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Study of multi-stage cadmium adsorption by riverine sediments

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ABSTRACT

Most riverine sediments have the high capability to adsorb and store heavy metal ions. In the present study, the adsorption capacity of the bed sediments collected from the Karaj River (Iran) were experimentally studied for cadmium ion adsorption. Multi-stage batch adsorption experiments were carried out for a constant sediment concentration of 20 g/L and different initial cadmium concentrations of 0.2, 0.5, 1, 10, 20, and 50 mg/L. The cadmium solutions with known concentrations were added to the bed sediment with the mean diameter of 0.53 mm in five stages to characterize the capacity of the sediments to adsorb cadmium. The batch adsorption experiments were conducted as both kinetics and equilibrium. The results showed that by adding cadmium ions to the sediment at each stage, the adsorption capacity was less than the previous stage, and for a cadmium concentration of 0.2 mg/L, the adsorption percent and the amount of adsorbed cadmium was reduced from 88 to 70% and 9 to 6.8 mg/kg, respectively. These changes decreased with increasing initial Cd concentrations. This process is useful for seasonal rivers in which a certain concentration of heavy metal pollution may occasionally flow over the bed.

1. Introduction

With the advancement of such industries as mining, fertilizers, and batteries, heavy metals are increasingly being discharged into aquatic environments. Therefore, the study of heavy metal pollution has become an environmental priority owing to the serious threats to the environment. Researchers have suggested several methods to remove heavy metals from water and wastewater: chemical precipitation, ion exchange, adsorption, membrane filtration, electrochemical treatment technologies, etc. [1]. The adsorption process is an effective and useful method for removing heavy metals from water and wastewater. Different studies have demonstrated the considerable contamination of riverine sediments by heavy metals [2-7]. In addition, many studies have been conducted to evaluate the partitioning and

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distribution of heavy metals in riverine sediments [8-11]. Kolemans and Lijklema [2] studied the uptake of cadmium by sediments and suspended particles in Lake Volkerak (Netherlands). Hung and Chen [3] investigated the adsorption process of heavy metals by the river, coast, and lake sediments. They concluded that the adsorption capacity of sediments ranged from 0.06-13.48 μM/g for Cu, 0.01-0.2I μM/g for Cd, 0.12-2.76 μM/g for Pb, and 0.12-0.46 μM/g for Zn. Their results also showed that the adsorption capacity of heavy metals for lake sediments was more than that for the riverine and coastal sediments. Jain and Ram [4] evaluated the adsorptive properties of heavy metal ions (lead and zinc) by riverine sediments. They concluded that by increasing the initial concentration of heavy metals, the adsorption of heavy metals increased. Furthermore, the adsorption of heavy metals increased with increasing sediment concentrations and decreased with the increasing size of sediment particles. Jain and Sharma [5] examined the adsorption of cadmium by the Hindon Riverbed sediments (India). They found that the optimum equilibration time was about 60 min, which was independent of the initial cadmium concentration. In addition, the adsorption of cadmium increased with increasing sediment concentrations and decreased with the increasing size of sediment particles. Jain et al. [6] concluded that the optimum contact time to reach equilibrium was about 60 min, which was independent of the initial concentration of the heavy metals. Their results showed that the adsorption rate increased by increasing the pH value and sediment concentrations. Also, the extent of adsorption decreased with the increasing particle size. They also evaluated their data using both Freundlich and Langmuir equilibrium adsorption models. Nasrabadi et al. [7] investigated the characteristics of cadmium adsorption by riverbed sands in a circular flume. They concluded that as the metal ion concentration increased, the cadmium adsorption was reduced in unit mass; however, the percentage of cadmium removal increased. They also observed that at a constant cadmium concentration, heavy metal adsorption decreased up to about 85% by increasing the sediment concentrations. The extent of adsorption increased from 41 to 80% by increasing the sediment concentrations from 3 to 20 g/L. Until now, many efforts have been made to study the adsorption of heavy metals by riverine sediments. However, the ultimate adsorption capacity of the sediments is still missing. Since the flow in natural rivers may be temporary (ephemeral rivers), sediments may encounter the pollution several times due to heavy metal dissolved in the stream. Therefore, studying the multi-stage adsorption of heavy metals by riverine sediments is very important from an environmental point of view. For this reason, this investigation aims to conduct a laboratory study by contaminating the sediments collected from the Karaj River in several stages and estimating the adsorption parameters for both the kinetic and equilibrium conditions at each stage to determine the degree of Cd ions the sediments can adsorb.

