Study of the removal of mercury(II) and chromium(VI) from aqueous solutions by Moroccan stevensite

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Abstract

The objective of the present study was to investigate the adsorption of the heavy metals mercury(II) and chromium(VI), from aqueous solutions, onto Moroccan stevensite. A mineralogical and physicochemical characterization of natural stevensite was carried out. In order to improve the adsorption capacity of stevensite for Cr(VI), a preparation of stevensite was carried out. It consists in saturating the stevensite by ferrous iron Fe(II) and reducing the total Fe by $Na_2S_2O_4$. Then, the adsorption experiments were studied in batch reactors at $25 \pm 3\,^{\circ}C$. The influence of the pH solution on the Cr(VI) and Hg(II) adsorption was studied in the pH range of 1.5–7.0. The optimum pH for the Cr(VI) adsorption is in the pH range of 2.0–5.0 while that of Hg(II) is at the pH values above 4.0. The adsorption kinetics were tested by a pseudo-second-order model. The adsorption rate of Hg(II) is $54.35\,mmol\,kg^{-1}\,min^{-1}$ and that of Cr(VI) is $7.21\,mmol\,kg^{-1}\,min^{-1}$. The adsorption equilibrium time for Hg(II) and Cr(VI) was reached within 2 and 12 h, respectively. The adsorption isotherms were described by the Dubinin–Radushkevich model. The maximal adsorption capacity for Cr(VI) increases from 13.7 (raw stevensite) to $48.86\,mmol\,kg^{-1}$ (modified stevensite) while that of Hg(II) decreases from 205.8 to $166.9\,mmol\,kg^{-1}$. The mechanism of Hg(II) and Cr(VI) adsorption was discussed.
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1. Introduction

Chromium(VI) and mercury(II) are two toxic metals found in various industrial waste waters. Several industrial activities can be at the origin of the contamination of water by these ions [1,2]: electroplating, leather tanning, pulp production, metal finishing, paint and petroleum refining. Various methods were used to remove metals from waste waters. These include chemical precipitation, membrane filtration, ion exchange and adsorption. The adsorbents commonly recommended for the removal of heavy metals are alumina, silica, iron oxide, and activated carbon [2]. We propose in this study the removal of Hg(II) and Cr(VI) by adsorption on an abun-

dant Moroccan stevensite. This clay mineral is the principal constituent of the clay called locally Rhassoul. The layer of Rhassoul is located in the east side of the middle-Atlas mountains of Morocco (Fig. 1) [3]. The Rhassoul clay is identified as a stevensite [4,5]. Faust and Murata [6] regarded stevensite as species of the montmorillonite group. Recently, Chahi et al. [7] provided a geochemical and mineralogical characterization of the Moroccan stevensite. Generally, montmorillonite can adsorb the metal ions via two different mechanisms [8]: (i) cation exchange resulting from the interactions between ions and negative permanent charge and (ii) the formation of inner-sphere complexes through $Si-O^-$ and $Al-O^-$ groups at the particle edges. The chromate anions such as $HCrO_4^-$ or CrO_4^{2-} are rarely adsorbed on negatively charged clay surfaces. To improve the retention of the Cr(VI), the methods often used consist in reducing the Cr(VI) to Cr(III) by an

