

Modeling of equilibrium isotherms and kinetic studies of Cr (VI) adsorption into natural and acid-activated clays

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Abstract Smectite clay has great potential for the removal of heavy metal ions from aqueous solution. This work aims to develop inexpensive, highly available, effective metal ion adsorbents from clay minerals as alternatives to existing commercial adsorbents. In particular, natural clay was modified with sulfuric acid to yield excellent adsorbent material. The adsorptive interactions of Cr (VI) ions with natural clay and their acid-activated derivative in aqueous solution are investigated in this study. The adsorption experiments were carried out under batch process with Cr (VI) concentration, pH, time, and temperature as the variables. The adsorption was strongly dependent on pH of the solution. Adsorption was very fast at low coverage, and equilibrium was approached within 35 min. The kinetic data were analyzed using different kinetic models. It was shown that the adsorption of Cr (VI) ions could be described by a pseudo-second-order equation and Elovich model. The experimental data were also analyzed using two- and three-parameter isotherm models of adsorption. Thermodynamic parameters such as ΔG^0 , ΔH^0 , and ΔS^0 have been evaluated, and it has been found that the sorption process was spontaneous and exothermic. From all our data, we conclude that the treated clay by sulfuric acid investigated

in this study showed good potential for Cr (VI) ions removal from aqueous solutions.

Keywords Cr (VI) · Adsorption · Acid-activated clay · Modeling · Isotherms · Kinetics

Introduction

Heavy metals are found in water, air, and soil. The major sources of heavy metals in water and soil are wastewater streams from many industrial processes (Olayinka et al. 2007).

The removal of toxic metal ions from wastewater is an important and widely studied research area. One of the heavy metals that have been a major focus in wastewater treatment is chromium. The increasing use of chromium in many industries has led to large amounts of polluted aqueous effluents which contain high levels of chromium. Due to its solubility, it is highly mobile in soil and aquatic environments and readily penetrates plant and animal epidermis where it irritates tissues (Olayinka et al. 2007; Chauhan and Sankaramakrishnan 2011).

In this respect, because of their toxicity applications, trivalent chromium and hexavalent chromium are two common existing oxidation states of chromium found in the environment. Most of the hexavalent compounds are toxic, carcinogenic, and mutagenic, and it can even cause lung cancer also by El-Sikaily et al. (2007) and Li et al. (2008). Major sources of chromium are effluents from electroplating, metal finishing, chromium mining pigments, leather tanning, wood protection, electrical and electronic equipments, manufactures, and catalysis (Mohan and Pittman 2006). Treatment of the chromium effluents poses a serious problem to ecosystems and cause great public concern. Therefore, it is necessary to eliminate chromium from the environment, and it is also essential that

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the effluents should be controlled before discharging hexavalent chromium into aquatic environments in order to prevent the deleterious impact of Cr (VI) on the ecosystem and public health (Rengaraj et al. 2001).

For this purpose, researchers in recent years investigated various physicochemical methods for removal of chromium and other heavy metals. The most important of these techniques include chemical precipitation, filtration, ion exchange, reverse osmosis, and membrane systems. However, all these techniques have their inherent advantages and limitations in application. In the last few years, adsorption has been shown to be an alternative method for removing dissolved metal ions from liquid wastes (Bayat 2002). The adsorption method is commonly used and several studies reported on various adsorbents (Olayinka et al. 2007; Chauhan and Sankaramakrishnan 2011; El-Sikaily et al. 2007).

The economic issue and the need for regeneration of used adsorbents forced researchers to investigate other inexpensive and low-cost adsorbents for the removal of chromium (Shen et al. 2012; Sahinkaya et al. 2012; Prigione et al. 2009; Sari et al. 2011). However, the literature is still insufficient to cover this problem, and more work and investigations are needed to deal with other locally available adsorbents to eliminate Cr (VI) from industrial wastewater samples with different compositions and characteristics (Sharma and Bhattacharyya 2004).

Clay minerals are effective adsorbents for the removal of heavy metals, owing to their high specific surface area with unique swelling, intercalation, and ion exchange properties, low cost and ubiquitous presence in most soils. To increase the adsorption capacity, clays are modified in various ways such as treatment by inorganic and organic compounds, acids, and bases (Sharma and Weng 2007). It was reported that heat treatment also enhanced the adsorption capacity of some clays (Lee et al. 2010). Acid or other reagents are used for activation of clays and are due to their high specific surface area, high chemical and mechanical stabilities, and various surface and structural properties. The study of the adsorption of Cr (VI) from aqueous solutions by natural or treated clay minerals was the subject of several investigations (Weng et al. 2008; Fritzen et al. 2006; Maryuk et al. 2005; Benhammou et al. 2007; Huang et al. 2008), but no study to date has considered the adsorption of Cr (VI) onto south Tunisian clay. Therefore, it was the objective of the present work to investigate the amenability of removal of Cr (VI) anionic species by smectite. The effects of various parameters affecting adsorption like contact time, initial metal ion concentration, and pH have been studied, and data have been presented using adsorption kinetic models. Two- and three-parameter isotherm models were used for the description of adsorption data obtained in this study.

Materials and experimental methods

Several factors influence the removal of heavy metals from water by the adsorption process, e.g., type and concentration of ion solution, adsorptive materials, pH, time, and temperature. The experiments were carried out by taking these as the variables and were investigated by varying any one of the process parameters and keeping the other parameters constant.

Materials

In the present work, green clay selected from site of Djebel EL'Aidoudi of "Hamma" area, located in south Tunisia, was used as raw material.

The as-received material was purified by aqueous dispersion and decantation. After a purification process, the clay remained free of quartz and the fraction with particle size less than 40 μm was separated and subjected to activation.

Acid activation

Acid activation was carried out with sulfuric acid H_2SO_4 in a jacketed glass reactor equipped with a reflux condenser, a thermometer, and a stirrer. At the end of each experiment, the solid content was immediately filtered, washed with water until the washing water was neutral, and dried.

The activated sample was obtained according to the following procedure: 100 g of material clay micro-powder was mixed with an aqueous H_2SO_4 solution from Scharlau Chemie (acid concentration of 35 %) in a jacketed glass reactor regulated at fixed temperature (96.6 °C) by a thermostatic bath for 3.75 h under mechanical stirring at 200 rpm and then washed by distilled water for many times until pH was achieved. The obtained samples were dried at 60 °C for 24 h.

