



Desorption Behaviour of Oxytetracycline onto Natural Sediment: A Case Study for the Middle Reaches of Weihe River in Shaanxi, China

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ABSTRACT

Desorption behaviour of oxytetracycline (OTC) onto natural sediment from the middle reaches of Weihe River was described. The impact factors in the process of desorption, such as contact time, temperature (simulative range of summer and winter), ionic strength and colloidal concentration were determined by experiments. The results indicated that desorption of OTC reached equilibrium in about 40 min, and its kinetics were found to follow a pseudo-first-order model. Thermodynamic parameters such as Gibbs-free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated, and the results demonstrated that desorption of OTC was feasible, spontaneous, exothermic in nature, and the desorption capacity decreased with increasing temperature, especially at the range of 296 to 302 K. The desorption process approached to saturation at a temperature range of 275 to 281 K. In addition, the presence of colloid and electrolytes in aqueous solution had a negative effect on OTC desorption onto sediment sample. Such results may help to provide the theoretical basis for the effective prevention of OTC pollution to the groundwater system in the Weihe River basin.

INTRODUCTION

Oxytetracycline (OTC) is one of the most widely used tetracycline antibiotics (TCs). Recent studies have confirmed that the residual OTC has been already detected from soils, rivers, sediments and even organisms in many countries and areas (Boonsaner & Hawker 2010, Done & Halden 2015). Therefore, the environmental risks caused by OTC become very concerned by the society (Bao et al. 2013), which may lead to enrichment (due to low biodegradability), biotoxicity (targeted goal of liver and kidney) and drug resistance. Thus, the migration and transformation of residual OTC in the environmental medium should be paid greater attention.

Sorption and desorption are both important processes for deciding the ultimate fate of organic chemicals in soils/sediments, as they are directly relevant to the prevention and detainment of pollutants. Studies on the environmental impacts from OTC mainly focused on the analysis of sorption behaviours, suggesting that soil/sediment types, or-

ganic matter content, particle size and cation species play an important role in the sorption process of OTC (Song et al. 2014).

The Weihe River is the biggest tributary of the Yellow River, many cities and livestock industries lie along its basin. Our previous survey along the Weihe River basin (Zhao et al. 2015) detected residue of OTC in the aquatic environment, and the concentration level reaches the degree of ngL^{-1} to μgL^{-1} with great seasonal variations. From the above, research on desorption behaviour of OTC onto sediment in the Weihe River is important to understand the fate of OTC in the Weihe River basin.

In this contribution, the desorption behaviour of OTC onto the sediment collected from the Weihe River was systematically analysed. The kinetic and thermodynamic parameters in the desorption process were calculated based on experimental data. Such research may provide the theoretical basis for the effective prevention of OTC pollution to the groundwater system in the Weihe River basin.

MATERIALS AND METHODS

Sediment sampling and analysis: Sediment samples were collected from the middle reaches of the Weihe River. From a hydrogeological point of view, this area belongs to the confluence sector of the Bahe River with the Weihe River in Shaanxi province. Sampling was conducted using the self-designed equipment (Zhao 2017) to collect the top 10 cm of the sediment for laboratory analysis, and a total mass of 3-5 kg was collected including a replicate sample for standby application. The sediment was directly used as natural for the lab analysis without further dispose. Basic physicochemical properties of the sediment are summarized in Table 1.

Chemical reagents: OTC ($C_{22}H_{24}N_2O_9$) was purchased from Boston Biomedical Inc. (Boston, U.S.A.) with United States Patent (USP) grade. Humic acid was purchased from Xideli Chemical and New Material Inc. (Zhengzhou, China) with analytical grade. Methanol in flowing phase was purchased from Waters Company (New York, U.S.A.) with high performance liquid chromatography (HPLC) grade. The other reagents are all in analytical grade with commercial resources.

