Modelling of the adsorption of the chromium ion by modified clays

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Abstract

This paper presents our contribution to the removal of chromium ions from aqueous solution by adsorption. The adsorbent used is bentonite clay coming from south Tunisian. This clay has been modified by several treatments such as aluminium pillaring, acid activation and pillared followed by acid activation. Acid activation involved a destruction partial of the octahedral layer by dissolution of the cations, Al^{3+}, Mg^{2+} and Fe^{3+} of this layer and an amorphous silica formation due to the destruction of the tetrahedral layer. This treatment involved a reduction in the cation capacity of exchange and an increase in the specific surface which reaches respectively 154, 354 m^2/g after treatment with HCl 0.5 M and HCl 3 M.

These adsorbent are used to fix chromium starting from the aqueous solutions at pH = 5. The maximum of adsorption differs according to the treatment. The retention of chromium is correlated with the variation of the values of the cation exchange capacities and not with the values of specific surfaces.

The concentrations of metal ions have been measured by batch techniques and with AAS (analysis adsorption).

The adsorption analysis has been correlated to Langmuir and Freundlich models.

Keywords: Clay; Acid activated clay; Pillared and acid activated clay; Chromium; Models of Freundlich and Langmuir

1. Introduction

Researchers are interested more and more in the elimination of pollutants implied directly in imbalance of the ecosystem. These pollutants are of the origin of serious harmful effects being able to lead to dead alive beings of fauna and flora.

The porous materials are abundantly used in the extraction of chemical species in aqueous phase or in gas phase because of their excellent capacity of adsorption, and their high surface specific and porosity.

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Clay minerals are non-pollutant and have very significant capacity adsorbing so they have a privileged place in the purification of water [1,2], decolourization of oils [3] and the fixing of metals [4].

Pillaring [5–11] and acid activated process are used in order to improve clay properties: Pillaring confers to the mineral a high thermal stability, a developed microporous surface and a great acidity [12]. While, acid activation [13,14] improves adsorption properties of clay by increasing the number of active sites of clay, the specific surface, acidity and porosity. These changes are dependent on several factors: pillaring agent, the force of the acid, the nature of clay, duration of treatment, the temperature.

Acid activation followed by a pillaring consists in gathering the two modifications; an acid activation followed by pillaring, with an aim of gathering the two properties of the two treatments.

In this work, we have studied the adsorption of chromium(III) by Tunisian bentonite before and after modification by acid activation, pillaring and by both the techniques. Two adsorption models are tested the Langmuir and Freundlich models.

2. Materials and methods

2.1. Material

A Tunisian interstratified illite/smectite bentonite mineral (H) from Haidoudi deposit is used in this study. The mineralogy and the purification protocol of this clay are presented in our previous work [1].

Acid activated clay has been prepared by immersion the mineral in 200 mL HCl at two different molarities (0.5 and 3 M) during 2 h. The acid activated clay mixture is separated by centrifugation. The solid phase is recovered and washed with the distilled water until having a constant pH then it is dried and crushed.

The transformation of natural clay into pillared clay requires essential operations resulting in the preparation of the solution pillaring by titrating an Al solution $(NO_3)_3 \cdot 9H_2O$ of concentration 0.2 M by a solution of sodium hydroxide 0.2 M with a discontinuous flow of OH/Al ratio 2, the agent intercalating is introduced by cation exchange into interlamellar space of clay by adding powder clay to the intercalating solution ages during 72 h with the free air with a 20 meq/g ratio of clay. The suspension obtained after a 24 h agitation is put to elutriate during one night to ensure a good insertion then it is put to dialyze after its separation of solution. This modified and washed clay is heated at temperature of 400°C during 2 h. Acid activated pillared clay is prepared in a first by acid activated followed by pillaring.

2.2. Methods of characterization

Analyses of the major elements Si, Al, Fe, Mg, K, Na and Ca present in clay were carried out by atomic absorption. The clay samples are attacked by a mixture of three concentrated acids (HCl, H_2SO_4, HNO_3) in known proportions. All the elements pass in solution except silicium.

