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Influence of Humic Acid Colloid on Adsorption of Oxytetracycline in Sediment

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Oscillating balance method was employed to study the adsorption of oxytetracycline (OTC) in sediment and its kinetic and thermodynamic properties with the presence of humic acid colloid (HA). The results showed that the equilibrium time of the adsorption of oxytetracycline in sediment with the existence of humic acid colloid was 12 h, while it was 24 h without humic acid colloid , which indicated that humic acid colloid can accelerate the adsorption of oxytetracycline in sediment. The adsorption kinetics was found to follow the pseudo first-order kinetics model. Langmuir and Freundlich model can preferably describe the isothermal adsorption process of oxytetracycline in sediment under different concentrations of humic acid colloid. But Langmuir model fitted better and four kinds of error function values were smaller. Thermodynamics results showed that the adsorption of oxytetracycline in sediment was spontaneous, endothermic and entropy-increasing. The value of ΔG° of adsorption process remained negative with humic acid colloid , but the absolute value decreased, indicating that it tended to physical adsorption. When adding humic acid colloid , the initial pH value greatly affected the adsorption of oxytetracycline in sediment. The adsorption quantity of oxytetracycline increased with the increase of pH when pH was 3-6, remained at a higher level when pH was 6-9 and decreased slightly when pH was greater than 9.

Keywords: Oxytetracycline, Humic acid colloid, Adsorption, Kinetic, Thermodynamic.

INTRODUCTION

Antibiotics were used widely and frequently in numerous kinds of Pharmaceuticals and Personal Care Products (PPCPs). Nowadays, only vestigial oxytetracycline (OTC) has been already detected from soils[1], rivers[2] and sediment[3], *etc*. in many countries and areas. Oxytetracycline is difficult to be biodegraded[4]. Therefore, the environmental risks caused by OTC are more and more concerned by all mankind. During the procedure of supplying underground water from polluted surface water (mainly river water), river sediment is the important medium which influences waters and solutes transportation. The adsorption characteristics of pollutants in river sediment directly influence transportation behaviors from surface layer downward. In a certain time, sediment is to adsorb and detain pollutants in sediment layers so as to just let waters get through, preventing the underground water from polluting[5,6]. The persistence of this function is directly relevant to the adsorption characteristics of pollutants in sediment. Therefore, the characteristics of adsorption behavior of pollutants in river sediment have caused widespread attention in the world. Some scholars have studied the adsorption of polycyclic aromatic hydrocarbons[7], florfenicol[8], *etc*. in different kinds of sediments in recent years. Our group has studied the adsorption behaviors of OTC in sediment[9]. However, adsorption is a complex physical and chemical process. Only for soil adsorption of organic pollutants, the main influence factors included the type of the soil[10], organic content[11], particle size[12], iron and aluminum oxide[13], cationic type[14], *etc*. Thus, it has an important scientific significance for adsorption process of OTC in sediment to research these factors.

Humic acid colloid (HA) as relatively stable composition component and high-content in the organic matter, which contains several functional groups, such as carboxyl, alcoholic hydroxy group, phenolic hydroxyl group and ketene hydroxyl. Humic acid colloid have acidic, hydrophilic, ion exchange and complexing power and high adsorption ability[15-17] and can interact with a lot of organic and inorganic substances[18-21]. Most of the reports on the adsorption of organic pollutants on humic acid colloid focused on polycyclic aromatic hydrocarbons (PAH)[15,22-24] and tetracycline antibiotics[25]. In addition, humic acid colloid can promote the adsorption of phenanthrene in soil[16] and exists widely in the sediment and natural water. But so far, the influence of humic acid colloid on adsorption behaviors of OTC in sediment is still an open question. Therefore, in this paper, the adsorption of OTC was studied by using humic acid colloid to discuss the influence of condition changes such as temperature and pH on the adsorption behaviors of OTC in

sediment, in order to provide the reference to clarify the OTC migration patterns in the environment.

EXPERIMENTAL

The supplied test sediment sample was collected from the overbank of Weihe river. The sediment sample was unpolluted by OTC, air-dried and sterilized for future use. Some basic physico-chemical properties of the supplied sediment sample are shown in Table-1.

Oxytetracycline was purchased from Boston Biomedical Inc., (USA) with United States Patent (USP) grade. Molecular formula of OTC is $C_{22}H_{24}N_2O_9$, and its molecular weight is 460.44. Methyl alcohol in flowing phase was purchased from Waters Company (USA) with High Performance Liquid Chromatography (HPLC) grade. The other reagents are all in analytical grade.

