Experimental investigation of the effect of flow turbulence and sediment transport patterns on the adsorption of cadmium ions onto sediment particles

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Abstract

The mechanism of flow turbulence, sediment supply conditions, and sediment transport patterns that affect the adsorption of cadmium ions onto sediment particles in natural waters are experimentally simulated and studied both in batch reactors and in a turbulence simulation tank. By changing the agitation conditions, the sediment transport in batch reactors can be categorized into bottom sediment-dominated sediment and suspended sediment-dominated sediment. It is found that the adsorption rate of bottom sediment is much less than that of suspended sediment, but the sediment transport pattern does not affect the final (equilibrium) concentration of dissolved cadmium. This result indicates that the parameters of an adsorption isotherm are the same regardless of the sediment transport pattern. In the turbulence simulation tank, the turbulence is generated by harmonic grid-stirred motions, and the turbulence intensity is quantified in terms of eddy diffusivity, which is equal to $9.84F$ (F is the harmonic vibration frequency) and is comparable to natural surface water conditions. When the turbulence intensity of flow is low and sediment particles stay as bottom sediment, the adsorption rate is significantly low, and the adsorption quantity compared with that of suspended sediment is negligible in the 6 h duration of the experiment. This result greatly favors the simplification of the numerical modeling of heavy metal pollutant transformation in natural rivers. When the turbulence intensity is high but bottom sediment persists, the rate and extent of descent of the dissolved cadmium concentration in the tank noticeably increase, and the time that is required to reach adsorption equilibrium also increases considerably due to the continuous exchange that occurs between the suspended sediment and the bottom sediment. A comparison of the results of the experiments in the batch reactor and those in the turbulence simulation tank reveals that the adsorption ability of the sediment, and in particular the adsorption rate, is greatly over-estimated in the batch reactor.

Key words: water flow; sediment transport; pollutant; interactions; turbulence, adsorption

Introduction

Over the past few decades, studies on the fate and transport transformation of trace heavy metals that enter natural waters have received increasing attention worldwide (Forster and Wittmann, 1981; Hart, 1986; Horowitz, 1995; Calmano et al., 1997; Ji et al., 2002; Monte et al., 2005; Mohamed and Hatfield, 2005). The potential influence of environmental variables on trace heavy metal partitioning have been widely identified and investigated through batch reactor experiments (McKinley and Jenne, 1991; Warren and Zimmerman, 1994; Patrick and Verloo, 1998; Wang and Chen, 2000). These studies mainly concentrate on the effects of the adsorbate itself, which include the type of heavy metal ion, the initial concentration of dissolved heavy metal, and the presence of other heavy

metal ions; the effects of the adsorbents, such as the mineral components of the sediment or the source of the sediment, the composition of the grain sizes, and the sediment concentration; the effect of the adsorption medium, such as the degree of mineralization in the water, the pH value, the oxidation-reduction potential, and the water temperature; and the effects of time that is required to reach an adsorption equilibrium of heavy metals onto sediment particles. A detailed review of these effects can be found in Huang (1993) and Huang and Wan (1995). However, these batch reactor experiments ignore the effects of the operational conditions in the reactor on the adsorption of heavy metal onto sediment particles, and few reports have intentionally been tried to quantify the effects of varying intensities of stirring, shaking, vibration, or oscillation in batch reactor experiments. This may be partly because it is very difficult to quantify the operational conditions, which makes it very difficult to compare the similarities of water flow and sediment transport in batch reactors and in natural waters. Moreover, in batch reactor experiments, the

reactors employ beakers that are generally less than 100 ml in volume (Huang and Wan, 1995) and the designed amount of water, sediment, and heavy metal ions that are continuously vibrated or oscillated, and thus the water, sediment, and heavy metal ion motions in such reactors may differ greatly from those in natural waters. For example, the turbulence intensities of flow in such reactors are more uniform and much larger than those in natural waters, which may cause the contact between sediment particles and trace metal ions to be more frequent.

In natural waters, the fate of many trace heavy metals is controlled to a large extent by adsorption processes and the dynamics of the sediment particles (Horowitz, 1995). However, research on the effects of sediment transport patterns and the dynamics of sediment particles on the fate and transport transformation of heavy metal pollutants in natural waters is seldom reported.

In this study, the effect of sediment transport patterns on the adsorption of cadmium ions onto sediment particles with changing agitation conditions in a commonly used batch reactor experiment is first simulated. Here sediment transport patterns are defined as either suspended sediment or bottom sediment for the sake of simplicity. The latter are the sediments other than suspended sediment. Second, a turbulence simulation tank (TST), in which a flow turbulence that is comparable to natural surface water conditions is generated by the harmonic motion of disturbed grids, is used to simulate the interactions between water, sediment, and cadmium ions, and special attention is paid to the effects of turbulence intensities of flow, sediment supply conditions, and sediment transport patterns on the adsorption of cadmium ions. Finally, the results obtained in the batch reactor experiment and in the TST experiment are compared.

