



Comparative study effects of calcinations, electrolytes, and Fe-bentonite, CaCO₃-bentonite on the removal of Cd(II) ions from aqueous solution

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Received 18 August 2014; Accepted 23 April 2015

ABSTRACT

This study presents the influence of different variables on Cd(II) adsorption in Iranian bentonite namely two different types of electrolytes (carbonate and chloride salts), calcination temperature, loading of Fe(III)–Fe(II) (synthesized Fe-bentonite) and CaCO₃ on bentonite. According to the experimental data, Na₂CO₃ is the best modifier electrolyte in comparison with other carbonate salts and chloride salts. The maximum removal (100%) of 1,000 ppm Cd(II) from aqueous solution was achieved in presence of 0.1 M of Na₂CO₃ and 5 g bentonite. Furthermore, Iranian bentonite was modified by CaCO₃ and Fe(III)/Fe(II) salts to have synthesized CaCO₃-bentonite and Fe-bentonite. For the equilibrium study of Cd(II) adsorption onto these compounds, the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) models have been examined. The Langmuir and Freundlich models explained the highest correlation coefficients for Fe-bentonite and CaCO₃-bentonite, respectively. According to the Langmuir (for Fe-bentonite) and Freundlich (for CaCO₃-bentonite) models, the maximum adsorption capacity were 32.39 mg/g and 1.97 mg^{1-1/n} L^{1/n} g⁻¹, respectively. The calculated results of DR models showed that Cd(II) adsorption onto modified bentonite is chemical adsorption or ion exchange interaction. The obtained thermodynamic parameters of Cd(II) adsorption indicated that Cd(II) adsorption onto modified one was spontaneous and Cd(II) adsorptions onto Fe-bentonite and CaCO₃-bentonite were exothermic and endothermic, respectively.

Keywords: Cadmium; Adsorption; Fe-bentonite; CaCO₃-bentonite; Equilibrium study; Thermodynamic

1. Introduction

One of the most hazardous heavy metals is cadmium. This metal is seriously polluting soil and water. The environmental protection agency states that the standard of maximum effluent discharge is 5 µg/L. These harmful effects that occur even by little concen-

tration of Cd(II) include kidney damage, bone lesions, renal damage, emphysema, diarrhea, stomach pain, sever vomiting, hypertension, lung insufficiency, protein metabolism disruption, damage of central nervous and immunity system, red blood cells reduction, and yellow coloration of teeth (Cd(II) ring formation) [1,2]. So the removal of Cd(II) ions from aqueous solutions which is attracting a great deal of attention and has

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been studied by various researchers, is essential and unavoidable. Among various methods that have been used for removing cadmium from aqueous solution [3], adsorption is one of the most efficient method which is simple, inexpensive, and easy to operate. Accordingly, adsorption of Cd(II) onto lots of different chemical and physical adsorbents such as active carbons [4], resin [5,6] and bio-sorbent [7] have already been studied. Oxide metals are an effective material to adsorb Cd(II), although they are not a low cost and easily handled adsorbents, therefore many studies have been doing to find a natural superseded adsorbents for the synthesized adsorbents which have high efficiency, low cost, and high availability. So far many researchers have been reported that natural mineral adsorbent such as waste Fe(III)/Cr(III) hydroxide [8], red mud and fly ash [9], refuse concrete, andesite, limestone, granite, nitrolite [10], zeolite and bentonite [11] have been recognized as a most useful adsorbent for Cd(II) due to attributes like high specific surface areas, high cation exchange capacities, and low cost [12,13]. Montmorillonite related to Smectitic clay minerals is the major constituent of bentonite. It has layer structure with the basic structural units of each unit being one octahedral coordinated layer of aluminum that is sandwiched between two tetrahedral coordinated layers of silicon. The electrostatic interaction between these layers is a weak Van Der Waals force which causes intercalate process to become more readily available. Net negative surface charge on the bentonite is due to the defect of crystal frame work that is originated from the substitution of aluminum ion for silicon ion and magnesium or iron ions for aluminum in the tetrahedral sheets and octahedral sheets, respectively [14]. Despite these properties of bentonite, the results of Cd(II) adsorption experimental data show that raw bentonite does not possess high efficiency for Cd(II) adsorption, and the maximum adsorption capacity of Cd(II) for raw bentonite from different areas of world is almost less than 30 mg/g. Therefore, different methods to modification of bentonite with several compounds have been considered to improve the adsorption capacity of bentonite. These methods include the chemical modification of the surface by using organic compounds as N-2-hydroxypropyl trimethyl ammonium chloride chitosan (HACC) [15], and hydroxy-8 quinoleine [12], Fe-montmorillonite [16], and surface chemical modification can be performed by using inorganic complex eses hydroxyl aluminum and hydroxyl aluminosilicate [17]. Table 1 shows the amount of Cd(II) adsorption onto different modified bentonite and clay adsorbents. The best modifier of bentonite to adsorb cadmium is related to organic compounds especially hydroxy-8

quinoleine compound that enhanced the adsorption capacity to more than 61 mg/g. After these compounds, iron salts are the best modifier to adsorb Cd(II) ions. Of course chemical and physical properties of bentonite are the effective parameters on the evaluation of modifiers.

This study tried to enhance the amount of cadmium adsorption by natural adsorbent and modified bentonite by investigating the different electrolytes effect, calcinations and to synthesize bentonite by CaCO₃ and Fe(III)/Fe(II) salts. In addition, Poly-hydroxy ferric and ferrous have been intercalated in layer of bentonite. The objective of this study is to investigate the isotherm and thermodynamic parameters of two kinds of modified bentonite for adsorption of Cd(II).

2. Materials and methods

2.1. Materials

Representative sample of bentonite was obtained from the Birjand area in southeastern of Iran which was ground and sieved by ASTM standard sieves to obtain the nominal particle size of $\sim 150 \mu\text{m}$ in diameter. The effect of electrolyte on this adsorption was investigated with different amount of carbonate and chloride such as CaCl, KCl, NH₄Cl, NaCl, CaCO₃, K₂CO₃, (NH₄)₂CO₃, and Na₂CO₃. To prepare modified bentonite, 0.1 mol/L of CaCO₃, FeCl₃, and FeSO₄ were used. All chemical compounds were purchased from Merck Company and used without further purification.

