



Preparation and characterization of pillared montmorillonite: application in adsorption of cadmium

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Abstract

This work concerns the pillaring of Algerian montmorillonite with polyhydroxymetal such as aluminum and chromium and its application in adsorption of inorganic pollutant in the water : the cadmium. A systematic study of different parameters was undertaken such as the ratio of Cr/Al (5, 10, 20, 50 and 80 mmoles/g) ; Cr/Al (0, 0.2, 0.6, 1.2 and 5 mol/mole), aging time of metallic hydrolysis (1, 4, 24 and 36 h) and temperature (25, 40, 60 and 95°C). The obtained pillared clays were characterized by X-ray diffraction, physisorption of nitrogen at 77 K and by transmission electronic microscopy. It has been shown that a high temperature and a long time of metallic polymerization (before the intercalation) are in favor to a good pillaring. Indeed, the chromium polymer resulted by the hydrolysis under 95°C for 36 h leads (after intercalation and burn-off at 150°C) to a pillared clays with an interesting and stable textural properties ($d_{001} = 19.13 \text{ \AA}$, $A_{sp} = 196 \text{ m}^2/\text{g}$ when calcined at 300°C). The effect of ratio Cr/Al shows that its increase is not favorable to the expansion of clay layers. When the ratio Cr/Al goes from 0.2 to 1.2, the basal spacing decreases from 17.8 to 16Å. The samples which have optimal properties were used as adsorbent of heavy metal. In this part of work, a systematic study optimizing the adsorption was also realized. The equilibrium time reaches 20, 40 and 80 min for the clays Mont.Al-Cr (Cr/Al = 0); Mont.Al-Cr (Cr/Al = 0.2) and Mont.Cr respectively. The adsorption yield is about 91%, 27% and 10% for an adsorption at 20 min for the above-mentioned clays respectively. These results reveals that the Al pillared clay (Cr/Al = 0) has a better affinity toward the cadmium in our conditions.

Keywords: Clay; Polymers; Adsorption; Pollutant; Basal spacing; Heavy metal

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1. Introduction

Pillared clays with different inorganic compounds have drawn much attention and many studies have been carried out during these two last decades. This class of materials is obtained from expansive clay such as montmorillonite, by cationic exchange with polycations.

Montmorillonite is a mineral clay that can hold guest molecules between its layers. Substitution of Si^{4+} with Al^{3+} and Al^{3+} with Mg^{2+} gives the lattice a net negative charge which is balanced by alkali metals and alkali earth cations (usually Na^+ and Ca^{2+}) located between the layer. These cations can be replaced by hydroxyl-metal cations oligomers which act as pillars that separate the lattice layers. By calcinations the pillars are fixed and the clay is converted into a rigid microporous material with substantial surface area. Numerous cations (hydroxyl aluminum [1], zirconium [2–4], chromium) have been used for the preparation of pillared montmorillonite characterized by surface area of 200–400 m^2/g ; pore volume of 0.15–0.30 cm^3/g and interlayer spacing of 1–2 nm. These microporous materials have shown catalytic ability in much organic reaction [4,5] and a high sorption capacity at adequate pH of heavy metals [6,7].

Adsorption of metals from aqueous solutions onto various soils or soil constituents plays an important role in influencing the metal transport in natural and engineering systems. Cadmium, as a result of its numerous uses, can pollute water and soils and it is well known that heavy metal pollution is a serious threat to the environment. In order to predict the fate of these contaminants in soil, it is necessary to improve the knowledge of their behavior in such a clay system. The most important processes regulating the free concentration of heavy metals in natural media, such as the adsorption by solid surfaces and the release from sediments, highly depend on an interfacial chemical reaction. Consequently, many research studies have focused on the interactions of

dissolved metals with surfaces of naturally occurring oxides [8–10]. Adsorption of heavy metals at oxide/water interface can be described as surface complexation mechanism [11]. The uptake of heavy metals by clay minerals is obviously more complicated and depends on pH.

In this present work, we propose to elaborate a microporous material starting montmorillonite by pillaring it with chromium and aluminum and to study cadmium adsorption ability of these pillared clays.

