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Effect of cadmium and chromium adsorption on the zeta potential of clays

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ABSTRACT

The aim of this study was to evaluate the efficiency of two Tunisian mineral clays to capture chromium(III) and cadmium(II) present in landfills leachate and to understand the corresponding mechanisms of sorption. Kinetic studies, adsorption isotherms, particle size distributions as well as zeta potential evolution with adsorbed amount, and pH were studied. The kinetic study revealed that a pseudo-second-order model agrees with the heavy metals adsorption experimental values for both clays. Negative zeta potential was obtained over the entire studied pH range (3–8) and no isoelectric point was found. Adsorption of Cr(III) had a significant effect on the zeta potential which goes from negative values to positive ones, indicating specific adsorption. Upon the addition of Cd(II), the clay surfaces stayed negatively charged whatever the cadmium concentration.

Keywords: Zeta potential; Smectite; Illite; Chromium; Cadmium; Sorption

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1. Introduction

Sites with clay soils are generally chosen to install landfills due to their physicochemical properties. In fact clays can retain organic and inorganic pollutants, thus preventing contaminants infiltration into the groundwater [1–3]. Clay minerals are often used in wastewater treatment [4–6]. They are characterized by a negative surface charge compensated by cations positioned in the interlayer spacing of the solid. These cations can be exchanged with other ions present in the surrounding solution. Studies showed that cations of heavy metals, in aqueous solution, exhibit a particular affinity for clays [7–9].

In previous works [10–12], we studied the adsorption of trivalent chromium and divalent cadmium on two clays from the local sites of two landfills located in Tunisia. Jebel Chakir landfill (northwest of Tunis), receives the highest volume of solid waste of Tunis City. Presence of chromium and cadmium ions was detected in the leachates. The second clay material was chosen as a comparative support for adsorption experiments and comes from Jebel Tejra (southeast Tunisia).

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The first clay contains mainly smectite and kaolinite. The second one is composed of illite and kaolinite. The choice of the two metals, chromium and cadmium, was due to their presence in the leachate from the decomposition of solid wastes in both landfills and also to their known toxicity for human being and environment. Toxic in all forms (metal, vapor, salts), even at low concentration, cadmium is one of the few elements with no known function in metabolism. Considerably mobile, cadmium and zinc have a great tendency to dissociate from insoluble inorganic and organic complexes to form soluble ionic species that remain stable at neutral or slightly alkaline pH [13,14]. They can be the cause of kidney problems and hypertension. Although molecular mechanisms of cadmium-induced carcinogenesis are not yet understood, several factors may contribute to it [15].

In vivo studies concerning trivalent chromium showed that exposure to chloride chromium and nitrate chromium induced DNA deletions in both mice and yeast [16].

Our aim in the present work was to improve our understanding of ions adsorption through acoustic and electroacoustic studies.

Three important characteristics regulating interactions in clay mineral suspensions are: mineralogy, particle size distribution (PSD), and zeta potential, the potential at the shear plane of the electric double layer [17]. Particle size and surface charge of clay minerals are important in sorption mechanisms and in transport properties of mineral colloids and associated contaminants, such as heavy metals [18].

There are a number of works related to the determination of the electrokinetic properties of clays. Hussain et al. [19] investigated the electrokinetic properties of three clays from Turkey (kaolinite, illite, and chlorite). They found that zeta potentials of all clays determined in water over a pH range from 2.5 to 11.0 were all negative, ranging from −15.1 to −49.5 mV. Kaolinite was the most negative clay, compared to chlorite and illite. Delgado et al. [20] employed the electrophoretic mobility of montmorillonite particles in different liquid media for the estimation of the zeta potential. In this work, the effect of cation adsorption was highlighted. Similar results were found by Au et al. [21]. They evaluated the zeta potential–pH behavior of pure kaolin and bentonite slurries, and mixed bentonite–kaolin slurries. They showed that both pure clays are negatively charged in the pH range of 2–12. However, the composite slurries displayed a more negative zeta potential at any given pH than the pure bentonite or the pure kaolin slurry.

Dohnalová et al. [22] have measured zeta potential and particle size distribution (PSD) by the ultrasonic techniques. The effects of solid concentration, temperature, pH, and type of supporting electrolytes on the zeta potential are investigated. At the opposite of the preceding reference, isoelectric points were observed for kaolinite samples. Kosmulski et al. [23,24] investigated electrokinetic properties of clay minerals and Anatase at high ionic strengths. Their results regarding clay minerals measurements indicated that the electrokinetic potential did not cease at high ionic strengths. Potassium and cesium salts induced a shift in the isoelectric points (IEP) of kaolin toward high pH. Inversion of sign was observed at very low pH. Mpofu et al. [25] studied the influence of hydrolysable metallic ions, Mn(II) and Ca(II), on smectite suspension stability. Specific adsorption of metallic ion, accompanied by a marked reduction in particle zeta potential was observed.

