

Application of Algerian Bentonite in the Removal of Cadmium (II) and Chromium (VI) from Aqueous Solutions

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Abstract

The aim of this study is to report batch adsorption results of Cd (II) and Cr (VI) onto Algerian bentonite. The equilibrium adsorption process was achieved at about 120 min contact time. The kinetic and isotherms aspects of Cr (VI) and Cd (II) adsorption were investigated by varying operation parameters such as pH (0.5 - 6), initial Cd (II) and Cr (VI) concentrations (50 - 200 mg/l) and temperature (293.15 K - 343.15 K). The optimum conditions obtained were: pH = 6.0 and 4.0 for Cd (II) and Cr (VI) respectively, initial concentrations of Cd (II) and Cr (VI) = 50 mg/L and T = 293.15 K. The kinetic of the adsorption process was studied by application of the most important kinetic models namely the pseudo-first order, the pseudo-second order and Elovich equations. The results showed that the pseudo-second order model fitted well the adsorption data of Cr (VI) whereas, and the Cd (II) adsorption data fitted best the Elovich equation. The equilibrium data fitted best the Langmuir isotherm, and the maximum adsorption capacity was determined through this model and was found to be 13.17 and 12.61 mg/g for Cd (II) and Cr (VI) respectively. The temperature had a reverse effect on the Cd (II) and Cr (VI) adsorption; our results showed that the removal efficiency increased to 82.4% and 55.70% for Cd (II) and Cr (VI) when the temperature decreased to 293.15 K. The negative figures of the Gibbs free energy ΔG°_{ads} values range from -15.23 kJ/mol to -14.37 kJ/mol for Cd (II) and from -9.70 kJ/mol to -9.64 kJ/mol for Cr(VI) at 293.15 K to 343.15 K showed that the adsorption process is spontaneous and favourable. These results confirmed the ability of the low-cost Algerian natural bentonite to efficiently and competitively adsorb the two toxic elements investigated: cadmium (II) and chromium (VI).

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Keywords

Adsorption, Cadmium, Chromium, Langmuir, Bentonite

1. Introduction

Many heavy metals have toxic effects at high concentration [1] [2]. Some of them, however, at trace level and under a specific valence play an important role as micronutrients in organisms

The presence of heavy metals such as cadmium and chromium in industrial wastewater and effluents has been a great concern due to their high toxicity and adverse accumulation characteristics [3] [4].

The most common oxidation states of chromium are trivalent Cr (III) and hexavalent Cr (VI) which are invariably found in various industrial processes. Chromium (VI) compounds are much more toxic than Chromium (III) ones [5] [6]. The former are reported to be a powerful carcinogen capable of modifying the deoxyribonucleic (DNA) transcription process in both animals and humans which result in important chromosome aberrations [7]. It is, therefore, essential to remove Cr (VI) from wastewaters of electroplating, cement, leather tanning and paint industries which may contain up to hundreds of mg/L of chromium though the tolerance limit of Cr (VI) for discharge into inland surface waters is only 0.1 mg/L and in waste water at the level of 0.05 mg/l [8] [9].

Cadmium (II) is a toxic inorganic pollutant with widely diffused emission sources, giving rise to a large scale environmental pollution. For these reasons, environmental severe regulations have been put up to limit the maximum cadmium concentration in natural water bodies as well as on the maximum allowed concentration for wastewater discharge [3]. Cadmium has been classified as a human carcinogen and teratogen affecting the lungs, the kidneys, the liver and the reproductive organs [1] [5]. The World Health Organization (WHO) has set a maximum guideline concentration of $0.003 \text{ mg}\cdot\text{L}^{-1}$ for Cd in drinking water [10].

Several processes have been suggested to remove heavy metals such as chemical precipitation, ion exchange, reverse osmosis, [11] [12]. These methods are either expensive or inefficient especially when the concentrations of metal ions are less than 10 mg/l.

In this study, we focused on the adsorption process, because it is inexpensive, widely applicable and has also been used in the water industry for the removal of colour, odour and organic matters [13]-[17].

The objective of the present study was to investigate the potential use of Algerian natural bentonite as a competitive adsorbent material for the removal of cadmium (II) and chromium (VI) from aqueous solutions. Batch experiments were carried out first, in order to determine an optimal contact time, then the influence of the most important parameters such as (pH, initial Cd (II) and Cr (VI) concentrations and temperature) was investigated. The Langmuir and Freundlich isotherm models were used to describe equilibrium data. The kinetic models of the Pseudo first-order, the second order-model and Elovich were applied to evaluate the mechanism of adsorption. The thermodynamic parameters derived from the Van't Hoff equation and the combination of the first and second law of thermodynamic (Gibbs free energy (ΔG°), molar enthalpy (ΔH°), and molar entropy (ΔS°) were determined.

2. Materials and Methods

2.1. Adsorbent

Natural bentonite (98% montmorillonite) from Maghnia (Western Algeria) used in this work was kindly supplied by ENOF (Entreprise Nationale des substances utiles et des produits non-ferreux). It was characterized by physicochemical analysis, by X-ray powder diffraction (XRD), by Infrared spectroscopy (FTIR) and scanning transmission microscopy (SEM). The apparent and true densities were determined by pycnometry method. The mean value of the pH was found to be 6.0.

The chemical composition, the granulometric distribution and both densities of the bentonite are reported in Table 1.

2.2. Preparation of Cr (VI) and Cd (II) Solutions and Sample Analysis

All the chemicals used are of analytical grade. The stock solutions of Cr (VI) and Cd (II) are prepared by

Table 1. Principal characteristics of our natural bentonite.

Chemical composition		Granulometric distribution		Densities	
constituents	Contents (% w/w)	Particle size (mm)	Mass (%)	d_p (g·cm ⁻¹)	d_s (g·cm ⁻¹)
SiO ₂	65.20	(0.200 - 0.165)	5.75	-	-
Al ₂ O ₃	17.25	(0.165 - 0.125)	5.23	-	-
Fe ₂ O ₃	2.10	(0.125 - 0.100)	9.80	-	2.36
MgO	3.10	(0.100 - 0.063)	29.99	1.04	2.34
CaO	1.20	(0.063 - 0.040)	37.26	1.02	2.24
Na ₂ O	2.15	(0.040 - 0.032)	7.32	0.93	2.20
TiO ₂	0.20	<0.032	2.00	0.88	2.19
K ₂ O	0.60				
Ignition loss	8.20				

d_p = carbon packed density (g·cm⁻¹), d_s = carbon solid-phase density (g·cm⁻¹).

dissolving potassium dichromate (K₂Cr₂O₇) and Cd (NO₃)₂·4H₂O (Merck) salts in distilled water. Experimental solutions at the desired concentration were then obtained by successive dilutions. The initial pH adjustments were carried out either by 0.1 M sulfuric acid or 0.1 M sodium hydroxide.