Detection method of OTC in solution: A Waters ACQUITY UPLC H-Class (New York, U.S.A.) outfitted with BEH Shield column (RP18 1.7 μ m 2.1 \times 150mm) was used for the quantification of OTC in the liquid phase. The chromatographic conditions were considered as: methanol/water = 50:50 (mobile phase), flow rate of 0.2 mL min⁻¹, column temperature of 20 \pm 0.1 $^\circ$ C, injection volume of 5 μ L, detected wavelength of 260 nm and retention time of 2.610 min. The typical chromatogram of OTC for standard and desorbed solutions is shown in Fig. 1.

Desorption experimental design: Desorption experiments were conducted based on the batch equilibrium method (Zhao et al. 2015) using a recommended sediment/water ratio of 1:5. For each time 0.2000 g sediment sample with previously sorbed OTC (sorbed for 24 h under the OTC concentration of 500 μ g L⁻¹, as determined to get sorption equilibrium according to the results of sorption kinetics, which is shown in Fig. 2) and 1 mL deionized water were mixed in a 5 mL centrifuge tube, which was then shaken in a thermostat shaker at 150 rpm.

Desorption kinetics: The kinetic studies were performed in a series of reactors with the same specification and following a similar procedure at 25 $^\circ$ C (298 K, pH 7.0). The liquid phase was separated at predetermined time intervals (1, 2, 5, 10, 15, 20, 30, 40, 50 and 60 min) by using filter membranes of 0.22 μ m. For each time interval, three replicate samples including one blank were available. The desorption quantity of OTC at time t , Q_t (μ g kg⁻¹), was calculated by the following equation:

$$Q_t = \frac{VC_t}{m} \quad \dots(1)$$

Where, C_t is the t time's concentration of the OTC (μ g L⁻¹) in the liquid phase, V is the volume of the solution (mL), and m is the weight of the sediment sample (g).

Desorption thermodynamics: In thermodynamic studies, the initial concentration of OTC ranged from 80 to 500 μ g L⁻¹ (80, 100, 200 and 500 μ g L⁻¹, pH 7.0) to meet with the upper limit of the residual level. As a typical semi-arid inland district, long summer and winter are two distinct seasons along the Weihe River basin with a mean annual outdoor temperature of about 4 $^\circ$ C and 24 $^\circ$ C, respectively (Zhao et al. 2015). Thus, desorption experiments were performed to simulate two seasons with a range of 2 $^\circ$ C to 8 $^\circ$ C (275 to 281 K) and 23 $^\circ$ C to 29 $^\circ$ C (296 to 302 K), respectively. The desorption equilibrium time was set as 40 min, which was long enough according to the kinetic studies. The desorption quantity of OTC at equilibrium, Q_e (μ g kg⁻¹), was calculated by the following equation:

$$Q_e = \frac{VC_e}{m} \quad \dots(2)$$

Where, C_e is the equilibrium concentration of the OTC (μ g L⁻¹) in the liquid phase.

Effect of ionic strength: The effect of ionic strength on OTC desorption was investigated by adjusting solutions to different concentrations of NaCl (0.85, 1.71, 3.42, 5.13, 8.56, 11.97 and 17.09 mmol/L), and desorption experiments were performed at 25 $^\circ$ C (298 K, pH 7.0) for 40 min with the initial OTC concentration of 500 μ g L⁻¹.

Effect of colloid: The effect of colloid on OTC desorption was investigated by adjusting solutions to different concentrations of humic acid (150, 300 and 450 μ g L⁻¹), and

Table 1: Physico-chemical properties of the sediment sample.

Organic content (weight %)	Moisture carbon (weight %)	Volume weight (g.cm ⁻³)	Mechanical composition (weight %)			
			Porosity %	Fine sand <0.35 mm	Medium sand 0.35-0.50 mm	Coarse sand >0.50 mm
0.52	6.38	1.61	45.17	55.38	40.35	4.27