1 Materials and methods

1.1 Pre-treatment of sediment samples

Sediment samples were taken from the Yellow River in China. Non-polluted deposits in the settling basin of the Zhengzhou Water Company of China were collected and freeze-dried at extra-low temperatures (–20°C to –25°C). The dried, scattered sediments were then sieved manually through five kinds of nylon sieves of 460-mesh (33 μm), 400-mesh (38 μm), 360-mesh (40 μm), 200-mesh (74 μm), and 100-mesh (149 μm) gauges to determine the classes of sediment size (Bowman, 2003). The size classes are less than 33 μm, 33–38 μm, 38–40 μm, 40–74 μm (not used here), and 74–149 μm. All of the samples were kept in a refrigerator until they were used. The content of organic matter of the sediment samples was measured (Huang, 2003a), and the sediment sample of less than 33 μm had an organic matter content of 2.05%.

1.2 Reagents and determination of concentrations

Cadmium, which is a typical heavy metal pollutant, was investigated in the experiments. Samples of 10-ml aliquots that were taken at certain time intervals were filtered

through a 0.5-μm membrane filter, and the concentration of cadmium ions in the filtrate was measured by conventional flame atomic absorption spectrophotometry using the standard procedures that are suggested by Lacerda *et al.* (1984) and Tan (1996). It is assumed that the difference between the cadmium that is added (the concentration of dissolved cadmium in the blank solution) and the cadmium that is left in the solution at the end of the experiment is absorbed onto the sediment. During the sampling process, the sediments in the vessel were kept in suspension by the agitation of the vessels. The temperature of the water was measured both at the beginning and at the end of each experiment, and the pH level was between 6–7 during all of the experiments. All of the experiments were operated in parallel.

The reagents were all chemical grade. All of the glass and plasticware was previously soaked in 10% (v/v) nitric acid overnight and rinsed five times with double deionized water.

1.3 Batch reactor experiments

The discharge of pollutants, the transport of water, and the sediment particles in natural waters are all simplified in batch reactor experiments, and sediment particles are simplified into the categories of suspended loads and bottom sediment.

In these experiments, 1000 ml beakers were used as reactors. Generally, 500 ml of double deionized water and a designed amount of sediment sample were added into the reactors, each of which had a rotating plastic propeller that was driven by electricity, and stirred, except in Run B1, in which the reactor had no propeller. Because the propeller was close to the bottom of the beaker, steady suspended sediment contributions in Runs B2, B3, and B4 were achieved very quickly, generally less than 10 min. The solution was sampled and the initial concentration of dissolved cadmium was measured. The cadmium ion solution of a designed concentration was added, and the time was recorded as $t=0$. The rotational speed and position of the propeller were kept constant during the experiments, except when they were changed intentionally.

Two sets of simulation experiments, each consisting of four runs, were conducted. A sediment sample of less than 33 μm was used, and the designed suspended sediment concentration was 10 kg/m^3 in all of the experiments. The concentration of the suspended sediment at the half-water depth of each reactor was measured, and as the water

Table 1 Agitation conditions in the reactor experiment

Run	Description of agitation conditions (the intensity is quantified by the concentration of suspended sediment)
B1	A clear glass rod was used to manually stir the solution gently at the beginning of the experiment to uniformly distribute the concentration of dissolved cadmium in the reactor (no further stirring)
B2	A propeller was slowly rotated for 2 h and then stopped, then the solution was kept stationary
B3	A propeller was quickly rotated for 2 h and then stopped, then the solution was kept stationary
B4	Strong stirring by a propeller continued for 7 h and then stopped, then the solution was kept stationary overnight

depth was very shallow (about 5 cm), the concentration of the suspended sediment at the half-water depth was taken as the average concentration in the reactor. Once the concentration was less than designed value, it was considered that some of the added sediment particles had settled at the bottom, and that there was bottom sediment in the reactor.

The agitations in each set, which moved the water, cadmium ions, and sediment particles and controlled the concentration of the suspended sediment in the reactor, are shown in Table 1. It was very hard to directly quantify and differentiate the agitation conditions, and the concentration of the suspended sediment was thus intended to represent these conditions in the different runs.

The experiment process can be divided into three time stages: 0–2 h, 2–7 h, and 7–24 h (32 h for Set 2).