2.2. Instruments

X-ray diffraction (XRD) was used to determine the mineralogy of the sample and its elemental analysis. XRD spectra was obtained by using a Philips X-ray diffractometer 1,140 ($\alpha = 1.54 \text{ \AA}$, 40 kV, 30 mA, calibrated with Si-standard). Infrared spectra from 4,000 to 400 cm⁻¹ were recorded on a Shimadzu 470 FT-IR instrument by using KBr pellets. Fourier transform infrared (FTIR) spectroscopy has been used for chemical functional groups. The concentration of Cd(II) solution after adsorption was determined by means of atomic absorption spectrometry of Unicomp 939. The Cd(II) adsorption was calculated with respect to the amount of Cd(II) in the solution. The adsorption percent (%) was calculated by using Eq. (1).

$$\text{Adsorption \%} = \frac{C_0 - C_{\text{eq}}}{C_0} \times 100 \quad (1)$$

Table 1
Summary of the Cd(II) adsorption on modified bentonite and clay adsorbents

Adsorbent	Experimental conditions	Adsorption capacity (mg/g)	Ref.
<i>Bentonite modified by 8-hydroxyquinolinium ion</i>			
Bentonite oxine complex (B-oxine)	C_0 : 4–100 mg/L, t : 60 min,	61.35	[12]
Sodic bentonite (B-Na)	Solid/solution: 1 g/L (B-Na) Solid/solution: 0.5 g/L (B-oxine)	29.41	
<i>Bentonite modified with N-2-hydroxypropyl trimethyl ammonium chloride chitosan</i>			
HACC-Bentonite	T : 20°C, pH 7, t : 40 min, m : 0.5 g, C_0 : 55–330 mg/L	22.23	[15]
Fe-montmorillonite	T : 25°C, pH 5, m : 0.2 g, t : 5 min, C_0 : 20–200 mg/L	25.7	[16]
<i>Bentonite clay modified with binary mixture of goethite and humic acid</i>			
Bentonite-goethite	T : 28°C, pH 6, m : 0.2 g, t : 8 h, C_0 : 50–700 mg/L	9.56	[33]
Bentonite-humic ACID		9.9	
Bentonite-goethite/humic acid		10.09	
Na-montmorillonite (Na ⁺ -Mt)	T : 25°C, pH 6.5, t : 8 h, C_0 : 11.2–224 mg/L	0.014	[34]
Al ₁₃ -pillared (Al ₁₃ -PMt)		0.016	
Al ₁₃ -pillared acid-activated(Al ₁₃ -PAAMt)		0.018	
Fe pillared bentonite (Fe-PB)	m : 2 g, C_0 : 0.178–5.34 mmol/dm ³ , t : 5–300 min, pH 3–9	86.893	[24]
Fe/Cr pillared bentonite (Fe/Cr0.5-PB)		71.155	
Cr pillared bentonite (Cr-PB)		47.549	
Fe-bentonite	pH 5.6, m/V : 50 g/L, T : 298 K, t : 30 min	32.39	In this study
CaCO ₃ -bentonite		11.22	

where C_0 is the initial concentration of Cd(II) and C_{eq} is the equilibration concentration of Cd (II) after analysis.

2.3. Effect of the modification agent

To achieve enhanced adsorption amount of cadmium by bentonite, these three methods have been used to modified bentonite

- (1) Carbonate salts and chloride salts electrolytes.
- (2) Modified bentonite by CaCO₃ and Fe(II)–Fe(III) salts.
- (3) Calcinations process.

2.3.1. Effect of electrolytes on adsorption of cadmium

In order to investigate the effect of electrolytes (chloride and carbonate solutions) on Cd(II) adsorption, 5 g bentonite was added to 100 mL of carbonate solution (0.004 mol/L) and chloride ion (0.1 mol/L)

along with other compounds (CaCO₃, K₂CO₃, (NH₄)₂CO₃, Na₂CO₃, CaCl, KCl, NH₄Cl, and NaCl). Cadmium adsorption experiments were carried out with prepared new adsorbent by using batch equilibrium. All of the adsorption experiments were conducted in a 250 mL glass reactor using a magnetic stirrer for mixing 5 g of certain adsorbent, 1,000 ppm Cd(II) initial concentration for 30 min at ambient temperature.

2.3.2. Modified bentonite with CaCO₃ and Fe(II)–Fe(III) salts

- (1) Preparation of bentonite modified by CaCO₃

Five grams of bentonite were suspended in 100 mL of CaCO₃ solution (0.1 mol/L) for overnight at room temperature then solid phase was separated and dried at room temperature for 24 h and was crushed and sieved to 150 μm in diameter.

(2) Preparation of bentonite modified by Fe(II)–Fe(III) salts

Six grams of bentonite were suspended in 80 mL of solution which mixed with Fe(III) 0.01 mol/L (0.162 g FeCl₃) and Fe(II) 0.005 mol/L (0.140 g FeSO₄) then 20 mL of NaOH solution (0.25 mol/L) was poured in the solution slowly. This obtained suspension was stirred at room temperature in 500 rpm for 30 min, then solid phase was separated by filter paper. After that the precipitation on the paper filter was dried in an oven at 343 K for 3 h and then ground to obtain a particle size 150 μm in diameter (200 mesh).

2.3.3. Effect of calcination temperature on cadmium adsorption

In order to investigate the effect of calcination temperature on Cd(II) adsorption onto bentonite. The bentonite was warmed in the range of 373–873 K in the oven for 1 h. Then Cd(II) adsorption onto raw bentonite and modified bentonite in the presence and absence of electrolyte experiments were carried out in a 250 mL glass reactor which contains 5 g of adsorbent and 100 mL of 1,000 ppm Cd(II) initial concentration for 30 min at ambient temperature.

2.4. Equilibrium studies

The relations between adsorbent and adsorbate in equilibrium state were characterized by isotherm models. Isotherm models have an important role in identifying an adsorption process and designing of adsorption system. To achieve this goal, 5 g of modified bentonite was suspended in 100 mL of cadmium solution at various initial concentrations from 100 to 1,500 ppm for 30 min at room temperature. Four different isotherm models (Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) models) were analyzed by the adsorption equilibrium data of cadmium onto bentonite. The equations of these models were represented in Table 2. The models were fitted by linear form of equations and their parameters were calculated by linear regression. In addition to correlation coefficient (r^2), standard deviation (SD) was used to evaluate the data of adsorption set to confirm the best fit of isotherm model according to Eq. (2):

$$SD = \sqrt{\frac{\sum [(q_{e,\text{exp}} - q_{e,\text{cal}})/q_{e,\text{exp}}]^2}{(n - 1)}} \quad (2)$$

where $q_{e,\text{exp}}$ is the experimental data of adsorption, $q_{e,\text{cal}}$ is the data obtained by calculation from adsorption models and number of experimental data. If the obtained data from this model are similar to the experimental data, SD will be a small number and data approach to zero but if SD value tends to 1, obtained data are not favorable.

2.5. Thermodynamic studies

Thermodynamic parameters could be explained with Eqs. (3) and (4):

$$q_e m = v(C_0 - C_e) \quad (3)$$

$$K_d = \frac{q_e}{C_e} \quad (4)$$

where q_e is the equilibrium capacity of Cd(II) on bentonite (mg/g of bentonite), C_0 is the Cd(II) initial concentration (mg/L), C_e is the equilibrium Cd(II) concentration in solution after absorption (mg/L), m is the mass of used bentonite (g), and V is the volume of solution (L). The K_d values were used in Eq. (5) to determine the Gibbs free energy of sorption process at different temperatures.

$$\Delta G^\circ = -RT \ln K_d \quad (5)$$

ΔG° is the free energy of Cd(II) adsorption (kJ/mol), R is the universal gas constant (8.314 J/mol K), and T is temperature (K) of solution during the adsorption process. The adsorption distribution coefficient may be expressed in terms of enthalpy change (ΔH°) and entropy change (ΔS°) as a function of temperature (Eq. (6)).

