Kinetics of Phosphorous Sorption by Sediment in a Subtropical Reservoir

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The kinetics of phosphorus sorption by sediments collected from the FUSHI reservoir in China was conducted to assess the sorption process and characteristics. Experiments showed that the sorption process consisted of fast sorption, slow sorption and equilibrium stages. Duration of each stage ranged from 10 min to 10 h. The kinetic process could be described by pseudo first-order, pseudo second-order and Evolich function. In the sorption process, ion exchange and ligand exchange were the dominant sorption actions. Sorption amount, sorption rate and sorption efficiency all increased with increasing initial concentration and decreased with extending sorption time. During the initial 0.25 h, sorption rate reached a maximum with 152.63 and 83.39 mg/(kg h^{-1}) while concentration were 0.5 and 0.3 mg/L, respectively. About 43.10-79.36 and 37.17-19.09 % of the sorption were completed in the fast stage and slow stage under concentration as 0.3 and 0.5 mg/L.

Key Words: Reservoir sediment, Sorption kinetic, Sorption rate, Sorption efficiency.

INTRODUCTION

Phosphorus can be found in the sediment in the form of calcium, iron, aluminum complex salts and organic species is one of the main nutrients or adsorbed on the surface of minerals and plays a predominant role to cell growth of plants including algae[1,2], but its excessive supply or leaching into watercourses can lead to eutrophication and other environmental ecosystem problems[3,4]. In recent years, much attention have been changed from nitrogen as a nutrient and pollutant[5] towards the less soluble and non-volatile contaminating nutrient P. Numerous studies have shown that high loading of P finally arrives in natural aquatic ecosystems and accumulates in sediments acting as a sink for P[6,7], which may result in serious problems of aquatic ecosystems, water environment and even human health.

The transformation processes of P on sediment-water interface are important for the availability of P and environment. The sorption of P on the sediments is one of the main processes used to regulate the mobilization and dynamic behaviour of P in aquatic sediments, because P is unlike other nutrients and has a strong affinity to react with sediment particles.

Substantial researches with respect to P sorption and sorption kinetics in soils and sediments have been carried out largely in temperate regions[8-13]. Soil sorption, desorption and kinetics process have a lot of information. However, little information is available with respect to non-steady-state kinetics in aquatic sediments. Information is limited on kinetic rates currently for each sorption phase and corresponding sorption efficiency. This substantially restricts the application of the sorption process in modeling of P dynamics in aquatic sediments.

The kinetic process of sorption includes chemical reaction and ion diffusion[14]. Chemical reaction usually contains the combination of functional group with other ions and ion change reaction on adsorbent surface. Ion diffusion is a complex process that free ions diffused into the interior micropores of particulate matter. Kinetic model could demonstrate the kinetics process that reaction between adsorbate and adsorbent and assess the characteristics and parameters during the sorption process.

In this study, the kinetics of P exchange between the sediment and water was investigated in order to understand sorption processes at different concentration. The objectives of the study are through the sorption kinetics to: (1) illustrate the kinetic process of P sorption to identify sorption stages (2) fitting the sorption process with kinetic models and determine the parameters and sorption types (3) calculate the sorption rates at different time periods (4) finally evaluate the sorption efficiency at each stage.

EXPERIMENTAL

Experiments were designed and conducted in Zhejiang University, China. Instruments were provided by College of

Environmental and Resource Sciences. The experiment included samples collection and preparation, sorption kinetics and data analyses.

Background of FUSHI reservoir: FUSHI reservoir is a subtropical reservoir located in Zhejiang Province, China. It was formed by damming the Xixi River in 1980. The reservoir has a maximum storage capacity of 218,000,000 m^3 and about 331 km^2 upstream areas. It provides 25,000 m^3/d drinking water, irrigates 8000 ha fields and generates 5,400 kW/y power. The upstream of FUSHI reservoir is mainly hills and foothills which are covered by bamboo and Chinese chestnut. Soils in hills are leanness and easy to be eroded. More fertilizers are used in order to improve the growth, which lead to heavy nutrient loss and soil erosion. The area experiences a typical subtropical marine-monsoon climate. The mean annual precipitation is 1344.1 mm and the mean annual temperature is 16.6 ℃. The concentration of P in the reservoir and river, which injectes into the reservoir, ranges from 0.012 to 0.07 mg/L.