Batch adsorption studies

Batch experiments, a technique commonly used to obtain data on the removal efficiency of a given adsorbent under static conditions was selected as an appropriate technique in the current study, with various natural and activated clays were conducted to investigate the parametric effects of initial adsorbate concentration on Cr (VI) adsorption. Chromium samples were prepared, a known quantity of potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$ (reagent grade from Merck, Darmstadt, Germany), by dissolving them in double-distilled water and used as a stock solution and diluted to initial concentration (range 10 to 100 mg/l), 50 ml of Cr (VI) solution of known concentration (C_0), and initial pH was taken in a 100-ml screw-cap conical flask with a required 0.05 g amount of adsorbent and was agitated at a speed of 200 rpm in a thermostatic shaker bath at 20 °C for a specified period of contact time. Then, the solution was filtered through a 0.45- μm membrane filter. The

initial pH of the solution was adjusted by using either 0.1 N NaOH or 0.1 N HCl.

All reagents used were of analytical grade, and all solutions were prepared in ultrapure water with a minimum resistivity of 18 MΩ cm obtained from a Milli-Q Millipore system (Billerica, MA, USA).

A colorimetric method was used to determine the remaining concentrations of Cr (VI) in the samples. The pink complex formed between 1,5-diphenylcarbazide and Cr (VI) was measured at 540 nm using a UV–visible spectrophotometer (Bandegharaei et al. 2010).

All experiments were carried out in triplicate, and the concentrations given are average values.

The filtrate was analyzed for the remaining Cr (VI) concentration. The amount of Cr (VI) adsorbed in (mg/g) at time t was computed by using the following equation:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where q_e is the amount of Cr (VI) ions adsorbed on the clay (mg/g), C_0 is the initial Cr (VI) ion concentration in solution (mg/l), C_e is the equilibrium Cr (VI) ion concentration in solution (mg/l), V is the volume (l), and m is the amount of clay (g).

Results and discussion

Characterization of the adsorbent

The X-ray diffraction analysis indicated that the mineralogical compositions of clays are mainly composed of smectite, quartz, and smectite-calcite (Fig. 1).

After acid activation, the disappearance of the characteristic peak of the smectite at 9.7 Å was observed (Fig. 1). They recommend that this phenomenon is due to treatment heat at high temperatures. This generates a burst of leaves which in turn changes the structure of the clay mineral (Weng et al. 2008). According to Table 1, the chemical analysis showed that the main constituents of clay are silica, alumina, and iron oxides. After acid activation, percentage of both the exchangeable ions and the octahedral cations decreased while that of silica increased due to its lower solubility in acid solution (Table 1). The acid-activated clay shows slowly increases in specific surface area (Table 1).

Effect of parameters on the adsorption of Cr (VI) onto clay

Various parameters for the effective removal of Cr (VI) from aqueous solutions by using natural smectite clay and their activated form as adsorbent were studied.

Effect of shaking time

The time-dependent behavior of chromium was measured by varying the equilibrium time between the adsorbate and adsorbent in the range of 5 to 200 min. The initial concentration of metal ions was varied from 20 to 40 mg/l. The pH values were kept at 5 and 4.2 for natural and activated clays, respectively, as while the amount of clay added was 1 g/l.

The results of the effects of shaking time and initial Cr (VI) ion concentration on adsorption from solution when using clay are shown in Fig. 2. It is found that the equilibrium is reached quickly only 60 min for the adsorption on natural clay and 30 min for their activated form. The removal of Cr (VI) increases rapidly with time, and then, it continues at a relatively slower rate and reaches saturation in about 15 min. Initially, the removal of Cr (VI) is rapid but it gradually decreases with time until it reaches equilibrium. It seems that at higher concentrations, there occur an initial fast adsorption of the metal ions into the clay, but some of it is lost again before equilibrium sets in. As time passed, the metal ion remained bound to the clay, showing strong metal-clay interaction.

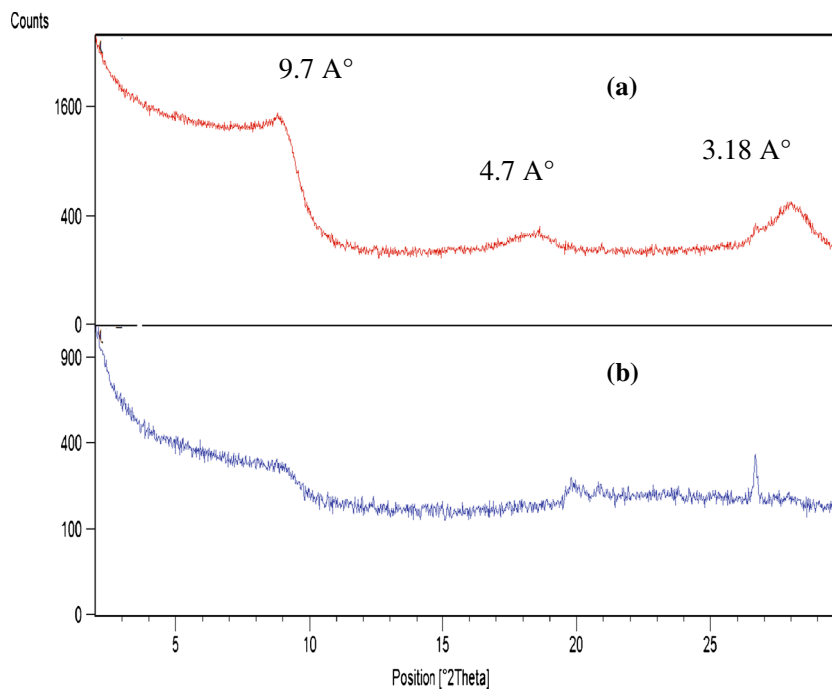
Effect of metal ion concentration

The amount adsorbed is highly dependent on the initial concentration of the chromium ions. This finding is in agreement with recent work by Shukla et al. (Yu et al. 2003), who found the same behavior by studying the adsorption capacity of maple sawdust for the removal of Cr (VI) from aqueous solutions.

The effects of the initial ion concentration on the removal of the Cr (VI) onto the adsorbents (natural and activated smectites) were investigated by changing the initial Cr (VI) concentration in the range of 20 to 40 mg/l at an optimized pH. The results are shown in Fig. 3. The removal of the Cr (VI) ion was found to be dependent on the initial concentration. At lower concentrations, all the Cr (VI) ions present in the solution would interact with the binding sites and facilitate about 96 % metal ion removal. At a higher concentration, more Cr (VI) ions are left unabsorbed in the solution, due to the saturation of the binding sites. This is due to the increase in the number of ions competing for available binding sites in the adsorbent (Dubey and Gopal 2007).

