Original Research

Adsorption and Hydrolysis Characteristics of Antibiotics in the Hyporheic Zone of Zaohe-Weihe River, China

Yali Xie^{1,2}, Shengke Yang^{1,2}*, Zongzhou Wang^{1,2}, Ruixin Hu^{1,2}, Siqi Shen³, Dan Zhang^{1,2}, Mengya Luo^{1,2}, Wenke Wang^{1,2}

¹Key Laboratory of Subsurface Hydrology and Ecology in Arid Areas, Ministry of Education, Chang'an University, Xi'an 710054, China

²School of Water and Environment, Chang'an University, Xi'an 710054, China ³China United Northwest Institute for Engineering Design and Research Co., Ltd., Xi'an 710077, China

> Received: 21 October 2021 Accepted: 20 January 2022

Abstract

To reveal the attenuation characteristics of antibiotics in completely different physical and chemical environments formed when surface water and groundwater complement each other, this paper selected the hyporheic zone of Zaohe-Weihe rivers as the study area, explored the adsorption and hydrolysis behavior of oxytetracycline (OTC), norfloxacin (NOR) and sulfamethoxazole (SMZ) by simulating the hyporheic zone. Results showed that the maximum adsorption capacity of the three antibiotics on sediment was SMZ (1008.14 mg/kg)>OTC (430.03 mg/kg)>NOR (128.47 mg/kg). The adsorption processes all were consistent with the Freundlich model. The hydrolysis rate of the three antibiotics in surface water was 2-10 times that in groundwater. In surface water, the half-lives of the three antibiotics were OTC (9.75 d)>SMZ (112. d)>NOR (14.2 d), respectively. In groundwater, the half-lives were OTC (14.78 d)>NOR (63.59 d)>SMZ (117.48 d), respectively. The hydrolysis rate of the three antibiotics under alkaline conditions was significantly greater than acidic and neutral conditions. High temperature and the adding of sediment or clay were conducive to the hydrolysis of antibiotics.

Keywords: hyporheic zone, antibiotics, adsorption, hydrolysis

Introduction

Antibiotics are widely used in medicine, agriculture and aquaculture [1-3]. Most antibiotics (about 25%-75%) cannot be completely metabolized and degraded by organisms, and are released into the environment in the form of parent or intermediate products [4, 5]. These antibiotics will pose a great threat to the survival of humans and animals [6, 7], so it is crucial to control the content of antibiotics in the environment. Antibiotics that enter the environment will be attenuated by biological and abiotic interactions [8-10]. Since antibiotics could inhibit or kill microorganisms at low concentrations [11-13], the biological attenuation effect that depends on the action of microorganisms

^{*}e-mail: ysk110@126.com

is negligible, abiotic attenuation plays an important role in the environmental fate of antibiotics. Therefore, it is necessary to pay more attention to which factors in different environmental media significantly influence the abiotic decline of antibiotics. The hyporheic zone between surface water and groundwater is a key zone of the earth with unique physical, chemical and biological dynamic gradients; pollutants are enriched, degraded and transformed under such a bidirectional hybrid drive. Therefore, it is of great significance to study the abiotic attenuation behavior of antibiotics in the hyporheic zone.

The forms of abiotic attenuation of pollutants in soil and water environment mainly include adsorption, hydrolysis and photodegradation, etc. At present, a large number of studies have focused on the adsorption behaviors of soil and organic matter on antibiotics. It has been found that the physical and chemical properties, composition, dissolved organic matter (DOM) and structure, properties and composition of soil can affect the adsorption of antibiotics [14-16]. Hydrolysis is an important degradation pathway of organic pollutants, especially in esters and amides. The hydrolysis products of esters and amides have higher water solubility and lower octanol water partition coefficients, which make them polar, resulting that its bioaccumulation may be lower than the parent [17]. The hydrolysis rate is a function of environmental conditions, which temperature and pH are the most important parameters. Some studies shown that the hydrolysis rate usually increases with the increase of temperature, and the rate of alkali-catalyzed hydrolysis was better than that of acid-catalyzed and neutral hydrolysis [18, 19]. Some scholars even believed that certain sulfonamides and fluoroquinolones antibiotics did not hydrolyze under any conditions [20-22]. However, these studies were focused on the hydrolysis of pure water in the laboratory, without considering the influence of other components of the actual water sample and its environmental factors [15]. The hydrolysis rate of antibiotics in the actual environment is much faster than the laboratory due to the combined action of various degradation processes. Interestingly, the bidirectional mixing of river water and groundwater in the hyporheic zone forms a unique physical, chemical and biological dynamic gradient, which is bound to affect the attenuation of antibiotics.

In recent years, some studies focused on the migration, distribution and redox process of traditional pollutants, such as N, P [23-26] and heavy metals (Fe, Mn, As, Hg, etc.) in the hyporheic zone [27-29]. The biogeochemical behavior of these pollutants in the hyporheic zone were mainly affected by the hydrological conditions, hydrodynamic conditions, climate, dissolved oxygen (DO), pH, and biological community structure. Among them, dissolved oxygen and pH were the most important factors [17, 23, 30]. Due to the complexity of organic pollutants, the current studies were still relatively thin. For antibiotics, they mainly focused on the distribution rules, the selection

of transport simulation tracers, migration rules, the influence of temperature, and microorganisms [18, 31-33]. But less attention was paid to the attenuation behavior of antibiotics in the hyporheic zone, such as adsorption and hydrolysis, these behaviors play an important role in the decay of antibiotics [18, 34-37]. Therefore, it is important to study the adsorption and hydrolysis behavior of antibiotics to predict their environmental persistence in the hyporheic zone.

This study used the Zaohe-Weihe River hyporheic zone as the study area, and chose oxytetracycline (tetracyclines), norfloxacin (fluoroquinolones) and sulfamethoxazole (sulfonamides) as the target pollutants, we studied the adsorption capacity of antibiotics in the sediments, and explored the hydrolytic behavior of antibiotics during different pH, temperature and sediment conditions in a simulated hyporheic environment. This study provides reference value for the environmental behavior of antibiotics in the hyporheic zone.

Material and Methods

Study Area and Sample Analysis

The study area is the intersection of the Weihe River and its first-level tributary Zaohe River, located in the Guanzhong Basin of Shaanxi Province, China. Weihe River, the largest tributary of the Yellow River, is responsible for regulating water flow, moisturizing, industrial and agricultural water and other functions. The Zaohe River is the main sewage river in Xi'an. It receives about 900,000 tons of domestic sewage every day. There are 6 domestic sewage treatment plants in the middle and lower reaches, in addition, part of the sewage from municipal pipelines will also leak directly into the Zaohe River, causing serious water pollution. The water quality of Weihe River is relatively well, thus this forms a sharp contrast. In the hyporheic zone, the water level of the river increases and the river supplies the groundwater laterally during the wet season; the water level of the river drops and the groundwater replenishes the river during the dry season. This creates a lateral recharge river-groundwater interaction zone.