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

ΔH° is the heat of adsorption (kJ/mol) and ΔS° is the standard entropy change in adsorption (kJ/mol) [18].

According to Eqs. (3)–(6), the parameters of thermodynamics of Cd(II) adsorption onto Fe-bentonite and CaCO₃-bentonite adsorbent were determined when 5 g of modified bentonite was added to 100 mL of Cd(II) solution at concentrations of 100 mg/L at pH 3. These were agitated for 30 min. The above procedure was carried out at 298, 303, and 313 K. These samples were subsequently filtered and the amount of Cd(II) adsorbed onto modified bentonite

was determined from the difference between the initial and remaining concentrations of Cd(II) solution after adsorption process.

3. Result and dissection

Investigating and understanding of the adsorption process onto bentonite are necessary for effective utilization of this mineral as commercial natural adsorbents for controlling the release of Cd(II). This study reports the modification of bentonite by inorganic compounds, its characterization, optimum equilibrium, and thermodynamic studies.

3.1. Effect of calcination temperature on cadmium adsorption

Cd(II) adsorption onto bentonite has been investigated as a function of the calcination temperature in the range of 373–873 K. As shown in Fig. 1, the percentage of cadmium removal is almost constant in the calcination of bentonite process by increasing calcination temperature from 73 to 573 K but from 573 to 673 K cadmium removal percentage increases to 48% which is related to loss of interlayer water that provides space Cd(II) ions adsorption. After calcination temperature 673 K remove of Cd(II) ions are decreased. This occurrence could be related to the movement of octahedral cations by increasing the temperature [19] which indicates the distortion of bentonite structure and a defective montmorillonite structure. On the other hand, high temperature (more than 673 K) could distort structure and decrease the specific surface area [20].

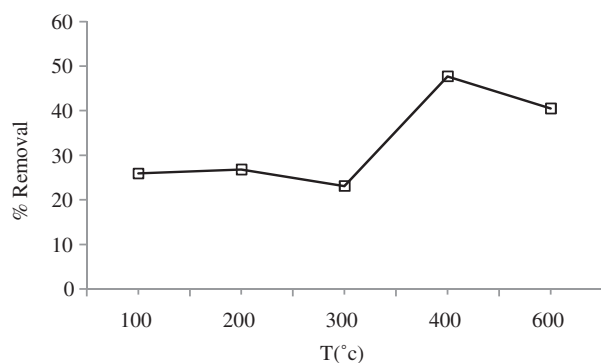


Fig. 1. Calcination temperature effect in the adsorption of cadmium onto bentonite, pH 5.6, m/V : 50 g/L, particle size: $-150 \mu\text{m}$, stirring speed: 500 rpm, contact time: 30 min.

3.2. Effect of electrolytes on adsorption of cadmium

The effects of carbonate salts (Na_2CO_3 , K_2CO_3 , $(\text{NH}_4)_2\text{CO}_3$, and CaCO_3) and chloride salts (NaCl , KCl , NH_4Cl , and CaCl_2) electrolytes on Cd(II) adsorption have been explained in following topics.

3.2.1. Effect of chloride electrolytes on adsorption of cadmium

Several adsorption experiments were performed with the aim of maximizing Cd(II) adsorption and minimizing adsorption of the other metallic ions. The effect of NaCl , NH_4Cl , and CaCl_2 electrolytes on Cd adsorption onto bentonite was determined for initial pH value of 5.6, solid to liquid ratio of 0.1 S/L, temperature of 298 K, particle size of $150 \mu\text{m}$, stirring speed of 500 rpm, contact time of 30 min, and 1,000 ppm Cd(II) ion. As seen in Fig. 2, the adsorption of cadmium in the presence of KCl , NaCl , NH_4Cl , and CaCl_2 solution (concentration of 0.1 M) has obviously decreased. It indicates that the competition between ions of the electrolyte such as Ca^{2+} , Na^+ , K^+ , and NH_4^+ with Cd(II) ions in adsorption onto bentonite. The highest amount of reduction of adsorption capacity is related to CaCl_2 electrolyte solution. Although negative influence of electrolyte on Cd(II) adsorption, NaCl electrolyte has least effect on the reduction of Cd(II) adsorption. However, all of the chloride electrolyte solutions which have negative effect on Cd(II) adsorption due to chloride ions has caused decrease in Cd(II) adsorption because container cation of chloride salts compete with Cd(II) in adsorption onto bentonite.

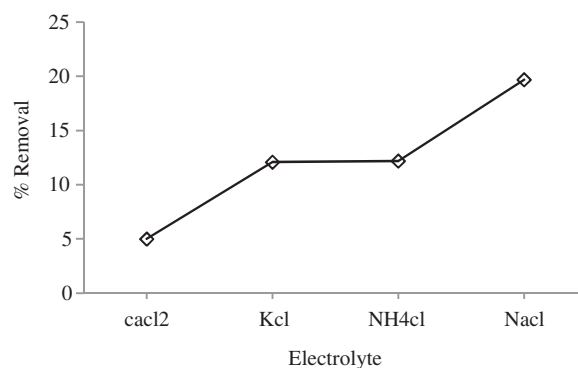


Fig. 2. Plot of different chloride electrolytes vs. removal of cadmium in the adsorption of cadmium onto bentonite, pH 5.6, m/V : 50 g/L, T : 298 K, particle size: $-150 \mu\text{m}$, stirring speed: 500 rpm, contact time: 30 min.

3.2.2. Effect of carbonate electrolytes on adsorption of cadmium

Generally, the amount of Cd(II) percentage uptake is increased in the presence of carbonate electrolytes. So, Fig. 3 shows that proximately 80% of Cd(II) ions were adsorbed onto bentonite in the presence of Na_2CO_3 electrolyte. This significant increase in the cadmium adsorption capacity of bentonite in presence of carbonate salt electrolytes can be attributed to surface negative charges by the carbonate ions. The effect of carbonate salts on Cd(II) percentage uptake is in order of $\text{Na}_2\text{CO}_3 > \text{K}_2\text{CO}_3 > (\text{NH}_4)_2\text{CO}_3 > \text{CaCO}_3$.

According to Fig. 4, it is obvious that the first adsorption of Cd(II) was slightly reduced in the range of 0.001–0.004 mol/L NaCO_3 and sequence is enhanced to maximum percentage (100%) by increasing in NaCO_3 concentration from 0.001 to 0.01 mol/L. The positive effect of carbonate salt electrolytes especially Na_2CO_3 on Cd(II) adsorption indicates that carbonate ions (CO_3^{2-}) play a role on the mechanism of Cd(II) adsorption. On the other words, carbonate ions could be participated in Cd(II) adsorption process.