The initial rapid rate of adsorption was maybe due to the availability of the positively charged surface of the adsorbent for anionic Cr (VI) species present in the solution. The later slow adsorption rate was maybe due to the electrostatic hindrance caused by already adsorbed negatively charged adsorbate species and the slow pore diffusion of the ions (Pandey et al. 2010). A higher initial concentration provides an important driving force to overcome all mass transfer resistances of the pollutant between the aqueous and solid phases, thus increases the uptake. Uptake of the Cr (VI) also increased with

Fig. 1 The X-ray diffraction patterns of natural (a) and acid-activated clays (b)



increasing the initial metal concentration tending to saturation at higher metal concentrations (Malkoc and Nuhoglu 2007).

Effect of pH on metal ion removal

In the adsorption studies, an optimization of the pH value plays a vital role for the adsorption medium. The effect of pH on the adsorption of Cr (VI) ions by natural and activated clays using different pH values ranging from 3 to 9 is illustrated in Fig. 4. The results show that the sorption is strongly pH-dependent. Therefore, the pH 5 and 4.2 were selected for

the other entire sorption test in this work. Meanwhile, at higher and lower pH, the capacities of chromium ion adsorption into the two types of adsorbents used in this study show a decline.

In general, a decrease in ion uptake at acidic pH is due to an increase of competition between hydrogen and metal ions for the same adsorption sites. However, an increase in alkalinity enhances metal adsorption rate, due to the predominant presence of hydrated species of heavy metals, changes in surface charge, and the precipitation of the appropriate salt. Therefore, there is an optimum pH in which the competition of hydrogen ions is minimized and metal ion precipitation is avoided, thus enhancing metal adsorption.

In acid solution, the main chromium species are HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, and H_2CrO_4 , so the attraction between these anionic

Table 1 Physicochemical properties of the studied clay samples

Chemical composition (% by weight)	Natural clay	Acid-activated clay
SiO_2	47.70	50.12
Al_2O_3	18.71	18.26
Fe_2O_3	12.11.33	9.12
CaO	2.59	1.93
MgO	2.59	1.89
K_2O	1.05	0.87
Na_2O	0.96	0.17
P_2O_5	0.32	0.02
SO_3	0.96	4.91
LOI	14	12
Structural parameters		
Specific surface of BET (m^2/g)	86	167
Total pore volume (cm^3/g)	0.1394	0.1986
Mean pore diameter (Å)	40.53	49.03

LOI loss on ignition

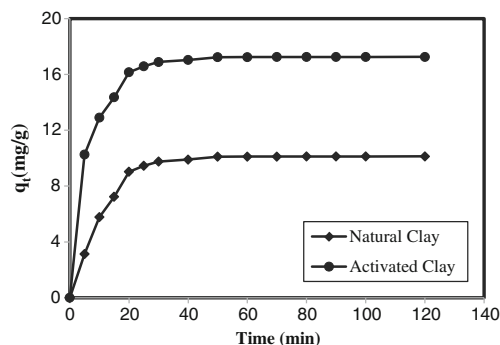
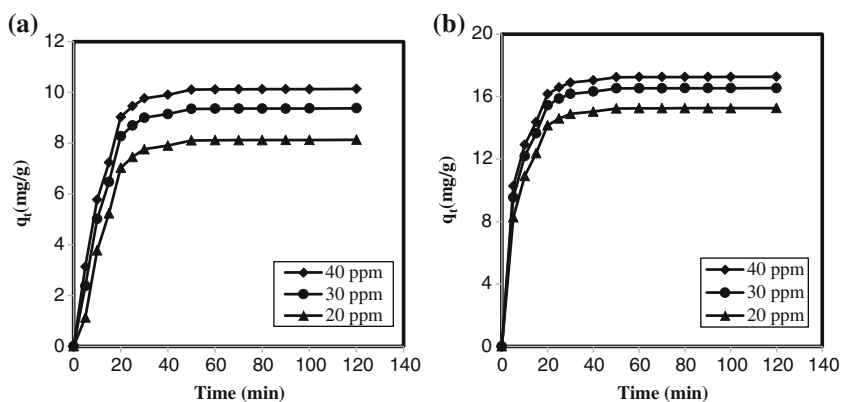


Fig. 2 Effects of contact time on the removal of Cr (VI) into natural and activated clays (dose 1 g/l, temperature 20 °C, agitation speed 200 rpm, and initial concentration 20 mg/l)

Fig. 3 Effects of initial chromium concentration into natural (a, pH=5) and acid-activated clays (b, pH=4.2) (dose 1 g/l, temperature 20 °C, and agitation speed 200 rpm)



species and positively charged adsorbent surface had been strongly increased (Olayinka et al. 2007).

In an alkaline solution, other negative ions, such as OH⁻, should compete with the major anion, CrO₄²⁻ ion, for the sorption sites on the adsorbent (Bhattacharyya and Sen Gupta 2006). So, the increase of pH suppresses the hydrolysis of chromium ions which causes a decrease in the adsorption amount. It is clear from Fig. 5 that acid activation increases the number of sites responsible for chromium adsorption and at any pH; the amount of Cr (VI) adsorbed per unit mass of acid-activated clay had a higher adsorption capacity compared to the non-activated clay.

Effect of temperature

To examine the effect of temperature effect on the Cr (VI) ion retention on both natural and activated clays, the same conditions were kept, contact time 2 h and Cr (VI) ion concentration of 40 mg/l, while changing the temperature from 20 to 65 °C. According to Fig. 5, when the temperature increases, the Cr (VI) adsorption capacities decrease, confirming that adsorption is an exothermic phenomenon. The same effect was observed for the activated form of kaolinite and montmorolinite clays (Eloussaief et al. 2011; Akar et al. 2009).

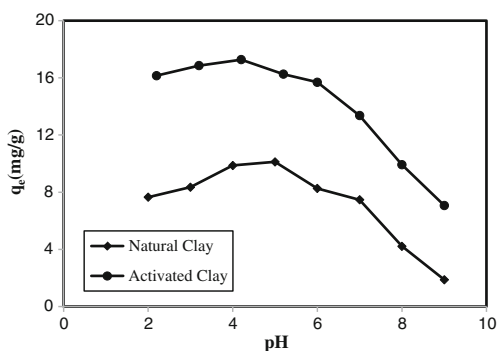


Fig. 4 Effects of pH on adsorption of Cr (VI) onto natural and acid-activated clays (dose 1 g/l and agitation speed 200 rpm)

Theoretical basis

Adsorption kinetic models

The kinetics of the adsorption process was studied by carrying out a set of experiments at constant temperature and monitoring the amount adsorbed with time. The sorption kinetic data for Cr (VI) on the various adsorbents studied were analyzed in terms of pseudo-first-order and pseudo-second-order sorption equations, intraparticle diffusion model, and Elovich model.