2. Experimental

2.1. Starting material

The clay used in this work is a bentonite from a deposit of northwest of Algeria (Maghnia). The parent material had the following chemical composition (in wt%): SiO_2 (69.4), Fe_2O_3 (1.3), MgO (1.1), Al_2O_3 (14.7), CaO (0.3), TiO_2 (0.2), Na_2O (0.5) and K_2O (0.8). The montmorillonite fraction is obtained by usual sedimentation and then saturated with 1 M NaCl solution to obtain a homionic compound. The sodium montmorillonite is then washed up to constant conductivity (Mont-Na). The cation exchange capacity of this clay determined from the ammonium exchanged from (microKjeldhal method) was 90 meq/100g.

2.2. Intercalation of montmorillonite

2.2.1. Chromium hydrolysis

The preparation of polyoxometal complexes for the pillaring montmorillonite is carried out by hydrolyzing metal ion solution by using Na_2CO_3 ($\text{CO}_3^{2-}/\text{Cr}^{3+} = 2$ meq/mmol). Generally, NaOH is avoided as source of base hydroxides. The effect of temperature of hydrolysis (25, 60, 95°C) aging time (1, 4, and 36 h) was studied.

2.2.2. Cr–Al hydrolysis

A certain amount of aqueous 0.1 M AlCl_3 was

gradually added to an aqueous CrCl_3 solution, resulting in product solutions having various Cr/Al ratios (0, 0.2, 0.6, 1.2 and 5). An aqueous Na_2CO_3 solution (0.1 M) was then added to these solutions with constant stirring until a final OH/(Cr+Al) ratio of 2.4 was reached. The resulting solutions were aged for 14 days at room temperature and for 4 h at 90°C [12].

2.3. Pillaring process

2.3.1. With chromium oligomer

The reaction of Na^+ montmorillonite with CrIII solution hydrolysed under various conditions of temperature and aging time is carried out with different ratios Cr/clays (2, 10, 50 and 80 mmole/g).

2.3.2. With Cr-Al oligomer

The pillaring agent solution with different Cr/Al ratios was added with rigorous stirring to clay slurry during 36 h at 95°C , aged for 7 days to ensure maximum swelling of the sheet. The final proportion in all case was 10 mmole/g of (Al+Cr)/g of clay.

2.4. Characterization of clays

These supports were characterized by different methods. The surface areas were determined from nitrogen adsorption isotherms measured at liquid nitrogen temperature using an ASAP 2010 sorptometer (Micromeretics).

The basal spacing of samples was measured by X-ray. Diffraction on a thin layer of the clay deposited on glass solids using a Philips vertical goniometer with nickel filtered Cu K_α radiation. The samples were also analysed by trans-mission microscopy which give the composition of pillared and non-pillared clay at different points of the surface.

2.5. Cadmium adsorption test

2.5.1. Adsorption kinetics

This part of experience is conducted in order to determine the effective equilibrium time of adsorption. The tests are carried out in pillared clays suspensions of 0.1 g in 100 ml of solution where the concentration of cadmium is 10 mg/l. After shaking, the sampling is accomplished each 10 min. These samples were centrifuged at 3000 rpm and the clear supernatants were collected. The determination of Cd in the supernatants was performed using an atomic adsorption spectrometer (Philips PU 9300 X).

2.5.2. Adsorption isotherm

Adsorption isotherms of the various prepared samples were measured for the screening properties of clays. The adsorption is conducted out with a constant concentration of cadmium. The mass of pillared and non-pillared clays varies from 10 to 150 mg. The mixtures are stirred at 25°C during 24 h when the real equilibrium is supposedly reached.

3. Results and discussion

3.1. Chromium hydrolysis

The behavior of the chromium polymer was studied by UV-visible and pH measurements. It has been shown that the $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution which is used for the preparation of the polymer is blue and have a maximum of absorption at 407 and 575 nm. When the solution is allowed to age, particularly at elevated temperature, the pH of the solution decreased. This result suggests that there is liberation of protons during the oligomerization. The change in pH is accompanied by a shift in the UV-visible absorption band of CrIII to longer wavelengths as shown in Fig. 1.