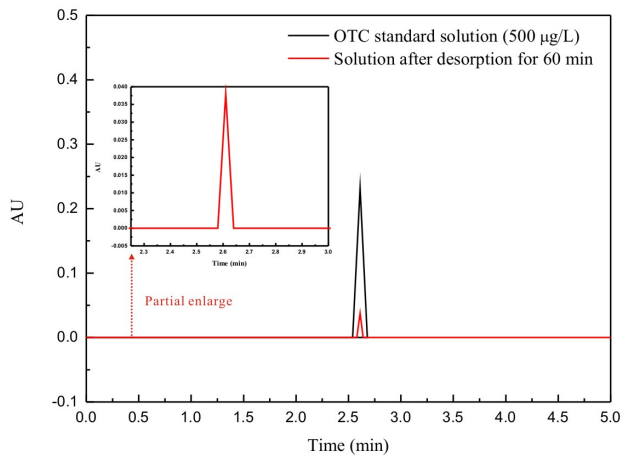


Fig. 1: Typical chromatogram of OTC for standard and desorbed solutions.

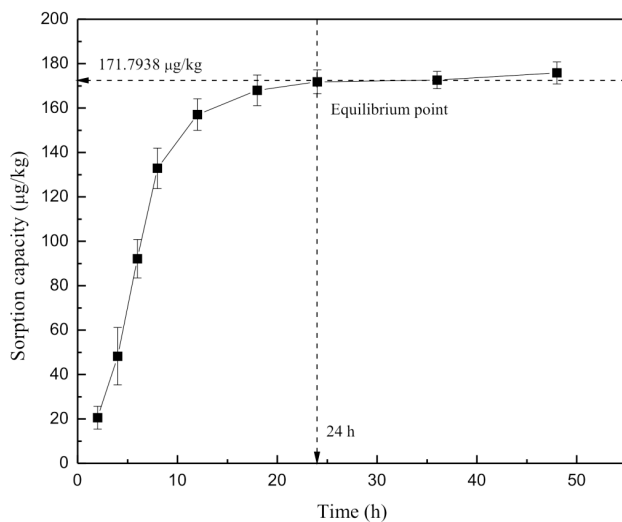


Fig. 2: Sorption kinetics of OTC onto the sediment sample.

desorption experiments were performed at 25°C (298 K, pH 7.0) for 40 min with the initial OTC concentration of 500 $\mu\text{g/L}^{-1}$.

Statistical analysis: The statistical analysis of desorption data was conducted in the StatTools 7.5 program (Palisade, Middlesex, U.K.). To perform a sensitive analysis of the factors (time, temperature, ionic strength and colloid) influencing desorption of OTC onto sediment, a Pearson's correlation analysis was conducted. Time (at each time point), temperature 1 (simulative summer, 23, 25 and 27°C), temperature 2 (simulative winter, 2, 4 and 6°C), ionic strength (3.42, 5.13 and 8.56 mmol/L) and colloidal concentration (150, 300 and 450 $\mu\text{g/L}^{-1}$) were all set as the independent numeric variables and desorption quantity of OTC was set as the dependent numeric variable.

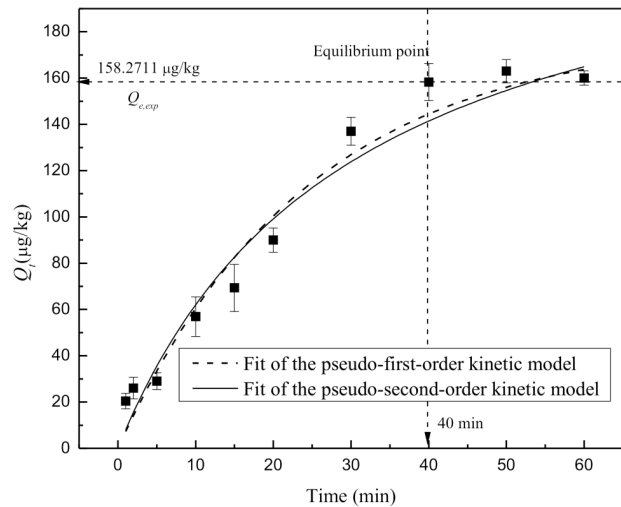


Fig. 3: Desorption kinetics of OTC onto the sediment sample.