3.3. Characterization of modified CaCO_3 -bentonite and Fe-bentonite

XRD pattern and main diffraction planes for CaCO_3 -bentonite and Fe-bentonite are shown in Fig. 5 and Table 3, respectively. The mineralogical study of these samples indicates that Quartz, Oligoclase, Gypsum, Montmorillonite, and Illite are the main constituents. This bentonite sample contains a low amount of Illite. As seen in Fig. 5, the main impurity of this sample is quartz which is obvious in the XRD pattern with the main diffraction peak at $27.7311^\circ (2\theta)$

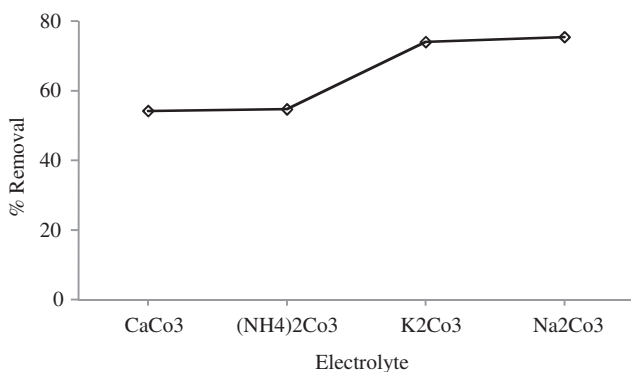


Fig. 3. Plot of different carbonate electrolytes vs. removal of cadmium in the adsorption of cadmium onto bentonite, pH 5.6, m/V : 50 g/L, T : 298 K, particle size: $-150 \mu\text{m}$, stirring speed: 500 rpm, contact time: 30 min.

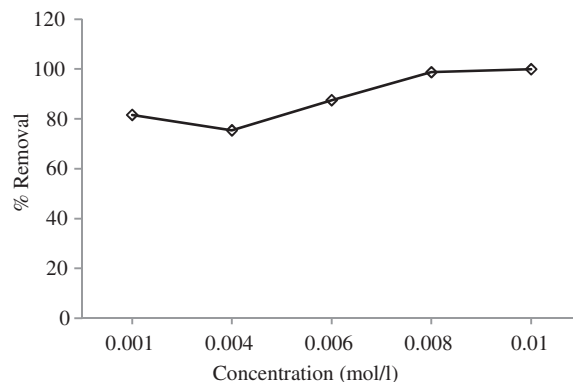


Fig. 4. Effect of different amount of Na_2CO_3 in the adsorption of cadmium onto bentonite, pH 5.6, m/V : 50 g/L, particle size: $-150 \mu\text{m}$, stirring speed: 500 rpm, contact time: 30 min.

[21,22]. The (0 0 1) diffraction at $8.93^\circ (2\theta)$ for raw bentonite [23] shifted to $7.31^\circ (2\theta)$ for Fe-bentonite and basal spacing (d_{001}) of raw bentonite increased from 10.59 to 12.01 Å by modification with iron. It was found as a shift of 1.42 Å value, this increase of basal spacing in XRD pattern of Fe-bentonite can be attributed to the incorporation of iron ions into inter-layer space [24]. This value in comparison with other reports is considerable [16,25]. It could be confirmed that poly-hydroxyl ferric-ferrous would intercalate in the interspaces of Fe-bentonite during synthesizing of Fe. The new major diffraction peaks at XRD of Fe-bentonite which was observed at $21.2^\circ (2\theta)$ and $35.5^\circ (2\theta)$ could be related to FeOOH , and Fe_3O_4 , respectively [25]. The XRD patterns of Fe-bentonite illustrate that iron element could have two forms: Fe-pillared and iron oxide.

For CaCO_3 -bentonite, the diffraction of (0 0 1) plane has disappeared due to the change in typical XRD patterns by adding CaCO_3 [26]. This absent peak of (0 0 1) plane in the patterns XRD may be taken as an evidence for high dispersion of CaCO_3 in the network structure of bentonite. Of course other (1 1 0), (1 0 0), and (1 0 1) diffraction planes are almost the same as the diffraction planes in XRD pattern of Fe-bentonite.

The infrared data of clays are usually using to predict their solid-state structures, to display functional groups and to explain their properties. Infrared spectra of modified bentonite are illustrated in Fig. 6 and Table 4. The presence of board bands at $3,627\text{--}3,626 \text{ cm}^{-1}$ on spectra of raw [23], CaCO_3 -bentonite, and Fe-bentonite concern to hydroxyl linkage (Si-OH, Al-OH) of bentonite structures. The stretching band between $3,429$ and $3,432 \text{ cm}^{-1}$ demonstrates O-H

