Study of Cadmium Desorption Kinetics from Riverine Sediments

Mohsen Nasrabadi (✉ nasrabadim@ut.ac.ir)

Arak University <https://orcid.org/0000-0001-8061-8836>

Mohammad Hossein Omid

University of Tehran

Ali Mahdavi Mazdeh

Imam Khomeini International University <https://orcid.org/0000-0002-9054-7661>

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The names of the authors:

1. Mohsen Nasrabadi*

Assistant Prof., Department of Water Science and Engineering Eng., Arak University. Karbala Sq., Arak, Iran, 31587-77871.

E-mail: nasrabadim@ut.ac.ir, m-nasrabadi@araku.ac.ir

Telephone No.: +989105080029

ORCID: 0000-0001-8061-8836

2. Mohammad Hossein Omid

Prof., Department of Irrigation & Reclamation Eng., University of Tehran. Daneshkadeh St., Karaj, Iran, 31587-77871.

3. Ali Mahdavi Mazdeh

Associate Prof., Department of Water Eng., Imam Khomeini International University. International University Blvd., Qazvin, Iran, 34149-16818.

Abstract

In natural streams, the majority of heavy metal ions are generally associated with sediment particles. Under some environmental conditions, these metal ions may release from the sediment particles. In such conditions, the desorption rate of heavy metals is very important for decision-makers of water quality assessment. In this study, the effect of cadmium desorption from the river bed sediments has been experimentally investigated. Artificially contaminated sediments were used for performing batch desorption experiments. The experiments were conducted by adding 1 gr of contaminated sediment ($D_{50} = 0.53$ mm) with a known concentration and shaking until observing a roughly constant cadmium concentration in the solution. It was concluded that the cadmium ions were strongly bond to the river bed sediment; meanwhile, at the equilibrium time, up to about 7 to 29 percent of cadmium ions were released from the artificially contaminated sediments. The experiments were followed by two agitation rates of 100 and 200 rpm. It was revealed that by increasing the flow turbulence, the amount of desorbed cadmium is slightly increased. Besides, the desorption kinetics was evaluated using eight models of Zero-, first-, second-, third-order, parabolic diffusion, double parabolic diffusion, two constant rate, and simple Elovich. The results of the evaluation showed that simple Elovich (with $R^2 = 0.991$), double parabolic diffusion (with $R^2 = 0.9882$), two constant rate (with $R^2 = 0.983$) and parabolic diffusion models (with $R^2 = 0.846$) have respectively the best performance in calculation of Cd desorption rate from the sediments.

Keywords: Desorption, Riverbed Sediments, Cadmium, Turbulence, Kinetics Models.

1. Introduction

The contamination of aquatic systems by heavy metal ions, especially in natural rivers, has become one of the most important environmental problems. Therefore, the existence of sediment particles in the water column and bed-layer may play an important role in the fate and transport of metal ions in natural rivers. When discharged into the rivers, heavy metals can be absorbed by sediment particles and transformed into a solid phase from an unsaturated liquid phase (adsorption process). On the other hand, the heavy metals may be also released from the contaminated sediment under favorable environmental conditions and become a secondary pollution source for the aquatic systems (desorption process). Meanwhile, the non-residual fractions of heavy metals may be conditionally released to water column through such disturbance as hydrological, physical, chemical and biological activities (Forster and Gottfried 1981; Hart 1986; Huang and Wan 1995; Wei et al. 2016; Liu et al. 2018; Huang et al. 2019).

Desorption of heavy metal from the sediment particles to the overlaying waters depend on the relative importance of the two counter-active processes of (i) desorption due to complexation with ligands in water medium and/or competition for sorption sites with other cations, and (ii) coagulation, precipitation and flocculation (Chapman and Wang 2001)

