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ORIGINAL ARTICLE

Competitive adsorption, release and speciation of heavy metals in the Yellow River sediments, China

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Abstract The competitive adsorption and the release of selected heavy metals and their speciation distribution before and after adsorption in the Yellow River sediments are discussed. The adsorption of metals onto sediments increases with increasing pH value and decreases with increasing ionic strength. The competitive coefficient K_c and the distribution coefficient K_d are obtained to analyze the competitive abilities of selected heavy metals, which are ranked as Pb > Cu >> Zn > Cd. The competition among selected heavy metals becomes more impetuous with increasing ion concentration in water. Speciation analysis was done by an improved analytical procedure involving five steps of sequential extraction. Cu, Pb and Zn were mainly transformed into the carbonate-bound form (50.8–87.7%) in adsorption. Most of (60.7–77.3%) Cd was transformed into the exchangeable form, and the percentage of carbonate-bound Cd was 19.7–30.4%. The release reaction was so quick that the release capacity of selected heavy metals from sediments to aqueous solution reached half of the maximum value only in 30 s. As opposed to adsorption, the release capacities of selected heavy metals were ranked as Cd > Zn >> Cu > Pb. In this study, Cd produces the most severe environmental hazards, because its concentration in the release solution is 85.8 times more than the human health criteria of US EPA.

Keywords Competitive adsorption · Heavy metals · Speciation analysis · The Yellow River

Introduction

Natural waters are found to be contaminated with many heavy metals (Christian Gischler 2005), so that the behavior of one heavy metal in the sedimentary phase and aqueous phase is affected by other metals. There have been many studies (Galvez-cloutier and Jean-sèbastien 1998; Petersen et al. 1997; Filius et al. 1998; Nicole et al. 2001; Huang et al. 1995; Du et al. 1996) about adsorption, speciation distribution and bio-availability of heavy metals. The Yellow River is the biggest sand transformation river in the world. As a result of serious pollution in recent years, the water–sand system has representative effects on the adsorption of pollutants, especially heavy metals. The competitive adsorption, speciation distribution after adsorption and the release of Pb, Cu, Zn and Cd into the Yellow River sediments are studied in this paper. The experiments were based on the sediments in relatively clean reach of the Baotou section of the Yellow River (Fig. 1) as the substrates and the selected heavy metals (Pb, Cu, Zn and Cd) in aqueous solution as the sorbent. The goal of this study is to reveal the rules of heavy metal transformation in sediment—water interface in competitive adsorption processes and to evaluate the potential hazards of heavy metals in the Yellow River sediments.

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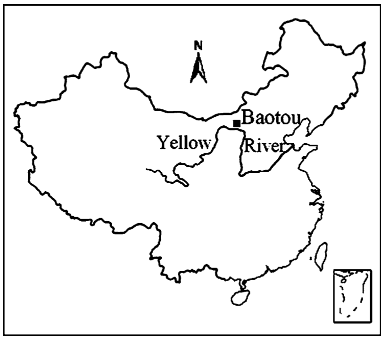

Fig. 1 Location of Baotou section in the Yellow River

Method

Sampling, background and geochemical characters of samples

The Baotou section includes the 216 km upper reach of the Yellow River. The sediment samples used as adsorbent were collected from the relatively clean reach in the Baotou section of the Yellow River (10 cm in depth, May 2004) using KC mod A och B from Swedaq company in Norway. The samples were put into polyethylene plastic bags and dried at low temperature (<60°C), then sieved and the portion smaller than 63 μm was chosen for analysis. The overlying water was passed through 0.45 μm of filtration membrane at the sampling sites and then analyzed directly after acidifying with nitric acid (GR) to obtain concentrations of soluble heavy metals.

The sediment characteristics such as mineral composition, organic content, carbonate content and cation exchange capacity (CEC) are listed in Table 1. Granularity distribution is shown in Table 2. The concentrations of soluble heavy metals (average values of heavy metal concentrations of eight sites in filtered water) and the physicochemical properties in the overlying water in the Baotou section of the Yellow River are shown in Table 3. The Yellow River flows across the arid region of North China that has higher salinity and concentration of suspended particulates, while the water shows low alkalinity and is a buffered carbonate–bicarbonate system. These characters play a key role in the migration of heavy metals toward sediments.

Experimental methods and conditions

Laboratory apparatus

Mineral analysis was accomplished using an X-ray diffractometer. Dichromate method was used to test

Table 1 Mineral composition and chemical characteristics of the sediments in the Baotou section of the Yellow River

	TOC %	Kaolinite %	Chlorite %	Calcium carbonate %	Ridbeckite %	Plagioclase %	Orthoclase %	Quartz %	CEC c mol/kg	Carbonate %
Average value	0.215	10.3	7.2	17.4	4.5	15.8	9.6	38.7	2.72	10.21
Number of samples	17	17	17	17	17	17	17	17	12	12
SD	0.079	3.4	1.7	3.3	2.0	1.2	2.5	5.3	0.18	1.18

Table 2 Granularity distribution of the sediments in the Baotou section of the Yellow River

Granularity extent (μm)	<4	4–16	16–32	32–50	50–63	63–125	125–250	>250
Proportion (%)	4.91	7.46	16.70	22.01	13.02	28.85	6.71	0.34
Number of samples	18	18	18	18	18	18	18	18
SD	1.58	3.34	7.50	4.12	1.62	9.31	5.91	0.62

the organic content. Acetic acid ammonia exchange method was used to test the cation exchange capacity. Acid–base indicator titration method was used to test carbonate, and acidimeter for pH. A new type of Marvin laser grain size analyzer named Master Sizer 2000 (MS2000), made in Britain, was used for the laser diffraction method in grain size analysis. Ion chromatograph was used to test the concentrations of chlorine ions and sulfate radicals. Analyses of selected heavy metals were done using atomic adsorption spectrophotometer (Z-5000) made by Hitach Company, Japan. Based on the different concentrations of selected heavy metals in the samples, flame spectrophotometry and graphite furnace method were used in the detection of heavy metals.

Experimental procedure of adsorption

The experiments were based on the sediment in relatively clean reach of the Baotou section of the Yellow River as the substrate and the selected heavy metals (Pb^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}) in aqueous solution as the sorbent. $Pb(NO_3)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$ and $Cd(NO_3)_2$ were chosen to confect a solution with [Pb]:[Cu]:[Zn]:[Cd] = 4:2:1:1, considering the intense adsorption to Pb^{2+} and Cu^{2+} and the higher atomic weight of Pb. The initial concentration of Pb in the solution was 10 mg/l and the concentrations of other ions were in accordance with the given proportion.

