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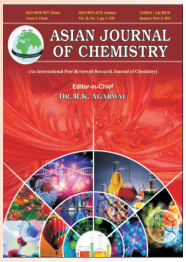

Influence of Humic Acid Colloid on Adsorption of DDT in the Riverbed Sediments

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Static experiments were conducted to investigate the influence of humic acid on adsorption of DDT in the Wei river sediments. The results of kinetics experiments showed that adsorptive equilibrium time of DDT in sediments without humus was 120 h and its adsorption kinetics conformed to the first-order kinetics equation; with humic acid colloid, the DDT equilibrium time was shortened to 48 h and the adsorption kinetics fitted the second-order kinetics equation. The results of adsorption thermodynamics experiments indicated that the forms of the adsorption isotherms of *o,p*'-DDT, *p,p*'-DDD and *p,p*'-DDE without humus were S-, L- and L-shaped and the correspondingly adsorption models accorded with Freundlich, Langmuir and Langmuir equation, respectively. The adsorption isotherms forms of *o,p*'-DDT, *p,p*'-DDD and *p,p*'-DDE with humus were L-, S- and L-shaped and the correspondingly adsorption models were Langmuir, Freundlich and Langmuir equation, respectively. Concentration of humic acid had a silght impact on adsorption kinetics and thermodynamics experiments.

Keywords: DDT, Humic acid colloid, Adsorption kinetics, Thermodynamics.

INTRODUCTION

Along with unceasingly cognition to transportation law of solute in groundwater system, colloid was found to be one of the important factors that affect pollutant migration. With the existence of colloid, there are some factors to impact the pollutant migration in groundwater, such as colloidal charge properties (electrokinetic potential positive and negative resistance), colloidal stability, chemical components of the solution, ion strength, pH value and flow velocity of water, *etc*. The pollutants collaborative with colloid cover VOC[1], PAHs[2-4] and some hydrophobic organic compounds[5]. Several kinds of models regarding vary factors were propounded to simulate the pollutants migration characteristics with colloid in theory and soil-column experiments[6-9].

Colloids that employed to underground include silicas, aluminosilicate, all kinds of chlorides (Fe^{3+}, Si^{4+}, Mn^{2+}), calcium carbonate and other inorganic colloids, humic acid, fulvic acid and other organic colloids and inorganic-organic composite gel. Effective experimental concentration was between few milligram per liter and hundreds milligram per liter. Because of a broad existence and mutable complicated nature of humic acid (HA), its effects for adsorbing solute catches attention of people. Wei and Shao[10] found that the following factors have a certain affect to adsorption and migration of HA, such as the content of soil clay particle, higher cation exchange capacity, pH value of soil and soil particle.

Tian *et al.*[11] and Ma[12] founded that HA colloid in underground can advanced the migration of U and ^{241}Am in subsurface layer of soil. Macromolecular humic acid could promote metal to transform steady state from unsteady one. Other raseach shows that HA would indeed accelerate the adsorption rate to Cu, especially in alkaline condition[13], its adsorbing effect to pH get stronger with the increasing of pH value[14]. Software SYSTAT was used to fit the isotherms of phenanthrene by Henry and Freundlich models, which demonstrated the adsorbing process of HA colloid to phenanthrene was nonlinear[15].

Hou and Yuan[16] studied positive ions were adsorbed by the Kaolinite-humic acid, montmorillonite-humic acid compound colloid and other organic-mineral composite colloids and the research results showed that they have a certain influence on adsorption capacity of Ca^{2+}, Fe^{3+}, Al^{3+} in different initial pH value.

The previous researches mainly focused on the migration of HA gel in soil/sediment and the adsorption of HA to metal ion and other pollutants and there is little study on the effects of HA adsorbing to organo chlorine pesticide (OCPs) in water-soil medium.