Detection method of oxytetracycline in solution: A Waters ACQUITY Ultra Performance Liquid Chromatography (UPLC) H-Class with ultraviolet/visible spectrophotometer detector and BEH Shield RP18 1.7 μm 2.1 × 150 mm column was used for the quantification of OTC in solution, under the optimized conditions as follows: methanol/water = 50:50 as mobile phase, 0.2 mL/min of flow rate, 20 ± 0.1 °C column temperature, 5 μL of injection volume, 260 nm detected wavelength and 2.610 min of retention time.

Adsorption procedure: Adsorption experiments were conducted by Organization for Economic Co-operation and Development (OECD) batch equilibrium method[26]. For each time 0.2000 g sediment,1 mL OTC solution and 1 mL humic acid colloid were mixed in a 5 mL centrifuge tube, which was then shaken in a thermostat shaker at 150 rpm and the aqueous samples were separated at predetermined time intervals by using filter membranes of 0.22 μm. Set with or without sediment, OTC and humic acid colloid as comparison, to remove the adsorption of OTC on humic acid colloid.

Adsorption kinetics: The kinetic studies were performed following a similar procedure at 25 °C (298 K), the initial concentration was set as 10 mg/L for each OTC in a series of reactors with the same specification. The uptake of OTC at time *t*, Q_t (mg/kg), was calculated by the following equation:

$$Q_t = \frac{V(C_0 - C_t)}{m} \quad (1)$$

where C_0 and C_t are the initial and after time (t) concentrations of the OTC (mg/L) in the solution, respectively. V is the volume of the solution (L) and m is the weight of the sediment sample (g).

Adsorption isotherm: In adsorption isotherm studies, solutions with different initial concentrations were added, which was ranging from 0.2 to 10 mg/L and the equilibrium time was set as 24 h, which was enough according to the kinetic studies. The uptake of OTC at equilibrium, Q_e (mg/L), was calculated by the following equation:

$$Q_e = \frac{V(C_0 - C_e)}{m} \quad (2)$$

where C_e is the equilibrium concentration of the OTC (mg/L) in the solution.

Thermodynamics: In thermodynamics study, the experimental temperature was set at 25, 30 and 35 °C.

Effect of solution pH: The effect of solution pH on OTC adsorption was investigated by adjusting OTC solutions (the initial concentration was 10 mg/L) to different initial pH values at 25 °C.

RESULTS AND DISCUSSION

Adsorption kinetics: The adsorption of OTC in sediment sample as a function of contact time is shown in Fig. 1. Without humic acid colloid, the equilibrium time of the adsorption of OTC in sediment was 24 h, while it was 12 h after adding humic acid colloid. It showed that adding humic acid colloid can accelerate the adsorption of OTC in sediment. The adsorption of OTC in sediment was attributed to a large number of adsorption sites existing on the surface of the sediment[27]. After adding humic acid colloid, during the first 12 h, the speed of the adsorption of OTC was faster and then came to balance. This may because the activity of adsorption sites on sediment surface enhanced, the resistance OTC gets reducing, to promote OTC to enter the internal microspores of sediment with the humic acid colloid . Thus, the equilibrium time of the adsorption of OTC in sediment was shortened. In addition, humic acid colloid and sediment may form hydrogen bonding after adding humic acid colloid, so that the adsorption of OTC in sediment was speeded up consequently.

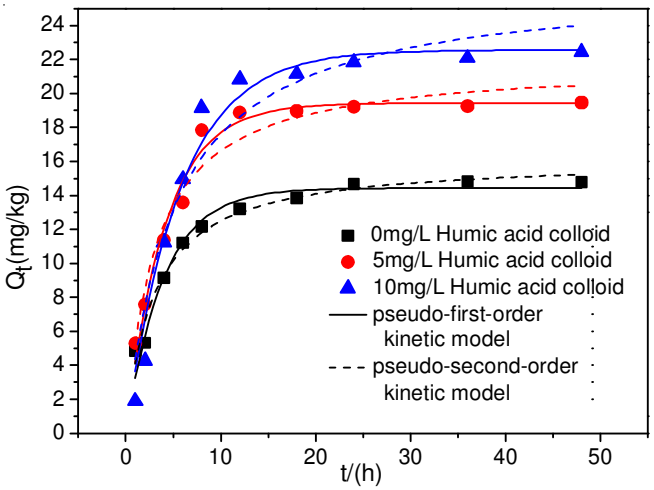

Fig. 1. Simulated results of pseudo-first-order kinetics and pseudo-second-order kinetics