We chose to collect samples in October and March of the following year when the river water level drops. We set a background section S0 on the Weihe River at 50 m before Zaohe River enters Weihe River and set the control section S1 on the Zaohe River at 100 m before Zaohe River enters the Weihe River. Then along the river, we set cut sections S2-S5 every 100 m. Surface water (0.3 m below the surface), groundwater (the depth of water sample was shown in Table 1), and sediment (0.1 m) were collected at each sampling point, we collected three samples each time and mixed them well before analysis, the water sample was collected by a convenient water sample collector (JC-8000B, China), and the sediment was collected by a gravity sediment sampler (JC-0203, China). The arrangement of sampling points was shown in Fig. 1.

Water sample collection: Place the collected surface water and groundwater samples in 1L brown ground glass, measure the pH, temperature and DO by a portable instrument, and label the sampling point number. The results were that the pH of the surface water was between 6.2 and 7.5, which conformed to GB 3838-2002 "Environmental Quality Standards for Surface Water". The pH of the groundwater was between 6.2 and 7.1, which met GB 14848-2017 "Environmental Quality Standard for Groundwater". The temperature of the surface water was between 12 and 20°C, the average temperature was 17°C. The temperature of the groundwater was between 9 and 14°C, the average temperature was 12°C. The DO of the surface water was between 7.14 and 14.78 mg/L, and the average DO was 9.33 mg/L. The DO of the groundwater was between 3.71 and 4.11 mg/L, and the average DO was 3.62 mg/L.

Collection of sediment: place the sediment in a black container, seal and transport it back to the experiment, and mix well after natural air drying. Then sample diagonally according to the four-point method and sieved. The resultswere shown in Fig. 2.

Sample	Longitude and latitude	Depth (m)
SO	N34°23′40″E108°51′00″	0.8
S1	N34°23′15″E108°51′15″	1.0
S2	N34°23′21″E108°51′25″	0.1
S3	N34°23′25″E108°51′27″	0.4
S4	N34°23′25″E108°51′35″	1.2
S5	N34°23′31″E108°51′46″	0.6

Table 1 The information of sampling points.

Determination of Antibiotics

Standard samples of oxytetracycline, norfloxacin and sulfamethoxazole were purchased from Sigma Company (purity>99%). Methanol, Na₂EDTA, ethyl acetate, acetonitrile and formic acid were purchased from Waters Corporation, USA.

Preparation of standard solution [36]: 10 mg of various antibiotic standards were accurately weighed and dissolved in a 10 mL brown volumetric flask. Tetracycline and sulfonamides antibiotics were dissolved in methanol, and fluoroquinolone antibiotics were dissolved in 0.03 mol/L NaOH and stored in a refrigerator at 4°C.



Fig. 1. Distribution map of study area and sampling points.



Fig. 2. Particle size distribution of sediments in the hyporheic zone.

The sample was centrifuged at 5000 r/min for 10min, the supernatant was filtrated through 0.45 µm filter membrane. The pH of the filtrate was adjusted to 3.85 with 1 mol/L hydrochloric acid, and 100 μ L of saturated Na₂EDTA solution was added. SPE solid phase extraction column (OASIS HLB column, 6 mL/500 mg) was eluted and activated successively with 5 mL ethyl acetate, 5 mL methanol and 5 mL pure water with pH = 3.85. Turn on the vacuum pump, control the flow rate to be about 3-5 mL/min, and load the membrane supernatant into the column with a sample volume of 5 mL. Then, the small columns were rinsed with 5 mL of 5% methanol water and 5 mL ultra-pure water respectively, and the HLB column was vacuumed and dried for 30 min. Finally, the eluents were eluted with 4.5 mL methanol and 4.5 mL of 50% methanol +50% ethyl acetate, and the eluents were collected and blown to near dry with N₂ at room temperature. Constant volume with 10% methanol to 1 mL, to be measured.

The chromatographic conditions were as follows: Agilent eclipse plus C18 (100 mm×2.1 mm, 1.8 μ m); The mobile phase was consisted of acetonitrile (a) and 0.1% formic acid (b). The column temperature was 35°C and the flow rate was 0.3 mL/min; Gradient elution procedure: 0-1 min, 90% A, 1-10 min, 90%-80% A; 10-20 min, 80%-50% A; 20-25 min, 50%-50% A; 25-26 min, 50%-90% A; 26-35 min, 90%-90% A, 10 μ L of the injection volume.

Mass spectrometry conditions [31]: electrospray ion source, positive ion scanning; the atomization gas, desolvent gas and cone hole gas are nitrogen, and the collision gas is argon; The source temperature and desolvent gas temperature are 90°C and 350°C, respectively; The flow rates of desolvent and cone hole gas were 500 and 70 L/H, respectively. The capillary voltage was 4 kV. The detection mode was MRM mode. ESI-MS / MS positive ion detection was used. The parent ion and daughter ion of each compound were determined directly by injection pump. The cone

Table 2. Ion characteristics, retention time and collision energy of the selected three antibiotics in the MRM mode.

Antibiotic	Parent ions (m/z)	Produce ions (m/z)	Quantitive ions (m/z)	Collision energy (eV)	Retention time (min)
OTC	461.3	443.3	426.1	5, 12	7.20
NOR	320.1	302.0	276.1	10, 15	5.98
SMZ	265.0	108.0	92.0	25, 25	4.11

hole voltage and collision energy were optimized, the tandem mass spectrometry detection conditions of the three antibiotics were shown in Table 2.

Adsorption Isotherm Experiment

Sediments played an important role in the migration, transformation and enrichment of pollutants in the hyporheic zone, which can truly reflect the environmental geochemical information of the study area. Batch adsorption experiments were carried out to study the adsorption capacity of sediments to three antibiotics. The initial concentrations of antibiotic were 0.1, 0.2, 0.5, 1, 2 and 5 mg/L, respectively. According to the preliminary kinetic experiment, it was determined that the adsorption equilibrium time was basically 30 h. Therefore, after placing the batch centrifuge tube in a constant temperature shaker for 30 h, took out the refrigerated centrifugation for 10 minutes (8000 r), and measured the concentration of the antibiotic remaining in the aqueous phase to calculate the equilibrium adsorption capacity:

$$Q_e = \frac{V(C_0 - C_e)}{m} \tag{1}$$

Where V (mL) represents the volume of the solution; C_0 (mg/L) is the initial concentration of the antibiotic, C_e (mg/L) is the equilibrium concentration of the antibiotic, and m (kg) is the mass of the sediment.

Two commonly used isotherm adsorption modes, Langmuir and Freundlich, are used to describe the adsorption process of sediments on antibiotics. The equations are as follows [38]: Langmuir:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \tag{2}$$

Freundlich:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{3}$$

Where Q_e (mg/kg) is the equilibrium adsorption capacity; Q_m (mg/kg) is the maximum adsorption capacity; K_L is the adsorption constant; K_F is the adsorption equilibrium constant; 1/n represents the adsorption strength.