Voluminous literature is available on the sorption of heavy metals by natural sediments (Gardiner, 1974; Jain and Sharma 2002; Jain and Ram 1997; Mahdavi et al. 2008; Mahdavi et al. 2013; and Ghoveisi et al. 2013; Nasrabadi et al. 2017, Nasrabadi et al. 2018); however, the study of heavy metal desorption, particularly cadmium ions, from riverine and natural sediments has not received much attention. Allen et al. (1995) examined the soil partition coefficients for cadmium ions and the difference between soil partition coefficients obtained from the column desorption and batch adsorption experiments with artificially contaminated soil. Franchi and Davis (1996) investigated the desorption kinetics of cadmium from natural sediments. They observed that the highest desorption rates at low pH and high concentrations of CaCl_2 and EDTA (a strong Cd chelator), with reduced rates at higher pH. They also concluded that the cadmium sorption and desorption were greatest and slowest to/from the sediments with the lowest sediment concentration. Huang et al. (1999) developed a model for heavy metal desorption from non-uniform sediments. They concluded that by increasing the content of active adsorption components, the adsorption ability of the sediments will be increased and desorption rate will be decreased. It was also found that the total amount of heavy metal desorbed from the sediments is directly proportional to the suspended sediment concentrations. Gao *et al.* (2003) evaluated the sorption/desorption hysteresis of lead (Pb) and cadmium (Cd) to/from the untreated and prewashed sediment particles. They observed the desorption hysteresis in both the untreated and the prewashed sediments using the replaced supernatant method, and desorption hysteresis was increased with aging time. Moreover, a large fraction of the adsorbed heavy metal ions were easily desorbed by EDTA. Loganathan *et al.* (2012) reported a critical review on the mechanisms and hysteresis of Cd adsorption and desorption to/from the soils and such factors as pH, ionic strength, index cation, other heavy metal cations, inorganic anions, organic ligands, Cd loading rate, and the type and amounts of organic matter and inorganic colloids influencing these processes. Li *et al.* (2015) investigated the selenite adsorption and desorption to/from the agricultural soils with varying physicochemical characteristics and mineralogical composition collected throughout China. They found out that the selenite desorption showed a reverse trend compared with adsorption: the correlations of desorption rates with soil pH and amorphous iron were positive and negative, respectively. They also concluded that the soils having strong selenite adsorption ability often showed low desorption rates. Huang et al. (2019) investigated the concentration and speciation of three typical heavy

metals (Cd, Cr and Cu) in a water-level fluctuation zone of TGR. They also simulated the adsorption and desorption behavior of heavy metals on soils. Their results showed that adsorption of Cd(II) was a chemical process and dissolved organic matters (DOM) in soils strengthened the combination of Cd(II) to soil surface which inhibited the desorption process. Cr(VI) was physically adsorbed and readily to be desorbed and DOM enabled deposition of Cr(VI) in soils. They found that the cation exchange was dominate mechanism in Cu(II) adsorption process, whereas DOM presented positive effects on desorption of Cu (II).

In the recent decades, different equations have been developed for desorption kinetics of the heavy metals from the absorbents. Of the most important desorption kinetics models reported are Zero Order, First Order, Second Order, Third Order (Dang *et al.* 1994), Parabolic Diffusion (Khater and Zaghloul 2002), Double Parabolic Diffusion (Dang *et al.* 1994), Two Constant Rate (Dang *et al.* 1994) and Simple Elovich (Polyzopoulos *et al.* 1986). There are many studies performed to evaluate these desorption kinetic models; among them, Krishnamurti *et al.* (1999) reported the kinetic data of cadmium desorption by M ammonium nitrate (NH_4NO_3) and M ammonium chloride (NH_4Cl) from the Canadian soils, with contrasting Cd-availability characteristics, pre-adsorbed with different amounts of Cd. They showed that the desorption kinetics were described best using the parabolic diffusion mathematical model. Khater and Zaghloul (2002) concluded that power function, parabolic-diffusion and first-order equations were the best-fitted equations used to describe Cu desorption. Ghasemi Fasaai *et al.* (2006) concluded that two-constant rate, Elovich, and simple Elovich were the best-fitted equations used to describe Cu desorption from highly calcareous soils of southern Iran. Reyhanitabar and Karimian (2008) studied experimentally the desorption kinetics of native Cu by DTPA from 12 calcareous soils of central Iran. They showed that two-constant and simple Elovich rate equations were the best-fitted equations among seven kinetic models studied. Yongkui *et al.* (2008) concluded that the two-constant equation and Elovich equation were applicable to describe the adsorption and desorption processes of Hg in soils. Esfandbod *et al.* (2010) investigated the kinetics of Cd desorption from 15 Cd-spiked surface soil samples collected from the northern part of Iran with a wide range of physical and chemical properties. Their results showed that two-constant rate, parabolic-diffusion and simple Elovich equations were the best-fitted equations among five kinetic models used. Reyhanitabar and Gilkes (2010) investigated the kinetics of Zn extraction by (DTPA) from the -2mm fraction of 12 calcareous soils using surface soil samples (0-30 cm). They concluded that Zero-, first-, second-, third order, parabolic diffusion, and simple Elovich equations did not adequately describe Zn extraction kinetics. The best model for describing extraction data for all soils was the exponential rate equation ($q=at^b$). Mohammadi *et al.* (2018) evaluated simultaneous desorption and desorption kinetics of PAHs (phenanthrene and anthracene) and heavy metals (lead,

nickel, and zinc) from artificially contaminated kaolinite soils with different organic matter content. The data obtained from desorption kinetics experiments were fitted with four kinetics models: pseudo-second-order equation, empirical power function, Elovich, and parabolic diffusion. The correlation coefficient of the pseudo second-order equation was higher than that of other model.