TABLE-1
PHYSICOCHEMICAL PROPERTIES OF THE SEDIMENT SAMPLE

Organic carbon (w %)	Moisture content (w %)	Volume weight (g/cm^3)	Porosity (%)	Mechanical composition (w %)			
				Silt < 0.25 mm	Fine sand 0.25-0.35 mm	Medium sand 0.35-0.5 mm	Coarse sand > .5 mm
0.33	5.84	1.54	41.81	1.52	48.50	39.82	10.16

TABLE-2
PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER RATE CONSTANTS FOR OTC ADSORPTION IN SEDIMENT SAMPLE

HA (mg/L)	$Q_{e,exp}$ (mg/kg)	Pseudo-first-order model			Pseudo-second-order model		
		R^2	k_1(1/h)	$Q_{e,cal1}$(mg/kg)	R^2	k_2(kg/mg h)	$Q_{e,cal2}$(mg/kg)
0	14.6716	0.9670	0.2524	14.4244	0.9765	0.0209	16.1693
5	18.8824	0.9772	0.2413	19.4330	0.9513	0.0147	21.8070
10	20.8331	0.9682	0.1767	22.5753	0.9272	0.0074	26.5409

Pseudo-first-order and pseudo-second-order kinetic model were used to fit the adsorption of OTC in sediment sample under different concentrations of humic acid colloid[9]. The fitting curves were shown in Fig. 1 and the results are given in Table-2.

In Table-2, $Q_{e,cal-1}$ and $Q_{e,cal-2}$ were the calculated values of the equilibrium adsorption quantity (mg/kg) from sediment sample adsorption dynamic curves according to the pseudo-first-order and pseudo-second-order fitting in different concentrations of humic acid colloid, respectively. $Q_{e,exp}$ was the equilibrium adsorption quantity (mg/kg) through experiments. It is demonstrated whether adding humic acid colloid or not, the calculated values of the equilibrium adsorption from the pseudo-first-order model fitting is closer to the equilibrium adsorption through the experiments and the correlation coefficient R^2 is higher. It indicated that adding humic acid colloid cannot change the dynamics model of the adsorption of OTC in sediment.

Adsorption isotherm: Langmuir and Freundlich model were used to analyze and predict adsorption behaviors of OTC in sediment sample with different concentrations of humic acid colloid[9]. The fitting curves were shown in Fig. 2 and the results are given in Table-3.

It can be seen from Table-3 that the values of R^2 for Langmuir model and the Freundlich model were all greater than 0.99 under different concentrations of humic acid colloid. Generally speaking, the value of R^2 is widely used to investigate the applicability of a model in fitting to data. However, it cannot be the only standard due to the inherent deviation of linear regression. For the purpose of quantitatively comparing the applicability of Langmuir and Freundlich adsorption isotherms in fitting to data, SSE, SAE, HYBRID and NPSD (%) four error functions were employed for error analysis[9]. The error analysis results are shown in Table-4.

By inspecting Table-4, it further proved that the Langmuir isotherm was more suitable to describe the adsorption behavior

TABLE-3
ISOTHERM PARAMETERS FOR ADSORPTION OF OXYTETRACYCLINE IN SEDIMENT SAMPLE

Humic acid (mg/L)	Langmuir isotherm				Freundlich isotherm		
	Q_m(mg/kg)	K_L(L/mg)	R^2	R_L	K_F/((mg/kg) (L/mg)$^{1/n}$)	1/n	R^2
0	70.35532	0.04181	0.99869	0.8977	2.86046	0.8871	0.99693
5	155.92857	0.02837	0.99925	0.9256	4.4601	0.9028	0.99923
10	229.64037	0.02201	0.99921	0.9402	5.04553	0.9292	0.99896

TABLE-4
ISOTHERM SIMULATED RESULTS WITH ERROR ANALYSIS FOR ADSORPTION OF OXYTETRACYCLINE IN SEDIMENT SAMPLE

Humic acid colloid (mg/L)	Langmuir isotherm				Freundlich isotherm			
	SSE	SAE	HYBRID	NPSD (%)	SSE	SAE	HYBRID	NPSD (%)
0	0.1888	0.8249	17.5310	90.4821	0.4420	1.5193	30.5847	117.6271
5	0.3092	1.0627	10.2020	44.3525	0.3164	0.9907	17.9308	62.3097
10	0.4112	1.3220	9.7031	37.2365	0.5408	1.5484	13.8631	47.8710