Preparation of Mixed Water Sample

Since the collected water and soil samples were tested and analyzed under natural conditions (open environment), some components had changed due to the influence of light and oxidation during the period, which was difficult to represent the real situation. In order to more truly reflect the migration and transformation of antibiotics in surface water and groundwater environment, simulated surface water and groundwater samples were configured for the adsorption and hydrolysis experiments of antibiotics in hyporheic zones. At the same time, in the process of configuring the simulated water sample, except the dissolved oxygen content was different, the concentration of other ions was kept the same to eliminate the experimental error caused by ionic strength.

Configuration process: we weighed 37.63 mg CaCl,, 76.89 mg MgCl₂, 3.53 mg KCl, 912.24 mg NaHCO₂, 152.43 mg Na₂CO₃, 55 mg KNO₃, dissolved and diluted them with Milli-Q water in a 1L round flask. Aerobic environment simulation: the conical flask is open, weigh it in time to replenish the missing water. Anaerobic environment simulation (Fig. 3): the serum bottle is wrapped in a black plastic bag and placed in a dark environment. The serum vial is placed in an anaerobic environment simulator and heated in a constant temperature water bath. At the same time, open the nitrogen bottle and fill nitrogen into the serum bottle to eliminate the dissolved oxygen in the simulated sample in the serum bottle and make it in the nitrogen atmosphere environment during the experiment cycle to ensure that no oxygen will be mixed in the degradation process.

Assuming that the hydrolytic products of antibiotics were unknown and the secondary hydrolysis and reaction of the hydrolytic products were ignored, the hydrolysis behavior of the hydrolytic products in the oxygen-free environment of groundwater conformed to:

$$RX+H_2O \rightarrow ROH+HX$$
 (4)

In the aerobic environment, since it is difficult for dissolved oxygen to directly oxidize antibiotics, it is assumed that oxygen does not directly participate in the hydrolysis reaction by means of interface reaction, and its hydrolysis behavior in the aerobic environment of surface water conforms to:

$$RX+H_2O \xrightarrow{O_2} ROH+HX$$
 (5)



Fig. 3. A multi-functional device of simulating groundwater system.

$$dx/dt = -kx \tag{6}$$

$$x(t) = x_0 e^{-k(t-t_0)}$$
(7)

pH Effects on Hydrolysis Characteristics

A simulated groundwater sample with a concentration of 10 mg/L was put in a 100 mL conical flask, and used HCl and NaOH to adjust the pH, and added 0.02% sodium azide as a biological preservative. Conical flask was protected from light. We took 24 h as a time interval for sampling and detection to study the hydrolysis rate of antibiotics under different pH conditions, and then used ln ([concentration at time (t)]/ [initial concentration]) and the time (t) to perform a linear fit.

Keeping the same conditions, the experimental device was placed in aerobic environment. Observe the effect of different pH on the hydrolysis of antibiotics in aerobic (surface water) and anaerobic (groundwater) conditions.

In order to facilitate the discussion of the changes in the hydrolysis rate of the three antibiotics caused by pH, we quoted Mabey and Mill's understanding of the hydrolysis of organic compounds, that is, the hydrolysis law of compounds can be reflected by the following equation [33]:

$$RX + H_2O \rightarrow ROH + HX$$
 (8)

Assuming that the hydrolysis under acid-base or neutral conditions is independent of each other, the hydrolysis rate constant should be:

$$-\frac{d(RE)}{dt} = K_h[RX] = K_B[OH^-][RX] + K_A[H^+][RX] + K_N'[H_2O][RX]$$
(9)

Where K_A , K_B , and K_N are the secondary hydrolysis rate of the compound under acid, base and neutral catalysis, respectively, and K_h is the cumulative hydrolysis rate or the total hydrolysis rate.

$$K_{h} = K_{B}[OH^{-}] + K_{A}[H^{+}] + K_{N}^{'}$$
(10)

$$[H^+][OH^-] = K_W (11)$$

So,

$$K_{h} = K_{B} \frac{[K_{W}]}{[H^{+}]} + K_{A}[H^{+}] + K_{N}'$$
(12)

Assuming that each reaction is independent under acid-base neutral conditions, the cumulative hydrolysis rate can be regarded as three parts,

$$\log K_h = \log K_A - pH \tag{13}$$

$$\log K_h = \log K_B K_W + pH \tag{14}$$

$$\log K_h = \log K'_N \tag{15}$$

Temperature Effects on Hydrolysis Characteristics

50 mL groundwater samples with 10 mg/L antibiotics were put in 100 mL conical flasks at 10°C (283 K, pH = 7.0), 15°C (288K, pH = 7.0), 20°C (293 K, pH = 7.0) and 25°C (298 K, pH = 7.0), respectively. The conical flasks were placed in both aerobic and anaerobic environments, and samples were taken every 24 hours to observe the effect of different temperatures on the hydrolysis of antibiotics under aerobic and anaerobic conditions. The time was plotted with ln ([concentration at time (t]]/ [initial concentration]) for linear fitting.

The change of hydrolysis rate caused by temperature was investigated by Arrhenius coefficient. The calculation formula is:

$$ln(k_h) = -\frac{E_a}{RT} + lnA$$
(16)

Where K_h represents the rate of hydrolysis, d⁻¹; Ea represents the activation energy of the reaction, J/mol; R represents the gas constant (8.3141 J/(mol•K); T represents the temperature, K; A is the Arrhenius coefficient.

$$f = e^{(\ln K_{298K} - \ln K_{288K})}$$
(17)

f represents the change in the rate of hydrolysis for every 10 degrees Celsius increase.

Sediment Effects on Hydrolysis Characteristics

2 g of disinfected sediments and clay were added to 50 mL of surface water and groundwater samples containing 10mg/L antibiotics respectively and adjusted pH to 7, and the samples were taken at intervals of 24 hours to study the effect of adding sediments on antibiotic hydrolysis. The time was plotted with ln([concentration at time (t)]/ [initial concentration]) for linear.

Results and Discussion

Adsorption Characteristics of Antibiotic in the Hyporheic Zone

In order to truly reflect the adsorption characteristics of antibiotics by sediments in the hyporheic zone, the water in this experiment was simulating the actual environment of the hyporheic zone, with a total ionic strength of 24.749mmol/L. The collected samples of undisturbed sediments were analyzed for particle size, and it was found that the sediments were mainly silt and clay in the hyporheic zone. According to the thermodynamic parameters of the adsorption of antibiotics by the sediments in the reciprocal zone studied by our team: $\Delta G < 0$, $\Delta H > 0$, and $\Delta S > 0$, we could know that for the adsorption process of antibiotics by the sediments in the reaction to move in the positive direction and the adsorption process was endothermic [1].