As a kind of OCPs, DDT played an important role in preventing and controlling the diseases-insect pests of agriculture and relieving the harm from malaria and typhoid, *etc.*[17]. But until 1960s, it was found DDT not only can hardly be degradated, but also can produce more damage through enriching and transferring by food chain[18-20], because of aforementioned reasons. Thus DDT was forced to suspend production and be out of service[21]. Even so, DDT residues can still be detected in environmental medium[22-30]. Therefore, scientists are paying much attention to its existential state, migration and transformation and migration destination.

The survey found that DDT was detected in soil of many countries and regions, such as Europe[31, 32], USA[33, 34], Tanzania[35], Beijing[36], Guangzhou[37], Sinkiang[30,39] of China and Taiwan straits, Xi'an[38].

DDTs exist in the atmosphere, water, soil and biology and their migration mainly occurs in single-medium and multimedium[39]. Generally speaking, the nongaseous diffusion occurs on the interface of water, atmosphere/water, water/soil (sediment) when DDT escaped from pollution source. Diffusivity mainly depends on its physico-chemical property and environmental conditions[20]. Hence, it is imperative to study the pollutants mass in different interface. In the meanwhile, there is few report about colloid in the underground adsorbing pesticide, especial hydrophobic organochlorine pesticide. Yang Feng[40] surveyed the hexachloro-cyclohexane (HCH) and DDT surviving situation in different kinds of soil profiles in Guanzhong basin such as Loess Plateau-Loess, Second terrance-Loess, First terrance-Clay and Floodplain-Aleurite. Consequently, this current paper defines DDT as research object, studies the effects of HA on adsorption and transportation DDT in sediments from Weihe river.

EXPERIMENTAL

Preparation of DDT: The deposit sediments were sampled from the floodplain of Weihe river in Caotan Town Xi'an City, China.

Preparation of standard stock solution and working liquid of DDT: Stock solutions for sorption studies were prepared by desolving 0.0100 g DDT isomer (each of *o,p*'-DDT, *p,p*'-DDD and *p,p*'-DDE 0.0100g) in 1000 mL normal hexane, the stock solutions were stored after mixing. Acording to the experimental needs, the stock solution was diluted to the targeting concentration and the working liquid of DDT has been prepared already.

Preparation of DTT for adsorption: Stock solutions for sorption studies were prepared by dissolving 0.0100 g DDT isomer (each of *o,p*'-DDT, *p,p*'-DDD and *p,p*'-DDE 0.0100 g) in 1000 mL methanol and concentration of each of the DDT isomer solution is 10 mg/L. In experimental process, different volume of DDT was transferred in 2000 mL volumetric flask with deionized water. The mixtures were stored after shaking well. The volume fraction of methanol was accounting for 1 % in order to avoid Eutectic effect.

Preparation of humic acid colloid

Extraction of humic acid colloid: A certain sample of HA was dissovled by 2 % sodium hydroxide solution and filtrated by 0.45 μm microporous menbrane. The filtrate liquor was acidified with hydrochloric acid and humic acid colloid was obained as a solid precipitate at pH 1.5 or even lower. It was seperated by centrifuging 0.5 h at 2500 rad/min. After the supernatant liquor was discarded, the precipitate was washed by deionized water repeatly until it was free-chloride, then, the humic acid colloid was obained aftering drying and stored in freezer.

Preparation of humic acid colloid: A certain mass of the colloid were dissolved in 2 % sodium hydroxide solution, the pH was adjusted to 8.0 and then filtrated by 0.22 μm microporous menbrane, the then reddish brown HA colloid was preparated.

Adsorption kinetics experiments: Weigh 2 g of sediments sample, 70 μg/L each of isomer of DDT solution (or with 5 mg/L humic acid colloid mixing liquor) in 250 mL conical flask with cover till the solution overflowing (the purpose is removing the air in conical flask), after capping, the vessels were vibrated in 110 ± 5 rpm at 25 ± 0.5 ºC. Samples were taken at 1, 2, 3, 4, 5, 6, 8, 10, 12, 24, 36, 48, 72, 96, 120, 168, 216 h and the concentrations of adsorpted samples were measured. The adsorption capacity of deposit sediments was caculated by minusing method. When investigating the effect of concentration of humic acid colloid to DDT adsorption kinetics, the concentrations of HA were 5, 20 and 50 mg/L, respectively.

