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Arabian Journal of Chemistry

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REVIEW

Competitive adsorption of heavy metals on local landfill clay

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Ibtissem Ghorbel-Abid *, Malika Trabelsi-Ayadi

Laboratoire des Applications de la Chimie aux Ressources et Substances Naturelles et à l'Environnement (LACReSNE), Faculty of Sciences of Bizerte, Zarzouna 7021, Tunisia

Abstract The aim of this study is to investigate the interaction of Cr^{III} and Cd^{II} ions in solution with the local landfill clay of Jebel Chakir (Ghorbel-Abid et al., 2009) located in the northwest of Tunis (Tunisia, North Africa). The adsorption properties of natural clay and the Na-purified clay in a chromium and cadmium rich aqueous solution have been studied by batch technique. The amount of adsorbed heavy metals ions, Q_e, was determined for the adsorption systems as a function of the contact time, the pH, and the metal ion concentration. The results show that the uptake of Cr^{III} by the purified clay is very fast. The quantity removed from the solution reached a maximum value 15 min after mixing, for the purified clay, and 1 h for the natural clay, although the latter removes greater quantities of Cr^{III} ions compared to the Na-purified clay. However, the uptake of Cd^{II} reached its maximum value approximately 2 h after mixing, for the purified clay, and 3.5 h for the natural clay, although the removed quantities of Cd^{II} ions are comparable in both the Na-purified and natural clay.
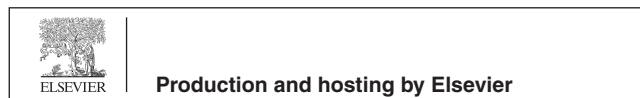
The experimental data points have been fitted to the Langmuir and Freundlich models. The competitive adsorption isotherms of Cr^{III} and Cd^{II} ions in similar conditions have been studied by the batch technique. The amount of adsorbed ions, Q_e was determined. The results show that the presence of Cd^{II} has an important effect on the uptake of Cr^{III}.

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* Corresponding author. Tel.: +216 21 024 843; fax: +216 72 590 566.
E-mail address: ibtissem.ab@planet.tn (I. Ghorbel-Abid).

Contents

1. Introduction

For decades, urban and industrial pollution has led to a gradual environmental degradation of the natural environment (atmosphere, water or soil). This phenomenon is serious and requires great efforts to correct the situation and prevent its proliferation. That is why the scientific knowledge of the contamination process is paramount. Demographic and economic changes in consumption patterns of Tunisia's residents resulted in an increase in the volume of household wastes to 1,800,000 metric tons per year (0.5 kg/person/day) with an annual growth rate production of 2% (ANPE-PRONAGDES, 2005). This required the creation of controlled landfills for household and similar wastes in the urbanized areas. Such landfills are adding to the environmental degradation which needs to be contained and redressed before it becomes irreversible.

Clays have been evaluated for their purifying qualities since they are thought to act as a filter and purifier of pollutants (Ghorbel-Abid et al., 2009, 2010; Coetzee et al., 2003; Bailey, 1999; Chakir et al., 2002; Ayari et al., 2005, 2007a,b; Vegal et al., 2005; Kaya and Hakan, 2005; Ramesh et al., 2007; Bellir et al., 2005; Yavuza et al., 2003; Abollino et al., 2003; Auboiroux et al., 1996; Barbier et al., 2000). Given their high impermeability, clays are often used as pollution barrier for waste storage sites (Bellir et al., 2005; Kouamel et al., 1970). In most cases, the nature of clay that seals the site floor is a criterion for selecting the landfill site.

The evolution process of waste degradation led to the production of leachates.

