

# Using Iranian Bentonite (Birjand Area) to Remove Cadmium from Aqueous Solutions

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**Abstract** Bentonite from the Birjand area of Iran was characterized by X-ray diffraction, X-ray fluorescence, and Fourier transform infrared spectroscopy. The removal of cadmium from aqueous solution by this bentonite was investigated as a function of conditions such as contact time, metal concentrations, pH, stirring speed, temperature, particle size, and amount of bentonite. The adsorption isotherm was studied with different models: the Freundlich and Dubinin–Radushkevich models had the highest correlation coefficients, 0.9922 and 0.9988, respectively. The corresponding Langmuir model indicates a maximum adsorption capacity of 13.50 mg/g. First-order, pseudo-second-order, and intra-particle diffusion equations were used to study the mechanism of adsorption; the experimental data fit well with pseudo-second-order kinetics. Thermodynamic parameters of adsorption were calculated at temperatures of 293, 303, 313, and 323 K, and indicated that the Cd adsorption was exothermic and spontaneous.

**Keywords** Adsorption · Kinetics · Thermodynamics · Isotherm

## Introduction

The presence of cadmium ions in industrial wastes affects human and aquatic lives (Godt et al. 2006; Lavelle 1995;

Sharma 1995). Hence, many processes for Cd removal have been studied (Bedoui et al. 2008; Jianru et al. 2007; Lodeiro et al. 2006; Namasivayam and Ranganathan 1995; Wu and Xiong 2003), and various types of bentonite have been used for the removal of metals and other pollutants (Babel and Kurniawan 2003; Koswojo et al. 2010; Li et al. 2011). The ability to absorb metals such as Cd, Zn, Fe, Hg, Cr, Cu, Mn, and Pb onto bentonite is well recognized (Chen et al. 2011; Inglezakis et al. 2007; Karapinar and Donat 2009; Vieira et al. 2010; Wang et al. 2011) and many studies have focused on optimum conditions, thermodynamics, isotherm models, and kinetics for removal of Cd using bentonite (Hamidpour et al. 2010; Huang et al. 2011; Purna et al. 2006; Zhao et al. 2011). The maximum removal of Cd onto raw and modified bentonite is summarized in Table 1, which shows that the best Cd adsorption belongs to a modified bentonite with an intercalation of 8-hydroxyquinolinium (Bentouami and Ouali 2006). However, the suitability of Iranian bentonite for Cd adsorption has not been characterized; this study was conducted to investigate its effectiveness and key factors involved in the adsorption process.

## Materials and Methods

A representative sample of bentonite from the Birjand area in southeastern Iran was used without any chemical pretreatment. The sample was ground and sieved by ASTM standard sieves to obtain the nominal particle size fractions of  $-600$  to  $+425$ ,  $-425$  to  $+300$ ,  $-300$  to  $+150$ , and  $-150$   $\mu\text{m}$  in diameter. X-ray diffraction (XRD) and X-ray fluorescence (XRF) were used to determine the mineralogy of the sample and its elemental analysis, respectively. XRD spectra and XRF were obtained using a Philips X-ray diffractometer

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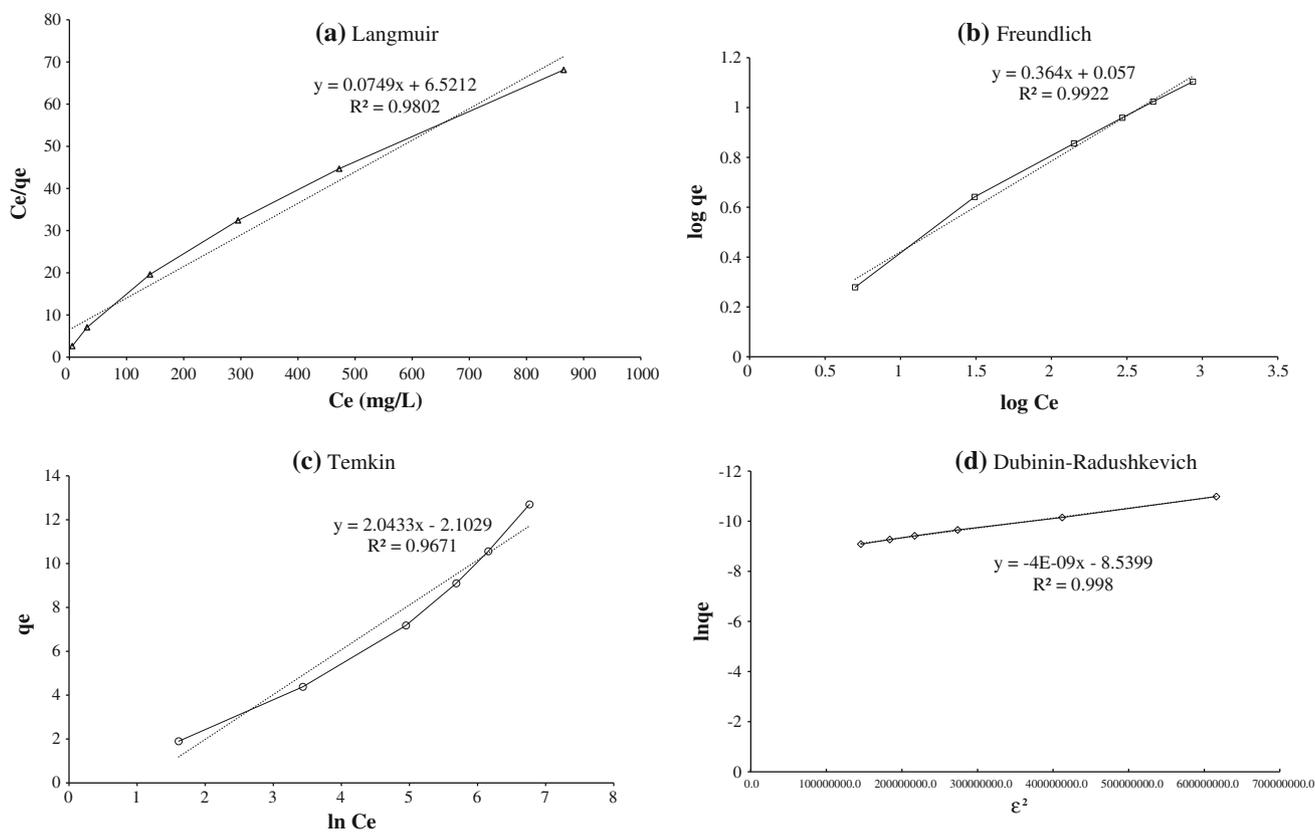
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**Table 1** Concise summary of the cadmium adsorption on bentonite