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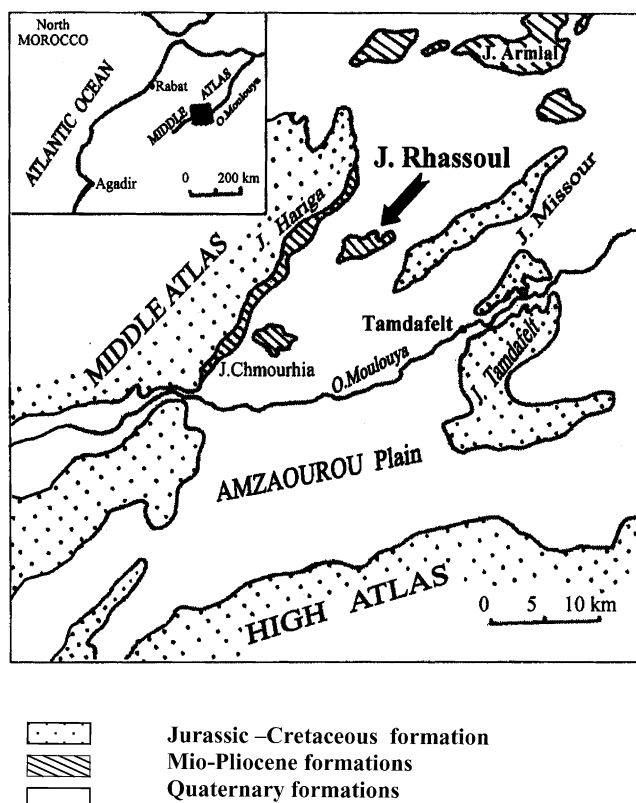*E-mail address:* benhammou_ab@yahoo.fr (A. Benhammou).

Fig. 1. Location of the Jbel Rhassoul in Morocco.

organic or inorganic reducer or using a surfactant modified clay [9–12]. Our approach consists in reducing the Cr(VI) to Cr(III) by ferrous iron Fe(II) released by stevensite saturated beforehand by Fe(II).

Our paper begins with a mineralogical and physicochemical characterization of stevensite. Therefore, the adsorption experiments will be carried out in batch reactors and will have as objectives: (i) the study of the kinetics and the isotherms of the adsorption of Hg(II) and Cr(VI), (ii) the study of the pH influence on the amount of Hg(II) and Cr(VI) adsorbed and (iii) the study of the effect of stevensite saturation by Fe(II) on the adsorption capacity of Cr(VI) and Hg(II).

2. Experimental

2.1. Characterization of raw stevensite

The chemical and mineralogical composition of the natural stevensite, dried at 250 °C and crushed to sizes lower than 200 μm, were given by X-ray fluorescence XRF (Philips PW 1666) and by X-ray diffraction XRD (Siemens D5000, Anton Parr HTK 10), respectively. The specific surface area was determined according to the BET method (NFX11-162) and the cation exchange capacity (CEC) was determined according to the ammonium acetate method (NFX 31-130). The exchangeable cations (Mg^{2+}, Ca^{2+}, Na^+, K^+) and the ammonium ion NH_4^+ were determined by GBC 904 flame atomic

absorption spectrometer (AAS) and GBC 911 UV–vis spectrophotometer at 420 nm, respectively. The zeta potential and the density were measured using a Zetaphotometer II (23000 model) and an Accupyc 1330 pycnometer.

2.2. Preparation of Fe(II)-stevensite

The adsorption of the anions such as $HCrO_4^-$ or CrO_4^{2-}, AsO_4^{3-} and CN^- on clayey minerals (montmorillonite, kaolinite, etc.) is generally weak [13]. This is explained by the permanent negative charge that these minerals possess. The method used in this work to improve the adsorption capacity consists in reducing Cr(VI) to Cr(III), in an acid medium, by ferrous iron Fe(II). The stages of saturation, reduction of Cr(VI) to Cr(III) and adsorption of both Cr(VI) and Cr(III) by stevensite are as follows: (i) saturation of stevensite by ferrous iron Fe(II) at 0.2 M $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ during 24 h with a ratio of stevensite to solution of 0.5 g/50 ml. The suspension obtained is centrifuged at 3600 rpm during 15 min. This operation of saturation–centrifugation is repeated three times, (ii) the deposit obtained is put again in suspension in a buffer solution citrate–bicarbonate (pH ≈ 8) at a temperature of 70 °C. To reduce the ferric iron Fe(III) to Fe(II), a mass of sodium dithionite $Na_2S_2O_4$ was added to have 0.2 M. This operation required 4 h. The deposit obtained is washed three times with double-distilled water to eliminate the excess of salts and (iii) the Fe-stevensite obtained is put in suspension in synthetic solutions of Cr(VI) to carry out the adsorption experiments.