The composition of leachates is highly variable from one discharge to another depending on waste composition.The chemical composition varies in a quasi-permanent pattern due to the complex nature of waste into rich organic and inorganic pollutants, especially heavy metals. Moreover, the composition of leachates changes over time due to the evolution process of waste degradation which is strongly linked to the physico-chemical and biological processes occurring in the landfill. Researchers (Coetzee et al., 2003) have studied the geochemical mechanisms that govern the vertical migration of some heavy metals to assess the risk of contamination of water by metals from the landfill leachates. The geochemical processes that govern the vertical migration of heavy metals indicate that adsorption is the dominant mechanism. The alkaline (7–10) and slight acidity (6–7) pH of the medium have a significant influence on the chemical form of metals and seem to favor the adsorption mechanism. Although the presence of heavy metals does not cause immediate danger to the population, it can lead to sustained, irreversible or wider contamination of the environment. This in turn could lead to long-term contamination of the surrounding soil and groundwater. The landfill in Jebel Chakir (north-west of Tunis), which received 7 M metric tons of waste in 2009, is the case we studied in this research.

We have focused our adsorption study on two heavy metals: cadmium and chromium, given their dangerous impact on heath and the environmental future of the site, and their significant presence in the leachates from the decomposition of solid waste landfill of Jebel Chakir. Their concentrations may reach $0.02 \, mg \, L^{-1}$ and $3.30 \, mg \, L^{-1}$ for cadmium and chromium, respectively. Cadmium is one of the few elements with no known function in human or animal life. However, its toxicity is known in all its forms (metal, vapor, salts, inorganic and organic compounds). For chromium, the chemical and toxicological properties are significantly different depending on the concentration and valence state it happens to be in.

Since the study of adsorption of heavy metals in leachates on clay in real conditions is difficult because of the complexity of the system involved, we resorted to studying synthetic systems using solutions containing one or both of these cations (Cd^{II}, Cr^{III}) and the natural or purified clay fractions.

2. Experimental set up

2.1. Materials

Local clay from Jebel Chakir has been characterized in an earlier study (Ghorbel-Abid et al., 2009). The chemical compositions in weight percentage for the raw material denoted as JCKb, and for the Na-purified clay denoted as JCKp are given in Table 1. Heavy metals are present in the natural and the purified clays in a trace amounts.

The cation exchange capacities (CEC) as well as the total internal plus external surface areas (SSA) were determined

Table 1 Chemical composition of Jebel Chakir clay.

wt%	SiO$_2$	Al$_2$O$_3$	CaO	Fe$_2$O$_3$	K$_2$O	MgO	Na$_2$O	MnO	Total
JCKb	42.35	16.06	22.51	13.36	2.50	1.68	1.56	0.03	100
JCKp	55.53	29.01	0.35	10.17	1.97	1.13	1.84	0.01	100

by the adsorption of methylene blue (MB) from the aqueous solutions. The (CEC) and (SSA) values for the natural fraction are 50 meq/100 g, 403m^2/g for the fired clay, and 77 meq/100 g and 628 m^2/g for the Na-purified fired clay fraction The specific surface area (SE) was calculated by applying the BET equation to the nitrogen adsorption isotherm at 77 K. Their values are 48.95 m^2/g for JCKb and 76.78 m^2/g for JCKp. The mineralogical composition (Table 2) of purified clay is smectite with a small proportion of kaolinite.

Natural clay from Jebel Chakir was powdered in an agate mortar and sieved through 63 μm mesh to obtain finer grains. The resulting clay powder was dried at 60 °C, before the experiments. JCKb indicated the raw select sample. The BEM (Fig. 1) is used to observe its morphology with a Cambridge Instrument S 90.

Table 2 Mineralogical composition (wt%).

Sample	Smectite	Kaolinite	Calcite	Quartz
JCKp	80	20	Trace	Trace
JCKb	43	11	22	24
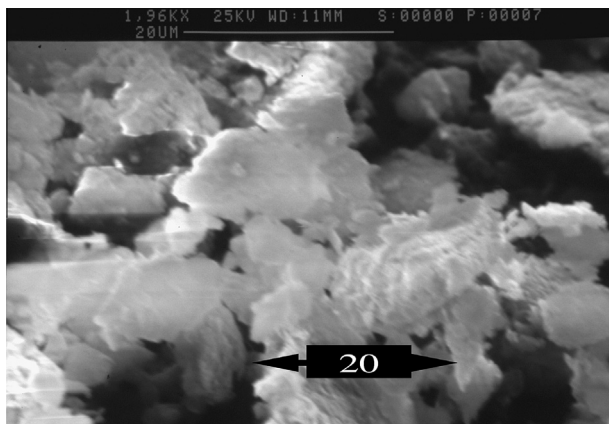
Figure 1 Scanned Electron Micrograph of Jebel Chakir Clay magnified 1960 times.