Pseudo-first-order kinetic model Pseudo-first-order kinetics using the Lagergren equation is applied (Ozturk and Kavak 2005).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

where q_e and q_t are the values of amount adsorbed per unit mass at equilibrium and at any time t and k_1 is the pseudo-first-order adsorption rate constant. The values of k_1 can be obtained from the slope of the linear plot of $\ln(q_e - q_t)$ versus t .

Second-order kinetic model The pseudo-second-order kinetic model was used to describe the sorption of metal ions (Soliman et al. 2011). It is applied when it is found that $\ln q_e$ is not equal to the intercept of the first-order plot as obtained from Eq. (2) by using the equation

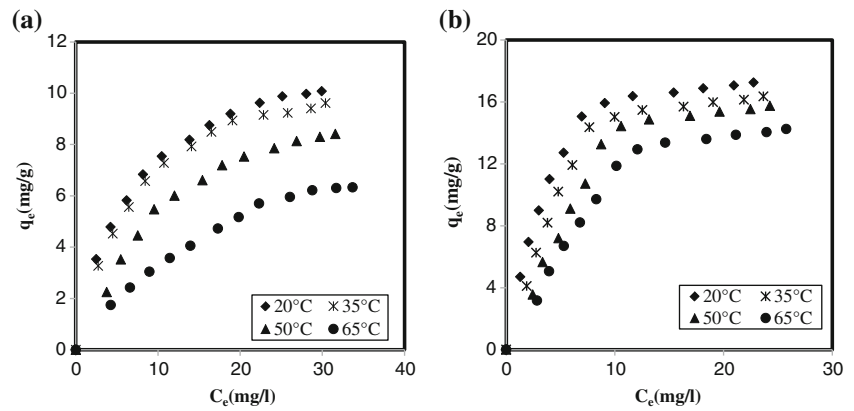
$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{1}{q_e} \cdot t \tag{3}$$

where $k_2 q_e^2$ is described as the initial adsorption rate at time 0.

The plot of $\frac{t}{q_t}$ versus t gives a straight line, which allows computation of q_e and k_2 .

The values of rate constants k_1 and k_2 obtained graphically for both adsorption models are listed in Table 2. The results show that the pseudo-second-order model provided a better approximation to the experimental kinetic data than the pseudo-first-order model (Fig. 6).

Fig. 5 Effects of temperature into natural (a, pH=5) and acid-activated clays (b, pH=4.2) (dose 1 g/l and agitation speed 200 rpm)



Again, correlation coefficients in Table 2 of second-order equation for all concentrations are higher than those of other kinetic models, and its calculated equilibrium sorption capacities fit well the experimental data.

Intraparticle diffusion model The possibility of intraparticle diffusion was explored by using an intraparticle diffusion model. It is of major concern because it is rate determining step in the liquid adsorption systems. The intraparticle diffusion that varies with square root of time is described as (Karthikeyan et al. 2005)

$$q_t = k_p \sqrt{t} + C \tag{4}$$

where C is the constant and k_p is the intraparticle diffusion rate constant ($\text{mg/g min}^{1/2}$), q_t is the amount adsorbed at a time (mg/g), and t is the time (min). The intraparticle diffusion rate constant was determined from the slope of the linear gradients of the plot q_t versus $t^{1/2}$. The rate constant of intraparticle diffusion at

different concentrations is shown in Table 2. The intraparticle diffusion process is controlled by the diffusion of ions within the adsorbent.

The mechanism of solute transfer to the solid includes diffusion through the fluid film around the adsorbent particle and diffusion through the pores to the internal adsorption sites. Initially, the concentration gradient between the film and the solid surface is large, and hence, the transfer of solute onto the solid surface is faster.

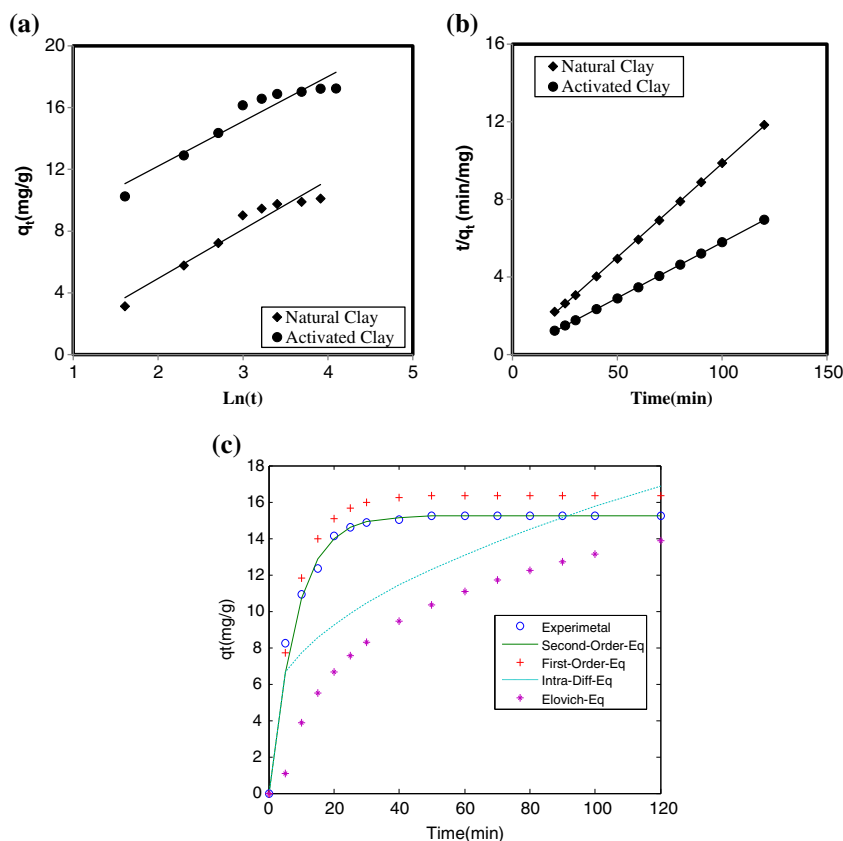
As time increases, intraparticle diffusion becomes predominant. Hence, solute takes more time to transfer from solid surface to internal adsorption sites through the pores (Babu and Gupta 2008).

