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Cadmium Adsorption Characteristics for Karaj Riverbed Sands

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Abstract

The adsorption characteristics of the bed sediments collected from Karaj River (North of Iran) have been studied for cadmium adsorption. The effect of various variables, such as, contact time and sediment concentration has been studied in a circular flume (with a width of 0.2 m) to get enhanced simulations of natural conditions in a river. The experimental conditions were adjusted similar to a natural river (pH=7.5, EC=800 µS/cm, and T=25°C). The sediment and cadmium concentrations were set in the ranges of 3-20 gr L^{-1} and 0.15-1 ppm, respectively. The results of kinetic tests demonstrated that the optimum equilibration time was found to be 5 hr, which was independent of initial cadmium concentration. The results showed that adsorption rate increased from 30 to 126.67 µgr gr^{-1} with increasing the initial concentration of cadmium, however the percent of cadmium elimination decreased from 50 to 41.3 percent. By increasing sediment concentration from 3 to 20 g L^{-1}, the adsorption rate reduced from 30 to 6.25 µgr gr^{-1}, 86.67 to 22.5 µgr gr^{-1}, and 126.67 to 36.5 µgr gr^{-1}. To interpret this result, these materials have been analyzed by the XRD technique. Also the adsorption data were analyzed using first- and second-order kinetics models.

1. Introduction

Heavy metal ions are the most toxic inorganic pollutants which usually occur in the riverine sediment and can be of natural or of industrial origin. Some of them are toxic even if their concentration is very low and their toxicity increases with accumulation in water and sediments. Adsorption is a major process responsible for accumulation of heavy metals. Therefore, the study of adsorption processes is of utmost importance for the understanding of how heavy metals are transferred from a liquid mobile phase to the surface of a solid phase [1]. When heavy metals enter the natural waters the majorities are adsorbed on suspended matters, and then transferred to the sediments. The adsorption capacity of heavy metal in sediments is influenced by the characterization of sediments and the physical and chemical properties of water [2]. Bradl [1] pointed out the most important parameters controlling heavy metal adsorption and their distribution between solid phase (soil/sediment) and water are soil/sediment type, metal speciation, metal concentration, soil pH, solid: solution mass ratio, and contact time.