The data of the sediment isotherm adsorption of the three antibiotics were fitted according to the Langmuir model and the Freundlich model of two single-molecule adsorption models. The fitting diagram was shown in Fig. 4, and the fitting parameters were shown in Table 3. Both adsorption models could reflect the OTC and SMZ adsorption process of sediments, and the correlation coefficient R^2 was greater than 0.9. However, Freundlich model could better reflect NOR adsorption process of sediments with a R² of 0.7596, which showed that the adsorption of NOR by sediments was not simply linear adsorption, and there were multilayer and reversible adsorption. These were consistent with the results of other researchers [39-43]. The maximum adsorption capacity of the three antibiotics was SMZ (1008.14 mg/kg) >OTC (430.03 mg/kg)>NOR (128.47 mg/kg), respectively. This might be related to the hydrophilicity of the three antibiotics. The octanol-water partition coefficients of the three antibiotics are OTC-1.22,

NOR-1.03, and SMZ-0.89. SMZ has the smallest octanol-water partition coefficient, indicating its hydrophilicity was smallest and was easier to adsorb to the solid phase [44, 45]. However, most scholars found that the adsorption of OTC and NOR by soil was better than SMZ [46, 47]. This might be because the adsorption strength of antibiotics in sediments was closely related to the content of organic matter and minerals in sediments, pH and ionic strength, etc [8, 37, 48]. The water samples used in this experiment simulated the hyporheic zone water samples in the actual environment, with high total ionic strength and accompanied by the hydrolysis of antibiotics in the adsorption process. In addition, there were differences in the types and quantities of organic carbon, cation exchange capacity and functional groups in the collected sediments, and their adsorption contributions to antibiotics were differnt.

Hydrolytic Characteristics of Antibiotic in the Hyporheic Zone

Under the natural condition, the hydrolysis behavior of three antibiotics in aerobic (surface water) environment and anoxic (groundwater) environment was studied. The concentration of antibiotics changed over time as shown in Fig. 5.

As time went on, the concentration of the three antibiotics decreased gradually, but the concentration of the antibiotics decreased faster in the aerobic environment than in the anaerobic environment, and fitted the hydrolysis process with Eq. 7. The experimental results were shown in Fig. 6

		Langmuir		Freundlich			
Antibiotics	Q _m (mg/kg)	K _L (L/mg)	R ²	K _F (mg/kg) (L/mg) ^{1/n}	1/n	\mathbb{R}^2	
OTC	430.0262	0.0720	0.9900	27.9129	0.9444	0.9882	
NOR	128.4694	1.6173	0.6319	73.9730	0.3538	0.7596	
SMZ	1008.1424	0.1027	0.9634	99.6368	1.0008	0.9618	

Table 3. Fitting parameters of the isothermal adsorption model of three antibiotics on sediments.



Fig. 4. Fitting curves of isothermal adsorption of three antibiotics on sediments.



Fig. 5. Hydrolysis of three antibiotics in the hyporheic zone.



Fig. 6. Hydrolysis of three antibiotics in the hyporheic zone a) anoxic b) aerobic.

and Table 4. The hydrolysis process of the three antibiotics in surface water and groundwater conformed to the first-order kinetic process. In the anoxic environment (groundwater), the hydrolysis rate was OTC ($0.047d^{-1}$)>NOR ($0.011d^{-1}$)>SMZ ($0.006d^{-1}$), respectively. In the aerobic environment (surface water), the hydrolysis rates of the three antibiotics were OTC ($0.071d^{-1}$)>SMZ ($0.062d^{-1}$)>NOR ($0.049d^{-1}$), respectively.

Effect of pH on Hydrolysis Characteristics

In groundwater, the hydrolysis process of the three antibiotics under different pH was shown in Fig. 7, and the relevant parameters were shown in Table 5. It can be seen that the hydrolysis rates of the three antibiotics under alkaline and neutral conditions were significantly higher than acidic conditions.

Table 4. Half- lives of the three antibiotics in the hyporheic zone.

Condition	OTC			NOR			SMZ		
Condition	k	R ²	Half life	k	R ²	Half life	k	R ²	Half life
Anoxic	0.047	0.991	14.78	0.011	0.742	63.59	0.006	0.673	117.48
Aerobic	0.071	0.984	9.75	0.049	0.991	14.20	0.062	0.998	11.20



Fig. 7. The hydrolysis of three antibiotics under different pH in groundwater.

nII	OTC			NOR			SMZ		
рп	k	R ²	Half life	k	R ²	Half life	k	R ²	Half life
4	0.051	0.805	13.49	0.033	0.983	16.66	0.016	0.891	44.43
6	0.053	0.777	12.98	0.033	0.961	20.88	0.016	0.889	42.79
7	0.050	0.776	14.29	0.033	0.981	19.08	0.016	0.924	41.55
8	0.046	0.775	15.07	0.032	0.978	17.24	0.017	0.800	41.76
10	0.057	0.909	12.14	0.037	0.990	18.58	0.021	0.794	32.39

Table 5. The half-lives of three antibiotics under different pH in groundwater.

The hydrolysis rate of the three antibiotics was OTC> NOR>SMZ. Among them, the hydrolysis rate of OTC was $0.050 \sim 0.057 d^{-1}$, and its half-lives were $12.14 \sim 15.07 d$; The hydrolysis rate of NOR was $0.032 \sim 0.037 d^{-1}$, and the half-lives were $16.66 \sim 20.88 d$; The hydrolysis rate of SMZ was $0.016 \sim 0.021 d^{-1}$, and its half-lives were $32.39 \sim 44.43 d$. Obviously, the hydrolysis rate of OTC was greatest and the half-life was shortest. This showed that tetracycline antibiotics were easy to hydrolyze in groundwater, while fluoroquinolone and sulfonamide antibiotics were difficult to hydrolyze and were relatively stable in the environment [19, 49].

In surface water, the hydrolysis process of the three antibiotics under different pH was shown in Fig. 8, and the relevant parameters were shown in Table 6. It can be seen that the hydrolysis rate of the three antibiotics under alkaline conditions was still greater than acidic and neutral conditions. The hydrolysis rate of OTC was greater than SMZ and NOR. Among them, the hydrolysis rate of OTC was $0.051 \sim 0.079 \text{ d}^{-1}$, and the half-lives were $9.01 \sim 13.5 \text{ d}$; the hydrolysis rate of SMZ was $0.053 \sim 0.074 \text{ d}^{-1}$, and the half-lives were $7.63 \sim 13.4 \text{ d}$; the hydrolysis rate of NOR was $0.010 \sim 0.057 \text{ d}^{-1}$, and the half-lives were $14.8 \sim 32.7 \text{ d}$. Kang et al. [48] found that OTC had a half-life of 7-10 days (under aerobic conditions) at a pH of 7, and neutral and alkaline were more conducive to the hydrolysis of OTC; Some scholars also found that the



Fig. 8. The hydrolysis of three antibiotics under different pH in surface water.