In the present study, the electroacoustic technique was used to determine the electrokinetic properties of the two Tunisian clays coming from Jebel Chakir and Jebel Tejra. Effects of heavy metallic cations Cd(II) and Cr(III) concentration and pH on the zeta potential and the PSD are investigated and discussed.

2. Experimental

2.1. Materials

Two natural clays were taken from Jebel Chakir and Jebel Tejra (northwest and southeast of Tunisia). They were powdered in an agate mortar and sieved through 63-μm mesh to obtain finer grains. Powdered clays were dried at 60°C, before the experiments. The lower than 63-μm fractions were purified by repeating cation exchange with NaCl solution (1 M) followed by washing, sedimentation, and dialyses [26].

In the following, JCKp and JTCp correspond to the purified samples of Jebel Chakir and Jebel Tejra, respectively. The chemical (Table 1) and mineralogical compositions of the materials (Table 2) were determined in previous works [10,11], by a variety of complementary techniques (IRTF, XRD, UV–vis, SEM, EDX, BET, and DTA–TGA). Results showed that the JCKp clay exhibited the highest BET surface area [10,11]. The same behavior is obtained when comparing the values of the specific surface areas obtained by the method of methylene blue [27]. This is due to the swelling of the smectite which gives access to the interlayer surface.

Table 1
Chemical composition of smectite from Jebel Chakir and illite from Jebel Tejra

Metal oxides	Percentage present[a]	
	JCK p	JTCp
Silica (SiO_2)	55.53	53.22
Alumina (Al_2O_3)	29.01	25.73
Lime (CaO)	0.35	0.17
Iron oxide (Fe_2O_3)	10.17	8.72
Magnesia (MgO)	1.13	3.19
Potassium oxide (K_2O)	1.97	5.85
Sodium oxide (Na_2O)	1.84	1.52
Manganese oxide(Mn O)	0.01	0.02
(P_2O_5)	–	0.77
(TiO_2)	–	0.11

[a] Measured with ICP in triplicates.

2.2. Experimental procedure

2.2.1. Kinetics

The experiments for the two metallic ions on JCKp and JTC p were obtained using the batch method for $CdCl_2$ and $CrCl_3$ solution at room temperature (22°C). In all cases, the solution to sorbent ratio was fixed at 1 g L^{-1}. After adding the purified clays, the pH of the suspension increased and was readjusted at about 3.5 by adding diluted NaOH or HCl solutions before stirring. The experiments were carried out in centrifuge tubes by subjecting 20 mg of clay to a fixed shaking period with 20 mL of ionic heavy metal solution on a vertical rotary shaker (50 turns/min).

The initial concentration of Cd(II) or Cr(III) was fixed at 200 mg L^{-1}. The time-dependent behavior of metal adsorption was measured varying the equilibrium time in the range of 10–1,200 min. The sorbent was separated using a centrifugation step. Quantitative analysis of cadmium and chromium in supernatant solution was made by inductively coupled plasma (ICP).

2.2.2. Adsorption isotherms

Adsorption isotherms of ions were obtained at pH 3.5 using the batch method. All studies were carried out in test tubes by contacting 20 mg of clay with 20 mL of metal solution on a vertical rotary stirrer (50 rpm) during 20 h. The sorbent was separated from the solution using a centrifuge. The supernatants were analyzed by ICP to determine the equilibrium concentration of heavy metals.

2.2.3. Determination of the PSD and zeta potential

A combined acoustic and electroacoustic spectrometer (DT-1200) developed by Dispersion Technology Inc. was used to determine the PSD of the clay (JCKp and JTCp) suspensions. This instrument has separate sensors for measuring acoustic and electroacoustic signals. The acoustic part of the instrument allows the determination of PSDs. The acoustic attenuation spectrum is used for calculating the PSD. The theoretical attenuation is calculated using the attenuation theory [28] and one of the model PSD distributions. The best fit is determined for each PSD model by searching for that PSD which minimizes the "error" between the theoretical attenuation and the experimental data. The electroacoustic sensor measures the magnitude and phase of the colloid vibration current (CVI) at 2 MHz. There is a correction for the speed of sound and attenuation measured with the acoustic sensor [29,30]. The total volume of sample required is about 100 ml. A special magnetic stirrer prevents sedimentation and ensures homogenization of the sample during experiment.

To measure the PSD and the zeta potential of the initial clays at constant pH, 1 g of clay (JCKp or JTCp) was dispersed in 100 mL of distilled water during 2 h under uninterrupted stirring to obtain a uniform suspension. This later was then introduced in the spectrometer.

To follow the evolution of particle size and zeta potential of clays during Cr(III) and Cd(II) adsorption at constant pH, 1 g of clay (JCKp or JTCp) was dispersed in 100 mL of chromium or cadmium solutions under the same conditions as adsorption isotherms (contact time, concentrations, pH, and temperature) under uninterrupted stirring to reach equilibrium.