Sampling and preparation of sediments: Four sediment samples S1, S2, S3 and S4 were taken from the FUSHI reservoir using a special messenger-activated core-sampler (ETC-200) in August, 2009. Water depths of the sample stations are about 6 m for S1 and S4 and 8 m for S2 and S3. The collected samples were stored in an ice box and transported to the laboratory immediately, centrifuged for 10 min at 5,000 rpm to remove most of pore water, then passed through 100 mesh and stored at 4 ℃ for experiment after air-dried.

The composition of P in sediments has been investigated and is shown in Table-1. Using the schemes of chemical extraction suggested by Hieljtes and Lijklema[15], the different species were ascertained to be loosely bound P, iron-and aluminum-bound P, calcium-bound P and residual P consisting of organic fraction mainly. The average value in Table-1 showed that iron-bound P accounting for 16.52-23.44 % was followed by the aluminum-bound phosphorus accounting for 2.35-3.70 % of total P. The results suggest that sorption characteristics of P in the FUSHI reservoir could be influenced by the performance of iron and aluminum.

Sorption kinetics: Artificial P solutions at 0.5 and 0.3 mg/L were prepared for sorption kinetic tests by dissolving a certain amount of analytically pure K_2HPO_4 in distilled water. Phosphorus sorption kinetics was conducted at 25 ± 1 ℃ and a series of two 50 mL polyethylene centrifugal tubes for each sample were prepared by mixing 0.25 g dried sediment with 25 mL solutions which contain P C_o at 0.5 and 0.3 mg/L, respectively. Two drops of 0.1 % chloroform was added to inhibit bacterial activity[16]. Then the tubes were shaken with 200 rpm at 25 ± 1 ℃. Solution samples were obtained after shaking with the different intervals for 0, 0.25, 0.5, 1, 1.5, 2.5, 5, 12, 18 and 24 h of sorption and were immediately centrifuged

at 4,000 rpm for 10 min, then filtered through 0.45 μm filter membrane, finally measured the P equilibrium concentration (C_{eq}) by the molybdate-blue method with a spectrophotometer (UV/VIS-2550)[17].

Definitions: The amount of sorbed P was calculated by the formula (1):

$$q = (C_o - C_{eq})\frac{v}{w} \quad (1)$$

where, q was the sorbed amount (mg/kg), w and v were, respectively the sample weight (g) and solution volume (mL) of K_2HPO_4.

Four typical kinetic equations, as described below were used for fitting the experimental kinetic data;

Pseudo first-equation: $\ln(q_e - q_t) = \ln q_e - k_1 t$

Pseudo second-equation: $\dfrac{t}{q_t} = \dfrac{1}{k_2 q_e^2} + \dfrac{t}{q_e}$

Elovich equation: $q = \alpha + \beta \ln t$

Intraparticle diffusion equation: $q_t = k_i h^{1/2}$

where q_t and q_e are the amount adsorbed at time t and equilibrium (mg/kg), respectively, t is the sorption time (h) and k_1 and k_2 are sorption contents, α and β are sorption rate content (mg/(kg h)) and desorption rate content (mg/(kg h)), k_i is diffusion rate content (mg/(kg h)).

The pseudo-first-order (and also the pseudo-second order) is based on the adsorption capacity, it only predicts the behaviour over the "whole" range of studies supporting the validity and is in agreement with chemisorption being the rate-control[18]. Elovich equation does not predict any definite mechanism, it emphasis on different kinetics, but it is useful in describing adsorption on highly heterogeneous adsorbents[19]. The intraparticle diffusion equation could identify weather or not the interior diffusion is dominant during the ion sorption process.

Sorption rate (SR) of phosphorus was calculated by the formula (6):

$$SR = \frac{(q_{t_2} - q_{t_1})}{(t_2 - t_1)} \quad (6)$$

In formula (6): SR, q_{t_2} and q_{t_1} were sorption rate, sorption amount at t_2 and t_1 and t_2 and t_1 were time points.

The sorption efficiencies (SE) for different phases were estimated according to final adsorbed amount of P and were calculated by the formula (7):

$$SE = \frac{(q_e - q_b)}{q_e} \quad (7)$$

In formula (7), the SE, q_e and q_b were respectively the sorption efficiency, sorption amount in the ending and

TABLE-1					
PHOSPHORUS COMPOSITION IN SEDIMENTS OF FUSHI RESERVOIR					
Samples	Loosely P (mg/kg)	Al-P (mg/kg)	Fe-P (mg/kg)	Ca-P (mg/kg)	Residual P (mg/kg)	TP (mg/kg)
S1	0.04	19.8	139.23	75.51	592.34	842.84
S2	0.04	23.96	174.6	68.56	549.18	821.69
S3	0.03	21.54	136.3	75.51	342.04	581.61
S4	0.02	14.91	104.24	72.20	310.27	510.13

beginning of any phase and the q_e was the sorption amount at final equilibrium point.