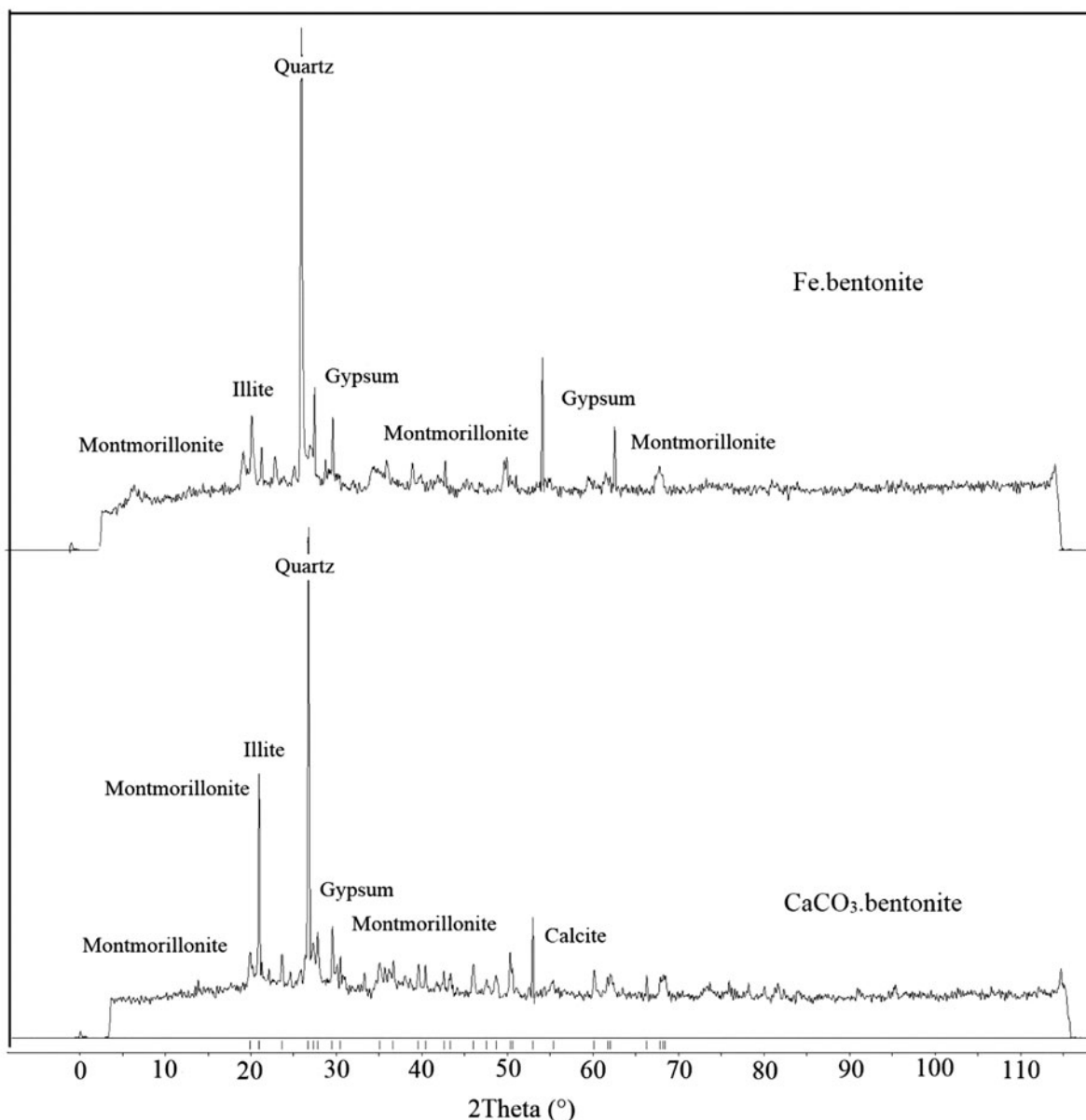


Fig. 5. XRD pattern of CaCO₃-bentonite and Fe-bentonite.

bonds of water molecules which were trapped on the bentonite structure. Of course bonding band on the Inferred spectra is due to hydrogen bonding between hydrogen and oxygen of different water molecules [27].

The bending vibration of H–O–H in water molecule in these samples is observed at 1,635–1,635 cm⁻¹. The strong and broad band at 1,040–1,039 cm⁻¹ is related to Si–O of stretching vibration in the Si–O–Si functional group in tetrahedral sheets, montmorillonite crystal in the raw, and modified bentonite [28]. Two bending vibration bands at 466–468 cm⁻¹ and

519–520 cm⁻¹ on the spectra of raw, CaCO₃-bentonite, and Fe-bentonite are demonstrated Si–O–Al and Si–O–Si bonds, respectively. The presence of quartz in this sample could be proved by FTIR with shoulder bonding at 796.68–777.01 cm⁻¹ [29,30]. The fingerprint area (400–1,000 cm⁻¹) of FTIR spectra of raw, CaCO₃-bentonite, and Fe-bentonite are almost the same which confirms that functional groups of modified bentonite were not converted by modification of CaCO₃ and FeCl₃, only basal spacing (*d*₀₀₁) of Fe-bentonite was changed by intercalation of Fe ions between montmorillonite layers.

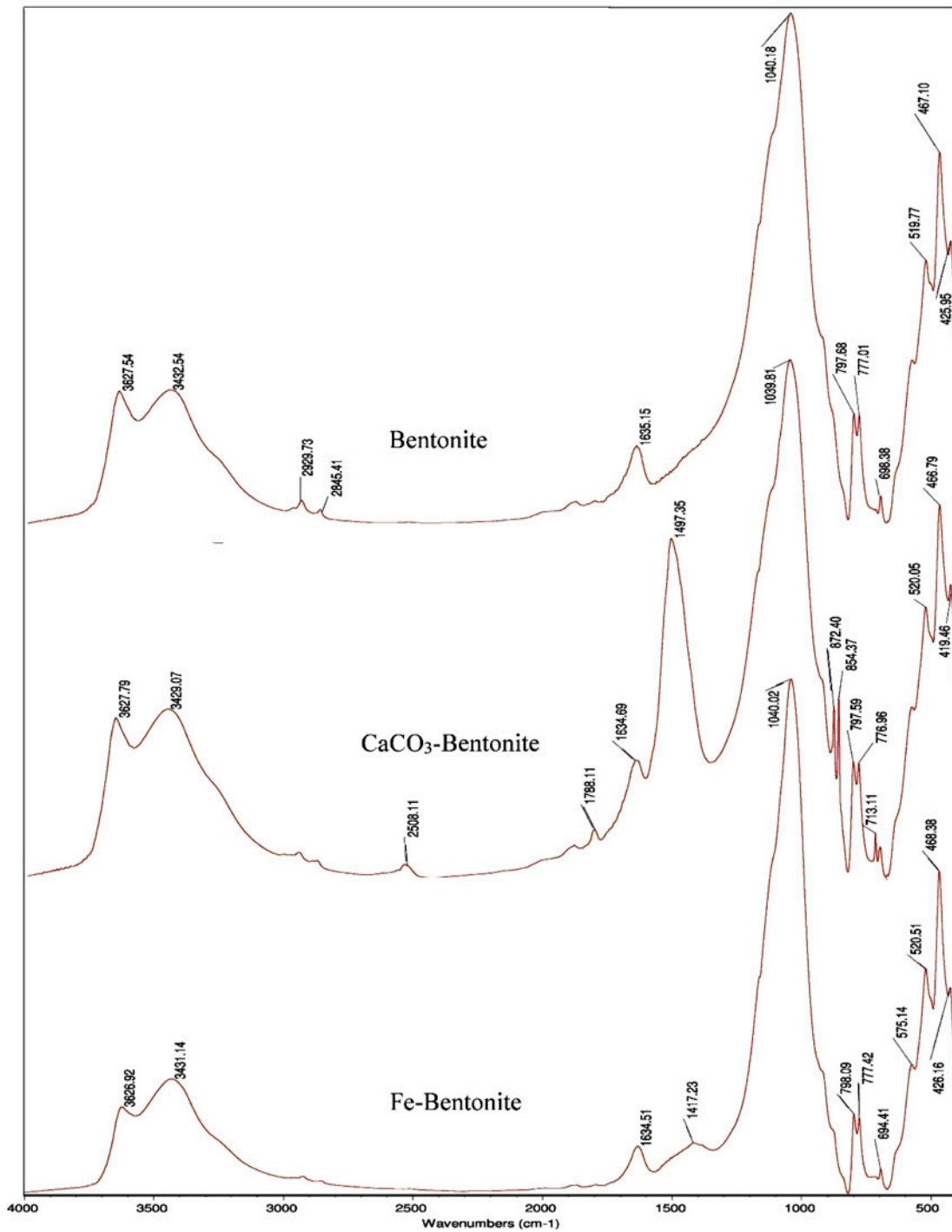


Fig. 6. FT-IR spectra of CaCO₃-bentonite and Fe-bentonite.