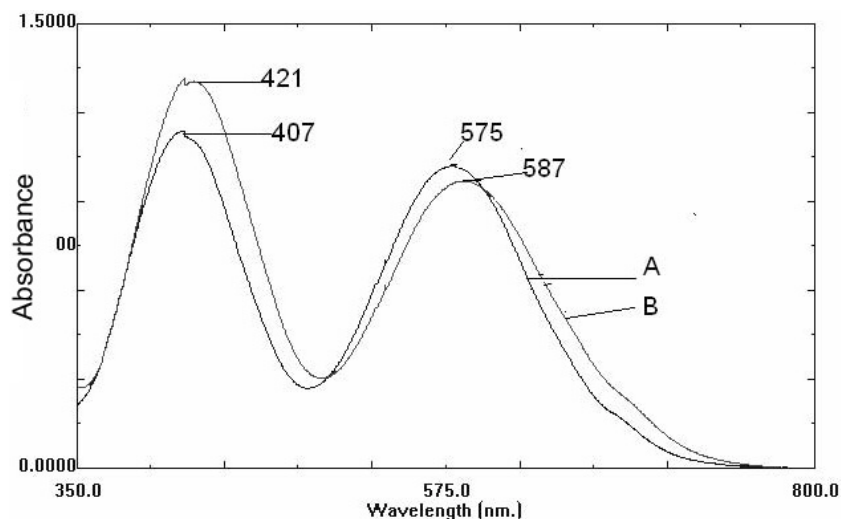


Fig. 1. UV-visible spectra of chromium solution. A: Fresh at 25°C; B: after 36 h at 95°C.

Table 1
pH values for 0.1 M chromium solution prepared by hydrolysis of Na_2CO_3 ($\text{CO}_3/\text{Cr}^{3+} = 2$ meq/mmol)

	25°C	60°C	95°C
1 h	374	293	248
4 h	362	279	234
36 h	349	265	223

The decrease of the pH (Table 1) and the change of spectral properties which occur upon ageing time indicate that the hydrolysis of chromium to higher polymers (dimer and trimer [13–15]) is a relatively slow process.

3.2. Al–Cr hydrolysis

The behavior of Al–Cr polymer is the same compared to the Cr polymer. Nevertheless, when shifted to the longer wave number, the bands were larger than remarked previously showing that new species were formed. But also the polymeric process is slow.

3.3. Pillared montmorillonite

3.3.1. With chromium

The intercalation of Na-montmorillonite with

Table 2
Effect of calcination temperatures of the pillared montmorillonite

Cr/clay (mmol/g)	DRX (Å)			
	Calcination temperature (°C)			
	200	250	300	350
5	18.23	17.98	17.38	15.58
10	18.59	19.67	19.13	14.43
50	19.74	19.41	19.23	14.16
80	11.23	10.52	10.11	10.01

CrIII solution hydrolysed at different ratios Cr/clay (5, 10, 20, 50 and 80 mmol/g) at 95°C during 36 h was studied. The calcination of the pillared clays is carried out at different temperatures as shown in Table 2. The pillared montmorillonite is affected by the treatment temperature but seems to be stable until 300°C. Indeed, the calcinated products at 300°C obtained from reaction mixture containing 2, 10, and 50 mmol/g of clay, gave basal spacing of 17.38, 19.13, and 19.23 Å respectively. Beyond this temperature, the basal spacing decreases by about 10.36, 24.57 and 26.36%.

Concerning the effect of Cr/clay ratios, it was studied at 95°C during 36 h under conditions of

Table 3

Effect of the time and the temperature of hydrolysis on basal spacing (Å)

Cr/clay (mmol/g)	25°C, 1 h	25°C, 4 h	25°C, 36 h	60°C, 36 h	95°C, 36 h
2e+06	14.31	14.47	14.62	16.01	17.38
	18.30	18.66	18.99	19.01	19.13
	—	—	—	—	19.23
	—	—	—	—	10.11

