

Chromium(VI) adsorption from aqueous solution onto Moroccan Al-pillared and cationic surfactant stevensite

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Abstract

Batch adsorption of the chromium(VI) onto Moroccan stevensite pillared by Keggin aluminium hydroxypolycation (Al-stevensite) and cationic surfactant cetyltrimethylammoniumbromide (CTA-stevensite) was investigated. The results showed that the CTA-stevensite has a higher affinity than that of Al-stevensite for chromium(VI) adsorption. The adsorption capacities for natural stevensite, Al-stevensite and CTA-stevensite calculated according to the Dubinin–Kaganer–Radushkevich isotherm (DKR) are 13.7, 75.4 and 195.6 mmol kg⁻¹, respectively. The study of the pH effect showed that the optimal range corresponding to the Cr(VI) maximum adsorption on Al-stevensite is pH 3.5–6 and that on CTA-stevensite is pH 2–6. The adsorption rates evaluated according to the pseudo-second-order model are 7.2, 207.2 and 178.5 mmol kg⁻¹ min⁻¹ for the natural stevensite, Al-stevensite and CTA-stevensite, respectively. The low values of the adsorption energy calculated by (DKR) suggest that anion exchange is the main mechanism that governs the chromate adsorption.

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1. Introduction

Chromium is present in the environment predominantly in one of two valence states: trivalent chromium Cr(III), which occurs naturally and is an essential nutrient, and hexavalent chromium Cr(VI) which is highly toxic and is classified as a human carcinogen [1,2]. In aqueous solution, Cr(VI) exists in the form: chromate CrO₄²⁻, dichromate Cr₂O₇²⁻ and hydrogen chromate HCrO₄⁻. Most studies seem to favour the dominant species dependence on the pH and the concentration of the solution: CrO₄²⁻ is predominant in basic solutions, H₂CrO₄⁻ is predominant at pH < 1 while HCrO₄⁻ and Cr₂O₇²⁻ are predominant at pH 2–6. Chromium is used in various industrial applications, including the production of stainless steels and refractory products like brick and mortar. It is also used in manufacturing pigments, the treatment of metal surfaces and in the tanning of leather [3,4]. Various methods were used to remove chromium from waste waters such as membrane filtration [5],

anion exchange resin [6] and adsorption onto different adsorbents [7].

The adsorption study of chromium(VI) from aqueous solutions by natural or modified clay minerals (kaolinite, bentonite, illite, etc.) was the object of several researches [8–10]. These studies reveal a weak adsorption of chromate anions by natural clay minerals due to the negative charge. Two methods are generally used to improve the affinity of clays for chromate removal: (i) the reduction of the chromium(VI) to chromium(III) by an organic or an inorganic reducing agent and the adsorption of chromium(III) [11–13] and (ii) surface modification by the adsorption of cationic surfactant or metallic hydroxypolycation [14,15].

Recent studies [16,17] showed that the clay minerals rich in Fe(II) can induce a considerable elimination of the chromium(VI) in solution by the reduction/adsorption mechanism. The effectiveness of retention increases with Fe(II) released in solution. Krishna et al. [18] showed that the adsorption of chromium(VI) onto montmorillonite is carried out via the anions exchange between the chromium(VI) and the anions bromide complexed on the cationic surfactant CTA-Br. Several studies have shown that clays modified

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with excess cationic surfactant can develop positive charges on their external surfaces [19,20]. Therefore, the surfactant bilayer formed on clay surfaces is responsible for the chromate adsorption.

The objectives of the present paper are: (i) to increase the affinity of Moroccan stevensite for Cr(VI) adsorption by the synthesis of an organo-stevensite and an inorgano-stevensite (ii) to study the pH effect on Cr(VI) adsorption by modified stevensite, (iii) to determine the kinetics and isotherms adsorption, and (iv) to investigate the mechanism of Cr(VI) adsorption on these modified clays.

2. Materials and methods

The stevensite-rich clay used in this study comes from a tertiary formation of Jbel Rhassoul located at the East of the middle- Atlas, in Morocco [21]. The chemical composition of this clay is: 57.49% SiO₂, 2.24% Al₂O₃, 1.35% Fe₂O₃, 1.46% CaO, 25.03% MgO, 0.73% K₂O and 0.51% Na₂O [22]. The chemical formula of stevensite is Si_{3.78}Al_{0.22}Mg_{2.92}Fe_{0.09}Na_{0.08}K_{0.08}O₁₀(OH)₂·4H₂O. The mineralogical composition is: stevensite 84.2%, quartz 11% and dolomite 4.8%. The surface area and the cation exchange capacity are 134 m²/g and 76.5 mequiv./100 g, respectively.