	OTC			NOR			SMZ		
рп	k	R ²	Half life	k	R ²	Half life	k	R ²	Half life
4	0.051	0.987	13.5	0.010	0.994	32.7	0.056	0.994	13.4
6	0.061	0.988	11.2	0.057	0.999	19.9	0.053	0.999	13.0
7	0.068	0.987	10.04	0.043	0.997	17.8	0.058	0.997	12.4
8	0.074	0.993	9.33	0.053	0.999	15.3	0.062	0.999	11.0
10	0.079	0.988	9.01	0.049	0.980	14.8	0.074	0.980	7.63

Table 6. The half-lives of three antibiotics under different pH in surface water.

hydrolysis rate of sulfonamide antibiotics in surface water was greater than groundwater [50-52]. It was consistent with the results of this study.

In summary, the hydrolysis rates of the three antibiotics under alkaline conditions were higher than acidic and neutral conditions. In order to more clearly explore the reasons, we quoted Mabey and Mill's knowledge on the hydrolysis of organic compounds, and this method defaulted to a linear relationship between logK_h and pH. The hydrolysis reaction under acid or base catalysis was a first-order kinetic process, that is, the relationship between the H⁺ concentration in the solution and the hydrolysis rate constant was completely linear. Mitchell et al. [53] used this method to calculate the hydrolysis rate of β -lactam antibiotics under different pH, and fitted the experimental values using Eq. (12). The hydrolysis process reflected in Eq. (12). It should be similar to the hydrolysis under acidic and neutral hydrolysis conditions, which the change of K_h was consistent with the value of $K_{N'}$ in a larger pH range.

The hydrolysis rate K_d of three antibiotics under different pH was fitted by the Eq. (12), as shown in Fig.9, the corresponding secondary hydrolysis rate constants were shown in Table 7. It can be seen that the secondary hydrolysis rates of the three antibiotics under different pH in surface water and groundwater were very different, especially under alkaline catalysis. This showed that the three antibiotic molecules contained groups such as amide groups, esters, sulfa groups, which will be attacked by the nucleophilic ion of OH, as a result, the hydrolysis rate constant remained basically unchanged under neutral conditions, but rose sharply under alkaline conditions [54, 55]. Among the three antibiotics, the hydrolysis of OTC was more sensitive to changes in acidic conditions, and the hydrolysis of SMZ was more sensitive to changes in alkaline conditions. Some researchers [56, 57] had found that fluoroquinolone antibiotics were not easily hydrolyzed. However, there were a large number of ions in the surface water and groundwater samples and the total ion concentration was 24.749 mmol/L, it could still be hydrolyzed. In addition, the hydrolysis rate constants K_d of the three antibiotics and H⁺ concentration in water simple were fitted by Eq. (12). Although the H^+ concentration and K_d value met the description of Eq. (12). to some extent, the correlation coefficient R² was relatively low, between



Fig. 9. Hydrolysis fitting of three antibiotics under different pH conditions.

Antibiotics	Condition	$K_{A}(M^{-1} \cdot d^{-1})$	$K_{B}(M^{-1} \bullet d^{-1})$	$K_{N}'(d^{-1})$	\mathbb{R}^2
OTC	Aerobic	-170.50	84.34	0.0686	0.8603
OIC	Anoxic	-12.56	44.35	0.0525	0.6256
NOP	Aerobic	-165.72	94.13	0.0375	0.6338
NOK	Anoxic	5.13	48.01	0.0324	0.7172
SM7	Aerobic	-60.65	334.03	0.0575	0.7761
SIVIZ	Anoxic	-5.011	53.18	0.0161	0.8411

Table 7. Hydrolysis rate of three antibiotics under different pH conditions.

0.6256-0.8603. This might be the existence of a large number of other ions destroyed the original linear relationship between H^+ and K_d , and promoted the progress of the hydrolysis reaction.

Effect of Temperature on Hydrolysis Characteristics

The hydrolysis results of three antibiotics with temperature changes were shown in Fig. 10, and the relevant parameters were shown in Table 8. It can be seen that the hydrolysis rates of the three antibiotics all increased with the increase in temperature. In surface water, the hydrolysis rate of OTC at 298 K was 0.47 times higher than 283 K, and the half-life was reduced by 3.93 d; The hydrolysis rate of NOR at 298 K was 0.85 times higher than 283 K, and the half-life was reduced by 8.48 d; The hydrolysis rate of SMZ at 298 K was 0.48 times higher than 283 K, and the half-life was reduced by 2.39 d. These results well proved the strong influence of temperature on the hydrolysis behavior of antibiotics, and NOR was more sensitive to temperature in the surface water.

In groundwater, the hydrolysis rate of OTC at 298 K was 1.32 times higher than 283 K, and the half-life was reduced by 12.48 d. The hydrolysis rate of NOR at 298 K was 1.10 times higher than 283 K, and the half-life was reduced by 15.72 d. The hydrolysis rate of SMZ



Fig. 10. The hydrolysis of three antibiotics under different temperature in surface water.

Antibiotics	Project	283K	288K	293K	298K
	K -O a	0.0539	0.0635	0.0740	0.0790
	Halflifa	11.69	0.72	8.02	7.75
	пан ше	11.08	9.75	8.03	1.13
OTC	R ²	0.9975	0.9966	0.8876	0.9871
010	K _h	0.0339	0.0412	0.0678	0.0786
	Half life	20.63	15.11	12.54	8.15
	R ²	0.8572	0.9080	0.9754	0.9860
	K _h -O ₂	0.0307	0.0397	0.0487	0.0569
	Half life	19.21	15.77	12.89	10.76
NOD	R ²	0.9990	0.9972	0.9994	0.9995
NOK	K _h	0.0176	0.0248	0.0324	0.0370
	Half life	34.25	27.64	21.21	18.53
	R ²	0.9697	0.9998	0.9991	0.9968
	K _h -O ₂	0.0572	0.0698	0.0839	0.0848
	half life	10.56	9.93	8.26	8.17
CM/7	R ²	0.9992	0.937	0.878	0.888
SIMZ	K _h	0.0065	0.0086	0.0115	0.0114
	half life	98.73	79.63	64.52	60.11
	R ²	0.9961	0.991	0.999	0.997

Table 8. Hydrolysis rate of three antibiotics under different temperature in surface water.

Note: a Kh-O2 represents the hydrolysis rate constant of antibiotics under aerobic conditions.

at 298 K was 0.75 times higher than 283 K, and the halflife was reduced by 38.62 d. These indicated that the hydrolysis of SMZ was more sensitive to temperature in groundwater.

Obviously, the hydrolysis rate of antibiotics under aerobic conditions was higher than anaerobic conditions. In order to explore the reasons for the obvious differences in the hydrolysis characteristics of antibiotic in the surface water and groundwater, and the Arrhenius coefficient was used to calculate the activation energy Ea. The results were shown in Table 9. It can be seen that the Ea value of OTC was 18273.75 J/mol under aerobic conditions, the Ea value of OTC was 42377.08 J/mol under anaerobic conditions, the Ea value under anaerobic conditions was 2.32 times that under aerobic conditions. Similarly, the Ea values of NOR and SMZ under anaerobic conditions were 1.22 times and 1.45 times that aerobic conditions, respectively. This showed that in surface water, due to the participation of dissolved oxygen, the activation energy required for the hydrolysis reaction of antibiotics was significantly reduced, and the hydrolysis reaction was easier to proceed. Schwarzenbach et al. [58] believed that some complex physical and chemical interactions could change the reaction site and conversion pathway by changing the activation energy. Based on this, it can be considered that the participation of dissolved oxygen

in surface water disrupted the hydrolysis reaction interface, reduced the reaction activation energy. Therefore, it increased the hydrolysis reaction rate of the antibiotic.