The Cr (VI) and Cd (II) concentrations were determined by the inductively coupled plasma method, (ICP Jovin Yvon instrument). X-ray diffraction and infrared spectroscopy analysis were carried out, respectively; with Philips instrument PW 1730 and Beckman acculab 9 spectrophotometer. The pH values were determined by means of a Tacussel digital pH meter.

2.3. Batch Experiments

Adsorption studies were carried out using the batch technique to acquire the rate and the equilibrium data. The batch adsorption experiments were performed in mechanically agitated beakers containing 100 mL under constant conditions of pH 0.5 - 6.0, Cr (VI) and Cd (II) concentrations 50 - 200 mg/L and temperature 293.15 K, 303.15 K, 313.15 K, 323.15 K, 333.15 K and 343.15 K. Only one parameter was changed at a time while others were maintained constant during the experiments. Aqueous solutions with 200 mg/L of Cr (VI) and Cd (II) were prepared at a desired pH values and at T = 293.15 K. Adsorption isotherms onto natural bentonite (particle size: 0.100 - 0.063 mm) were obtained by mixing 100 ml of a 200 mg/l of Cr(VI) and Cd (II) concentrations with an amount of bentonite (2.5 g). The system was agitated at a constant stirring rate of 200 rpm, as for higher values the agitation has a strong negative effect [18]. After filtration, the residual Cd (II) and Cr (VI) concentrations were determined using ICP.

2.4. Calculations

The percentage removal of each metal ion was calculated using the following equation:

$$R\% = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

The distribution coefficient K_d (mL/g) is calculated by the following equation:

$$K_d = \left(\frac{C_0 - C_t}{C_t} \right) v/m \quad (2)$$

K_d = amount of metal in adsorbent/amount of metal in solution $\times v/m$ (mL/g)

C_0 , C_t are respectively the initial and final metal concentration expressed in mg/L

Where v is the volume of the solution (mL) and m is the weight of the adsorbent (g) at equilibrium time.

The amount of metal ion sorbed at time t , q_t , was calculated from the mass balance equation: is represented by the expression

$$q_t = (C_0 - C_t) \cdot v/m \quad (3)$$

C_0 , C_t are defined just above and q_t is the adsorption capacity in mg/g (milligram of solute per gram of adsorbent) where t is equal to the equilibrium contact time, $C_t = C_e$, $q_t = q_e$, then the amount of metal ion sorbed at

equilibrium, q_e .

All the adsorption experiments were carried out in duplicate. The errors in the data were typically less than 5%.

3. Theory

3.1. Equilibrium Isotherm Models

Three models were used to fit the experimental data, Langmuir isotherm [19] and Freundlich isotherm [20].

3.1.1. Langmuir Isotherm

The Langmuir isotherm is based on assuming a monolayer sorption onto a surface with a fixed number of well defined sites; the equation is given below:

$$1/q_e = [(1/Q_0b) \times (1/C_e) + (1/b)] \quad (4)$$

where, b is the adsorption equilibrium constant ($\text{L} \cdot \text{mg}^{-1}$) related to the apparent energy of adsorption, Q_0 is the quantity of adsorbate required to form a single monolayer per unit mass of adsorbent ($\text{mg} \cdot \text{g}^{-1}$), considered as the maximum adsorption capacity and q_e is the amount adsorbed on unit mass of the adsorbent ($\text{mg} \cdot \text{g}^{-1}$) when the equilibrium concentration is C_e ($\text{mg} \cdot \text{L}^{-1}$).

A further analysis of the Langmuir equation can be made on the basis of a dimensionless parameter, R_L [21], also known as the separation factor, given by Equation (5):

$$R_L = 1/(1 + bC_e) \quad (5)$$

The values of R_L indicate the type of Langmuir isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$).

3.1.2. Freundlich Isotherm

The Freundlich adsorption isotherm is an empirical equation used to describe heterogeneous system. The linear form of Freundlich isotherm is represented as:

$$q_e = K_f C_e^{1/n} \quad (6)$$

where, K_f is the Freundlich constant, which indicates the relative adsorption capacity of the adsorbent related to the bonding energy, and n is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient. The Freundlich coefficients can be determined by linear regression from the plot of $\log q_e$ versus $\log C_e$ on the basis of the linearized equation given by Equation (7)

$$\log q_e = \log K_f + 1/n \log C_e \quad (7)$$

The plot of $\log q_e$ as a function of $\log C_e$ at 293.15 K will lead us to determine the Freundlich constants (K_f , $1/n$).

3.2. Adsorption Kinetics

In order to understand the mechanism of adsorption and potential rate controlling step, a number of kinetic models have been employed to test experimental data of Cd(II) and Cr(VI) adsorption. These include various ordered equations such as pseudo-first order equation [22], pseudo-second order equation [23], Elovich equation [24]. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients r^2 . A relatively high r^2 value indicates that the model successfully describes the kinetics of adsorption of Cd (II) and Cr (VI).

3.2.1. Pseudo-First- Order Kinetics

The pseudo-first order model has been widely used to predict the metal adsorption kinetics. It was historically suggested by Lagergren in 1898 to deal with the adsorption of solid/liquid systems and it is expressed as:

$$dq_e/dt = k_1 (q_e - q_t) \quad (8)$$

After integration and at the initial condition $q_t = 0$ at $t = 0$, it becomes:

$$\text{Log}(q_e - q_t) = \text{Log}q_e - k_1 t / 2.303 \quad (9)$$

where, q_e and q_t are the amounts of Cr (VI) and Cd (II) adsorbed ($\text{mg}\cdot\text{g}^{-1}$) at equilibrium time and at any instant of time t , and k_1 ($1\cdot\text{min}^{-1}$) is the rate constant of the pseudo first order adsorption. The plot of $\log(q_e - q_t)$ vs. t gives a straight line for the first-order adsorption kinetics, which allow the computation of the adsorption rate constant, k_1 .