3.4. Adsorption isotherm models

In order to investigate equilibrium isotherm models in this study, Langmuir, Freundlich, Temkin, and D-models were examined. The equations of the models and their parameters value were represented in Tables 2 and 5, respectively.

3.4.1. Langmuir isotherm

The plot of linear form of Langmuir has correlation coefficient (r^2) 0.985 and 0.995 for CaCO₃-bentonite and Fe-bentonite, respectively, as is shown in Fig. 7(a). It was clear that Langmuir model was fitted well for Fe-bentonite. This indicates that homogeneous Cd(II)

Table 2
Equations of different isotherm models

Models	Equation (linear form)	Descriptions	Ref.
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m \cdot b} + \frac{C_e}{q_m}$	q_m maximum adsorption capacity (mg/g), b adsorption intensity or Langmuir coefficient (L/mg)	[32,33]
Freundlich	$\log q_e = \log K_F + 1/n \log C_e$	K_F the constant indicative of the relative adsorption capacity ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$) and n indicative of the intensity	[32,33]
Temkin	$q_e = RT/b \ln A_T + RT/b \ln C_e$	A_T and b_T are Temkin constant that b is related to the heat of adsorption (J/mol), R is the gas constant (8.314 J/molK) and T is absolute temperature (K)	[3,32]
Dubinin–Radushkevich	$\ln q_e = \ln q_{\max} - \beta \varepsilon^2$ $\varepsilon = RT \ln (1 + 1/C_e)$	β is the activity coefficient related to sorption energy (mol^2/KJ^2), E : free energy per molecule of adsorbate (kJ) which represent:	[32]

- If $E < 8$ kJ/mol: physical adsorption
- If $8 < E < 16$ kJ/mol: chemical adsorption or ion exchange
- For $E > 16$ kJ/mol: particle diffusion governs the reaction

$$E = \frac{1}{\sqrt{2\beta}}$$

adsorption onto Fe-bentonite has been predominated. Qualification of experimental data of Cd(II) adsorption onto Fe-bentonite for Langmuir isotherm model has been confirmed by standard deviation (SD) value (0.0736) which indicates no interaction between adsorbed Cd(II) ions. Correlation coefficient (r^2) for Langmuir isotherm model could not describe Cd(II) adsorption onto CaCO₃-bentonite well. The values of the Langmuir constants b and Q_0 (mg/g) are presented in Table 5. Thus, the adsorption capacity (Q_0) of Fe-bentonite is approximately 70 times higher than raw Iranian bentonite [23].

3.4.2. Freundlich isotherm

A plot of $\log q$ vs. $\log C_e$ gives a straight line of slope $1/n$ and intercepts K_F as seen in Fig. 7(b). The Freundlich constants for Fe-bentonite adsorbent, K_F and n are 4.043 [(mg g⁻¹)/(mg/L)^{1/n}] and 3.8212, respectively, and regression coefficient (r^2) is 0.8827.

Table 3
The main XRD plane of CaCO₃-bentonite and Fe-bentonite

CaCO ₃ -bentonite			Fe-bentonite		
2θ (°)	d (Å)	Plane	2θ (°)	d (Å)	Plane
19.9257	4.4522	1 1 0	7.3531	12.0124	0 0 1
20.9987	4.2271	1 0 0	20.2288	4.3862	1 1 0
26.7406	3.331	1 0 1	20.8377	4.2594	1 0 0
29.5245	3.023	1 0 4	26.1446	3.4056	1 0 1

The Freundlich constants for CaCO₃-bentonite adsorbent, K_F and n are 1.9742 (mg g⁻¹)/(mg/L)^{1/n} and 3.9904, respectively. Freundlich isotherm was well in agreement with the data for Cd(II) ion adsorption onto CaCO₃-bentonite with r^2 values of 0.998 but the Cd(II) adsorption onto Fe-bentonite is not well descriptive by Freundlich model. This data indicate multilayer adsorption on the CaCO₃-bentonite surface as like raw bentonite [23]. The n value shows the degree of non-linearity between Cd(II) concentration in solution and adsorption. The adsorption process is favorable because n is more than one. The K_F value for CaCO₃-bentonite and Fe-bentonite shows force binding between Cd(II) and bentonite has been improved when compared to raw bentonite (1.140

Table 4
The main vibrational modes of IR spectra

Assignment	Bentonite samples (cm ⁻¹)	
	Fe-bentonite	CaCO ₃ -bentonite
$\sqrt{(X-O-H)}$, X=Al, Si	3,626.92	3,627.79
$\sqrt{(H-O-H)}$	3,431.14	3,429.07
σ (H-O-H)	1,634.51	1,634.11
$\sqrt{(Si-O)}$	1,040.02	1,039.81
δ (Al-Al-OH)		
$\sqrt{(Si-O, -SiO_2)}$	798.09	797.59
δ (Al-O-Si)	468.38	466.79
δ (Si-O-Si)	520.05	520.51

Table 5

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

Model	Parameter	CaCO ₃ -bentonite	Fe-bentonite
Langmuir	q_m (mg/g)	11.22	18.657
	r^2	0.9853	0.995
	SD	3.99	0.736
	R_L	0.3756–0.03855	0.129–0.00979
	b	0.02	0.067
Freundlich	K_F (mg ^{1-1/n} L ^{1/n} g ⁻¹)	1.9742	4.043
	n	3.9904	3.8212
	r^2	0.9982	0.8827
	SD	0.0124	0.323
Temkin	b	1.2813	2.0799
	A (L/mg)	2.6541	10.2052
	r^2	0.9379	0.9842
	SD	0.2046	0.2382
Dubinin–Radushkevich	β	2.00E-09	2.00E-09
	E (kJ)	15.8114	15.8113
	r^2	0.9838	0.9103
	SD	0.0209	0.0331