The main purpose of this study is to provide quantitative information about the behavior of desorption cadmium in river bed sediments. The artificially contaminated samples were subsequently subjected to a wide range of conditions that may occur in natural systems to study their effects on heavy metal desorption. In addition, desorption kinetics were evaluated using eight models developed in the literature. The experimental results of the present study will show how changes in the concentrations and flow turbulence affect the heavy metal desorption rates.

2. Materials and Methods

2.1. Preparation of Contaminated Sediments

The sediment samples were collected from shallow waters nearer to the bank of the Karaj River and were taken from upper 0-15 cm layer of the deposits at the places with low flow rates as sedimentation was assumed to occur (Jain and Ram 1997b). The samples were washed several times with distilled water to remove physical earthen impurities. Then, prior to experiments, they were dried in a hot air oven at 110°C for 24 hrs. A sediment size of 0.53 mm was selected by using standard sieving apparatus (particles remained between sieves No. 30 and 40). The cation exchange capacity (CEC) of the riverine sediments was measured using Bower's method (Bower et al. 1952) equal to 13.873 meq/100gr. In addition, the physicochemical composition and particle size distribution of the sediments are listed in Tables 1 and 2. In table 2, σ_g is geometric standard deviation of the sediment particles, d_g is geometric diameter of the sediment particles, C_c is coefficient of curvature and, C_u is uniformity coefficient, D_{90} , D_{60} , D_{50} , D_{30} , D_{10} , are, respectively, the portions of particles with diameters smaller than this value is 90%, 60%, 50% 30%, and 10%.

Table 1. The physicochemical analysis of the sediments

Constituents	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MnO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	MnO	S	L.O.I
% By weight	54	14.4	7.5	0.7	6.4	3	1.9	3	0.3	< 1	0.2	-	8.34

Table 2. The particle size distribution of the sediments

σ_g	d_g	CC	CU	D_{90}	D_{60}	D_{50}	D_{30}	D_{10}
1.13	0.52	0.98	1.234	0.6	0.54	0.53	0.485	0.44

Because the Karaj River is a seasonal and temporal river, it may flow several times a year, therefore, the sediments may be encountered several times to the pollution due to heavy metal dissolved in the river. As a result, the sediment samples were artificially contaminated in several stages. Furthermore, as the background cadmium concentrations of the original Karaj River sediment samples were too low, the sediments were contaminated with cadmium by adding 1 gr (dry wt.) of sediment to a 50 mL cadmium solution by adjusting pH = 7.5 using NaOH and EC = 700-800 $\mu\text{S/cm}$ (similar to the values encountered in Karaj River). First, the sediment samples were put in different pre-cleaned flasks with cadmium concentrations of 0.2, 0.5, 1, 10, 20, and 50 ppm. The flasks were then placed in a constant-temperature (25°C) vibration case. After being vibrated in a constant agitation rate (100 rpm) for about 5 hrs, the case was stopped. Overlaying water on the sediment surface in each flask was then taken to analyze the dissolved cadmium concentrations. The amount of Cd adsorbed to the sediments was calculated as follows:

$$q_e = \frac{C_0 - C_e}{W} \times V \quad (1)$$

where, C_0 is the initial cadmium concentration (mg L^{-1}), C_e is the cadmium concentration after adsorption (mg L^{-1}), V is the volume of the aqueous phase (50 mL), and W is the amount of the sediment (gr). Cadmium measurement was conducted by using an ICP-OES Varian VISTA-MPX device.

In the next stage, new solutions with the same Cd concentration were again added to the sediment samples and the mixtures were shake for another 5 hrs. This process was repeated for five stages and the amount of Cd adsorbed at each stage were determined (Eq. 1). After contamination of the sediments for five stages, they were removed from the flasks. Then, they were allowed to air-dry for one week at ambient temperature of the laboratory. The results of these measurements are given in Table 3.

Table 3 .The amount of Cd adsorbed at each stage

Stage	0.2 ppm	0.5 ppm	1 ppm	10 ppm	20 ppm	50 ppm
	q_e (mg/kg)	q_e (mg/kg)	q_e (mg/kg)	q_e (mg/kg)	q_e (mg/kg)	q_e (mg/kg)
Stage1	9	22	48.75	425	730	1610

Stage2	8.5	21	47.5	345	620	1310
Stage3	8	19.5	42.5	275	405	875
Stage4	7.25	18.25	37	190	345	650
Stage5	6.8	18	32.5	125	225	450
Adsorbed Cd (mg/kg)	39.55	98.75	208.25	1360	2325	4895

As can be observed in this table, total adsorbed cadmium by the sediments for five initial concentrations of 0.2, 0.5, 1, 10, 20, and 50 ppm are, respectively, 39.55, 98.75, 208.25, 1360, 2325 and, 4895 mg kg⁻¹.