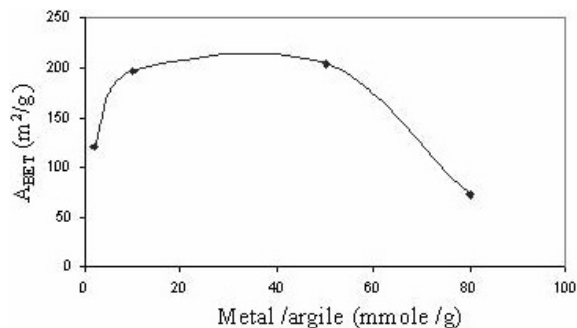


Fig. 2. Effect of ratio Cr/clay on specific surface area of pillared clay.

hydrolysis and is presented in Table 3. The X-ray basal spacing of the calcinated pillared clays at 300°C is affected by the reaction stoichiometry. Thus, between 2 and 50 mmol/g, the increase of the Cr/ clay ratio raises the d_{001} . Beyond this ratio, a change of the behavior is noticed.

Indeed, for 80 mmol/g, the basal spacing equals only 10.11 Å, suggesting that there is no intercalation because of the big size of the chromium polymer which is impossible to be inserted between the layers of the clay.

Concerning the time of hydrolysis study, it has been shown that the increase of aging time of hydrolysis rises slightly the basal spacing. This behavior confirms the evolution the pH values (Table 1) which suggests that the polymerization process is slow. The obtained polymers are approximately the same and lead to a similar basal spacing.

Fig. 2 shows that the specific surface area increases with the ratio. Nevertheless, 50 mmol/g

Table 4

Effect of Cr/Al ratio on basal spacing of pillared montmorillonite

Cr/Al (mol/mol)	d_{001} (Å)		
	150°C	300°C	400°C
0	208	19	19.4
2	2092	18.9	17.8
6	2033	18.5	17.1
12	1843	17.1	16
5	1361	12.8	10

seems to be the optimum and the surface is 196 m²/g. This behavior is the same compared to the evolution of X-ray basal spacing suggesting the formation of porosity.

3.3.2. With aluminum-chromium

Table 4 shows the evolution of d_{001} of Cr-Al pillared montmorillonite [(Al + Cr)/clay = 10 mmole/g] prepared with different ratios (0.2, 0.6, 1.2 and 5 mol/mol). Cr/Al ratio equal to zero was also prepared under the same conditions.

The effect study of the ratio Cr/Al shows that its increase is not favorable to the expansion of the clay layer. Nevertheless, Cr/Al equal to 0.2 seems to be the optimum value for which the basal spacing of Cr-Al clay is 20.92 Å (maximum) when air dried at 150°C. These results show that the pillars of Cr-Al intercalated with larger Cr/Al ratios have a larger degree of chromium polymerization. This suggests that the