Table 2
Mineralogical composition (wt %) of the clays[a]

Sample	Smectite	Illite	Kaolinite	Calcite	Quartz	Feldspar
JTCp		65	35	Nd[b]	Nd[b]	Nd[b]
JCKp	80	–	20	Trace	Trace	Nd[b]

[a] Determined by X-ray diffraction (XRD.

[b] Not detected.

The influence of pH on PSD and zeta potential was studied using similar experimental conditions. During the measurements, the spectrometer allowed to keep constant the pH of clay suspensions by adjusting it by a dropwise addition of sodium hydroxide or hydrochloric acid solutions. A particularity of this study is that each sample is a mixture of two components: smectite–kaolinite and illite–kaolinite for JCK and JTC, respectively. The electroacoustic signal of such a mixture is a sum of signals of its components, but it is not possible to split the sum into its components. Then the zeta potentials and particle sizes reported by the instrument software represent a sort of "average" properties of the two types of particles, but the contributions of the components to the average are not easy to assess, and probably they are not proportional to their mass fractions.

For example, the calculations of the zeta potential involve the specific density of solid particles (which is slightly different for component 1 and component 2). Another problem is that of particle shape. The data are calculated by the instrument assuming a spherical shape for the particles, whereas clays are mainly under the form of platelets [31]. An equivalent diameter is then obtained. Consequently, the results provided by these analyses are mainly quantitative but they can used to follow the evolution of suspension properties under the variation of a parameter (ion concentration, pH etc.).

3. Results and discussion

3.1. Clays behavior in water at constant pH

3.1.1. Kinetics

The amounts of adsorbed cadmium and chromium per gram of clay are plotted as a function of contact time in Fig. 1.

Generally, the adsorption kinetics are described as expressions of the pseudo-first-order and pseudo-second-order equations originally given by Lagergren [32–35].

The kinetic model of adsorption is the pseudo-first-order equation as given by Eq. (1):

$$dQ_t = k_{1,s}\,(Q_\mathrm{e} - Q_t)dt \tag{1}$$

where $k_{1,s}$ is the constant rate of adsorption and Q_e is the adsorbed amount at equilibrium. Integration of the Eq. (1) at the limit conditions for $t = 0$ to t_o and $Q_t = 0$ to Q_e gives Eq. (2):

$$\ln(Q_\mathrm{e} - Q_t) = \ln(Q_\mathrm{e}) - k_{1,s}t \tag{2}$$

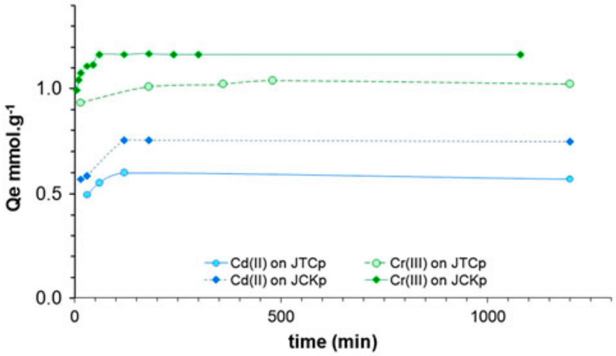

Fig. 1. Effect of contact time on Cr(III) and Cd(II) adsorption onto purified clay samples.

On the other hand, a pseudo-second-order equation based on the equilibrium adsorption capacity can be expressed as the Eq. (3):

$$\frac{\mathrm{d}Q_t}{\mathrm{d}_t} = k_{2,s}\,(Q_\mathrm{e} - Q_t)^2 \tag{3}$$

where $k_{2,s}$ is the pseudo-second-order rate constant.

After linearization and integration, we obtain the Eq. (4):

$$\frac{t}{Q_t} = \frac{1}{k_{2,s}Q_\mathrm{e}^2} + \frac{1}{Q_\mathrm{e}}t \tag{4}$$

The fitting validity of these models is traditionally checked by the linear plots of $\ln(Q_\mathrm{e} - Q_t)$ vs. t and t/Q_t vs. t, respectively. The slope and intercept of the straight line obtained allows calculating the kinetic constants $k_{1,s}$, $k_{2,s}$ and equilibrium concentration Q_e.

The obtained results indicated that the adsorption of heavy metals onto the studied clay did not follow the pseudo-first-order model, while the pseudo-second-order model (Fig. 2) agrees with experimental values. The correlation coefficients for pseudo-second-order kinetic model were greater than 0.999 in all cases.

The slopes and intercepts of plots t/Q_t vs. t were used to calculate the pseudo-second-order rate constants ($k_{2,s}$) and Q_e. The obtained kinetic parameters are summarized in Table 3.

3.1.2. Adsorption isotherms

The adsorption isotherms (Fig. 3a) were performed at pH 3.5 where free cations of cadmium and chromium are the predominant species in solutions [11,36].