Adsorbent	$Q_m$ (mg/g)	Kind of investigation	References	About adsorbent
B–Na	29.40	Isotherm, kinetic and thermodynamic studies	Bentouami and Ouali (2006)	Bentonite was purified and modified by intercalation of 8-hydroxyquinolinium ion in Algeria
B–oxine	61.40	Isotherm, kinetic and thermodynamic studies	Bentouami and Ouali (2006)	Bentonite was purified and modified by intercalation of 8-hydroxyquinolinium ion in Algeria
HACC–bentonite	22.23	Optimum condition, isotherm, kinetic and thermodynamic studies	Huang et al. (2011)	Bentonite modified with N-2-hydroxypropyltrimethyl ammonium chloride chitosan (HACC) in China
GMZ bentonite	10.96	Optimum condition, isotherm and thermodynamic studies	Wang et al. (2011)	Bentonite from Gaomiaozi county, China (abbreviated as GMZ bentonite)
Organophilic-bentonite	2.80	Isotherm study	Andini et al. (2006)	In Italy
Natural bentonite	–	Isotherm study	Hamidpour et al. (2010)	Bentonite was obtained from Anarak and Firouzko mines in central and northern Iran
Bentonite	28.34	Optimum condition, isotherm, and kinetic studies	Purna et al. (2006)	In India
Bentonite	21.00	Optimum condition, isotherm, kinetic, and thermodynamic studies	In this study	Bentonite was obtained from east of Iran

**Fig. 1** a Langmuir isotherms, b Freundlich isotherms, c Temkin isotherm, and d Dubinin–Radushkevich isotherm for Cd(II) adsorption on bentonite: pH: 5.5, m/V: 50 g/L, T: 298 K, particle size:  $-150 \mu\text{m}$ , stirring speed: 500 rpm, contact time: 30 min

1140 ( $\alpha = 1.54 \text{ \AA}$ , 40 kV, 30 mA, calibrated with Si-standard) and a Philips X-ray diffractometer Xunique II (80 kV, 40 mA, calibrated with a Si-standard), respectively. The XRD of the sample is shown in Fig. 1, and the elemental analysis of the sample is shown in Table 1. This result indicated that the main mineral of the sample is montmorillonite. All chemical compounds were purchased from Merck and used without further purification.

Infrared spectra from 4,000 to 400  $\text{cm}^{-1}$  were recorded on a Shimadzu 470 FT-IR instrument, using KBr pellets. Fourier transform infrared (FTIR) spectroscopy has been used for chemical functional groups. The Cd concentration after adsorption was determined using a Unicam 939 atomic absorption (AA) spectrometer. The Cd adsorption was calculated by the amount of Cd in solution.

The Cd adsorption experiments were carried out using batch equilibrium. All of the adsorption experiments were conducted in a 250.0 mL glass reactor using a magnetic stirrer for mixing at ambient temperature. In this study, the influence of the parameters, such as mass of bentonite from 5.00 to 60.00 g/L, particle size from  $-150$  to  $-600 \mu\text{m}$ , initial Cd concentration from 50.0 to 2,000.0 ppm, contact time from 15 to 180 min, and stirring speed from 400 to 900 rpm were investigated, and the optimized conditions for maximizing Cd adsorption were determined. All other parameters were held constant for the investigation of each parameter in each test. The adsorption isotherms models of Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) were studied using 5 g of bentonite added to 100 mL of solution containing different concentrations of Cd, ranging from 50 to 2,000 ppm. All of the solutions were immediately filtered after each test.