1.4 TST experiments

The turbulence simulation tank (TST) (Fig.1), in which turbulence is generated by the up and down vibration of a set of grids, was first introduced by Rouse (1938) to study the mechanism of particles in suspension. Yang and Chien (1986), Chien and Wan (1999) used a similar device to investigate the flocculent structure of clay slurries. The device was modified by Huang (1993), who replaced all of the submerged parts with parts that were made of plexiglass. The coefficient of the vertical turbulent diffusion in a TST, E_y, can be calculated by the empirical equation $E_y=9.84F$ (Yang and Chien, 1986), in which F is the vibrating frequency of the grids in 1/s, and E_y is in units of cm^2/s. The TST has the advantage of being able to produce water and sediment motions that are similar to those in natural waters, and the design concept of the tank has been rigorously investigated (Rouse, 1938; Yang and Chien 1986; Chien and Wan, 1999).

In the TST of this experiment, four plexiglass tubes were mounted onto one wall of the tank at different depths, and were connected to rubber tubes for sampling. Before each sampling, the leftover solution in the rubber tubes was discarded.

Before carrying out the experiments, the tank was first soaked in 10% (v/v) nitric acid overnight and rinsed three times with double deionized water. A pre-determined volume of double deionized water was added to the tank before the vibrating grids were started up. A given amount
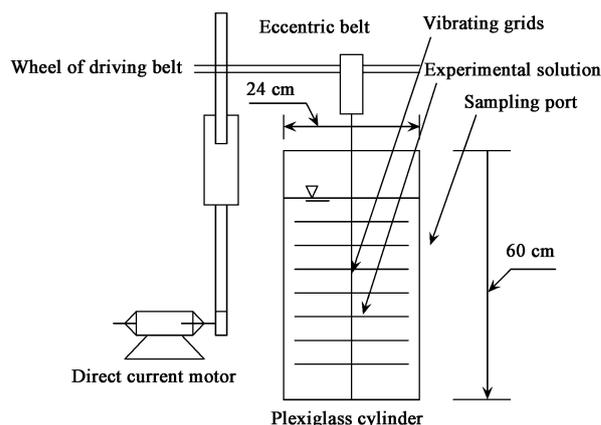

Fig. 1 Turbulence simulation tank (TST).

of sediment was added to the tank, and after the grids had vibrated at the designed frequency for about 2 h, stable (equilibrium) distributions of the suspended sediment in the tank were achieved. Muddy water samples from all the four tubes were taken to measure the concentrations of the suspended sediment and the initial dissolved cadmium, with the concentration of the suspended sediment being measured by the volume method (Yang and Chien, 1986). It was found that the initial concentration of dissolved cadmium was below the limit of detection. A pre-determined volume and concentration of cadmium ion solution was then added at the surface of the water (the top of the tank) at a time that was defined as zero ($t=0$). Muddy water samples from the four tubes in the tank were sampled at certain time intervals, and were filtered with a 0.45-μm filter membrane. The extracted filtrate was then used to measure the concentration of dissolved cadmium. The determination of the concentration of dissolved cadmium in the filtrate followed the aforementioned procedure. All of the labware and equipment that had come into contact with the sediment and muddy water were washed in acid and thoroughly rinsed five times with double deionized water.

The experiment was run nine times, and the experimental conditions are listed in Table 2. The water depth in all of the experiments was 50.5 cm, the temperature of the solution in the TST for Runs 1 and 7 was 27–28°C and for Runs S8 and S9 was 23–24°C, and the pH values were all 6–7.

Table 2 Experimental conditions and results in the TST

Run	F (1/s)	E_y (cm^2/s)	W (g)	D (mm)	H (cm)	s^* (kg/m^3)	W_1 (g)	W_2 (g/cm^2)	D_1 (cm)	D_1/D	Time (h)	V_a (mg/L)	Remarks
S1	4.55	44.7	300	0.033–0.038	45.5	3.5	220	0.49	0.51	140.5	5.3	4.0-1.3	No
S2	4.55	44.7	80	0.033–0.038	45.5	3.5	0	0	0	0	5.5	4.8-2.95	Yes
S3	1.63	16.1	80	0.074–0.149	45.5	≈0	80	0.18	0.19	16.5	5.5	4.5-4.4	Ny
S4	4.79	47.1	80	0.074–0.149	45.5	1.0	60	0.13	0.14	11.9	5.5	3.8-2.1	Yes
S5	1.83	18.0	270	0.074–0.149	45.5	≈0	270	0.60	0.62	54.9	6.0	4.3-4.2	Ny
S6	1.44	14.2	200	<0.033	45.5	0.3	190	0.42	0.43	>129.2	6.0	4.0-3.4	Yes
S7	4.76	46.9	200	<0.033	45.5	4.5	100	0.22	0.22	>68.1	6.0	2.8-0.5	Yes
S8	4.55	44.7	300	0.038–0.400	45.5	3.0	242	0.54	0.54	70.3	8.0	2.9-0.6	No
S9	4.55	44.7	58	0.038–0.400	45.5	3.0	0	0	0	0	8.0	4.1-3.2	Yes

No: means that the adsorption of cadmium ions by the sediment has not reached an equilibrium; Yes: means that the equilibrium adsorption of the cadmium ions by the sediment has been reached; Ny: means that the adsorption of the cadmium ions by the sediment is unremarkable.