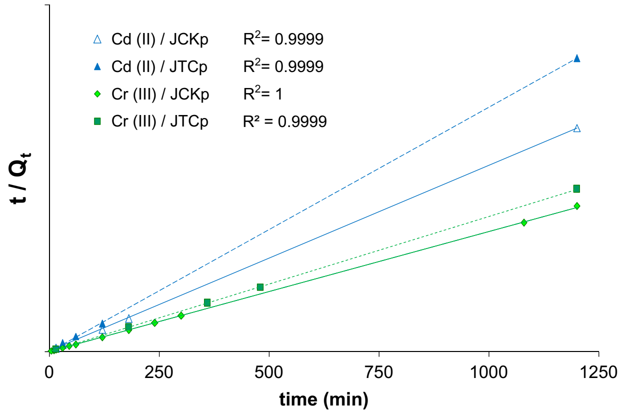

Fig. 2. Pseudo-second-order sorption kinetics of Cd(II) and Cr(III) onto JCKp and JTCp clays at initial concentrations.

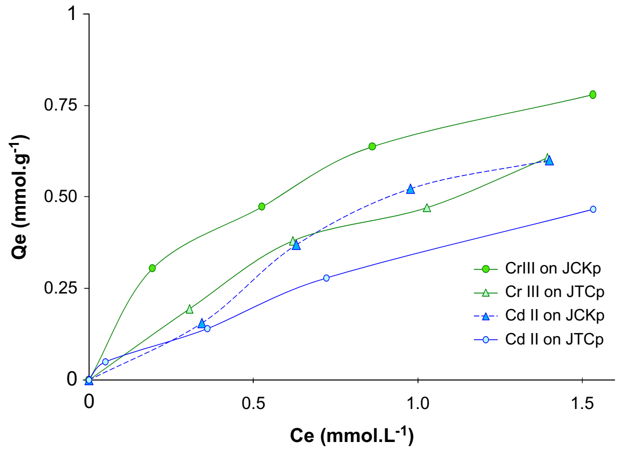

Fig. 3a. Adsorption isotherms of Cd(II) and Cr(III) on JTCp and JCKp at pH 3.5.

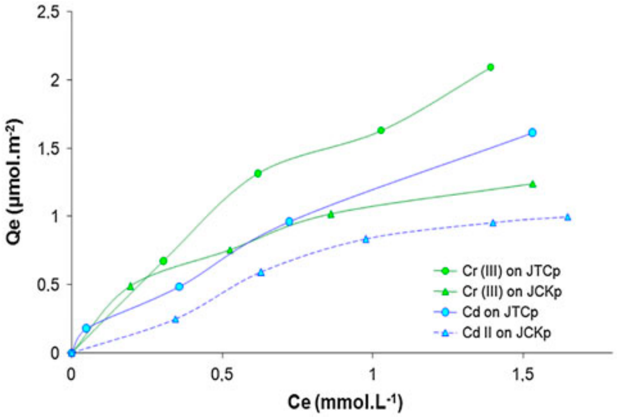

Fig. 3b. Adsorption isotherms of Cd(II) and Cr(III) on JTCp and JCKp at pH 3.5 Q_e reported to methylene blue surface area of JTCp and JCKp.

Reported to the weight of adsorbent, the removal of Cr(III) and Cd(II) by the smectite clay (JCKp) was more efficient than by JTCp. This is expected from the difference in surface area between the two samples when they are immersed in an aqueous solution (see Table 4). If reported to methylene blue surface area (Fig. 3b), the affinity, as evidenced by the initial slope of the adsorption isotherm, was apparently slightly higher for the JTCp sample. Nevertheless, because the dispersion state of the smectite and consequently the number of accessible sites are not known, the real affinity of cations for the JCKp sample cannot be clearly established.

For better isotherms analysis, Freundlich and Langmuir models are used [11,12]. The following linearized form of the Langmuir and Freundlich equations were used:

$$\frac{C_e}{Q_e} = \frac{1}{K_L} + \frac{a}{K_L} C_e \tag{5}$$

$$\log Q_e = \log K_F + n \log C_e \tag{6}$$

where C_e and Q_e are the equilibrium concentration and adsorbed quantities of metallic ions and K_L, a, K_F, and n are the constants for the Langmuir and Freundlich models, respectively

The experimental data for Cr(III) and Cd(II) by the smectite clay (JCKp) and the illitic clay JTCp, in the studied concentration range (0–2 mmol L^{-1}) are in

Table 3
Kinetic parameters pseudo-second-order sorption of Cr(III) and Cd(II) onto purified clays

Heavy metal/clay	$1/Q_e$ (g $mmol^{-1}$)	Q_e (mmol g^{-1})	$k_{2,s}$ (g $mmol^{-1}$ min^{-1})	R^2
Cd/JCKp	1.34	0.75	7.164	0.999
Cd/JTCp	1.76	0. 57	1.580	0.999
Cr/JCKp	0.29	3.45	0.033	1
Cr/JTCp	0.98	1.03	0.270	0.999

Table 4
Physical characteristics of Jebel Chakir and Jebel Tejra clays

Materials	(SE)[a] ($m^2\ g^{-1}$)	SSA[b] ($m^2\ g^{-1}$)	CEC[b] (meq/100 g)
Purified clay (JCK p)	76.8	628	77
Purified clay (JTC p)	61.9	290	31

[a] Determined by applying the BET equation to the nitrogen adsorption isotherm at 77 K.
[b] Obtained using the absorption of methylene blue from aqueous solutions.

good correspondence with Freundlich model (Fig. 4). This result is explained by multilayer adsorption.