In addition, the f value was the change value of the hydrolysis rate constant for every 10°C increase in temperature, which calculated by Eq. (17). Table 9 showed that the f value of the three antibiotics in groundwater was higher than surface water, and the hydrolysis of antibiotics in groundwater was more sensitive to temperature changes.

Table 9. Activation energy and Arrhenius coefficient of the hydrolysis reaction of three antibiotics.

Antibiotics	Project	Aerobic	Anaerobic	
	Ea (J/mol)	18273.75	42377.08	
OTC	$LnA(d^{-1})$	4.86	14.60	
	f	1.24	1.91	
	Ea (J/mol)	28867.23	35101.82	
NOR	$LnA(d^{-1})$	8.81	10.92	
	f	1.43	1.49	
	Ea (J/mol)	19231.66	27843.47	
SMZ	$LnA(d^{-1})$	5.35	6.85	
	f	1.21	1.32	

Effect of Sediment on Hydrolysis Characteristics

In order to explore the impact of sediments on the hydrolysis of antibiotics in the hyporheic zone, sandy sediments and clays were selected for experiments as shown in Fig. 11. In view of the fact that the adsorption of antibiotics by sediments generally reached equilibrium within 30 hours, it is believed that the reduction of antibiotics after 48 hours was caused by hydrolysis. For OTC, the hydrolysis rate in surface water was still significantly greater than groundwater. In surface water, the hydrolysis rate was 0.0711 d⁻¹, after adding 2 g/50 mL sediment and 2 g/50 mL clay, the hydrolysis rate changed to 0.1041 d⁻¹ and 0.1031 d⁻¹, respectively, and the half-lives were reduced by 1.45 d and 1.39 d, respectively. It showed that the sediment and clay had a promoting effect on the hydrolysis of OTC. In groundwater, the hydrolysis rate also increased significantly after adding different masses of 2 g/50 mL sediment and 2 g/50 mL clay, the antibiotic hydrolysis rate increased to 0.100 d⁻¹ and 0.0980 d⁻¹, respectively. The half-lives were reduced from 12.74 d to 7.16 d, respectively. It indicated that both sediment and clay can promote the hydrolysis of OTC in groundwater. For SMZ, after adding 2 g/50 mL sediment and 2 g/50 mL clay, its hydrolysis rate in surface water changed from 0.0619 d-1 to 0.0875 d-1 and 0.0851 d-1, respectively and the half-lives were reduced by 0.33 d

and 0.11 d, respectively. This showed that sediment and clay had a very weak promotion effect on the hydrolysis of SMZ in surface water; In groundwater, the hydrolysis rate increased significantly after adding 2g/50 mL sediments and 2 g/50 mL clay of different quality. When adding 2 g sediment and clay, the antibiotic hydrolysis rate increased to 0.042 d⁻¹ and 0.058 d⁻¹, respectively. The half-lives of 64.17 d when never added was reduced to 47.18~52.22 d, and the fastest was reduced by 2.51 d. This showed that the addition of sediments also promoted the hydrolysis of SMZ in surface water and groundwater, and the promotion effect was more obvious under groundwater, which was consistent with the hydrolysis behavior of OTC. In addition, adding the same quality of sediment, the hydrolysis rates of antibiotics in surface water and groundwater were not the same, and it was faster in groundwater.

Whether it was adding sediment or clay, the hydrolysis of antibiotics was significantly enhanced. This might be due to the presence of certain substances that could catalyze the hydrolysis of antibiotics. Chen et al. [59] found that the increase of manganese oxide content in soil or sediments would promote the adsorption of lincosamide antibiotics in environmental media and accelerate their degradation and transformation. Kang et al. [48] also found that the hydrolysis of antibiotics was significantly accelerated on the surface of silica minerals, indicating that silica may



Fig. 11. The effect of sediment on the hydrolysis of two antibiotics in surface water and groundwater.

be a catalyst to catalyze the hydrolysis of antibiotics. The two representative hyporheic zone media selected in this experiment, sediments and clays, were mainly SiO_2 and also contained other aluminosilicate components, which could significantly accelerate the hydrolysis process of antibiotics.

Conclusions

This paper studied the adsorption and hydrolysis behavior of antibiotics in the Zaohe-Weihe hyporheic zone. The maximum adsorption capacity of the three antibiotics in the typical sediments was SMZ (1008.14 mg/kg)>OTC (430.03 mg/kg)>NOR (128.47 mg/kg). The hydrolysis rate of the three antibiotics in surface water was higher than in groundwater environment. Compared with NOR, the hydrolysis effect of dissolved oxygen on OTC and SMZ was more obvious. The hydrolysis of antibiotics was accelerated by oxygen, alkaline, high temperature and the addition of sediment. Changes in these conditions had a greater effect on the hydrolysis of antibiotics in groundwater than in surface water.

Acknowledgments

This work was supported by National Natural Science Foundation of China (Grant numbers 41977163), National Key Research and Development Program of China (Grant numbers 2020YFC1808304), Along the Yellow Ecological Economic Zone Project of Ningxia Finance Department (Grant numbers 6400201901273), and the Natural Science Foundation of Shaanxi Province (Grant number 2020JQ-352). The authors are also thankful to all experts involved for their valuable outputs and help.

References

- ZHANG D., YANG S.K., WANG Y.N., YANG C.Y., CHEN YY., WANG R.Z., WANG Z.Z., YUAN X.Y., WANG W.K. Adsorption characteristics of oxytetracycline by different fractions of organic matter in sedimentary soil. Environmental Science and Pollution Research, 26 (6), 5668, 2019.
- CHEN K., ZHOU J.L. Occurrence and behavior of antibiotics in water and sediments from the Huangpu River, Shanghai, China. Chemosphere, 95, 604, 2014.
- XU J., ZHANG Y., ZHOU C.B., GUO C.S., WANG D.M., DU P., LUO Y., WAN J., MENG W. Distribution, sources and composition of antibiotics in sediment, overlying water and pore water from Taihu Lake, China. Science of The Total Environment, s 497–498 (3), 267, 2014.
- JIANG Y.H., LI M.X., GUO C.S., AN D., XU J., ZHANG Y., XI, B.D. Distribution and ecological risk of antibiotics in a typical effluent–receiving river (Wangyang River) in north China. Chemosphere, **112**, 267, **2014**.