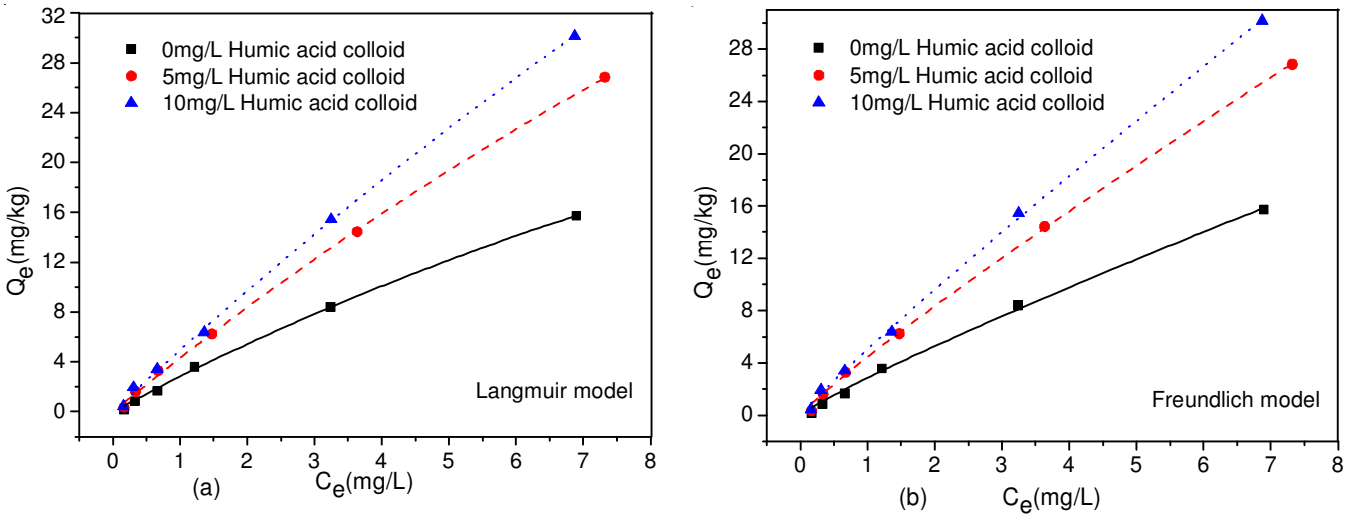

Fig. 2. Langmuir and Freundlich model fit of adsorption isotherm (298 K)

of OTC in sediment sample as it gave a comparatively lower error function compared with the Freundlich model.

For the isothermal adsorption of OTC in sediment sample under different concentrations of humic acid colloid, the values of R_L with the Langmuir model fitting were shown in Table-3, respectively. It was found that the values were less than 1, which indicated that the adsorption process was favorable[28,29]. It is generally acknowledged that in Freundlich adsorption isotherm, *1/n* value is usually 0-1. If *1/n* value is 0.1- 0.5, it is easy for adsorption[30]. In our study, it was found that after adding humic acid colloid, although *1/n* value increased, the equilibrium time of the adsorption of OTC shortened and the adsorption quantity increased. Thus, humic acid colloid can contribute to the adsorption of OTC in sediment apparently, for which reason should be further studied.

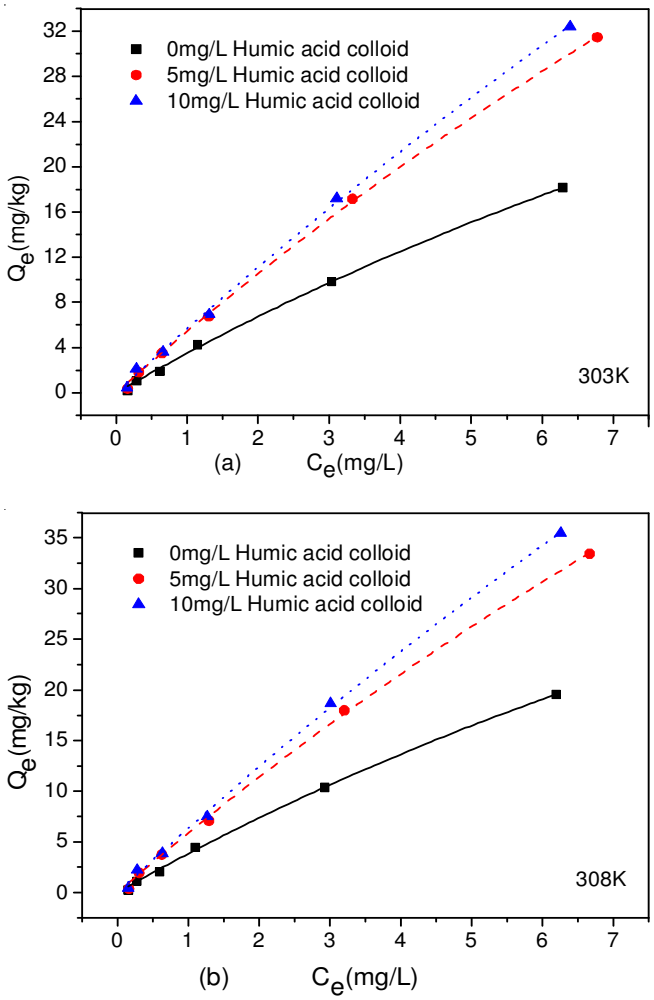

Fig. 3. Langmuir fit of adsorption of OTC in sediment sample under different concentration of humic acid colloid at different temperatures