2.3. Adsorption tests

The adsorption experiments of mercury(II) and chromium(VI) by stevensite, crushed and sieved beforehand to a size lower than 100 μm, were carried out in batch reactors. The synthetic solutions of Hg(II) and Cr(VI) were prepared by dissolution of the appropriate mass of $Hg(NO_3)_2 \cdot H_2O$ (Fluka Chemika) and $K_2Cr_2O_7$ (Panreac Quimica SA, PA) in distilled water. A ratio of stevensite to solution of 10 and 1 g/l was used for all adsorption experiments of Cr(VI) and Hg(II), respectively. At the end of every adsorption test, the suspensions were centrifuged at 3600 rpm for 15 min.

The effect of pH on the adsorption capacity was investigated at the pH range 1.5–7. The ionic force of the electrolyte is 0.05 M ($NaNO_3$). The Hg(II) and Cr(VI) concentrations are 0.5 and 2 mmol/l, respectively.

After determining the optimum time for Hg(II) and Cr(VI) adsorption, the kinetic study was performed at a room temperature of 25 ± 3 °C. The pH of the suspensions was maintained constant during the experiments at pH 4 and 3, respectively, for the adsorption of Hg(II) and Cr(VI). Samples were collected at appropriate time intervals in order to analyze the chromium and mercury concentrations.

The adsorption isotherms of Cr(VI) and Hg(II) on the stevensite were investigated when the optimum pH and equi-

librium time were evaluated. The concentration ranges used to carry out the adsorption isotherms for Hg(II) and Cr(VI) are 0.125–1 and 0.5–6 mmol/l, respectively. During the experiments, the solution pH was adjusted to 4 for Cr(VI) and 3 for Hg(II). The equilibrium time selected for Cr(VI) adsorption was 12 h while that of Hg(II) was 2 h.

2.4. Analytical methods

The concentrations of Hg(II) in the filtrate were determined by GBC 904 atomic absorption spectrometer (SAA) in an air acetylene flame. The addition of $SnCl_2$ as a reducing agent of Hg(II) to Hg(I) at the samples and standards makes it possible to reduce the interference. The Cr(VI) residual concentration was measured by GBC 911 spectrophotometer UV-vis at 560 nm using the diphenylcarbazide reagent in the acid solution [14]. To determine the total Cr concentration, all chromium in the solution was converted into hexavalent state by oxidation with potassium permanganate. Thereafter, total Cr concentration was analyzed by GBC 904 SAA in nitrous oxide acetylene flame. Ferrous iron Fe(II) was analyzed according to the ferrozine method using GBC 911 spectrophotometer UV–vis at 562 nm.

3. Results and discussions

3.1. Characterization of stevensite

The mineralogical composition of Rhassoul clay shows that it is made up of essentially stevensite (84.2 wt.%) with the presence of quartz (11 wt.%) and dolomite (4.8 wt.%) [15]. Table 1 summarizes the chemical composition of raw stevensite and Fe-stevensite using XRF analysis. As seen in Table 1, the iron concentration of Fe-stevensite (representing as Fe_2O_3) increases from 1.35 wt.% for raw stevensite to 10.37 wt.% for Fe-stevensite. The empirical chemical formula of raw stevensite is $Si_{3.78}Al_{0.22}Mg_{2.9}Fe_{0.09}Na_{0.08}K_{0.08}O_{10}(OH)_2 \cdot 4H_2O$. The physical and chemical properties of raw stevensite such as specific surface area (133 m^2/g) and cation exchange capacity (76 meq/100 g) are presented in Table 2.

