



# Speciation and Release Kinetics Simulation of Zn and Cd from River Sediment Contaminated by Gold Mining

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**Abstract** Heavy metals release from contaminated sediments is one of the most important chemical processes affecting overlying water quality in river, lake, and ocean. The objective of this study was to determine the leaching properties, kinetic rate, and leaching amount of zinc (Zn) and cadmium (Cd) from the river sediment contaminated by gold mining. Speciation of Zn and Cd in the sediments was extracted by a modified BCR extraction procedure. Release kinetics of Zn and Cd were studied by a simulated leaching experiment using a stirred-flow reactor and a two-site equilibrium-kinetic model. The sediments we studied were significantly contaminated by Zn (620–5878 mg kg<sup>-1</sup>) and Cd (2–67 mg kg<sup>-1</sup>), and both have high content of weak acid extractable forms. There were much more smaller par-

ticles on the surface of sediment JH01 and JH02 than sediment JH03 and JH04. The two-site equilibrium-kinetic model fits the release data of Zn and Cd well, and it was demonstrated as an effective tool to describe the kinetic release of Zn and Cd from river sediments. Kinetic rates obtained from curve fitting showed large variation among sediments indicating different reaction mechanisms. The rapid release stage (before the second stop-flow) of Zn and Cd was controlled both by the equilibrium sites and the kinetic sites, while the slow release stage (after the second stop-flow) was mainly controlled by the kinetic sites. The total leaching amount of Zn and Cd in JH01 (27.1 mg kg<sup>-1</sup>, 0.4 mg kg<sup>-1</sup>), JH02 (474 mg kg<sup>-1</sup>, 7.5 mg kg<sup>-1</sup>), JH03 (320 mg kg<sup>-1</sup>, 7.6 mg kg<sup>-1</sup>), and JH04 (52.4 mg kg<sup>-1</sup>, 2.0 mg kg<sup>-1</sup>) demonstrated that large amount of Zn and Cd in sediments can be leached into solution. Thus, effective measures should be taken to prevent leaching of heavy metals from river sediment.

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## 1 Introduction

Heavy metals usually have high toxicity; once entering into rivers, they will cause water pollution and transport with hydrologic gradients for a long distance and then settled on the bottom sediments by adsorption or precipitation, etc. (Li et al. 2013; Resongles et al. 2014). Sediment is a sink for contaminants by removing them

from the water column. However, subsequent release of contaminants from the sediment will increase heavy metals in overlying waters under favorable conditions (Chen et al. 2019; Deng et al. 2020). These heavy metals may enter into the food chain and thereafter pose health risks to human consumers (Di Palma and Mecozzi 2007; Kalnejais et al. 2015; Li et al. 2020; Soliman et al. 2018; Urien et al. 2018). Thus, heavy metals release from contaminated sediments is one of the most important chemical processes affecting overlying water quality in river, lake, and ocean.

Cadmium is toxic to humans, animals, and plants (Khaokaew et al. 2012). Although Zn is an essential element for plants, it can be toxic at a high level (Khaokaew et al. 2011). Nowadays, in addition to considering the total amount of heavy metals, the bioavailable fractions of heavy metals are considered to be more effective and accurate to estimate the toxicity of heavy metals; so, it is indispensable to investigate heavy metal speciation in soils or sediments (Dutta et al. 2017). The sequential extraction procedure has successfully been used to extract the speciation of heavy metals in soils and sediments and estimation of heavy metal toxicity and risk (Król et al. 2020; Zhao et al. 2020). Both Zn and Cd have high mobility especially in acid environment (Gao et al. 2018; Król et al. 2020; Rausch et al. 2005; Zhao et al. 2020). Mining and smelter activities can result in Zn and Cd contamination in environments, including river sediments (Ren et al. 2016; Resongles et al. 2014). Earlier studies demonstrated that the content of toxic metals can even exceed hundreds of milligrams per kilogram in river sediment contaminated by mining (Chen et al. 2019; Pagnanelli et al. 2004). Therefore, the contaminated sediment is a potential threat to ecological environment. So a quantitative understanding of the kinetics of heavy metal adsorption/desorption reactions in sediment is required. And it will provide basis for further predicting the behavior of heavy metals and developing remediation strategies in the watershed.

This study aimed to investigate Zn and Cd speciation and release kinetics in the Zn-Cd-contaminated river sediments. Sequential extraction procedure (SEP) was employed to determine Zn and Cd speciation in the sediment. A stirred-flow experiment and a two-site equilibrium-kinetic model were used to measure Zn and Cd release kinetics. Results reported in this study will be useful in choosing the best strategy to remediate Zn and Cd in contaminated river sediments, especially in the Jiehe River watershed.

## 2 Materials and Methods

### 2.1 Sediment Characterization

The four contaminated sediments used in this study were collected along the main stem of the Jiehe River which is located in the northwest of Shandong province, China, with a latitude 37°05' N–37°33' N and a longitude 120°08' E–120°38' E. The locations of all sediment samples are as follows: JH01 (120°29.26' E, 37°25.19' N), JH02 (120°27.39' E, 37°23.82' N), JH03 (120°22.97' E, 37°25.24' N), and JH04 (120°21.96' E, 37°26.05' N). The main stem of the Jiehe River flows northwest into the Laizhou Bay of Bohai Sea, and the length is about 42 km (Cai et al. 2017). The distances of the four sediments from the river source are 4.5, 8.4, 17.3, and 19.2 km, respectively. Our earlier studies have demonstrated that abundance of heavy metals was released into the Jiehe River by the rapid development of mining industry, and the river sediment was contaminated by the mine water and tailings (Cai et al. 2017; Zhang et al. 2014b). Composite samples of surface (0–5 cm) sediment were grabbed from the bottom of stream channel and stored in sealed plastic bags. Stream sediment samples were air dried and passed a 2-mm sieve before chemical analysis.