Langmuir model was used to fit the adsorption of OTC in sediment sample under different concentrations of humic acid colloid at temperatures of 298, 303 and 308 K, respectively. The fitting curves were shown in Figs. 2 and 3. It can be seen that the adsorption quantity of OTC in sediment increased obviously after adding humic acid colloid compared with that without humic acid colloid. This may because humic acid colloid reacted with OTC, forming the structure absorbed more easily by the sediment, such as the combination of humic acid colloid carboxylic and phenol hydroxyl of OTC. It may also because humic acid colloid acted on the sediment, making originally hydrophilic surface have hydrophobicity, which changed the adsorption properties of sediment and enhanced the activity of adsorption sites on sediment surface, thus the adsorption was promoted. In addition, humic acid colloid and sediment may form hydrogen bonds.

Thermodynamics: The obtained data of the adsorption of OTC in sediment sample under different concentrations of humic acid colloid at 298, 303 and 308 K were fitted by Langmuir model and the fitting curves were shown in Fig. 4

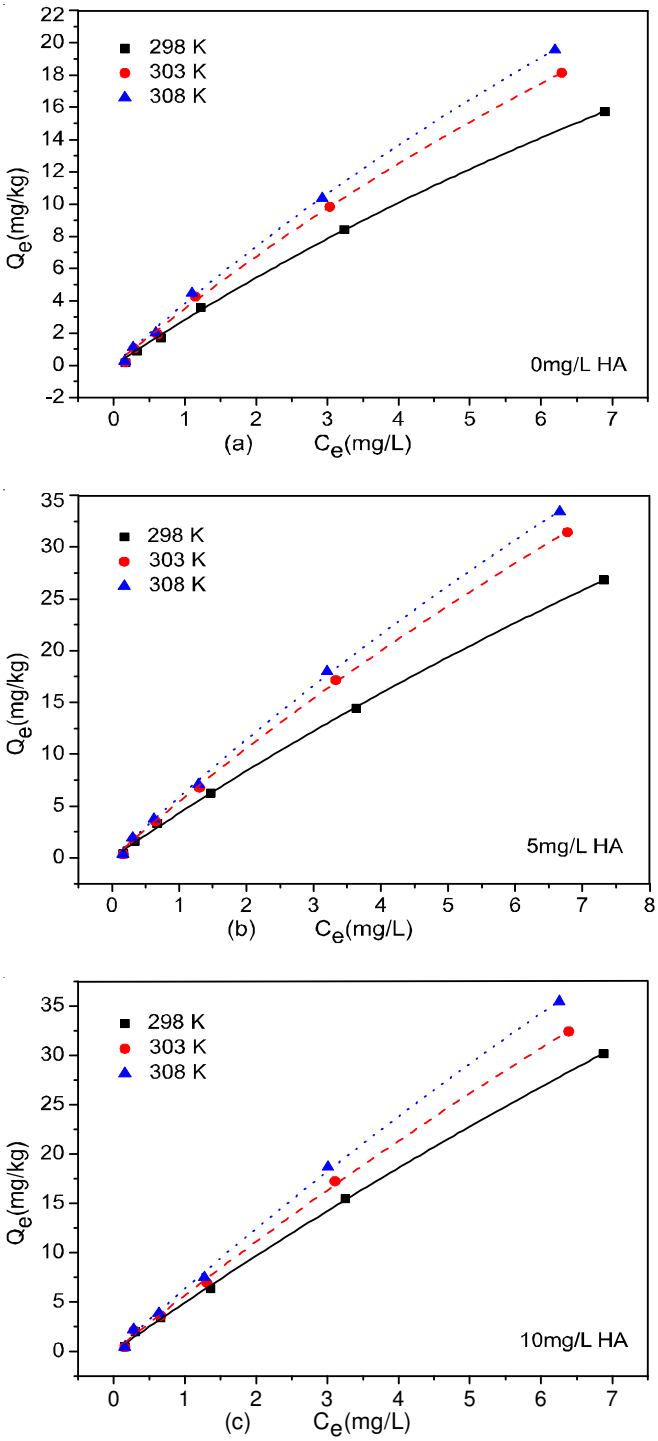

Fig. 4. Langmuir fit of adsorption of OTC in sediment sample under different concentration of humic acid colloid at different temperatures

and the fitting parameters shown in Table-5. The linear plot of ln K_L *versus* 1/T for calculating thermodynamic parameters for OTC adsorption in sediment sample was shown in Fig. 5. The values of thermodynamic parameters such as Gibbs-free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated with reference to the literature[9] and shown in Table-6.