Date analyses: All data presented are the mean values. The measurement was done with 3 replicates. The software of Office Excel and Origin 8.0 were used to calculate, fit and analyze data.

RESULTS AND DISCUSSION

Phosphorus sorption kinetics: Phosphorus sorption by sediments is considered to be a time dependent process[8] and has been regarded as a (multiple) compound kinetic process involving at least an initial fast adsorption stage followed by a slow adsorption stage[20]. The kinetics plots for the adsorption of P are depicted in Fig. 1.
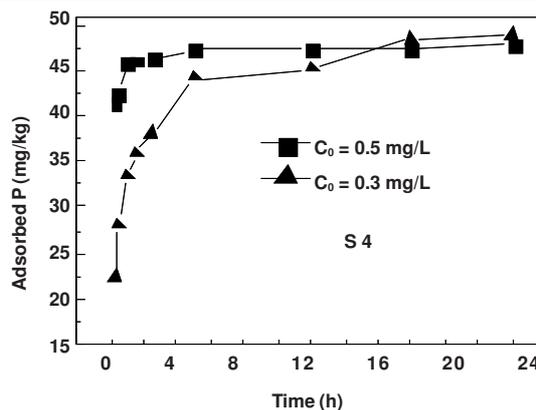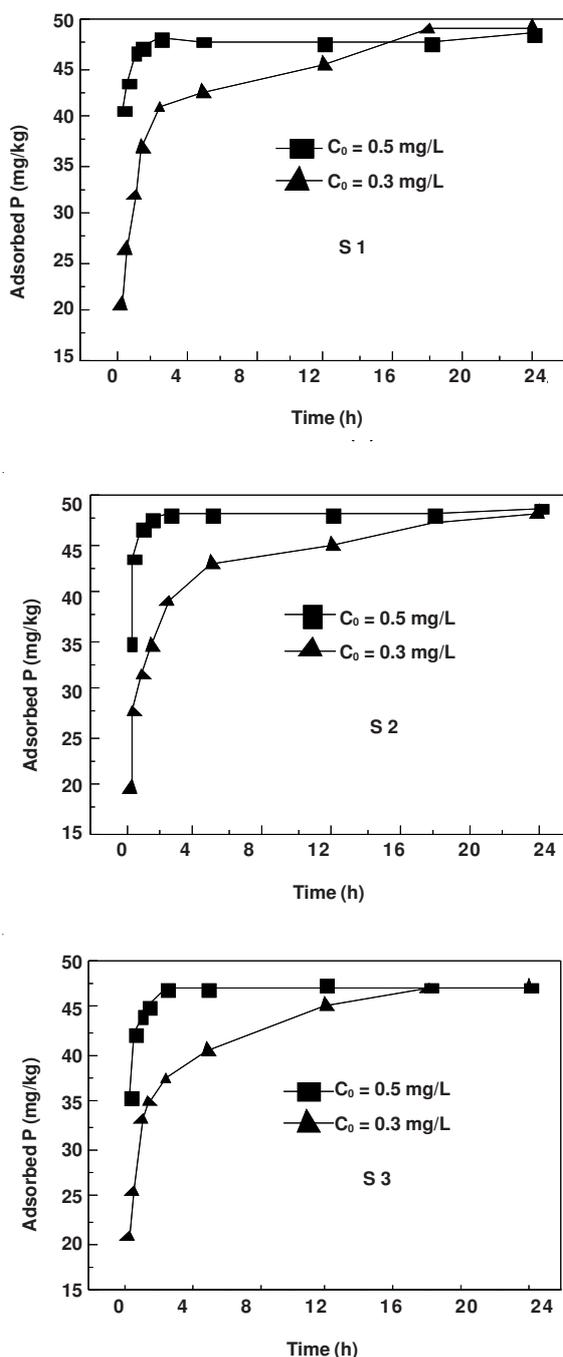
Fig. 1. Kinetic process of phosphorus adsorption on sediments with different concentration