2.2. Reagent

To establish the adsorption isotherms of the two metals on the two clays we opted for the use of solutions of chlorides of these metals (CdCl$_2$) and chromium trichloride (CrCl$_3$) solution. This choice is closer to natural compositions of leachates (Table 3). All the reagents used in our study are of high purity (i.e., analytical grade). The ultrapure water used is produced with a Millipore Milli-Q system. A pH meter was used to measure the pH, standard solutions at pH 4.0, 7.0 and 10 have served for its calibration. Centrifugation was done with a Sigma 2–15 centrifuge at 4000 rpm. Table 3 shows the natural compositions of leachates of Jebel Chakir's landfill. The quantitative analysis of cadmium and chromium solutions was made by inductive coupled plasma-atomic emission spectroscopy (ICP-AES, Optima 3300. Perkin–Elmer).
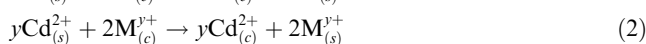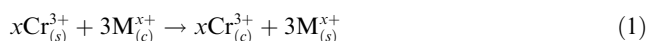
3. Experiments and results

3.1. Batch studies

The experiments for the two metallic ions on JCKb and JCKp were performed using the batch method for CdCl$_2$ and CrCl$_3$ solution at room temperature (22 ± 3 °C). In all the cases considered, the solution to sorbent ratio was fixed at 1 g L^{-1}. The experiments were carried out in centrifuge tubes by subjecting 20 mg of clay to a fixed shaking period of 20 h with 20 mL of metal solution on a vertical rotary shaker (50 turns/min). After adding the clays, the pH of the suspension increased and was readjusted to a preselected pH value. The sorbent was separated using a centrifugation step. After centrifugation, the supernatant liquid was used for measurements. Quantitative analysis of cadmium and chromium in solution was made by ICP. The batch adsorption experiments were also conducted at different pH levels [pH 3–7] and solution pHs were adjusted by adding diluted NaOH and HCI solutions.

3.2. Amount of adsorbed heavy metal ions on clays

The equilibriums that describe the interaction between the *heavy metals* ions and clay are:

$$xCr^{3+}_{(s)} + 3M^{x+}_{(c)} \rightarrow xCr^{3+}_{(c)} + 3M^{x+}_{(s)} \tag{1}$$

$$yCd^{2+}_{(s)} + 2M^{y+}_{(c)} \rightarrow yCd^{2+}_{(c)} + 2M^{y+}_{(s)} \tag{2}$$

Table 3 Natural compositions of leachate of Jebel Chakir landfill, pH 6.65 (at 19.9 °C).

Parameter	(CO$_3^-$)$_2$	SO$_4^{2-}$	NH^{4+}/N	CN$^-$	NO$_3^-$	P$_{Total}$	Cl	Na	K
Concentration (mg L^{-1})	22.2 × 10^3	625	2.2 × 10^3	54.7	< 1.1	12.5	3.8 × 10^3	3.7 × 10^3	2.4 × 10^3
Parameter	Al	Cd	As	Sn	Cu	Fe	Pb	Mn	Ni	Zn
Concentration (mg L^{-1})	0.554	0.006	< 0.05	< 0.025	0.030	228	0.150	9.14	1.16	0.942

where x and y are the exchangeable cations valence M (Na, K, Ca, Mg, Mn) and subscripts (s) and (c) denote solution and clay phases, respectively.

The amount of adsorbed metallic ions in the clay can be expressed as:

$$Q_e = \frac{C_i - C_e}{S} \qquad (3)$$

where, Q_e, C_i, C_e and S are the adsorbed metallic ion onto the clays (mg/g), the initial concentration (mg/l), the equilibrium concentration of metallic ion (mg/l) and the slurry concentration, respectively.

In the case of the cadmium and chromium solutions, pH was adjusted before adding clays, by adding diluted NaOH and HCl solutions. NaOH and HCl solutions were prepared in 0.01 N stock solutions. After adding the clays, the solution pH increased and was readjusted.