Because the adsorption data for all cases did not fit in the Langmuir equation, the results using this model are not reported.

3.1.3. Determination of PSD and zeta potential in water

Fig. 5 shows the attenuation curves for initial clays (pH 3.5, 295 K) at the same concentration. Similar behavior was observed for both suspensions: the attenuation decreased at low frequencies, reached a minimum, and then increased sharply at high frequencies. At low frequencies, the attenuation values were higher for JTCp indicating slightly bigger particles for this solid compared to JCKp.

The corresponding PSDs calculated from attenuation spectra are shown in Figs. 6 and 7. In this case, the PSD was judged to be unimodal according to the PSD criteria's (smaller fitting error). The average particle size was slightly larger in the case of JTCp indicating a more aggregated system (Table 5).

Zeta potential measurements of purified clays showed negative values as expected from their compositions [18,25]. Au et al. [21] showed that the composite suspensions show a more negative zeta potential at any given pH than pure bentonite or pure kaolin slurry. This may be an explanation of the high absolute values of JCKp and JTCp clays zeta potential. Table 6 allows a comparison of these values and that reported in the literature.

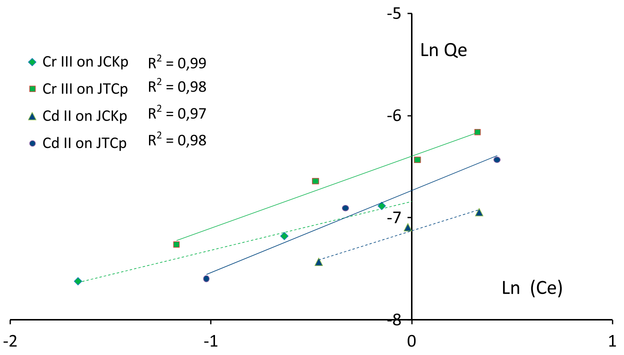

Fig. 4. Linearized Freundlich isotherms for Cd(II) and Cr (III) removal by JCKp and JTCp

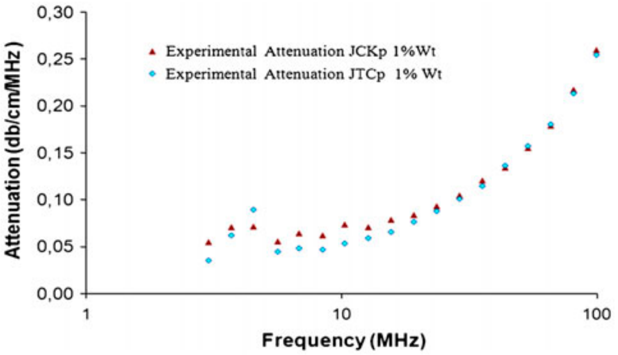

Fig. 5. Experimental attenuation curves for JCKp and JTCp suspensions (1 wt %) in water.

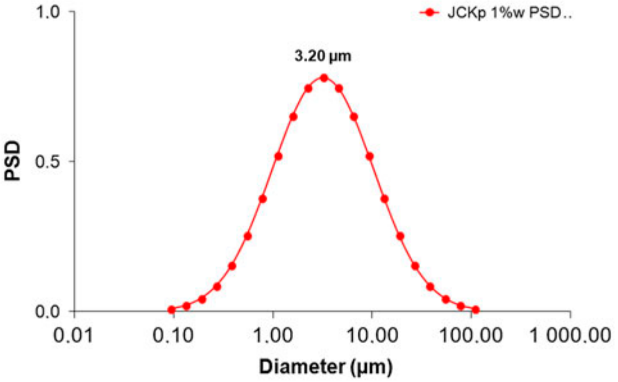

Fig. 6. PSD of JCKp calculated from the attenuation spectra of Fig. 5.

3.1.4. Effect of heavy metal adsorption on zeta potential and PSD

Zeta potential of clay particles in suspension was measured at constant pH (3.5) and room temperature at different heavy metal concentrations. Figs. 8 and 9

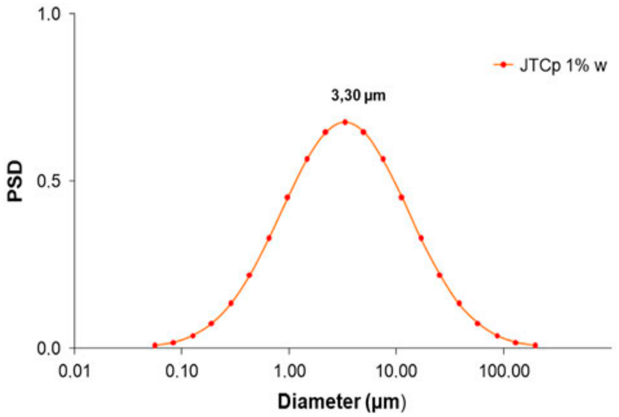

Fig. 7. PSD of JTCp calculated from the attenuation spectra of Fig. 5.