2. Materials and methods

The Karaj riverbed sediments were collected by dredging the river bed. These samples were taken from the upper layer (0-15 cm) of the deposits where the flow rate was low and sedimentation occurred [12]. Immediately after collecting the samples, the particle-size distribution, physicochemical characteristics, and cation-exchange capacity (CEC) of the sediments were analyzed. All of the sediments were washed five times with deionized water to eliminate the background heavy metal contents in various areas and remove any impurities and turbidities. The sediments were then placed in an oven at 105°C for 24 hours. The physicochemical composition and particle-size distribution of the prepared sediments are given in Tables 1 and 2, respectively. In Table 1, σ_g is the geometric standard deviation of the sediment particles, d_g is the geometric diameter of the sediment particles, C_C is the coefficient of curvature, C_U is the uniformity coefficient, and D_{90}, D_{60}, D_{50}, D_{30}, and D_{10} are respectively 90%, 60%, 50% 30%, and 10%, the portions of the particles with diameters smaller than this value. A cadmium ion was the heavy metal used in all the experiments. A 1000 ppm (mg/L) stock solution of Cd ion (Merck) was prepared. The concentration of the Cd was measured using an ICP-OES device. The detection range for the Cd ion was 0.0005 ppm (mg/L). In all the experiments, the values of pH and

EC were using dilute HNO_3 and NaOH (Merck) solution and sodium chloride (NaCl), respectively. It should be mentioned that for the simulation of natural conditions, the values of the environmental parameters of pH, EC, and temperature were considered and adjusted to the values encountered in natural rivers (pH = 7.5 ± 0.1, EC = 800 ± 10 μS/cm, and T = 25°C). Multi-stage batch adsorption experiments were performed using 1 g of sediment prepared with 50 ml of the cadmium solution with a certain concentration, using pre-cleaned flasks of 100 ml in volume. The initial concentrations of cadmium solution used were 0.2, 0.5, 1, 10, 20 and 50 mg/L. First, the sediment samples were put in different pre-cleaned flasks with cadmium concentrations of 0.2, 0.5, 1, 10, 20, and 50 mg/L. After that, all the flasks were placed in a constant-temperature vibration case. All the flasks were shaken in a shaker for 5 hours at a rate of 100 rpm to ensure sufficient cadmium adsorption by the sediments; the shaking process was stopped. The overlying water on the sediment surface in each flask was analyzed for Cd concentrations in the solution. In the next stage, new solutions with the same cadmium concentration were again added to that sediment sample, and the mixture was re-shaken for another 5 hrs. For five stages, total time was 1500 min (25 hr). This process was repeated for five stages and five Cd concentrations, and the amount of cadmium adsorbed at each stage was determined. It should be mentioned that all analyses were performed in two replicates.

Table 1. The size distribution of the riverine sediments.

σ_g	d_g	CC	CU	D_9	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

Table 2. Physico-chemical properties of sediments.

Constituents	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MnO	Na_2O	K_2O	P_2O_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

In order to determine the adsorption capacity of the sediments, the amount of cadmium adsorbed per unit weight of the sediments (q_e, mg/kg) was calculated using Equation (1):

$$q_e = \frac{(C_0 - C_e).V}{m} \tag{1}$$

where q_e is the amount of cadmium adsorbed at equilibrium time, C_o is the initial Cd concentration (mg/L), C_e is the Cd concentration at equilibrium condition (mg/L), V is the volume of the aqueous phase, and m is the weight of the sediment (g). To quantify the performance of the different fractions of the sediments, the cadmium removal percent was calculated using Equation (2):

$$\text{Adsorption}(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

3. Results and discussion

In this study, the sediment was mostly composed of sand (more than 99%; d_{50} = 0.53 mm), and the organic content of the sediment was negligible (0-1%). In addition, the weight percentages of the geochemical constituents for the sediments showed that the main constituent was SiO_2 (54%), and CaO was also present in a significant amount (6.4%) in the sediment (Table 2). In addition, as previously mentioned by different researchers (Kolemans and Lijklema, 1992; Jain et al., 2004), the most important geochemical phases (iron and manganese) may play an important role in the adsorption process. As shown in Table 2, the amounts of Fe_2O_3 and MnO are 7.5% and 3%, respectively. These values indicate that two geochemical phases may act as supportive materials for Cd adsorption by sediments [2,6].

3.1. Initial Cd concentration

In order to evaluate the effect of the initial Cd concentration on adsorption by the sediments, many experiments were carried out with different cadmium concentrations in the range of 0.2 to 50 mg/L with a constant sediment dose of 20 g/L and fixed values of environmental parameters (pH = 7.5 ± 0.1, EC = 800 ± 10 μS/cm, and T = 25°C). Figure 1 shows the results of these experiments for different initial Cd concentrations. The results show that the Cd adsorption by sediments increases with increasing initial Cd concentration. So that by increasing the Cd concentration from 0.2 to 50 mg/L, the adsorption rate increases from 9 to 1610 mg/kg, while the adsorption percent decreases from 88 to 63 percent.