Adsorption thermodynamics experiments: Adsorption thermodynamics experiment of DDT was studied with batch equilibrium method. Weigh 2 g sediments sample in 250 mL conical flask with cover, add 2, 5, 10, 20, 30, 50, 70 μg/L each of isomer of DDT solution (or with 5 mg/L humic acid colloid mixing liquor), respectively, till the solution overflowing (the purpose is same as former), after capping, the vessels were vibrated with 110 ± 5 rpm at 25 ± 0.5 ºC. After adsorption equilibrium, the concentrations of adsorbed samples were measured. The adsorption capacity of deposit sediments was caculated by minusing method. When investigating the effect of concentration of humic acid colloid to DDT adsorption thermodynamics, the concentrations of humic acid were 1, 2 and 5 mg/L respectively. The DDT was 70.0 μg/L.

Analysis and test methods: Conductivity meter was adopted to measure the chloride ion concentration. The concentration of humic acid colliod was measured by Ultraviolet-visible spectrophotometer in 225 nm wave band; mass spectrometry (M-S) was used to determine the concentration of DDT. Add 10 mL sample and 2 mL *n*-hexane into colorimetric tube, fully vibrate for 3 min, after 3 min standing, two phase were seperated and the water-phase was discarded, the organic phase was dehydrated by anhydrous sodium sulphate and preparing for M-S analysis.

Data analysis

Amount of DDT: The amount of DDT that adsorbed in deposit sediment is determined by minusing, the formula is as follows:

$$C_s = \frac{(C_o - C_e)V}{W} \qquad (1)$$

where C_o is initial mass concentration of DDT solution (μg/L); C_e is residual concentration of DDT solution after adsorbing (μg/L); V is volume of DDT adding in adsorption experiment (L); W is mass of soil sample adding in adsorption experiment (g); C_S is amount of DDT adsorbed in the deposit sediment (μg/g).

Adsorption kinetics curve fitting equation

Two-constant equation:

$$Q_t = at^b \tag{2}$$

where t is adsorption time (h); Q_t is adsorption capacity at t hour (μg/L); a and b are the model parameters, a has something to do with adsorption capacity and b is have relation to dynamic curve bending degree.

Elovich equation:

$$Q_t = a + b \ln t \tag{3}$$

where a and b are the adsorption parameters;

Parabolic diffusion equation:

$$Q_t = a + bt^{1/2} \tag{4}$$

where b is diffusion rate constant (g/(mg min)).

First-order kinetic model:

$$Q_t = Q_{max} - Q_{max}e^{-K_1 t} \tag{5}$$

$$\ln (Q_e - Q_t) = \ln Q_e - k_1 t \tag{6}$$

where Q_e(mg/g) is equilibrium adsorption capacity of HA to DDT; Q_t(mg/g) is adsorption capacity in t h; k_1 (1/min) is the rate constant of pseudo-first-order kinetic model. The linear plot of $\ln (Q_e - Q_t)$ *versus* t in eqn. 6 was employed to calculate and from slope and intercept, respectively.

Second-order kinetic model:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{7}$$

where (1/min) is the rate constant of pseudo-second-order kinetic model. The linear plot of *versus* t in eqn. 7 was employed to calculate and from intercept and slope, respectively.

Adsorption thermodynamic curve fitting equation: In the current study, Henry, Langmuir, Freundlich and Temkin four common patterns were successively used to fit the sorption conduction. The linear expressions of those patterns were listed as follows:

Henry: $$Q_e = K_d C_e \tag{8}$$

where Q_e (mg/g) is adsorption capacity of HA to DDT; C_e (mg/L) is the equilibrium concentration of solution; K_d is partition coefficient.

Langmuir $$\frac{C_e}{Q_e} = \frac{1}{Q_{max} k_L} + \frac{C_e}{Q_{max}} \tag{9}$$

where C_e (mg/L), Q_e (mg/g) and Q_{max} (mg/g) are equilibrium concentration of solution, adsorption capacity and the maximum adsorption capacity for meerschaum, respectively and k_L (L/mg) is Langmuir isotherm constant. The linear plot of C_e/Q_e *versus* C_e was used to calculate the Q_{max} and k_L from the slope and intercept of the fitting straight line.