There are many papers in the literatures which have investigated the adsorption of heavy metals by riverine sediment. Gardiner [3] studied the effect of various factors on the adsorption of cadmium on river mud and other naturally occurring solids. Koelmans and Lijklema [4] studied the adsorption of cadmium onto sediment and suspended solids for Lake Volkerak in the Netherlands and reported that cadmium is bound almost completely to the geochemical iron, manganese and organic phases, the first being exclusively associated with clay fraction. Wiley and Nelson [5] examined the influence of various factors on the adsorption of cadmium onto the sediments of Sturgeon Lake, Oregon and reported pH as the most critical parameter affecting cadmium adsorption. Jain and Sharma [6] investigated the effects of several parameters such as initial concentration, solution pH, sediment dose, contact time, particle size and temperature. The results of their study showed that the pH of the solution was the most important parameter in the control of cadmium adsorption, so the adsorption of cadmium increased with an increase in pH. Furthermore, the adsorption of cadmium increased with increasing adsorbent concentration and decreased with adsorbent particle size. They stated that the most important geochemical phases, iron and manganese oxide, support the adsorption of cadmium ions. Hung and Chen [2] studied the characterization of sediments collected from the various (as river, lake and coast) locations, the physical and chemical properties of sea water collected off the northern Taiwan, the processes of heavy metal adsorption in sediments, and finally, the correlations between those parameters and the adsorption capacity of heavy metals in Taiwan sediments. The results showed that the adsorption capacities of heavy metal in sediments for a unit μM/L of sea water ranged from 0.06-13.48 μM/g for Cu, 0.010.2l μM/g for Cd, 0.12-2.76 μM/g for Pb, and 0.12-0.46 μM/g for Zn. They also found that higher capacities of heavy metal adsorption found in the lake sediments than those in the riverine and coastal sediments were due to the higher contents of clay (36.5%), TOC (12.3%), CEC (43.7 meq/100g) in the lake sediments and DOC (3.65 mg/L) in the interstitial water of sediments. Jain and Ram [7] investigated the adsorption characteristics of the bed sediments collected from the River Kali, India, for the uptake of lead and zinc ions. They found that heavy metal adsorption increases with increasing the initial metal ion concentration. They pointed out that the adsorption of the two metal ions on the bed sediments follows two phases: a linear phase of adsorption and then a quasi-equilibrium state. The quasi-equilibrium state was attained within 45 min for both the metal ions. It is observed that the extent of adsorption increases with the increase of pH of the solution and metal ion concentration decreases with increase in pH value. In addition, the adsorption of metal ions increases with increasing adsorbent doses and decreases with adsorbent particle size. The geochemically important elements such as Fe and Mn have also been determined in various grain size fractions of the sediments and correlated with the adsorption of metal ions. The adsorption data of the two metal ions was also analyzed with the help of the Langmuir and Freundlich models to evaluate the mechanistic parameters associated with the adsorption process, viz. monolayer capacity and sorption intensity. Jain and Sharma [8] studied the adsorption characteristics of cadmium on bed sediments of river Hindon, India. They concluded that the optimum equilibration time was found to be 60 min, which was independent of initial concentration of cadmium ions. The adsorption curves were smooth and continuous leading to saturation, suggesting the possible monolayer coverage of cadmium ions on the surface of the adsorbent. The adsorption of cadmium increased with an increase in pH. Furthermore, the adsorption of cadmium increased with increasing adsorbent concentration and decreased with adsorbent particle size. Jain et al. [9] investigated the optimum contact time needed to reach equilibrium was of the order of 60 min and was independent of initial concentration of zinc ions. The extent of adsorption increased with an increase of pH. Furthermore, the adsorption of zinc increases with increasing adsorbent doses and decreases with the adsorbent particle size. The content of iron, manganese and organic matter in various fraction of sediment decreases with increasing particle size indicating the possibility of the two geochemical phases to act as the active support material for the adsorption of zinc ions. The adsorption data follows both Langmuir and Freundlich adsorption models.

Ghoveisi et al. [10] investigated four linear regression of kinetic model of pseudo second order to describe the adsorption of cadmium by fine sediment. They determined the adsorption parameters by means of nonlinear method of pseudo second order as well as four linear regression methods. Their results showed that the nonlinear method of pseudo second order is a suitable method in estimating of adsorption parameters. Ghoveisi et al. [11] conducted an experimental work in a circular flume and a reactor device to show the effect of flow velocity, sediment movement type and concentration on the kinetic adsorption and transport of cadmium in both bed and suspended load conditions. Their results showed that the rate of adsorption is directly related to the sediment motion type and flow velocity. They found that the equilibrium capacity increased by 20% as the flow velocity changed from 0.35 to 0.7 m s^{-1}. Moreover, the use of batch reactors overestimates sorption capacity. However, for suspended load conditions, the equilibrium capacity was not significantly affected by the flow velocity or sediment motion type (comparing flume and batch reactor results). It was experimentally deduced that increasing the sediment concentration load by 300% would decrease the equilibrium cadmium adsorption in unit mass by 170% and 250% for bed and suspended loads respectively.

Until now, little attempt has been made to study the kinetics of adsorption to riverbed sediments in their naturally occurring state. In this paper, the adsorption characteristics of bed sediments of Karaj River (North of Iran) have been studied to determine the tolerance of the system for the heavy metal load in a circular flume. Moreover, different riverine sediments, certainly, have significant different physicochemical properties and type and composition of sediment's mineral and organic fractions vary simultaneously. Therefore, the study of the adsorptive characteristics of the sediment from each river is so important from environmental point of view.