The amount of sorbed P in sediments increased with time (Fig. 1). The kinetic processes of sorption appeared to be a very fast adsorption at the initial 0.25 h, followed by a slow adsorption stage which was completed within 0.25-2.5 h. From the sorption kinetic (Fig. 1), it was noted that sorption amounts were 42.98 mg/kg, 26.92 mg/kg, 45.65 mg/L and 33.43 mg/L at an average value during the initial 0.25 h and 0.25-2.5 h as concentration was 0.5 and 0.3 mg/L, respectively. The sorption amounts have a slow increasing in the periods from 0-0.25 h to 0.25-2.5 h, so the first 0.25 h was usually recognized as fast adsorbing stage and during 0.25-2.5 h was as slow adsorption stage. The fast sorption time was nearly the reported data that fast sorption completed in about 10 min[8,21]. Sorption amounts have only a tiny increasing or decreasing, but the tendency was reached an equilibrium stage basically. This process lasted in the scale of more than 10 or 20 h, continuous adsorption or desorption appeared to take place at a very low rate, this was accordance with the reported result[22,23], so this process was regarded as equilibrium stage.

In all, it indicated that both sorption time and C_o affected the sorption amount of sediments at each stage. Sorption amount increased with the increasing of C_o and the extending of sorption time, which was accordance with the reports[22,24].

Model calibration and calculated parameters: Kinetic sorption processes of P on sediments of FUSHI reservoir could be described by the pseduo first-order, second-order kinetics function and Elovich equation. The results were listed in Table-2. It showed that pseduo second-order function (average, $R^2 = 0.99$) was better to describe the sorption kinetic process than Elovich equation (average, $R^2 = 0.80$) and pseudo first-order (average, $R^2 = 0.79$). Concentration didn't influence the fitting of kinetic process by pseudo-second function ($R^2 = 0.99$). However, pseudo first-order function described the sorption kinetics process of P better under concentration at 0.5 mg/L (average, $R^2 = 0.80$) than at 0.3 mg/L (average, $R^2 = 0.64$), while the Elovich function was better at concentration as 0.3 mg/L (average, $R^2 = 0.86$) than 0.5 mg/L (average, $R^2 = 0.79$).

The parameters α and β in Elovich model were the constants of sorption rate and desorption rate, respectively. Table-2 demonstrated that sorption and desorption simultaneously occurred during the sorption process whatever concentration as 0.5 or 0.3 mg/L and always existed $\alpha > \beta$ in the whole sorption process.

Sample	C_o (g/kg)	Pseudo first-order kinetic			Pseudo second-order kinetic			Simple Elovich equation		
		q_e (mg/kg)	k_1 (mg (g/h))	R^2	q_e (mg/g)	k_2 (mg/(g h))	R^2	α (mg/(g h))	β (mg/(g h))	R^2
S1	0.5	47.45	7.35	0.78	48.33	0.38	0.99	45.10	1.31	0.62
	0.3	44.97	1.56	0.83	50.09	0.03	0.99	31.72	6.10	0.95
S2	0.5	47.93	5.03	0.98	48.64	0.30	0.99	43.76	2.10	0.50
	0.3	43.8	1.60	0.80	48.86	0.03	0.99	31.05	5.94	0.96
S3	0.5	46.34	5.63	0.89	47.39	0.36	0.99	42.69	1.98	0.66
	0.3	42.80	1.73	0.79	48.06	0.04	0.99	30.83	5.71	0.97
S4	0.5	46.46	8.32	0.55	47.71	0.03	0.99	44.43	1.25	0.77
	0.3	43.96	1.88	0.74	49.56	0.04	0.99	32.43	5.63	0.97

TABLE-2
SORPTION KINETIC PARAMETERS OF PSEUDO EQUATION

The sorption kinetics could not be described by the intra-particle diffusion equation. It indicated that interior diffusion didn't affected the P sorption process of P on FUSHI reservoir sediments obviously. However, it could not demonstrate the occurrence of interior diffusion during the sorption process. So, ion exchange and ligand exchange were likely the two most dominant sorption actions for sediment samples.

Phosphorus sorption rate: The sorption rate data (Table-3) of each time scale showed sediments reached the maximum sorption rate with 162.98, 138.71, 142.90 and 165.92 mg/(kg h) during the initial 0.25 h as concentration equal 0.5 mg/L and with 82.50, 78.71, 82.42, 89.92 mg/(kg h) at concentration equal 0.3 mg/L, respectively for S1, S2, S3 and S4. These sorption rate values were close to other similar reports[13,21,22].