Table 1
Chemical composition (in wt.%) of stevensite as determined using XRF analysis

Elements	Raw stevensite	Fe-stevensite
SiO_2	57.49	53.68
Al_2O_3	2.24	1.58
Fe_2O_3	1.35	10.37
CaO	1.46	0.52
MgO	25.03	20.48
K_2O	0.73	0.44
NaO_2	0.51	0.02
Loss on ignition at 1000 °C	8.31	11.18

Table 2
Chemical and physical properties of raw stevensite

Parameters	Values
Exchangeable cations (meq/100 g)	
Ca^{2+}	7.10
Mg^{2+}	53.31
Na^+	12.14
K^+	1.56
Cation exchange capacity (meq/100 g)	76.50
Specific surface (m^2/g)	133.68
Density (g/cm^3)	2.24
Zeta potential (mV)	−21.00
Equilibrium pH	8.65
pH of zero point charge, pH_{ZPC}	2.0

3.2. Adsorption study

The results of the pH influence on the adsorption capacity of stevensite for Hg(II) are given in Fig. 2. It was found that the amount adsorbed of Hg(II) increases with increasing pH from 1.5 to 4. This can be explained by the diminution of the competition between H^+ protons and Hg(II) cations towards the adsorption sites and the deprotonation of the particle edges [16]. At pH values above 4, the Hg(II) adsorption was not significantly affected by the solution pH. This is because at the pH range of 4–6, the predominant specie is $Hg(OH)_2^0$ [17]. Similar results to ours were observed in other studies of the pH influence on the Hg(II) adsorption by kaolinite [18] and activated carbon [19,20]. The Hg(II) adsorption can be illustrated by the surface complexation reactions [18]:

$$S-OH^0 + Hg^{2+} + H_2O \rightarrow S-O^- -HgOH^+ + 2H^+ \quad (1)$$

$$S-OH^0 + Hg(OH)_2^0 \rightarrow S-OHg(OH)_2^- + H^+ \quad (2)$$
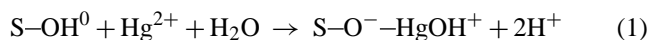
where S–OH is the amphoteric surface hydroxyl groups (Si–OH or Al–OH).

Fig. 3 shows the pH effect on the amount of chromium adsorbed by Fe-stevensite. We note that the Cr(VI) adsorption is optimal in the pH range of 2–5 and decreases with
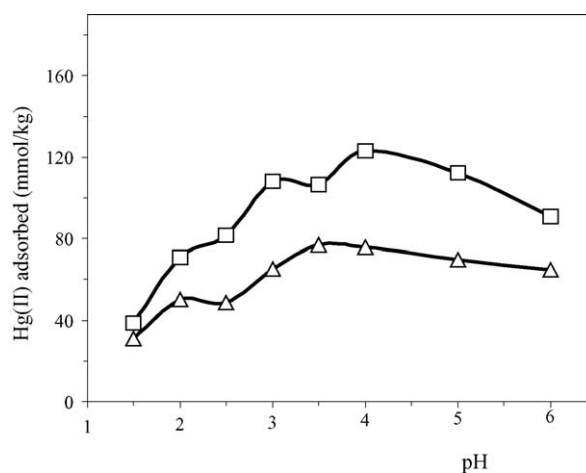

Fig. 2. Effect of pH on Hg(II) adsorption: (△) raw stevensite; (□) Fe-stevensite.
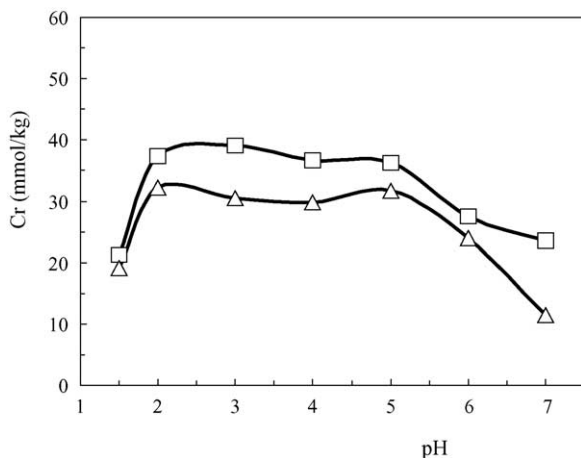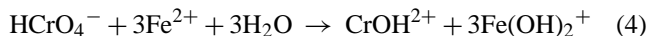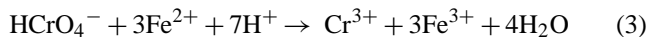
Fig. 3. Effect of pH on chromium adsorption onto Fe(II)-stevensite: (□) Cr(VI) disappeared; (△) Cr total adsorbed.