For the kinetic investigation, 5 g of bentonite was mixed with 100 mL of Cd at various concentrations of 100.00, 250.00, 500.00, 750.00, 1,000.00, and 1,500.0 mg/L. Each batch test was conducted at various time intervals to determine the period required to reach the adsorption equilibrium and maximum removal of Cd. For the thermodynamic investigation, 5.00 g of bentonite was added to 100 mL of Cd solution at concentrations of 100.0 mg/L and the amount of removed Cd was determined at various temperatures (293, 303, 313, and 323 K). The amount of Cd adsorbed onto the bentonite was determined from the difference between the initial and remaining concentrations of Cd in solution after adsorption.

## Result and Discussion

### Characterization of the Bentonite

The mineralogical study indicated that quartz, oligoclase, gypsum, montmorillonite, and illite were the main

constituents of this sample (Supplementary Fig. 1; supplementary files appear with the on-line version of this paper). The diffraction peaks at  $8.9329^\circ$ ,  $19.8985^\circ$ , and  $26.6978^\circ$  ( $2\theta$ ) correspond to planes (001), (002), and (003), although plane (001) overlapped with the illite diffraction peak. The bentonite contains little illite; the main impurity in this sample was quartz, which is observed in the XRD pattern with the main diffraction peak at  $27.7311^\circ$  ( $2\theta$ ) (Caglar et al. 2009). The main mineral is montmorillonite; the presence of iron likely indicates that some adsorption has already taken place (Supplementary Table 1).

Infrared data are usually used to identify solid-state structures and functional groups of clays. Presence of two stretching bands at 3,627.54 and 3,432.54  $\text{cm}^{-1}$  indicate O–H bond linkage (Supplementary Fig. 2). The stretching band at 3,627  $\text{cm}^{-1}$  is due to the hydroxyl linkage of the bentonite structure and the broad band at 3,432  $\text{cm}^{-1}$  indicates the presence of water molecule in the structure, due to hydrogen bonding between hydrogen and oxygen of different water molecules (Wang et al. 2009). The bending vibration band of H–O–H in the water molecule of bentonite is observed at 1,635  $\text{cm}^{-1}$ . The strong and broad band at 1,040  $\text{cm}^{-1}$  can be attributed to Si–O of stretching vibration in the Si–O–Si functional group in tetrahedral sheets, for the montmorillonite structure (Wang et al. 2011). Two bending vibration bands at 467 and 519  $\text{cm}^{-1}$  represent Si–O–Al and Si–O–Si bonds, respectively. The vibration band at 693  $\text{cm}^{-1}$  and its small shoulder band (with a lower intensity, which is not assigned in Supplementary Fig. 2) can be related to the deformation and bending modes of the Si–O–Si bond. The presence of quartz in this sample is indicated by the FTIR shoulder bonding at 796–777  $\text{cm}^{-1}$  (Klinkenberg et al. 2006; Yang et al. 2010).

### Adsorption Characteristics

In order to study the effect of bentonite quantity on the removal of Cd from solution, experiments were conducted with weights of 5.00–60.00 g/L, with the same concentration (1,000.00 ppm  $\text{Cd}^{2+}$ ) at 25 °C, a stirring speed of 500 rpm, and a particle size of  $-150 \mu\text{m}$ . Supplementary Fig. 3 presents the results of Cd adsorption with different bentonite values. It is obvious that the adsorption percentage is a function of bentonite mass. The increase in adsorbent to liquid ratio caused the percentage of adsorption to increase, to a maximum value at 50.0 g/L of bentonite, as the amount of available sites for ion exchange increased with the increasing mass of bentonite (Abollino et al. 2003). The maximum value of Cd removed from solution for 1.00 g of bentonite was 160.00 mg, which is considerable compared with other reported values (Bentouami and Ouali 2006; Hamidpour et al. 2010; Purna et al.

2006; Zhao et al. 2011). The distribution coefficient constant is calculated by Eq. (1):

$$K_d = \frac{C_0 - C_{eq}}{C_0} \times V/m \quad (1)$$

where  $C_0$  (mg/L) is the initial Cd concentration,  $C_{eq}$  (mg/L) is the equilibrium Cd concentration in solution after adsorption,  $V$  (L) is the volume of the solution, and  $m$  (g) is the mass of bentonite. Supplementary Fig. 4 shows that the  $k_d$  value decreases with an increase in bentonite content from 5.00 to 60.00 g/L. Since the increase in mass of bentonite was done in a fixed volume, there was competition among available sites on the bentonite, which limited the activity of available sites; therefore, the distribution coefficient constant decreased with increased bentonite content (Chaari et al. 2008; Ding et al. 2009).

The effect of contact time on the adsorption of Cd(II) onto bentonite was investigated using a constant Cd concentration of 1,000 mg/L and a particle size of bentonite of  $-150 \mu\text{m}$ , at room temperature (Supplementary Fig. 5.) Different contact times from 15 to 180 min were studied for adsorption of Cd(II) onto bentonite. The adsorption efficiency improved from 33.0 to 53.0 % when contact time increased from 15 to 30 min. There was no significant difference on adsorption efficiency after 30 min of contact time. Therefore, a 30 min contact time was found to be appropriate for maximum adsorption and was used in all subsequent experiments. It seems that this phenomenon is controlled by the diffusion of Cd from the surface sites to the interlayer of the solid (Chaari et al. 2008). The fast adsorption of Cd(II) onto bentonite indicates that Cd(II) adsorption is mainly chemical adsorption. It seems that, Cd (II) ions quickly interact with negative permanent charge such as silanol ( $\text{Si-O}^-$ ) and aluminol ( $\text{Al-O}^-$ ) groups on edges of the bentonite surface (Xu et al. 2008).