2.2. Desorption Experiments

For the desorption tests, 1 gr (dry wt.) contaminated sediment, containing different amounts of adsorbed Cd, was shake with 50 mL of distilled water for different times (0, 5, 15, 30, 60, 120, 300, and 720 min) to reach an equilibrium desorption rate. The amount of desorbed Cd from unit weight of the sediments (D_s , in mg g⁻¹) and desorption percent (R , %) were determined using the following equations:

$$D_s = \frac{CV}{m} \quad (2)$$

$$R = \frac{D_s}{S} \times 100\% \quad (3)$$

where, V is the volume of the solution (lit), C is the Cd concentration at equilibrium condition (mg/lit) m is the weight of sediments (g), S is the adsorbed Cd (mg kg⁻¹).

In this study, to investigate the effect of turbulence on cadmium desorption the mixtures were shake with different agitation rates of 100 and 200 rpm. The Cd concentration in the supernatant was determined after dilution using an ICP-OES Varian VISTA-MPX device. The amount of Cd desorbed from the sediments was calculated as the difference between the amount of Cd pre-adsorbed onto the sediments and the amount released to the solution.

2.3. Desorption Kinetics

As mentioned before, in this study, eight desorption kinetic models including Zero-order, First-order, Second order, Third order, Parabolic diffusion, Double Parabolic diffusion, Two Constant Rate, and simple

Elovich equations were evaluated using the experimental data Table 4 presents the details and parameters of each model.

Table 4. Developed kinetics models for desorption of heavy metals from the absorbents

No.	Model	equation	Parameters
1	Zero-order	$q_t = q_0 - k_0 t$	k_0 , zero-order rate constant (mg Cdkg ⁻¹ s ⁻¹)
2	First-order	$\ln q_t = \ln q_0 - k_1 t$	k_1 , first-order rate constant (s ⁻¹)
3	Second order	$\frac{1}{q_t} = \frac{1}{q_0} - k_2 t$	k_2 , second-order rate constant ((mg Cdkg ⁻¹) ⁻¹)
4	Third order	$\frac{1}{q_t} = \frac{1}{q_0^2} - k_3 t$	k_3 , third-order rate constant ((mg Cdkg ⁻¹) ⁻²)
5	Parabolic diffusion	$q_t = q_0 + k_p t^{0.5}$	k_p , diffusion rate constant ((mg Cdkg ⁻¹) ^{-0.5})
6	Double Parabolic diffusion	$q'_t = a_1 + k_1 t^{0.5}$ $q_t^n = a_2 + k_2 t^{0.5}$	k_1 and k_2 , first and second stage diffusion rate constants ((mg Cdkg ⁻¹) ^{0.5})
7	Two Constant Rate	$q_t = at^b$	a , initial Cd desorption rate constant (mg Cdkg ⁻¹ S ⁻¹) ^b and b , desorption rate coefficient
8	simple Elovich	$q_t = \frac{1}{\beta_s} \ln \alpha_s \beta_s + \frac{1}{\beta_s} \ln t$	α_s , initial Cd desorption rate (mgCdkg ⁻¹ S ⁻¹) and β_s , Cd desorption constant ((mgCdkg ⁻¹) ⁻¹)

In order to analyze the accuracy of the best fitted model, the coefficient of determination (r^2) and the standard error of estimate (SE) were calculated as follows:

$$SE = \left[\frac{\sum (q_{cal} - q_{meas})^2}{(N - 2)} \right]^{0.5} \quad (4)$$

where, q_{cal} and q_{meas} are estimated and observed values, respectively. A relatively large coefficient of determination (r^2) and small SE were used as criteria for the best fit.

3. Results and Discussion

After the sediments were artificially contaminated by different concentrations of cadmium ions, desorption experiments were conducted to evaluate the effect of Cd concentrations and flow turbulence on the desorption rate of cadmium from the river bed sediments. After that, the analysis for the desorption kinetics models are represented in order to select the best fitted model for cadmium release from the sediments.