In Table 2, W is the mass of the added sediment, D is the grain size of the added sediment, H is the water depth at the fourth sampling place, which was closest to the bottom of the TST, $s*$ is the concentration of the suspended sediment at the fourth sampling place (from top to bottom), W_1 is the calculated mass of the bottom sediment, W_2 is the average mass of the bottom sediment on the bed (= W_1/A), A is the area of the bottom of the TST, D_1 is the calculated thickness of the bottom sediment (=$W_1/A/\rho_s/p$), ρ_s is the density of the sediment (=2.65 g/cm^3), p is the porosity of the sediment (=0.37), D_1/D is the relative thickness of the bottom sediment, V_a is the difference of the dissolved cadmium concentration at a water depth of y=45.5 cm between the measured initial value and the last, Remarks is a qualitative description in whether the adsorption reaches equilibrium or not, and the time is the duration of an experiment.

2 Results and discussion

2.1 Results of the batch reactor experiments

The concentration of dissolved cadmium and suspended sediment in the two sets in the first seven hours are shown in Fig.2 (stages 1 and 2 only), and the results after seven hours are shown in Table 3 (stage 3), in which c denotes the concentration of dissolved cadmium.

From Fig.2, it can be seen that the concentration of suspended sediment in the four runs was significantly different as a result of the different agitation conditions in the first two hours of the experiment. Although the added sediment in the four runs was the same, the sediment transport patterns were significantly different. The sediment particles mainly stayed as bottom sediment in Runs B1 and B2 of the two sets, and were mainly suspended in Runs B3 and B4.

The extent and rate of descent of the dissolved cadmium concentration differed greatly for different initial concentrations of suspended sediment because of the variation in agitation conditions. The concentration of suspended sediment in the four runs in Set 1 was 0.5, 1.6, 9.1, and 8.8 kg/m^3 during the first stage of the experiment, as shown in Fig.2a, and the concentration of dissolved cadmium correspondingly decreased by 1.28, 1.4, 2.63, and 2.49 mg/L, and the average rate of decrease of the dissolved cadmium concentration was 0.64, 0.7, 1.32, and 1.25 mg/(L·h), although the amount of total sediment
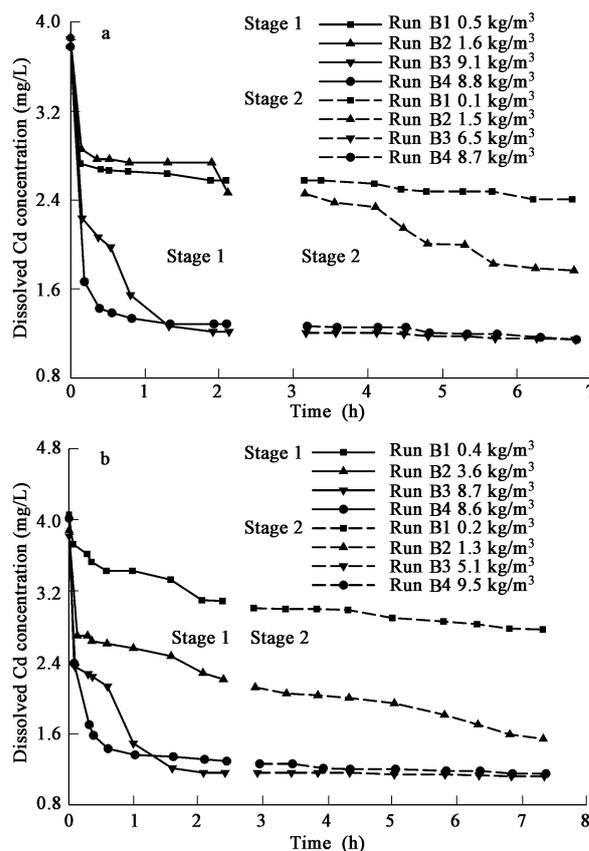

Fig. 2 Variation in the concentration of dissolved cadmium over time for different sediment transport patterns in Set 1 (a) and Set 2 (b).

particles in the four runs was the same. In the four runs of Set 2, the concentration of suspended sediment was 0.4, 3.6, 8.7, and 9.0 kg/m^3 in the first stage, as shown in Fig.2b, the concentration of dissolved cadmium decreased by 0.97, 1.68, 2.66, and 2.82 mg/L, and the average rate of decrease was 0.49, 0.84, 1.33, and 1.41 mg/(L·h). These results indicate that the adsorption rate of cadmium ions by suspended sediment is much greater than that by bottom sediment.