Total organic carbon (TOC) and particle size of the sediments were determined using an elemental analyzer (Vario MACRO cube, Elementar, Germany) and a laser particle size analyzer (Malvern Mastersizer 2000F, Malvern, UK), respectively. The sediment microscopic morphological characteristics were analyzed by a Scanning Electron Microscope-Energy Dispersive Spectrometer (SEM-EDS) (S-4800, Hitachi, Japan). Sediment pH was measured in a 1:10 soil-water suspension after stirring for 30 min. Combined forms of Zn and Cd were analyzed by a sequential extraction method (Table 1), which contained different sequential extraction schemes that vary in number of steps, shaking times, extracting reagents, etc. (Król et al. 2020; Tessier et al. 1979). The three-step sequential extraction procedure proposed by the Commission of the European Communities Bureau of Reference (BCR) has been applied commonly for the fractionation of heavy metals (Table 1) and is utilized in our study (Nemati et al. 2011; Pueyo et al. 2008; Soliman et al. 2018). About 0.10 g sediment sample was digested with a mixture of HNO<sub>3</sub>-HClO<sub>4</sub>-HF (5 mL-2 mL-1 mL) for 12 h at 180 °C. The total metal concentration in sediment was determined by

**Table 1** Modified sequential extraction procedures used in this study

Steps	Speciation	Reagents used
1	Weak acid extractable	0.11 mol L <sup>-1</sup> CH <sub>3</sub> COOH (20 mL); 24 h at 25 °C on shaker table (200 rpm)
2	Reducible	0.5 mol L <sup>-1</sup> NH <sub>2</sub> OH·HCl (20 mL); 24 h at 25 °C on shaker table (200 rpm)
3	Oxidizable	30% H <sub>2</sub> O <sub>2</sub> (10 mL) 1 h at 85 °C; 1 mol L <sup>-1</sup> CH <sub>3</sub> COONH <sub>4</sub> (25 mL), pH 2; 24 h at 25 °C on shaker table (200 rpm)
4	Residual	Aqua regia

Dried sediment (1.0 g) was extracted using the steps below. Steps 1–3 were washed with deionized water; the wash solution for each step was analyzed for Zn and Cd

inductively coupled plasma-mass spectrometry (ICP-MS, ELAN DRC II, PerkinElmer, USA). All sediment analysis followed the standard operation procedures and quality control procedures to ensure accurate analysis of sediment and solution samples, including replication, calibration, external standards, blank samples, etc.

## 2.2 Stirred-Flow Experiments

A stirred-flow reactor system was used in our kinetic experiments by leaching sediment with a 10 mM Ca(NO<sub>3</sub>)<sub>2</sub> solution (pH 6.5) as the background electrolyte. The stirred-flow reactor system which was successfully used in earlier studies was to specifically study the short-term kinetic reactions in diluted soil suspensions (Liu et al. 2019; Shi et al. 2005). The reactor (25 mm i.d.) has a reaction cell of 42 cm<sup>3</sup>. Sediment sample (1.0 g) was placed in the reactor, together with a magnetic stir bar. A filter membrane (0.45 μm) was placed in the reactor to prevent the sediment particles flow out of the reactor. After sealing the reactor, the reactor was fully filled with the Ca(NO<sub>3</sub>)<sub>2</sub> solution, and stirred immediately. The suspension was stirred for 20 min without flow in the background electrolyte (pre-equilibration). After pre-equilibration, the background electrolyte was injected into the reactor with a peristaltic pump (BT102S, Leadfluid, China) at a fixed flow rate (2 mL min<sup>-1</sup>). To diminish diffusion, the suspension was well mixed during the whole experiments. To prevent the back reactions, the reaction products were continuously flowing out of the reactor during the metal release process. The leaching effluent was collected with a fraction collector (BS-100A, BaiXian, China) using 5-min fixed time intervals for each sample. Samples were preserved at 4 °C before they were analyzed for Zn

and Cd by ICP-MS. A stop-flow experiment was carried out by turning off pump for 30 min two times (60 min and 260 min) to determine whether metal release is kinetically controlled or instantaneous.

## 2.3 Model Description

Heavy metals release from contaminated sediments is controlled by some reactions: sorption/desorption, precipitation/dissolution, etc. (Gwimbi et al. 2020; He et al. 2019). In this study, all sediment samples were leached by neutral solution (pH 6.5), and we did not expect any significant amount of metal release by precipitates dissolve in the original sediment samples. Therefore, only adsorption/desorption reactions were considered in the equilibrium-kinetic model described below. There are many functional groups in sediment particles with different capabilities of binding metals. For simplification of the metal release process, we assume that there are a set of equilibrium sorption sites and a set of reversible kinetic sites in the sediment particles. Based on this assumption, we established an equilibrium-kinetic model to describe the release of Zn and Cd from the contaminated sediment. The competitive adsorption of Ca is not considered in the model, as there is constant concentration of Ca in the background electrolyte. The formulations of the model are described as:

$$S_e = K_d C \quad (1)$$

$$\frac{\partial S_k}{\partial t} = k_1 C - k_2 S_k \quad (2)$$

where  $C$  is the concentration of the metals in solution,  $S_e$  and  $S_k$  are the amount retained on equilibrium sites and kinetic sites (mg g<sup>-1</sup>),  $K_d$  is equilibrium constant (L g<sup>-1</sup>),

and  $t$  is the reaction time (h).  $k_1$  and  $k_2$  are the adsorption ( $\text{L g}^{-1} \text{min}^{-1}$ ) and desorption ( $\text{min}^{-1}$ ) reaction rate. The total amount of solute retention on sediment is:

$$S = S_e + S_k \quad (3)$$

To simulate the release of Zn and Cd from the sediments, we incorporated the two-site equilibrium-kinetic formulations into the steady-state convection-dispersion equation (CDE) in the form of (Selim et al. 1989; Zhang et al. 2014a):