3.3. Effect of shaking time

To determine the time required for equilibrium adsorption, we varied the contact time between adsorbent and adsorbed in the range [15–1800] min at pH 4, the initial concentrations of Cd(II) and Cr(III) have been fixed at 200 mg L^{-1}, and the concentration of clay in the suspension at 1 g L^{-1}. The quantities of adsorbed cadmium and chromium per gram of clay were calculated by the method of residues using Eq. (2). These quantities are plotted as a function of contact time in Fig. 2.

The adsorption of Cd II on JCKp and JCKb reached equilibrium around 120 min. and showed a slight decrease in the case of JCKp and a decrease for the largest raw clay JCKb that could be attributed to desorption of cadmium. Also, some other studies that analyzed the kinetics of adsorption of Cd II on kaolinite noted a decrease after 12 h (Srivastava et al., 2005). Similarly, the adsorption of cadmium on vermiculite exhibits this decrease of retention after 65 h (da Fonseca et al., 2006). However, the adsorption of Cr$^{(III)}$ on JCKp is almost instantaneous, since after 15 min, a plateau is reached. The adsorption of Cr$^{(III)}$ on JCKb is slower since it is completed after 30 min.
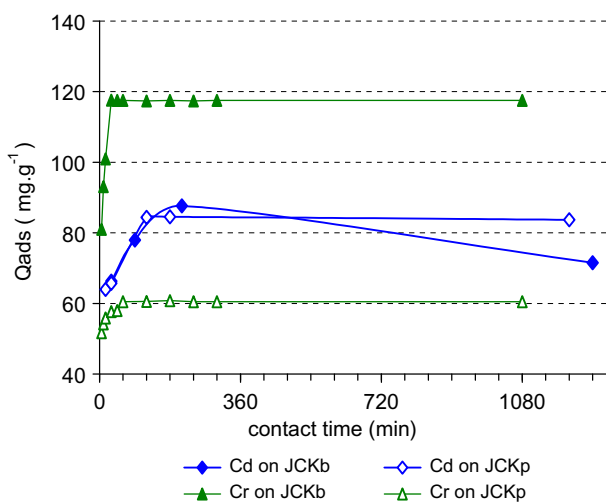
Chakir et al. (2002) studied the retention of Cr$^{(III)}$ by bentonite at pH 3 with an initial concentration of 5×10^{-3} mol L^{-1}. They found that the equilibrium is also reached after 30 min.

We can deduce from these experiments that the equilibrium times of adsorption are achieved faster for chromium. The equilibrium adsorption of cadmium is slower to reach but did not exceed 210 min in all the analyzed cases. Thus, given these results and for convenience reasons, the contact times were set at night (960 min) for the adsorption experiments on the effects of pH and initial concentrations of Cr III solutions and Cd II.

3.4. Effect of pH

The influence of pH of the clay suspension on cadmium retention has been observed and reported in Fig. 3.

Studying the behavior of chromium was limited by the precipitation of chromium, in the (Coetzee et al., 2003; Bailey, 1999; Chakir et al., 2002) pH range. The study of the effect of pH of the clay suspension was made under the same conditions for chloride concentrations of cadmium and chromium, temperature, and concentration of adsorbent suspensions. The results are reported in Table 4.

These results show the influence of the pH level on the adsorption capacity of chromium by JCKb, JCKp. Fig. 3 shows that when the pH increases, the amount adsorbed at equilibrium increases for all clay fractions studied (Table 4). Conversely, it seems that the adsorption capacity of cadmium
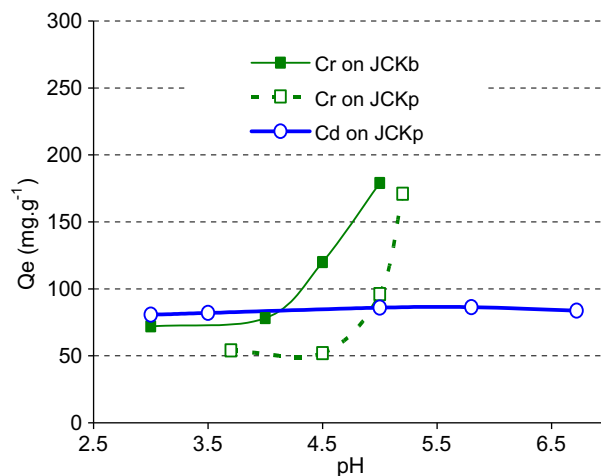
Figure 3 Effect of pH on adsorption of Cd(II) and Cr(III) on JCKb and JCKp.