Elovich model Elovich equation is one of the most useful models for describing the kinetic adsorption and is also used successfully to describe second-order kinetics, assuming that the actual solid surfaces are energetically heterogeneous, but

Table 2 Kinetic models for the adsorption of chromium ions into natural and acid-activated clays at various concentrations

Kinetic models	Parameters	Natural clay			Acid-activated clay		
		20 (mg/l)	30 (mg/l)	40 (mg/l)	20 (mg/l)	30 (mg/l)	40 (mg/l)
Pseudo-first order	$q_{e\text{calc}}$ (mg/g)	11.846	12.629	17.76	16.346	12.025	12.403
	k_f (min^{-1})	0.109	0.267	0.304	0.128	0.111	0.114
	R^2	0.973	0.979	0.983	0.959	0.975	0.978
Pseudo-second order	$q_{e\text{exp}}$ (mg/g)	8.12	9.30	10.12	15.25	16.500	17.200
	$q_{e\text{calc}}$ (mg/g)	8.403	9.615	10.4167	15.625	16.950	17.544
	k_2 (g/mg min)	0.047	0.048	0.049	0.0512	0.051	0.0524
Elovich equation	R^2	0.999	0.999	0.999	0.999	0.999	0.999
	β (g/mg)	0.284	0.344	0.313	0.344	0.376	0.345
	α (mg/g min)	1.049	1.739	2.022	13.25	28.632	26.408
Intra-particle diffusion	R^2	0.962	0.909	0.937	0.909	0.883	0.909
	k_p (mg/g min)	1.89	1.68	1.72	2.107	1.72	2.107
	C (mg/g)	0.321	0.262	0.249	4.021	6.659	6.021
	R^2	0.974	0.962	0.894	0.962	0.894	0.962

Fig. 6 Plots of sorption kinetic equations for sorption of Cr (VI) into natural and acid-activated clays. The Elovich equation (a), the pseudo-second order (b), and the comparison between the measured and kinetic modeled time profiles (c)



the equation does not propose any definite mechanism for adsorbate–adsorbent which the linear form of this equation is given as (Ozacar and Sengil 2005)

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \tag{5}$$

where α is the initial adsorption rate (mg/g min) and the parameter β is related to the extent of surface coverage and activation energy for chemisorption (g/mg).

Table 2 lists the kinetic constants obtained from the Elovich equation. It will be seen from the data that the values of α and β varied as a function of the initial chromium concentration. Thus, on increasing the initial Cr (VI) concentration from 20 to 40 ppm, the value of α increased from 1.049 to 2.022 (mg/g min) and from 13.25 to 26.408 (mg/g min), and the value of β increased from 0.284 to 0.313 (g/mg) and from 0.344(g/mg) to 0.345(g/mg) for natural and activated clays, respectively. Significant observation is that α increased by ~12 times from natural to activated clays and the other coefficient, β , did not show much variation for all the four adsorbents.

These values indicated rapid uptake of Cr (VI) on the clay surface before coverage becomes appreciable. If the interactions are carried out with a sufficiently large amount of the clay, the surface area available will be very large, giving rise to considerably bigger uptake of the metal ions in a very short

time interval. This will enhance the overall rate many times as has been observed by other workers in equivalent situations (Lakshmi and Srinivasan 2004).

Again, in this case, the linear correlation coefficient values obtained from Elovich equation were in the range of 0.88–0.96 for chromium initial concentration of 20–40 mg/l (Fig. 6) for both natural and acid-activated clays and once more demonstrated a high degree of correlation between the experimental data and the theoretical data predicted by the Elovich model.

Kinetic model results

A comparison of calculated and measured results for 20-mg/l initial chromium concentration is shown in Fig. 6. The pseudo-second-order equation provides the best correlation for all of the sorption processes, whereas the Elovich equation also fits the experimental data well. The pseudo-first-order and intraparticle equations do not give a good fit to the experimental data for the sorption of chromium into both natural and acid-activated clays. The kinetics of Cr (VI) adsorption onto smectite and their acid-activated forms, as expected, are not a simple process, and no definite kinetic mechanism could be proposed. The rates are very close to second-order kinetics, but other processes may also be operating simultaneously, in

which the number of adsorption sites on the clay surface and the number of Cr (VI) ions in the liquid phase determine the kinetics. Depending on pH, different chromium species that may be held to the clay surface at appropriate ion exchange site suggest any particular mechanism of interaction.

Adsorption isotherm

Adsorption isotherms, which are the presentations of the amount of solute adsorbed per unit of adsorbent, as a function of equilibrium concentration in bulk solution at constant temperature were studied in Fig. 7. If a quantity q_e of solute is absorbed by a porous solid adsorbent at constant temperature and the steady state equilibrium concentration, then the function q_e describes the adsorption isotherm. It shows the adsorption isotherms for the Cr (VI) adsorption on natural and activated clays. The isotherm rises in the initial stages with higher slope at low C_e and q_e values. This indicates that, initially, there are numerous readily accessible sites. At higher C_e values, a plateau occurs. This confirms the monolayer coverage of Cr (VI) onto natural and activated clay particles. A variety of isotherm equations have been in use, some of which have a theoretical foundation and some being of mere empirical nature.

Equilibrium isotherm modeling

The isotherm equations describe the equilibrium relationship between the amount of the adsorbed metal ions and the remaining concentration in the liquid phase. It gives important information about the main mechanisms involved in the removal of heavy metal.

In this study, the adsorption equilibrium data for Cr (VI) into natural and activated clays were analyzed using program MATLAB 7.9, to fit the two- and three-parameter isotherm models.

The experimental values of q_e and C_e are initially treated with the models in order to determine the equation parameters, and the isotherms are reconstituted using the determined values.

Langmuir isotherm Langmuir isotherm model is based on the assumption of monolayer adsorption, assuming that all surface sites are energetically identical and surface itself is homogeneous (Eloussaief et al. 2011). It also assumes that intermolecular forces decrease rapidly with the distance from the adsorption surface.