- ZHANG Q.Q., YING G.G., PAN C.G., LIU Y.S., ZHAO J.L. Comprehensive Evaluation of Antibiotics Emission and Fate in the River Basins of China: Source Analysis, Multimedia Modeling, and Linkage to Bacterial Resistance. Environmental Science & Technology, 49 (11), 6772, 2015.
- 6. BAGUER A.J., JENSEN J., KROGH P.H. Effects of the antibiotics oxytetracycline and tylosin on soil fauna. Chemosphere, **40** (7), 751, **2000**.
- 7. LTD B., Tetracyclines stain children's teeth. Drug & Therapeutics Bulletin, **5** (16), 61, **1967**.
- KIM S.C., YANG J.E., OK Y.S., CARLSON K. Dissolved and Colloidal Fraction Transport of Antibiotics in Soil under Biotic and Abiotic Conditions. Water Quality Research Journal of Canada, 45 (3), 275, 2010.
- WANG Y., RODDICK F.A, FAN L. Direct and indirect photolysis of seven micropollutants in secondary effluent from a wastewater lagoon. Chemosphere, 185, 297, 2017.
- LI Y., RASHID A., WANG H.J., HU A.Y., LIN L.F., YU C.P., CHEN M., SUN Q. Contribution of biotic and abiotic factors in the natural attenuation of sulfamethoxazole: A path analysis approach. Science of The Total Environment, 633, 1217, 2018.
- BERENDONK. Tackling antibiotic resistance: the environmental framework. Nature Reviews Microbiology, 13 (5), 310, 2015.
- AMINOV R.I. Horizontal Gene Exchange in Environmental Microbiota. Frontiers in Microbiology, 2, 2011.
- ZAINAB S.M., JUNAID M., XU N., MALIK R.N. Antibiotics and antibiotic resistant genes (ARGs) in groundwater: A global review on dissemination, sources, interactions, environmental and human health risks. Water Research, 187, 2020.
- OH, SANGHWA., SHIN WON SIK., KIM HONG. TAE. Effects of pH, dissolved organic matter, and salinity on ibuprofen sorption on sediment. Environmental Science & Pollution Research International, 23 (22) 22882, 2016.
- KVHNE M., IHNEN D., MOLLER G., AGTHE O. Stability of tetracycline in water and liquid manure. Journal of Veterinary Medicine A Physiology Pathology Clinical Medicine, 47 (6) 379, 2010.
- MINGYUN, JIA., FANG, WANG., YONGRONG, BIAN., ROBERT D, STEDTFELD., GUANGXIA, LIU., JINPING, XU., XIN, JIANG. Sorption of sulfamethazine to biochars as affected by dissolved organic matters of different origin. Bioresource Technology, 248, 36, 2017.
- CHRISTOPHER C., FULLER., JUDSON W., HARVEY. Reactive Uptake of Trace Metals in the Hyporheic Zone of a Mining-Contaminated Stream, Pinal Creek, Arizona. Environmental Science & Technology, 34 (7), 2000.
- MITCHELL S.M., ULLMAN J.L., TEEL A.L., WATTS R.J. pH and temperature effects on the hydrolysis of three beta-lactam antibiotics: Ampicillin, cefalotin and cefoxitin. Science of The Total Environment, 466, 547, 2013.
- KEITH A., LOFTINA CRAIG D., ADAMSB., MICHAEL T., MEYERA, and RAO S. Effects of Ionic Strength, Temperature, and pH on Degradation of Selected Antibiotics. Journal of Environmental Quality, **37** (2), 378, **2008**.
- ALAM G., TROVO., RAQUEL F.P., NOGUEIRA., ANA, AGVERA., CARLA, SIRTORI., AMADEO R., FERNANDEZ-ALBA. Photodegradation of sulfamethoxazole in various aqueous media: Persistence, toxicity and photoproducts assessment. Chemosphere, 77 (10), 1292, 2009.

- RUI XIN, GUO., JIANQIU, CHEN. Application of alga-activated sludge combined system (AASCS) as a novel treatment to remove cephalosporins. Chemical Engineering Journal, 260, 550, 2015.
- RADKA, ALEXY., TINA, KUMPEL., KLAUS, KUMMERER. Assessment of degradation of 18 antibiotics in the Closed Bottle Test. Chemosphere, 57 (6), 505, 2004.
- PETER J., HANCOCK., ANDREW J., BOULTON. The Effects of an Environmental Flow Release on Water Quality in the Hyporheic Zone of the Hunter River, Australia. Hydrobiologia, 552 (1), 75, 2005.
- TREVOR K., LAURA T. Collocation of hydrological and biological attenuation of nitrate in an urban stream. Hydrological Processes, **30** (17), 2948, **2016**.
- LAMONTAGNE S., COSME F., MINARD A., HOLLOWAY A. Nitrogen attenuation, dilution and recycling in the intertidal hyporheic zone of a subtropical estuary. Hydrology & Earth System Science Discussions, 22 (7), 4083, 2018.
- 26. WANG W.Z., SONG J.X. ZHANG G.T., LIU Q., GUO W.Q., TANG B., CHENG D.D., ZHANG Y. The influence of hyporheic upwelling fluxes on inorganic nitrogen concentrations in the pore water of the Weihe River. Ecological Engineering, **112**, 105, **2018**.
- 27. HINKLE S.R., BENCALA K.E., WENTZ D.A., KRABBENHOFT D.P. Mercury and Methylmercury Dynamics in the Hyporheic Zone of an Oregon Stream. Water Air & Soil Pollution, 225 (1), 2014..
- MOSER D.P., FREDRICKSON J.K., GEIST D.R., ARNTZEN E.V., PEACOCK AD., LI S.W., SPADONI T., MCKINLEY J.P. Biogeochemical processes and microbial characteristics across groundwater-surface water boundaries of the Hanford Reach of the Columbia River. Environmental Science & Technology, 37 (22), 5127, 2003.
- PALUMBO-ROE B., BANKS V.J., BONSOR H.C., HAMILTON E.M., WATTS M.J. Limitations on the role of the hyporheic zone in chromium natural attenuation in a contaminated urban stream. Applied Geochemistry, 83, 108, 2017.
- ANDREA, BUTTURINI., FRANCESC, SCBATER. Importance of transient storage zones for ammonium and phosphate retention in a sandy-bottom Mediterranean stream. Freshwater Biology, 41 (3), 593, 2010.
- CHAI Y.F., FENG Y.Q., ZHANG Y.X., CHEN M.X., WANG R. Optimization of the simultaneous detection method of 24 antibiotics in pig farm wastewater. Environmental Chemistry, 36 (010) 2147, 2017 [In Chinese].
- 32. WEATHERILL J.J., ATASHGAHI S., SCHNEIDEWIND U., KRAUSE S., ULLAH S., CASSIDY N., RIVETT M.O. Natural attenuation of chlorinated ethenes in hyporheic zones: A review of key biogeochemical processes and insitu transformation potential. Water Research, **128**, 362, **2018**.
- MABEY W., MILL T. Critical review of hydrolysis of organic compounds in water under environmental conditions. Journal of Physical & Chemical Reference Data, 7 (2), 383, 1978.
- 34. LIU X.H., ZHANG H.B., LUO Y.M., ZHU R.S., WANG H.Z., HUANG B.H. Sorption of oxytetracycline on particulate organic matter in soils and sediments: Roles of pH, ionic strength and temperature. Science of The Total Environment, **714**, 136628, **2020**.
- BERGES J., MOLES S., ORMAD M.P., MOSTEO R., GOMEZ J. Antibiotics removal from aquatic environments:

adsorption of enrofloxacin, trimethoprim, sulfadiazine, and amoxicillin on vegetal powdered activated carbon. Environmental Science and Pollution Research, **28** (7), 8442, **2020**.