2.1. Purification of raw stevensite

A mass of 10 g of raw stevensite, with a size lower than 80 μm, is put in suspension in 100 ml of 1 M NaCl solution. After 4 h of agitation, the particles are separated by centrifugation at 3600 rpm for 15 min. This operation is repeated four times. The homogenisation operation is followed by several washings with distilled water, to eliminate excess of Cl⁻ anions, until the AgNO₃ test is negative.

To dissolve carbonates, the obtained homoionic stevensite is dispersed in a buffer solution of the acetic acid and sodium acetate (8.2 g of sodium acetate and 6 g of acetic acid for 100 ml of distilled water, pH ≈ 4.6). The suspension was stirred until the disappearance of bubbles that indicate the presence of carbonates. After that, the suspension was centrifuged.

The stevensite, free from carbonates, is put in suspension in a series of graduated cylinder of 0.5 l and the fraction <2 μm was separated by sedimentation using the Stokes equation. Practically, several taking are necessary to extract the totality of the clay fraction. Thereafter, the clay particles are separated by centrifugation and dried at 100 °C.

2.2. Pillaring solution

The aluminium pillaring solution was prepared according to the method of Khalaf et al. [23]. The titration of 0.4 M AlCl₃, 6H₂O solution (Panreac Quimica, purity >95%) by 0.4 M NaOH solution is achieved at a flow rate of 1.5 ml/min under strong stirring. The final concentration of aluminium is 0.1 M and the volume of NaOH added corresponds to a [OH⁻]/[Al] molar ratio of 2. This solution is maintained under constant agitation for a

minimum 24 h until no precipitation is present. Under these conditions, the solution contains mostly Keggin aluminium hydroxypolyocation [Al₁₃O₄(OH)₂₄(H₂O)₁₂]⁷⁺.

The solutions pillaring are obtained by the dissolution of a suitable quantity of cationic surfactant cetyltrimethylammoniumbromide CTA-Br (AMRESKO, purity 99%) of chemical formula CH₃(CH₂)₁₅N(CH₃)₃⁺-Br⁻, in distilled water heated before at 40 °C in order to increase the CTAB solubility.

2.3. Pillared stevensites synthesis

The organo-stevensite (CTA-stevensite) is prepared by adding 1 g of Na-stevensite into 100 ml of cationic surfactant solution at a CTA⁺/stevensite ratio of 1.14 mmol/g equivalent to 150% CEC. The mixture is stirred for 4 h. The particles clay are separated by centrifugation at 3600 rpm for 15 min and washed several times with distilled water until the disappearance of the excess of CTA-Br which appears in the bubbles form. The organo-stevensite is dried at 100 °C during 12 h.

Al-stevensite is synthesized by intercalating Na-stevensite with aluminium hydroxypolyocation. The pillaring solution containing [Al₁₃O₄(OH)₂₄(H₂O)₁₂]⁷⁺ is added to the stevensite suspension (1 g stevensite/100 ml distilled water) in order to obtain a ratio of 10 mmol Al/g stevensite. The obtained suspension stirred for 4 h. The pillared form was centrifuged, washed until no chloride was present in the washing water (no AgCl precipitation upon treatment with Ag⁺) and dried at 100 °C for 12 h.

2.4. Chromate adsorption experiments

To study the pH effect on the Cr(VI) adsorption, 0.25 g of natural stevensite or modified stevensite is combined with 50 ml of Cr(VI) solution. The suspension is titrated to different pH, ranging from 1.5 to 6.0 using 0.1 M NaOH or HNO₃. Initial solution concentration was 5 mmol/l K₂Cr₂O₇ (Panreac Quimica SA, PA). The mixtures were stirred at room temperature for 4 h and then centrifuged at 3600 rpm for 15 min. The supernatant solutions were analyzed for equilibrium Cr(VI) concentrations by GBC 904 flame atomic absorption spectrometer (AAS) in a nitrous oxide acetylene flame. Duplicate samples were prepared for similar conditions.