The spectrometer of atomic absorption used is of type AAS vario 6. To eliminate the phenomena of interferences between the elements is introduced solution of lanthanum oxide.

For the identification and the study of argillaceous minerals we have used the X-ray diffractometer Philips PW 1900 with Cu-K radiation.

N_2 BET surface area determinations: The specific surface areas of the samples were determined from nitrogen adsorption isotherms at 77 K obtained in a sorptomatic 1900 after pre-degassing the samples at 120°C for 12 h. The BET method was used for the corresponding calculation.

3. Results and discussions

3.1. Physico-chemical properties

The chemical analysis of the natural bentonite and solids resulting from the HCl treatment given in Table 1 showed a decrease in octahedral cations (Al, Mg and Fe) and enrichment in SiO_2. This relative increase results of the removal of the octahedral cations. The octahedral cations pass into the solution while silica, owing to its insolubility in acid solution, remains in the solids obtained. In the other hand, extraction rate of these elements increases with the concentration of the acid. In the case of pillared clay we noted a reduction in the percentage of sodium and an increase in the aluminium indicating the intercalation of aluminium in the interlayer.

Moreover the acid activation of clays generates changes in the crystalline phase which depends on the concentration of acid (Table 2). After acid activation with HCl (0.5 M) d_{001} moves to 15.5 Å which indicates that sodic clay is transformed into aluminic clay coming from the octahedral layer, whereas the acid activation with HCl (3 M); leads to total disappearance of the 001 reflexion.

Aluminium pillared clay show a displacement of d_{001} from 1.35 nm for sodic clay to 1.7 nm. After pillaring acid activated samples show slight increasing of d_{001} value.

By identification with the classification of the UIPAC [15], it is noted that crude, purified and pillared clay present similar isotherms (*type II* with *H4* hysteresis). The purification as well as pillaring does not modify the type of the isotherm. On the other hand the isotherm of adsorption of the acid activated clays for the two concentrations 0.5 and 3 M present an adsorption similar to that of crude clay, but changes of hysteresis. The latter is of *H3 type*. This is due to the changes of the type of pores; which passes to a mesoporous material. After pillaring, this sample changes the texture. Hysteresis regains its initial shape; it passes from H3 type to H4.

Surface area increases with the acid concentration (Table 2). The S_{BET} value increase from 105.8 to 354.3 m²/g. We notice also an increase in the porous volume from 0.62 to 0.51 cm³/g. This is due to the formation of the pores and empty spaces accessible to the nitrogen molecules. Pillared clay has a higher surface S_{BET} than that of purified clay; this is due the intercalation of the polycation between the layers which maintains a structure opens accessible to nitrogen.

The cation exchange capacities decrease after modification by acid activation and pillaring that indicates the destruction of interlayer cation by acid and intercalation of polycations in interlayer.

Table 1
Centesimal composition in oxides of the crude and the modified samples

	H1	H2	H3	H4	H6
SiO_2	63.35	61	59	68.33	84.05
Al_2O_3	21.76	24.7	29.69	19.59	11.06
Fe_2O_3	8.01	8.7	7.55	5.35	2.42
MgO	1.89	1.8	1.52	1.31	0.05
Na_2O	2.08	2.4	0.96	0.24	0.22
K_2O	1.03	1.2	1.15	0.8	0.45
CaO	1.58	0.3	0.08	0.09	0.068
Total	99.97	100.1	99.95	95.99	98.8

Table 2
$d_{(001)}$ reflexion, S_{BET}, V_p and CEC of crude, purified and modified clays

	d(001) Å	S_{BET}	V_p	CEC
Clay crude (H1)	12.62	93.5	0.062	75
Clay purified (H2)	13.5	105.8	0.085	88
Pillared clay (H3)	17.24	135	0.120	40
Acid activated clay (0.5 M) (H4)	15.9	153.8	0.196	59.6
Acid activated pillared (0.5 M) (H5)	16.9	113.2	0.133	34.3
Acid activated clay (3 M) (H6)	–	354.3	0.502	31.12
Acid activated pillared (3 M) (7)	16.5	236.2	0.412	24.39