RESULTS AND DISCUSSION

Desorption kinetics: Fig. 3 shows the desorption kinetics of OTC onto the sediment sample. Results showed that the rate of desorption was rapid during the first 30 min and gradually decreased with increasing contact time until equilibrium was attained, which was considered at 40 min. These results are comparable to those reported by Duran-Alvarez et al. (2012) for the carbamazepine, naproxen and triclosan using soils with similar contents. There are three possible explanations for the changes of OTC desorption with increasing contact time (Özer et al. 2005). Firstly, there existed enough amount of OTC sorbed on to the surface of sediment sample, which was easy to desorption at the beginning. Secondly, the initial concentration of OTC in solid phase was much higher than that in aqueous phase, which provided the necessary driving force to overcome the resistance of mass transfer. Thirdly, the desorption of OTC on the surface of sediment sample was close to saturation with increasing contact time, which made desorption of OTC transfer from the surface into a void of sediment sample. Due to the increase of the resistance function, the rate of desorption was gradually decreased until equilibrium was attained. In addition, the retardation of sediment for OTC seem to be negligible by comparing equilibrium sorption and desorption capacity (171.7938 and 158.2711 μgkg^{-1} , see in Figs. 2 and 3 respectively), which could be further speculated that OTC could move through the sediment layer and came into the vadose zone, bringing a potential health risk to the groundwater system in the Weihe River basin that makes people concern. Actually, these inferences still need to be proved by the seasonal survey of OTC contami-

Table 2: Fitting results of the pseudo-first-order and pseudo-second-order kinetic models.

$Q_{e,exp}$ (μgkg^{-1})	Pseudo-first-order model			Pseudo-second-order model		
	R^2	k_1 (min^{-1})	$Q_{e,cal}$ (μgkg^{-1})	R^2	k_2 ($\text{kgug}^{-1}\text{min}^{-1}$)	$Q_{e,cal}$ (μgkg^{-1})
158.2711	0.9756	0.0413	178.7463	0.9736	0.0002	246.7499

Table 3: Thermodynamic parameters for OTC desorption onto sediment sample.

Simulative season	T (K)	ΔG° (kJmol^{-1})	ΔH° (kJmol^{-1})	ΔS° (kJmol^{-1})
Summer	296	-22.3817	-41.8205	0.0496
	298	-23.5022		
	300	-23.9986		
	302	-24.0076		
Winter	275	-18.7533	-29.1251	0.0098
	277	-18.9268		
	279	-19.3979		
	281	-19.8007		

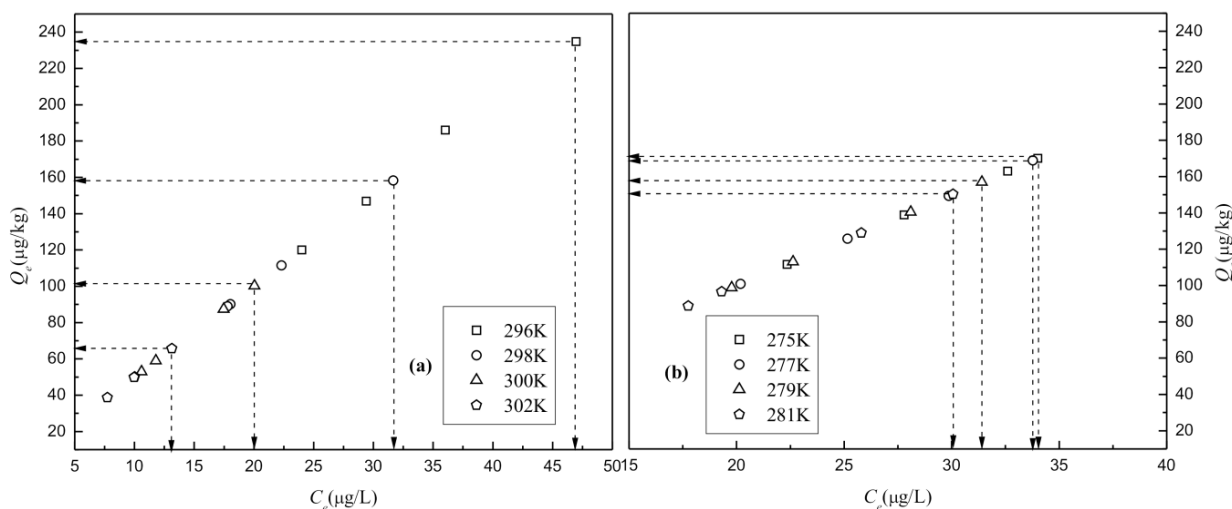


Fig. 4: Desorption of OTC onto the sediment sample in simulative (a) summer and (b) winter as a function of temperature.