increasing pH from 5 to 7. The quantity of Cr(VI) adsorbed is 32 and 12 mmol kg^{-1} for pH 2 and 7, respectively. The higher adsorption of Cr(VI) at low pH (2–5) may be due to the reduction of Cr(VI) to Cr(III) by Fe(II) released from Fe-stevensite, and adsorption of Cr(III) onto negative permanent charge of particles. As seen in Fig. 4, Fe(II) released in solution at different pH decreases with increasing pH from 1.5 to 5 and becomes negligible in the pH range of 5–7. The reduction of Cr(VI) to Cr(III), in acidic medium, can be described by the following reactions:

$$HCrO_4^- + 3Fe^{2+} + 7H^+ \rightarrow Cr^{3+} + 3Fe^{3+} + 4H_2O \quad (3)$$

$$HCrO_4^- + 3Fe^{2+} + 3H_2O \rightarrow CrOH^{2+} + 3Fe(OH)_2^+ \quad (4)$$

The decrease of the Cr(VI) adsorption with increasing pH may also be attributed to the surface complexation [21]. Table 2 shows that the pH of zero point charge pH$_{ZPC}$ is 2. This indicates that at pH greater than pH$_{ZPC}$ the aluminol and silanol sites are present mainly as Al–O$^-$ and Si–O$^-$. Therefore, the adsorption of Cr(VI) anions decreases with an increase in pH. Previous studies have shown that Cr(VI) ex-
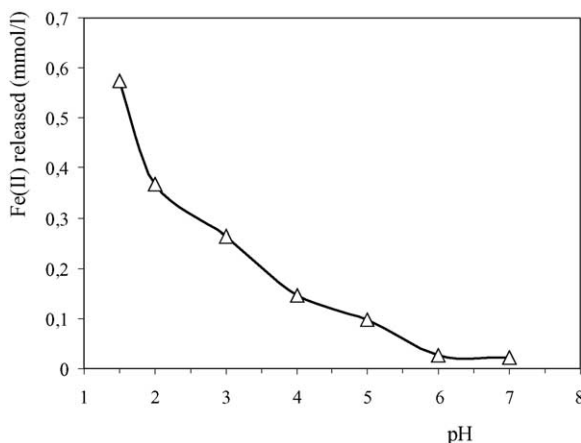
ists predominantly in solution as HCrO$_4^-$ at low pH values and CrO$_4^{2-}$ at high pH values [22]. The adsorption of these species on the particle edges (S–OH$_2^+$) can be described by the following complexation reactions:

$$S-OH_2^+ + HCrO_4^- \rightarrow S-OHCrO_4^- + H^+ \quad (5)$$

$$S-OH_2^+ + CrO_4^{2-} \rightarrow S-OHCrO_4^{2-} + H^+ \quad (6)$$

The experimental results of the adsorption kinetics for three concentrations of Hg(II) are illustrated in Fig. 5. The rate of adsorption of Hg(II) was followed by looking at the increase in the adsorption as a function of time until the adsorption remained constant, implying equilibrium was reached. As seen in Fig. 5, the adsorption of Hg(II) is rapid during the first 20 min and the equilibrium is then attained within 40 min. The amount adsorbed increases with agitation time and Hg(II)concentration in solution. Fig. 6 presents the adsorption kinetics of Cr(VI) on raw stevensite and Fe-stevensite. It was found that equilibrium was attained at about 6 h. Therefore, an agitation period of 2 and 12 h was selected to establish the adsorption isotherms of Hg(II) and Cr(VI), re-
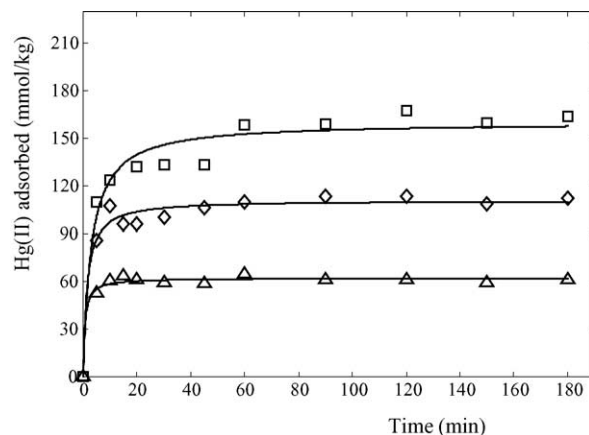