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) - v \frac{\partial C}{\partial x} - \frac{\partial S}{\partial t} \quad (4)$$

where  $x$  is distance (cm),  $D$  is hydrodynamic dispersion coefficient ( $\text{cm}^2 \text{min}^{-1}$ ), and  $v$  is flow rate ( $\text{cm min}^{-1}$ ).

The coefficient of determination ( $r^2$ ) and the root mean square error ( $RMSE$ ) were used in this study to estimate the goodness-of-fit of our model to the observed data:

$$RMSE = \sqrt{\frac{\sum (C_{\text{obs}} - C_{\text{mod}})^2}{n_{\text{obs}} - n_{\text{par}}}} \quad (5)$$

where  $C_{\text{obs}}$  is the observed Zn and Cd concentration,  $C_{\text{mod}}$  is the simulated Zn and Cd concentration,  $n_{\text{obs}}$  is the number of measurements, and  $n_{\text{par}}$  is the number of fitted parameters.

### 3 Results and Discussion

#### 3.1 Sediment Characteristics

Basic physical and chemical properties of the four sediments are showed in Table 2. The pH of the four sediment samples increase with their distance from the river source. Sediment JH01 shows the lowest pH 4.2, and sediment JH04 has the highest pH 7.8. This can be explained by the discharge of acid mine drainage (AMD) caused by oxidative dissolution of sulfide minerals such as pyrite, containing various toxic trace elements (Cai et al. 2017; Zhang et al. 2014b). There is a big difference of the content of TOC among the four sediments. The TOC of sample JH04 is especially high ( $116 \text{ g kg}^{-1}$ ) compared to the other three sediments. This may be caused by the vermicelli factories along the downstream of the Jiehe River, which discharged large amount of wastewater with high concentration of organic materials. Sediments JH01 and JH02 have similar

particle size distribution; it might be because there are amount of tailings in the upstream of the river channel (Cai et al. 2017). Sand is the major composition in sediment JH03 and JH04, and sand is especially high in JH03 (86%). Total Fe in sediment JH01 and JH02 were higher than in sediment JH03 and JH04, while on the contrary, total Mn in JH01 and JH02 were lower than in JH03 and JH04. The high content of Fe in upstream sediment may be due to the high content of primary minerals caused by mining waste. The lower pH in the upstream sediment and water (Cai et al. 2017) may cause the release of Mn from minerals and transport to downstream. Zn and Cd in the four sediments are very high, especially in downstream sediment. There is a same trend as Mn that the content of Zn and Cd in upstream sediment is lower than the downstream sediment.

The microscopic morphological characteristics of the four sediments showed some differences in Fig. 1. The particle sizes of sediment JH01 and JH02 in upstream were smaller than JH03 and JH04, which is consistent with the results analyzed by a laser particle size analyzer (Table 2). The particles on the surface of sediment JH03 have the biggest grain size than the other three sediments as this sediment has 86% of sand particles (Table 2). The major element on the surface of the sediments analyzed by SEM-EDS is shown in Table 3. Carbon (C), oxygen (O), aluminum (Al), and silicon (Si) accounted for more than 80% of the total mass in the surface of the four sediments. The content calcium (Ca) and sodium (Na) increases with the distance increases from the source. This may be caused by the discharge of domestic sewage from nearby villages along the Jiehe River. The content of Fe on the surface of the four sediments are 5.7%, 4.5%, 4.8%, and 5.3%, which is much different from the total amount analyzed by ICP-MS. This just shows the heterogeneity of surface structure in four sediments.

#### 3.2 Speciation of Zn and Cd in Sediment

The reliability of our continuous extraction experiment can be evaluated by the recovery rate of the element we extracted. The recovery rates of Zn and Cd in the four sediments are 90–109% and 94–109%, respectively (Table 4). The results showed that the modified BCR extraction experiment that we used here is an effective and reasonable method to analyze Zn and Cd speciation in the stream sediment.