In the experiment of adsorption isotherm, the initial concentration of Pb^{2+} was in the range of 1–40 mg/l, and the concentrations of Pb^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} were in accordance with the ratio given above. The experiments were carried out under the conditions of temperature 25 ± 1°C, ionic strength 0.01 mol/l ($NaNO_3$) and pH 7.00.

In the experiments of adsorption dynamics, the initial concentrations of Pb^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} were 12, 4, 2 and 4 mg/l, respectively. Into a 1,000 ml beaker, 500 ml of mixed solution and 2.5 g sediments were added and a magnetic stirrer was used for stirring. The solution was sampled at 30 s, 1 min, 2 min, 4 min, 8 min, 16 min, 30 min, 1 h, 2 h and 4 h and then passed through 0.45 μm of filtration membrane for analysis.

The pH adsorption edges experiments were carried out under the conditions of temperature 25 ± 1°C, ionic strength 0.01 mol/l ($NaNO_3$) and different values of pH. To test the effects of ionic strength on heavy metal adsorption, the experiments were carried out under pH 7.00, temperature 25 ± 1°C and different ionic strengths. To test the effects of temperature on heavy metal adsorption, the experiments were carried out under pH 7.00, ionic strength 0.01 mol/l ($NaNO_3$) and different temperatures.

In all the experiments, 0.1000 ± 0.0005 g of sediments were accurately weighed in 50 ml centrifuge tubes, and then 20 ml confected solution was added in. After 3 h of continual oscillation in a homothermal shaker at the given temperature, and 12 h of equilibrium at constant temperature, the samples were centrifuged and passed through 0.45 μm of filtration membrane, then acidified with nitric acid (GR) for analysis.

Analytical procedure of speciation

Firstly, for polluting the sediments, which were sampled from the relatively clean reach in the Baotou section of the Yellow River, series of adsorption experiments were carried out. Secondly, the samples (S_2) for speciation analysis were obtained by drying at low temperature (<60°C) after adsorption. To see the speciation distribution of heavy metals in sediments after adsorption, sediments (S_1) from the relatively clean reach in the Baotou section were subjected to form analysis simultaneously. The sequential extraction procedure established by Tessier et al. (1979) was applied in the study.

In the first step, the initial concentrations of Pb^{2+} in the solution were 12, 20 and 30 mg/l, respectively, and the concentrations of Pb, Cu, Zn and Cd were in accordance with the ratio given in the adsorption experiment. The experiment was carried out at pH 6.90 (±0.05), temperature 25 (±1) °C and ionic strength 0.01 mol/l ($NaNO_3$). The solution was oscillated continuously for 3 h, followed by 12 h equilibrium at constant temperature.

Release experimental procedure

Firstly, the adsorption experiment was carried out similar to the speciation analysis. A system was

Table 3 The concentration of heavy metal in soluble form and the physicochemical properties in the overlying water in the Baotou section of the Yellow River

	Cu (µg/l)	Pb (µg/l)	Zn (µg/l)	Cd (µg/l)	pH	K^+ (mg/l)	Na^+ (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Cl^{1-} (mg/l)	SO_4^{2-} (mg/l)	CO_3^{2-} (mg/l)	HCO_3^- (mg/l)	Concentration of suspended matter (g/l)
Average value	1.877	2.68	2.825	0.496	8.21	4.3	187.4	87.4	32.6	141.3	200.2	8.3	210.7	2.388
Number of samples	8	8	8	8	12	8	8	8	8	8	8	8	8	12
SD	0.425	0.48	0.549	0.073	0.25	0.6	55.3	4.7	3.7	10.1	12.7	3.8	17.1	0.432
Coefficient of variation%	22.6	17.9	19.4	14.7	1.8	14.9	29.5	5.4	11.3	7.2	6.3	46.2	8.1	18.1

established with a solid to liquid ratio of 1:100, and the initial concentrations of the four ions in the solution were [Pb]:[Cu]:[Zn]:[Cd] = 20:10:5:5 (mg/l).

Secondly, 5 ± 0.0005 g of polluted sediment sample was rapidly added into a beaker. At a given pH (6.90 ± 0.05) and ionic strength ($I = 0.02$ mol/l, average value in the Yellow River) 500 ml $NaNO_3$ solution was added to the beaker and then mixed continually at 25 ± 1°C with an electromagnetic stirrer. The solution was filtered through 0.45 µm syringe filters each time. Finally, the sample was acidified with nitric acid (GR) for analysis.

Heavy metal analysis was accomplished using flame atomic absorption spectrophotometer and graphite furnace method, and the adsorption capacity was calculated as the difference between the primal and final heavy metal concentrations in adsorption. All the acids used in the experiments were guaranteed reagents, the other chemicals were all analytically pure, and the water was ultra-pure deionized water (18 MΩ). The samples were digested in polytetrafluoroethylene (PTFE) vessels. All the glass and polyvinyl vessels in the sampling and experiments were soaked in nitric acid (14%) about 24 h, washed with deionized water and then dried at low temperature.

Results and discussion

Results and discussion of the adsorption experiment

Adsorption isotherm

The adsorption isotherms of Cu^{2+}, Pb^{2+}, Zn^{2+} and Cd^{2+} are presented in Fig. 2. The Freundlich isotherm-type model and Langmuir isotherm-type model were used in this study, and the parameters are presented in Table 4.

The linearized form of the Langmuir equation is:

$$C/q = 1/\alpha\beta + C/\beta \tag{1}$$

where C is the concentration or activity of the free metal in solution, q is the quantity of the metal ion sorbed by the sediments (i.e., mg of metal sorbed/kg of sediments), β is the maximum sorption capacity of the sediments and α is the coefficient related to bonding energy. When C/q is plotted as a function of C, the slope is the reciprocal of the sorption capacity β and the intercept is $1/\alpha\beta$.

The Freundlich expression is an empirically derived equation to describe the logarithmic decrease in adsorption energy with increasing surface coverage. The linearized form of the Freundlich equation is:

$$\ln q = b \log C + a \qquad (2)$$

where q and C have the same definition as above and a and b are constants fitted from the experimental data.

The Freundlich isotherm model was found to fit the experimental equilibrium concentration data of Cu^{2+} and Pb^{2+} better; however, the Langmuir isotherm model fitted only the equilibrium data of Zn^{2+} and Cd^{2+}, suggesting that selected heavy metal ions are in different adsorption stages at the given initial concentration range due to their different adsorption abilities. As shown in Fig. 2, the adsorption capacities of Cu and Pb increase smoothly with increasing equilibrium concentration of the adsorption isotherm; while the adsorption capacities of Zn and Cd tend to increase first and decrease slightly from 2.5 to 6 mg/l of the equilibrium concentration, then increase thereafter, because the strong adsorption abilities of Cu and Pb greatly affect the adsorption of Zn and Cd and further lead to desorption of Zn and Cd. Therefore, higher competitive abilities of Cu and Pb than Zn and Cd in the mixed system are observed. Furthermore, the competitive coefficient K_c and distribution coefficient K_d were cited to interpret the adsorption abilities and adsorption processes of Cu, Pb, Zn and Cd with the impacts of pH, initial concentration, ionic strength and temperature (as controlling factors) well. The impacts of controlling factors on adsorption of selected metals can be seen from the variations of K_c and K_d.