Freundlich: $$\ln Q_e = \ln k_F + \frac{1}{n} \ln C_e \tag{10}$$

where k_F ((mg/g) (L/mg)$^{1/n}$) and 1/n are the Freundlich constants which are related to the bonding energy and heterogeneity factor of adsorption curve in Freundlich isotherm, respectively. The linear plot of $\ln Q_e$ *versus* $\ln C_e$ in eqn. 10 was used to calculate the 1/n and k_F from the slope and intercept of the fitting straight line.

Temkin: $$Q_e = \frac{RT}{k_T} \ln A + \frac{RT}{k_T} \ln C_e \tag{11}$$

where k_T was Temkin constant.

RESULTS AND DISCUSSION

Adsorption dynamics behavior of DDT: The effect of time on equilibrium concentration of DDT that adsorbed by deposit sediment was given in Fig. 1.

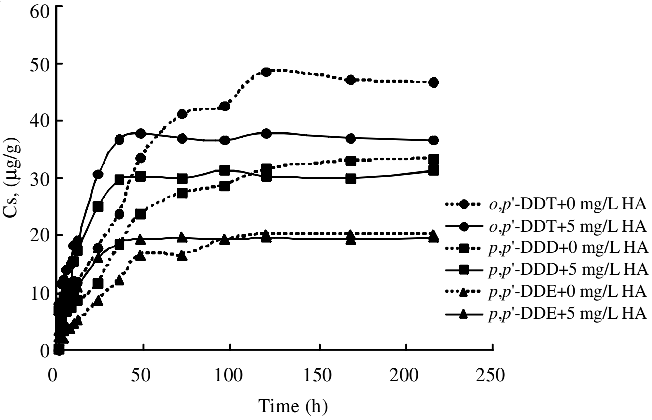

Fig. 1. Effect of adsorption time

As shown in Fig. 1, the adsorption process of DDT can be separated into two stages. During the fast adsorption phase (from 0-48 h), the adsorption rate of sedimentary to DDT was faster and the adsorption capacity rapidly increased. During the slow adsorption phase (from 48-120 h), the adsorption rate relative decreased and the adsorption capacity raises slightly, when the process reached adsorption equilibrium (in 120 h), the adsorption amount of sediments to DDT was stable and the adsorption processes achieved apparent balance. In conclusion, 120 h was regarded as the equilibrium time. When humic acid colloid existed in sediments, the sediments' adsorption rate of DDT was accelerated and the time to reach equilibrium was shortened from 120 h to the 48 h.

As the Fig. 1 described, the curve forms of *o,p*'-DDT, *p,p*'-DDD and *p,p*'-DDE with or without humic acid were basically similar. Comparaed with the adsorption processes without HA colloid, the adsorption rate with HA was faster and the adsorptive equilibrium can easily reach, while the equilibrium adsorptive amount and the adsorption rate diminished, which resulted from that part of the HA was adsorbed to deposit sediment of water-sediment system and the other part of the humic acid was detached in water. Humic acid colliod adsorbed to sedimentary can speed up adsorptive rate of deposit sediment to DDT, accelerate to balance, while humic acid collid free-in-water can also adsorb DDT. In addition, because of high adsorptive strength of humic acid collid free-in-water indeed adsorb DDT even from that originally adsorbed in sediments, which resulted in DDT adsorbed in sediments lessen[41,15].

DDTs adsorption dynamics equation simulation: DDT adsorption dynamics curves were fitted by two-constant equation, elovich equation, parabolic diffusion equation, first-order-kinetic model and second-order kinetic model and the results were demonstrated in Table-1.