3.1. Effect of Cd Concentrations

The results of cadmium desorption from the artificially contaminated sediments were given in Fig. 1 for different Cd concentrations of 0.2, 0.5, 1, 10, 20, and 50 mg/l. In fact, according to the results presented in Table 6, total adsorbed cadmium by the river bed sediments for five initial concentrations are, respectively, 39.55, 98.75, 208.25, 1360, 2325 and 4895 mg/kg. As can be seen in Fig. 1, by increasing the cadmium concentration, desorption rate from the sediments is increased. So that, for low cadmium concentrations, the cadmium desorption percentage (R) is about 7 percent; however, with increasing cadmium concentrations, the rate of release of cadmium reaches 29 percent. In addition, the release pattern of cadmium ions in all contaminated sediment samples consists of a fast stage (short-term) and a slow stage (long-term), so that within the first 2 h of the experiment, about 83 to 92 % of Cd(II) was released. A slow leaching process occurred after then, and desorption rate reached an equilibrium state. This process indicated that different mechanisms may control the cadmium desorption rate. At the first 2 hrs of the exposure, the cadmium desorption is occurred in internal or external surfaces of macro-aggregates. Fewer desorption potential may be attributed to the trapping of cadmium ions into the cracks in the texture of the sediment particles or due to the special adsorption on high energy sites in sediments. This finding also reveal a difference in the release site in two stages (such as the outer and inner surfaces of the aggregates), or the cadmium release of various absorbent compounds that absorb cadmium ions with different energies. It should be mentioned that these changes are the same for all Cd concentrations.

Figure 1. Cadmium desorption from contaminated sediment for different Cd concentrations.

Findings of Dang et al. (1994) on desorption kinetics of zinc showed that most of the zinc desorption occurred over a period of 4 hours. They concluded that the time required for reaching equilibrium desorption is approximately 2 hrs; after that, desorption rate reaches a constant value. The slight amount of cadmium desorption represents a strong bonding of cadmium ions with sediment particles. The results of the present study are consistent with the Franchi and Davis (1996) showed that almost all of desorption processes occurred within the first 30 min of the test. They also concluded that the cadmium sorption and desorption were greatest and slowest to/from the sediments with the lowest sand content.

As previously mentioned, there are generally two methods for the study of desorption process. The present paper confirms the first method. The predictable result of this type of studies is that the absorption and desorption of cadmium are reversible processes (physical bonding). However, the results of this study showed that most of the sediment particles and cadmium have been strongly bonded. It can be said that the cadmium adsorption and desorption are irreversible by Karaj River bed sediments. These findings are consistent with the results of Li *et al.* (2015), who studied the adsorption and desorption of selenium in different soils of China.

3.2. The effect of turbulence

As the flow turbulence can play an important role in desorption and release of heavy metal ions from the sediments. Accordingly, the effect of turbulence on desorption process was investigated for two agitation rates of 100 and 200 rpm. It should be noted that, with the increase in the agitation rates from 100 to 200 rpm, the temperature of the solution did not change significantly. The results of measurement of cadmium desorption in different concentrations and agitations rates are presented in Table 5 and Figure 2. As can be seen, with the increase of agitation rate (flow turbulence), the amount of cadmium desorption is slightly increased. So that, in high Cd concentrations, the amount of cadmium desorption in both agitation rates is very negligible and can be ignored. It can be concluded that by increasing the turbulence intensity, the collisions between the sediment particles are increased, resulting in more cadmium release from the sediments. According to Huang (2003)'s study, these results show that in the rivers with contaminated sediments, the flow turbulence may cause sediment re-suspension through dredging, tides, floods and cleaning the silting basins and may lead to the release of heavy metals from sediments. This phenomenon is also noteworthy for contaminated sediments in the upstream of the dam reservoirs.

Table 5. Adsorbed and desorbed cadmium ions with desorption percentages at different concentrations and agitation rates

V (rpm)	C (ppm)	q _{cd} (mg/kg)	D _s (mg/kg)	R (%)
100	0.2	39.55	3	7.85
	0.5	98.75	6.5	6.58
	1	208.25	13.5	6.48
	10	1360	275	20.22
	20	2325	650	27.95
	50	4895	850	17.36
200	0.2	39.55	3.5	8.84
	0.5	98.75	8	8.1
	1	208.25	21.5	10.32
	10	1360	375	27.57
	20	2325	675	29.03
	50	4895	875	17.87

Figure 2. Cadmium desorption from contaminated sediment for two agitation rates of 100 and 200 rpm.

3.3. Evaluation of desorption kinetics models

Figures 3 to 10 shows the results of kinetics desorption rate calculated by various models for different concentrations. As can be observed, zero-, first-, second-, and third order equations have large errors in estimating the desorption rates. So far, many researchers have evaluated these models, and nearly all of them have described the first four models as inappropriate and incorrect ones (Krishnamurti et al. 1999; Ghasemi Fasaei et al. 2006; Reyhanitabar and Karimian 2008; Yongkui et al. 2008; Esfandbod et al. 2010; and Reyhanitabar and Gilkes 2010). On the other hand, simple Elovich, double parabolic diffusion, two constant rate, and parabolic diffusion models

have better performance in calculation of desorption rate. In addition, the parameters of each model were estimated using for different concentrations (Table 6).