#### Effect of Particle Size on Cadmium Adsorption

Particle size has an important effect on Cd adsorption; the finer the particle size, the greater the geometric surface area and the greater the degree of contact between Cd ions and the bentonite. Supplementary Table 2 shows that decreasing the bentonite particle size from  $-600$  to  $-150 \mu\text{m}$  increased adsorption of Cd ions. This can be attributed to increased contact with the surface of the bentonite particles. On the other hand, the number of active sites and effective collisions increased when bentonite particle size decreased. When particle size was in the range of  $-600$  to  $+450 \mu\text{m}$ , Cd adsorption was lowest, 30.1 %. It appears that an increase in bentonite particle size causes the effective interaction between Cd ions and bentonite particles to decrease. Therefore, a particle size of  $-150 \mu\text{m}$  was

selected for the adsorption experiments (Supplementary Table 2).

#### Effect of Stirring Speed on Cadmium Adsorption

Experiments were conducted to determine the effect of stirring speed using a solid to liquid ratio of 50.00 (g/L) at 25 °C. The Cd adsorption onto bentonite (Supplementary Fig. 6) peaked at a stirring speed of 500 rpm, at 53 %, and then decreased at a stirring speed of 600 rpm. Increasing the stirring speed over 600 rpm did not affect the uptake of Cd ions because there was an adequate suspension of solid particles in solution as well as an adequate distribution of Cd ions in solution.

#### Effect of Initial Cd(II) Concentration on Cd Removal

The adsorption of Cd onto bentonite was studied at different initial concentrations of Cd ranging from 50 to 2,000 mg/L at a ratio of mass of bentonite to liquid (m/V) of 50 g/L and a particle size of  $-150 \mu\text{m}$  (Supplementary Fig. 7). The Cd removal percentage decreased with increased initial Cd concentrations. This shows that Cd uptake was limited to active bentonite adsorption sites.

#### Effect of pH on Adsorption of Cd

The influence of pH was investigated at ambient temperatures and a solid to liquid ratio of 50.00 (g/L), over a pH range of 1.10–7.60. The pH was adjusted by adding 0.1 M HCl and 0.1 M  $\text{NH}_3$ . Previous researchers, such as Huang et al. (2011) and Zhao et al. (2011), observed a rapid increase in adsorption to pH 3 and then a moderate increase in adsorption to pH 7. Supplementary Fig. 8 shows that the adsorption percentage increased by more than 33 % from pH 1.10 to 2.70, while the adsorption of Cd(II) onto bentonite from pH 2.7 to 7.6 was approximately constant, increasing by only 7 %. The Cd ion in solution was Cd (II) and Cd was not precipitated as  $\text{Cd}(\text{OH})_2$ . Adsorption of Cd at a pH less than 2.7 is hindered because the  $\text{H}^+$  ions compete with Cd adsorption onto active bentonite sites. Increasing the pH increases the dissociation of functional groups such as  $\text{Si-OH}$  and  $\text{Al-OH}$ , which enhanced Cd absorption.

#### Adsorption Isotherm Models

The adsorption capacity, surface properties, mechanism of adsorption and affinity of the adsorbents were investigated using the equilibrium concentration of dissolved adsorbate (Cd ions), amount of bentonite, and adsorbate on bentonite. In this study, four different isotherm models (for multilayer and monolayer adsorption surfaces) were examined.

**Table 2** Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm constants for cadmium adsorption

Model	Parameter	Bentonite
Langmuir	$q_m$ (mg/g)	13.35
	$R^2$	0.980
	$R_L$	0.46–0.05
	$b$	0.011
	SD	0.670
Freundlich	$K_F$ ( $\text{mg}^{1-1/n} \text{L}^{1/n}/\text{g}$ )	1.140
	$n$ (g/L)	2.75
	$R^2$	0.992
	SD	0.061
	Temkin	$b$ (J/mol)
	$A$ (L/mg)	0.36
	$R^2$	0.967
	SD	0.188
Dubinin–Radushkevich	$q_m$ (mg/g)	21.90
	$\beta$ ( $\text{mol}^2/\text{kJ}^2$ )	0.004
	$E$ (kJ/mol)	11.18
	$R^2$	0.998
	SD	0.003

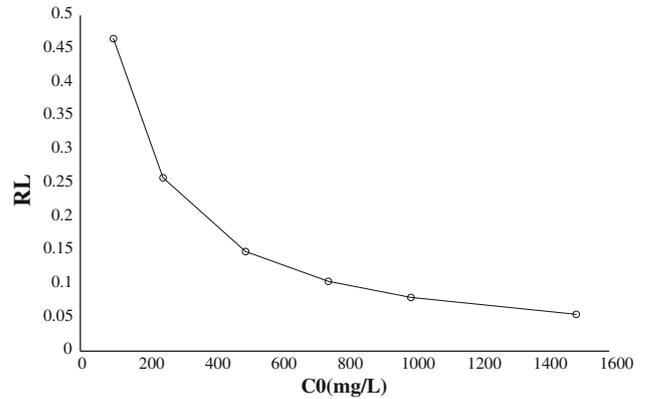
*Langmuir Isotherm*

The linear form of the Langmuir isotherm model assumes that adsorption occurs onto a homogeneous (uniform) surface with a finite number of adsorption sites, and a monolayer adsorption process. The model assumes that the adsorptive molecules interact with active sites on the bentonite surface that have identical energy. The Langmuir isotherm model is represented by Eq. (2):