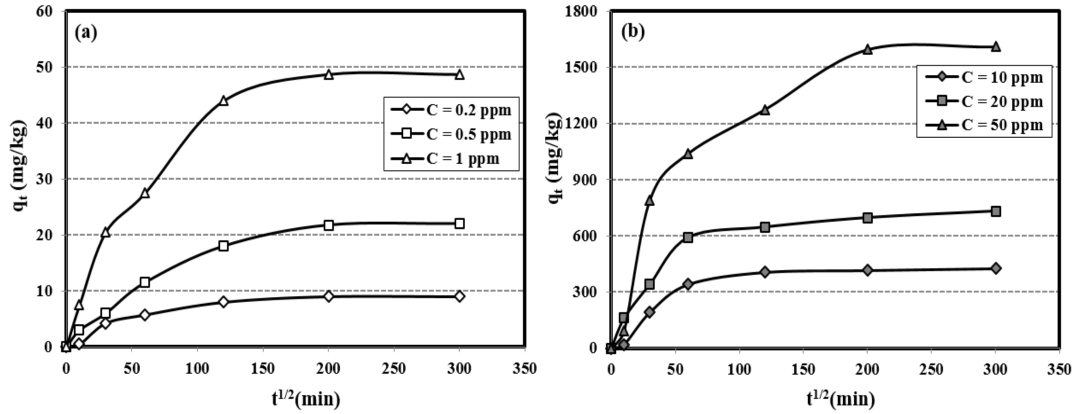

Fig. 1. The adsorbed cadmium ions versus time (min) (a) for C = 0.2, 0.5, 1 mg/L (b) C = 10, 20, and 50 mg/L.

It is also evident from Figure 1 that the Cd adsorption increases rapidly in the initial stages; then, the increase in the removal of cadmium from the solution decreases gradually and reaches a constant value (at equilibrium time of 200 min). For these experiments, the quasi-equilibrium state was attained at the first 60 min. Jain and Ram [4] found that the pseudo-equilibrium phase was achieved within 45 min for both tested metals. On the other hand, Jain and Sharma [5] concluded that the optimum equilibration time was about 60 min. In addition, Jain et al. [6] concluded that the optimum contact time to reach the equilibrium was about 60 min, which was independent of the initial concentration of heavy metals. As can be seen, the Cd adsorption by the riverine sediment followed three phases: (1) rapid adsorption phase (Phase I), (2) transition phase (phase II), and (3) an almost flat phase (Phase III). It is noteworthy that the cadmium concentration is not affected by these phases (Figure 1). As shown in phase I, about 50% of the cadmium is adsorbed in the first 60 min. It is related to the simultaneous utilization of the most accessible adsorbing sites on the sediment surfaces [4-6].

3.2. Contact time

Figure 2(a) shows the plots of cadmium adsorption as a function of time for a constant sediment concentration of 20 g/L with an initial cadmium concentration of 0.2, 0.5, 1, 10, 20, and 50 mg/L for a mean diameter of 0.53 mm. On the other hand, according to Weber and Morris [13], for most adsorption processes, the amount of heavy metal adsorbed is approximately proportional with $t^{1/2}$ [14]. Therefore, the value of cadmium adsorbed, q_t, against $t^{1/2}$ is also shown in Figure 2(b). The adsorbed cadmium by the sediments vs. $t^{1/2}$ can be observed in a certain trend with a constant slope during the experiment.

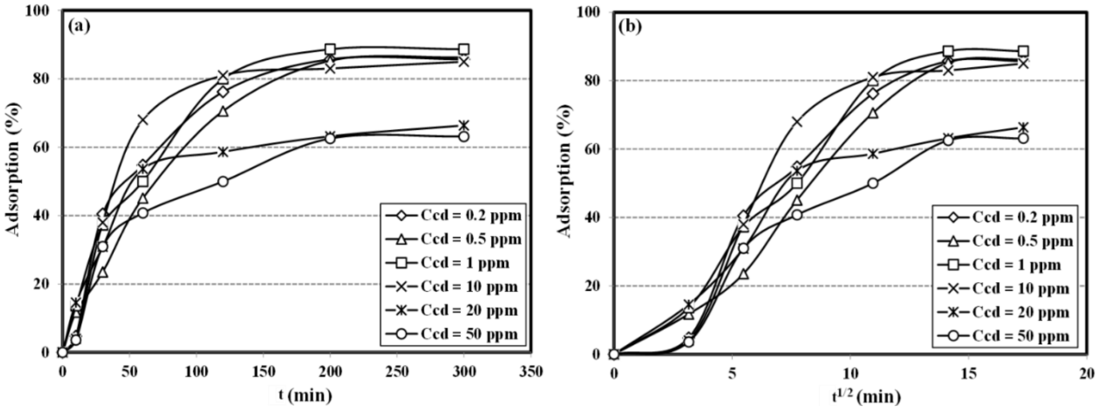

Fig. 2. a) Adsorbed cadmium by sediments vs. t; b) Adsorbed cadmium by sediments vs. $t^{1/2}$.