2. Experimental details

A circular flume (Fig. 1) with the mean diameter of 1.6 m, width of 0.2 m and depth of 0.15 m was used in the study. The flume was placed on a stationary 2×2 m^2 platform and a water-sediment flow was made by using two rotating pedals within the flume. Before each experiment, the flume was filled with 0.1% nitric acid (HNO_3) and run for 1 h to remove any possible impurities. It was then thoroughly rinsed up to a level of 0.13 m (130 lit) with deionized water [12].

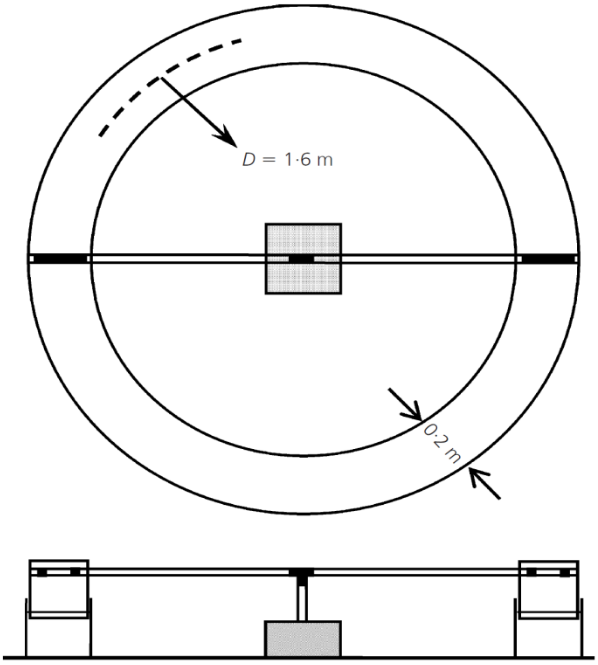

Figure 1: Plan and cross-section of the circular flume.

Cadmium was the heavy metal which used in whole experiments. Stock solution 1000 ppm cadmium was prepared for all experiments. Cadmium measurements were conducted by using an ICP-OES (Varian VISTA-MPX device). The detection limit for the cadmium ion was 0.0005 mg L^{-1}.

Bottom sediment samples were collected by dredging from Karaj River. A sediment size of 0.53 mm was selected by using standard sieving apparatus (particles remained between sieves 30 and 40) and then was carefully washed with distilled water. Then they were dried at 105°C for 24 hrs .Samples were taken from the upper 5 cm of the sediments at places where flow rates were low and sedimentation was assumed to occur [13, 14]. The organic content of the sediment was of the order of 0–1%. The background cadmium level in the various fractions of the sediments was negligible (below detection limits) in the unpolluted zone, compared to the amount of adsorbate added for the adsorption tests. This confirms the absence of any particulate cadmium attached to the sediment particles. The pH value of 7.5 ± 0.1 was maintained throughout the experiment using dilute HNO_3 and NaOH solutions. EC values of the system were adjusted using sodium chloride (NaCl) at 800 ± 10 µS/cm. The solution pH and EC for the adsorption experiments was chosen to be as close to that encountered in the Karaj River water. In addition, all the experiments were conducted at 25°C. The temperature was adjusted using two 300 W aquarium heaters.

The sediment concentrations were 3, 12 and 20 gr/lit and cadmium concentrations were considered as 150, 460 and 770 µgr L^{-1}. During the experiments, first the cadmium solution was injected throughout the flume. The cadmium cloud was then spread through the flume, until it dispersed and the concentration was equal at the whole flume. After adjusting the temperature, pH and EC, the experiment was started by taking 50 mL samples at a given point of the centerline of the flume in different times (0, 1, 2, 5, 10, 15, 30, 45, 60, 90, 120, 180, 240, and 300 minute). These samples were immediately moved to the laboratory for cadmium analysis by ICP-OES. The list of experiments is given in the Table 1 (C_{cd} is the cadmium concentration in the solution).