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \tag{2}$$

where  $q_e$  (mg/g) is the amount of Cd adsorbed per unit weight of bentonite and  $C_e$  (mg/L) is the Cd concentration in solution at equilibrium (after adsorption). The  $b$  is the Langmuir isotherm constant that indicates the free energy of adsorption;  $b$  is related to the binding energy of the active bentonite site.  $Q_0$  is the maximum monolayer adsorptive capacity (Chingombe et al. 2006; Foo and Hameed 2010; Tan and Xiao 2009). Figure 1a shows the linear Langmuir plot with a correlation coefficient ( $R^2$ ) of 0.980; the values of the Langmuir constants  $b$  and  $Q_0$  (mg/g) are listed in Table 2. This data shows that the maximum adsorptive capacity (13.350 mg/g) of the unmodified Iranian bentonite (from the Birjand area) is considerable according to the Langmuir model.

The Langmuir isotherm model can be displayed in terms of a dimensionless constant that is called the range of



**Fig. 2** Plot of separation factor versus initial cadmium concentration

separation factor  $R_L$ ; it is also called the equilibrium parameter (Crini et al. 2007; Ofomaja and Ho 2007; Özacar and Şengil 2004b).

$$R_L = \frac{1}{1 + bC_0} \tag{3}$$

where  $C_0$  (mg/L) is the initial Cd concentration and  $a_L$  (L/mg) is the Langmuir constant related to the energy of adsorption. Figure 2 shows the plots of separation factor ( $R_L$ ) versus the initial Cd concentration of solution ( $C_0$ ). If  $R_L > 1$ ,  $R_L = 0$ ,  $R_L = 1$ , and  $0 < R_L < 1$ , the adsorption will be unfavorable; irreversible and linear, and; favorable, respectively. The  $R_L$  of the Birjand bentonite is 0.05–0.46 for initial concentrations of Cd between 100.00 and 1,500.00 ppm. This data indicates that Cd adsorption onto bentonite in different Cd concentrations (especially in high initial Cd concentration) is favorable and reversible because  $0 < R_L < 1$ .

In addition to the correlation coefficient ( $r^2$ ), the standard deviation (SD) is used to evaluate the adsorption data set to confirm the best fit isotherm model for the system (Bulut et al. 2008a):

$$SD = \sqrt{\frac{\sum [(q_{t,exp} - q_{t,cal})/q_{t,exp}]^2}{(n - 1)}} \tag{4}$$

This equation shows that the SD of the adsorption process is equal to the sum of the squares of the differences between the experimental adsorption data ( $q_{t,exp}$ ) and the data obtained from the adsorption models ( $q_{t,cal}$ ), with each squared difference divided by the corresponding data obtained from the models. In this equation,  $n$  is the number of data points. If the obtained data from this model is similar to the experimental data, the SD will be a small number, but if the SD approaches 1, it will be a large number and means that the data for the model differs from the experimental data.

### Freundlich Isotherm

The Freundlich isotherm model describes processes of non-ideal adsorption, multilayer adsorption, and adsorption on heterogeneous surfaces, and assumes that the adsorption process is reversible. Equation (5) represents the Freundlich isotherm model (Crini et al. 2007).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where  $K_F$  ( $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$ ) and  $n$  ( $\text{g/L}$ ) are Freundlich constants that represent the adsorption capacity of the bentonite and the adsorption intensity (or surface heterogeneity) of the adsorbent, respectively. If  $1 < n < 10$ , the adsorption process is favored. This equation indicates that stronger binding sites are occupied at the beginning of the adsorption process; the decrease in adsorption energy is observed as an exponential reduction (Foo and Hameed 2010; Ofomaja and Ho 2007).

Figure 1b shows the linear Freundlich plot with an  $r^2$  of 0.992; the values of the Freundlich constants  $K_F$ ,  $n$ ,  $Q_0$  ( $\text{mg/g}$ ), and correlation coefficient are listed in Table 2. The slope of the plot of  $\log q$  versus  $\log C_e$  gives the Freundlich isotherm parameter,  $1/n$  ( $\text{L/g}$ ). This coefficient value indicates the adsorption intensity of Cd ions on the clay. The slope of linear plots in Fig. 1b shows that  $n$  for raw bentonite is 2.75, which indicates that heterogeneous adsorption dominated in this experiment.