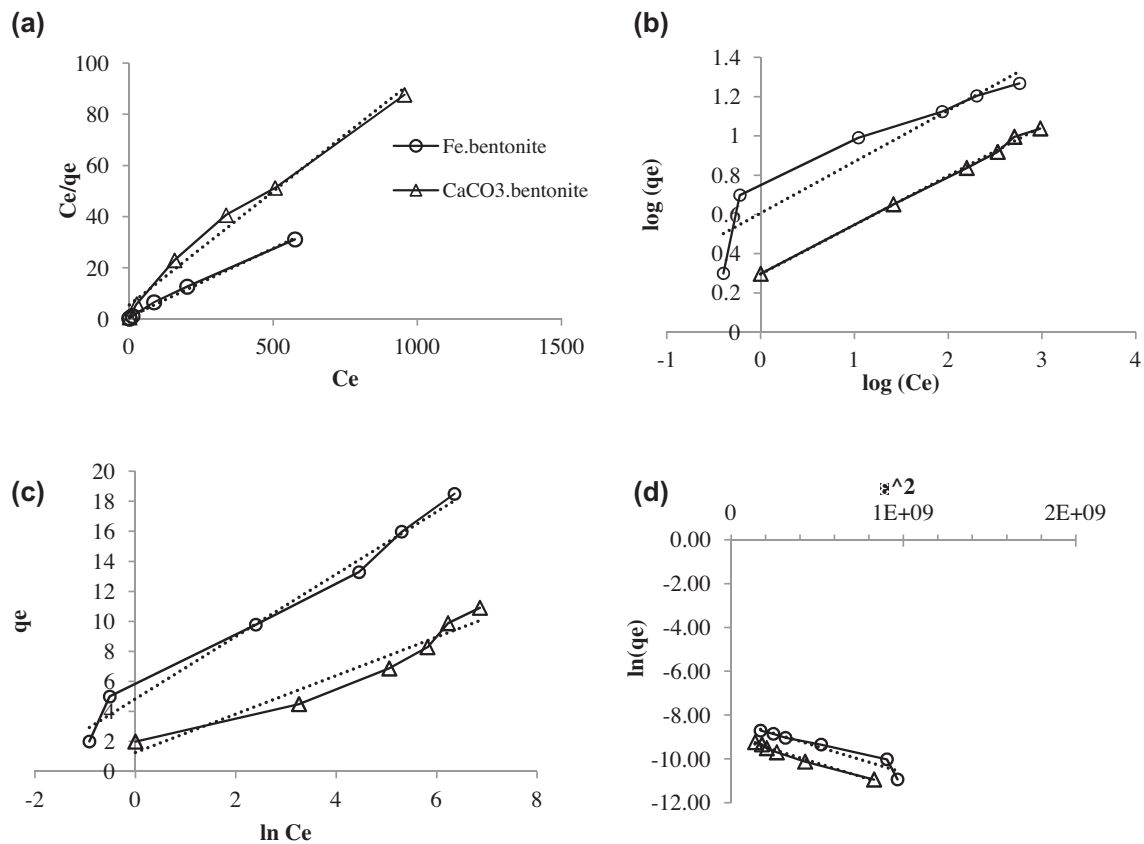


Fig. 7. (a) Langmuir isotherms, (b) Freundlich isotherms, (c) Temkin isotherm, and (d) Dubinin–Radushkevich isotherm for Cd(II) adsorption on Fe-bentonite and CaCO₃-bentonite. pH 5.6, m/V : 50 g/L, T : 298 K, particle size: $-150 \mu\text{m}$, stirring speed: 500 rpm, contact time: 30 min.

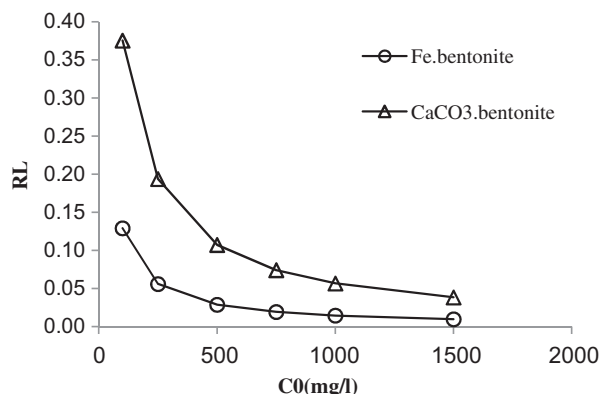


Fig. 8. Plot of separation factor vs. initial concentration of cadmium between 100 and 1,500 ppm for the range of CaCO_3 -bentonite and Fe-bentonite.

$(\text{mg g}^{-1})/(\text{mg/L})^{1/n}$ [23]. It means that calcium carbonate and ions are effective on interaction between Cd(II) and bentonite.

3.4.3. Temkin isotherm

The equilibrium data were also fitted to linear Temkin equation for the adsorption of Cd(II) onto CaCO_3 -bentonite and Fe-bentonite. Fig. 7(c) shows the plots of linear form of Temkin and the values of the Temkin constants A , b (b constant calculated at $T = 298 \text{ K}$), SD, and r^2 are listed in Table 5. A and b constants are determined from the interception and slope of the linear plots of q_e vs. $\ln C_e$. According to Temkin model, correlation coefficient (r^2) of model for Fe-bentonite (0.9842) is not only the value more acceptable than CaCO_3 -bentonite (0.9379) but also the obtained A values of Fe-bentonite and CaCO_3 -bentonite indicated a higher Fe-bentonite potential for Cd(II) adsorption. The b (the binding energy) value of Fe-bentonite is 2.079 kJ/mol. Literature survey shows that for b values less than 8 kJ/mol, physical adsorption and weak interactions have been predominated at adsorption process [31].

RT/b constant value is related to heat of Cd(II) adsorption with respect to RT/b values of modified bentonite which is 1,933.6 and 1,191.2 for CaCO_3 -bentonite and Fe-bentonite, respectively, therefore heat of cadmium ions adsorption onto Fe-bentonite is higher than CaCO_3 -bentonite indicating that interaction between Cd(II) and Fe-bentonite is favorable.

So it is reasonable to discuss the parameter of Temkin model for Fe-bentonite. In other words, the fitting of Temkin model for Cd(II) adsorption onto Fe-bentonite was emphasized by Langmuir model (as both are suitable for monolayer adsorption)

3.4.4. D-R isotherm

The plots of linear form of $\ln q_e$ vs. $\ln^2(1 + c^{-1})$ for Cd(II) adsorption onto CaCO_3 -bentonite and Fe-bentonite are observed in Fig. 7(d). The parameters q_m and B are calculated from the intercepts and slopes, respectively. The values of adsorption free energy (E) mean are an indication of whether or not the adsorption process is done by particle diffusion, physical or chemical interaction. As seen in Table 5, adsorption free energy (E) of Cd(II) adsorption onto CaCO_3 -bentonite and Fe-bentonite are 15.8114 and 15.8113 kJ, respectively. These values are between 8 and 16 kJ, that is to say, the adsorption of Cd(II) by modified bentonite is chemical adsorption or ion exchange process [32].

3.4.5. Evaluation of adsorption isotherm models

By equilibrium study, it could be concluded that the adsorption of Cd(II) onto Fe-bentonite and CaCO_3 -bentonite could be better described by Langmuir and Freundlich model with correlation coefficients (r^2) 0.995 and 0.998, respectively. These conclusions are confirmed by SD values. According to Langmuir isotherm model (monolayer adsorption process) the maximum Cd(II) adsorption capacity of Fe-bentonite is 32.39 mg/g. The base on Freundlich isotherm model (multilayer adsorption process) Cd(II) adsorption onto CaCO_3 -bentonite is $1.97 \text{ mg}^{1-1/n} \text{ L}^{1/n} \text{ g}^{-1}$. The adsorption free energy (E) of D-R model and the binding energy (b) from Temkin model emphasized that Cd(II) adsorption onto modified bentonite is chemical or ion exchange adsorption with strong interaction between cadmium ions and functional groups of modified bentonite. These results in comparison with other reports of Cd(II) adsorption are considerable [24,33,34]. Generally, the Cd(II) has been adsorbed onto Fe-bentonite by monolayer mechanism. As shown in Table 6, it is one of the best reported result Cd(II) adsorption onto Fe-bentonite that could be related to synthesizing bentonite under calcinations low temperature.