Competitive coefficient

In the study of competitive adsorption, the distribution coefficient K_d (US EPA 1999, 402-R-99-004A-B) (Gomes et al. 2001) is always cited to compare the competitive abilities of ions in adsorption. The K_d model originates from thermodynamic chemistry (Alberty 1987). It is a measure of sorption and defined as the ratio of the quantity of the adsorbate adsorbed per gram of solid to the amount of the adsorbate remaining in solution at equilibrium. The mass action expression is the partition coefficient (K_d, ml/g):

$$K_d = \frac{A_i}{C_i} \qquad (3)$$

where C_i = total dissolved adsorbate concentration remaining in solution at equilibrium (mol/ml or µg/ml), and A_i = concentration of adsorbate on the solid at equilibrium (mol/g or µg/g).

Competitive adsorption of heavy metal is affected by environmental conditions, such as pH, ion concentration and so on. Whereas, as a natural attribute, K_d describes intension of interaction between adsorbate and sorbent, it reflects neither the competitive ability of heavy metals in adsorption in a quantifiable manner, nor the status of each competitor in the adsorption site. Therefore, competitive coefficient (K_c) has been cited in this study to reflect intension of interaction among heavy metal ions in the system.

The competitive coefficient, which originates from adsorption dynamics describes competitive adsorption and it has led in this study to depict competitive adsorption of elements in the solid–liquid system. Its equation is as follows:

$$K_c = \frac{A_i/C_i}{\sum_{i=1}^{n} A_i/C_i} \qquad (4)$$

where, K_c = competitive coefficient of heavy metal i, A_i = average adsorption capacity of heavy metal I and C_i = initial concentration of heavy metal i. The competitive coefficients of all selected heavy metals in the system amount to 1.

Impacts of pH on competitive adsorption

The adsorption capacity on selected heavy metals increases with increasing pH (Fig. 3), because H^+ (or

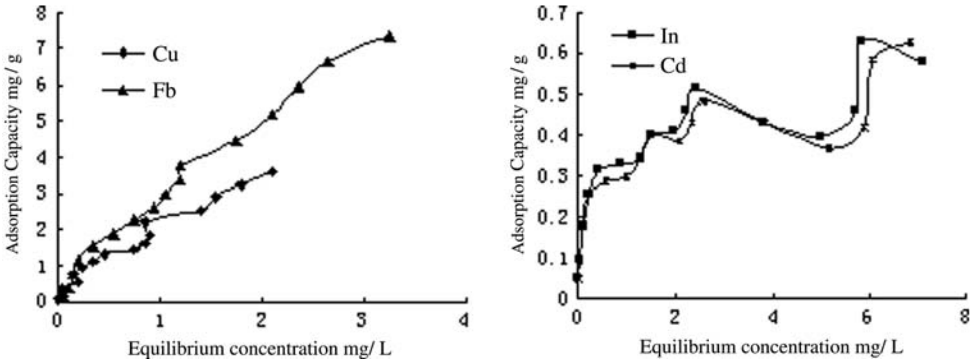

Fig. 2 Adsorption isotherms of Cu, Pb, Zn and Cd on Yellow River sediments in mixed ions system (25°C)

Table 4 The estimated parameters of heavy metals adsorption isotherms to sediments based on a linear correlation analysis (25°C)

Equation		*a*	*b*	r^2
Langmuir equation	Cu	0.2408	0.2010	0.7871
$C/q = a + bC$	Pb	0.2404	0.0711	0.7718
	Zn	0.7658	1.8417	0.9382
	Cd	0.8737	1.9048	0.9051
Freundlich equation	Cu	0.7577	0.7099	0.9594
$\ln q = a + b \ln C$	Pb	1.0936	0.8181	0.9773
	Zn	–1.1346	0.3352	0.9118
	Cd	–1.1824	0.3291	0.9099

H_3O^+) occupies more adsorption sites at lower pH values. Hsu (1989) suggested that exchange adsorption should be viewed as the competition between M^{2+} and H^+ for the surface O on the basis of the cation relative affinity for this surface O. Schwertmann and Taylor (1989) postulated that pH is the main force governing the adsorption of metal cations, and the fact that pH of maximum increase in adsorption is found to be linearly related to the first hydrolysis constant of the metal $K_1 = (MOH^+)/(M^{2+})\cdot(OH^-)$ indicates that the hydrolyzed species (MOH^+) is preferentially adsorbed over the unhydrolyzed one (M^{2+}). Based on the study of Pb^{2+} adsorption by fly ash, Ricou et al. (1999) pointed out that heavy metal adsorption is divided into three stages, for example, plumbum mainly precipitates when pH > 6 in the solution, it is adsorbed or has surficial deposition when 5 < pH < 6, and there is competitive adsorption between Pb^{2+} and H_3O^+ when pH < 5. The adsorption process includes reversible ion exchange and irreversible precipitation. Both of them are evidently influenced by the different pH value of the system.