### Temkin Isotherm

The obtained adsorption data was investigated for the Temkin isotherm model. The linear form of the Temkin isotherm (Mall et al. 2005; Özacar and Şengil 2005) is represented as Eq. (6):

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \quad (6)$$

where  $b$  and  $A$  are Temkin isotherm constants;  $b$  is a constant that is related to the heat of adsorption ( $\text{J/mol}$ );  $R$  is the gas constant ( $8.314 \text{ J/mol K}$ ); and  $T$  is the absolute temperature. The  $q_e$  ( $\text{mg/g}$ ) is the equilibrium concentration of Cd adsorbed onto the bentonite. Equation (6) shows that the amount of adsorption in the layer is related to the logarithm of equilibrium concentration of adsorbate in solution and that  $A$  and  $b$  are determined from the intercept and slope of the linear plots of  $q_e$  versus  $\ln C_e$ . In this model, the binding energies of adsorbent–adsorbate interactions are assumed to be uniformly distributed, which causes a linear decrease in the heat of adsorption. On the other hand, the Temkin model has modified the Langmuir model by considering the effect of temperature in the adsorption processes (Mall et al. 2005; Özacar and Şengil 2005).

### Dubinin–Radushkevich (D–R) Isotherm

The Dubinin–Radushkevich model isotherm was presented in 1947 and assumes homogenous surface adsorption (Hobson 1969). This model can be distinguished between physical and chemical adsorption of metal ions. The model is presented by Eq. (7):

$$\ln q = \ln q_{\max} - \beta R^2 T^2 \ln^2(1 + 1/C) \quad (7)$$

where  $R$  is the gas constant ( $8.314 \text{ J/mol K}$ ),  $T$  is the absolute temperature,  $q_m$  is the maximum capacity of adsorption ( $\text{mg/g}$ ), and  $\beta$  is a constant related to adsorption energy ( $\text{mol}^2/\text{kJ}^2$ ). Equation (8) can be used to calculate  $E$ , the free energy per molecule of adsorbate (Bulut et al. 2008a).

$$E = \frac{1}{\sqrt{2\beta}} \quad (8)$$

If the adsorption energy,  $E_a < 8 \text{ kJ/mol}$ , physical adsorption dominates; chemical adsorption or ion exchange are most important if the adsorption energy is  $8 < E_a < 16 \text{ kJ/mol}$ , and; for  $E_a$  values  $> 16 \text{ kJ/mol}$ , particle diffusion governs the reaction (Bulut et al. 2008b; Özcan et al. 2006).

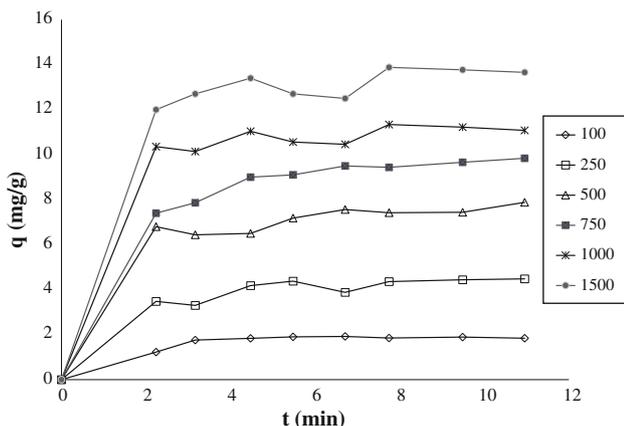
Linear plots of  $\ln q_e$  versus  $\ln^2(1 + c^{-1})$ , with a  $r^2$  of 0.998 are observed in Fig. 1d. The parameters  $q_m$  and  $B$  are calculated from the intercepts and slopes respectively. The adsorption free energy ( $E$ ) is  $11.18 \text{ kJ}$  (Table 2), which means that adsorption of Cd by bentonite is a chemical adsorption or ion exchange process.

### Evaluation of Adsorption Isotherm Models of Cd onto Bentonite

As seen from Table 2 and Fig. 1, the highest  $r^2$  value and the lowest SD value are associated with the D–R model, with the Freundlich model having the next highest value of  $r^2$ , so these (Freundlich and D–R models) fit the data better than the Langmuir and Temkin models. The fit of the experimental data with the D–R model shows that Cd was adsorbed onto the bentonite surface by chemical processes. However, the fact that heterogeneous (multilayer surface) Cd adsorption was dominant (Fig. 1b) indicates that the data is best described by a Freundlich isotherm model.

### Adsorption Kinetics of Cd Ions onto Iranian Bentonite

Adsorption kinetics of Cd onto bentonite has been investigated by studying the effect of contact time and initial Cd concentration on adsorption of the Cd ion. Figure 2 shows that the amount of Cd adsorbed increased with increased contact time and reached equilibrium after 60 min. Figure 3 indicates that increasing the initial Cd concentration



**Fig. 3** Adsorption kinetics of Cd on bentonite at different initial Cd concentration; conditions: particle size:  $-150\ \mu\text{m}$ , speed stirrer: 500 rpm, temperature: 298 K, pH: 5.4

caused the amount of Cd absorption to increase sharply. At higher concentrations of Cd(II), the adsorption of Cd reached equilibrium more quickly than did lower concentrations of Cd(II). It is obvious that the physical and chemical characteristics of the bentonite greatly affected the adsorption (Bektaş et al. 2004).

In order to find effective processes regarding Cd adsorption onto bentonite, three kinetic equations, pseudo-first-order, pseudo-second-order, and intra-particle diffusion models were examined.