3.5. Thermodynamic studies

The ΔH° and ΔS° values of Cd(II) adsorption could be calculated from the slope and intercept of the plot of $\ln K_d$ vs. $1/T$, respectively. Those are reported in Table 7. The values of ΔH° and ΔS° of Fe-bentonite were obtained $-10.33 \text{ (kJ mol}^{-1}\text{)}$ and $-15.89 \text{ (J mol}^{-1} \text{ K}^{-1}\text{)}$, respectively, and ΔH° and ΔS° values of CaCO_3 -bentonite were obtained $12.06 \text{ (kJ mol}^{-1}\text{)}$ and $54.06 \text{ (J mol}^{-1} \text{ K}^{-1}\text{)}$, respectively. The values of ΔH° for Fe-bentonite and CaCO_3 -bentonite indicate exothermic

Table 6

Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm constants for Cd(II) adsorption on modified bentonite and clay adsorbents

Clay adsorbent	Langmuir			Freundlich			Ref.
	q_m	b	r^2	K_F	n	r^2	
Na-montmorillonite	0.124 (mmol/kg)	2.582 (L/mmol)	0.9949	0.0706	0.3874	0.9408	[34]
Fe-montmorillonite	25.7 (mg/g)	0.0671	0.962	16.9	8.31	0.86	[16]
Bentonite	7.73 (mg/g)	0.486	0.9426	0.82	2.174	0.9518	[33]
Goethite-modified bentonite	9.56 (mg/g)	0.07	0.9243	0.7	1.754	0.9846	
Humic acid-modified bentonite	9.90 (mg/g)	1.152	0.9195	1.89	2.439	0.947	
Fe pillared bentonite	0.773 (mmol/g)	0.469	0.984	0.451	2.75	0.932	[24]
Fe-bentonite	18.657 (mg/g)	0.067	0.995	4.043	3.8212	0.8827	In this study
CaCO ₃ -bentonite	11.22	0.02	0.9853	1.974	3.9904	0.9982	In this study

Table 7

Values of thermodynamic parameters for cadmium removal with CaCO₃-bentonite and Fe-bentonite

Clay adsorbent	ΔH° (kJ/mol)	ΔS° (J/mol (K))	ΔG° (kJ/mol)		
			293 K	303 K	313 K
Fe-bentonite	-10.337	-15.89	-5.68	-5.523	-5.364
CaCO ₃ - bentonite	12.06	54.04	-3.8	-4.3	-4.85

and endothermic Cd(II) adsorption, respectively. These mean that adsorption efficiency of Cd(II) onto Fe-bentonite and CaCO₃-bentonite decreases and increases by increasing temperature, respectively [35].

This data show that modification of bentonite has caused the increase in ΔH° value. So, it was observed that the process would change from exothermic to endothermic by changing from Fe-bentonite to CaCO₃-bentonite. The entropy of Cd(II) adsorption onto Fe-bentonite and CaCO₃-bentonite has been decreased relative to raw bentonite.

Generally, the negative value of entropy is logical because adsorption process would cause decrease in the number of ions in solution but it seems that the positive value for ΔS° of CaCO₃-bentonite and raw bentonite [23] is related to release of cation and anion ions in solution in adsorption process.

Negative ΔG° values at different temperatures were indicative of the fact that the adsorption process is spontaneous. The ΔG° value of Cd(II) adsorption onto Fe-bentonite decreases from -5.68 to -5.36 kJ/mol with enhancing of temperature from 293 to 313 K but ΔG° value for CaCO₃-bentonite increases from -3.80 to 4.85(J/mol K) with increasing in temperature from 293 to 313 K. These phenomena are confirmed by enthalpy standard changes (ΔH°). In other words, the increasing of temperature has positive and negative effects on

ΔG° value of Cd(II) the same as the ΔH° value of Cd(II) adsorption onto CaCO₃-bentonite and Fe-bentonite, respectively.

These Gibbs free energy (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) are considerable in comparison with other reports of Cd(II) adsorption onto bentonite. As seen in Table 7, generally Cd(II) adsorption onto modified bentonite is endothermic but in this study Fe Iranian bentonite for Cd(II) adsorption has exothermic process.

4. Conclusions

- (1) The experimental data illustrated that Na₂CO₃ compound is the best modifier electrolyte in comparison with other carbonate salts and chloride salts so the removal of 1,000 ppm Cd(II) from aqueous solution in presence of 0.1 M Na₂CO₃ by 5 g bentonite has maximum uptake (100%).
- (2) The uptake of Cd(II) on bentonite is affected by calcination temperature so the best temperature is 673 K. Increasing calcination temperature causes the loss of adsorption capacity of Cd(II) which is related to distortion of bentonite structure and defective montmorillonite structure (dehydroxylation).

- (3) The characterization structure of CaCO₃-bentonite and Fe-bentonite by XRD and FTIR spectroscopy displayed that the increase in basal spacing in XRD pattern of Fe-bentonite could confirm this fact that poly-hydroxyl Fe(III)–Fe(II) would intercalate in the interspaces of Fe-bentonite in synthesizing of Fe compounds.
- (4) The Langmuir and Freundlich models were fitted very well for Cd(II) adsorption onto Fe-bentonite and CaCO₃-bentonite, respectively, and were indicating that homogenous (monolayer) and heterogeneous (multilayer) adsorption process are predominated in Cd(II) adsorption onto Fe-bentonite and CaCO₃-bentonite, respectively. Equilibrium studies illustrated that adsorption characteristic for modified bentonite includes physical adsorption and weak interaction Cd(II) ions and available sites of bentonite surface.
- (5) The modification of Iranian bentonite by Fe(II)–Fe(III) and CaCO₃ for adsorption of Cd(II) adsorption improved maximum adsorption capacity corresponding to Langmuir (for Fe-bentonite) and Freundlich (for CaCO₃-bentonite) relative to raw bentonite.
- (6) Thermodynamic studies show that higher temperature results in both positive and negative effect on Gibbs free energy changes (ΔG°) for Cd(II) adsorption onto CaCO₃-bentonite and Fe-bentonite, respectively. In other words, the increase in temperature is favorable for Cd(II) adsorption onto CaCO₃-bentonite.
- (7) Adsorption process for the removal of Cd(II) from aqueous solution by Fe-bentonite is exothermic with decrease in entropy. Although ΔH° and ΔS° values have been reported with positive effect on Cd(II) adsorption onto raw and modified bentonite. This late subject could be related to especial effect of Fe(II) and Fe(III) ions on the Cd(II) adsorbed.

Acknowledgments

The authors thank the Vice-President's Office for Research Affairs of Amirkabir University of Technology for supporting this project. We acknowledge the contribution of Milad Armaghan.

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