In addition, the remaining cadmium concentration is asymptote with the time axis so that there is no significant change in the cadmium concentration after 1 hour. This time was considered as the equilibrium time, in which an equilibrium concentration was presumably achieved. It is noteworthy that the equilibrium time is not dependent on the cadmium and sediment concentrations. The following explanations can be expressed for these changes: 1) at the initial stage of the adsorption process, the sediment surface provided more adsorption sites, attributing rapidly increased adsorption rate. Due to the negative-charged surface of the sediments, it could combine with metal cations through Coulomb force, and this process could be considered as pseudo-adsorption; 2) Specific adsorption happened through a chemical reaction between Cd and sediment surface was followed. However, it would change the property of surface electric charge. Increased positive sites would prevent the adsorption of Cd; and 3) Available sorption sites became a limiting factor along with the increasing adsorption [15-18]. The results of Jain and Ram [4], Jain and Sharma [5], Ho [19-20], Mahdavi et al. [21]are consistent with the results of the present study.

3.3. Multi-stage adsorption

One of the main hypotheses of this research is that riverine sediments have the ability to adsorb heavy metals in several stages due to adsorption sites at the sediment surface. As previously mentioned, for multi-stage adsorption experiments, different concentrations of Cd ions (0.2, 0.5, 1, 10, 20, and 50 mg/L) were successively added to the sediments to determine the degree of adsorption of the cadmium ions by the sediments. To answer this question, some multi-stage adsorption experiments were performed for cadmium concentrations ranging from 0.2 to 50 mg/L with a fixed sediment dose of 20 g/L. Figure 3 shows the results of multi-stage adsorption experiments for different concentrations and at different stages. The results showed that with the continuous injection of cadmium (at a known concentration) to the sediments, the sediments continued to adsorb cadmium, but the adsorption capacity in each stage was lower than in the previous stage. For example, for a Cd concentration of 0.2 mg/L, the adsorption percent decreased from 88 (at the first stage) to 70% (at the fifth stage), and the amount of cadmium adsorbed declined from 9 mg/kg (at the first stage) to 6.8 mg/kg (at the first stage). As it is observed in Figure 3, these changes decreased while the adsorption rate increased. On the other hand, at the first stage of the tests, by increasing the Cd concentration from 0.2 to 50 mg/L, the adsorption rate increased from 9 to 1610 mg/kg, and the adsorption percent decreased from 88 to 63 percent; while, at the fifth stage, these changes declined and the adsorption rate increased from 6.8 to 450 mg/kg, and the adsorption percent decreased from 64 to 17 percent. It can be found that with continuous Cd injection to the mixture, the amount of Cd (mg) in the unit weight of the sediment (kg) increased while the adsorption capacity decreased.

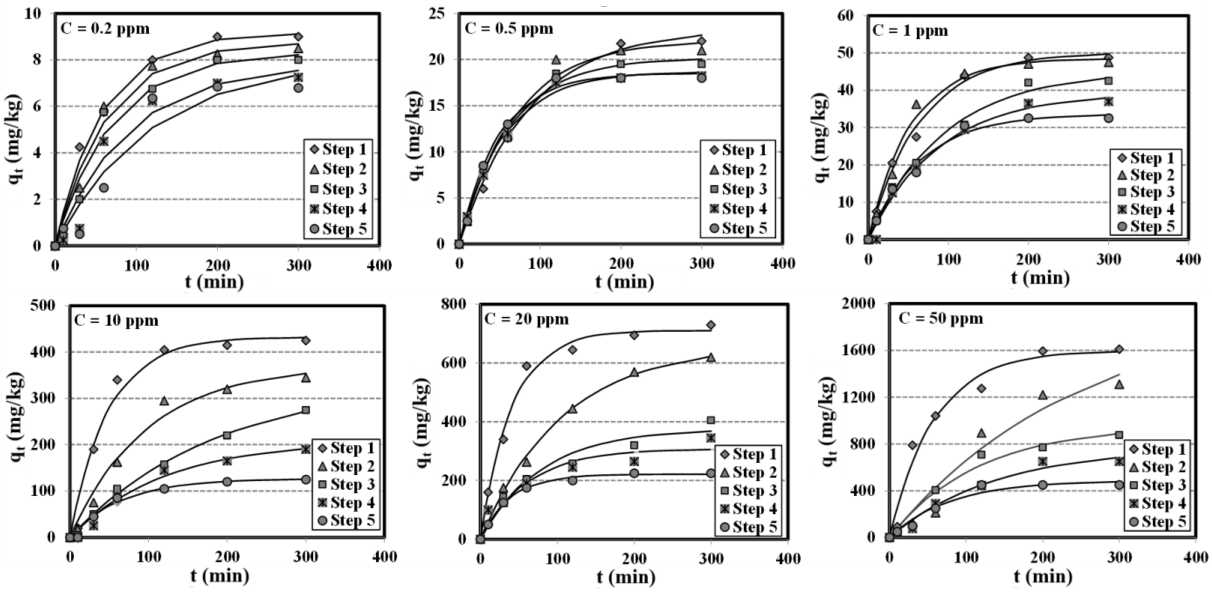

Fig. 3. The amount of Cd adsorption vs. time (min) at different stages.