*Pseudo-first Order Equation*

The pseudo-first-order equation (Crini et al. 2007; Yuh-Shan 2004) is presented as:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \tag{9}$$

where  $q_t$  and  $q_e$  are the amounts of Cd adsorbed after  $t$  units of time and time of reach to equilibrium (mg/g), respectively, and  $k_1$  is the pseudo-first order rate constant for the adsorption process (1/min). After integration and applying boundary conditions values of  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = t$ , the integrated form of Eq. (9) becomes:

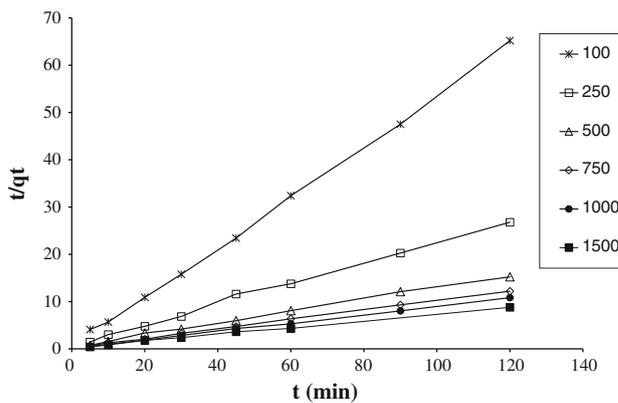
$$\ln\left(\frac{q_e}{q_e - q_t}\right) = K_1 t \tag{10}$$

Equation (10) can be rearranged to obtain a linear form:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{11}$$

*Pseudo-second-Order Equation*

The pseudo-second-order chemisorption kinetic rate equation (Ho and McKay 1999; Özacar 2003; Özacar and Şengil 2004a) is expressed as:



**Fig. 4** Pseudo-second order rate expression for the adsorption of cadmium by 5 g of bentonite at various initial Cd concentrations; conditions: particle size:  $-150\ \mu\text{m}$ , speed stirrer: 500 rpm, temperature: 298 K, pH: 5.4

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{12}$$

where  $k_2$  is the equilibrium rate constant of the pseudo-second-order equation (g/mg min). Integrating Eq. (12) for the boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$  gives:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + K_2 t \tag{13}$$

Equation (13) can be rearranged to obtain the following linear form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{14}$$

Figure 4 shows the linear plots of  $t/q_e$  versus  $q_e$  at different initial Cd concentrations.

*Intra-particle Diffusion Equation*

The intra-particle diffusion equation (Özacar 2003; Özacar and Şengil 2005) is presented as:

$$q_t = K_i t^{1/2} \tag{15}$$

where  $K_i$  is the intra-particle diffusion rate constant (mg/g min<sup>1/2</sup>).

*Evaluation of Adsorption Kinetic Model of Cd onto Bentonite*

The values of the different parameters of each model were calculated from the linear equations (Table 3). With respect to the  $r^2$  values ( $>0.997$ ) describing the experimental results at different initial Cd concentrations, the pseudo second-order adsorption mechanism dominated in these experiments (Fig. 4). In other words, the  $r^2$  and SD

**Table 3** Kinetic parameters for the adsorption of cadmium onto bentonite

C <sub>0</sub> (mg/L)	q(exp) (mg/g)	First-order kinetic eq.				Second-order kinetic eq.				Intraparticle diffusion eq.		
		q <sub>1</sub> (mg/g)	k <sub>1</sub> (1/min)	r <sub>1</sub> <sup>2</sup>	SD	q <sub>2</sub> (mg/g)	k <sub>2</sub> (g/mg min)	r <sub>2</sub> <sup>2</sup>	SD	k <sub>int</sub> (mg/g min <sup>1/2</sup> )	r <sup>2</sup>	SD
100.00	1.93	1.41	0.099	0.9518	0.642	1.88	0.952	0.9989	0.105	0.047	0.9443	0.009
250.00	4.49	1.19	0.038	0.9641	0.364	4.56	0.074	0.9973	0.096	0.105	0.7330	0.053
500.00	7.89	2.97	0.045	0.9381	0.675	7.94	0.038	0.9974	0.166	0.137	0.8074	0.031
750.00	9.85	3.39	0.047	0.9709	0.396	9.94	0.049	0.9995	0.041	0.277	0.9072	0.035
1,000.00	18.13	7.98	0.001	0.9207	0.006	11.22	0.089	0.9996	0.051	0.099	0.8983	0.012
1,500.00	15.61	3.36	0.005	0.9774	0.032	13.93	0.028	0.9973	0.157	0.155	0.9379	0.013

were better for the pseudo-second-order equation than the fit for the pseudo-first-order and intra-particle diffusion models. The k (the rate constant), declined from 0.017 to 0.003 g/mg min when the Cd(II) initial concentration increased from 100.0 to 1,500.0 mg/L (Table 3). The rate-controlling step was chemisorption interaction. This means that both the concentration of adsorbate (Cd ions) and the number of active bentonite sites affected the adsorption mechanism and the rate of adsorption.