It was also found that the extent and rate of descent of dissolved cadmium concentration were quite different at the end of the second stage of the experiment. For Set 1, the extent of descent of the dissolved cadmium concentration in Runs B1 to B4 was 0.24, 0.68, 0.04, and 0.01 mg/L from the 2 h to the 7 h. Correspondingly, the average rate of decrease was 0.05, 0.14, 0.01, and 0.00 mg/(L·h),

Table 3 Variation in the concentration of dissolved cadmium over time after the agitation was stopped (stage 3)

Set	Run B1 [a]			Run B2 [b]			Run B3 [c]			Run B4 [d]		
	Time (h)	Time (min)	C (mg/L)	Time (h)	Time (min)	C (mg/L)	Time (h)	Time (min)	C (mg/L)	Time (h)	Time (min)	C (mg/L)
1	6	45	2.41	6	45	1.77	6	47	1.15	6	48	1.15
	All runs were kept stationary											
	24	0	1.97	24	0	1.49	24	0	1.09	24	0	1.10
2	7	19	2.77	7	20	1.54	7	21	1.12	7	22	1.15
	All runs were kept stationary											
	24	0	2.26	24	0	1.33	24	0	1.10	24	0	1.11
	32	0	2.11	32	0	1.23	32	0	1.07	32	0	1.06

[a] Stationary; [b] stirring gently, then stationary; [c] stirring strongly, then stationary; [d] stirring strongly.

which indicates that the adsorption of cadmium ions by the sediment in Runs B3 and B4 approached equilibrium. This can be verified from the data at the third stage (Table 3), which shows that the concentration of dissolved cadmium in Runs B3 and B4 decreased by 0.06 and 0.05 mg/L from about the 7 h to the 24 h. For Set 2, the extent of decrease of the dissolved cadmium concentration in Runs B1 to B4 was 0.24, 0.58, 0.04, and 0.11 mg/L, respectively, from 2 h to the 7 h. The corresponding average rate of decrease was 0.05, 0.12, 0.01, and 0.02 mg/(L·h). Moreover, as shown in Table 3, from the 7 h to the 32 h, the extent of decrease of the dissolved cadmium concentration in Runs B3 and B4 of Set 2 was 0.05 and 0.09 mg/L, respectively. This also indicates that the adsorption of cadmium ions by the sediment in these runs approached equilibrium. In summary, it can be found that the adsorption of cadmium ions by the sediment in Runs B3 and B4 of the two sets was negligible in the second and third stages compared with the initial stage. These results imply that the time that is required to reach adsorption equilibrium for suspended sediment is much shorter than that required for bottom sediment.

The concentration of suspended sediment in Runs B1 and B2 of the two sets were always low during the course of the experiment, and were zero after the solution was kept in a stationary state for some time in stage 3. The extent of decrease and the concentration of dissolved cadmium in Runs B1 and B2 in the first stage were larger than in the second stage, although it should be noted that the decreases remain at a considerable value after the first stage. For example, in Run B1 of Set 2 (Table 3 and Fig.2b), the concentration of suspended sediment was 0.2 kg/m^3 at the very beginning of the second stage, and the concentration of dissolved cadmium was reduced by 3.01–2.77=0.24 (mg/L). When the concentration of suspended sediment was almost zero between the 7 h and the 24 h, the concentration of dissolved cadmium lessened by 2.77–2.26=0.51 (mg/L), and decreased by 2.26–2.11=0.15 (mg/L) between the 24 and the 32 h. It can therefore be deduced that the differences in the concentrations of dissolved cadmium among Runs B1, B2, B3, and B4 became less over time. For example, the difference between Runs B1 and B3 of Set 2 was 3.09–1.16=1.93 (mg/L) at the 2 h, 2.77–1.12=1.65 (mg/L) at the 7 h, 2.26–1.10=1.16 (mg/L) at the 24 h, and 2.11–1.07=1.04 (mg/L) at the 32 h. Thus, it can be concluded that regardless of the transport pattern that the sediment takes, the final (equilibrium) concentration of dissolved cadmium and the final (equilibrium) concentration of particulate cadmium will be the same in different runs in the same set provided that the duration of the experiment is long enough. As the parameters in adsorption isotherms are determined by the concentration of equilibrium particulate heavy metals and the equilibrium concentration of dissolved heavy metals (Huang, 2003a, b), the fact that the final (equilibrium) concentration of dissolved cadmium and the final (equilibrium) concentration of particulate cadmium will be the same regardless of the transport patterns that the sediment takes means that the parameters of the adsorption isotherms are the