Figure 3. Results of zero-order model for different concentrations

Figure 4. The results of first-order model for different concentrations

Figure 5. Results of the second-order model for different concentrations

Figure 6. Results of the third order model for different concentrations

Figure 7. The results of parabolic model for different concentrations

Figure 8. The results of Double Parabolic diffusion model for different concentrations

Figure 9. The results of Two Constant Rate model for different concentrations

Figure 10. The results of the simple Elovich model for different concentrations

Table 6. Estimated parameters of high accurate desorption kinetic models

D_s (mg/kg)	k_p	q_0	k_1	a_1	k_2	a_2	a	b	α_s	β_s
39.55	0.09	1.08	0.34	0.26	0.05	1.79	1.11	0.16	2.92	2.82

98.75	0.17	3.28	0.87	0.98	0.07	5	3.79	0.09	641.52	2.06
208.25	0.38	6.24	1.88	1.30	0.15	10.27	6.8	0.12	88.6	0.75
1360	6.66	151.74	43.75	33.26	1.5	242.02	177.43	0.08	93521	0.05
2325	21.09	219.42	85.05	0	8.91	438.28	217.05	0.18	218.91	0.01
4895	22.70	391.91	124.52	64.32	7.91	651.94	430.84	0.11	7047	0.01

290

291 Figure 11 shows the experimental values versus the calculated values by the four models with high
292 accuracy. As can be seen, among these four models, simple Elovich (with $R^2 = 0.991$), double parabolic diffusion
293 (with $R^2 = 0.9882$), two constant rate (with $R^2 = 0.983$) and parabolic diffusion model (with $R^2 = 0.846$) have
294 respectively the best results in calculation of desorption rate. The details of statistical evaluation for different
295 concentrations was given in Table 7.

296 For the purpose of comparison, Krishnamurti et al. (1999) and Esfandbod et al. (2010) reported that
297 parabolic diffusion and two constant rate equations was best-fitted for Cd desorption kinetics. On the other hand,
298 Ghasemi Fasaei et al. (2006), Reyhanitabar and Karimian (2008), and Yongkui et al. (2008) found that two
299 constant rate equation has the best performance in calculation of Cu and Hg desorption kinetics. This discrepancy
300 between our results and the previous studies may due to the fact that batch experiments set-up such as enhancing
301 agents and contaminants physicochemical properties and concentrations, physicochemical properties of the
302 sediments such as organic matter content and aging history were different.

303

304 **Table 7. The results of statistical analysis**

D _s (mg/kg)	Zero Order		First Order		Second Order		Third Order		Parabolic Diffusion		Two- Constaant Rate		Simple Elovich		Double Para. Diff.	
	SE	R ²	SE	R ²	SE	R ²	SE	R ²	SE	R ²	SE	R ²	SE	R ²	SE	R ²
39.55	0.52	0.76	0.54	0.68	0.56	0.63	0.56	0.63	0.41	0.95	0.19	0.98	0.19	0.98	0.29	0.97
98.75	1.06	0.68	0.62	0.95	1.04	0.62	1.04	0.62	1.01	0.87	0.25	0.99	0.24	0.99	0.82	0.97
208.25	2.51	0.68	2.51	0.63	2.54	0.60	2.54	0.60	9.22	0.30	0.78	0.98	0.61	0.99	1.24	0.98
1360	50.15	0.63	49.41	0.60	49.08	0.58	49.08	0.58	49.24	0.81	16.05	0.98	14.12	0.99	28.06	1.01
2325	156.53	0.66	160.59	0.59	163.53	0.45	171.76	0.36	127.66	0.88	80.33	0.91	56.62	0.96	38.58	0.92
4895	154.86	0.68	115.06	0.90	262.31	0.28	224.51	0.80	140.39	0.87	54.57	0.97	42.92	0.99	57.24	1.01

Figure 11. The experimental values versus the calculated values by four models with high accuracy.

Conclusions

In this study, the cadmium desorption kinetics from artificially contaminated bed sediments was experimentally investigated. Besides, the effect of Cd concentrations and flow turbulence was examined. The results of cadmium desorption experiments showed that within 2 hr, about 83 to 92 % of Cd(II) was released. Meanwhile, at the equilibrium time, up to about 7 to 29 percent of cadmium ions were released from the artificially contaminated sediments. The results of this study showed that most of the sediment particles and cadmium have been strongly bonded. It can be said that the cadmium adsorption and desorption are irreversible by Karaj River bed sediments. Furthermore, by increasing the flow turbulence (increasing the agitation rate from 100 to 200 rpm), the amount of desorbed cadmium is slightly increased. The results of the evaluation of eight desorption kinetics models showed that simple Elovich (with $R^2 = 0.991$), double parabolic diffusion (with $R^2 = 0.9882$), two constant rate (with $R^2 = 0.983$) and parabolic diffusion model (with $R^2 = 0.846$) were respectively the best-fitted equations among all kinetic models studied.