Figure 2 Effect of shaking time on adsorption of Cd(II) and Cr(III) on JCKb and JCKp.

Table 4 Adsorption capacity at different pH values.

	pH	Qe (mg g^{-1})
Cd (II)/JCK p	3.5	86
	6.8	87
Cr (III)/JCK p	3.7	54
	5	96
Cr (III)/JCK b	3	72
	5	179

on JCKp is weakly influenced by the pH. The increased fixing capacity for $Cr^{(III)}$ when the pH increases may be attributed to the exchange adsorption of hydrolyzed species that compete for exchange sites with H^+. The study of sepiolite and kaolinite gives different results because of the presence of silanol in this type of clays.

Alvarez-Ayuso and Garcıa-Sanchez (2003) studied this influence in the case of sorption on sepiolite. They observed that the amount of adsorbed Cd II increases when the pH of the solution increases in the interval (Coetzee et al., 2003; Bailey, 1999; Chakir et al., 2002; Ayari et al., 2005). They justified this phenomenon by the fact that sepiolite has a large number of silanol sites on the outer surface and that when the pH decreases, the proportion of these groups decreases.

The effect of pH on the adsorption of Cd II by kaolinite was examined by Srivastava et al. (2005). Their work focused on two modes of ion binding Cd on kaolinite namely ionic exchange sites of permanent charge, and complexation of amphoteric Si-OH groups and Al-OH on the edges of particles. These sites are dependent on the pH. When the pH of the clay suspension increases, the second mode of binding is weak which explains the low value of the adsorbed quantities.

3.5. Isotherms for exchange

The study of the isotherms has often been regarded as the best approach in the study of the theoretical aspects of all adsorption systems. These isotherms are graphs where the amounts adsorbed are plotted against the pressure (or concentration

of the adsorbate) in the external phase at constant temperature and usually under conditions of equilibrium as in Gilles (1974). The adsorption results were analyzed in terms of Langmuir and Freundlich isotherms.
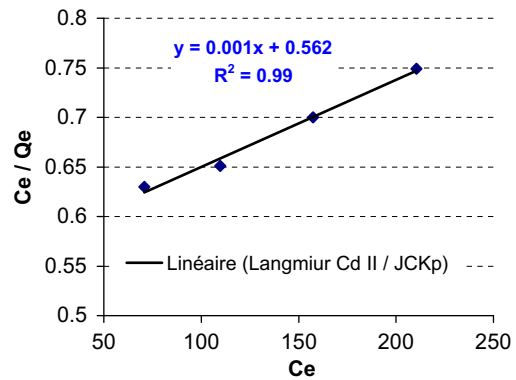

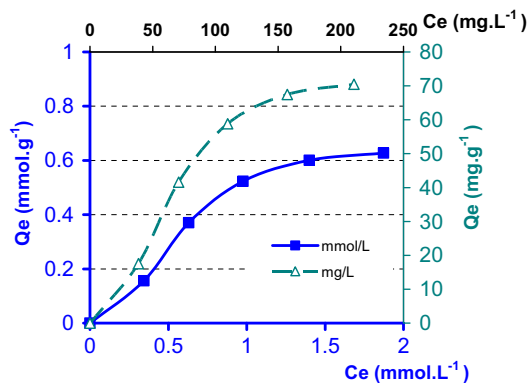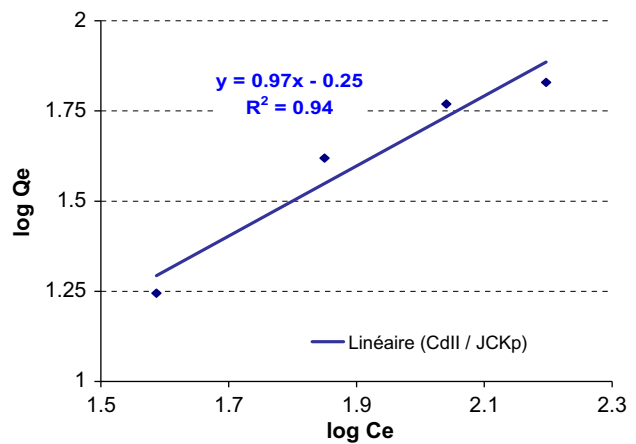**Figure 6** Linearized Langmuir adsorption isotherm of Cd(II) by JCKp at pH 3.5.