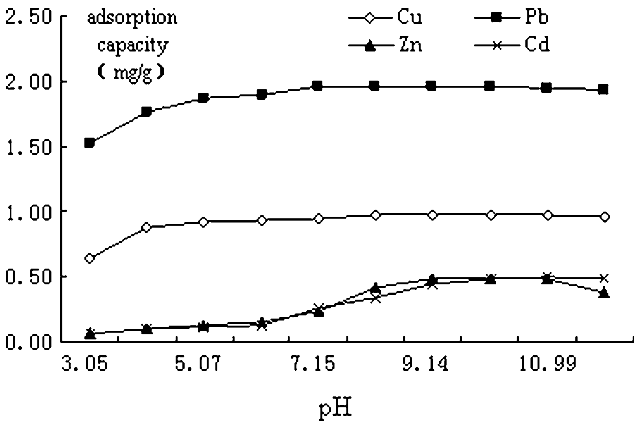

Fig. 3 pH adsorption edges

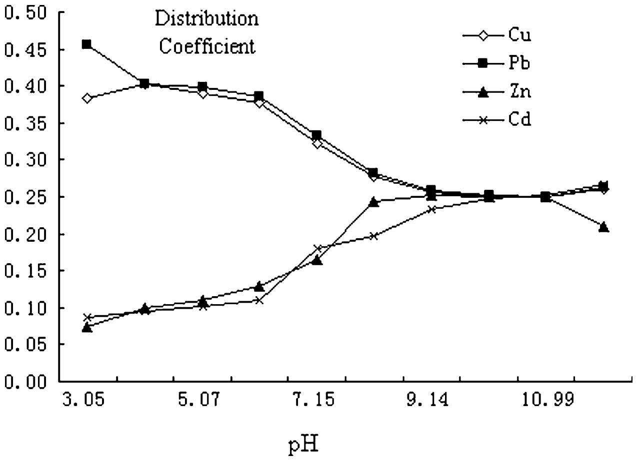

Fig. 4 K_c with different pH

As can be seen in Fig. 3, over 60% of Pb and Cu are adsorbed at pH = 3, because Pb and Cu can hydrolyze at lower pH and the hydrolysate makes them easier to be adsorbed than Zn and Cd. In the low pH condition, the main competitive cation is H_3O^+. The adsorption capacities of Pb and Cu increase very fast and rise to maximum values as the pH varies from 3 to 6. Figure 4 shows that the competitive coefficients of Pb and Cu are far higher than those of Zn and Cd at lower pH values and no sharp evolution is observed for the adsorption capacities of Zn and Cd. It is mainly due to the inactivity of Zn and Cd in hydrolytic reaction that they lack the ability to compete. When pH is in the range of 6–9, the accelerating hydrolytic reaction promotes the adsorption of Zn and Cd. Meanwhile, the competitive coefficient increases fast with increasing adsorption. However, no sharp evolution is observed for the adsorption capacities of Pb and Cu, and their competitive coefficients decrease gradually because of the precipitation and the decreasing concentrations of soluble ions. When pH > 9, the concentrations of

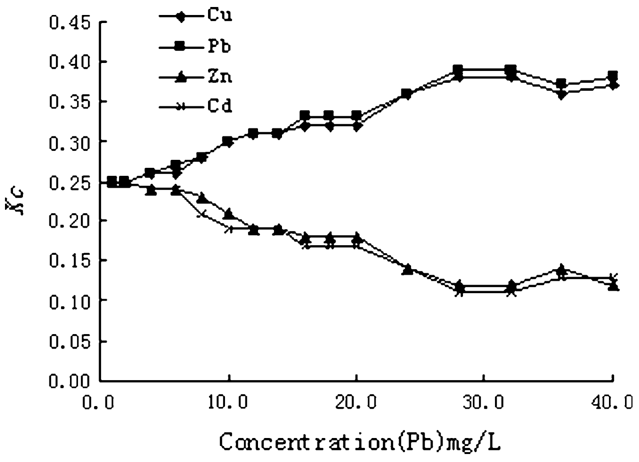

Fig. 5 K_c with different heavy metal concentration (by Pb)

Table 5 The adsorption capacity with different heavy metal initial concentrations (by Pb)

Heavy metal initial concentration (mg/l)	Adsorption capacity of Cu (mg/g)	Adsorption capacity of Pb (mg/g)	Adsorption capacity of Zn (mg/g)	Adsorption capacity of Cd (mg/g)
1.00	0.10	0.19	0.05	0.05
2.00	0.19	0.38	0.10	0.10
4.00	0.39	0.77	0.18	0.18
6.00	0.56	1.16	0.26	0.26
8.00	0.77	1.53	0.31	0.29
10.00	0.95	1.89	0.33	0.30
12.00	1.13	2.25	0.34	0.34
14.00	1.31	2.61	0.40	0.40
16.00	1.45	2.99	0.41	0.39
18.00	1.63	3.36	0.46	0.43
20.00	1.82	3.76	0.51	0.48
24.00	2.23	4.45	0.43	0.43
28.00	2.52	5.18	0.40	0.37
32.00	2.89	5.93	0.46	0.42
36.00	3.24	6.67	0.63	0.59
40.00	3.58	7.35	0.58	0.63

Table 6 The adsorption capacity with different ionic strength (mg/g)

Ionic strength $NaNO_3$ (mol/l)	Adsorption capacity of Cu	Adsorption capacity of Pb	Adsorption capacity of Zn	Adsorption capacity of Cd
0.001	0.97	1.94	0.31	0.28
0.005	0.94	1.95	0.30	0.27
0.010	0.97	1.93	0.29	0.26
0.020	0.91	1.87	0.21	0.17
0.050	0.92	1.79	0.12	0.09
0.100	0.88	1.71	0.08	0.07
0.150	0.84	1.68	0.07	0.06
0.200	0.82	1.67	0.06	0.03
0.500	0.78	1.62	0.05	0.02

soluble ions are so low that the competitive coefficients tend to be equal to each other because of the precipitation. It indicates that there is no competitive adsorption, yet. As the pH value increases to 12, Zn rebounds to the soluble form due to its amphoteric nature and the adsorption capacity of Zn declines. This could be expressed as follows:

$$Zn(OH)_2 + 2OH^- \rightarrow Zn(OH)_4^{2-}$$

Figure 3 well presents the changes in adsorption capacities in pH adsorption edges, and Fig. 4 offers the competitive adsorption capacities of selected heavy metals at given pH values.

Impacts of ion concentration on competitive adsorption

Competitive adsorption could be understood as the competition of the adsorbate for the limited adsorption sites; therefore, competitive adsorption becomes more impetuous with increasing ion concentration. Figure 5 and Table 5 indicate that there is no competitive adsorption in solution when the initial concentration of Pb is lower than 2 mg/l, because there are sufficient adsorption sites in the surface for adsorption. With the increasing heavy metal concentrations in the solution, competitive adsorption becomes more impetuous, and the differentiation of competitive coefficients becomes more obvious. When the concentrations of heavy metals increase to 28 mg/l, the competitive coefficients stabilize again. Cu and Pb capture most of the adsorption sites on the adsorbent, and their competitive coefficients are approximately three times as high as those of Zn and Cd. It is observed that there is no obvious differentiation between Cu and Pb in adsorption while the ion concentrations are increasing, indicating that their competitive abilities are almost equal to each other, and they get almost equal adsorption sites; so do Zn and Cd.

Impacts of ionic strength on competitive adsorption

The increase of ionic strength, which means increase of cation content in solution, could be understood as the joining of new competitors. It leads to the decrease of total adsorption capacity and differentiation of K_c. The experiment results are showed in Fig. 6 and Table 6.