3.2.2. Pseudo-Second-Order Kinetics

Ho's pseudo-second-order model has been successfully applied to the adsorption of metal ions, organic substances dyes [25]. It was expressed as:

$$dq_t/dt = k_2 (q_e - q_t)^2 \quad (10)$$

Integrating Equation (10) for the bounding conditions gives:

$$1/q_t = 1/k_2 q_e^2 + 1/q_e \quad (11)$$

where k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) is the second order rate constant of the pseudo-order adsorption and $h = k_2 q_e^2$ is the initial adsorption rate.

3.2.3. Elovich Kinetics Model

The Elovich equation is of general application to chemisorption kinetics. It has been applied satisfactorily to some chemisorption processes and has been found to cover a wide range of slow adsorption rates [26]. The same equation is often valid for systems in which the adsorbing surface is heterogeneous, and is formulated as:

$$dq_t/dt = \alpha e^{-\beta q_t} \quad (12)$$

where, α ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}$) is the initial adsorption rate and β ($\text{mg}\cdot\text{g}^{-1}$) is the desorption constant related to the extent of the surface coverage and activation energy for chemisorption. Integrating Equation (12) for the bounding conditions gives:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \quad (13)$$

3.3. Thermodynamic Studies

In order to determine the thermodynamic feasibility and the thermal effects of the sorption, the Gibbs free energy (ΔG°), the molar entropy (ΔS°) and the molar enthalpy (ΔH°) were determined. The ΔG° is the fundamental criterion to determine if a process occurs spontaneously. Data about the adsorbed Cd (II) and Cr (VI) at equilibrium at different temperatures have been used to evaluate the thermodynamic parameters ΔG° , ΔS° and ΔH° for the adsorption system by means of the following equations [27]:

$$\text{Ln } k_d = \Delta S^\circ / R - \Delta H^\circ / RT \quad (14)$$

where T is temperature in Kelvin and R is the universal gas constant ($8.31 \text{ J/mol}\cdot\text{K}$)

The plot of $\text{Ln}k_d$ as a function of $1/T$ should give a linear relationship with slope of $\Delta H^\circ/R$ and an intercept of $\Delta S^\circ/R$. Then, ΔG° value was obtained at any temperature from the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (15)$$

4. Results and Discussion

4.1. Characterization of Adsorbent

Some chemical and physical characteristics of natural bentonite are presented in **Table 1**.

From **Table 1**, it is clear that clay mineral was rich in various oxides.

4.1.1. Analysis by DRX

X-ray diffraction (XRD) analysis was carried out with X-ray diffractometer (Philips instrument PW 1730), using CuK_α radiation. Patterns were recorded from 5° to 70° 2θ at a scan rate 1° min^{-1} . The XRD patterns for the ben-

tonite are shown in **Figure 1**.

Analysis by X-ray diffraction showed that the natural bentonite belongs to the montmorillonite clay family. It is characterized, respectively, by a series of big peaks at $\theta = 5.78^\circ$ and $d_{hkl} = 15.3 \text{ \AA}$, $\theta = 17.27^\circ$ and $d_{hkl} = 5.13 \text{ \AA}$, $\theta = 19.9^\circ$ and $d_{hkl} = 4.46 \text{ \AA}$ and a few small peaks at $\theta = 25.9^\circ$ and $d_{hkl} = 33.3 \text{ \AA}$, $\theta = 49.2^\circ$ and $d_{hkl} = 1.81 \text{ \AA}$ which is characteristic of the presence a small amount of quartz.

4.1.2. FTIR Spectral Analysis

In order to determine which functional groups were responsible for metal uptake, an infrared analysis in solid phase was performed on bentonite in a KBr disk. An infrared spectrum was obtained for the adsorbent solid sample before the adsorption process. As illustrated in **Figure 2**, we can show the presence of absorption bands of clay phase and the adsorption characteristic bands of impurities.

Two absorption peaks are observed between 3200 and 3800 cm^{-1} , and 1600 and 1700 cm^{-1} . The first corresponds to the OH vibration band of silicate skeleton at 3290 cm^{-1} , assigned by several authors to the montmorillonite mineral [28] [29]. The second peak at 1640 cm^{-1} showed the presence of absorbed water between the foils. Another intense peak appeared at 1000 cm^{-1} , characterizing the main vibration bands of montmorillonite.

4.1.3. Scanning Electronic Microscopy SEM

All the samples were analyzed, examined and studied by means of Scanning electron microscope make PHILIPS ESEM XL 30 FEG. **Figure 3** represents a microphotograph of the natural Algerian bentonite. The morphological analysis of the structure and the form of our material shows that our bentonite exists in aggregates, and in non uniform plate.

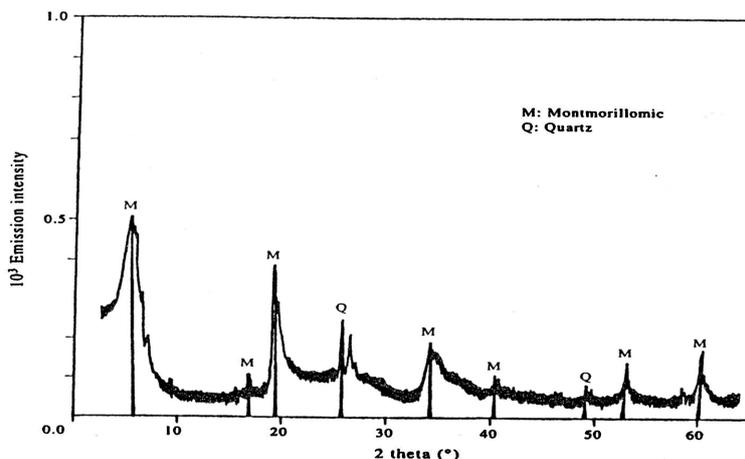


Figure 1. XRD pattern of natural Algerian bentonite.