Fig. 5. Adsorption kinetics of Hg(II) onto stevensite at pH 4: (□) 0.5 mmol/l; (◇) 0.25 mmol/l; (△) 0.125 mmol/l.

Fig. 4. Effect of pH on Fe(II) released from Fe-stevensite: stevensite dose = 10 g/l, t = 12 h, 0.05 M (NaNO$_3$).
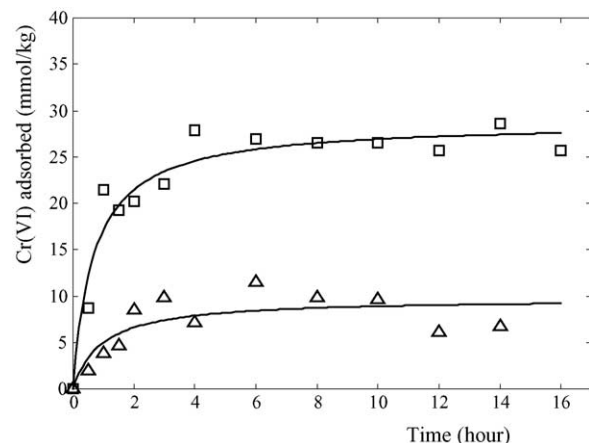

Fig. 6. Adsorption kinetics of Cr(VI) adsorption at pH 3: (△) raw stevensite; (□) Fe(II)-stevensite.

spectively. An increase of the amount of Cr(VI) adsorbed by Fe-stevensite was observed. This may be due to the reduction of Cr(VI) to Cr(III) preferentially adsorbed by clayey minerals. The concentration of Fe(II) released in solution at pH 3 was found to be 0.264 mmol/l (Fig. 4).

Several simplified kinetic models, namely, pseudo-first-order, intra-particle diffusion, external mass transfer and pseudo-second-order can be used to analyze the experimental data of the adsorption kinetics. In our study, only the last model was used to identify the nature of the mechanism responsible for the Hg(II) and Cr(VI) adsorption. According to Ho and Mckay [23], the pseudo-second-order model (Eq. (7)) agrees with the complexation reaction:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \tag{7}$$

where k (g mmol^{-1} min^{-1}) is the rate constant, $v_0 = kq_e^2$ the initial adsorption rate (mmol g^{-1} min^{-1}), q_t, q_e (mmol/g) are the adsorbed quantity at time 't' and equilibrium.

The initial rates and the adsorption capacities of stevensite at equilibrium for Hg(II) and Cr(VI) are given in Table 3. The results show that the Hg(II) adsorption is rapid compared with Cr(VI) and the initial rate for Hg(II) is 54.35 mmol kg^{-1} min^{-1} while those of raw stevensite and Fe-stevensite for Cr(VI) adsorption are 7.21 and 42.39 mmol kg^{-1} min^{-1}, respectively. The good description of Hg(II) and Cr(VI) adsorption by the pseudo-second-order model ($R^2 > 0.97$) indicates that the adsorption reaction can be controlled by surface complexation mechanism [23].