Ionic strength has no obvious effects on heavy metals in competitive adsorption when it is lower than 0.01 mol/l. When the ionic strength is 0.01–0.10 mol/l, the impacts become more and more obvious, and there is a quick differentiation among selected heavy metals, because most of the adsorption sites for Zn and Cd are captured by Cu and Pb. In addition, impacts of ionic strength on Cd are obviously greater than on Zn.

Impacts of temperature on competitive adsorption

The impacts of temperature on competitive adsorption are not as strong as that of pH, initial concentration and ionic strength. It is clear from Fig. 7 and Table 7 that the competitive coefficients of Cu and Pb decrease below 25°C and increase above 25°C, while the competitive coefficients of Zn and Cd increase below 25°C and decrease above 25°C. Generally speaking, the temperature of the solution has no obvious effects on competitive adsorption.

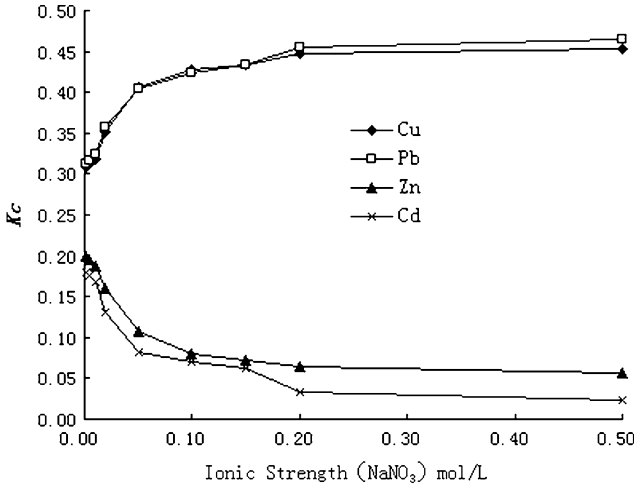

Fig. 6 K_c with different ionic strength

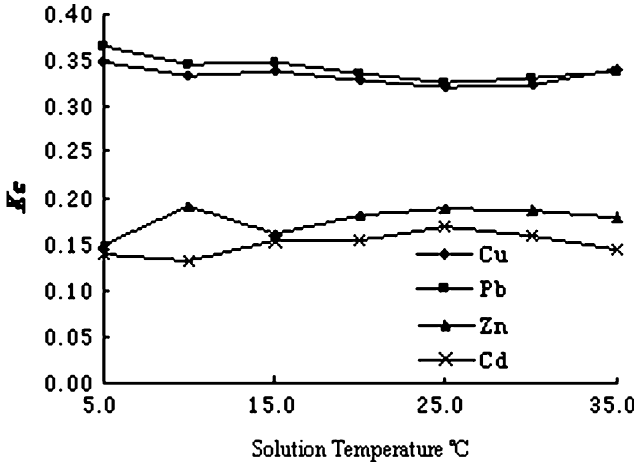

Fig. 7 K_c with different solution temperatures

The order of competitive adsorption capacity

Whatever the experimental condition (pH, heavy metal concentration, ionic strength and temperature) considered, the adsorption capacities are always ranked as Pb > Cu >> Zn > Cd (obtained from K_c). Table 8 shows K_d obtained in the release experiments. According to K_d, the adsorption capacities of selected heavy metals in the sediments of the Yellow River are also ranked as Pb > Cu >> Zn > Cd. The order of competitive adsorption capacity implies that the adsorption capacities of the Yellow River sediments to Cu^{2+}, Pb^{2+}, Zn^{2+} and Cd^{2+} are notably different from each other, indicating the different self-purification capacities of sediments to heavy metals. In the order of competitive adsorption capacity, the selected heavy metal has a more serious potential hazard on the Yellow River than the frontal one.

Table 7 The adsorption capacity with different temperatures (mg/g)

Temperature (°C)	Cu	Pb	Zn	Cd
5.0	0.9	1.87	0.19	0.18
10.0	0.91	1.89	0.26	0.18
15.0	0.92	1.91	0.22	0.21
20.0	0.93	1.92	0.26	0.22
25.0	0.93	1.93	0.27	0.24
30.0	0.93	1.9	0.27	0.23
35.0	0.96	1.88	0.25	0.2

Table 8 The difference of K_d and adsorption capacities of heavy metals

Items	Cu	Pb	Zn	Cd
Concentration added (mg/l)	10	20	5	5
Equilibrium concentration (mg/l)	0.070	0.076	2.265	2.802
Adsorption capacity (mg/g)	0.993	1.9924	0.2735	0.2198
K_d (l/g)	14.186	26.216	0.121	0.078

Adsorption dynamics

The data were collected from 30 s to 4 h in the experiments on adsorption dynamics. As we can see from Fig. 8, the adsorption reaction is very fast in the beginning, suggesting that the adsorption is mainly surficial adsorption. About 30 min later, the adsorption speed tends to increase smoothly. As shown in Table 9, the Elovich equation, double constant equation, parabolic diffusion equation and first-order equation were used to analyze the adsorption of selected heavy metals in the Yellow River sediments. The Elovich equation and the double constant equation were the optimal model to describe the adsorption of selected heavy metals,

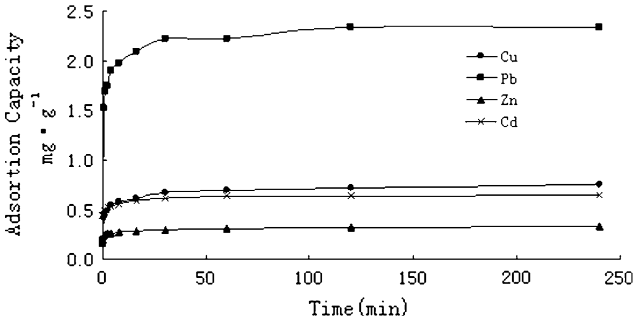

Fig. 8 Dynamics curves of heavy metals adsorption on the Yellow River sediments

Table 9 The estimated parameters of heavy metals adsorption dynamic to sediments based on a linear correlation analysis

Equation		a	b	r^2
Elovich equation $q = a + b \ln t$	Cu	0.4557	0.0578	0.9872
	Pb	1.6755	0.1367	0.9742
	Zn	0.2538	0.0149	0.9879
	Cd	0.5084	0.0280	0.9675
Double constant equation $\ln q = a + b \ln t$	Cu	–0.7818	0.1009	0.9698
	Pb	0.5171	0.0701	0.9595
	Zn	–1.3678	0.0513	0.9931
	Cd	–0.6748	0.0491	0.9663
Parabolic diffusion equation $q = a + bt^{1/2}$	Cu	0.4817	0.0219	0.7859
	Pb	1.7438	0.0503	0.7363
	Zn	0.2585	0.0060	0.8965
	Cd	0.5206	0.0107	0.7815
First-order equation $\ln q = a + bt$	Cu	–0.6327	0.0019	0.4949
	Pb	0.6227	0.0013	0.4593
	Zn	–1.2987	0.0011	0.6597
	Cd	–0.6037	0.0010	0.5251

q Adsorption capacity, t time, a, b coefficients

whereas the first-order equation and the parabolic diffusion equation were not suitable ones.