Table 1: Experimental conditions

Run No.	C_s (gr L^{-1})	C_{cd} (mg L^{-1})
AS01	3	0.15
AS02	3	0.46
AS03	3	0.77
AS04	12	0.15
AS05	12	0.46
AS06	12	0.77
AS07	20	0.15
AS08	20	0.46
AS09	20	0.77

3. Results and Discussion

The physicochemical composition of the minerals was measured using X-ray diffraction (XRD). The physicochemical analysis of the riverbed sand revealed that SiO_2 is its major (54%) constituent and CaO is also present (6.4%) in the sediment in significant amount (Table 2). In addition, the most important geochemical phases, Fe and Mn oxides, are existed in the sediment samples. These elements play an important role in the adsorption process.

Table 2: The physicochemical analysis of the riverbed sands

Constituents	% By weight
SiO_2	54
Al_2O_3	14.4
Fe_2O_3	7.5
TiO_2	0.7
CaO	6.4
MnO	3
Na_2O	1.9
K_2O	3
P_2O_5	0.3
SO_3	< 1
MnO	0.2
S	-
L.O.I	8.34

3.1. Equilibrium Time (t)

The plots of cadmium adsorption with different contact times are shown in Fig. 2(a) for a fixed adsorbent dose of 3 g L^{-1} with an initial cadmium concentration of 150, 460 and 770 μgr L^{-1} for a particle size 0.53 mm.

For most adsorption processes, the uptake varies almost proportionately with $t^{1/2}$ rather than with the contact time [15]. Therefore, plots of cadmium adsorbed, q_t vs $t^{1/2}$, are also presented for the two particle sizes of adsorbent in Figure 2(b). It is clearly evident from these plots that adsorption of cadmium ions on the bed sediments followed three phases: (1) a rapid uptake (Phase I); (2) a transition phase (phase II) and (3) an almost flat phase (Phase III). The interesting thing is that the cadmium concentration does not affect these phases.

As can be seen, the remaining concentration of cadmium ions became asymptotic to the time axis such that there is no appreciable change in the remaining concentration after 5 hrs. This time was presumed to represent the equilibrium time at which an equilibrium concentration was presumably attained. It should be mentioned that this time is approximately independent of cadmium and sediment concentrations. All the further experiments were conducted for 5 hrs.

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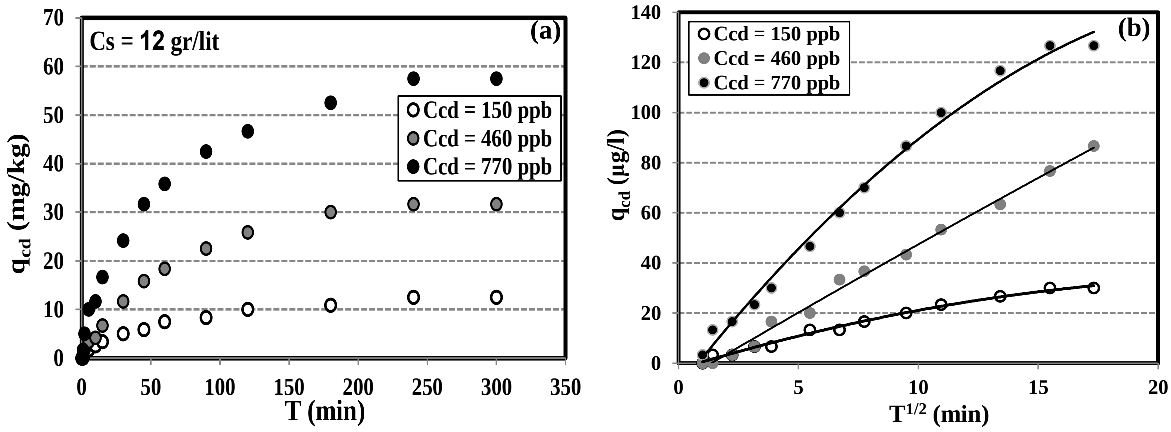

Figure 2: Effect of contact time on adsorption Cadmium by riverbed sand.