**Table 2** Basic physical and chemical properties of the four sediments

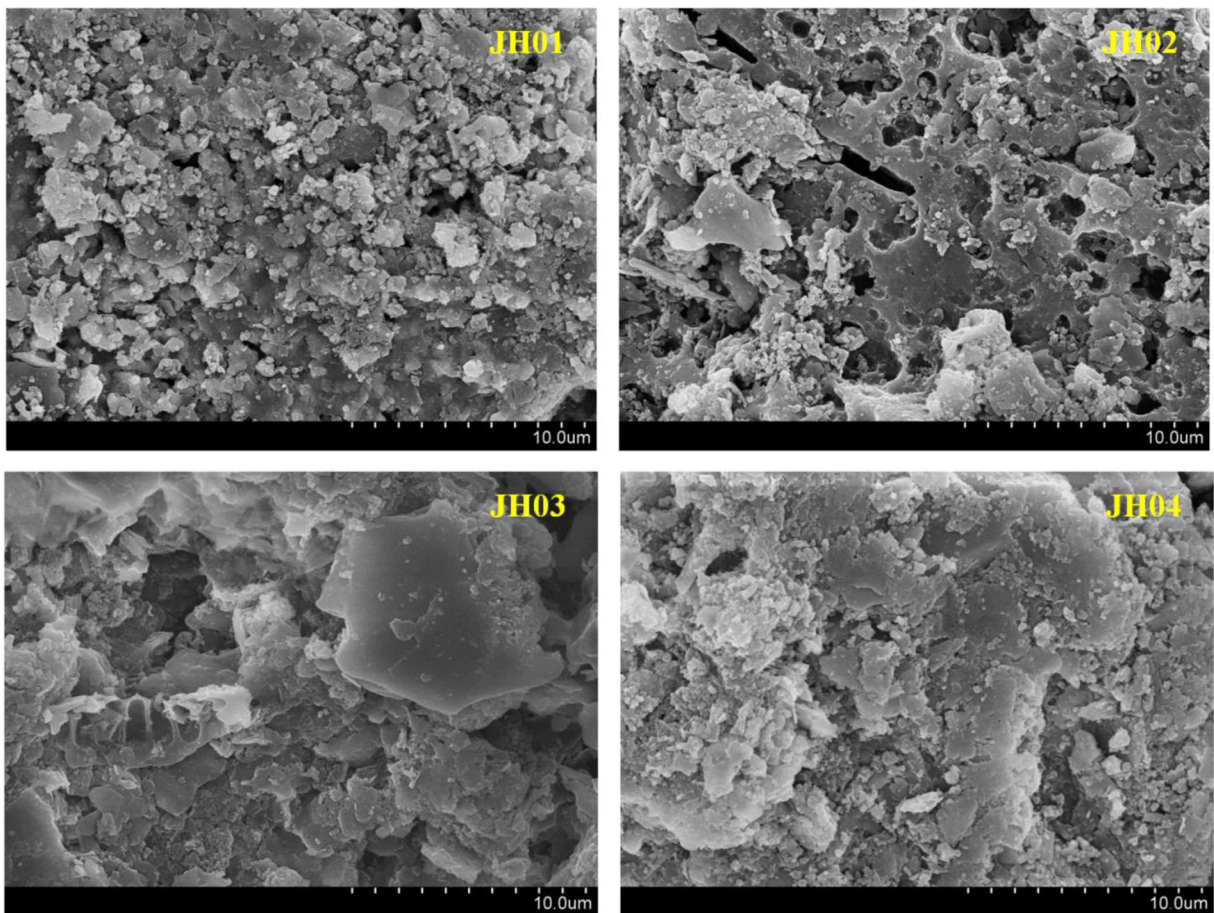
Sediment	Distance (km)	pH	TOC <sup>a</sup> (g kg <sup>-1</sup> )	Clay <sup>b</sup> (%)	Silt (%)	Sand (%)	Fe (g kg <sup>-1</sup> )	Mn (mg kg <sup>-1</sup> )	Zn (mg kg <sup>-1</sup> )	Cd (mg kg <sup>-1</sup> )
JH01	4.5	4.21	17.7	6.90	40.9	52.2	74	227	620	2
JH02	8.4	5.58	38.1	8.41	49.3	42.3	35	246	1920	15
JH03	17.3	6.66	11.8	1.74	12.2	86.0	29	351	5878	67
JH04	19.2	7.84	116	5.46	34.0	60.5	32	439	3701	34

<sup>a</sup> TOC total organic carbon

<sup>b</sup> Grain size distribution: clay (<2 μm), silt (2–20 μm), sand (20–2000 μm)

The releases of heavy metals present in sediment could threaten the quality of local water resources and aquatic organisms (Deng et al. 2020), and the risk is not only related to their total contents but also their speciation (Wang et al. 2019). The sequential extraction results (Fig. 2) showed that Zn and Cd were similarly present in high labile fractions compared to other fractions. It means that these two elements in the sediment have high

mobility and bioavailability, which is consistent with other studies (Kim and Hyun 2015; Nemati et al. 2011; Xiao et al. 2019). Most of Zn and Cd in sediment JH02, JH03, and JH04 are in the weak acid extractable form and little of them in oxidizable form and residual form. Weak acid extractable forms include carbonate and water exchangeable forms, which can be easily released and cause risks to organisms directly. So there could be

**Fig. 1** SEM pictures of the four sediments

**Table 3** Major element of the particles on the sediment surface (wt%)

Sediment	Distance (km)	C	O	Na	Mg	Al	Si	P	S	K	Ca	Fe
JH01	4.5	10.41	55.88	0.53	0.51	8.48	12.07	0.15	1.10	3.24	–	5.67
JH02	8.4	15.92	48.17	0.38	0.59	11.66	8.97	1.55	4.83	0.80	0.75	4.51
JH03	17.3	9.29	47.77	1.36	0.52	10.82	17.29	0.66	0.76	1.97	3.12	4.81
JH04	19.2	17.84	44.83	2.15	0.56	6.73	10.87	2.90	1.50	1.63	3.09	5.32