Table 5
Mean particle size of the initial clays (1 wt % in water)

Sample	Peak maximum particle diameter (μm)
JCKp	3.2
JTCp	3.3

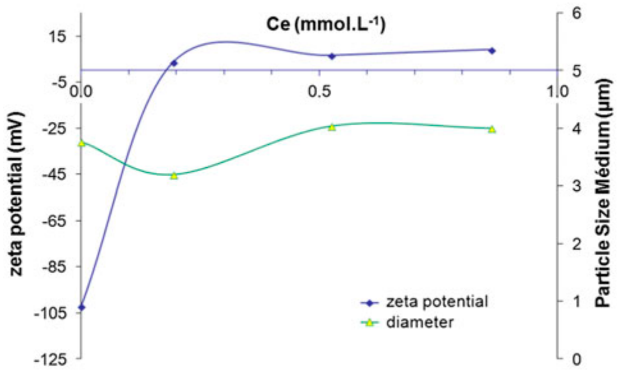

Fig. 8. Variation of zeta potential and mean particle size with Cr(III) adsorption on JCKp.

show the evolution of zeta potential and mean particle size as a function of chromium concentration. The results demonstrate that the addition of chromium and cadmium ions at constant pH value can significantly modify the zeta potential of clay particles. The chromium adsorption lead to an increase in the zeta potential on both clays with a reversal of zeta potential from negative to positive values, which can be directly related to the specific adsorption of chromium (III) species [25,36,37]. In the case of JCKp, the sign inversion was located at about 0.18 mmol L^{-1}. This point was located at higher concentration for JTCp (about 0.35 mmol L^{-1}) which seems to show a higher chromium affinity for the JCKp, which was not possible to be clearly deduced from adsorption isotherms.

In both cases (Figs. 7 and 8), the amount of chromium adsorbed at the isoelectric point, expressed in meq/100 g clay, was greater than the CEC of the clays (Table 7).

In contrast, the adsorption of cadmium (Figs. 10–11) showed no isoelectric point in the studied pH range. This is a surprising result, since the adsorbed amount of cadmium was higher than the CEC. It may show that some cadmium is adsorbed under a neutral form (for example with a co-ion). In addition, other factors (chemical potential, electronegativity) as suggested by Mc Bride [38] could be at the origin of the cadmium behavior.

The adsorption of metal ions on the interface solid/aqueous solution is not only governed by the concentration of free metal ions, but also by complexes of these metals [39]. Metal adsorption is often a highly pH-dependent phenomena. Most important in determining the effect of complexation on adsorption is the adsorbability of the resulting complexes [40].

Table 6
The zeta potential–pH of clays over a pH range

	pH range	Zeta potential (mV)	Refs.
JCKp (Mixed smectite–kaolinite)	4.5–8.0	−103 to −122	
JTCp (Mixed illite–kaolinite)	3.5–7.5	−66 to −65	
Kaolinite	2.5–11.0	−24.0 to −49.5	[19]
Illite	2.5–11.0	0.0 to −42.0	[19]
Chlorite	2.5–11.0	0.0 to −36.5	[19]
Montmorillonite	2–11	−25 to −42.5	[20]
Kaolin	2–12	−14 to −36	[21]
Bentonite	2–12	−30 to −35	[21]
Mixed bentonite–kaolin	2–12	−29 to −44	[21]
Mixed bentonite–kaolin 1:1	2–12	−31 mV to −39	[21]

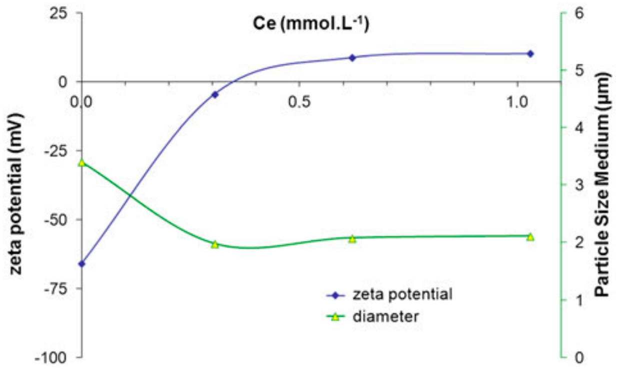

Fig. 9. Variation of zeta potential and mean particle size with Cr(III) adsorption on JTCp.