Table-1 indicated, the first-order kinetic equation and second-order kinetic equation were preferably fitting with coefficient association R^2 greater than 0.95 by existence of humic acid. It was proved that the equilibrium capacity calculated value Q_e(cal) obtained from first-order kinetic fitting equation was close to experimental value Q_e(exp) by comparing with Q_e(exp) and Q_e(cal), which illustrated that first-order kinetic equation can more perfectly represent the adsorptive behavor of sediments to DDT. When humic acid colloid existed in sediments, all the the fitting coefficient assciations R^2 of *o,p*'-DDT, *p,p*'-DDD and *p,p*'-DDE were above 0.99. The equilibrium capacity calculated value [Q_e(cal)] obtained from second-order kinetic fitting equation was very close to experimental value Q_e(exp) with relative error of only ± 1 %, which indeed explain second-order kinetic fitting equation can well describe the adsorption process of sediment to DDT by existence of humic acid, while the adsorption process of sediment to DDT without humic acid can be described by first-order kinetic fitting equation and the existence of humic acid colloid has something to do with adsorption equation.

Adsorption isotherms of DDTs: Adsorption isotherm was separated into four types by the slope of the curve changes near the orginal: S-type, L-type, H-type and C-type. The results of adsorption isotherms of DDT were represented in Fig. 2.

It was inferred from Fig. 2 that the form of the sediments' adsorption isotherms by *o,p*'-DDT, *p,p*'-DDD and *p,p*'-DDE without humic acid colloid were S-shaped, L- and L- shaped and they became L-shaped, S-and L- shaped with existence of humic acid colloid in this experiental system. The type of L stands for monolayer adsorption on the surface of sediment to DDT and the type of S stands for multimolecular layer adsorption. Therefore, by the influence of HA colloid, the adsorption method of sediment to *o,p*'-DDT changed from multimolecular layer adsorption to monolayer adsorption and that of *p,p*'-DDD changed from monolayer adsorption to multimolecular layer one, while the isotherms of *p,p*'-DDE belonged to monolayer adsorption pre- and post-HA-additon.

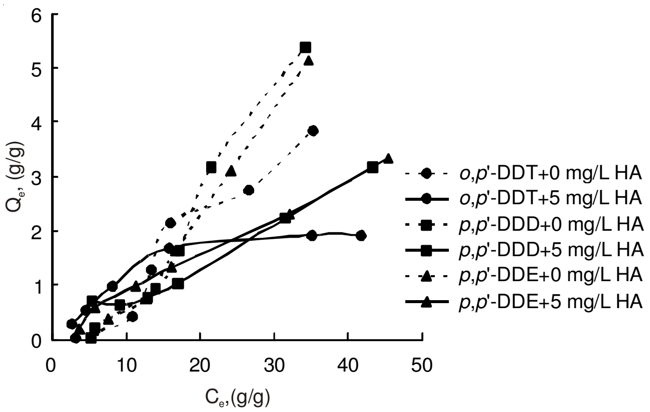

Fig. 2. Adsorption isotherms of DDT

The effects of humus to sediment adsorbing DDTs vary from equilibrium concentration. When the concentration of *o,p*'-DDT, *p,p*'-DDD and *p,p*'-DDE were below 14.60, 12.90 and 15.90 μg/L, respectively, humic acid colloid would strenthen adsorbing, but on the contrary, HA would block adsorbing.

Simulation of DDT adsorption thermodynamic equation: Henry, Langmuir, Freundlich and Temkin Equation were emplyed to simulate the DDT adsorption thermodynamic equation (Table-2).

As described in Table-2, to *o,p*'-DDT, when humic acid was absent, R^2 of Freundlich equation is maximal, with the isotherm style of *o,p*'-DDT (S-type), the conclusion was made that sediment adsorbing *o,p*'-DDT should be depicted by Freundlich equation. The parameter n < 1 illustrated that relationship between adsorption quantity and equilirium concentration is linear[42-44]. Chemical adsorption can explain the adsorbing process of sediment to *o,p*'-DDT. When humic acid was present, R^2 of Langmuir equation is maximal, with the isotherm style of *o,p*'-DDT(L-type), the conclusion can be easily made that sediment adsorbing *o,p*'-DDT should be depicted by Langmuir equation.