same. Of course, the coefficients of the adsorption rate (or the coefficients of the desorption rate) are significantly different in different runs with different sediment transport patterns, because the rates of decrease of the dissolved cadmium concentration are markedly different in different runs. For example, if the Langmuir adsorption isotherm is used, then the saturation adsorption content of a unit weight of sediment, b, and the constant of the adsorption-desorption rate, k, are the same regardless of the transport pattern that the sediment takes, but the coefficients of the adsorption rate and the coefficients of the desorption rate are different for different sediment transport patterns. Thus, the different sediment transport patterns, which either keep the sediment in the water as a suspended load or let it stay on the bed as bottom sediment, have significantly different adsorption rate coefficients (desorption rate coefficients) in the adsorptive reaction kinetics equation, and have the same adsorption isotherm parameters. The adsorptive reaction kinetics equation can be found in references (Huang, 2003a, b).

In Run B3 of the two sets, the solution was kept in a stationary state after strong stirring for 2 h, and the concentration of suspended sediment gradually descended to zero. Afterwards, the variation in the concentration of dissolved cadmium was nearly the same as that in Run B4, in which the strong stirring was kept up continuously during the first 7 h, and no obvious difference was found between the two runs. This implies that after the adsorption equilibrium of heavy metal pollutants by the sediment has been reached, which is here denoted by the fact that the concentration of dissolved cadmium hardly changed, the equilibrium persists, regardless of the sediment transport pattern thereafter. These results also indicate that the sediment transport pattern has no effect on the equilibrium concentration of cadmium (or the equilibrium concentration of particulate cadmium), and thus the sediment transport pattern has no effect on the parameters of the adsorption isotherm.

2.2 Results of the TST experiments

Because the TST was not very large, the distribution of the dissolved cadmium concentration at all water depths became uniform in 30 min (Huang, 2001). The results of the TST experiments at a water depth of 45.5 cm are shown in Table 2. The variation in the concentration of dissolved cadmium at a water depth of y=45.5 cm is shown in Fig.3.

2.2.1 Effect of different turbulence intensities

The same coarse sediment was used in Runs S3, S4, and S5, and the turbulence intensities and amounts of sediment that were added were varied to simulate the sediment supply condition of natural bodies of water. The turbulence intensities in Runs S3 and S5 were quite low, the concentration of suspended sediment was nearly zero for the duration of the experiment, and all of the added sediment (80 g in Run S3 and 270 g in Run S5) was bottom sediment, as is shown in Table 2. The extent of decrease of the dissolved cadmium concentration in the two runs was small for the duration of the experiment (5.5 h). In Run S4, the total amount of added sediment was 80 g,
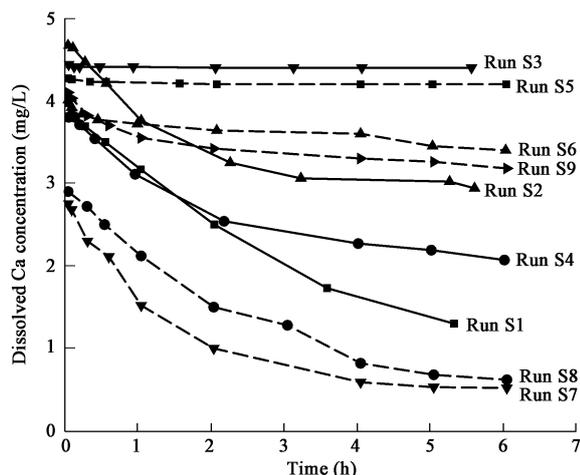
Fig. 3 Variation in the concentration of dissolved cadmium at a water depth of y=45.5 cm over time.

of which 20 g was suspended because of the high turbulence intensity. The concentration of dissolved cadmium decreased significantly from 3.8 to 2.1 mg/L after 6 h, and gradually approached a constant, as shown in Fig.3 and Table 2. A comparison of the experimental conditions and the results of the variation in the concentration of dissolved cadmium in the three runs reveals that even when the amount of added sediment and the grain size of the sediment are the same, the variation in the concentration of dissolved cadmium will be significantly different over time because of the different sediment transport patterns, which vary with the turbulence intensity and sediment supply conditions. The rate of adsorption by the bottom sediment is small for the duration of the experiment, and the time thus required to achieve adsorption equilibrium is rather long.