a massive release of Zn and Cd in sediment JH02, JH03, and JH04. While in sediment JH01, Zn and Cd in weak acid extractable form are 13% and 28%, far lower than their amount in JH02, JH03, and JH04. This indicates that Zn and Cd have the similar geochemical properties, that is, they were easily released from upstream sediment JH01 and transported to JH02, JH03, and JH04. This can also be explained by the total contents of Zn and Cd in the four sediments (Table 2). The total contents of Zn and Cd in JH01 is an order of magnitude lower than the other three sediments. And the low pH value (4.2) may have caused amount of Zn and Cd in weak acid extractable forms released and transported to downstream and adsorbed in downstream sediments (Król et al. 2020). Thereafter, the rest of Zn and Cd in JH01 mainly in residual forms. Heavy metals in residual forms are very stable and mostly in primary minerals and secondary silicate mineral lattice. They can hardly participate in sediment-water interactions and have lower mobility and bioavailability and will not cause pollution in short term (Gao et al. 2018). Extractable heavy metals (weak acid extractable, reducible, oxidizable) are not stable; if environmental conditions changed, they can easily release and cause secondary pollution. Sediments in the Jiehe River were heavily contaminated and have high content of Zn and Cd in weak acid extractable forms, which would easily release and cause long-term pollution to the Jiehe River. So it is necessary to clarify the release mechanisms of Zn and Cd for choosing better remediation techniques.

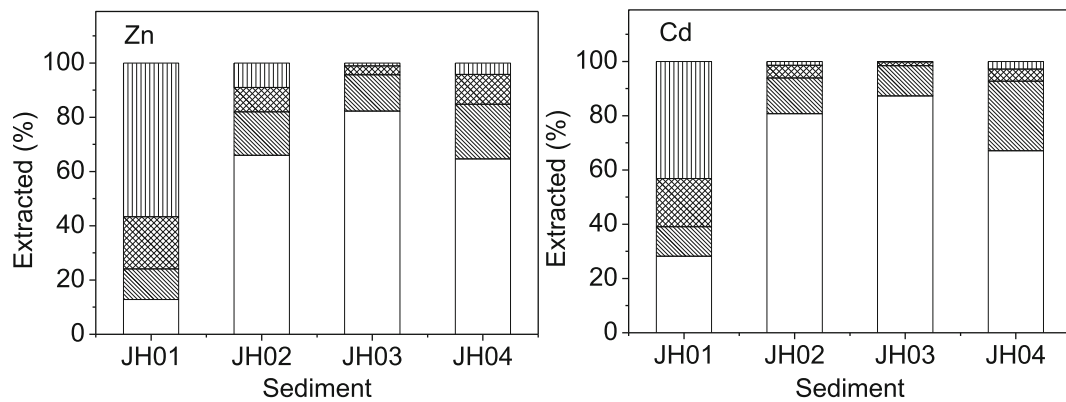
**Table 4** Recovery rate of Zn and Cd of sequential extraction procedure (%)

Sediment	JH01	JH02	JH03	JH04
Zn	90	96	109	96
Cd	94	102	109	101

### 3.3 Modeling Zn and Cd Release Kinetics

Figure 3 shows the pH values of the effluent during the leaching experiment of the four sediments. Since the pH of the four sediments themselves varies considerably (Table 2), the pH of the solution in the leaching reactor is different even if the same background solution (pH 6.5) is used. We assume that the pH of the collected leach solution is the pH of the solution in reactor at the time of the reaction. The four sediments had strong acid-producing potential, and the pH values were basically consistent with the pH values of the sediments themselves. The leachate of the upstream sediments JH01 and JH02 was acidic and tends to increase slowly, while the sediments JH03 and JH04 in the downstream were basically neutral. The pH values of the input solution during leaching might be an important factor affecting the release of heavy metals in the sediments.

The kinetics of Zn and Cd release from the four sediments at same flow rates ( $2 \text{ ml min}^{-1}$ ) under different pH values (Fig. 3) are presented in Fig. 4 and Fig. 5. Zn and Cd demonstrated as two mobile elements with averaged concentration of 46, 777, 580, and  $79 \mu\text{g L}^{-1}$  and 0.8, 13, 14, and  $3 \mu\text{g L}^{-1}$  in the leachate of sediments JH01, JH02, JH03, and JH04, respectively. Higher concentrations of Zn and Cd released from sediment JH02 and JH03 than JH01 and JH04 may be caused by lower content of weak acid extractable forms of Zn and Cd in sediment JH01 (Fig. 2) and high content of TOC in sediment JH04 (Table 2). Long term of wastewater discharge from a vermicelli production factory located near the sampling site might cause high content of organic matters accumulated in sediment JH04. The concentrations of Zn and Cd released decreased with the influent of background solution and quickly approached to a plateau. This trend is consistent with the release of Zn and Cd desorption from contaminated soils (Liu et al. 2019; Peng et al. 2018).