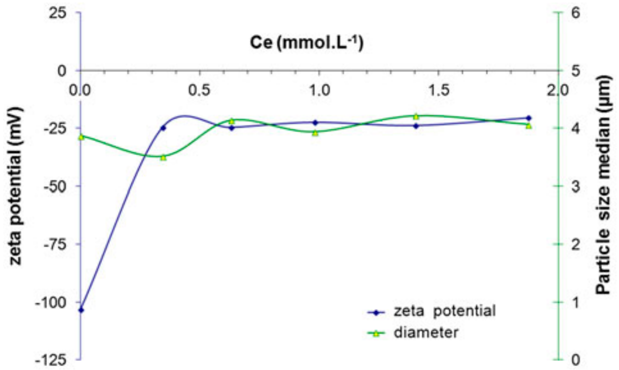

Fig. 10. Variation of zeta potential and mean particle size with Cr(III) adsorption on JCKp.

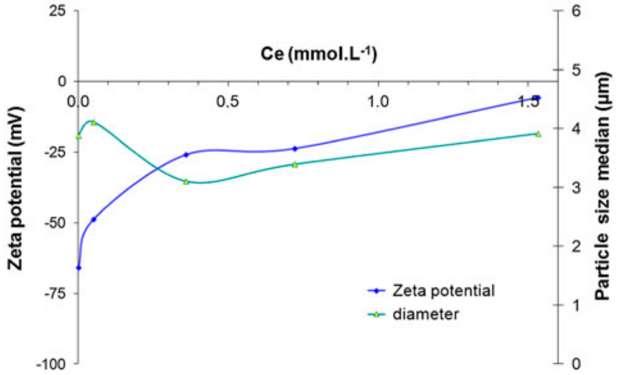

Fig. 11. Variation of zeta potential and mean particle size with Cd(II) adsorption on JTCp.

Aqueous metal cations hydrolysis yields a series of soluble metal complexes, according to the general equation:

$$M_{aq}^{z+} + n\,H_2O \Leftrightarrow M(OH)_n^{z-n} + n\,H^+ \tag{7}$$

$M(OH)_n^{z-n}$: hydroxo complexes

The nature and the distribution of the resulting hydroxo complexes depend on the concentration of ligands and soluble metals. Experimental data on adsorption allow considering that the hydrolysis and adsorption of metals are related phenomena. Thus, it was suggested that the hydroxo complex species are active in the adsorption process [40]. In addition, the absorption of the species MOH^+ was used to explain the observed retention of Cu(II) [41,42] and Zn(II) [43] beyond the exchange capacity of cationic clays. Adsorption of metal complex may be largely a electrostatic phenomenon. However, this adsorption is sometimes not clearly coulombic as in the case of bonds between the surfaces and neutral complexes. The surface complexation, the hydrogen bond, and hydrophobic effects are frequently proposed as mechanisms of specific adsorption (binding relatively strong, in our case with chromium) [42].

This is indicative of a lower affinity of cadmium than that of chromium and a non-specific adsorption for this cation. Mpofu et al. [25] studied the influence of hydrolysable metallic ions, Mn(II) and Ca(II), on smectite suspension stability. Specific adsorption of metallic ion, accompanied by a marked reduction in particle zeta potential was observed.

It is interesting to note that the mean particle size remained constant when the metal concentration increased (Figs. 8, 9) This fact may be due to the existence of initial agglomerated particles of clay for which the size is not modified by the adsorption of chromium or cadmium at constant pH value.

Table 7
Adsorbed quantity and CEC at the isoelectric point

JCKp/Cr(III)			JTCp/Cr(III)		
Q_e meq/100 g	CEC meq/100 g	Q_e/CEC	Q_e meq/100 g	CEC meq/100 g	Q_e/CEC
90.0	77.0	1.2	67.5	31.0	2.2

3.2. Effect of pH on the electrokinetic properties of clays

The results showed that, whatever the clay be (Figs. 12 and 13), a negative zeta potential was obtained in the studied pH range (3–8) and that no isoelectric point was found. The solid JCKp is the most negatively charged clay, ranging from −100 to −120 mV. In the case of JTCp, zeta potential remained constant for all pH range. Although these measurements were performed on complex mixtures of clay, the results are consistent with those obtained from electrokinetic measurements for pure clay [21,44]. JCKp is principally composed of smectite (Table 2), which conferred it a high negative surface charge partially compensated by hydrated cations; whereas for JTCp, mainly composed of illite, the dominating negative charge is due to isomorphic substitution [19] which can partially explain the lower value of zeta potential.

Fig. 12 shows also the variation of zeta potential with pH in solutions with increasing concentrations of chromium. With increasing pH, the zeta potential of JCKp reached a maximum and then decreased. Depending on chromium concentration, an isoelectric point could be observed [45,46]. For example, the isoelectric point was at pH 8 for a chromium concentration of 0.5 mmol L^{-1}. Such maximum was already observed for other clays [19]. At low pH, there is a competition for adsorption on the negative surface of clays between chromium and protons. When pH increases, the chromium adsorption increases because of the decrease in proton equilibrium concentration. This increase is limited by the formation of chromium hydroxides as pH increases (see Table 8). The isoelectric point of the hydroxide, which may be deposited on the clay surface, is around 8 [47]. The apparent surface charge is a mixture of clay surface charge and deposit surface charge for the clay JCKp.