In these experiments, similar to the first experiments (section 3.1), the adsorption curves are smooth, indicating the monolayer coverage of metal ions on the riverine sediment surfaces. As observed in Figure 3, this time is also 4 hours, and it is presumed to represent the equilibrium time. Similar to the first set of experiments, the equilibrium time is not dependent on the cadmium concentrations. Figure 4 shows the cumulative adsorbed cadmium to the riverine sediments by adding the different cadmium concentrations in five stages and a total time of 1500 min. In this figure, q_s is the sum of the cadmium adsorbed (total adsorbed cadmium) by the sediments during the five stages of the tests. The results of these experiments also showed that with the continuous injection of cadmium (at a known Cd concentration) to the sediments, the sediments continue to adsorb cadmium. As can be observed, the total adsorbed cadmium by the sediments for five initial concentrations of 0.2, 0.5, 1, 10, 20, and 50 mg/L are 39.55, 98.75 ,208.25, 1360, 2325and , 4895 mg/kg, respectively.

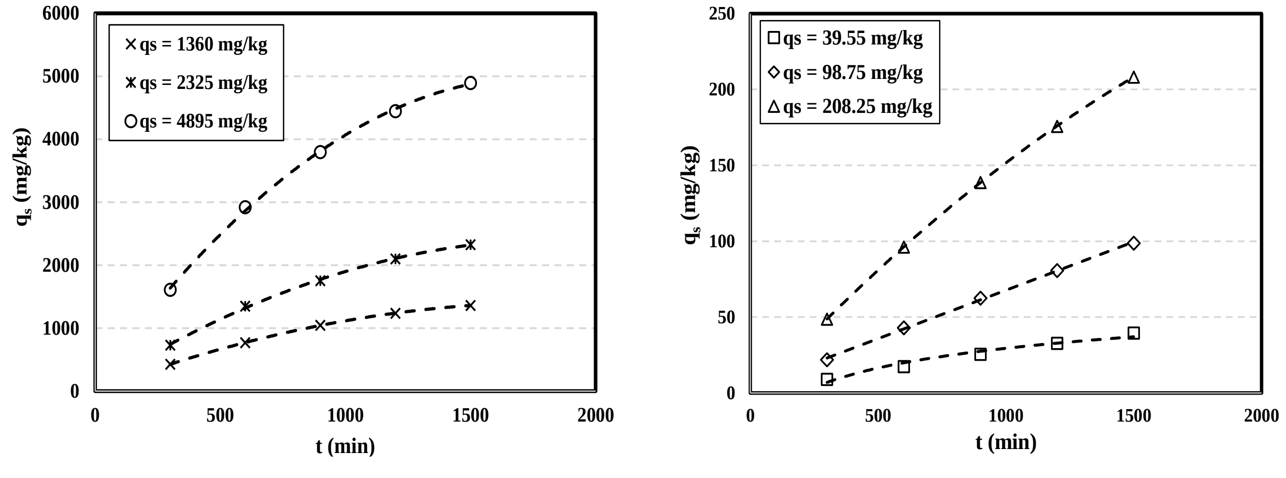

Fig. 4. Cumulative adsorption by sediments due to injecting different cadmium concentrations at five stages.

Figure 5 shows the Cd adsorption percent versus the equilibrium cadmium concentration (q_e) at different stages. It can be concluded that for a given equilibrium time, the adsorbed cadmium increases by increasing the initial cadmium concentrations. In other words, for a low Cd concentration, the adsorption percent is high, and it decreases by increasing the initial Cd concentrations. These changes can be attributed to more efficient utilization of the adsorptive capacities of the sediments because of a greater driving force. These changes are the same for all stages of the experiments. As shown in Figure 5, by adding the Cd continuously to the sediment (at the known Cd concentration), the adsorption percent decreases, indicating the reduction in adsorption capacity of sediments with a continuous injection of the Cd ions.

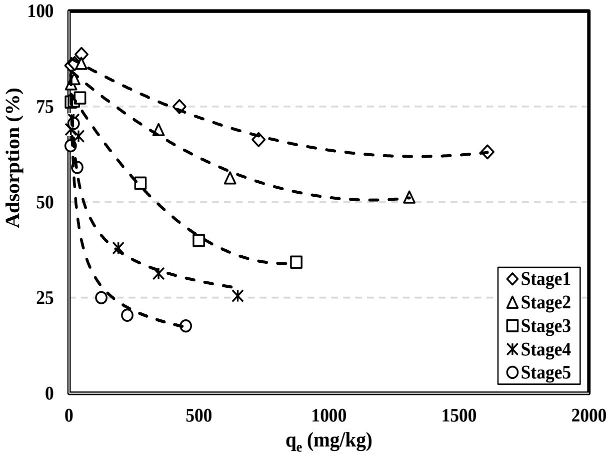

Fig.5. Cadmium adsorption percent on bed sediments versus Cd adsorbed at equilibrium conditions (mg/kg) at different stages.

3.4. Equilibrium adsorption

In this study, equilibrium adsorption data were analyzed using the Freundlich and Langmuir models to investigate the monolayer capacity and adsorption intensity.