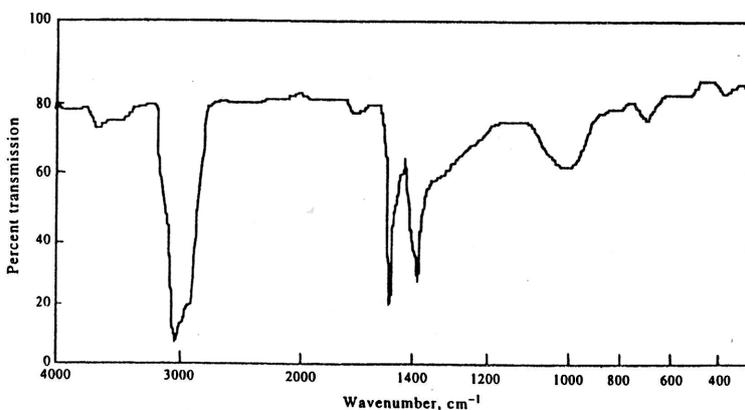


Figure 2. FTIR spectra of natural Algerian bentonite

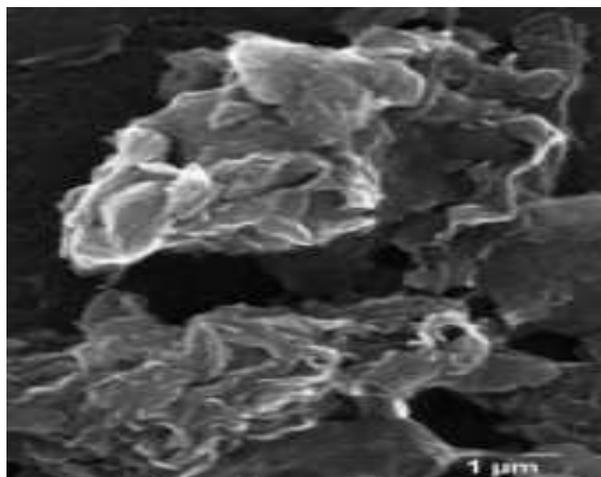


Figure 3. SEM image of the natural Algerian bentonite used in this study.

4.2. Effect of Parameters on Adsorption Process

Various parameters for the effective removal of Cd (II) and Cr (VI) from aqueous solutions by using Algerian bentonite as adsorbent were studied.

4.2.1. Determination of the Optimum Contact Time

The influence of contact time on adsorption of metal ions was investigated within the time range of 30 to 180 min at 20°C. **Table 2** listed our kinetic results at the following conditions: bentonite sample = 0.5 g with 50 ml of Cd (II), Cr (VI) solutions and pH = 4). It was shown that the adsorption efficiency of Cd (II) and Cr (VI) ions increased with increasing contact time up to 120 min and later, it would remain constant. For instance, during 120 min, the adsorption efficiencies of Cd (II) and Cr (VI) ions reached 43.62 (II) % and 28.45% respectively. Therefore, the optimum contact time was fixed at 120 min for the further experiments. The results indicated that the equilibrium was reached slowly similar to the results reported by A. Zeid [30].

4.2.2. Effect of pH

The pH of the solutions plays an important role in the adsorption process as the adsorbent surface acquires positive or negative charge in response to change in pH [31] [32]. The effect of pH on adsorption of Cd(II) and Cr(VI) ions was investigated by varying the pH from 0.5 - 6.0 at different times. The effect on the uptake adsorption of Cd (II) and Cr (VI) is shown in **Figure 4** and **Figure 5**.

It can be seen from **Figure 4** and **Figure 5**, that the percent removal of Cd (II) and Cr (VI) ions on the adsorbent increased with increasing pH and significantly decreased at lower pH values. The minimal adsorption at low pH may be due to the higher concentration and high mobility of the H⁺, which were preferentially adsorbed rather than the metal ions [33]. It was found that the adsorption of Cd(II) and Cr(VI) ions was to be maximum at 6.0 and 5.0 respectively.

4.2.3. Effect of Initial Cd(II) and Cr(VI) Concentrations

The adsorption of Cd (II) and Cr (VI) ions onto bentonite as a function of the initial concentrations were studied in the concentration range of 50 - 200 mg·L⁻¹ while keeping all the other parameters constant. The results are shown in **Figure 6** and **Figure 7**. It was clear that, the adsorption efficiencies increased when the metal ions concentrations decreased. For example, when Cd (II) and Cr (VI) ions concentrations increased from 50 mg·L⁻¹ to 200 mg·L⁻¹, the adsorption efficiencies decreased from 78.35% to 48.50% for Cd (II) and from 27.50% to 37.75% for Cr (VI). This may be explained by an increase in the number of Cd (II) and Cr (VI) ions to bind on the adsorbent surface and saturation of adsorbent surface with metal ions [25] [26]. Similar observations have been reported for Cr (VI) removal by using jatropha oil cake, sugarcane bagasse and maize corn cob [34] and Cd (II) onto untreated coffee grounds [35].

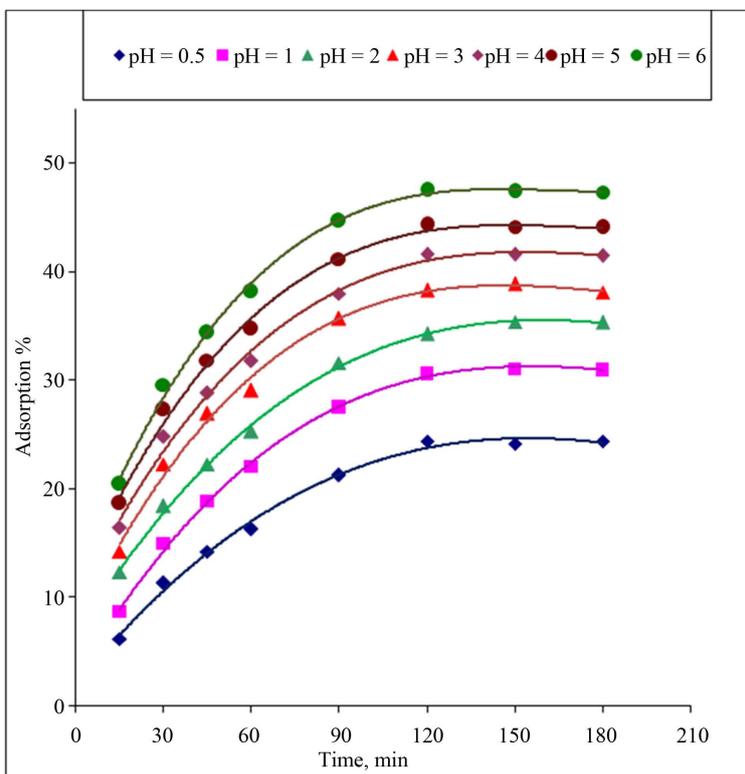


Figure 4. Effect of pH on the removal of Cd (II) at 293.15 K.