3.2. Adsorption of Cr^{3+} by the different samples

3.2.1. Effect of adsorbent and adsorptive doses

A relatively simple calculation makes it possible to obtain the quantities of fixed product. Quantity of product adsorbed expressed in moles of aqueous solution per gram of adsorbent solid is given by the following relation:

$$Q = (C_0 - C_f) \cdot V/m$$

where Q is the quantity of chromium per unit of clay mass (in meq/100 g), C_0 the initial concentration (mol L^{-1}), C_f the final concentrations with balance (mol L^{-1}), V the volume of the adsorbate (L), m the mass of adsorbent (g).

The analysis of remaining chromium after exchange with the various clay samples enabled us to trace the isotherms of adsorption $Q = F(C_f)$. The isotherms are curves indicating the chromium content in the solid phase (clay) according to its concentration in the liquid phase after reaching equilibrium (Fig. 1).

The adsorption of chromium(III) at a fixed bentonite dose of 2 g/L at room temperature is shown in Fig. 1. The sample H2 showed the maximum adsorption. The adsorption decreased in the order H1 > H2 > H3 > H4 > H5 > H6 > H7. The purified bentonite showed a considerable adsorption, which was reduced after modification by pillaring and acid activation. The amount of

the chromium adsorbed showed a continuous decrease with all modifications.

3.2.2. Isotherm modelling

Adsorption isotherms of clays for chromium ion were expressed mathematically in terms of the Langmuir and Freundlich models.

3.2.3. Langmuir model

It is a simple model and largely used. It is based on the following assumptions:
- The adsorbed species is located on a well defined site of the adsorbent (localised adsorption).
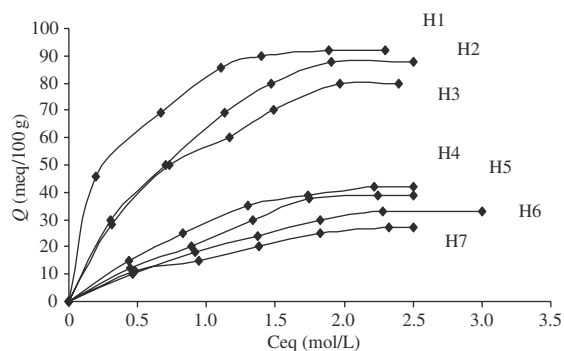- Each site is likely to fix only one adsorbed species.

Fig. 1. Cr^{3+} adsorption isotherm of studied samples.

- The energy of adsorption of all the sites is identical and independent of the presence of the species adsorbed on the close sites (homogeneous surface and absence of interactions between adsorbed species). It is applicable to the monomolecular adsorption in aqueous solution on the surface of the adsorbent at equilibrium. In the case of a small quantity of adsorbed aqueous solution, the $K \cdot C_e$ term can be much lower than 1 and it is then neglected. The relation of Langmuir is reduced then to a direct relation between the capacity of adsorption and the concentration at equilibrium of the adsorbate in solution:

$$Q = Q_m \cdot K \cdot C_e$$

In the case of a strong quantity of aqueous solution adsorbed, the $K \cdot C_e$ term becomes largely higher than 1. That implies that Q tends towards Q_m.

In addition, the linearization of the function of saturation per passage of the opposite gives

$$1/Q = [(1/Q_m \cdot K) \cdot (1/C_e) + (1/Q_m)]$$

The obtained equation is that of a line of slope $1/Q_m \cdot K$ and ordinate in the beginning $1/Q_m$; which makes it possible to determine two parameters of the relation at equilibrium: Q_m and K.