3.4.1. Langmuir model

The Langmuir isotherm model is valid for monolayer adsorption onto the adsorbent surfaces having limited identical sites. It is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface with constant adsorption energy, and there is no transmigration of adsorbate in the plane of the surface [22]. The nonlinear form of Langmuir isotherm equation is represented by the following equation:

$$q_e = \frac{q_m K C_e}{1 + K C_e} \tag{3}$$

where q_e is the metal ion adsorbed at equilibrium (mg/kg), C_e is the equilibrium concentration of cadmium in the solution (mg/L), and K (mg/g) and q_m (l/mg) are Langmuir constants related to the maximum adsorption capacity of the riverine sediments and adsorption energy, respectively. These values were used to compare the adsorptive properties of the sediments.

3.4.2. Freundlich model

Another equilibrium model that has been extensively used is the Freundlich isotherm. It is an empirical model representing the isothermal variation of heavy metal adsorption by an adsorbent. The general form of the Freundlich equation is defined as Equation (4):

$$q_e = K_f C_e^{1/n} \tag{4}$$

The Freundlich equation is basically empirical, but it is often used for data description. The equilibrium adsorption data are usually fitted to the logarithmic form of the Equation (5):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{5}$$

where K_F (mg/g) and n (l/mg) are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. By plotting $\log q_e$ vs. $\log C_e$, a straight line with the slope of 1/n and intercept $\log K_f$ is obtained. The intercept of the line, $\log K_f$, approximately represents the adsorption capacity, and the slope, 1/n, indicates the adsorption intensity [23]. Figure 6 shows the cadmium adsorption isotherms on the riverine sediments with a constant sediment concentration of 20 g/L. As mentioned before, the experiments were carried out at the constant environmental factors of pH = 7.5 ± 0.1, EC = 800 ± 10 µS/cm, and T = 25°C. It was evident that for the same equilibration time, the cadmium adsorbed increased by increasing the initial cadmium concentrations. Furthermore, for low Cd concentrations, the adsorption percent was high, and it decreased with increasing initial Cd concentration. The reason for these changes was that more efficient utilization of the adsorptive capacities of the adsorbent was due to a greater driving force. The results also showed that the Freundlich isotherm model well described the adsorption of the cadmium ions.