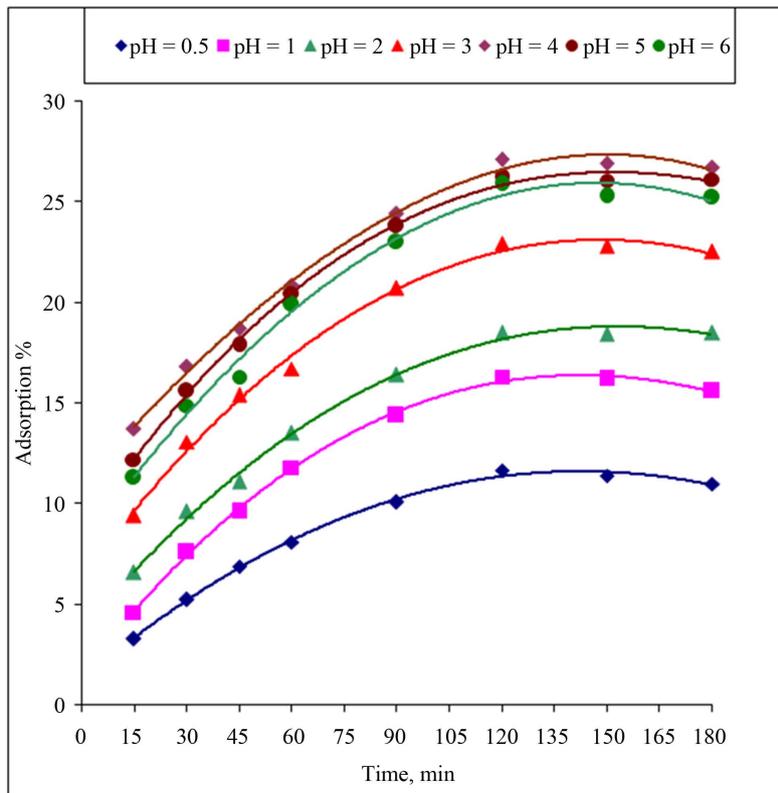


Figure 5. Effect of pH on the removal of Cr (VI) at 293.15 K.

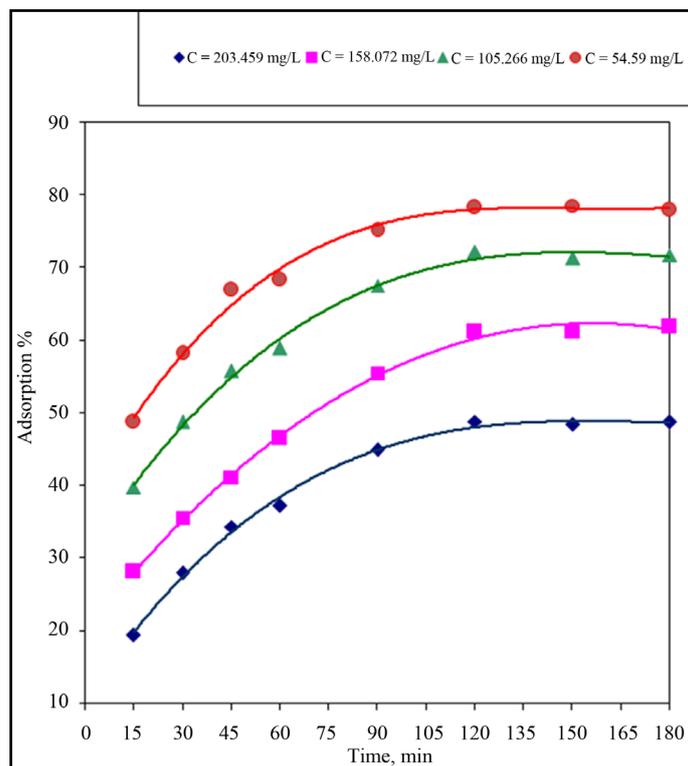


Figure 6. Effect of initial Cd (II) ions concentration on the adsorption at 293.15 K.

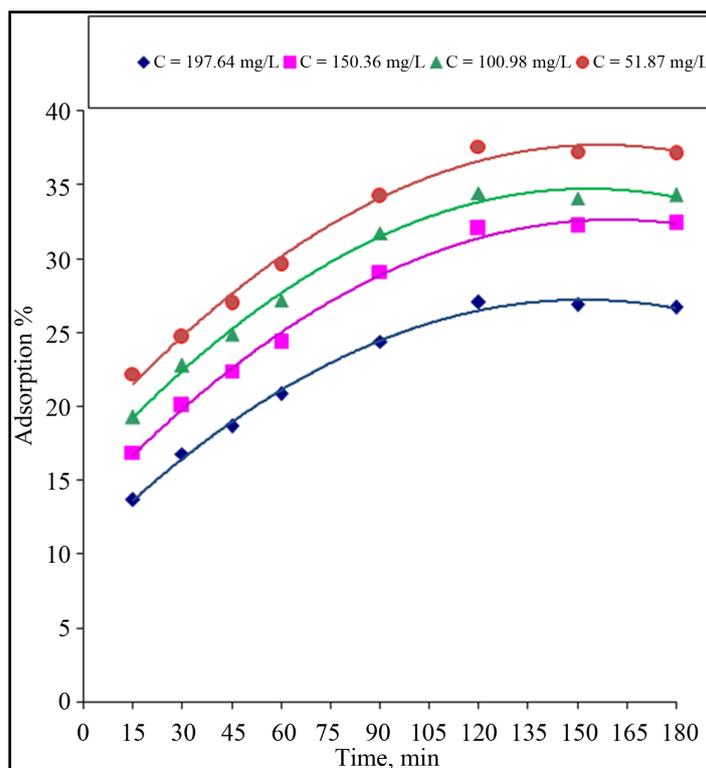


Figure 7. Effect of initial Cr (VI) ions concentration on the adsorption at 293.15 K.

Table 2. Effect of contact time on the rate of adsorption of Cd (II) and Cr (VI).