The adsorption isotherms of Hg(II) and Cr(VI) on the stevensite are presented by Figs. 7 and 8, respectively. The Dubinin–Radushkevich model (D–RM) was tested to describe the adsorption experimental results because it is more general compared with other models such as that of Langmuir which supposes a homogeneous surface. This model, which assumes a monolayer adsorption, permits to evaluate the maximal adsorption capacity and provide the mechanism responsible for metals uptake [24]. The (DR) equation is expressed by:

$$q_e = q_D \exp\left(-B_D\left[RT\ln\left(1 + \frac{1}{C_e}\right)\right]^2\right) \tag{8}$$

where C_e is the equilibrium concentration of the solute (mmol/l), q_e the amount adsorbed at equilibrium, q_D (mmol/g) the monolayer maximal adsorption capacity, T (K) the absolute temperature, R (J/mol K) the universal gas con-
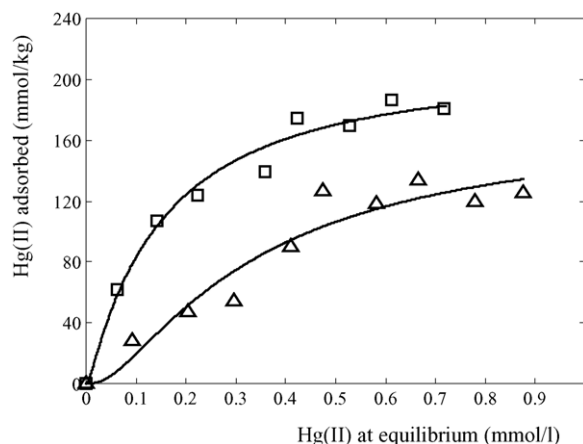

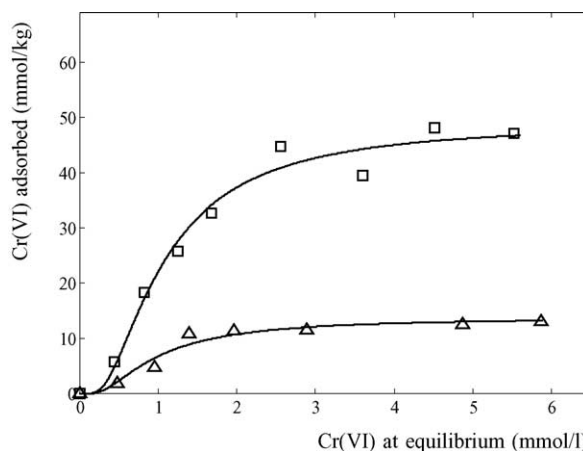Fig. 7. Adsorption isotherms of Hg(II) onto stevensite at pH 4. (△) Raw stevensite; (□) Fe(II)-stevensite.

Fig. 8. Adsorption isotherms of Cr(VI) at pH 3: (△) raw stevensite; (□) Fe(II)-stevensite.

stant and B_D (mol^2/J^2) a constant related to the mean energy of adsorption of the sorbate as it is transferred to the surface of the solid from infinite distance in the solution.

The mean energy of adsorption E (kJ/mol) is given by:

$$E = \frac{1}{\sqrt{2B_D}} \tag{9}$$

The (D–R) parameters, obtained by non-linear least-square regression analysis, and mean energy are given in Table 4. The adsorption capacity of raw stevensite for Cr(VI) (13.7 mmol kg^{-1}) was nearly four times less than that of Fe-stevensite (48.86 mmol kg^{-1}). This may be due to the reduc-

Table 3
Adsorption kinetics parameters of Hg(II) and Cr(VI) by stevensite

		k (g mmol^{-1} min^{-1})	v_0 (mmol g^1 min^{-1})	q_e (kJ/mol)	R^2
Raw stevensite	Hg(II)	0.74	7.21	9.79	0.98
	Cr(VI)	0.34	54.35	160.32	0.98
Fe-stevensite	Hg(II)	0.05	42.39	28.47	0.97
	Cr(VI)	–	–	–	–