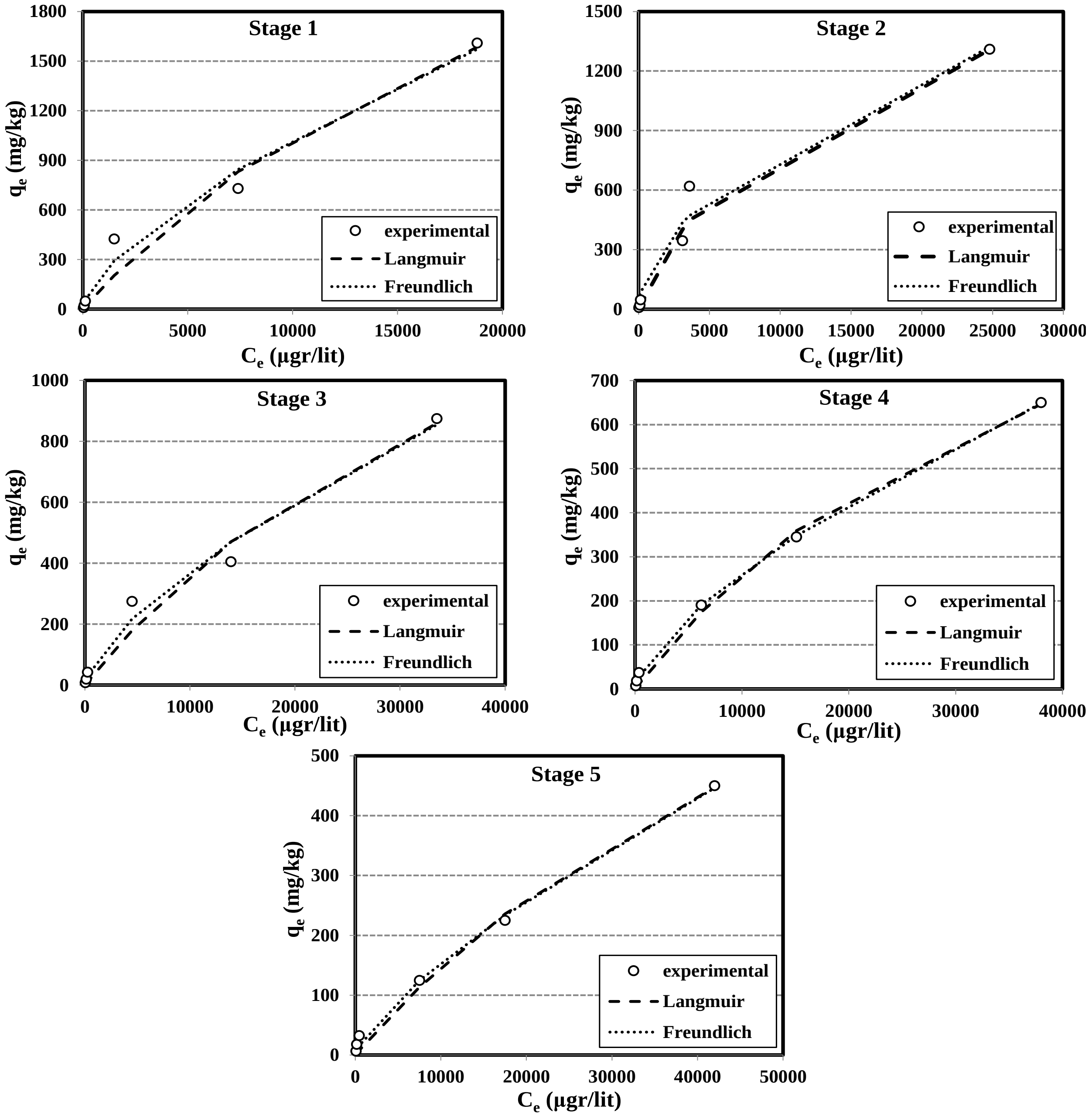

Fig. 6. Langmuir and Freundlich isotherms for cadmium ion adsorbed on riverine sediments.

The results of the calculation of the Langmuir and Freundlich isotherm constants for Cd adsorbed by riverine sediments are presented in Table 3. As can be seen, the adsorption capacity (K_F) is reduced from 2.254 for the first stage to 0.169 for the fifth stage of the tests, while the values of n increase from 0.665 to 0.739 (decreasing 1/n), indicating the adsorption intensity decrease in comparison with the first stage of the experiments.

Table 3. Langmuir and Freundlich isotherm constants for cadmium ion adsorbed on riverine sediments

Stage	Freundlich		Langmuir	
No.	K_f	n	K	q_m
1	2.252	0.665	0.000037	3863
2	5.96	0.533	0.00008	1936
3	0.714	0.68	0.000021	2077
4	0.53	0.67	0.000024	1366
5	0.169	0.739	0.000013	1249

3.5. Adsorption kinetics

In this study, equilibrium adsorption and the kinetic data for cadmium adsorption on riverine sediments were measured at different times. For this purpose, the pseudo-first-order and pseudo-second-order equations were investigated. The pseudo-first-order equation is defined as:

$$\frac{dq}{dt} = k_1(q_e - q) \quad (6)$$

where k_1 is the pseudo- first-order rate constant. By integrating and applying the boundary conditions defined as q_t = 0 to q_t = q_t at t = 0 to t = t, the following expression yields:

$$\log(q_e - q) = \log q_e - \frac{k_1 t}{2.303} \quad (7)$$

when $\log(q_e - q_t)$ is plotted against t, a straight line is obtained, from which k_1 and q_e can be determined from the slope and intercept of the line. As a result, the analytical form of the equation can be represented as:

$$q_t = q_e[1 - \exp(-k_1 t)] \quad (8)$$

In addition, the following pseudo-second-order model has been proposed by Ho and Mckay [24] and Azizian [13]:

$$\frac{\partial q}{\partial t} = k_2(q_e - q)^2 \quad (9)$$

where k_2 is the pseudo-second-order rate constant. By integrating and applying the boundary conditions defined as q_t = 0 and q_t = q_t at t = 0 to t = t, the integrated form of the equation yields:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

By plotting t/q_t against t, a straight line is obtained, from which k_2 and q_e can be determined:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (11)$$

Different researchers have suggested two methods for estimating the kinetic adsorption parameters. The first one applies the least-squares method to the linear transformed kinetic model (Eqs. 7 and 10), while the second one utilizes the non-linear least-squares method. However, some researchers (e.g., Goveisi et al. [25] and Jiang et al. [26]) have shown that the use of the non-linear least-squares method is better for the original non-linear equation. The kinetic adsorption parameters (k and q_e) were estimated and are shown in Table 4 for the linear and non-linear methods and the pseudo-first-order and pseudo-second-order models. In addition, the value of the statistical index of SSE (Eq. 12) was calculated for each experiment to show the difference between the estimated and observed values and expressed as:

$$SSE = \sum(q_{cal} - q_{meas})^2 \quad (12)$$

where q_{cal} and q_{meas} are the estimated and observed values of cadmium adsorbed by the riverine sediments, respectively. As can be seen, the pseudo-first-order mode (nonlinear) obtained the least values of SSE in comparison with the other models, and therefore best describes the adsorption rate of cadmium by riverine sediment. This model is also plotted in Figure 3 as the solid line along with the experimental data.