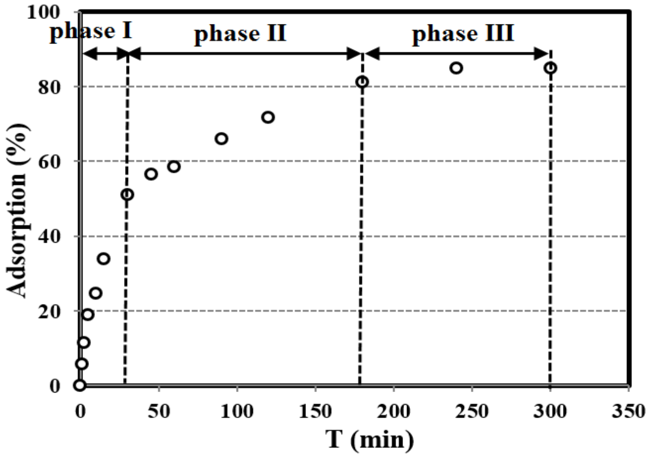

Figure 3. The percent adsorption vs. time (min)

As it is observed, in phase I, about 50% of the cadmium is uptake within the first 30 minutes. This is attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface.

3.2. Sediment Concentration (C_s)

The effect of sediment concentration on the adsorption properties of bed sediments of Karaj river was studied with different doses varying from 3 to 12 g L^{-1} and at the initial cadmium concentrations of 150, 460, and 770 µg L^{-1} (Figure 4. a, b, c). The experiments were conducted in a flow velocity of 0.35 ms^{-1}.