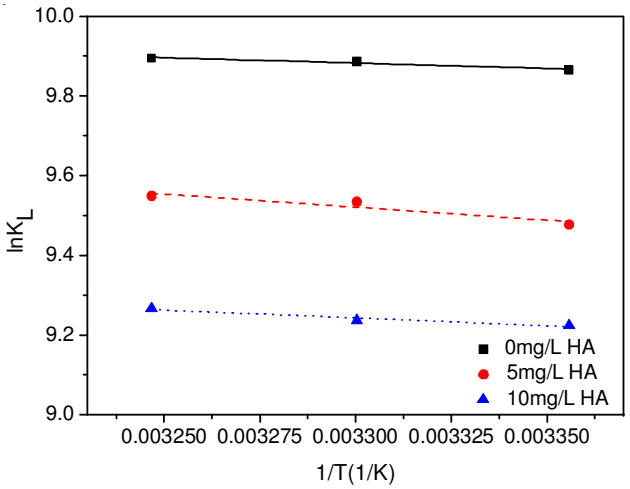

Fig. 5. Linear plot of ln K_L *versus* 1/T for calculating thermodynamic parameters for adsorption of OTC in sediment sample

From Table-6, the values of ΔG° of OTC adsorption in sediment sample under different concentrations of humic acid colloid at 25, 30 and 35 °C were negative, which indicated that the adsorption process was spontaneous and the values of ΔG° decreased with the addition of humic acid colloid, as well as the increase of temperature, which referred to the more spontaneous the process. This indicated that the adsorption of OTC in sediment is mainly physical adsorption, while after adding humic acid colloid , ΔG° decreases gradually and the adsorption tends to physical adsorption better than without humic acid colloid[31]. Studies have shown that humic acid colloid absorbed into kaolin can change its physical and chemical properties, making the originally hydrophobic surface possess hydrophobicity[32]. The reasons for the phenomenon may be that after adding humic acid colloid, low molecular humic acid colloid instead of water molecules on the surface of the sediment, makes the hydrophobicity of the sediment stronger, the water film on the surface thinner. The space steric hindrance of the sediment decreases with the decrease of the number of water molecules on the unit surface, which leads to the physical adsorption and that may play a leading role. In addition, the carboxyl group, phenolic hydroxyl group and amino group are bonded with the sediment, resulting in surface energy increasing and the surface properties of sediment changing, which leads to the chemisorptions.

Effect of solution pH: Solution pH usually influences the adsorption largely, as it affects the properties of both adsorbent and adsorbate. Studies have shown that the pH of the solution affects the degree of ionization and the speciation of tetracycline hydrochloride which subsequently leads to a change in adsorption kinetics and equilibrium characteristics[33]. The effects of solution pH as well as OTC existence forms on OTC adsorption in sediment sample were shown in Fig. 6. The properties of charge on the surface of the soil and sediment were related to the pH value of zero point charge (pHZPC). When environmental pH < pHZPC, soil and sediment surface is positively charged or negatively charged[34,35].

Without humic acid colloid, the adsorption quantity of OTC in sediment was rather large and change little from solution pH 3 to 7, decreased significantly from solution pH 7 to 8 while was very small and changed little in a solution of pH > 8.

With the existence of humic acid colloid , the adsorption quantity of OTC in sediment sample increased with the increase of solution pH at solution pH < 6, was relatively large and there was no significant change at solution pH 6-9 and remained at a high level and decreased slightly at solution pH > 9. The

TABLE-5
LANGMUIR ISOTHERM PARAMETERS FOR ADSORPTION OF OTC IN SEDIMENT SAMPLE AT DIFFERENT TEMPERATURES

Parameters	Humic acid colloid (mg/L)	Temperature		
		298 K	303 K	308 k
Q_m/(mg/kg)	0	70.35540	85.69410	92.94474
K_L/(L/mg)		0.041810	0.04272	0.04306
K_L/(L/mol)		19250.9964	19669.9968	19826.5464
R^2		0.99869	0.99840	0.99861
Q_m/(mg/kg)	5	155.92857	186.22731	198.52302
K_L/(L/mg)		0.02837	0.03004	0.03047
K_L/(L/mol)		13062.6828	13831.6176	14029.6068
R^2		0.99925	0.99927	0.99896
Q_m/(mg/kg)	10	229.64037	260.31182	282.75838
K_L/(L/mg)		0.02201	0.02231	0.02298
K_L/(L/mol)		10134.2844	10272.4164	10580.9112
R^2		0.99921	0.99872	0.99866