The results of Runs S6 and S7 also indicate that the rate of adsorption by the bottom sediment is small compared with that of the suspended sediment. If there is some suspended sediment, then the bottom sediment is not able to adsorb the cadmium ions in a short space of time. As shown in Table 2 and Fig.3, the same amount of fine sediment was added in the Runs S6 and S7, but the turbulence intensity was different. Because the high turbulence intensity result in high concentration of suspended sediment in Run S7, the concentration of dissolved cadmium decreased significantly, and gradually approached a constant after 6 h. In Run S6, however, the concentration of dissolved cadmium decreased by only 0.6 mg/L, although it also approached a constant after 6 h, because of the low turbulence intensity and the resultant low concentration of suspended sediment.

A comparison of the results of Runs S3 and S5 gives some data on the effect of the thickness of the bottom sediment on the adsorption. In these two runs, all of the experimental conditions were the same, except for the amount of sediment (bottom sediment) that was added. In Run S5, the bottom sediment weighed 270 g, the calculated thickness was 0.62 cm, and the relative thickness was 55, which is the calculated thickness multiplied by the grain size of the added sediment. In Run S3, the bottom sediment

was only 80 g, the calculated thickness was 0.19 cm, and the relative thickness was 17. Although there was a large difference in the amount of added sediment in the two runs, no obvious difference in the concentration of dissolved cadmium was found. This implies that the effect of the thickness of bottom sediment on the adsorption of heavy metal pollutants is at most seventeen times the grain size of the added sediment. In this regards, more study is needed in the future.

2.2.2 Effect of strong turbulence intensities with or without bottom sediment

The same uniform sediment was added and kept at a same high turbulence intensity in Runs S1 and S2, but the amount of added sediment was different, being 300 g for Run S1 and 80 g for Run S2. Under a condition of strong turbulence, the concentration of suspended sediment was almost uniformly distributed at all depths in both runs. There was no bottom sediment in Run S2, and 220 g of bottom sediment in Run S1, and the sediment supply condition was different in the two runs. The concentration of dissolved cadmium decreased significantly after 5.3 h and was not stable in Run S1 (Fig.3 and Table 2), whereas the concentration of dissolved cadmium in Run S2 was basically stable after 5.5 h. The extent of decrease of the dissolved cadmium concentration in Run S1 was 2.7 mg/L (= 4.0–1.3 (mg/L)), which is larger than the extent of decrease of 1.85 mg/L (= 4.8–2.95 (mg/L)) in Run S2. As noted from the results of the batch reactor experiments that the rate of adsorption by the bottom sediment was small, and the effect of the adsorption by the bottom sediment in a short time was not obvious, these differences were not created by the bottom sediment itself directly, but were caused by the continuous exchange between the suspended sediment and the bottom sediment due to the strong turbulence. Although the concentration of suspended sediment was the same in both runs, there was a considerable amount of added sediment in Run S1, and about 220 g of it settled at the bottom of the device (TST) as bottom sediment. Under a strong turbulence intensity, the bottom sediment did not stay on the bottom all of the time, but continuously exchanged with the suspended sediment. Some of the suspended sediment settled at the bottom and turned into bottom sediment, and at the same time, the same amount of bottom sediment was lifted up into the water and turned into suspended sediment (Chien and Wan, 1999). In this way, the total amount that was adsorbed by the sediment particles increased considerably, and the concentration of dissolved cadmium thus decreased significantly. Moreover, because of the continuous exchange between the suspended sediment and the bottom sediment, the time that was required to reach adsorption equilibrium increased significantly.

The foregoing conclusion can also be seen in the results of Runs S8 and S9. The two runs had the same high turbulence intensity, the same sized sediment, and thus the same concentration of suspended sediment. Although the amount of added sediment was different, with 300 g in Run S8 and 58 g in Run S9, the sediment in Run S8 was not

fully suspended, and some settled at the bottom. Due to the continuous exchange between the suspended sediment and the bottom sediment in Run S8, the concentration of dissolved cadmium seemed unstable after 6 h (Fig.3), and was 0.6 mg/L at 6 h, 0.53 mg/L at 7 h, and 0.45 mg/L at 8 h (not plotted in Fig.3). In Run S9, the extent of decrease of the dissolved cadmium concentration was not as great as that in Run S8, because there was no bottom sediment and thus no exchange due to the limited amount of added sediment. Moreover, the concentration of dissolved cadmium seemed stable after 6 h. In Run S9, the concentration of dissolved cadmium was 3.18 mg/L at 6 h, 3.17 mg/L at 7 h, and 3.14 mg/L at 8 h (not plotted in Fig.3). This indicates that the basic adsorption equilibrium was reached in Run S9.