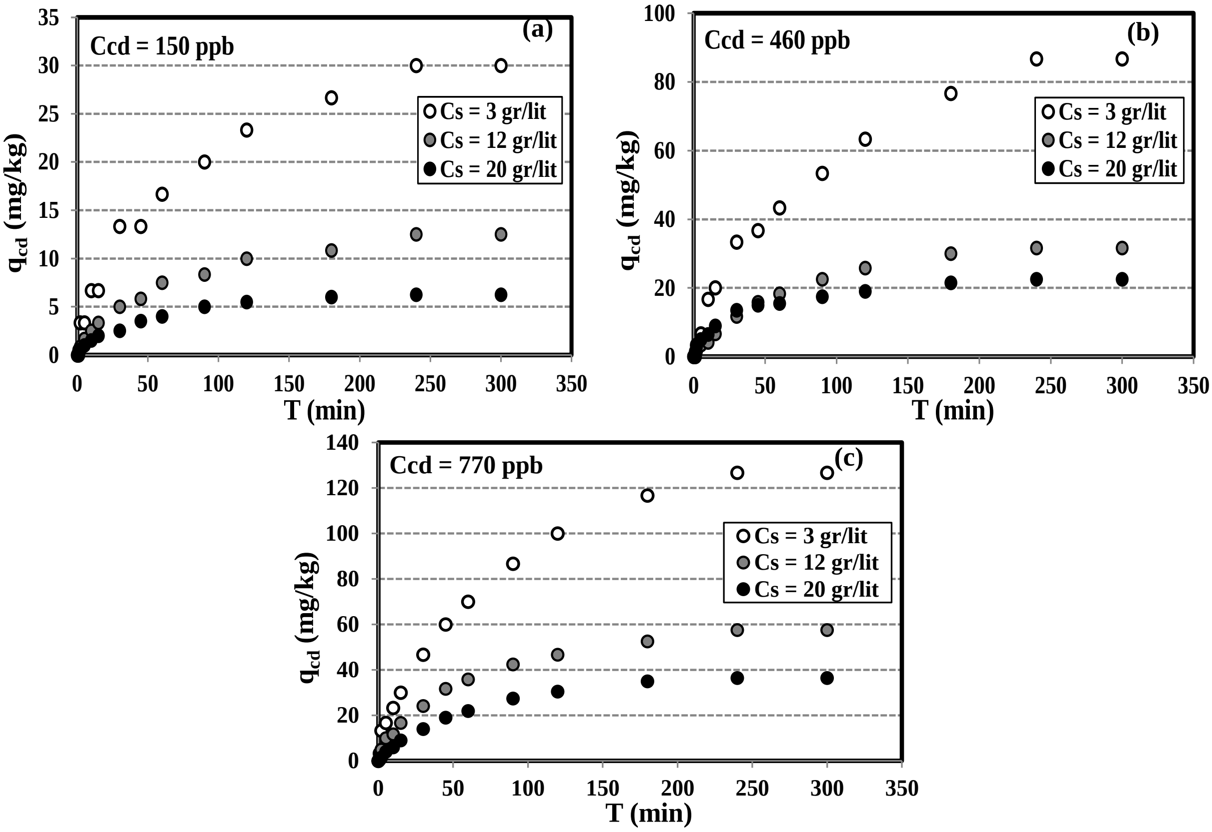

Figure 4: Adsorption of cadmium ions on bed sediments at different concentrations at the initial cadmium concentrations of a) 150, b) 460, and c) 770 µg L^{-1}.

It can be observed that as the concentration of sediment increases the adsorption rate of Cd in unit mass is decreased. It is noteworthy to acknowledge that although the adsorption rate of cadmium in unit mass is decreasing but the percentage of cadmium elimination is increasing. In other words, increasing the sediment concentration in the solution would bring in a decrease of adsorption rate in unit mass while the cumulative adsorption becomes higher, which is due to the competition among sediment particles [11].

Table 3 shows the percent adsorption at the equilibrium time for different sediment and cadmium concentrations. It can be concluded that at a given initial cadmium concentration, the adsorption of cadmium decreased up to about 85 percent with increasing adsorbent load. On the other hand, percent adsorption increased from 41.3 to 80.21% with increasing adsorbent load from 3 to 20 g L^{-1}.

Table 3: The value of percent adsorption (%) at the equilibrium time for different sediment and cadmium concentrations

Cadmium Conc. (ppb)	**Sediment Conc. (gr/lit)**		
	3	**12**	**20**
150	50	83.33	78.12
460	47.77	31.67	84.90
770	41.1	73.4	80.21

3.3. *Adsorption Kinetics*

For the kinetics modelling, the following pseudo first-order equation was used:

$$\frac{dq}{dt} = k_1(q_e - q) \tag{1}$$

where, k_1 is the pseudo first-order rate constant. After integration and applying the boundary conditions $q_t = 0$ to $q_t = q_t$ at t = 0 to t = t; the integrating form of equation becomes:

$$\log(q_e - q) = \log q_e - \frac{k_1 t}{2.303} \tag{2}$$

a plot log (q_e - q_t) versus t gives a straight line from which k_1 and q_e can be evaluated from the slope and intercept. Its analytical equation can be expressed as:

$$q_t = q_e[1 - \exp(-k_1 t)] \tag{3}$$

Ho and Mckay [14] and Azizian [15] proposed the following pseudo second-order model as a best fit to the experimental data:

$$\frac{\partial q}{\partial t} = k_2(q_e - q)^2 \tag{4}$$

where k_2 is the pseudo second-order rate constant. The boundary conditions qt = 0 and $q_t = q_t$ at t = 0 to t = t, respectively. The integrated form of equation becomes:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

A plot t/q_t versus t gives a straight line from which k_2 and q_e can be evaluated:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{6}$$

There are two methods for estimating the kinetics sorption parameters. The first is to apply the least-squares method to the linear transformed kinetic model (Eqs. 2 and 5). However, Goveisi et al [10] showed that it is better to use a non-linear least-squares method for the original non-linear equation.

Also, the "solver tool" in excel software was used to determine the required parameters for pseudo-second order method where it was attempted to minimize the Sum of Square Error (SSE), as follows:

$$SSE = \sum (q_{cal} - q_{meas})^2 \tag{7}$$

where, q_{cal} and q_{meas} are estimated and observed values, respectively. This parameter is used as an optimality criterion in parameter selection and model selection.