The kinetic study is performed at room temperature and at Cr(VI) initial concentration of 5 mmol/l. A mass of 1 g of the natural stevensite or modified stevensite is combined with 200 ml of Cr(VI) solutions and the pH of the suspensions was adjusted to optimum value during the experiments. Samples were collected at appropriate time intervals in order to analyze the Cr(VI) concentrations.

The Cr(VI) adsorption isotherms were carried out at room temperature and at initial concentrations of 0.5–10 mmol/l. A mass of 0.25 g of each sample was mixed with 50 ml of Cr(VI) solution for 2 h and the mixture was stirred. After Cr(VI) adsorption, solutions were centrifuged at 3600 rpm for 15 min and the Cr(VI) concentrations were analyzed. All the adsorption experiments were performed in duplicate. Quantity of Cr(VI) anions adsorbed was determined by the difference between initial and

final concentrations:

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

where C_i and C_e are the initial and equilibrium concentration (mmol/l), q_e the amount adsorbed at equilibrium (mmol/g), m the mass of adsorbent (g) and V is the volume of solution (l).

2.5. Characterization of stevensite

X-ray diffraction patterns are obtained by a Philips X' PERT MPD diffractometer with copper anticathode ($\lambda_{K\alpha} = 1.5406 \text{ \AA}$). The field observed of angle 2θ is between 5° and 20° with a step of 0.02° . The analyzed samples are natural stevensite, Al-stevensite and CTA-stevensite dried at 100°C .

3. Results and discussion

3.1. Stevensite characterization by XRD

Values of the basal distance d_{001} of XRD patterns of natural stevensite (a), Al-stevensite (b) and CTA-stevensite (c) dried at 100°C are illustrated in Fig. 1. This one shows that the basal spacing d_{001} increases from 14.7 \AA for the natural stevensite to 17.6 and 17.5 \AA for the pillared stevensites by the intercalation of the Al_{13}^{7+} and CTA^+ polycations. This indicates that the increase in d_{001} spacing is attributed to the adsorption of these polycations in the interlayer space. Studies showed that the adsorption of cationic surfactant is bilayer type and that organo-

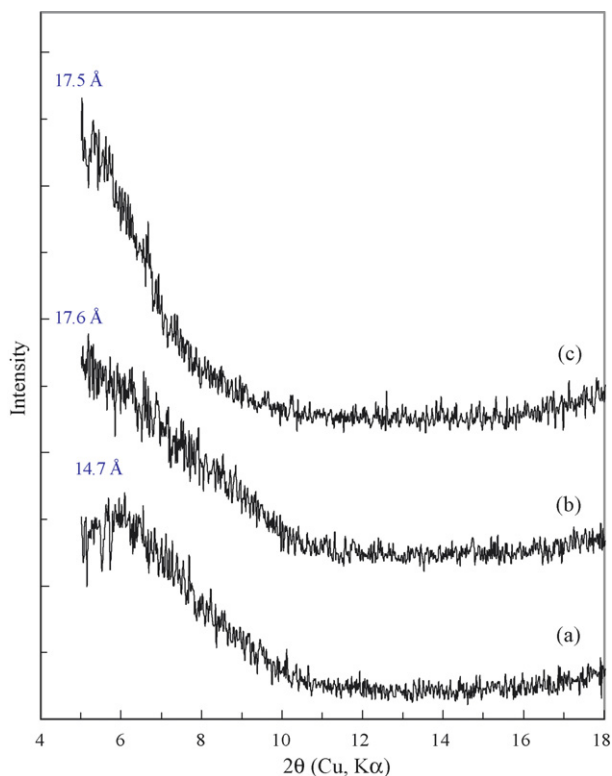


Fig. 1. X-ray diffraction patterns for natural stevensite (a), Al-stevensite (b) and CTA-stevensite (c).

