water was deionized water (18.25 MΩ / cm). Levofloxacin standard was dissolved in deionized water to make a standard solution of 100 mg/l.

The silty clay samples were used after air drying, grinding and sieving.

| Water content (%) | Wet density (g / cm\(^3\)) | Dry density (g / cm\(^3\)) | proportion | Porosity |
|-------------------|---------------------------|---------------------------|-------------|----------|
| 20.2              | 2.04                      | 1.75                      | 2.71        | 33.0     |

Table 1 Physical and chemical properties of tested silty clay soil

| Specific surface area | Major minerals                        |
|-----------------------|---------------------------------------|
| 12.10                 | Calcite, quartz, plagioclase, feldspar, illite, chlorite, kaolin, montmorillonite |

| Particle composition  | Grit | Powder | Cosmid | Colloidal particles |
|-----------------------|------|--------|--------|--------------------|
|                        | 11.50| 54.90  | 33.60  | 18.60              |

2.2 Adsorption experiment

2.2.1 Adsorption kinetics test.
Weighed 2 g of silty clay in a 30 ml brown bottle, The prepared 100 mg/l levofloxacin standard solution was diluted to 10 mg/l levofloxacin solution standard stock solution, and the CaCl\(_2\) concentration was adjusted to 0.01 mol/l. Adjusted pH value 1.85, 3.63, 7.01, 7.93, 10.96, mixed with the ratio of soil to liquid 1:10. Shook in a shaker at 25°C and 120 rpm for 24 hours in a dark place. Took out the solution and stand the solution for 30 minutes. Took the supernatant in a centrifuge tube and centrifuge at 25°C for 15 minutes. Transferred a small amount of liquid to the quartz cuvette and measured the solution Levofloxacin concentration.

2.2.2 isothermal adsorption experiment.
Weighed 2 g of silty clay in a 30 ml brown bottle, The prepared 100 mg/l levofloxacin standard solution was diluted to 5 mg/l, 10 mg/l, 20 mg/l, 30 mg/l, and 50 mg/l levofloxacin solution standard stock solution, and the CaCl\(_2\) concentration was adjusted to 0.01 mol/l. Adjusted pH value 1.85, 3.63, 7.01, 7.93, 10.96, mixed with the ratio of soil to liquid 1:10. Shook in a shaker at 25°C and 100 rpm for 24 hours in a dark place. Took out the solution and stand the solution for 30 minutes. Took the supernatant in a centrifuge
tube and centrifuge at 25°C for 15 minutes. Transfer a small amount of liquid to the quartz cuvette and measure the solution Levofloxacin concentration

2.3 Data processing
This experiment takes Quasi-second-order kinetic equations and Langmuir Model fits adsorption data

Quasi-second-order kinetic equation: \[ y = \frac{a^2 \times k \times x}{1 + a \times k \times x} \]

Langmuir model: \[ y = \frac{q \times k \times x}{1 + k \times x} \]

\( a \) was the amount of adsorption (mg/l) at equilibrium, \( y \) was the amount of adsorption (mg/l) at time \( x \); \( x \) was the adsorption time (h); \( k \) was the quasi-secondary adsorption rate constant

\( y \) was the equilibrium adsorption amount mg / g; \( x \) was the equilibrium concentration mg/l; \( q \) was the saturation adsorption amount mg / g. Generally, the larger the value of \( k \), the stronger the adsorption capacity, and \( k \) has the dimension of the inverse concentration

3. Results and discussion

3.1 Fitting of adsorption kinetics curve
The fitting results of quasi-second-order kinetic equations were listed in Table 2. Figure 1 describes the process of adsorption kinetics curve. The correlation coefficient was above 0.999, which indicated that the quasi-second-order kinetic equation had a good fit to the levofloxacin adsorption kinetic curve. The adsorption rate was determined by the square of the number of unoccupied adsorption vacancies on the surface of the adsorbent. The mechanism of chemisorption controlled the adsorption process. This chemisorption involved electron sharing or electron transfer between the adsorbent and the adsorbate. The original levofloxacin solution was neutral with a pH value of 7.01. Overall, the maximum adsorption time of levofloxacin was basically unaffected by changes in pH value. With the decrease of pH value, the adsorption of levofloxacin in silty clay decreased, and the maximum adsorption capacity decreased. With the increase of the pH value, after the pH value exceeded 8, the adsorption amount of levofloxacin would increase rapidly after 10 hours, and the maximum adsorption amount was higher. Overall, levofloxacin had better adsorption in silty clay at low pH value

3.2 Isothermal adsorption curve fitting
Table 3 lists the Langmuir model fitting data, and Figure 2 describes the unadsorbed capacity. The correlation coefficient was above 0.999, which indicates that Langmuir model. The fitting degree of levofloxacin isotherm was better. This indicates that interaction between the adsorption layers may not exist. By comparing the value of \( K \), combined with the difference between the maximum adsorption amounts of each group at the same concentration and different pH value, it can be seen that the adsorption performance was best when the pH value was 1.85. It decreases as the pH value goes up. When the pH value reached 7.93, the adsorption rate increased again and continued to decrease as the pH value increased. The results were consistent with the adsorption kinetics experiments

| pH value | a   | K    | R²    |
|----------|-----|------|-------|
| 1.85     | 9.640 | 18.994 | 0.99994 |
| 3.63     | 9.585 | 18.202 | 0.99992 |
| 7.01     | 9.424 | 17.990 | 0.99966 |
| 7.93     | 9.316 | 15.751 | 0.99991 |
| 10.96    | 9.272 | 16.836 | 0.99938 |