Results and discussion of the speciation analysis

Table 10 and Fig. 9 show the heavy metal form distribution of the Yellow River sediments before adsorption. The contents of Cu, Pb, Zn and Cd in the sediments were 23.53, 14.95, 62.37 and 0.238 mg/kg respectively, which agree with the studies of Chen (2000a, b).

For form distribution of Cu, Pb and Zn, the major form was the residual form (V); the second was the Fe, Mn-oxidex-bound form (III); the contents of the carbonate-bound form (II) and the exchangeable form (I) were low. Except that the organic-bound form (IV) of Cd (5.9%) was low, the other forms were distributed at an average. It showed that the hazard of Cd cannot be ignored, because the exchangeable Cd (20.2%) might release easily.

The percentages of form transformation of heavy metals before and after adsorption, which are obtained from the ratio of the difference in concentrations between S_2 and S_1 of the respective forms to the difference in amounts between S_2 and S_1, are given in Figs. 9, 10 and Tables 10, 11. The content of heavy metals in the residual form (V) had no variation in the process of adsorption. Only a small fraction (0–1.9%) of heavy metals were transformed into the organic-bound form (IV) in the adsorption process, due to the slight organic content in the sediments of the Yellow River. However, Cu, Pb and Zn, for the most part (50.8–87.7%), were transformed into the carbonate-bound form (II). The Yellow River is a buffered carbonate–bicarbonate system (Tables 1 and 3), and the ksp of selected heavy metal carbonates is low, which causes the precipitation of heavy metals on the surface of particulates ($M^{2+} + CO_3^{2-} \rightarrow MCO_3$). Therefore, the carbonate radical and bicarbonate radical play a controlling role in the transformation process. Cu, Pb and Zn were transformed partially into Fe, Mn-oxidex-bound form (III) during adsorption. Cu showed slight transformation into the exchangeable form during adsorption, followed by Pb; whereas up to 32% of Zn was transformed into the exchangeable form. Most of Cd was transformed into the exchangeable form, which accounted for 77.3% at the highest, and secondly into the carbonate-bound form.

All the discussion above show that in the hypergene zone of sediments, heavy metals in the primary phase (residual form) were not concerned with the transformation between the water and sediments, while artificial contamination was mainly accumulated in the secondary phase (bio-available form). Therefore, the

Table 10 Form distribution of heavy metals in sediments in the Baotou section of the Yellow River before adsorption

Form	Cu		Pb		Zn		Cd	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
I	0.787	3.3	0.126	0.8	5.716	9.2	0.048	20.2
II	0.501	2.1	0.866	5.8	2.943	4.7	0.053	22.3
III	2.121	9.0	4.562	30.5	12.703	20.4	0.072	30.3
IV	0.791	3.4	0.888	5.9	4.235	6.8	0.014	5.9
V	19.329	82.1	8.505	56.9	36.772	59.0	0.051	21.4
Total	23.530	100.0	14.948	100.0	62.369	100.0	0.238	100.0

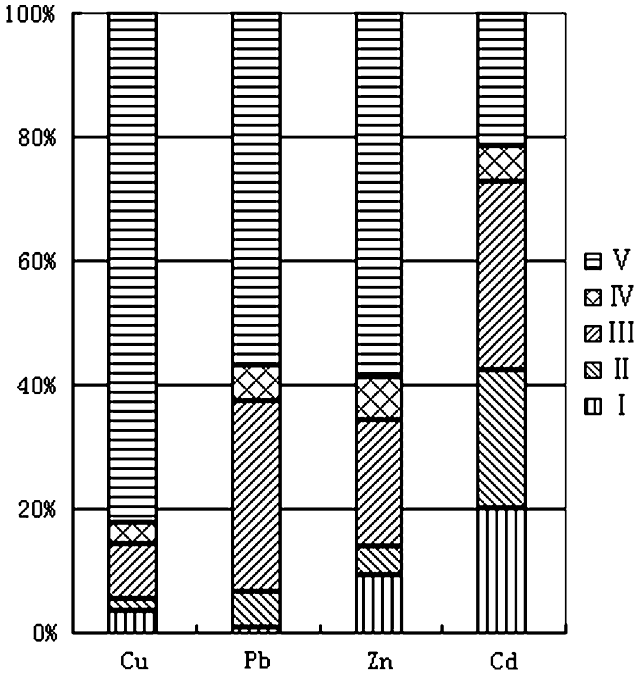

Fig. 9 The heavy metal form distribution of the Yellow River sediments before adsorption

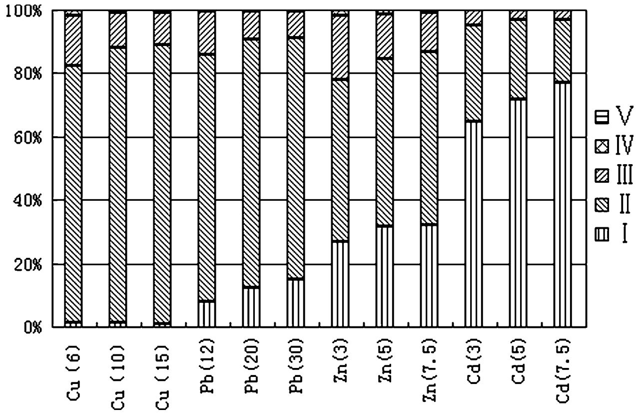

Fig. 10 The form distribution of the Yellow River sediments after adsorption with different concentration of initial metals (mg/l)

percentage of heavy metals in the secondary phase indicates their mobility from sediments to water, which may cause secondary contamination. Cd causes the most serious environmental hazard because its toxicity is the highest of the selected heavy metals, and most part of Cd transformed into the exchangeable form, which is easy to release.

Results and discussion of the release experiments

Adsorption and release of sediments to heavy metals were in dynamical variation. At low heavy metal concentration, competitive adsorption was feeble because there were sufficient adsorption sites for heavy metal ions leading to low release capacity. Released solution concentrations and released percentages of heavy metals at different times are given in Table 12.