TABLE-6
RMODYNAMIC PARAMETERS FOR ADSORPTION OF OTC IN SEDIMENT SAMPLE

Humic acid colloid (mg/L)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	ΔG°(kJ/mol)			
			298 K	303 K	308 K	R^2
0	2.2535	0.0896	-24.4420	-24.9064	-25.3377	0.87659
5	5.4668	0.0972	-23.4812	-24.0193	-24.4520	0.79615
10	3.2840	0.0877	-22.8523	-23.2699	-23.7296	0.90374

reason for this phenomenon is probably that at solution pH < 3.5, OTC and sediment is positively charged, additionally, humic acid colloid can provide more H^+, which leads to the electrostatic repulsion between sediment and OTC. Thus the adsorption quantity decreases. At solution pH 3.5-6, the form of OTC is $OTCH_2^0$.The presence of humic acid colloid enhanced the activity of the sediment adsorption sites, thus the adsorption quantity increases gradually as the activity of the sediment adsorption sites increases. At solution pH 6-9, the pHZPC of sediment may form at a larger pH value in the presence of humic acid colloid, which caused that the adsorption quantity was relatively large with no significant change. At solution pH > 9, OTC and sediment were both negatively charged. With the increase of solution pH, the repulsion increases and adsorption quantity decreased.

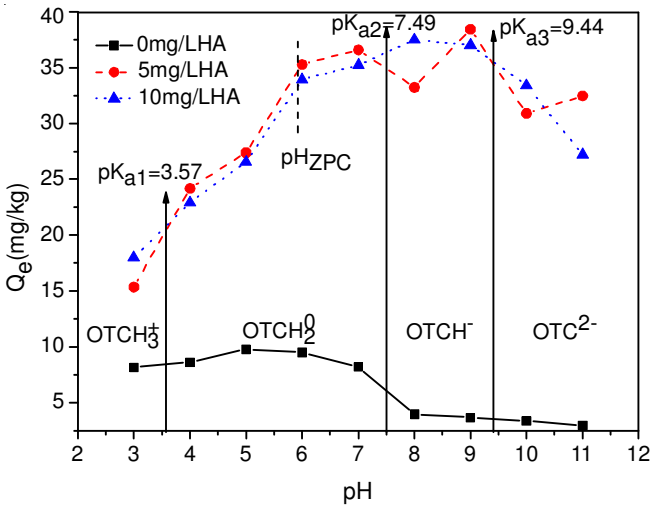

Fig. 6. Effect of solution pH on adsorption of OTC in sediment sample

Conclusions

The conclusions of this study are shown as follows:

(1) The results showed that the adsorption equilibrium time of OTC in sediment without adding humic acid colloid was 24 h, while it was 12 h in the presence of humic acid colloid, which showed that humic acid colloid could accelerate the process of adsorption of OTC in sediment. Adsorption kinetics was in line with the pseudo first-order kinetics model. (2) Langmuir and Freundlich model can better describe the process of isothermal adsorption of OTC in sediment and the Langmuir model fitted better and four kinds of error function values were smaller. (3) The thermodynamics research results showed that the process of the adsorption of OTC in sediment was spontaneous, endothermic and entropy-increasing. Adding humic acid colloid and increasing temperature both contributed to the obvious increase of the adsorption capacity and the adsorption tended to physical adsorption.(4) The adsorption quantity of OTC increased with an increase in solution pH from 3 to 6, decreased slightly when pH was greater than 9 and remained at a higher level when pH was 6-9. (5) However, absorption is a complex process and the structure of humic acid colloid is rather complicated, the impact of humic acid colloid on the adsorption of OTC in sediment remains to be studied in the next step.