Time (min)	R % (Cd (II))	R % (Cr (VI))
30	17.30	16.95
60	25.10	22.50
90	38.50	23.50
120	43.62	28.45
150	43.64	28.47
180	43.65	28.46

4.2.4. Effect of Temperature

The temperature dependence of Cd (II) and Cr (VI) adsorption by natural bentonite was studied with a constant metal ion concentration of $50 \text{ mg}\cdot\text{L}^{-1}$ for different temperatures (293.15 K, 303.15 K, 313.15 K, 323.15 K, 333.15 K and 343.15 K). The results of the studies are presented in **Figure 8** and **Figure 9** which showed that adsorption efficiencies of Cd (II) and Cr (VI) decreases with increase in temperature. For example, with increase in temperature from 293.15 K to 343.15 K, the uptake adsorption decreased for Cd (II) from 82.75% to 52.50% and for Cr (VI) from 38.75% to 22.45%. The decrease in percentage of adsorption with rise in temperature may be due to desorption caused by an increase in the available thermal energy [36]. Higher temperature induces higher mobility of the adsorbate causing desorption. This indicates that the adsorption process is spontaneous and exothermic in nature.

4.3. Equilibrium Isotherm Models [37] [38]

To examine the relationship between adsorbent and adsorbate at equilibrium, and to search for the maximum sorption efficiency of adsorbent, sorption isotherm models such as Langmuir and Freundlich isotherms have been applied for Cd(II) and Cr(VI) ions and represented in (**Figures 10-13**) respectively.

The values of the Langmuir parameters Q_0 , b and Freundlich parameters K_f , n and the calculated regression correlation coefficients were reported in **Table 3**.

The Langmuir constants Q_0 and b showed in these results were determined by linear regression and found to be 13.17 and 4.1×10^2 , 12.61 and 0.56×10^2 for Cd (II) and Cr (VI), respectively and the regression coefficients ($r^2 = 0.990$ and 0.997) suggest that the adsorption of Cd (II) and Cr (VI) can be modelled by Langmuir as well as Freundlich model with a slight preference to Langmuir. The adsorption process was also favourable according to Langmuir's dimensionless constant separation factor ($R < 1$).

4.4. Adsorption Kinetics [39] [40]

Various sorption kinetics models have been used to describe the removal of metals from solution, whereas most often used are Lagergren pseudo-first order and pseudo-second order Elovich equations. For evaluating the sorption kinetics of Cd^{2+} ions, pseudo-first order, pseudo-second order and Elovich kinetics models were used to find fit of the experimental data. The results are given in **Tables 4-6**. The kinetic rate constants obtained from these models showed that the Elovich and pseudo-second order equations possess relatively the highest correlation coefficient values (0.984 - 0.998) and (0.989 - 0.978) as a function of increasing values of pH for Cd (II) and Cr (VI). Therefore, it can be concluded that the pseudo-second order model fitted well the adsorption data of Cr (VI) whereas, the Cd (II) adsorption data fitted best the Elovich equation.

4.5. Thermodynamic Study [41] [42]

In order to describe thermodynamic behaviour of the removal of Cd (II) and Cr (IVI) ions onto natural bentonite, thermodynamic parameters including the change in free energy, enthalpy and entropy were calculated from the general Equations (14) and (15).

The values of thermodynamic parameters were given in **Table 7**. The negative value of heat of reaction ΔH° indicated that the sorption is exothermic. On the other hand, the decrease in entropy ΔS° , showing that the metal ions were stable on the solid surface. The values of ΔG found were small and negative indicating that the adsorption of both metal ions onto natural bentonite was spontaneous. However, increasing temperature does not seem to significantly change ΔG .

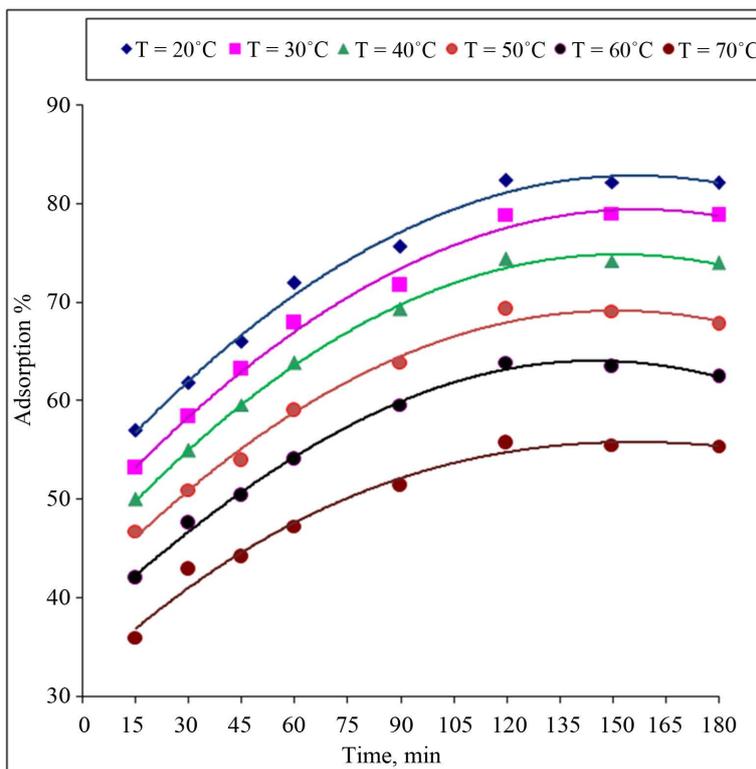


Figure 8. Effect of temperature on the adsorption of Cd (II).