During the sorption process, existed some fluctuations between sorption or desorption at different time intervals. The negative values in Table-3 meaning the sorption rate in this time interval was less than the former interval. It indicated sediment desorption P at this time scale. For example, the sorption rate was -0.08 mg/(kg h) in period of 2.5-5.0 h, it indicated sediment released P. But the basic tendency of sorption rate changed less with the time extending. This change tendency was accordance with the sorption principle. In fact, sorption and desorption occurred simultaneously during the sorption process. Sediment will adsorb P if sorption rate was more than desorption rate. On the contrary, sediments will release P when sorption rate was less than desorption rate. When sorption rate and desorption rate were equal, the sediment-water system is already in a dynamic equilibrium without net adsorption and desorption.

Phosphorus sorption efficiency: Sorption kinetics part has defined the first 0.25 h as fast sorption phase, during the 0.25-2.5 h as slow sorption phase and from 2.5-24 h as

equilibrium phase. There are two hypotheses in the process of calculated sorption efficiency, firstly, assumed at 24 h sorption reached the final equilibrium, so q_{24} equal q_e; secondly, the total sorption efficiency was 100 % and the sorption efficiency at equilibrium stage was calculated by 100 % minus the sum of phase 1 and phase 2. The sorption efficiency at different phases was calculated based on the above definitions, hypothesis and function (7), then it was plotted in Fig. 2.

The results indicated that, both fast and slow sorption phase had completed about 98.45 % at an average value and with an average 79.36 and 19.06 %, respectively, while concentration was 0.5 mg/L. However, under concentration as 0.3 mg/L, both fast and slow sorption phase completed 80.27 % at an average value, with an average 43.10 and 37.17 %, respectively. So, 1.55 and 19.73 % of q_e were completed at equilibrium stage.

At fast sorption phase, average 79.36 and 43.10 % of q_e was completed respectively as concentration at 0.5 and 0.3 mg/L. This demonstrated that the concentration had a positive relationship with the efficiency of fast sorption phase. At slow and equilibrium sorption stages, average 19.09, 37.17, 1.54 and 19.73 % of sorption were completed, respectively, as concentration at 0.5 and 0.3 mg/L, this demons-trated concentration had a negative-relationship with the sorption efficiency of slow and equilibrium sorption phase.

Conclusion

The sorption kinetic of P on reservoir sediments with a special P concentration was designed to investigate the process and characteristics of sorption kinetic. In conclusion, this study has demonstrated that the kinetic processes of P sorption on sediments of FUSHI reservoir appear to have three clear stages-an initial fast stage, followed by a slow sorption stage and

TABLE-3
SORPTION RATE OF P ON DIFFERENT TIMES SCALES (mg/kg h)

Time (h)	S1		S2		S3		S4	
	0.5 (mg/L)	0.3 (mg/L)	0.5 (mg/L)	0.3 (mg/L)	0.5 (mg/L)	0.3 (mg/L)	0.5 (mg/L)	0.3 (mg/L)
0-0.25	162.98	82.50	138.71	78.71	142.90	82.42	165.92	89.92
0.25-0.5	5.42	11.23	17.55	15.55	12.93	9.61	1.67	11.17
0.5-1	6.55	10.89	5.94	7.48	3.72	15.04	6.72	10.50
1-1.5	0.20	3.37	0.66	2.07	0.57	1.25	0.19	1.71
1.5-2.5	0.92	4.06	0.63	4.49	1.85	2.42	0.19	2.12
2.5-5	-0.08	0.64	0.03	1.60	0.04	1.27	0.38	2.39
5-12	-0.03	0.41	-0.04	0.28	0.05	0.67	0.00	0.14
12-18	0.03	0.60	0.00	0.43	-0.01	0.28	0.02	0.56
18-24	0.11	0.06	0.14	0.12	0.00	0.04	0.07	0.07

Fig. 2. Sorption efficiency of P on different sorption phases

exchange were the two most dominant sorption actions for sediment and interior diffusion did not obviously affect the P sorption process on reservoir sediments. The sorption rate and sorption efficiency of P sorption in sediments drops with the decreasing of concentrationb and time extending. These suggested that the concentration of adsorbate and sorption time were two key factors for the pollution manages and control, it determined what kind of sorbent will be selected and the major expense. The optimum collocation among adsorbate, sorbent and sorption time was a critical step during the processes of the environment manages and pollution control, because environment manage and pollution control are complicated systems engineering.

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finally an equilibrium stage and the duration of each sorption stage ranged from 0-0.25, 0.25-2.5 and 2.5-24 h, respectively. This result suggested sorption process usually completed within the hours and this may be useful for the environment manage and pollution control. Sorption kinetics can be described by the pseudo first-order, pseudo second-order and Elovich function and this indicated ion exchange and ligand