Figure 7 Linearized Freundlich adsorption isotherm of Cd(II) by JCKp at pH 3.5.

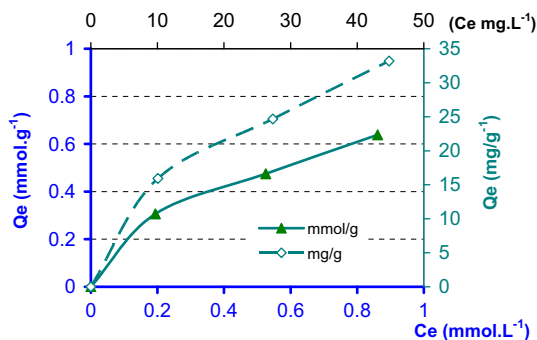**Figure 4** Adsorption isotherm of Cd(II) by JCKp at pH 3.5.

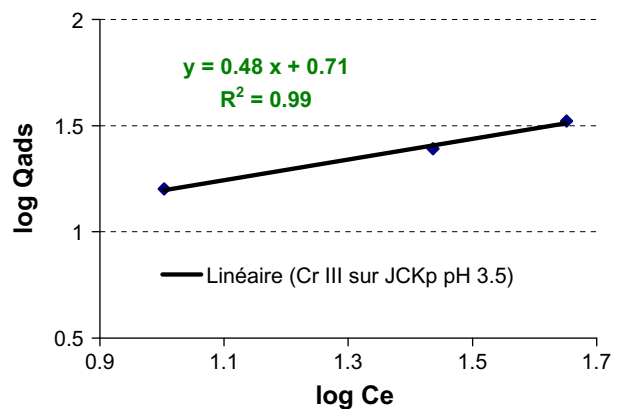**Figure 5** Adsorption isotherm of Cr(III) by JCKp at pH 3.5.

Figure 8 Linearized Freundlich adsorption isotherm of Cr(III) by JCKp at pH 3.5.

The data obtained for the experiments were fitted to the Langmuir and Freundlich isotherms (Langmuir, 1918; Freundlich, 1906) as reported in Figs. 4 and 5.

The following linearized form of the Langmuir and Freundlich isotherms was also used for this purpose. To do this, the adsorbed metallic ion Q_e, onto the clays (mg/g) is expressed as:

$$Q_e = \frac{K_L C_e}{1 + aC_e} \qquad (4)$$

$$Q_e = K_F C_e^n \qquad (5)$$

where K_L, a, K_F and n are the constants for the Langmuir and Freundlich models respectively.

The linear forms of these equations are:

$$\frac{C_e}{Q_e} = \frac{1}{K_L} + \frac{a}{K_L} C_e \qquad (6)$$

$$\log Q_e = \log K_F + n \log C_e \qquad (7)$$

Table 5 The parameters of Langmuir and Freundlich isotherms.