**Thermodynamic Study**

Thermodynamics of Cd adsorption onto bentonite was studied at various concentrations from 100 to 1,000 mg/L of Cd at 293, 333, 343, and 353 K. Thermodynamic parameters can be explained by these equations:

$$q_e m = V(C_0 - C_e) \tag{16}$$

$$K_d = q_e / C_e \tag{17}$$

where q<sub>e</sub> is the equilibrium adsorption capacity of Cd (mg/g), C<sub>0</sub> is the initial Cd concentration (mg/L), C<sub>e</sub> the equilibrium Cd concentration in solution after Cd absorbed by bentonite (mg/L), m the mass of bentonite used (g) and V is the volume of solution (L). The K<sub>d</sub> values are used in following equation to determine the Gibbs free energy of sorption process at different temperatures.

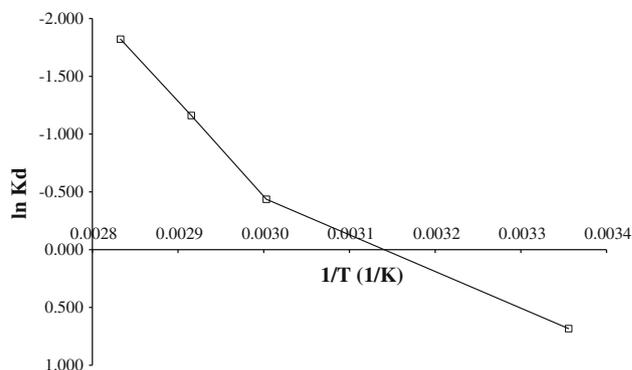
$$\Delta G^\circ = -RT \ln K_d \tag{18}$$

ΔG° is the free energy of Cd adsorption (kJ/mol), R is the universal gas constant (8.314 J/mol K), and T is the temperature (K) of solution during adsorption process. The adsorption distribution coefficient may be expressed in terms of enthalpy change (ΔH°) and entropy change (ΔS°) as a function of temperature:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{19}$$

ΔH° is the heat of adsorption (kJ/mol) and ΔS° is the standard entropy change of adsorption (kJ/mol) (Ho 2003; Ho et al. 2002; Smith and Van Ness 1987).

According to Eq. (19), the linear plot of lnK<sub>d</sub> versus 1/T has an r<sup>2</sup> value of 0.9393. The ΔH° and ΔS° parameters of adsorption can be calculated from the slope and intercept of the plot of lnK<sub>d</sub> versus 1/T, respectively (Fig. 5; Table 4). The values of ΔH° and ΔS° are −37.57 and −119.4 J/mol K, respectively. The negative value of ΔH° indicates that the adsorption reaction is exothermic; this means that with increasing temperature, adsorption of Cd onto bentonite decreases. The negative value of entropy changes is logical because the adsorption process causes the numbers of ions in the solution to decrease. These enthalpy changes (ΔH°) and entropy changes (ΔS°) are considerable when compared with other reports of Cd adsorption onto bentonite (Huang et al. 2011; Zhao et al. 2011).



**Fig. 5** Plot of ln K<sub>d</sub> versus 1/temperature to determine enthalpy and entropy of the adsorption reaction

**Table 4** Thermodynamic parameters for the adsorption of cadmium onto bentonite

r <sup>2</sup>	ΔH° (kJ/mol)	ΔS° (J/mol(K))	ΔG° (kJ/mol)
			293 K 303 K 313 K
0.939	−37.57	−119.4	−2.585 −1.391 −0.197

Negative  $\Delta G^\circ$  values at different temperatures indicate that the adsorption process is spontaneous. Table 4 shows that  $\Delta G^\circ$  values decreased from  $-2.585$  kJ/mol at  $293^\circ\text{K}$  to  $-0.197$  kJ/mol at  $313^\circ\text{K}$ , which indicates that temperature increases can cause the adsorption process to spontaneously decrease.

## Conclusions

The optimum conditions for achieving maximum Cd adsorption on bentonite at room temperature with initial Cd concentrations of 1,000.0 ppm were a pH of 3.1, a particle size  $\leq 150$   $\mu\text{m}$ , a solid to liquid ratio of 50.0 g/L, a contact time of 30 min, and a stirrer speed of 500 rpm. The adsorption data obtained for an unmodified Iranian bentonite were best described by a Freundlich isotherm model, since heterogeneous (multilayer surface) Cd adsorption or ion exchange processes was dominant. The maximum adsorption capacity corresponding to the Langmuir model was 13.50 mg/g.

Given the  $r^2$  values ( $>0.997$ ) and suitable SD for the linear plots, the kinetic study demonstrated that the experimental data fit the pseudo-second-order kinetics well. The rate-controlling step is chemisorption interaction. This means that both adsorbate (Cd ions) concentration and the number of active bentonite sites affected the adsorption mechanism and the rate of adsorption.

The thermodynamic parameters of adsorption were determined at temperatures of 293, 303, 313, and 323 K: enthalpy  $\Delta H^\circ$  ( $-37.57$  kJ/mol) and entropy  $\Delta S^\circ$  ( $-119.4$  J/mol K). The negative  $\Delta H^\circ$  value indicated that the adsorption reaction was exothermic. Negative  $\Delta G^\circ$  values at different temperatures indicate that the adsorption process is spontaneous.

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