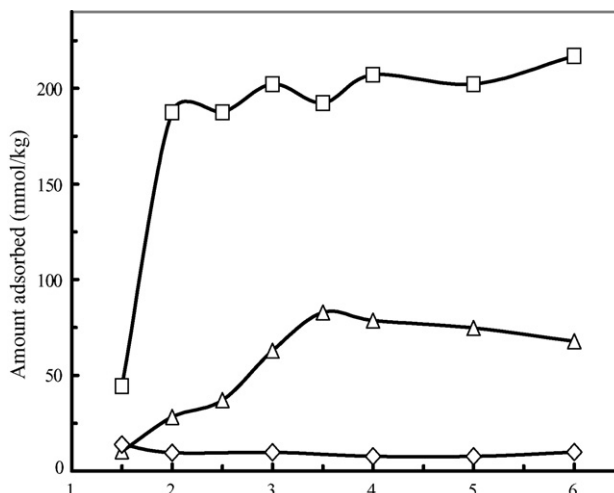


Fig. 2. Effect of pH on Cr(VI) adsorption: (\diamond) natural stevensite; (Δ) Al-stevensite; (\square) CTA-stevensite.

clay can develop positive charges, on external surface, capable of adsorbing the anion contaminants such as the chromium(VI) [24–26]. Kasama et al. [27] showed that the smectite intercalated by Al_{13}^{7+} in interlayer has as results the increase in surface groups Al–OH having an affinity for the anions.

3.2. Chromate adsorption

3.2.1. pH influence

The results of the pH effect on the Cr(VI) adsorption by natural stevensite, stevensite pillared by aluminium hydroxy-polycations Al_{13}^{7+} (Al-stevensite) and stevensite intercalated by cationic surfactant CTA^+ (CTA-stevensite) at pH range of 1.5–6 are presented in Fig. 2. The pH is adjusted using 0.1 M NaOH or HNO_3 solutions. Chromium(VI) speciation is dependent on the pH of solution according to following reactions [28]:



The results show that the quantity of Cr(VI) adsorbed by Al-stevensite increases gradually between pH 1.5 and 3.5 and attain a maximum for a values of pH higher than 3.5. The Cr(VI) adsorption onto Al-stevensite is optimal in the pH range of 3.5–6. The results show also an important increase of the Cr(VI) adsorption onto CTA-stevensite by increasing the pH of 1.5–2 and an optimal adsorption in the pH range of 2–6. The decrease of the effectiveness of Cr(VI) adsorption onto Al-stevensite and CTA-stevensite by decreasing the pH may be explained by the increase of the competition of the NO_3^- anions and Cr(VI) for adsorption sites. As the pH decreases, the ionic strength of the solution increases and as a consequence the affinity of Cr(VI) adsorption decreases. The results from this experiment are in agreement with chrome(VI) competitive adsorption by chloride [28]. Similar results of Cr(VI) adsorption by organo-kalinite at

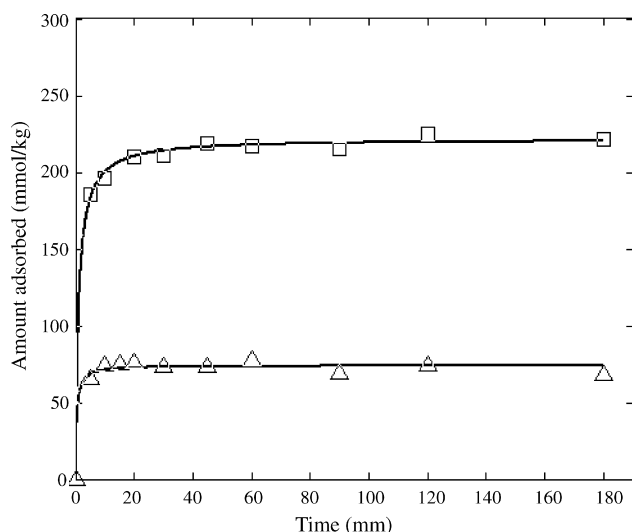


Fig. 3. Adsorption kinetics adjusted by second-order model at pH 3: (Δ) Al-stevensite and (\square) CTA-stevensite.

different NaCl background concentrations showed that as the ionic strength increases the Cr(VI) adsorption decreases [24].

3.2.2. Chromate adsorption kinetics

The chromium(VI) adsorption kinetics by Al-stevensite and the CTA-stevensite at pH 3 are presented in Fig. 3. The examination of this figure reveals a rapid adsorption during first 10 min and equilibrium is attained within 30 min. An optimum equilibrium time of 2 h was selected for the adsorption isotherm experiments.