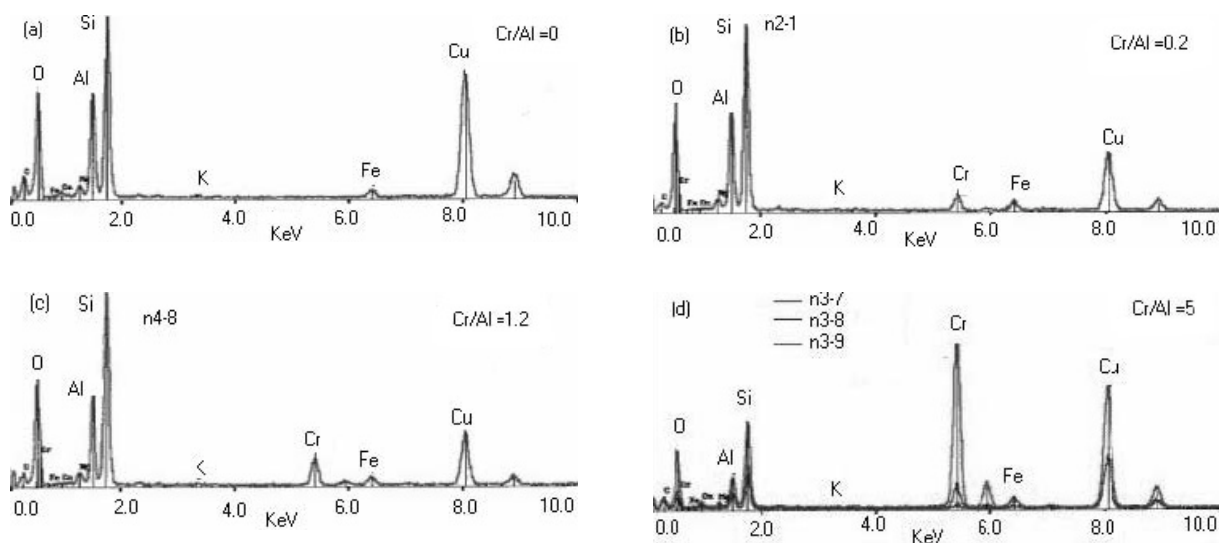


Fig. 3. Principal elements in Cr-Al pillared clays prepared with different ratios Cr/Al.

biggest polymers could not to be inserted in the clay layer. The Al-Cr pillared clay seems to be stable when calcined at 300°C. But the pillars are not stable at 400°C.

The evolution of specific surface area confirms the d_{001} behavior. The surface decreases when the ratio Cr/Al increases. Indeed, when the ratio rises from 0.2 to 5, the specific surface area diminishes about 31%.

Fig. 3 shows the presence of different elements, principally Si, Al, Mg, Fe, O and K in Cr-Al pillared clays when Si and Al constituents are major. Generally, the increase of Cr/Al ratio raises the content of Cr and diminishes the Al one as shown in Table 5, and which is 12 times higher when Cr/Al is equal to 5. Nevertheless, and for a same sample, the analysis of different zones shows that the contents of chromium are different.

3.4. Adsorption of cadmium

The samples which have optimal properties were used as adsorbent of cadmium metal. Fig. 4 shows that the adsorption is divided into three zones:

Table 5

Surface composition of pillared clays with different ratios Cr/Al

Oxide	Cr/Al = 0 (%)	Cr/Al = 0.2 (%)	Cr/Al = 1.2 (%)	Cr /Al = 5 (%)
MgO	265	274	313	132
Al ₂ O ₃	3359	3056	2603	1854
SiO ₂	6075	5910	5952	4980
K ₂ O	55	28	34	0
Fe ₂ O ₃	245	266	239	279
Cr ₂ O ₃	0	466	858	2751

- Important and fast adsorption: all the sites on montmorillonite are free and the fixation of the cations is very easy. (0–15), (0–20), (0–35) and (0–75) min respectively from Mont-Cr-Al (Cr/Al = 0), Mont-Cr-Al (Cr/Al = 0.2) and Mont-Cr.
- Slow adsorption: the min sites are occupied, and in addition to this, there is repulsion between the Cd adsorbed and Cd in solution [16]. So, there is a need to develop a higher energy of adsorption and the phenomenon becomes slow: (15–20), (20–25), (35–40) and (75–80) min respectively from Mont-Cr-Al

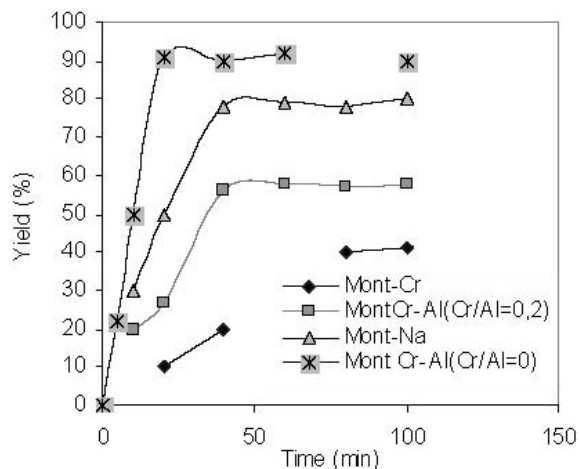


Fig. 4. Adsorption kinetics of cadmium onto different clays.

(Cr/Al = 0), Mont-Cr-Al(Cr/Al = 0.2) and Mont-Cr.

- Equilibrium: the adsorption has reached the maximum, all the sites are occupied and there is equilibrium between the Cd in solution and Cd on solid.