- 36. SHEN S.Q., YANG S.K., JIANG Q.L., LUO M.Y., LI Y., YANG C.Y., ZHANG D. Effect of dissolved organic matter on adsorption of sediments to Oxytetracycline: An insight from zeta potential and DLVO theory. Environmental Science and Pollution Research, 27 (2), 1697, 2019.
- LI J., CUI M. Kinetic study on the sorption and degradation of antibiotics in the estuarine water: an evaluation based on single and multiple reactions. Environmental Science and Pollution Research, 27 (33), 42104, 2020.
- WEATHERILL J.J., ATASHGAHI S., SCHNEIDEWIND U., KRAUSE S., ULLAH S., CASSIDY N., RIVETT M.O. Natural attenuation of chlorinated ethenes in hyporheic zones: A review of key biogeochemical processes and insitu transformation potential. Water Research, 128, 362, 2018.
- ZONGZHOU WANG., QIANLI JIANG., RUIZE, WANG., XIAOYU, YUAN., SHENGKE YANG., WENKE WANG., YAQIAN ZHAO. Effects of Dissolved Organic Matter on Sorption of Oxytetracycline to Sediments. Geofluids, 2018.
- XU X.R., LI X.Y. Sorption and desorption of antibiotic tetracycline on marine sediments. Chemosphere, 78 (4), 430, 2010.
- HUANG Y.Q., WANG Y., HUANG Y.Z., ZHANG L.X., YE F., WANG J.L., SHANG J.G., LIAO Q.J.H. Impact of sediment characteristics on adsorption behavior of typical antibiotics in Lake Taihu, China. Science of the Total Environment, **718**, 137329.1, **2020**.
- 42. ZHANG DAN., YANG S.K., WANG Y.N., YANG C.Y., CHEN Y.Y., WANG R.Z., WANG Z.Z., YUAN X.Y., WANG W.K. Adsorption characteristics of oxytetracycline by different fractions of organic matter in sedimentary soil. Environmental Science and Pollution Research, 26 (6), 5668, 2019.
- KONG J.J., PEI Z.G., WEN B., SHAN X.Q., and CHEN Z.L. Adsorption behavior of sulfadiazine and sulfathiazole in soil. Environmental Chemistry, 2008 [In Chinese].
- 44. CONGLIANG, ZHANG., YAN WANG., FUAN WANF. Determination and Temperature Dependence of n-Octanol/ Water Partition Coefficients for Seven Sulfonamides from (298.15 to 333.15) K. Bulletin of the Korean Chemical Society, 28 (7), 1183, 2007.
- 45. CARDENAS-YOUNGS G.M., BELTRAN J.L. Dissociation Constants and Octanol-Water Partition Equilibria for Several Fluoroquinolones. Journal of Chemical and Engineering Data, 60 (11), 3327, 2015.
- 46. HUANG Y.Q., WANG Y., HUANG Y.Z., ZHANG L.X., YE F., WANG J.L., SHANG J.G., LIAO J.H. Impact of sediment characteristics on adsorption behavior of typical antibiotics in Lake Taihu, China. Science of The Total Environment, **718**, 137329.1, **2020**.
- 47. LI J., WANG P.F., JI L.L., QIAN J., HOU J. Adsorption mechanism of antibiotics in sediments and its influencing factors. Sichuan Environment, **32** (002), 87, **2013** [In Chinese].
- 48. KANG HYUN-JOONG., LIM MI-YOUNG., KWON JUNG-HWAN. Effects of adsorption onto silica sand particles on the hydrolysis of tetracycline antibiotics. J Environ Monit, 14 (7), 1853, 2012.
- NORVILL Z.N., SHILTON A., GUIEYSSE B. Emerging contaminant degradation and removal in algal wastewater treatment ponds: Identifying the research gaps. Journal of Hazardous Materials, 313, 291, 2016.

- 50. LAI H.T., HOU J.H., Light and microbial effects on the transformation of four sulfonamides in eel pond water and sediment. Aquaculture, **283**, 50, **2008**.
- BOREEN A.L., ARNOLD W.A., MCNEILL K. Photochemical Fate of Sulfa Drugs in the Aquatic Environment: Sulfa Drugs Containing Five-Membered Heterocyclic Groups. Environmental Science & Technology, 38 (14), 3933, 2004.
- 52. JUNG J.Y., KIM Y.H., JEONG D.H., CHOI K.H. Environmental levels of ultraviolet light potentiate the toxicity of sulfonamide antibiotics in Daphnia magna. Ecotoxicology, **17** (1), 37, **2008**.
- 53. MITCHELL S.M., ULLMAN J.L., TEEL A.L., WATTS R.J. pH and temperature effects on the hydrolysis of three β -lactam antibiotics: ampicillin, cefalotin and cefoxitin. Science of The Total Environment, **466**, 547, **2014**.
- 54. FENG H., DING J.J., ZHU D.Y., LIU X.H., XU X.Y., ZHANG Y., ZANG S.S., WAND D.C., LIU W. Structural and Mechanistic Insights into NDM-1 Catalyzed

Hydrolysis of Cephalosporins. Journal of the American Chemical Society, **136** (42), 14694, **2014**.

- 55. CHOW C., XU H., BLANCHARD J.S. Kinetic characterization of hydrolysis of nitrocefin, cefoxitin, and meropenem by β -lactamase from Mycobacterium tuberculosis. Biochemistry, **52** (23), 4097, **2013**.
- WU Y.B., LIAO X.D., WANG Z.S., CHEN Z.L., ZHOU Y. Hydrolysis characteristics of enrofloxacin. Chromatography, 17 (3), 258, 2006 [In Chinese].
- 57. GAO X. Study on the hydrolysis rate constants and products of antibiotics and other organic substances. **2016** [In Chinese].
- SCHWARZENBACH R.P., GSCHWEND P.M., IMBODEN D.M. Environmental Organic Chemistry, 3rd Edition. 2016.
- CHEN W.R., DING Y.J., JOHNSTON C.T., TEPPEN B.J., BOYD S.A., LI H. Reaction of lincosamide antibiotics with manganese oxide in aqueous solution. Environmental Science & Technology, 44 (12), 4486, 2010.