To determine the equilibrium adsorption capacities and the adsorption rates, the experimental data are adjusted by the Ho and Mckay's pseudo-second-order model [29]:

$$q_t = \frac{kq_e^2 t}{1 + kq_e t} \quad (5)$$

where k is the rate constant ($\text{g mmol}^{-1}/\text{min}$), $v_0 = kq_e^2$ the initial adsorption rate ($\text{mmol g}^{-1}/\text{min}$), q_t the adsorbed quantity at the instant t (mmol/g) and q_e is the amount adsorbed at equilibrium (mmol/g).

The validity of this model can be determined by calculation of the standard deviation Δq (%) between the experimental and theoretical data:

$$\Delta q (\%) = \sqrt{\frac{\sum [(q_{t,\text{exp}} - q_{t,\text{cal}})/q_{t,\text{exp}}]^2}{n - 1}} \times 100 \quad (6)$$

where the subscripts "exp" and "cal" are, respectively, the experimental and calculated data, and n is the number of data points.

The pseudo-second order parameters calculated by linear regression analysis are presented in Table 1. The examination of this table shows a good description of the experimental results ($\Delta q < 4.7\%$). The Cr(VI) adsorption rates by Al-stevensite and CTA-stevensite are 178.54 and 207.2 $\text{mmol kg}^{-1} \text{min}^{-1}$, respectively. The results show also a greater affinity for Cr(VI) adsorption by CTA-stevensite than by Al-stevensite: the adsorption capacity of the CTA-stevensite is nearly three times more than

Table 1

Adsorption kinetic parameters for Cr(VI) adsorption onto natural stevensite, Al-stevensite and CTA-stevensite at pH 3

Parameters	Al-stevensite	CTA-stevensite
K ($\text{kg mmol}^{-1} \text{min}^{-1}$)	0.013	0.005
v_0 ($\text{mmol kg}^{-1} \text{min}^{-1}$)	178.54	207.2
q_e (mmol kg^{-1})	74.08	221.67
Δq (%)	4.77	1.53

that of Al-stevensite. Similar results were obtained for Cr(VI) adsorption onto Al-montmorillonite and CTA-montmorillonite [15].

3.2.3. Chromate adsorption isotherm

The results of the Cr(VI) adsorption isotherms by Al-stevensite and CTA-stevensite at pH 3 and at room temperature are illustrated in Fig. 4. The Dubinin–Kaganer–Radushkevich model (DKR) is used to describe the adsorption experimental results. This model permits to evaluate the maximal adsorption capacity and to provide the mechanism responsible for metals uptake. The (DKR) adsorption isotherm has the form [30]:

$$q_e = q_D \exp \left(-B_D \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2 \right) \quad (7)$$

where C_e (mmol/l) is the equilibrium concentration, q_e and q_D are the amount adsorbed at equilibrium and maximal adsorption capacity, T (K) the absolute temperature, R (J/mol K) the universal gas constant and B_D (mol^2/J^2) a constant related to the adsorption energy E (kJ mol^{-1}):

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

The (DKR) parameters, calculated by linear regression analysis and the adsorption energy are given in Table 2. Maximum

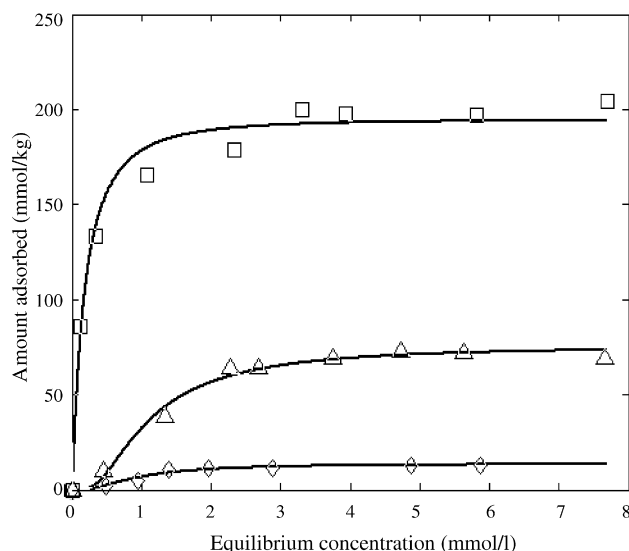


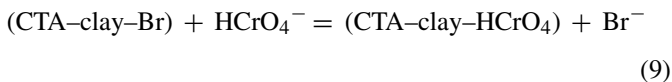
Fig. 4. Adsorption isotherms adjusted by the (DKR) model at pH 3: (\diamond) natural stevensite; (Δ) Al-stevensite; (\square) CTA-stevensite.