Ethics approval

Not applicable

324

325 **Consent to participate**

326 Not applicable

327

328 **Consent to Publish**

329 Not applicable

330

331 **Authors Contributions**

332 Mohsen Nasrabadi, as former PhD Candidate, performed the experiments and analyzed and interpreted the
333 data and he was a major contributor in writing the manuscript. Mohammad H. Omid is the main supervisor of this
334 PhD thesis and Ali Mahdavi Mazdeh is the co-supervisor of this PhD thesis. All authors read and approved the
335 final manuscript.

336

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339

340 **Competing Interests**

341 The authors declare that they have no competing interests.

342

343 **Data Availability**

344 Some or all data, models, or code that support the findings of this study are available from the
345 corresponding author upon reasonable request.

346

347 **References**

348 Allen HE, Chen YT, Li YM, Huang CP (1995) Soil partition coefficients for Cadmium by column desorption and
349 comparison to batch adsorption measurements. *Envir Sci Technol*, 29(8): 1887-1891.

350 Bower CA, Reitmeir RF, Fireman M (1952) Exchangeable cation analysis of saline and alkali soils. *Soil Sci*. 73:
351 251-261.

352 Chapman PM and Wang F (2001) Assessing Sediment Contamination in Estuaries. *Environmental Toxicology*
353 *and Chemistry*. 20: 3-22.

354 Dang YP, Dalal DG, Edwards DG, Tiller KG (1994) Kinetics of Zinc adsorption from vertisols. *Soil Sci America*
355 J, 58: 1392-1399.

356 Esfandbod M, Adhami E, Rezaei Rashti CM Esfandbod M (2010) Kinetics of cadmium desorption from some
357 soils of Iran. 19th World Congress of Soil Science, Soil Solutions for a Changing World. Brisbane,
358 Australia.

359 Fornster U and Gottfried TW (1981) *Metal pollution in the aquatic environment*, 2nd Ed., Berlin: Springer-Verlag.

360 Franchi A and Davis AP (1997) Desorption of cadmium (ii) from artificially contaminated sediments. *Water, Air,*
361 *and Soil Pollution*. 100: 181–196.

362 Gao Y, Kan AT, Tomson MB (2003) Critical evaluation of desorption phenomena of heavy metals from natural
363 sediments. *Environ Sci Technol*. Dec 15; 37(24): 5566-73. doi: 10.1021/es034392w.

364 Gardiner J (1974) The chemistry of cadmium in natural waters. The adsorption of cadmium in river muds and
365 naturally occurring soils. *Water Res*, 8: 157-164.

366 Ghasemi Fasaei R, Maftoun M, Ronaghi A, Karimian N, Yasrebi J, Assad MT and Ippolito JA (2006) Kinetics of
367 copper desorption from highly calcareous soils. *Commun. Soil Sci. Plant Analysis*. 37: 797-809.

368 Ghozeisi H, Mahdavi Mazdeh A, Farhoudi J, Omid MH (2014) The effect of sediment motion on adsorption of
369 cadmium. *Proceedings of the ICE - Water Management*, 167(4): 238–245. doi:10.1680/wama.12.00103.

370 Hart BT (1986) *Water Quality Management-The role of particulate matter in the transport and fate of pollutants*,
371 Water Studies Center, Chisholm Institute of Technology, Melbourne.

372 Huang SL (2003) Investigation of cadmium desorption from different sized sediments. *J. Environ. Eng. ASCE*
373 129(3): 241–247.

374 Huang SL and Wan ZH (1995) Present state of experimental research on heavy metal pollutant adsorption-
375 desorption by sediment, *International Journal of Sediment Research*, 10(3): 69–81.

376 Huang SL, Onyx Wai WH, and Sheung Li Y (1999) Determination of cadmium ion desorption from non-uniform
377 sediment particles, *Toxicological & Environmental Chemistry*, 72:3-4, 195-213.

378 Huang Y, Fu C, Li Z, Fang F, Ouyang W, Guo J (2019) Effect of dissolved organic matters on adsorption and
379 desorption behavior of heavy metals in a water-level-fluctuation zone of the Three Gorges Reservoir, China.
380 *Ecotoxicology and Environmental Safety*, 185, 109695–. doi:10.1016/j.ecoenv.2019.109695.

381 Jain CK and Ram D (1997a) Adsorption of lead and zinc on bed sediments of the river Kali, *Water Res.*, 31(1):
382 154–162.

383 Jain CK and Ram D (1997b) Adsorption of metal ions on bed sediments, *Hydrol. Sci. J.*, 42(5): 713–723.

384 Jain CK and Sharma MK (2002) Adsorption of cadmium on bed sediment of river Hindon: adsorption models and
 385 kinetics, *Water, Air, and soil pollution*, 137: 1-19.