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REFERENCES

1. E. Zuccato, D. Calamari, M. Natangelo and R. Fanelli, *Lancet*, **355**, 1789 (2000).
2. D.W. Kolpin, E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber and H.T. Buxton, *J. Environ. Sci. Technol.*, **36**, 1202 (2002).
3. A.K. Sarmah, M.T. Meyer and A. Boxall, *Chemosphere*, **65**, 725 (2006).
4. P.A. Blackwell, A.B. Boxall, P. Kay and H. Noble, *J. Agric. Food Chem.*, **53**, 2192 (2005).
5. H. Kang, S.K. Yang, W.K. Wang, F. Li, Y.Z. Li, Y.L. Wang and G.X. Mu, The International Symposium on Water Resource and Environmental Protection (ISWREP), vol. 2: pp. 1526-1528 (2011).
6. P.J. Dillon, M. Miller, H. Fallowfield and J. Hutson, *Hydrology*, **266**, 209 (2002).
7. G.Y. Luo, H. Zhu, X.Y. Xu, W.L. Cai and J.F. Dou, *Environ. Sci. Technol.*, **33 (12F),** 1 (2010).
8. J.T. Hu, H.M. Zong, J.Y. Wang and D.Y. Ma, *Environ. Chem.*, **27**, 482 (2008).
9. D.H. Cheng, S.K. Yang, Y. Zhao and J. Chen, *J. Chemistry,* **Article ID 652930** (2013).
10. S.A. Sassman and L.S. Lee, *Environ. Sci. Technol.*, **39**, 7452 (2005).
11. Y.Y. Bao, Q.X. Zhou, Y. Wan and X.J. Xie, *China Environ. Sci.*, **29**, 651 (2009).
12. R.A. Figueroa, A. Leonard and A.A. MacKay, *J. Environ. Sci. Technol.*, **38**, 476 (2004).
13. P. Jacobsen and L. Berglind, *Aquaculture*, **70**, 365 (1988).
14. Y.Y. Bao, Q.X. Zhou and H. Zhang, *J. Environ. Sci. (China)*, **30**, 552 (2009).
15. L. Li, Z.Q. Yu, G.Y. Sheng, J.Z. Fu, P.A. Peng and W.L. Huang, *Environ. Chem.*, **23**, 381 (2004).
16. B. Wen, J.J. Zhang, S.Z. Zhang, X.Q. Shan, S.U. Khan and B. Xing, *J. Environ. Sci. Technol.*, **41**, 3165 (2007).
17. B. Xing, *Environ. Pollut.*, **111**, 303 (2001).
18. M. Chen, H.M. Yu, C.J. Ge, W.H. Tang, H. Deng, C.R. Li and P. Jiao, *Eco. Environ. Sci.*, **21**, 1891 (2012).
19. M.E. Parent and D. Velegol, *Colloids Surf. B*, **39**, 45 (2004).
20. M. Arias, M.T. Barral and J.C. Mejuto, *Chemosphere*, **48**, 1081 (2002).
21. J.M. Zachara, C.T. Resch and S.C. Smith, *Geochim. Cosmochim. Acta*, **58**, 553 (1994).
22. J.H. Zhang, M.C. He and Y.H. Shi, *J. Hazard. Mater.*, **166**, 802 (2009).
23. T. Nielsen, K. Siigur, C. Helweg, O. Jørgensen, P.E. Hansen and U. Kirso, *Environ. Sci. Technol.*, **31**, 1102 (1997).
24. M.J. Simpson, B. Chefetz and P.G. Hatcher, *J. Environ. Qual.*, **32**, 1750 (2003).
25. C. Gu and K.G. Karthikeyan, *J. Environ. Qual.*, **37**, 704 (2008).
26. B. von Oepen, W. Kördel and W. Klein, *Chemosphere*, **22**, 285 (1991).
27. A. Özer, D. Özer and H. Ibrahim EkIz, *Adsorption*, **10**, 317 (2005).
28. M.A. Wahab, S. Jellali and N. Jedidi, *Bioresour. Technol.*, **101**, 5070 (2010).
29. Q.S. Liu, T. Zheng, P. Wang, J.P. Jiang and N. Li, *Chem. Eng. J.*, **157**, 348 (2010).
30. K.G. Bhattacharyya and A. Sharma, *Dyes Pigments*, **65**, 51 (2005).
31. Y. Yu, Y.Y. Zhuang, Z.H. Wang and M.Q. Qiu, *Chemosphere*, **54**, 425 (2004).
32. A.M. Li, Y. Zhu and J.Y. Dai, *Acta Petrol. Mineral.*, **24**, 145 (2005).
33. M. Sathishkumar, A.R. Binupriya, D. Kavitha, R. Selvakumar, R. Jayabalan, J.G. Choi and S.E. Yun, *Chem. Eng. J.*, **147**, 265 (2009).
34. K. Sakurai, Y. Ohdate and K. Kyuma, *Soil Sci. Plant Nutr.*, **35**, 89 (1989).
35. W.H. Hendershot, G.A. Singleton and L.M. Lavkulich, *Soil Sci. Am. J.*, **43**, 387 (1979).