**Fig. 2** Speciation of Zn and Cd in the four sediments. Different pattern illustrate Zn and Cd distribution in the four different forms (from bottom to top): weak acid extractable form, reducible form, oxidizable form, and residual form

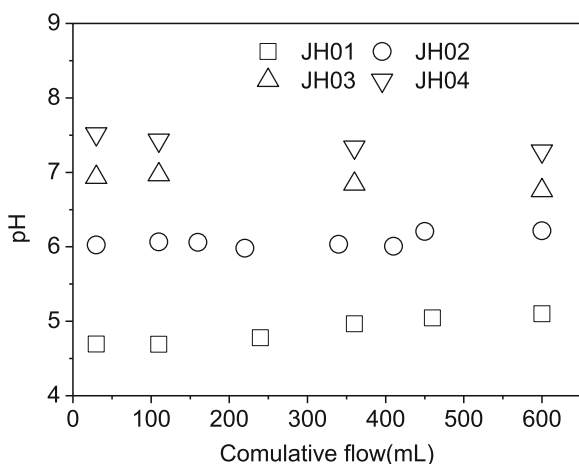
Two times of stop-flow were carried out at the cumulative flow of 120 mL and 420 mL, respectively. There is a certain amount of increase for the concentration of Zn and Cd in the leachate after stop-flow. This increase of Zn and Cd concentrations after stop-flow demonstrates that the release of Zn and Cd from sediment is a time-dependent process. The time-dependent leaching process is likely due to the speciation of elements transformed between recalcitrant and leachable forms (Kim and Hyun 2015). Zn and Cd showed a quick release from the fast leaching fraction followed by retarded leaching from the slow leaching fraction. This is consistent with the release of Zn and Cd from abandoned mine soils which was fitted with two-site first-order leaching model (Kim and Hyun 2015).

The kinetic rate of Zn and Cd release from sediment can vary in a wide range depending on characteristics of the river sediments (Table 5). Sediment JH04 showed

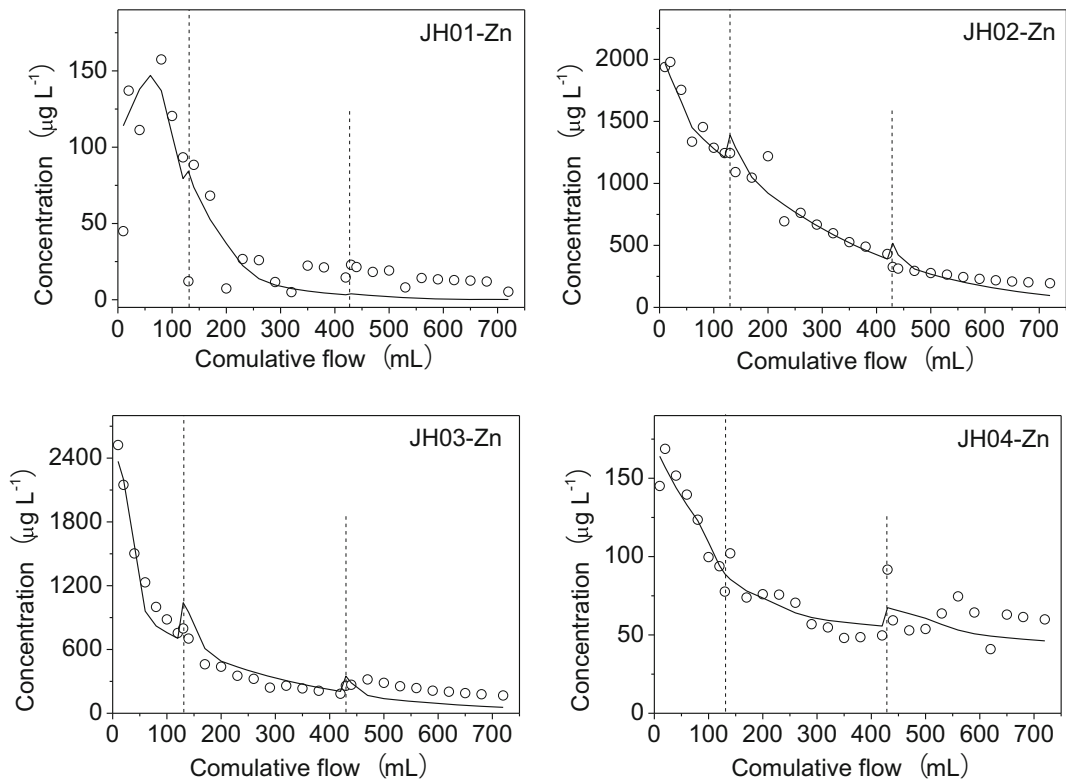
higher  $K_d$  value than the other three sediments, meaning that Zn and Cd release from sediment JH04 are mainly controlled by equilibrium sites. The coefficients of determination ( $r^2$ ) and the root mean square error (RMSE) of the simulated results demonstrate that our kinetic model fit to Zn and Cd release experiment especially for Cd and can well reproduce the stop-flow results. Kinetic rates obtained from curve fitting (Table 4) showed large variation among sediments, indicating different reaction mechanisms. The rapid release stage (before the second stop-flow) of Zn and Cd was controlled both by the equilibrium sites and the kinetic sites, while the slow release stage (after the second stop-flow) was mainly controlled by the kinetic sites. Overall, the release kinetics of Zn and Cd from the contaminated river sediments can be well described by our two-site equilibrium-kinetic model.