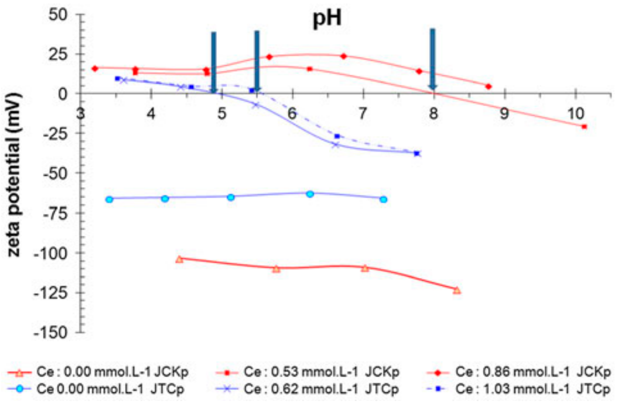

Fig. 12. Effect of Cr(III) adsorption on JCKp and JTCp on the zeta potential.

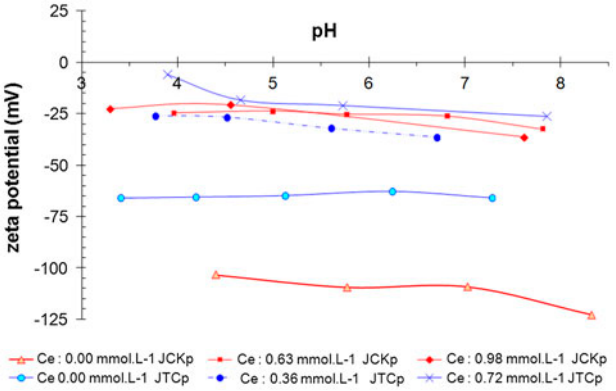

Fig. 13. Effect of Cd(II) adsorption on JCKp and JTCp on the zeta potential.

Table 8
Principle species of cations as a function of pH [26]

pH		% species			
Cation	Species	1.15	3.50	5.20	9.00
Cd^{2+}	Cd^{2+}	99.997	99.997	99.997	93.92
	$Cd(OH)^+$	<0.001	<0.001	<0.001	0.811
	$Cd2(OH)^{3+}$	<0.001	<0.001	<0.001	4.988
	$Cd(OH)_2(aq)$	<0.001	<0.001	<0.001	0.275
Cr^{3+}	Cr^{3+}	99.810	60.448	0.064	<0.001
	$Cr(OH)_2^+$	<0.001	0.0250	35.140	0.219
	$Cr(OH)^{2+}$	<0.124	24.570	62.780	<0.001
	$Cr_2(OH)_2^{4+}$	<0.001	14.189	0.143	<0.001
	$Cr_2(OH)_4^{5+}$	<0.001	0.796	0.015	<0.001
	$Cr(OH)_3(aq)$	<0.001	<0.001	1.853	99.790

For JTCp clay, the zeta potential decreases with an isoelectric point around pH 5. This is another indication of the lower affinity of chromium ion for this sample.

Upon the addition of cadmium, the clays surface was always negatively charged and the zeta potential (Fig. 13) followed the same trend for both clays: it slowly decreased to reach similar values, whatever the cadmium concentration. Similar behavior was observed for Ca(II) and Mn(II) ions adsorption on smectite [18]. Free cation of cadmium (Cd^{2+}) is the predominant species in solution at all pH [39].

4. Conclusion

The behavior of two clay minerals JCKp and JTCp toward metallic cation adsorption, chromium(III), and cadmium(II), has been evaluated. For this, sorption capacities, potential zeta, and PSD were determined.

Adsorption isotherms indicated that the removal of chromium and cadmium by the smectite clay JCKp is more efficient. The addition of chromium and cadmium ions at constant pH significantly modifies the zeta potential of clays particles. Chromium adsorption on both clays showed reversal of zeta potential from negative to positive values which was directly related to the specific adsorption of chromium(III) species. In the case of cadmium adsorption, a significant increase in the zeta potential for both clays was observed, but it remained negative at all Cd(II) concentrations. This is indicative of a lower affinity and a non-selective adsorption of this cation. This study revealed also that the zeta potential of clays was pH dependent during the adsorption of cations. Here, the effect of chromium(III) adsorption was highlighted. In contrast, the adsorption of cadmium(II) showed no isoelectric point in the pH range studied.

The results of this study may be used to predict the uptake efficiency of these adsorbents in view of their application for the removal of metal ions from contaminated effluents. The clay JCKp could be successfully used for the removal of chromium(III) and cadmium(II) ions and also may constitute a barrier in the landfills.

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