Table 4 shows the results of estimation of adsorption parameters (k and q_e) by using linear and nonlinear methods and for pseudo first and second orders are given. The value of SSE is also calculated for each test to show the difference between estimated and observed values. As can be seen in this table, nonlinear pseudo second order is the most accurate method for estimation the adsorption parameters.

Table 4: The results of estimation of adsorption parameters (k and q_e)

			AS01	AS02	AS03	AS04	AS05	AS06	AS07	AS08	AS09
Pseudo first order	nonlinear	k_1	0.0146	0.0124	0.0142	0.0144	0.0143	0.0169	0.0184	0.0306	0.0161
		q_e	29.61	86.7	126.7	12.6	31.7	57.6	6.3	22.6	36.5
		SSE	31.571	183.397	305.527	4.276	5.024	86.797	0.803	46.273	5.223
	linear	k_1	0.0260	0.0421	0.0348	0.0308	0.0393	0.0278	0.0288	0.0233	0.0286
		q_e	30.1	86.67	126.7	12.51	31.67	57.6	6.26	22.6	36.6
		SSE	218.468	5831.929	7139.710	49.588	521.906	514.020	4.756	36.740	261.273
Pseudo second order	nonlinear	k_2	0.0004	0.0001	0.0001	0.0001	0.0003	0.0003	0.0029	0.0016	0.0004
		q_e	36.62	112.70	159.55	36.52	40.71	67.17	7.42	23.94	45.71
		SSE	18.549	104.358	179.438	43.260	4.204	28.926	0.484	7.950	4.789
	linear1	k_2	0.0005	0.0001	0.0001	0.0013	0.0004	0.0004	0.0036	0.0016	0.0004
		q_e	34.88	107.71	149.16	14.47	39.47	65.31	7.15	24.33	44.76
		SSE	25.837	130.974	353.767	2.698	5.278	46.321	0.677	8.847	5.416
	linear2	k_2	0.0062	0.0002	0.0014	0.0051	0.0018	0.0016	0.0105	0.0053	0.0004
		q_e	16.47	86.44	70.36	9.34	22.06	41.48	5.08	17.83	42.76
		SSE	638.696	531.661	11681.052	41.870	485.342	1074.05	8.953	96.180	11.739

Figure 5 shows the estimated and observed values of q_e by using different methods (linear and nonlinear).