### 3.4 Leaching Amount of Zn and Cd

Figure 6a and b illustrate the leaching amount of Zn and Cd include observed and simulated. The observed leaching amount of Zn and Cd in JH01 (27.1 mg kg<sup>-1</sup>, 0.4 mg kg<sup>-1</sup>), JH02 (474 mg kg<sup>-1</sup>, 7.5 mg kg<sup>-1</sup>), JH03 (320 mg kg<sup>-1</sup>, 7.6 mg kg<sup>-1</sup>), and JH04 (52.4 mg kg<sup>-1</sup>, 2.0 mg kg<sup>-1</sup>) were compared to the weak acid extractable forms and total amount in the four sediments and shown in Fig. 6c, d. High amount of Zn and Cd were released from sediment JH02 and JH03, especially for Zn. The percentage of Zn and Cd released to weak acid extractable forms of the four sediments were JH01 (38%, 73%), JH02 (39%, 61%), JH03 (6%, 12%), and JH04 (2%, 9%), respectively (Fig. 6c, d). While sediment JH01 and JH02 showed higher leaching rate for



**Fig. 3** The pH values of the effluent during the leaching experiment of the four sediments



**Fig. 4** Kinetics of Zn release from stream sediment. The white cycles and solid line depict the observed and simulated concentration of Cd, respectively. The dash line indicates two times of stop-flow

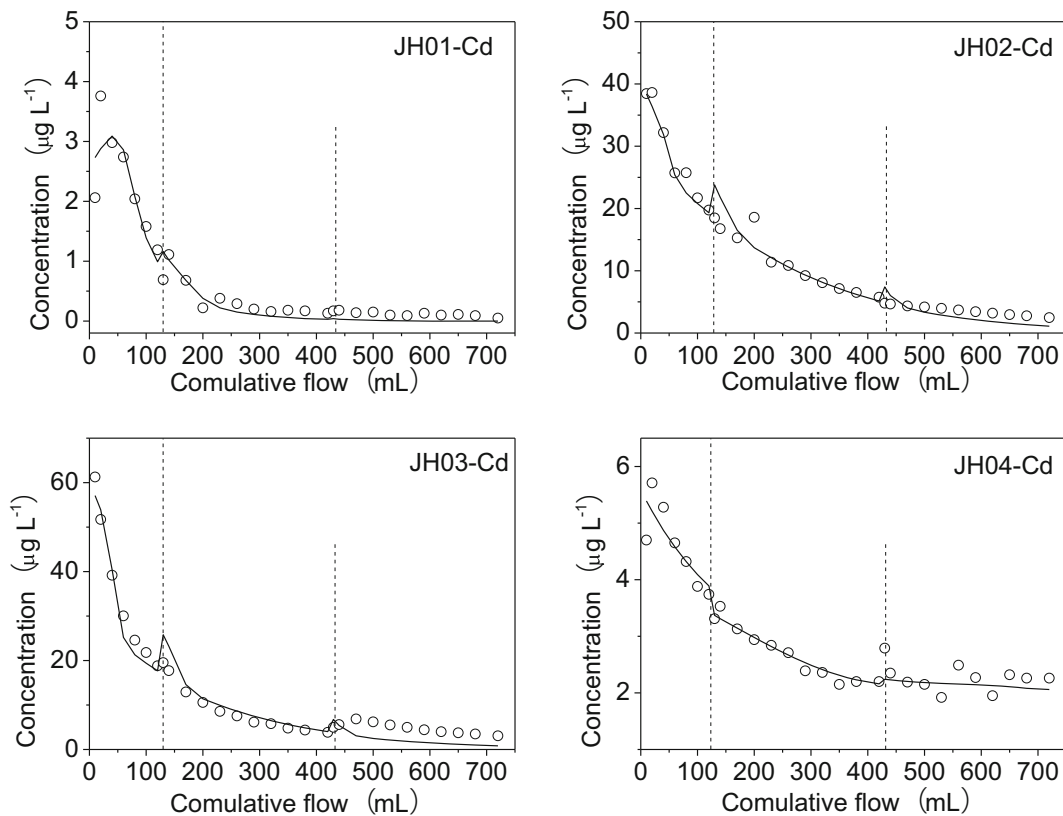
both Zn and Cd, this may be caused by the lower pH of the solution in the reactor. Though with high content of Zn ( $3701 \text{ mg kg}^{-1}$ ) and Cd ( $34 \text{ mg kg}^{-1}$ ) in sediment JH04, the leaching amount and leaching rate of Zn and Cd were much lower. This might be related to the slightly alkaline solution environment and high content of phosphorus (2.9%, Table 2), which could bind with Zn and Cd to form precipitates. Furthermore, the weak acid extractable forms of metals include water exchangeable form and carbonate bounded form, and only water exchangeable form can be released in this experiment conditions (Izquierdo et al. 2017). And even the two elements showed different leaching characteristics in the four sediments, the observed and simulated values of leaching amount are very close, so our two-site model could simulate the kinetic release of Zn and Cd well from sediments with different geochemical properties. Generally, the release of Zn and Cd from sediments not only was controlled by their total content but also impacted by its chemical speciation in solid phases (Wang et al. 2019). Extractable forms (water exchangeable form and weak acid extractable form) of heavy metals

always have high mobility and should be the major contributor to metals release in leaching experiment.

#### 4 Conclusions

With high total contents of Zn and Cd and relatively high percentages present in the weak acid extractable forms especially in downstream sediments, the river sediments contaminated by gold mining serve as a key source of Zn and Cd to the surrounding environment. The four sediments had strong buffer capacity, and the pH values were basically consistent with the pH value of the sediments themselves. Zn and Cd demonstrated as two mobile elements with averaged concentration of 46, 777, 580, and  $79 \mu\text{g L}^{-1}$  and 0.8, 13, 14, and  $3 \mu\text{g L}^{-1}$  in the leachate of sediments JH01, JH02, JH03, and JH04, respectively. The two-site equilibrium-kinetic model fits the release data of Zn and Cd well and can reproduce the stop-flow experimental results. It was demonstrated as an effective tool to describe the kinetic release of Zn and Cd from sediments to waters. The kinetic rate of Zn and