Concentrations of Cu, Pb, Zn and Cd in the release solution at different times are shown in Fig. 11. It is clear from Fig. 11 and Table 11 that the average release percentages of Pb and Cu at the 24 h point were merely 0.33 and 0.85%, which were far less than 25.25 and 39.48% of Zn and Cd, respectively. So, the order of release capacity is Cd > Zn >> Cu > Pb, which is opposite to the order of adsorption capacity. Although the ionic strength in the release solution only accounts for 1/100 of the ionic strength (1 mol/l $MgCl_2$) in the extracting solution for exchangeable form, large amounts of heavy metals, mostly in the exchangeable form, release to the solution. The release capacities of Cu, Zn and Cd were respectively 70.1, 80.2 and 54.8% of their contents in the exchangeable form. Due to the solubility product of $PbCO_3$ (7.4×10^{-14}), which accounted for 1/70 of $CdCO_3$, the release capacity of Pb was just 2.7% of exchangeable Pb. With varying solution conditions, Pb may capture the chance of combining with the carbonate of other heavy metals in the release experiment, then redistribute in the system.

It makes sense that in 24 h of release reaction, the concentrations of Cu and Zn in the solution were less than the values of Quality Criteria for Water in the

Table 11 Form distribution of heavy metals in sediments in the Baotou section of the Yellow River after adsorption

Form	Cu			Pb			Zn			Cd		
	6[a]	10	15	12	20	30	3	5	7.5	3	5	7.5
I	1.3	1.2	1.1	8.1	12.3	15.1	27.0	31.5	32.0	64.7	72.0	77.3
II	81.2	86.8	87.7	78.0	78.3	76.2	50.8	53.1	54.6	30.4	24.9	19.7
III	15.6	11.1	10.4	13.3	8.8	8.2	20.4	14.1	12.4	4.9	3.1	3.0
IV	1.9	0.9	0.8	0.6	0.6	0.5	1.8	1.3	1.0	0.0	0.0	0.0
V	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Equilibrium concentration mg/l	0.023	0.07	0.141	0.034	0.076	0.156	0.973	2.265	4.126	1.317	2.802	5.112

[a] The line is initial concentration of heavy metal (mg/l)

Red Book (US EPA 1976) and Gold Book (US EPA 1986) (Cu:1.0 mg/l, Zn:5.0 mg/l) of US EPA. Concentration of Pb was 65μg/l, which was a little higher than 50μg/l in the quality criteria for water. However, the concentration of Cd was 85.8 times more than the Human Health Criteria 10μg/L, which indicates Cd has the most serious potential hazard of the selected heavy metals.

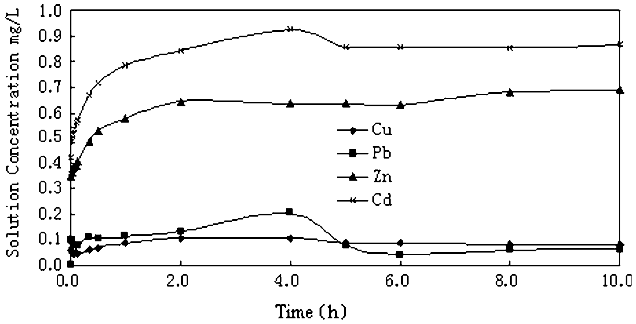

Fig. 11 Concentrations of Cu, Pb, Zn and Cd against time in release solution

The release reaction went very fast. As shown in Table 12, the release capacities of Cu, Pb, Zn and Cd from sediments reached half of the maximum release capacity or so in only 30 s. It implies that most of the heavy metals released were in the exchangeable form and some were in the adsorptive form, and that the released heavy metals were adsorbed into the external surface of particles before release. This is related to the grain surface and geochemical characteristics of the Yellow River sediments (Tables 1 and 2). The Yellow River sediments have characteristics as follows: the organic matter content is very low, while the inorganic constituent is in a dominant status; the grain size of sediments mainly varies from 16 to 125 μm; the contents of cosmid (0–16 μm) and coarse sand (>125 μm) are low; there is no adsorbent with micro aperture in the sediments, according to granularity. All these characteristics lead to quick adsorption and release of heavy metals in the system. Figure 11 illustrates that the release capacity of Zn continuously increases, while the others reach a maximum value in 4 h and drop thereafter. Variations in the values of Pb are most obvious; the release capacity at the 24 h point accounts for 31.6% of the maximum value, and at the 30 s point, 65%. It indicates that most of the Pb released is adsorbed back to the sediments again. By calculating the mole number of heavy metals in the release reaction, it is found that the readsorption capacities of Cu, Pb and Cd after the maximum value at the 4 h point is two times as large as the release capacity of Zn. It reveals that on one hand they capture parts of the external adsorption sites of Zn; on the other hand, they capture parts of the internal adsorption sites through migration and balanced reaction. Competition of heavy metals also exists in release reaction according to release dynamics.

Release dynamical equation dealing with first-order reaction is shown in Table 13. During the first 30 min, Cu is in accordance with the first-order reaction, of which the correlation coefficient is 0.8331 and confidence level is over 98%. Pb is not in accordance with the first-order reaction under the high influences of other heavy metals, of which the release capacity tends to decrease and increase later. During the first 1–30 min, Zn and Cd are well in accordance with the first-order reaction, and their confidence level of cor-

Table 12 Released solution concentrations and released percentages of heavy metals at different time

Release time	Cu		Pb		Zn		Cd	
	RSC mg/l	R_i %	RSC mg/l	R_i %	RSC mg/l	R_i %	RSC mg/l	R_i %
30 s	0.058	0.58	0.100	0.50	0.3462	12.66	0.4230	19.24
1 min	0.052	0.52	0.100	0.50	0.3672	13.43	0.4890	22.25
2 min	0.046	0.46	0.092	0.46	0.3782	13.83	0.5166	23.50
4 min	0.046	0.46	0.076	0.38	0.3881	14.19	0.5360	24.39
6 min	0.049	0.49	0.076	0.38	0.3932	14.38	0.5604	25.50
8 min	0.046	0.46	0.076	0.38	0.4057	14.83	0.5690	25.89
20 min	0.061	0.61	0.108	0.54	0.4835	17.68	0.6659	30.30
30 min	0.070	0.70	0.107	0.54	0.5279	19.30	0.7189	32.71
1 h	0.086	0.87	0.112	0.56	0.5752	21.03	0.7843	35.68
2 h	0.104	1.05	0.133	0.67	0.6417	23.46	0.8466	38.52
4 h	0.107	1.08	0.206	1.03	0.6336	23.17	0.9255	42.11
5 h	0.089	0.90	0.076	0.38	0.6334	23.16	0.8600	39.13
6 h	0.086	0.87	0.043	0.22	0.6314	23.09	0.8590	39.08
18 h	0.080	0.81	0.060	0.30	0.6824	24.95	0.8552	38.91
24 h	0.084	0.85	0.065	0.33	0.6905	25.25	0.8677	39.48

RSC Released solution concentration, R_i released percentage

Table 13 Release dynamics parameters of heavy metals

	Cu	Pb	Zn	Cd
Time (min)	1–30	1–30	1–30	1–30
Number of samples n	7	7	7	7
Rate equation	$\ln C = 0.8337\,t - 3.0932$	$\ln C = 0.5301\,t - 2.501$	$\ln C = 0.7572\,t - 1.0025$	$\ln C = 0.7532\,t - 0.6814$
Correlation coefficient r^2	0.8331	0.3408	0.9909	0.9611
Significance level α	0.02	Inconspicuous	0.001	0.001
Rate constant of release reaction k	0.834	0.530	0.757	0.753

relation coefficients are over 99.9%. According to rate constants attained from first-order reaction, the order of release speed of the previous 30 min with Zn = Cd > Cu > Pb is obtained.