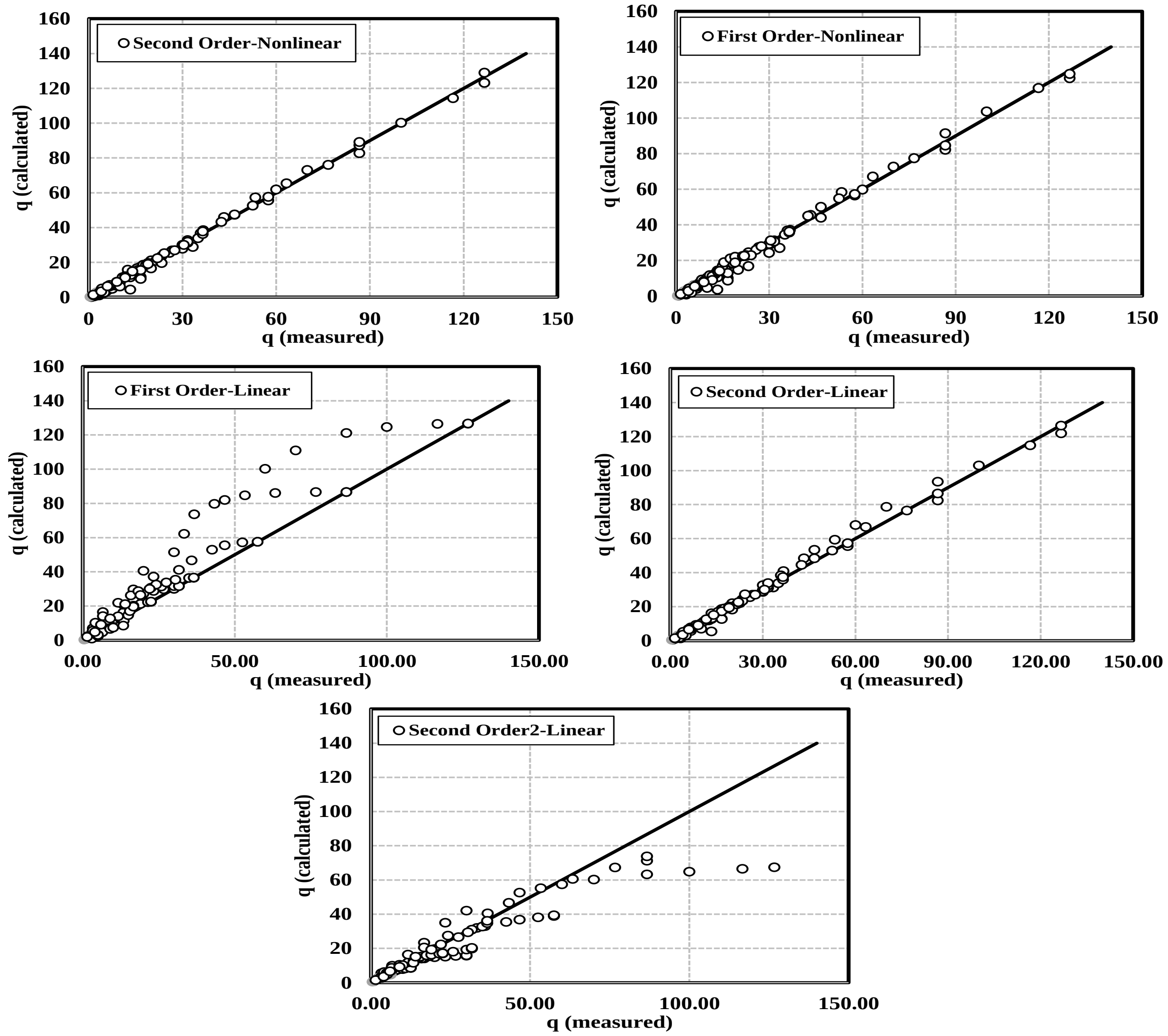

Figure 5: The estimated and observed values of q_e by different methods.

Conclusions

In this paper, effects of various important parameters such as contact time and sediment concentration on adsorption of cadmium by riverbed sands have been experimentally investigated. This study showed that riverbed sands are a good adsorbent matter for adsorptive separation of cadmium from aqueous solutions and they will provide a non-toxic and economically viable treatment for cadmium rich waters and wastewaters. Kinetics modelling of the adsorption process have been discussed. Analysis of the experimental data was led to the following conclusions:

- two important geochemical phases, iron and manganese oxide, play an important role in the adsorption process,
- as the concentration of sediment was increased, the adsorption rate of Cd in unit mass was decreased. It is noteworthy to acknowledge that although the adsorption rate of cadmium in unit mass is decreasing but the percentage of cadmium elimination is increasing,
- at a given initial concentration of cadmium, the adsorption of cadmium decreased up to about 85 percent with increasing adsorbent load. On the other hand, percent adsorption increased from 41.3 to 80.21% with increasing adsorbent load from 3 to 20 g L^{-1},
- based on the SSE values, pseudo-second order model was selected as the best model to describe the adsorption behavior for all these types of cadmium ions. It was also shown that the nonlinear pseudo second order is the most accurate method for estimation the adsorption parameters (k and q_e),
- kinetic tests demonstrated that adsorption equilibrium reached within 5 hrs for cadmium, which was independent of initial cadmium and sediment concentrations, and
- the removal percentage increases with increasing the sediment concentration, but the adsorption capacity of sediment decreases.

In general, the results of the study are highly useful and may be extended for other rivers with coarser sediments. The relative contribution of individual components could not be obtained from the present studies because in natural systems, type and composition of sediment's mineral and organic fractions vary simultaneously and the effect of individual constituents could not be isolated.

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