Langmuir isotherm is expressed as

$$q_e = \frac{q_m k_l C_e}{1 + k_l C_e} \quad (6)$$

The above equation can be rearranged to its linear form.

$$\frac{C_e}{q_e} = \frac{1}{q_m k_l} + \frac{C_e}{q_m} \quad (7)$$

Both q_m and k_l could be determined from the slope and intercept of the linear plot C_e/q_e against C_e , respectively. C_e is the equilibrium concentration of Cr (VI) ion (mg/l), q_e is the adsorbed amount of Cr (VI) (mg/g), q_m (mg/g) is the maximum adsorption capacity, and k_l is the Langmuir constant related to the adsorption energy, especially the adsorption enthalpy (Kundu and Gupta 2006).

Our experimental data were fitted to the Langmuir isotherm to calculate the maximum adsorption capacity of the studied clay samples. The results indicated that higher removal efficiency was achieved by activated clay sample (Table 3). The maximum adsorption capacity (q_m) was 12.5 (mg/g) and 19.23 (mg/g) for natural and activated clays, respectively. This may indicate that the acid treatment of the collected clay sample enhanced its textural properties that would contribute to the higher adsorptive capacities. Furthermore, the high coefficients of determination R^2 further confirmed that our experimental data fit better to the Langmuir model in Fig. 7. This is indicative of the homogenous clay surface as supported by k_l values were 0.149 and 0.429 ($l \text{ mg}^{-1}$) for natural and activated clays, respectively, at 20 °C.

The Langmuir isotherm can be expressed in terms of the dimensionless constant (R_l) defined as (Aluyor et al. 2009)

$$R_l = \frac{1}{1 + k_l C_0} \quad (8)$$

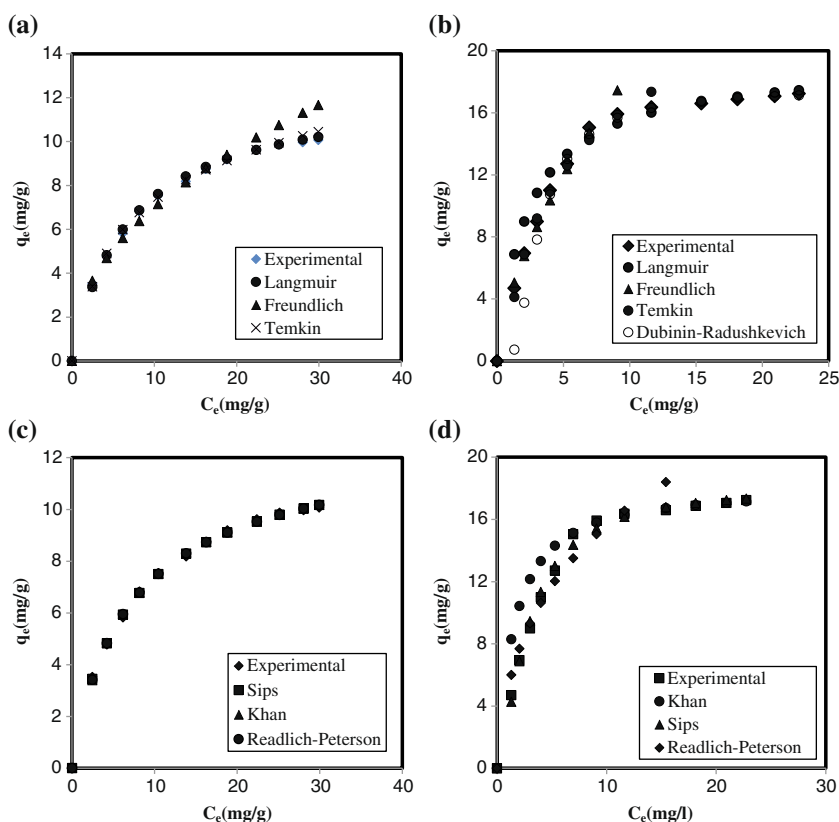
where C_0 is the initial metal concentration. The value of R_l indicates whether the adsorption process is favorable as follows:

- $R_l > 1$ unfavorable adsorption
- $R_l = 1$ linear
- $0 < R_l < 1$ favorable
- $R_l = 0$ irreversible.

Therefore, our results indicated that R_l ranged between 0 and 1 for the adsorption of Cr (VI) on natural and activated clays, indicating a favorable and high adsorption (Table 5). According to the values of the dimensionless parameter, R_l is 0.173 and 0.085 for natural and activated clays that is consistent with the requirement for favorable adsorption. This is in great agreement with the findings regarding to R_l values (Babu and Gupta 2008).

Freundlich isotherm Freundlich isotherm describes multilayer adsorption on energetically heterogeneous surfaces. It is an empirical equation suitable for high and middle range of solute concentration but not for low concentrations. Freundlich

Fig. 7 Experimental and predicted isotherm models of Cr (VI) into natural (a two parameter and c three parameter) and acid-activated clays (b two parameter and d three parameter)



isotherm is usually described by the following equation (Babel and Kurniawan 2004):

$$q_e = k_f C_e^{1/n} \tag{9}$$

This equation can be arranged in its linear form.

$$\ln(q_e) = \frac{1}{n} \ln(C_e) + \ln(k_f) \tag{10}$$

where k_f and n are the Freundlich constants related to the adsorption capacity and intensity of adsorption, respectively. K_F and n were determined from the linear plot of $\ln q_e$ versus $\ln C_e$.

Our data showed a good fitting to the Freundlich model in Fig. 7. The high correlation coefficient $R^2 > 0.95$ and $R^2 > 0.97$ for natural and activated clays, respectively, may confirm this hypothesis.

The results in Table 3 appeared that the value of $1/n$ is less than unity, indicating that the Cr (VI) is favorably adsorbed by both natural and activated clays.

Temkin isotherm The derivation of the Temkin isotherm assumes that due to adsorbate/adsorbent interaction, the heat of

adsorption decreases linearly rather than logarithmically, as implied in the Freundlich equation (Kim et al. 2004).

The Temkin isotherm is usually applicable for a heterogeneous liquid and solid interface. It is given in the following:

$$q_e = \frac{RT}{b} \ln(A) + \frac{RT}{b} \ln(C_e) \tag{11}$$

where b is the adsorption heat (kJ/mol) and A is the equilibrium binding constant (l/g) corresponding to the maximum binding energy. The results presented in Table 3 indicated that a high value of b shows a fast sorption of adsorbate at initial stage. Similarly, a low value of A is related to weak bonding of adsorbate onto the medium. Based on this model, the orders of adsorption heats were 0.861 and 0.404 kJ/mol for activated and natural smectite clays, respectively, showing that the highest sorption of chromium at initial stage was onto natural clay rather than others. On the other hand, the lowest value of A was observed for natural clay rather than activated form, indicating a weak bonding of chromium on natural clay (Fig. 7).