Conclusions

Adsorption capacities of selected heavy metals increase obviously with increasing pH. Adsorption of Cu and Pb increase rapidly at 3 < pH < 6, while adsorption of Zn and Cd increase rapidly at 6 < pH < 9. Competition of selected heavy metals decrease with increasing pH of the solution, and the competition nearly disappears as precipitation is at the highest flight in the system.

Adsorption on selected heavy metals decreases with increasing ionic strength and is barely influenced by the temperature of the system. But increasing salinity of the Yellow River in recent years (Chen 2000a, b) has led to decrease in the sediment adsorption on heavy metals and to increase in the potential environmental hazard.

Both competitive coefficient K_c and distribution coefficient K_d describe the competitive abilities of heavy metals well. But K_c, more accurately than K_d, describes the competition of selected heavy metals, while K_d mainly describes the natural quality of heavy metals and sediments. Calculating K_c and K_d, the same order of adsorption ability is attained as Pb > Cu >> Zn > Cd. Competition of heavy metals intensifies with the increasing concentrations of heavy metals.

None of the selected heavy metals transformed into the residual form after adsorption. Only 0–1.9% of heavy metals were transformed into the organic-bound form (IV). Most part of Cu, Pb and Zn (50.8–87.7%) were transformed into the carbonate-bound form (II). Cu had less transformation (1.2%) into the exchangeable form (I), while transformation of Pb and Zn into the exchangeable form and Fe, Mn-oxidex-bound form (III) were 8.2–32.0% after adsorption. Most (60.7–77.3%) of Cd was transformed into the exchangeable form, and 19.7–30.4% of Cd transformed into the carbonate-bound form.

In contradiction to adsorption, the order of release ability is Cd > Zn >> Cu > Pb. The release capacities of Cu, Zn and Cd account for 70.1, 80.2 and 54.8% of their contents in exchangeable form, respectively, while Pb merely accounts for 2.7%. The study also shows that concentrations of Cu, Zn and Pb in the release solution are lower than the Human Health Criteria; however, the release concentration of Cd is 85.8 times more than the Human Health Criteria of US EPA. So, there is a great environmental risk from Cd in the Yellow River, which needs to be controlled.

Release reaction goes very fast. The release capacities of Cu, Pb, Zn and Cd from sediments reach half of the maximum release capacity or so in only 30 s. Except Zn, the other heavy metals reach the maximum release value at the 4 h point and drop thereafter. During the first 1–30 min of release, Cu, Zn and Cd are in accordance with first-order reaction; the confidence level of Cu in correlation test is over 98% and the confidence levels of Zn and Cd are over 99.9%. Pb is not in accordance with first-order reaction, which decreases before increasing later in release. According to the rate constants attained from first-order reaction, the order of release speed in 1–30 min with Zn = Cd > Cu > Pb is obtained.

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References

Alberty RA (1987) Physical Chemistry. 7th edn. Wiley, New York

Chen JS, Hong S, Wang LX, Wang FY (2000a) Geo-chemical parameters of river particulate in Eastern China. Acta geographica sin 55(4):417–427

Chen JS, Li HB, Xia XH, Zhai XH (2000b) A study on water-quality trend in the Yellow River system from 1960's to 1990's. Environ Chem 19(2):97–101

Christian Gischler (2005) Pathways of heavy metals and implication for stakeholders, Sonso Lagoon, Colombia. TRITA-LWR Master Thesis LWR -EX-05–13. Stockholm-Sweden

Du Q, Wen XH, Li LL, Tang HX (1996) Adsorption behaviours of the natural sediment on heavy metals. Environ Chem 15(3):199–206

Filius Angelika, Streck Thilo, Richter Jorg (1998) Cadmium sorption and release in limed topsoils as influenced by pH: isotherms and simulated leaching. J Environ Qual 27:12–18

Galvez-cloutier R, Jean-sѐbastien D (1998) An evaluation of fresh water sediments contamination: the Lachine canal sediments case, Montrѐal, Canada. Part II: heavy metal particulate speciation study. Water Air Soil Pollut 102:281–301

Gomes PC, Fontes MPF, Da Silva AG, Mendonça de ES, Netto AR (2001) Selectivity sequence and competitive adsorption of heavy metals by Brazilian soils. Soil Sci Soc Am J 65:1115–1121

Hsu PH (1989) Aluminum oxides and oxyhydroxides. In: Dixon JB, Weed SB (eds) Minerals in soil environments. ASA and SSSA, Madison, pp 331–378

Huang SL, Wan ZH, Wang LX (1995) Study on the effects of concentrations of heavy metals in sediment and initially in water phase on their adsorption. Acta Scientiae Circumstantiae 15(1):66–75

Nicole ML, Robert PM, Jean-Michel L (2001) The fate and transport of mercury, methylmercury, and other trace metals in chesapeake bay tributaries. Wat Res 35:501–515

Petersen W, Willer E, Willamowski C (1997) Remobilization of trace elements from polluted anoxic sediments after resuspension in oxic water. Water Air Soil Pollut 99:515–522

Ricou P, Hѐquet V, Lecuyer I, Le Cloirec P (1999) Influence of operating conditions on heavy metal cation removal by fly ash in aqueous solutions. In: International ash utilization symposium. University of Kentucky

Schwertmann U, Taylor RM (1989) Iron oxides. In: Dixon JB, Weed SB (ed) Minerals in soil environments. ASA and SSSA, Madison, pp 379–438

Tisser A, Campdell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem 51:844–851

US EPA (1976) Quality criteria for water (Red Book)

US EPA (1986) Quality criteria for water (Gold Book). EPA 440/5-86-001

US EPA (1999) Understanding variation in partition coefficient, K_d, values. EPA 402-R-99-004A-B, August