4. Conclusions

This paper evaluated the adsorption capacity of cadmium by riverine sediments. The effects of such important parameters as contact time and the cadmium concentration on the adsorption process were experimentally investigated. The main findings of this study are as follows:

- By increasing the cadmium concentration from 0.2 to 50 mg/L, the adsorption rate in a constant sediment dose of 20 g/L increased from 9 to 1610 mg/kg, while the percent adsorption decreased from 88.63 to 63.13 percent.
- The results showed that by adding cadmium ions to the sediment at each stage, the adsorption capacity was less than before. So that, for cadmium concentration of 0.2 mg/L, the adsorption percent and the amount of adsorbed cadmium were reduced from 88 to 70% and 9 to 6.8 mg/kg, respectively. These changes decreased with increasing cadmium concentrations. On the other hand, at the first stage of the tests, by increasing the cadmium concentration from 0.2 to 50 mg/L, the adsorption rate increased from 9 to 1610 mg/kg, and the percent adsorption decreased from 88 to 63 percent; still, at the fifth stage, these changes declined and the adsorption rate increased from 6.8 to 450 mg/kg, and the percent adsorption decreased from 64 to 17 percent.
- The adsorption data showed that the

pseudo-first-order and Freundlich adsorption models best described the adsorption rate of cadmium by riverine sediment, respectively, for kinetics and equilibrium conditions.

Table 4. Kinetic parameters for Cd adsorbed on riverine sediments.

Cd Conc. (mg/l)	Stage No.	Second-order-nonlinear			First-order-nonlinear			Second-order-linear			First-order-linear		
		k	q_e	SSE	k	q_e	SSE	k	q_e	SSE	k	q_e	SSE
0.2	Stage1	0.002	11.30	1.93	0.017	9.2	1.3	0.0005	14.5	7.9	0.023	9.1	3.6
	Stage2	0.001	11.1	3	0.016	8.8	1.8	0.0004	14.2	7.8	0.022	8.6	4.5
	Stage3	0.001	10.7	3.1	0.014	8.3	2.2	0.0004	13.7	6.6	0.024	8.1	6.9
	Stage4	0.0008	10.7	4.1	0.011	7.8	3.3	10^{-5}	67	15.2	0.027	7.3	15.4
	Stage5	0.0005	11.7	4.9	0.008	8.0	4.1	4×10^{-5}	31.8	9.7	0.011	6.9	5
0.5	Stage1	0.0003	30.8	5.3	0.012	23.4	2.1	0.0003	30.4	5.6	0.013	22.1	3.7
	Stage2	0.0005	28	11.2	0.014	22.1	5.4	0.0004	28.1	13.1	0.016	21.1	6.8
	Stage3	0.0007	24.9	6.6	0.016	20.2	2.9	0.0007	24.3	7.1	0.016	19.6	3.9
	Stage4	0.0008	22.7	5	0.018	18.7	1.3	0.0009	22.2	1.6	0.019	18.3	1.6
	Stage5	0.001	22.2	7.8	0.02	18.5	2.3	0.0009	21.9	9.9	0.022	18.1	2.7
1	Stage1	0.0003	62.1	28.7	0.016	50.2	16.0	0.0003	61.0	30.4	0.016	48.9	18.6
	Stage2	0.0003	59.1	64.6	0.019	48.6	27.9	0.0003	59.0	77.9	0.02	47.6	29.6
	Stage3	0.0002	59.8	14.3	0.011	45.3	12.4	0.0002	58.9	14.5	0.012	42.6	18
	Stage4	0.0002	52.4	31.4	0.011	39.4	21.9	0.08	0.1	4044.2	0.013	37.1	26.9
	Stage5	0.0004	41.8	20.4	0.015	33.7	11.8	0.0004	40.8	21.6	0.017	32.6	13.7
10	Stage1	10^{-5}	524	9180	0.02	432	5084	10^{-5}	729	38089	0.021	425	5198
	Stage2	10^{-5}	510	3225	0.01	371	2090	10^{-5}	732	7876	0.012	345	2659
	Stage3	10^{-5}	517	306	0.005	341	331	10^{-5}	1597	8537	0.008	275	1098
	Stage4	10^{-5}	301	1183	0.008	209	980	0.082	0.1	92875	0.0000	190	1548
	Stage5	0.0001	161	572	0.015	127	408	0.082	0.1	50148	0.016	125	412
20	Stage1	10^{-5}	833	7071	0.025	711	4039	0.00003	823	7406	0.023	730	4852
	Stage2	10^{-5}	895	2462	0.009	663	2419	10^{-5}	834	3225	0.011	620	3522
	Stage3	10^{-5}	466	4433	0.013	376	7158	3×10^{-5}	460	4705	0.011	405	7688
	Stage4	0.0001	370	3639	0.016	308	5815	5×10^{-5}	379	3748	0.012	345	7115
	Stage5	0.0001	256	248	0.026	221	198	0.0001	254	272	0.025	225	234
50	Stage1	10^{-5}	1964	63293	0.017	1600	64211	10^{-5}	2524	224473	0.017	1610	64372
	Stage2	10^{-5}	1961	161138	0.004	1986	96253	10^{-5}	10089	226021	0.008	1310	160758
	Stage3	10^{-5}	1377	30473	0.009	962	24839	10^{-5}	2700	73415	0.01	875	29345
	Stage4	10^{-5}	1141	13376	0.007	774	10763	10^{-5}	1679	22692	0.01	650	17732
	Stage5	10^{-5}	641	12796	0.013	488	8552	10^{-5}	679	15843	0.015	450	10478

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