2.3 Comparison of the effect of bottom sediment on the adsorption of cadmium ions in the batch reactor experiment and the TST experiment

A comparison of the effect of bottom sediment on the adsorption of cadmium ions in the batch reactor experiment and the TST experiment is shown in Table 4. It can be seen that under nearly the same conditions, the adsorption of cadmium ions per unit weight of sediment in the TST experiment was much less than that in the batch reactor experiment, which is deduced from the extent of decrease of the dissolved cadmium concentration at about the same time. It can also be noted that in the TST experiment, as shown in Table 3, bottom sediment was only present in Runs S3 and S5. The extent of decrease of the dissolved cadmium concentration in both runs was small after about 6 h, and it seems that the adsorption ability of the sediment in the batch experiment was greater than in the TST experiment.

There is a significantly different water flow, sediment transport, and thus pollutant transport transformation in a batch reactor compared with natural waters or a TST. This is mainly because batch reactors are generally very small, and no similarity either in the geometry, the movement, or the dynamics (acting forces) of the reactors is taken into consideration. For example, the adsorption of heavy metal pollutants by sediment particles in batch reactors may occur much faster than it does in natural waters, because the reactor is so small that the heavy metal pollutants (ions) come into contact more frequently with the sediment particles than they would in natural waters or in a TST. The explanation of this difference from the

point of view of environmental chemistry or a combination of environmental chemistry and hydraulics requires further study.

3 Conclusions

Sediment transport patterns were simplified and simulated in the commonly used batch reactor experiment. By changing the agitating conditions, which is nearly equivalent to the variation in flow conditions in natural rivers and is qualified by the concentration of suspended sediment, the effect of sediment transport patterns (here either suspended sediment or bottom sediment) on the adsorption of cadmium ions was clarified. It was found that the adsorption rate of bottom sediment was significantly less than that of suspended sediment, but after a long time the equilibrium concentration of dissolved cadmium was the same regardless of the sediment transport pattern. This indicates that the sediment transport pattern does not affect the parameters of an adsorption isotherm due to the fact that they are determined only by the equilibrium concentration of dissolved cadmium and the equilibrium concentration of particulate cadmium.

The effects of flow turbulence intensities, sediment supply conditions (different amounts of added sediment), and sediment transport patterns on the adsorption of cadmium ions were simulated and studied in a TST, in which the water flow and sediment transport were comparable to those in natural waters.

The results of the experiment indicate that when the turbulence intensity is low and the sediment particles stay as bottom sediment, the adsorption rate is significantly small, and the adsorption quantity compared with that achieved by suspended sediment is negligible in an experiment period of 6 h. This result greatly favors the simplification of the numerical modeling of heavy metal pollutant transport transformation in natural rivers.

The results also indicate that when the turbulence intensity is high, the presence of bottom sediment greatly influences the variation in the concentration of dissolved cadmium due to the continuous exchange between bottom sediment and suspended sediment that occurs when bottom sediment is present. The results demonstrate that when bottom sediment is present and this exchange occurs, the rate and extent of descent of the dissolved cadmium concentration noticeably increases, and the time that is required to reach adsorption equilibrium also increases

Table 4 Comparison of the effect of bottom sediment on the adsorption of cadmium ions in the batch reactor experiment and the TST experiment

Item	Batch reactor experiment		TST experiment	Remarks
Run no.	B1 of stage 1	B1 of stage 2	S6	
Sediment composition	<0.033 mm	<0.033 mm	<0.033 mm	The same
Designed sediment concentration (kg/m^3)	10	10	Nearly 10	Nearly the same
Measured initial concentration of suspended sediment (kg/m^3)	0.5	0.4	0.3	Nearly the same
Extent of decrease of the dissolved cadmium concentration in 2 h (mg/L)	1.28	0.97		
Extent of decrease of the dissolved cadmium concentration in 7 h (mg/L)	1.28+0.24=1.52	0.97+0.24=1.21	4.0–3.4=0.6 in 6 h	Markedly different

considerably.

A comparison of the results of the batch reactor experiment and the TST experiment reveals that the adsorption ability of the sediment, and in particular the adsorption rate, is greatly over-estimated in the batch reactor experiment. This may be because batch reactors are so small with strong stirring in it or strong vibration that heavy metal pollutants (ions) come into contact more frequently with the sediment particles than would occur in natural waters or in a TST. However, further study is needed to identify the other chemical mechanisms that are involved.

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