Dubinin–Radushkevich model This model has been used instead of Langmuir isotherm, since it is more general than the Langmuir model, as its deviations are not based on ideal

Table 3 Adsorption isotherm constants of two- and three-parameter models for chromium adsorption onto natural and acid-activated Tunisian clays

Isotherm models	Parameters	Natural clay				Acid-activated clay			
		20 °C	35 °C	50 °C	65 °C	20 °C	35 °C	50 °C	65 °C
Langmuir	q_m (mg/g)	12.5	11.904	11.949	11.11	19.230	18.518	17.241	16.129
	R_l	0.173	0.200	0.246	0.399	0.085	0.105	0.078	0.111
	k_l (l/mg)	0.149	0.1433	0.0874	0.043	0.429	0.339	0.473	0.319
	R^2	0.997	0.998	0.997	0.988	0.999	0.993	0.998	0.998
Freundlich	$1/n$	0.465	0.510	0.565	0.507	0.636	0.716	0.944	0.881
	k_f (l/mg)	2.401	2.079	1.419	1.111	4.288	2.995	1.648	1.439
	R^2	0.995	0.984	0.974	0.950	0.981	0.946	0.986	0.971
Dubinin–Radushkevich	E (kJ/mol)	0.666	0.944	0.804	0.570	1.613	1.718	1.020	0.934
	β (mol ² /kJ ²)	9.007	4.486	6.183	12.31	1.537	1.355	3.842	4.585
	q_m (mg/g)	10.69	9.497	7.950	6.456	17.426	17.218	16.560	14.805
	R^2	0.998	0.966	0.979	0.937	0.989	0.991	0.985	0.981
Temkin model	A (l/mg)	1.339	1.0705	1.067	0.366	1.5825	1.124	1.015	1.431
	b (kJ/mol)	0.861	0.8687	1.114	1.085	0.404	0.4326	0.508	0.682
	R^2	0.997	0.997	0.982	0.989	0.993	0.957	0.905	0.860
Sips model	q_{ms} (mg/g)	13.01	11.230	9.673	10.82	18.094	16.078	15.711	14.092
	m_s	0.157	1.1245	1.404	1.015	1.5048	3.5609	2.8582	3.9520
	k_s (l/mg)	0.919	0.1269	0.050	0.043	0.2083	0.0048	0.0114	0.0005
	R^2	0.999	0.999	0.999	0.997	0.9966	0.9869	0.986	0.9954
Khan model	q_m (mg/g)	10.83	17.204	9.354	6.317	19.692	24.267	29.01	30.648
	b_k	0.179	0.0879	0.107	0.083	0.5720	0.230	0.1517	0.0992
	a_k	0.942	1.2086	0.880	0.740	1.0244	1.122	1.2482	1.3508
	R^2	0.999	0.9992	0.994	0.996	0.9916	0.9505	0.9771	0.9796
Readlich–Peterson	k_{RP} (l/g)	2.003	1.7687	0.744	0.976	12.445	10.500	5.508	4.020
	P_e (l/mg)	0.189	0.1636	0.0179	0.491	1.3697	0.5910	0.2576	0.2922
	g	0.957	0.9720	1.000	0.591	0.7128	1.000	1.000	0.936
	R^2	0.999	0.9978	0.9979	0.9932	0.9696	0.994	0.9731	0.9253

assumptions such as equipotential of sorption sites, absence of steric hindrances between sorbed and incoming particles, and surface homogeneity on microscopic level (Monika et al. 2009).

The linear form of this isotherm model is represented by this equation (Agrawal et al. 2008).

$$\ln(q_e) = \ln(q_s) - \beta \varepsilon^2 \quad (12)$$

where q_s is the theoretical maximum capacity (mg/g) and it is related to the degree of sorbate sorption by the sorbent surface, β is the D–R model constant (mol²/kJ²), and ε is the Polanyi potential equal to

$$\varepsilon = RT \left(1 + \frac{1}{C_e} \right) \quad (13)$$

The plots of $\ln q_e$ versus ε^2 yielded straight lines and indicate a good fit of the isotherm to the experimental data. The values of q_s and β calculated from the intercept slopes of the

plots, respectively, are shown in Table 3. According to these results, the highest value of q_s was observed for activated clay with sulfuric acid, showing higher sorption capacity of activated adsorbent compared to natural form (Fig. 7).

The mean free energy E (kJ/mol) is a parameter used in predicting the type of adsorption mechanism; it can be calculated using the following relationship:

$$E = \sqrt{1/2\beta} \quad (14)$$

When the E value is less than 8 kJ/mol, it indicates physical adsorption. When E is between 8 and 16 kJ/mol, it indicates the ion exchange, and when E is between 20 and 40 kJ/mol, it indicates chemisorptions (Marjanovic et al. 2011).

The calculated value of E for this study is below 8 kJ/mol and is an indication of physico-sorption. This constant gives an idea about the mean free energies which were valued as 0.666 and 1.613 kJ/mol for natural clay and activated clay

with sulfuric acid, respectively, showing physico-sorption nature of hexavalent chromium on used adsorbents.

Redlich–Peterson isotherm Redlich–Peterson equation that is an empirical isotherm included three parameters. This equation is widely used as combined elements between Langmuir and Freundlich equations (Prasad and Srivastava 2009). The equation for this model is

$$q_e = \frac{k_{RP}C_e}{1 + C_e^g P_e} \tag{15}$$

where k_{RP} is the Redlich–Peterson constant having unit of (l/g), P_e is also a constant (l/mg), and g is an exponent that lies between 0 and 1.

When the value of g is equal to 1, the above equation is reduced to the Langmuir isotherm, while it reduced to a Freundlich isotherm, in case the value of the parameter $C_e^g P_e$ is much bigger than 1. The ratio of k_{RP}/P_e indicates the adsorption capacity.

From Table 3, the results show that the k_{RP}/P_e has a similar variation to q_m . Thus, for each parameter, the values show an increase with increasing pore volume and surface area of activated clay. The higher R^2 values for Redlich–Peterson isotherm model suggest the applicability of this model to represent the equilibrium sorption of Cr (VI) by natural and activated clays (Fig. 7).

Sips model Sips model predicts a monolayer sorption capacity for high sorbate similar in form to the Freundlich equation, but it has a finite limit when the concentration is sufficiently high (Gunay et al. 2007).