Table 4
Dubinin–Radushkevich parameters deduced from the adsorption isotherms of Hg(II) and Cr(VI)

		q_D (mmol kg^{-1})	β_D (mol^2/kJ^2)	E (kJ/mol)	R^2
Raw stevensite	Hg(II)	205.8 ± 12.6[a]	0.025 ± 0.008	4.47 ± 0.7	0.991
	Cr(VI)	13.7 ± 2.6	0.24 ± 0.08	1.44 ± 0.41	0.98
Fe-stevensite	Hg(II)	166.94 ± 15.6	0.061 ± 0.014	2.89 ± 0.44	0.97
	Cr(VI)	48.86 ± 5.6	0.26 ± 0.07	1.38 ± 0.42	0.99

[a] Mean ± standard deviation (95% confidence level).

tion of Cr(VI) to Cr(III) by Fe(II) released from Fe-stevensite and adsorption of Cr(III). The adsorption capacity of Fe-stevensite for the Cr(VI) adsorption was compared with the capacities of other adsorbents. The q_m values for the Cr(VI) adsorption on the raw bentonite and kaolinite [25] were insignificant while the adsorption capacity of modified-zeolite [26], modified kaolinite [25] and Na-montmorillonite [21] were 10, 30 and 11.5 mmol kg^{-1}, respectively. The adsorption capacity of raw stevensite and Fe-stevensite for Hg(II) was, respectively, 205 and 167 mmol kg^{-1}. The decrease of Hg(II) adsorption may be attributed to the replacement of the interlayer cations (Na$^+$, K$^+$, Ca^{2+}, Mg^{2+}) by Fe^{2+} (Table 1). This can decrease the affinity of Fe-stevensite for the Hg(II) adsorption. The adsorption capacity for Hg(II) on montmorillonite, sepiolite [27] and activated carbon [19] were 250, 170 and 309 mmol kg^{-1}, respectively. The mean energy values for adsorption of Hg(II) onto raw stevensite and Fe-stevensite are 4.47 and 2.89 kJ/mol while those of Cr(VI) are 1.44 and 1.38 kJ/mol. They are lower than the energy range of the ion-exchange reaction 8–16 kJ/mol, confirming that the ion-exchange may also play a significant role in the adsorption mechanism [24]. From the results of the kinetics and isotherms of adsorption, one can conclude that the removal of Hg(II) and Cr(VI) may be controlled by the ion exchange mechanism and also the surface complexation mechanism.

4. Conclusion

The mineralogical and physicochemical characterization of Rhassoul clay show that this material is made up mainly of stevensite (84.2 wt.%) with the presence of dolomite and quartz. The values of the specific surface (133.6 m^2/g) and cation exchange capacity (76.5 meq/100 g) are relatively important. The chemical composition of Fe-stevensite reveals an increase in the iron concentration from 1.35 to 10.37 wt.%.

The study of the pH effect on the adsorption shows that the amount of Hg(II) adsorbed increases with pH and becomes insignificant for a value of pH above 4.0. Also, the Cr(VI) adsorption was optimal at the pH between 2.0 and 5.0 and decreases at the pH range of 5.0–7.0.

The adsorption kinetics study of the Hg(II) and Cr(VI) reveals a rapid adsorption of Hg(II) compared with Cr(VI) and are in accordance with the pseudo-second-order model. This indicates that the adsorption may be controlled by the surface complexation mechanism. The adsorption rates

of Hg(II) and Cr(VI) on raw stevensite are 54.35 and 7.21 mmol kg^{-1} min^{-1}, while that of Cr(VI) on Fe-stevensite is 42.3 mmol kg^{-1} min^{-1}.

Concerning the adsorption isotherms study, the maximal adsorption capacity of raw stevensite for Hg(II) decreases from 205.8 to 166.94 mmol kg^{-1} while that of Fe-stevensite for Cr(VI) adsorption increases from 13.7 to 48.8 mmol kg^{-1}. The values of mean energy calculated from the Dubinin–Radushkevich equation show that the adsorption may also be attributed to the ion exchange mechanism. Then, Surface complexation and ion exchange are the major removal mechanisms involved.

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