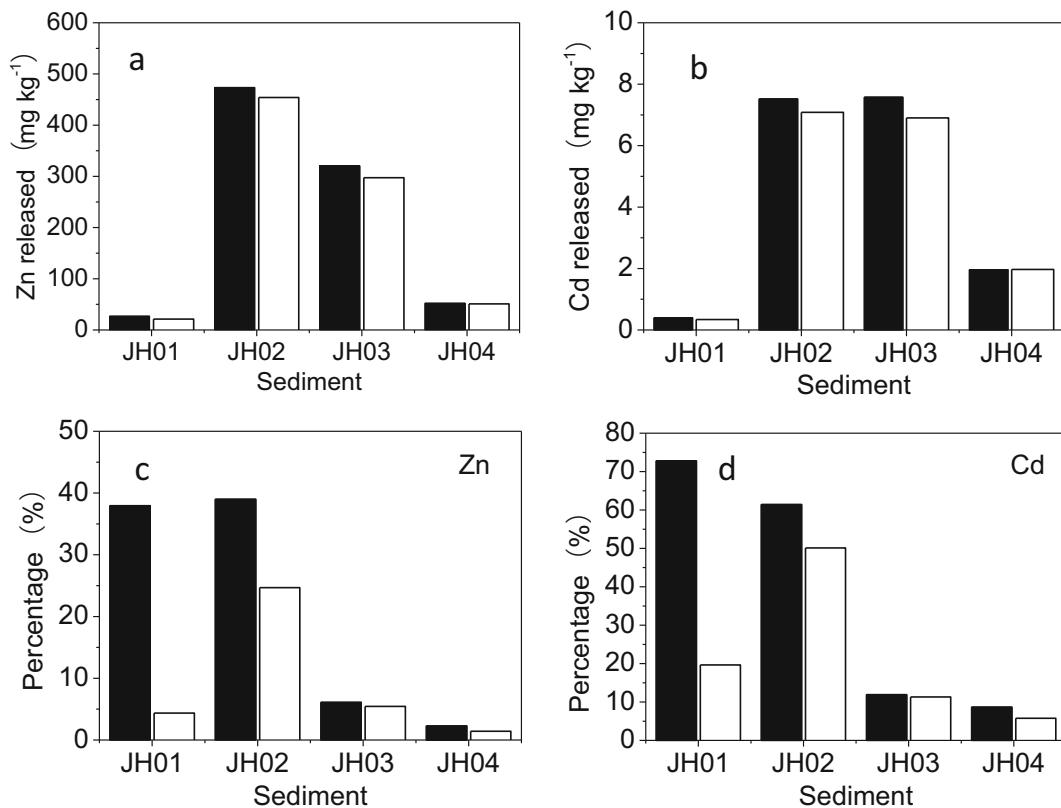
**Fig. 5** Kinetics of Cd release from stream sediment. The white cycles and solid line depict the observed and simulated concentration of Cd, respectively. The dash line indicates two times of stop-flow

Cd release from sediment can vary in a wide range depending on characteristics of the river sediments, indicating different reaction mechanisms. The total leaching amount of Zn and Cd in JH01 (27.1 mg kg<sup>-1</sup>, 0.4 mg kg<sup>-1</sup>), JH02 (474 mg kg<sup>-1</sup>, 7.5 mg kg<sup>-1</sup>), JH03 (320 mg kg<sup>-1</sup>, 7.6 mg kg<sup>-1</sup>), and JH04 (52.4 mg kg<sup>-1</sup>, 2.0 mg kg<sup>-1</sup>) demonstrated that large amount of Zn and Cd in sediments can be leached into solution. Overall,

the findings of this study indicate the risk of contaminated river sediment as a source of heavy metals to the surrounding water and even soil environment. Thus, effective measures should be taken to prevent leaching of heavy metals from river sediments. River dredging and stabilization/solidification method could potentially serve as an effective measure to minimize the releases of heavy metals from contaminated river sediments.

**Table 5** Model fitting parameters for Zn and Cd release kinetics using an equilibrium-kinetic model

Element	Sediment	r <sup>2</sup>	RMSE	K <sub>d</sub> (L g <sup>-1</sup> )	k <sub>1</sub> (L g <sup>-1</sup> min <sup>-1</sup> )	k <sub>2</sub> (min <sup>-1</sup> )
Zn	JH01	0.856	29.1	0.057	7.08E-18	0.016
	JH02	0.989	107.02	0.046 ± 0.017	0.05 ± 0.01	0.018 ± 0.002
	JH03	0.976	138.76	1.2E-16	0.044	0.012
	JH04	0.975	14.75	0.095 ± 0.025	0.020 ± 0.004	0.002 ± 0.001
Cd	JH01	0.96	0.27	0.034 ± 0.004	0.007 ± 0.010	0.024 ± 0.013
	JH02	0.985	2.17	0.008 ± 0.008	0.066 ± 0.018	0.017 ± 0.002
	JH03	0.98	3.03	0.0007 ± 0.003	0.043 ± 0.007	0.014 ± 0.002
	JH04	0.989	0.359	0.295 ± 0.119	0.013 ± 0.002	0.0006 ± 0.0003



**Fig. 6** The leaching amount and leaching rate of Zn and Cd. (a, b) Amount of Zn and Cd released include observed (black pattern) and simulated (white pattern). (c, d) Percentage of Zn and Cd

released to weak acid extractable form (black pattern) and to total amount (white pattern)

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#### Compliance with Ethical Standards

**Conflict of Interest** The authors declare that they have no conflict of interest.

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