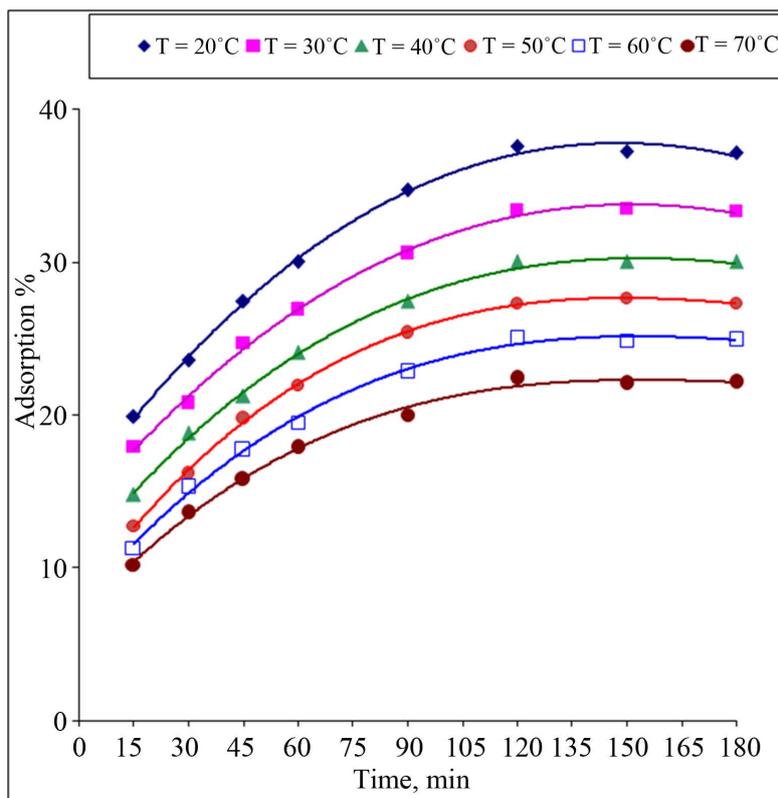


Figure 9. Effect of temperature on the adsorption of Cr (VI).

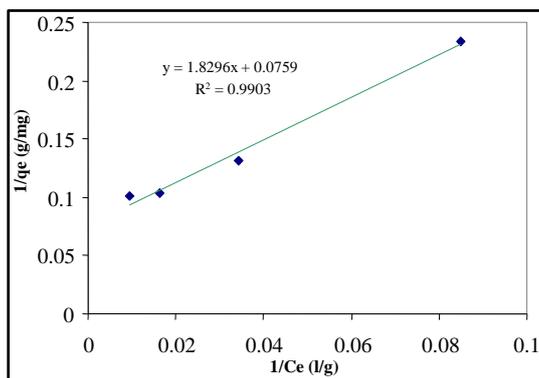


Figure 10. Langmuir Adsorption isotherm of Cd (II) onto natural bentonite at 293.15 K.

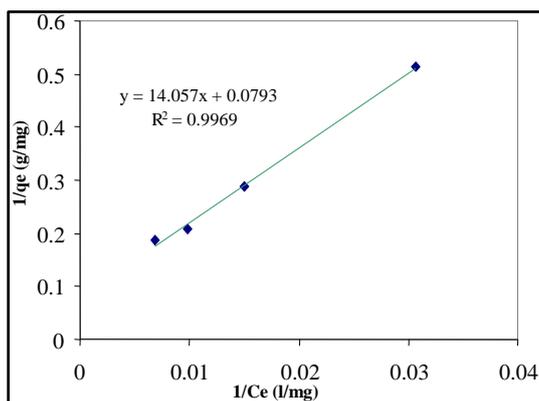


Figure 11. Langmuir Adsorption isotherm of Cr (VI) onto natural bentonite at 293.15 K.

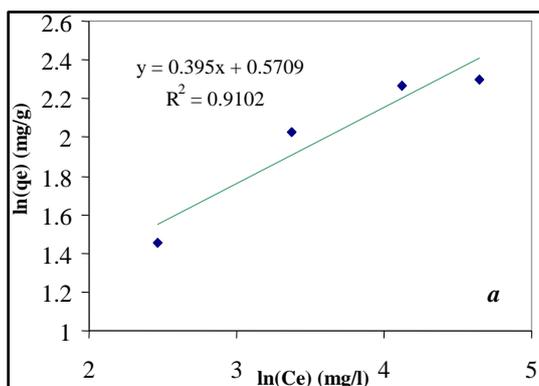


Figure 12. Freundlich adsorption isotherm of Cd (II) onto natural bentonite at 293.15 K.

Table 3. The value of parameters for each isotherm model used at 293.15 K.

Metal ions	Langmuir model				Freundlich model		
	Q_0 ($\text{mg}\cdot\text{g}^{-1}$)	$B \times 10^2$ ($\text{l}\cdot\text{mg}^{-1}$)	R_L	r^2	K_F ($\text{mg}\cdot\text{g}^{-1}$)	n	r^2
Cd (II)	13.17	4.1	0.30	0.990	2.17	3.16	0.910
Cr (VI)	12.61	0.56	0.77	0.997	0.17	1.42	0.979

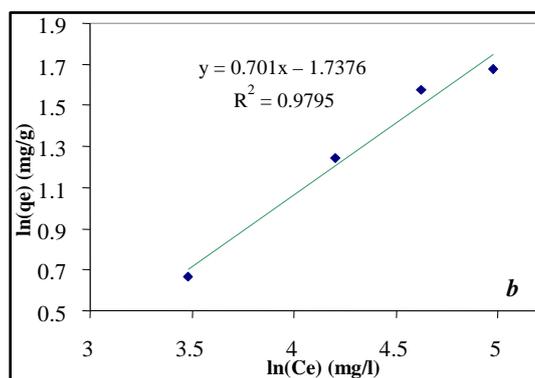


Figure 13. Freundlich adsorption isotherm of Cr (VI) onto natural bentonite at 293.15 K.

Table 4. Kinetic constants (pseudo-first order) for Cd (II) and Cr (VI) adsorption at different pH.

pH	Kinetic constants (pseudo-first order) for Cd(II) adsorption				Kinetic constants (pseudo-first order) for Cr(VI) adsorption			
	$q_{e(\text{exp})}$ ($\text{mg}\cdot\text{g}^{-1}$)	$q_{e(\text{cal})}$ ($\text{mg}\cdot\text{g}^{-1}$)	$K_1 \times 10^{-2}$ (min^{-1})	r_1^2	$q_{e(\text{exp})}$ ($\text{mg}\cdot\text{g}^{-1}$)	$q_{e(\text{cal})}$ ($\text{mg}\cdot\text{g}^{-1}$)	$K_1 \times 10^{-2}$ (min^{-1})	r_1^2
0.5	6.34	5.52	2.53	0.974	2.30	2.46	2.23	0.974
1.0	9.28	7.08	2.579	0.980	3.22	3.58	2.41	0.980
2.0	11.25	7.57	2.74	0.961	3.65	3.61	2.30	0.961
3.0	11.67	8.11	2.87	0.966	4.53	4.07	2.32	0.966
4.0	12.29	7.70	2.51	0.982	5.35	3.93	2.12	0.982
5.0	13.46	8.28	2.74	0.977	5.18	4.27	2.32	0.977
6.0	14.97	9.28	2.97	0.978	5.11	4.30	2.16	0.978