TABLE-1
KINETIC FUNCTIONS AND FITTING PARAMETERS OF DDT

Fitted equation		DDT + 0 mg/L HA			DDT + 5 mg/L HA		
		o,p'-DDT	*p,p*'-DDD	*p,p*'-DDE	*o,p*'-DDT	*p,p*'-DDD	*p,p*'-DDE
Two-constant equation	a	5.1953	3.8129	2.4870	4.5155	3.6825	3.4039
	b	0.4382	0.4259	0.4190	0.5717	0.5708	0.4665
	R^2	0.9251	0.9454	0.914	0.9518	0.9489	0.9694
Elovich equation	a	4.0279	2.2884	1.5492	3.7931	3.1436	0.4122
	b	9.3887	6.3952	4.0801	9.4314	8.5040	4.7327
	R^2	0.8609	0.8838	0.8703	0.9631	0.9624	0.9586
Parabolic diffusion equation	a	1.8853	1.7778	1.1410	3.9324	3.2476	0.3302
	b	3.6958	2.5109	1.5853	6.5757	5.3578	2.9892
	R^2	0.9186	0.9377	0.9029	0.9664	0.9645	0.9661
First-order kinetic model	Q_e(exp) (μg g^{-1})	46.7523	33.3253	20.2564	37.8472	30.3495	20.2564
	Q_e(cal) (μg g^{-1})	48.2848	32.8345	20.4497	40.3907	32.6448	19.2366
	K_1/g (μg h)$^{-1}$	0.0239	0.0255	0.0278	0.0239	0.0255	0.0277
	R^2	0.9543	0.9518	0.9569	0.9807	0.9884	0.9681
Second-order kinetic model	Q_e(exp) (μg g^{-1})	46.7523	33.3253	20.2564	37.8472	30.3495	20.2564
	Q_e(cal) (μg g^{-1})	55.2486	37.8788	23.5294	39.8406	33.3333	20.6186
	K_2/g ((μg h)$^{-1}$)	0.0006	0.0009	0.0015	0.0023	0.0025	0.0062
	R^2	0.9589	0.9692	0.9674	0.9911	0.9938	0.9981

TABLE-2
ADSORPTION THERMODYNAMIC FITTING RESULTS OF DDT

Fitted equation	DDT	DDT + 0 mg/L HA		DDT + 5 mg/L HA	
		Model parameter	R^2	Model parameter	R^2
Henry equation	*o,p*’-DDT	$K_d = 0.1195$	0.9100	$K_d = 0.0657$	0.6862
	p,p’-DDD	$K_d = 0.1292$	0.8254	$K_d = 0.0630$	0.9178
	p,p’-DDE	$K_d = 0.1169$	0.7873	$K_d = 0.0753$	0.9662
Langmuir equation	*o,p*’-DDT	$Q_m = 2.47, K_L = 2.07$	0.8921	$Q_m = 3.5557, K_L = 0.0374$	0.8657
	p,p’-DDD	$Q_m = 1.63, K_L = 1.26$	0.7905	$Q_m = 10154.526, K_L = 6.2016 \times 10^{-16}$	0.8903
	p,p’-DDE	$Q_m = 1.50, K_L = 1.28$	0.7447	$Q_m = 12.8566, K_L = 0.0069$	0.9687
Freundlich equation	*o,p*’-DDT	$K_F = 0.0286, n = 0.6975$	0.9469	$K_f = 0.2156, n = 1.5758$	0.8131
	p,p’-DDD	$K_F = -6.84 \times 10^{15}, n = 1.6268$	-0.2	$K_f = 0.0148, n = 0.6871$	0.9909
	p,p’-DDE	$K_F = -1.32 \times 10^{26}, n = 1.6128$	-0.2	$K_f = 0.0997, n = 1.0890$	0.9620
Temkin equation	*o,p*’-DDT	$a = -0.8285, b = 1.1032$	0.5717	$a = -0.5662, b = 0.7012$	0.8431
	p,p’-DDD	$a = -3.8322, b = 2.1904$	0.6836	$a = -2.1930, b = 1.1947$	0.8552
	p,p’-DDE	$a = -3.1195, b = 1.8494$	0.5742	$a = -1.3333, b = 1.0028$	0.9327