3.2.4. Freundlich model

It is about an equation which is often employed in the practical representation of the adsorption between the aqueous solution and the surface of the solid. It is presented in the form:

$$Q = K_F \cdot C_e^{1/n}$$

Linearization by scaling of the relation of Freundlich led to the following equation:

$$\log Q = \log K_F + 1/n \log C_e$$

It is about the equation of a line of slope $1/n$ and ordinate in the beginning $\log K_F$. The extrapolation of this equation for $C = C_0$, provided that C_0 = constant (initial concentration in aqueous solution), gives the ultimate capacity of adsorption (Q_mF) in the area of studied concentration. In addition to the experimental data, the linearized form of Langmuir and Freundlich isotherms for chromium ion removal by samples can be seen in (Fig. 2).

The values of the constants (K, Q_{max}, K_F and $1/n$) obtained from both models are presented in Table 3.

Fig. 2 show that chromuim(III) adsorption on the clays can be described by the Freundlich and also Langmuir equation. The Freundlich exponent $1/n$ between 0.3 and 0.73 indicates favourable
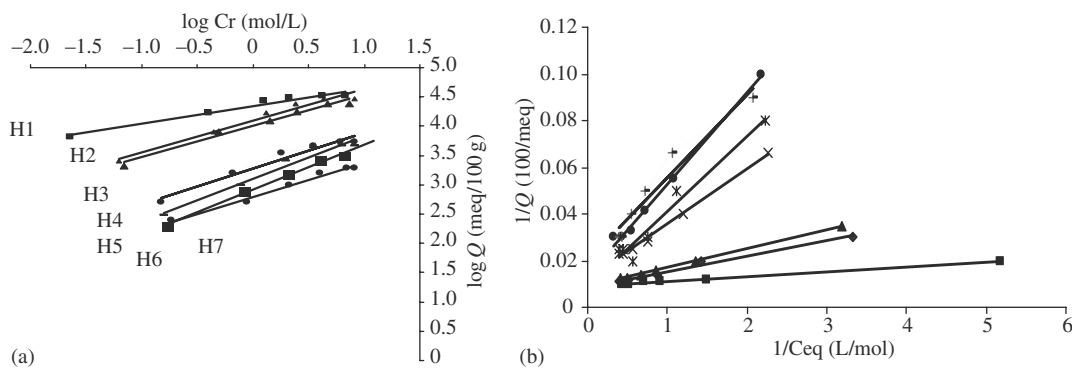

Fig. 2. The linearization obtained using the equations of Langmuir (a) and Freundlich (b) for the adsorption of chromium on clay before and after modification.

Table 3
The parameters for Langmuir and Freundlich isotherms

	Langmuir			Freundlich		
	Q_{max}	K	R^2	K_F	$1/n$	R^2
H1	113	1	0.96	59.7	0.54	0.98
H2	109	4	0.96	77	0.3	0.99
H3	112	1	0.97	54.6	0.53	0.99
H6	74	0.34	0.95	18.19	0.6	0.99
H7	50	0.5	0.94	16.37	0.58	0.98
H4	83	0.5	0.95	26.5	0.67	0.99
H5	103	0.3	0.96	22.3	0.73	0.98

adsorption for which $0 < 1/n < 1$. The coefficient $1/n$ is less 1, this means the isotherms of adsorption of all samples are of type L. The Freundlich constant K_F is appreciable for all the samples in general agreement with strong adsorption. The purified clay has the largest value of K_F. The crude clay has the lowest K-value.

The increase in K_F of the adsorbent corresponds to more active sites while the decrease in $1/n$ may be regarded as increased surface heterogeneity after modification. On the other hand Q_{max} values for the samples follow the order H1 > H3 > H2 > H5 > H4 > H6 > H7.

The comparison of the experimental values with the values of Q obtained by both models is shown in (Fig. 3). As it is seen from Fig. 3, Freundlich isotherms fitted better with the experimental data rather than Langmuir isotherms. Also, some other studies showed that Langmuir and Freundlich isotherms correspond well with the experimental results of some heavy metals [16].