The non-linear Sips isotherm equation can be represented as

$$q_e = \frac{q_{ms}k_s C_e^{m_s}}{1 + k_s C_e^{m_s}} \tag{16}$$

where k_s is the Sips equilibrium constant (l/mg) and m_s is the Sips model exponent.

The values of this isotherm model are presented in Table 3. According to the Sips isotherm model, the maximum sorption capacities were 13.016 and 18.094 mg/g at 20 °C for natural clay and activated clay with sulfuric acid, respectively (Fig. 7).

Khan model The Khan isotherm model (Padmeh et al. 2006) is given by the following equation:

$$q_e = \frac{q_m b_k C_e}{(1 + b_k C_e)^{a_k}} \tag{17}$$

where q_m and b_k are the Khan model constants and a_k is the Khan model exponent.

According to the results given in Table 3, q_m values were 10.835 and 19.69 mg/g for natural smectite and activated clays with sulfuric acid, respectively. The values of b_k were 0.179 and 0.572 for natural Tunisian clay and their activated form, respectively.

Equilibrium data were fitted (Fig. 7) onto the entire investigated three-parameter isotherm models very well. However, the highest correlation coefficient was observed with the Sips isotherm model. Among the tested two-parameter equations, and based on higher determination coefficient, the Dubinin–Radushkevich isotherm model was the best model to describe the adsorption of hexavalent chromium ion on the natural and acid-activated clays. Comparing all the used isotherm models, it seems that three-parameter isotherm model is the best to describe adsorption of hexavalent chromium on the used adsorbents.

Thermodynamic parameters of adsorption

For designing adsorption batch adsorption systems, the designer should be able to understand the following: what changes can be expected to occur and how fast will they take place. The fast of the reaction can be calculated from the knowledge of kinetic studies. But, the changes in reaction that can be expected during the process require the brief idea of thermodynamic parameters. The concept of thermodynamic assumes that in an isolated system where energy cannot be gained or lost, the entropy change is the driving force (Atia 2008). The thermodynamic parameters that must be considered to determine the process are enthalpy of adsorption (ΔH^0), free energy change (ΔG^0), and entropy change (ΔS^0) due to transfer of unit mole of solute from solution onto the solid–liquid interface. The important thermodynamic function ΔH^0 is very useful whenever there is a differential change that occurs in the system. Enthalpy is an additive property that its value is additive. The negative value of ΔH^0 indicates the exothermic process, and positive value indicates the endothermic process.

The other important thermodynamic parameter is the change in entropy ΔS^0 . The parameter ΔS^0 is used to identify the spontaneity in the adsorption process. The values of ΔH^0 and ΔS^0 were computed using the equation as follows (Donat 2009):

$$\ln(k_l) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{18}$$

where

- R Universal gas constant (8.314 J/mol K)
- T Absolute solution temperature (K)
- k_l The Langmuir constant that is related with the energy of adsorption.

Table 4 Thermodynamic parameters of adsorption of Cr (VI) onto natural and acid-activated clays

Adsorbents	$-\Delta G^0$ (kJ/mol)				$-\Delta S^0$ (J/mol K)	$-\Delta H^0$ (kJ/mol)
	293 K	308 K	323 K	338 K		
Natural clay	5.245	6.565	7.888	9.931	101.63	24.661
Activated clay	3.151	2.411	1.915	0.435	56.713	19.874

The value can be calculated from the slope and intercept of plot between $\ln k_t$ versus $1/T$. Another most important thermodynamic parameter involved in the adsorption process is the free energy change and can be calculated using the relation (Wang et al. 2010).

$$\Delta G^0 = -RT \ln(k_t) \quad (19)$$

The calculated thermodynamic parameters based on the above functions are listed in Table 4. Negative values of ΔH^0 suggest the exothermic nature of the adsorption. However, the negative values obtained for ΔG^0 indicated the spontaneous nature of adsorption (Table 4). Moreover, the increase of ΔG^0 with temperature indicated that adsorption was unfavorable at higher temperatures. Exothermic adsorption of Cr (VI) ion was also observed on Tunisian clay (Bhattacharyya and Sen Gupta 2006).

Comparison of adsorption capacities of natural and activated clays with other adsorbents

A comparison was made, in term of adsorption capacity (q_m) of our clay with other adsorbents. For a better valorization of our clay, the adsorbent capacity is compared in the same operating condition with different types of adsorbents in this study and in literature for Cr (VI) adsorption. The results show

that the retention of Cr (VI) ions onto acid-activated clays was better than their natural forms for all type of clays. The present study shows that natural and activated clays are effective low-cost adsorbents for the removal of Cr (VI) from aqueous solutions. Furthermore, the adsorbents used during our work have higher maximum adsorption capacities than commercial clay and much other types of adsorbents reported in Table 5, which indicated the effectiveness of the Tunisian smectite clay used in the present work.

Conclusions

This study indicates that the natural and activated clays can be used as effective and inexpensive adsorbents for the removal of toxic Cr (VI) ions from aqueous solutions. The pH of the medium is the controlling parameter of this adsorption process. Increases in the initial metal ion concentration and contact time were found to increase the removal of Cr (VI) ions. The adsorption of Cr (VI) onto natural clay followed the pseudo-second-order kinetic and Elovich model. The experimental data fit well with two- and three-parameter isotherm models.

The results of this study indicate that Tunisian smectite clay especially their activated form has the potential to be used as an alternative adsorbent material for the removal of Cr (VI)

Table 5 Comparison of adsorption capacity of different adsorbents for the adsorption of hexavalent chromium

Adsorbent	Adsorption capacity (mg/g)	References
Clay C1	10.6	(Bhattacharyya and Sen Gupta 2006)
Clay C2	4.45	
Kaolinite	11.6	(Malkoc and Nuhoglu 2007)
Acid-activated kaolinite	13.9	
Poly(oxozirconium) kaolinite	10.9	
TBA-kaolinite	10.6	
Sulfuric acid-treated groundnut husk	7.01	(Atia 2008)
Silver nitrate impregnate	11.4	
Indigenous waste	12.57	(Donat 2009)
Coconut shell carbon	10.88	(Babel and Kurniawan 2004)
Activated alumina	7.44	(Mor et al. 2007)
CTA-stevensite	10.27	(Benhammou et al. 2007)
BDMODA-bentonite	13	(Maryuk et al. 2005)
PEI/palm shell-activated carbon	20.5	(Owlad et al. 2010)
Natural clay	12.5	Present study
Activated clay	19.23	

ions from aqueous solutions owing to its low cost and simple regeneration.

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