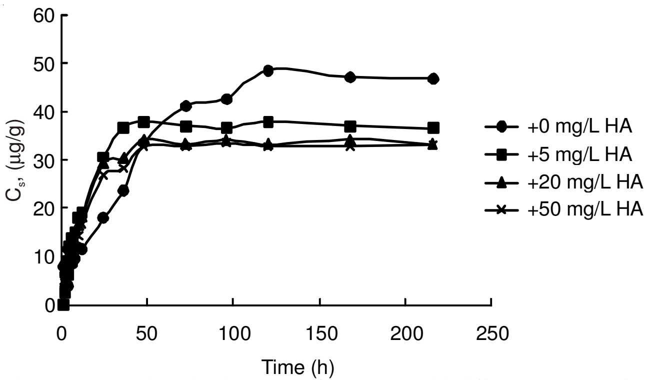

Fig. 3. Adsorption kinetics curve of *o,p*'-DDT with different concentration of humic acid

Dynamics model of DDTs: Calculated from first-order-kinetic equation no matter with/without humic acid, the order of K_1 from big to small was *p,p*'-DDE > *p,p*'-DDD> *o,p*'-DDT, which revealed the adsorptive rate of *p,p*'-DDE was fastest. The adsorptive rate was diverse is the difference of octanol/water partition coefficient. It was also manifested from Fig. 1 that the maximum adsorptive capacity of *o,p*'-DDT without was 48.2848 g/g, which was 1.47 and 2.36 times to these of *p,p*'-DDD and *p,p*'-DDE, respectively. When the system worked with humic acid, the maximum adsorptive capacity of *o,p*'-DDT without was 40.3907 g/g, which was 1.24 and 2.10 times to these of *p,p*'-DDD and *p,p*'-DDE, respectively. The adsorptive amount of sediment to *o,p*'-DDT was still most perfect with maximum amount of a little decline, which accorded with the conclusion from Fig. 1.

K_2 is adsorptive rate constant of second-order-kinetic. the order of K_2 from big to small was *p,p*'-DDE > *p,p*'-DDD > *o,p*'-DDT with/without humic acid, which also revealed the adsorptive rate of *p,p*'-DDE was fastest. The adsorptive amounts of sediments to DDTs declined which accorded with the conclusion from Fig. 1 and first-order-kinetic.

The value of a has something to do with adsorptive capability in elovich equation. The a value of *o,p*'-DDT was maximal, which betrayed that sediment had the strongest adsorptive capability to *o,p*'-DDT.

The states aforementioned declared that adsorptive capacities of sediments to *o,p*'-DDT was always maximum, while the adsorptive rate to *p,p*'-DDE was still fastest with/without humic acid.

Effect of various concentrations of HA to adsorption capacity and rate of DDT was shown in Fig. 3.

Adsorption equilibrium times of DDTs scarcely changed with the concentrations of humic acid vary from 5-50 mg/L, but the equilibrium adsorptive capacity had a slight decline with the increase of concentrations of humic, which resulted from too much HA colloid and part of them free-in-water that adsorbed a great quantity of DDT, which made the adsorptive capability weaken.

Thermodynamic model of DDTs: To *p,p*'-DDD and *p,p*'-DDE, when humic acid was absent, R^2 of Henry and Langmuir equation were essentially equal, but taking isotherm styles of *p,p*'-DDD and *p,p*'-DDE (L-shaped) into consideration, sediment adsorbing *p,p*'-DDD and *p,p*'-DDE should be described by Langmuir equation. Studies showed that organic molecule adsorbed on the surface of solid body may be the results of joint action of several mechanisms[45]. Consequently, both Henry and Langmuir equation could perfectly fit the adsorptive action of *p,p*'-DDD and *p,p*'-DDE. The processes of sedimentary adsorpting *p,p*'-DDD and *p,p*'-DDE were both physical absorption and chemisorption.