nation in the groundwater along the Weihe River basin, which will be carried out in our future study.

Two widely used kinetic models, pseudo-first-order and pseudo-second-order kinetic models, were employed to interpret the kinetics results (see the dotted line and solid line in Fig. 3). The linearized forms of the two models are given as follows (Anirudhan & Senan 2011):

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad \dots(3)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad \dots(4)$$

Where, k_1 (min^{-1}) and k_2 ($\text{kgug}^{-1}\text{min}^{-1}$) are the rate constants of pseudo-first-order and pseudo-second-order kinetic models, respectively.

Table 2 shows the fitting results of the two mentioned kinetic models with experimental data. It was obvious that the obtained values of determination coefficient (R^2) were both high (>0.95), however, by considering the curvature tolerance between calculated Q_e value ($Q_{e,cal}$) and experimental result ($Q_{e,exp}$), the pseudo-first-order kinetic model was found to be more suitable to describe the desorption kinetics data of OTC onto the sediment sample, which further suggests that the dominant mechanism of OTC

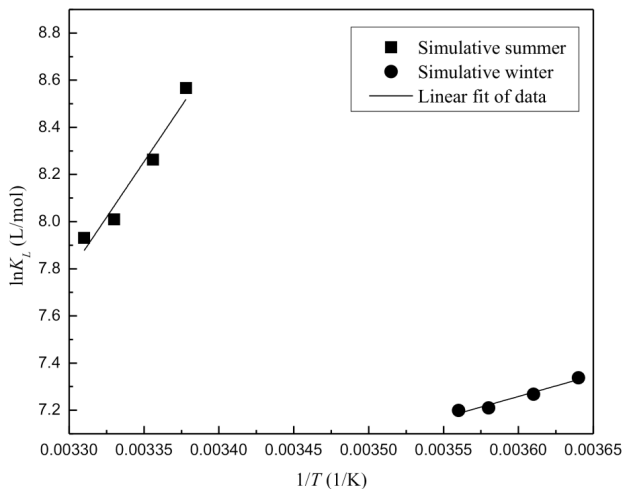


Fig. 5: Linear plot of $\ln K_L$ versus $1/T$.

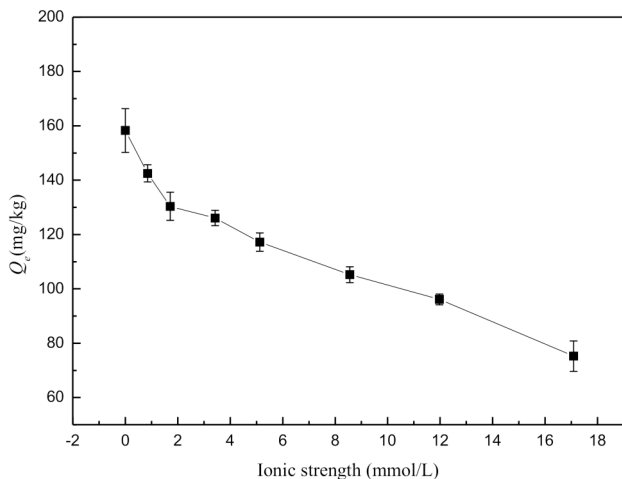


Fig. 6: Effect of ionic strength on OTC desorption onto sediment sample.

desorption is the physical process that can be well attributed to the pseudo-first-order kinetic model (Rahmanian et al. 2018).