4. Conclusion

In general, adsorption involves the accumulation of molecules from a solvent onto the exterior and interior surfaces of an adsorbent. This surface phenomenon is a manifestation of complicated interactions among the three components involved, the adsorbent, the adsorbate and the solvent. Normally, the affinity between the adsorbent and the adsorbate is the main interaction force controlling adsorption. However, the adsorbate–solvent affinity can also play a significant role in adsorption. In order the natural and modified clays are used to fix chromium starting from the aqueous solutions at pH = 5. The maximum of adsorption differs according to the treatment followed by clay. The fixing of chromium is correlated with the variation of the values cation exchange capacities and not with the values of specific surfaces. The study of the behaviour of these modified clays in the adsorption of the ions chromium showed that

- Although the curves of isotherms show more or less marked differences, according to the nature of modified clay we conclude that the various isotherms of adsorption are of type L.
- The isotherms of adsorption of crude, purified and modified clays give coefficients $1/n < 1$ which shows that the retention of the aqueous solution somewhat modifies the capacity of adsorption of the samples through the creation of new sites of adsorption.
- The experimental results were well fitted with the Freundlich and Langmuir isotherms. The Freundlich isotherms correspond better with the experimental findings rather than Langmuir isotherms.
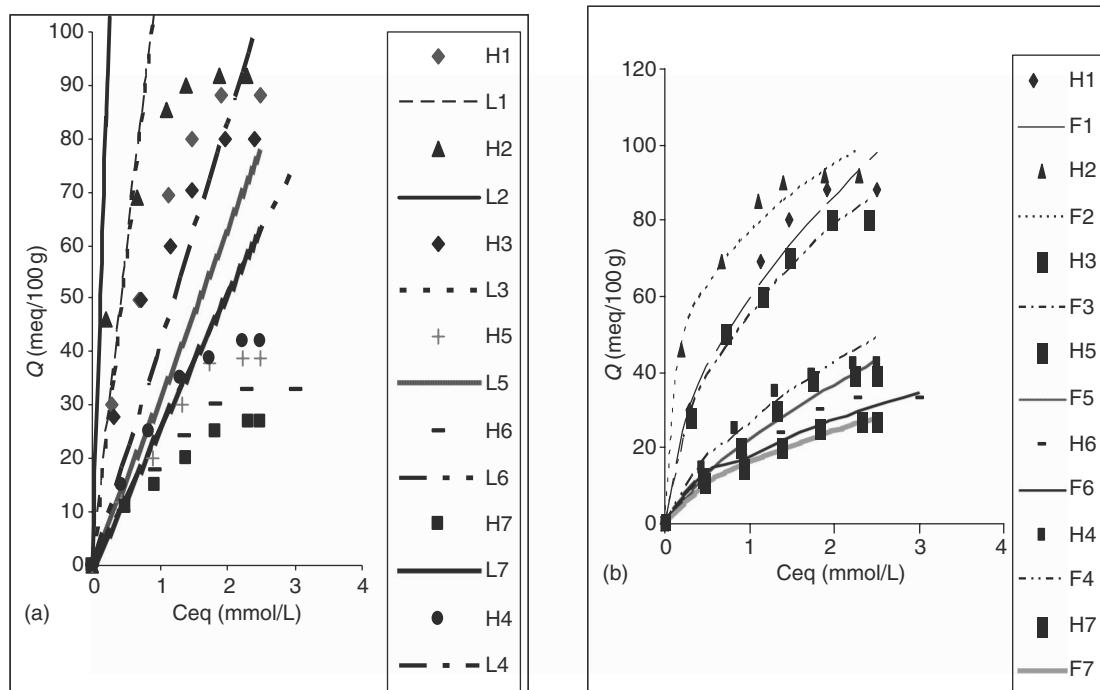
Fig. 3. Adsorption isotherms (a) Langmuir (L) and (b) Freundlich (F) of samples before and after modification.

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