Table 3. Langmuir Model fitting levofloxacin isotherm adsorption curve
3.3 Study on the effect of pH value on the adsorption of levofloxacin

According to some studies [11], pH may affect the adsorption of quinolones in soil or sludge by affecting soil ions, such as Ca\(^{2+}\). Combined with the results of isothermal adsorption experiment, in order to explore whether levofloxacin had similar behavior in farmland silty clay in North China, the comparative experiment was carried out under the alkaline condition (pH value > 10), changing the solution into equal concentration NaCl solution and deionized water. The amount of unabsorbed was shown in Figure 3.

3.4 Effect of different pH values on levofloxacin adsorption

The experimental results show that the morphology of levofloxacin is strongly pH-dependent. According to research [12], In an acidic environment, levofloxacin mainly exists as a cation; in an alkaline environment, it mainly exists as an anion; and in a neutral environment, the zwitterion reaches a maximum distribution. Nuclear magnetic resonance method [13] has been proved that only the carboxyl group of quinolones and the amino group of nitrogen-containing heterocyclic substituent group have obvious proton binding ability, while the electron absorption effect and conjugation effect of aromatic
ring make the proton binding ability of nitrogen atom directly connected with benzene ring greatly weakened. Another study shows that in an acidic environment, the cation of the quinolone compound can form an ion pair with negative ions such as phosphate or chloride in the buffer.

In order to simulate the soil solution conditions in the original state as much as possible in the experiment, CaCl$_2$ solution was used as the solute. On the one hand, protonated levofloxacin may be bound to Cl$^-$ ions in the soil in large quantities, which increases the adsorption of levofloxacin in the soil. On the other hand, levofloxacin combined with anion showed a neutral ion state, which made levofloxacin hydrophobic. According to research by Vaz et al., hydrophobic effect will significantly increase the adsorption capacity of humic acid for antibiotics. Therefore higher hydrophobicity may further enhance the adsorption of levofloxacin in soil.

When the pH value rises to neutral, the neutral ions or zwitterions in the levofloxacin solution gradually increase, and it cannot bind well to the anions in the soil. Therefore, as the pH value increases, the levofloxacin adsorption amount gradually decreases.

According to research of Wang, physical adsorption play the leading role in the process of the adsorption of antibiotic, such as van der Waals force, hydrogen bonding, and mineral pore adsorption. It is consistent with Wang Chang. Chen et al. believe that the formation of hydrogen bonds by combining carboxyl groups with oxygen atoms on the surface of clay minerals may be one of the main mechanisms for adsorption in soil. It was observed in the experiment that with the increase of the pH value of the solution, the turbidity of the solution after shaking was high and it was difficult to settle. This may be due to the decrease of soil viscosity and soil hardening under alkaline conditions, resulting in the decrease of mineral pores and oxygen atoms on the surface of clay minerals, which causes the adsorption capacity of levofloxacin decreased. Previous studies focused on the effect of pH value change on the electrical properties of levofloxacin. This experiment shows that pH value not only affects the adsorption by directly changing the levofloxacin itself, but also affects the adsorption by changing the physical properties of soil.

When the pH value was further increased, the amount of levofloxacin adsorbed increased instead. At this time, levofloxacin was mainly present in the anion in the soil.

According to Qin, the high valence metal cations play the role of bond bridge, forming the three-phase complex of antibiotics metal ions adsorption medium at high pH value. This is consistent with the experimental results. According to the experimental phenomenon, it is observed that at high pH, one group of solution with deionized water as solvent is relatively turbid and difficult to precipitate compared with the other two groups. In addition to the above adsorption mechanism, it is speculated that under alkaline conditions, alkali soluble minerals in the soil, such as quartz, will become colloidal particles, which will expose more binding points on the surface, and produce flocculation under the action of external ions, increasing the adsorption capacity.

Liu et al. When studying the adsorption behavior of another class of quinolone antibiotics, levofloxacin, it was also found that the adsorption amount of levofloxacin in soil increased with the increase of the concentration of neutral / amphoteric molecules, and the highest concentration of neutral molecules was at pH value 7. The maximum adsorption capacity. Results are different. This may be related to the different soils used in the experiment.

4. Conclusion
(1) In the North China Agricultural silty clay, the adsorption capacity of levofloxacin increased with the decrease of pH value, and the adsorption capacity was the lowest from neutral to weak alkaline. With the increase of pH value, the adsorption capacity also increased. The maximum adsorption time was not affected by pH value.

(2) There are two ways for pH value to affect the adsorption of levofloxacin in silty clay. One is to change the electrical property of levofloxacin itself, and the cationic levofloxacin is more likely to combine with the anions in the soil under low pH value; the other is to change the physical properties of the soil, such as viscosity, porosity, and the impact on the soil components, organic matters and inorganic minerals, so as to change the adsorption point on the soil surface.
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