Desorption thermodynamics: Fig. 4 shows desorption of OTC onto the sediment sample in two typical seasons as a function of temperature (275 to 281 K and 296 to 302 K, respectively) at solution pH 7.0. It was obvious that the OTC desorption capacity was increased with the increasing equilibrium OTC concentration for the same temperature, which reflected a good linear relationship both in simulative summer and winter. In addition, the OTC desorption capacity was found to be decreased significantly with the increasing temperature in simulative summer compared with it in winter, suggesting that the desorption behaviour of OTC may belong to an exothermic process. It was worth noting that the desorption capacity of OTC approached its equilib-

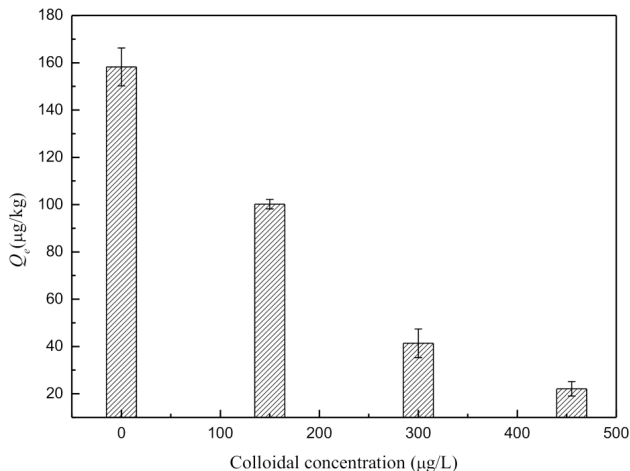


Fig. 7: Effect of colloid on OTC desorption onto sediment sample.

rium sorption capacity at all temperature points in winter with initial OTC concentration of $500 \mu\text{gL}^{-1}$. In other words, desorption capacity of OTC was near saturation at low temperature range (275 to 281 K), which further indicated that the detainment of OTC onto the sediment from the middle reaches of the Weihe River was limited, especially in winter season.

Thermodynamic parameters such as Gibbs-free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) of the OTC desorption process were calculated using the following equations (Anirudhan & Senan 2011):

$$K_L = \frac{C_e}{C_r - C_e} \quad \dots(5)$$

$$\Delta G^\circ = -RT \ln K_L \quad \dots(6)$$

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \dots(7)$$

Where, K_L (Lmol^{-1}) is the equilibrium constant. C_r is the concentration of sorbent (μgL^{-1}). R ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$) is the gas constant. T (K) is the absolute temperature. The values of ΔH° and ΔS° can be calculated from the intercept and the slope of the linear plot of $\ln K_L$ versus $1/T$ (Fig. 5).

The obtained values of thermodynamic parameters for OTC desorption onto sediment sample are shown in Table 3. Results showed that the negative values of ΔG° suggest the feasibility of OTC desorption onto sediment sample and the spontaneous nature of the desorption process (Bera et al. 2013). The negative values of ΔH° further indicated that the desorption process was exothermic in nature (Bera et al. 2013), which was in good agreement with the experimental data mentioned before. The positive values of ΔS° showed an increase in randomness at the solid/liquid interface during the desorption process (Akpomie et