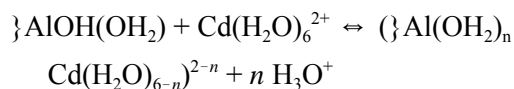
The equilibrium time was 20, 25, 40 and 80 min for Mont-Cr-Al (Cr/Al = 0); Mont-Na; Mont-Cr-Al(Cr/Al = 0.2) and Mont-Cr respectively, showing that the adsorption of Cd is a very low process onto Cr-pillared montmorillonite compared to the other pillared montmorillonites. In addition to that, and for a same contact time of 20 min, the yields are 91, 78, 27 and 10% respectively. These results show that the Mont-Na and Mont-Al are more interesting than Mont-Cr-Al and Mont-Cr in adsorption of cadmium in our conditions (pH = 5.8). This low adsorbed quantity of cadmium could be attributed to the competition between H⁺ of the clay suspension and Cd²⁺.

Adsorption of heavy metals at the oxide/water interface can be described as the surface complexation mechanism [11]. The uptake of heavy metals by clay minerals is obviously more complicated. The chemical nature of metal clay interaction changes with increasing pH: at low pH

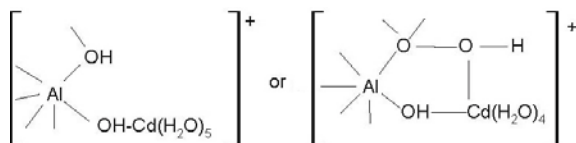
values cation exchange is dominating process [11,17,18], whereas at high pH values, the uptake of heavy metal ions is accompanied by release of hydrogen ions, and seems to be more specific than the uptake at low pH values. Thus, the classical ion exchange model does not cover the whole range of adsorption phenomena and a part of heavy metal adsorption occurs at sites created by displacement of protons from surface hydroxyls (i.e. surface complexation) [19].

In the Mont-Na and Mont-Al case, and as seen in Fig. 5, the adsorption is carried out in two possible ways: (1) non-specific and (2) specific adsorption. It has been established [20] that at pH < 5, only the }Al(OH)₂⁺ species is present between pH 5 and 7, and the AlOH(OH₂) groups are preponderant.

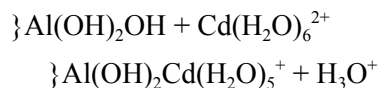
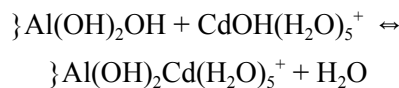
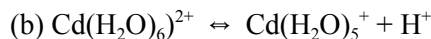
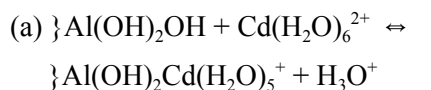
In the first case the adsorption is carried out without proton H⁺ elimination, when the second case is accompanied by H⁺ separation as shown:



So, the adsorbed entity is probably



and the equilibrium is presented as:



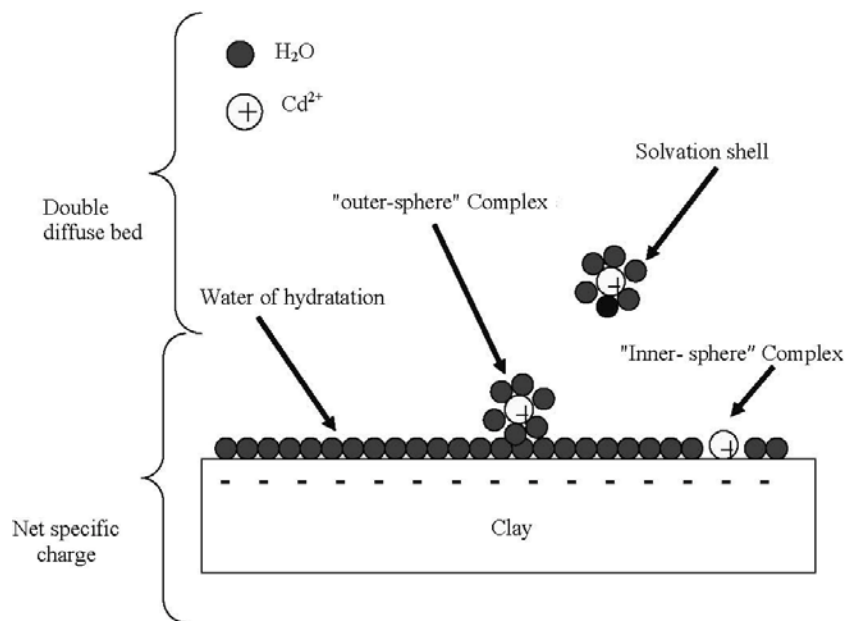


Fig. 5. Solid–liquid adsorption.

Thus, for the Cr-Al-Mont pillared clay, and especially for the low Cr/Al ratio (0.2), the specific adsorption is probably carried out only on the Al pillared clays because of the low attraction between the metal and the chromium pillared clays as seen for Cr-Mont material. Nevertheless, we can notice the non-selective adsorption on this adsorbent.

In the case of the Na-Mont support, the ionisable groups of the layers of the clay constitute the sites of adsorption. For this reason, the Cd²⁺ ions can be adsorbed on Mg(OH)₂, SiOH, Al(OH) which constitute the sites of adsorption. In addition to that, the silanol groups of the side of the clay layers are transformed in SiO-Na⁺ form and the adsorption of these silanol sites is not accompanied by H⁺.

The adsorption isotherm is shown in Fig. 6. The maximum adsorption capacities are around 16.10⁻⁴, 5.10⁻⁴, 4.10⁻⁴ and 1,2.10⁻⁴ mol/g respectively for Mont-Cr-Al (Cr/Al = 0), Mont-Na, Mont-Cr-Al (Cr/Al = 0.2) and Mont-Cr.

The isotherms show that the adsorption on Mont-Na and Mont-Cr-Al (Cr/Al=0.2) is carried out on a monolayer when the adsorption on

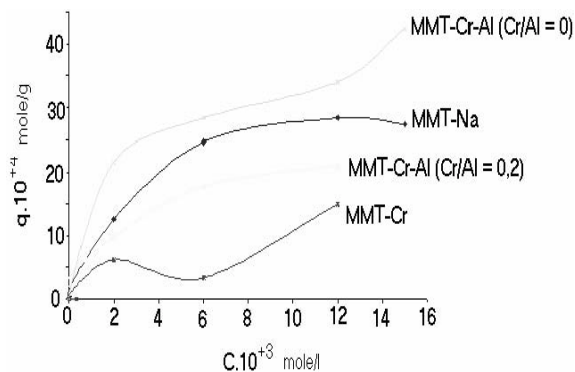


Fig. 6. Cd adsorption isotherm on different pillared clays.

Mont-Cr and Mont-Cr-Al (Cr/Al = 0) occurs on different layers.

The application of the Freundlich model has been further extended considering the influence of adsorption sites and the competition between different ions for adsorption on the available sites. The Freundlich model constitutes a distribution of the energy sites which characterise the heterogenic surface sites.

The linearization of Freundlich equation, $\ln Q = \ln K + 1/n \cdot \ln C$ leads to the calculation of $1/n$ and

Table 6
Freundlich constants of cadmium adsorption

	Mont-Cr-Al (Cr/Al = 0)	Mont-Cr-Al (Cr/Al = 0,2)	Mont-Cr	Mont-Na
$1/n$	506	6420	6614	6637
K	123	134	32	59
R^2	98	0.98	99	96

K constants as shown in Table 6. These results suggest that the Freundlich model can be applicable because of the value of $1/n$, which is in the interval $[0, 1]$. All the values of $1/n$ are less than 1, suggesting that the adsorption sites are heterogeneous. In addition to this, the lower value of $1/n$ (0.5) confirms that the Mont-Cr-Al (Cr/Al = 0) is the better adsorbent for the cadmium, showing the interaction between Al and Cd. A similar study [21] demonstrated that the adsorption properties depend from several parameters as the nature and the distribution of pillars in the clays.

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