Table 2
Dubinin–Kaganer–Radushkevich parameters for Cr(VI) adsorption onto natural stevensite, Al-stevensite and CTA-stevensite at pH 3

	Natural stevensite	Al-stevensite	CTA-stevensite
q_D (mmol/kg)	13.7 ± 2.6	75.47 ± 3.54	195.66 ± 5.82
B_D (mol ² /kJ ²)	0.24 ± 0.08	0.28 ± 0.012	0.03 ± 0.002
E (kJ/mol)	1.44 ± 0.41	1.34 ± 0.14	4.08 ± 0.1
Δq (%)	14.8	13.07	5.44

adsorption was observed to occur in CTA-stevensite, followed successively by Al-stevensite and natural stevensite. The adsorption capacities of natural stevensite, Al-stevensite and the CTA-stevensite are 13.7, 75.4 and 195.6 mmol/kg, respectively. This shows a significant increase of the Cr(VI) adsorption capacity on modified stevensites. The increase in affinity of the Al-stevensite may be attributed to the increase in the Al–OH₂⁺ functional groups located in the edges of layer [27]. The adsorption of HCrO₄[−] species at low pH may be attributed to the Al–OH₂⁺–HCrO₄[−] surface complexes.

The increase in affinity of CTA-stevensite for Cr(VI) adsorption is probably due to the positive charges resulting from formation of surfactant bilayer on the external surface [25]. The adsorbed CTA⁺ bilayer on the clay minerals results in a positively charged surface compensated by adsorption of the Br[−]. Recently, it has been shown that adsorption of a cationic surfactant onto negatively charged clay minerals involves both cation exchange and hydrophobic bonding and that anion exchange is the major mechanism that governs the Cr(VI) adsorption [20]. At low pH values, the anion exchange reaction of HCrO₄[−] for Br[−] can be written as



The E values for Cr(VI) adsorption onto Al-stevensite and CTA-stevensite are 1.44 and 1.34 kJ/mol, respectively. These values are of the typical order of an ion-exchange mechanism [29]. Krishna et al. [18] have made a similar observation on the Cr(VI) adsorption mechanism onto CTA-montmorillonite. Table 3 gives a comparison between the affinity of Al-stevensite, CTA-stevensite and various modified clay minerals for Cr(VI)

Table 3
Comparison between the modified stevensite and other modified clay minerals for Cr(VI) adsorption

Samples	Adsorption capacities (mmol/kg)	References
Al-stevensite	75.5	This study
CTA-stevensite	195.7	This study
CTA-smectite	53	[20]
CTA-sepiolite	34	[25]
CTA-palygorskite	42	[25]
CTA-illite	18	[14]
CTA-zeolite	11	[31]
CTA-montmorillonite	340	[18]
Al-montmorillonite	50	[15]
CTA-kaolinite	13	[15]

adsorption. As this table shows, the modified stevensites may be considered as effective adsorbents to remove Cr(VI) from aqueous solutions.

4. Conclusion

From this research it is concluded that:

- the optimum pH ranges for the maximum adsorption of Cr(VI) onto Al-stevensite and CTA-stevensite were found to be 3.5–6 and 2–6, respectively.
- Cr(VI) adsorption is rapid during first 10 min and equilibrium is attained within 30 min. The adsorption kinetics are well described by pseudo-second-order model and the rates for Al-stevensite and CTA-stevensite are 178.54 and 207.2 mmol kg^{−1} min^{−1}, respectively
- both Al-pillared and cationic surfactant stevensite are an effective adsorbents for Cr(VI) adsorption. The Cr(VI) adsorption capacities for natural stevensite, Al-stevensite and CTA-stevensite calculated according to (DKR) isotherm are 13.7, 75.4 and 195.6 mmol kg^{−1}, respectively.
- the values of the adsorption energy obtained by (DKR) model are found to be 1.44 and 1.34 kJ mol^{−1} for Cr(VI) adsorption on Al-stevensite and CTA-stevensite, respectively. These values are of the order expected of an ion-exchange mechanism.

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