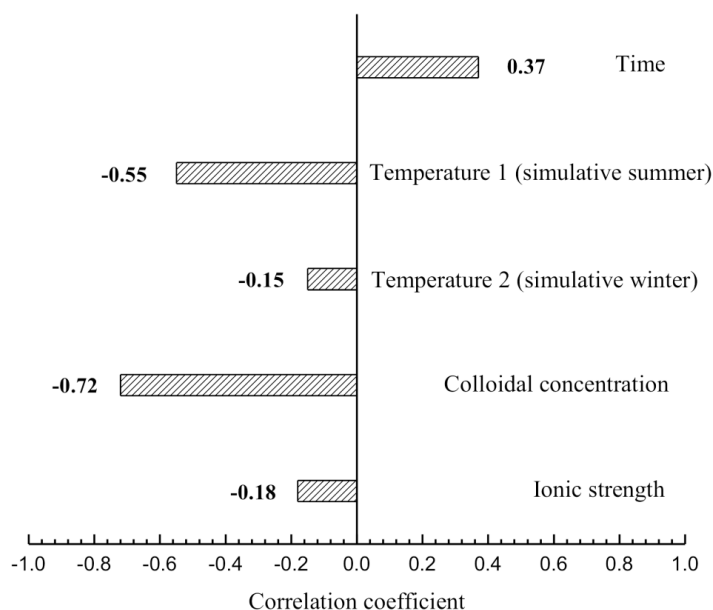


Fig. 8: Sensitivity analysis demonstrating the effect of each experimental parameter on OTC desorption onto sediment sample.

al. 2015). It should be noted that the degree of feasibility and randomness at interface for OTC desorption onto sediment was different at two simulative seasons, comparatively weaker values were observed at low temperature range (275 to 281 K), which may also be attributed to the saturation of desorption process that was discussed previously.

Effect of ionic strength: The desorption of OTC onto sediment sample as a function of ionic strength is shown in Fig. 6. The result confirmed that the presence of electrolytes such as NaCl in aqueous solution had a significant negative effect on OTC desorption onto sediment sample. When the ionic strength of the aqueous solution increased from 0 to 17.09 mmolL⁻¹, the OTC desorption capacity decreased from 158.2711 to 22.1526 µgkg⁻¹. This result is comparable with previous work by Xu et al. (2008) who presented the influence of ionic strength on the sorption of Ni²⁺ on montmorillonite. During the sorption process, the competition between the electrolytes and the sorbate in the aqueous solution may lead to the decrease of sorbate onto solid phase. However, in the case of OTC desorption, the inhibition of electrolytes may be attributed to the high concentration gradient in liquid phase, impeding the release of sorbed OTC.

Effect of colloid: The desorption of OTC onto sediment sample as a function of colloidal concentration is shown in Fig. 7. It was obvious that the presence of colloid in aqueous solution had an inhibition effect on OTC desorption onto sediment sample. For example, when the colloidal concentration of the aqueous solution increased from 0 to 450

µgL⁻¹, the OTC desorption capacity decreased from 158.2711 to 1.1526 mgkg⁻¹. As suggested by Severino et al. (2007) and Heidmann et al. (2005), colloidal particles play an important role in the groundwater system, and they have a strong affinity with pollutants due to their large specific surface area, which may lead to an inhibition effect on the desorption process.

Statistical analysis: To demonstrate the effect of each experimental parameter on OTC desorption, the sensitive analysis was conducted based on Pearson's correlation coefficient and the result is shown in Fig. 8. It was obvious that the colloidal concentration had the most prominent influence on the release of OTC from the sediment sample, followed by temperature 1, time, ionic strength and temperature 2. The plant residue (natural colloidal material) and ionic strength buffer solution might be considered as emergency measures to prevent leakage of OTC along the Weihe River basin. In addition, the temperature 1 is denoted as having a negative impact on OTC desorption, which would suggest the potential use of effective local heating and ventilate technology to limit OTC exposure to the aquifer layer in arid summer. Although the time did have a positive impact on OTC desorption, the equilibrium concentration of OTC in solution was reached within 40 min and therefore, limits the number of applications that could reduce the release effectively from the beginning, which made people concerned about the potential risk of groundwater, especially in winter season.

CONCLUSIONS

The present study demonstrated that the desorption of OTC onto the sediment sample from the middle reaches of the Weihe River reached equilibrium in about 40 min. The desorption kinetics of OTC onto the sediment sample was found to follow a pseudo-first-order model, and the dominant mechanism is a physical process. The calculated thermodynamic parameters showed that the desorption of OTC was feasible, spontaneous, exothermic in nature, and the desorption capacity decreased with increasing temperature, especially in summer season. Saturation of the desorption process was easy to occur in winter. In addition, the presence of colloid and electrolytes in aqueous solution had a negative effect on OTC desorption onto sediment sample. Such results may help to provide the theoretical basis for the effective prevention of OTC pollution to the groundwater system in the Weihe River basin.

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