Table 5. Kinetic constants (pseudo-second order) for Cd (II) and Cr (VI) adsorption at different pH.

pH	Kinetic constants (pseudo-second order) for Cd(II) adsorption				Kinetic constants (pseudo-second order) for Cr(VI) adsorption			
	$q_{e(\text{exp})}$ ($\text{mg}\cdot\text{g}^{-1}$)	$q_{e(\text{cal})}$ ($\text{mg}\cdot\text{g}^{-1}$)	$K_2 \times 10^{-2}$ (min^{-1})	r_1^2	$q_{e(\text{exp})}$ ($\text{mg}\cdot\text{g}^{-1}$)	$q_{e(\text{cal})}$ ($\text{mg}\cdot\text{g}^{-1}$)	$K_2 \times 10^{-2}$ (min^{-1})	r_1^2
0.5	6.34	5.52	2.53	0.974	2.30	2.46	2.23	0.989
1.0	9.28	7.08	2.579	0.980	3.22	3.58	2.41	0.988
2.0	11.25	7.57	2.74	0.961	3.65	3.61	2.30	0.977
3.0	11.67	8.11	2.87	0.966	4.53	4.07	2.32	0.966
4.0	12.29	7.70	2.51	0.982	5.35	3.93	2.12	0.977
5.0	13.46	8.28	2.74	0.977	5.18	4.27	2.32	0.984
6.0	14.97	9.28	2.97	0.978	5.11	4.30	2.16	0.978

Table 6. Kinetic constants (Elovich model) for Cd (II) and Cr (VI) adsorption at different pH.

pH	Kinetic constants (Elovich model) for Cd(II) adsorption			Kinetic constants (Elovich model) for Cr(VI) adsorption		
	β ($\text{g}\cdot\text{mg}^{-1}$)	α ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$)	r_1^2	β ($\text{g}\cdot\text{mg}^{-1}$)	α ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$)	r_2^2
0.5	0.57	0.21	0.984	1.25	0.10	0.983
1.0	0.46	0.30	0.993	0.89	0.153	0.988
2.0	0.45	0.42	0.987	0.78	0.33	0.980
3.0	0.42	0.53	0.995	0.88	0.21	0.975
4.0	0.41	0.62	0.996	0.79	0.61	0.968
5.0	0.39	0.75	0.997	0.74	0.47	0.982
6.0	0.37	0.83	0.998	0.72	0.40	0.966

5. Comparison with Other Adsorbents

In order to justify the validity of the Algerian natural bentonite as an effective adsorbent for Cd (II) and Cr (VI) adsorption, we compared our results with other works carried out elsewhere using other adsorbents for similar purpose. We used as a basis of comparison, the maximum adsorption capacities of Cd (II) and Cr (VI) on different adsorbents. The results are reported in **Table 8** including the adsorbent used in this study.

From the results given in **Table 8**, we can observe:

- As for Cd (II), Na-bentonite has a great adsorption capacity 26.2 (mg·g⁻¹) followed by our adsorbent 13.17 (mg·g⁻¹).
- Fe-montmorillonite and bagasse fly ash have the lowest values of adsorption capacities 2.89 (mg·g⁻¹) and 2.0 (mg·g⁻¹) respectively.
- As for Cr (VI), micellar compounds has a slightly higher adsorption capacity than ours 17.89 (mg·g⁻¹) and activated carbon (Merck) has the lowest value of adsorption capacity 0.09 (mg·g⁻¹).

6. Conclusions

According to the results obtained in the adsorption process study of Cd (II) and Cr (VI) on natural bentonite, we can conclude that:

- The natural Algerian bentonite used in this study was found to be an effective and low-cost adsorbent for the adsorption of Cd (II) and Cr (VI) ions from aqueous solutions.
- The kinetic experiments show that the adsorption is rapid and maximum efficiencies adsorption achieved in 120 min.
- The pH of solution has a positive effect, however, the temperature has an inverse effect on adsorption.
- Optimum conditions were found at pH 6 and 5 for Cd (II) and Cr (VI), a concentration of 50 mg·L⁻¹ and temperature 293.15 K.
- The pseudo first-order, pseudo second-order kinetic and Elovich models were used to analyze data obtained for Cd (II) and Cr (VI) adsorption. The results indicated that the pseudo second-order and Elovich equations provided the best correlation for the adsorption data.
- Langmuir and Freundlich, equilibrium isotherms were used to describe the adsorption of Cd (II) and Cr (VI). Langmuir model has better correlation coefficient than Freundlich model.

Table 7. thermodynamic parameters for Cd (II) and Cr (VI) adsorption at the studied temperatures.

	ΔH (kJ·mol ⁻¹)	ΔS (J·mol ⁻¹ ·K ⁻¹)	ΔG (kJ·mol ⁻¹)					
			T = 293.15 K	T = 303.15 K	T = 313.15 K	T = 323.15 K	T = 333.15 K	T = 343.15 K
Cd (II)	-20.58	-17.07	-15.23	-15.06	-14.89	-14.72	-14.55	-14.37
Cr (VI)	-10.10	-1.26	-9.70	-9.69	-9.68	-9.67	-9.65	-9.64

Table 8. Adsorption capacity of Cd (II) and Cr (III) by various adsorbents.

Adsorption capacity of Cd(II) by various adsorbents			Adsorption capacity of Cr(VI) by various adsorbents		
Adsorbent	Q ₀ (mg·g ⁻¹)	Ref.	Adsorbent	Q ₀ (mg·g ⁻¹)	Ref.
Low-grade phosphate	7.5	[43]	Bentonite	0.57	[50]
Fe-montmorillonite	2.89	[44]	Oak sawdust (Quercus coccifera) treated by HCl	1.72	[51]
Kaolinite	9.9	[45]	Activated carbon (Merck))	0.09	[52]
Na-bentonite	26.2	[46]	Activated carbon (BDH)	0.93	[53]
Red mud	10.6	[47]	Iron (III) hydroxide	0.47	[54]
Bagasse fly ash	2.0	[48]	micellar compounds	17.89	[55]
Ca-bentonite	7.3	[49]	Sawdust	2.29	[56]
Natural Algerian bentonite	13.17	Present study	Natural Algerian bentonite	12.61	Present study

- Thermodynamic analysis showed that the adsorption process was exothermic and spontaneous in nature.
- The sorption capacity of bentonite was comparable to the other available absorbents and it was much cheaper.

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