With the existence of humic acid, the R^2 of Freundlich for *p,p*'-DDD was more than 0.99, further more, taking it's isotherm style (S-shaped) into account, sediment adsorbing *p,p*'-DDE should be described by Freundlich equation; But for *p,p*'-DDE, it could well explained that *p,p*'-DDE adsorbed by sediment with HA accorded with Langmuir model by combining considerations both the maximal R^2 of Langmuir and the isotherm of L-shaped.

Adsorption models of sediment to *o,p*'-DDT, *p,p*'-DDD and *p,p*'-DDE without humic acid accorded with Freundlich, Langmuir and Langmuir equation, respectively, but with HA it accordingly changed for Langmuir, Freundlich and Langmuir. With the absence of humic acid, it was both physical absorption and chemisorption for *p,p*'-DDD and *p,p*'-DDE and chemisorption for *o,p*'-DDT. When HA participated in this action, all of them shold be chemisorption.

Effect of varying concentrations of HA to isotherm of *o,p*'-DDT was shown in Fig. 4. Take the isotherms of *o,p*'-DDT for an example to investigate the effect of different concentrations of HA to isotherm of DDTs. It was manifested from Fig. 4 that the isotherm style changed from S-type to L-type with humic acid colloid, but the style, adsorption equilibrium time and the maximum adsorption capacity had no changes with the increasing of concentration of HA.

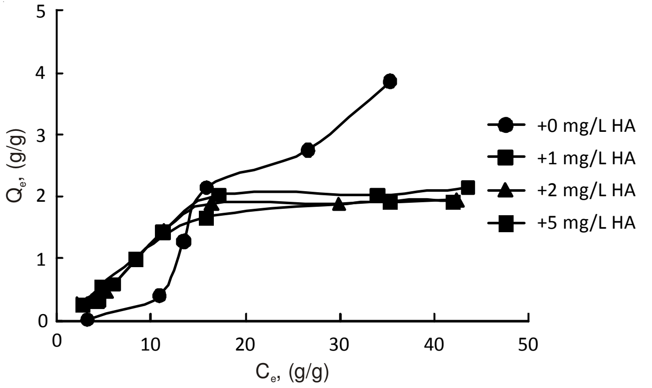

Fig. 4. Adsorption isotherms of *o,p*'-DDT with various concentrations of HA

Conclusion

This paper mainly studied the influence of humic acid colloid on adsorption of DDT in the Wei river sediments in shallow groundwater. Humic acid colloid can speed up the adsorption rate of DDT in sediment, the equilibrium time was shorten from 120 to 48 h. The adsorption kinetics of DDT in sediments without HA conformed to the first-order kinetics equation; that conformed to the first order kinetics equation when humic acid existed in this system. When the systems without humic acid colloid, the forms of the adsorption isotherms of *o,p*'-DDT, *p,p*'-DDD and *p,p*'-DDE in sediments were S-, L- and L- shaped; when the sediments with HA colloid within the experimental concentration range, the forms of the adsorption isotherms of *o,p*'-DDT, *p,p*'-DDD and *p,p*'-DDE in sediments were L-, S- and L- shaped. With the absence of HA, the adsorption of *o,p*'-DDT in sediments were in line with Freundlich equation, the adsorption of both *p,p*'-DDD and *p,p*'-DDE were in line with Langmuir equation. Both physical absorption and chemisorption for *p,p*'-DDD and *p,p*'-DDE and chemisorption for *o,p*'-DDT. When HA participated in this action, the adsorption of *o,p*'-DDT and *p,p*'-DDE in sediments were all in line with Langmuir equation, the adsor-ption of *p,p*'-DDD in line with Freundlich equation. All of them should be chemisorption. Results about adsorption dynamics indicated that equilibrium time of DDT has been less affected by vary concentrations of HA; while the adsorp-tion rate and the amounts would decrease with the increasing of concentration of HA. Results about thermodynamics showed that vary concentrations of HA cannot change the isotherms and the models in the current studies.

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