386 Khater AH and Zaghloul AM (2002) Copper and zinc desorption kinetics from soil: Effect of pH, paper presented
 387 in 17th world conference on Soil science, Thailand, 47: 1-9.

388 Krishnamurti GSR, Cieslinski G, Huang PM, and Van Rees KCJ (1997) Kinetics of cadmium release from soils
 389 as influenced by organic acids: Implication in cadmium availability. *J. Environ. Qual.* 26: 271–277.

390 Li Z, Man N, Wang S, Liang D (2015) Selenite adsorption and desorption in main Chinese soils with their
 391 characteristics and physicochemical properties. *J Soils Sediments* 15(5): 1150–1158.

392 Liu J, Liu YJ, Liu Y, Liu Z, Ning Zhang A (2018) Quantitative contributions of the major sources of heavy metals
 393 in soils to ecosystem and human health risks: A case study of Yulin, China. *Ecotoxicol. Environ. Saf.* 164:
 394 261–269. DOI: 10.1016/j.ecoenv.2018.08.030.

395 Loganathan P, Vigneswaran S, Kandasamy J, Naidu R (2012) Cadmium Sorption and Desorption in Soils: A
 396 Review. *Critical Reviews in Environmental Science and Technology*, 42(5): 489–533.
 397 doi:10.1080/10643389.2010.520234.

398 Mahdavi A, Omid MH and Ganjali MR (2008) Effect of bed load transport on kinetic sorption in a circular flume.
 399 Proceedings of International Conference on Fluvial Hydraulics, RiverFlow2008, Cesme-Izmir, Turkey.
 400 Kubaba Congress Department and Travel Services, Ankara, Turkey, pp. 2485–2491.

401 Mahdavi A, Kashefipour SM and Omid MH (2013) Effect of sorption process on cadmium transport. Proceedings
 402 of the Institution of Civil Engineers-Water Management. 166(3): 152-162.

403 Mohammadi A, Saeedi M, Mollahoseini A (2018) Simultaneous Desorption and Desorption Kinetics of
 404 Phenanthrene, Anthracene, and Heavy Metals from Kaolinite with Different Organic Matter Content. *Soil*
 405 *and Sediment Contamination: An International Journal*, 1–21. doi:10.1080/15320383.2017.1339666.

406 Nasrabadi M, Omid MH, Mahdavi Mazdeh A (2017) Cadmium Adsorption Characteristics for Karaj Riverbed
 407 Sands. *Journal of Materials and Environmental Sciences*, 8(5): 1729-1736.

408 Nasrabadi M, Omid MH, Mazdeh AM, Shahriari T (2018) Cadmium adsorption by natural zeolite in a circular
 409 flume. *International Journal of Environmental Technology and Management* 21 (3-4): 174-189.

410 Polyzopoulos NA, Keramidas VZ, Kiosse H (1986) Phosphate Sorption by Some Alfisols of Greece as Described
 411 by Commonly Used Isotherms. *J Soil Sci*, 37: 183-189.
 412 <https://doi.org/10.2136/sssaj1985.03615995004900010016x>.

413 Reyhanitabar A and Gilkes RJ (2010) Kinetics of DTPA extraction of zinc from calcareous soils from Iran. 19th
 414 World Congress of Soil Science, Soil Solutions for a Changing World. Brisbane, Australia.
 415 Reyhanitabar A and Karimian N (2008) Kinetics of Copper Desorption of Selected Calcareous Soils from Iran
 416 American-Eurasian J. Agric. & Environ. Sci. 4(3): 287-293.
 417 Xin W, LanFang H, Bo G, HuaiDong Z, Jin Lu, XiaoHong W (2016) Distribution, bioavailability, and potential
 418 risk assessment of the metals in tributary sediments of Three Gorges Reservoir: the impact of water
 419 impoundment. Ecol. Indic. 61: 667–675.
 420 Yongkui Y, Li L, Dingyong W (2008) Effect of dissolved organic matter on adsorption and desorption of mercury
 421 by soils. Journal of Environmental Sciences. 20: 1097–1102.
 422 Zhang HH, Cao XY, Wang H, Ma Z, Li J, Zhou LM, Yang GP (2019) Effect of black carbon on sorption and
 423 desorption of phosphorus onto sediments. Marine Pollution Bulletin, 146: 435–441.
 424 doi:10.1016/j.marpolbul.2019.06.059.
 425 Zhou Y, Yang Y, Liu G, He G, Liu W (2020) Adsorption mechanism of cadmium on microplastics and their
 426 desorption behavior in sediment and gut environments: The roles of water pH, lead ions, natural organic
 427 matter and phenanthrene, Water Research, 184, 116209, <https://doi.org/10.1016/j.watres.2020.116209>.