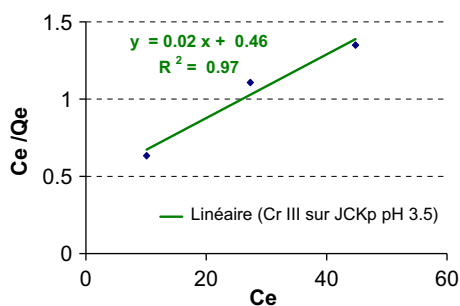|	Langmuir parameters			Freundlich parameters		
	K_L (g L^{-1})	a (L g^{-1})	R^2	K_F (L^{-1} g)	n	R^2
Cd/JCK p	1.78	0.002	0.99	–	–	0.94
Cr/JCKp	0.47	0.10	0.99	5.13	0.49	0.99

Figure 9 Linearized Langmuir adsorption isotherm of Cr(III) by JCKp at pH 3.5.
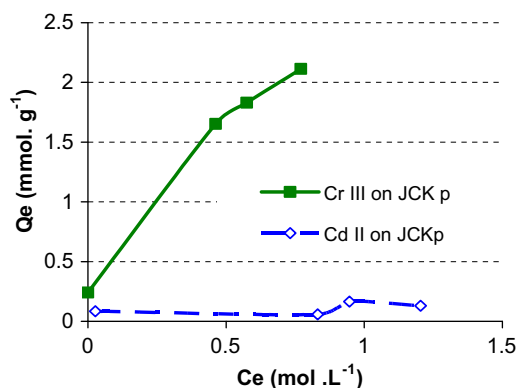

Figure 10 Competitive adsorption isotherm of Cr(III) ad Cd(II) on JCKp.

Table 6 Comparative adsorption capacity of JCKp (pH 3.5).

	Single-element systems Qe (mg g^{-1})	Binary-element systems Qe (mg g^{-1})
Cd (II)/JCK p	62.5	20.0
Cr (III)/JCK p	64.5	110.0

Table 7 Chemical properties of chromium and cadmium ions.

Cation	Electronegativity	Ionic radius (nm)	Charge density z/r	Ionic potential z^2/r
Cr^{3+}	1.66	0.061	49.18	147.55
Cd^{2+}	1.69	0.097	20.62	41.23

Fig. 6 shows the adsorption isotherms of trivalent chromium and divalent Cadmium on JCKp, at room temperature (22 °C) and pH 3.5 (see Fig. 7).

The experimental data fit very well the Linearized Langmuir isotherm (Fig. 6) for Cd(II). It is most significant that the adsorption model corresponds to a monolayer model.

For Cr(III) the experimental data also fit well with the Freundlich model (Fig. 8). This result is explained by multilayer adsorption. The parameters of Langmuir and Freundlich isotherms, given in Table 5, confirm those models (see Fig. 9).

3.6. Competitive adsorption isotherms

Using the solution containing the two-metal ions Cd and Cr, we analyzed their competitive behavior. The competitive adsorption isotherms of Cd(II) and Cr(III) JCKp are represented in Fig. 10.

The experimental isotherm shows a significant increase in the adsorption capacity of Cr(III) on JCKp. In the presence of Cd(II), the chromium adsorbed quantity reached 110.0 mg g^{-1} in the binary-element system, up from 64.5 in the single system. However, in the presence of Cr(III), adsorption capacity of Cd(II) fell to 20.0 mg g^{-1} in the binary-element system, while it was 62.5 mg g^{-1} in the single-element system (see Table 6).

This result is in agreement with Mc Bride's (1989) who linked the specific adsorption of heavy metals in the order of affinity based on the chemical properties of each element (chemical potential, electronegativity, position in the series of Irving Williams) [34]. Taking into account all these factors, Table 7 shows that the chromium stands as the strongest ion.

4. Conclusion

This study indicates that the smectic clay JCK could be used as an efficient low-cost adsorbent. In single-element systems we have observed an increase in the pH-enhanced adsorption capacity for chromium. The adsorption capacities for the Cr(III) and Cd(II) by purified Jebel Chakir Clay are 64.5 and 62.5 mg g^{-1}, respectively, in single-element systems. Thus, the removal efficiency is strongly modified when the two metals are present in a solution. A significant 110 mg g^{-1} increase for chromium uptake and a 20 mg g^{-1} decrease for cadmium were observed in binary-element systems.

Clays have been evaluated for their purifying qualities since they are thought to act as a filter and purifier for pollutants. Our results provide further support of this view reaffirming that certain clays could be a promising agent in the fight against heavy metal pollutants in waste landfills when used as pollution barriers in waste storage sites.

Acknowledgments

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