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Removal of trivalent iron and chromium from aqueous solution by local clay

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ABSTRACT

The ability of local clay from Jebel Kebir (north of Tunisia) to remove heavy metal ions from wastewater was tested. The original clay was characterized using several techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM) and infrared spectroscopy (IR). The cation exchange capacities (CEC) as well as the specific surface area (SSA) were determined using the adsorption isotherm obtained with methylene bleu in aqueous solution. Chemical compositions were determined by the inductively coupled plasma technique (ICP). The results show that the material is a smectite with a small proportion of kaolinite. The CEC and SSA values for the raw clay sample (JKb) are respectively 25 meq/100 g, 206 m²/g of fired clay; and 50 meq/100 g and 403 m²/g of fired clay for Na-purified clay. During the removal process, batch technique is used, and the effects of heavy metal concentration and agitation time on adsorption efficiency are studied. The adsorption mechanism of Cr (III) and Fe (III) ions onto adsorbents was evaluated in terms of kinetics and equilibrium. The Langmuir and Freundlich isotherms are applied in order to determine the efficiency of raw and Na-purified clay used as an adsorbent. In all cases results show that both Fe (III) and Cr (III) adsorption isotherms have a positive retention. In addition, it is concluded that natural clay can be used as an effective adsorbent for removing Fe (III) and Cr (III) from wastewater.

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KEYWORDS

Clay mineral;
Smectite;
Kaolinite;
Chromium;
Iron;
Adsorption;
Kinetic;
Isotherm;
Freundlich;
Langmuir.

INTRODUCTION

Chromium and iron are two typical widespread heavy metal pollutants in natural water environment.

Chromium (III) is an essential microelement that can be toxic in large doses (100 mg/L). However, the toxicity of chromium compounds depends on the ox-

idation state of the metal. Hexavalent chromium is known to be much more dangerous than trivalent chromium.

All forms of chromium can be toxic at high levels. Allergic people to chromium may have asthma attacks after breathing high levels of chromium (III) in air.

Various techniques have been developed for removal metals from wastewater^[1-7]. The ion exchange,

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chemical precipitation, solvent extraction, reverse osmosis, adsorption are the most commonly used processes; each has its merits and limitations in application.

Clays constitute the low cost and available materials that could be used as adsorbents to remove organic and inorganic pollutant from wastewater. The adsorption of impurity in aqueous medium by clays is one process highly used in decontamination of industrial effluents with satisfactory performance in heavy metals removal^[8-14].

It is well known that smectitic clays have very high cation exchange capacities (90–120 meq/100 g) due to substitutions of Mg^{2+} and Fe^{2+} in place of Al^{3+} in the octahedral positions and, to a higher degree, to substitutions of Al^{3+} in place of Si^{4+} in the tetrahedral positions. Moreover, they possess higher elasticity and plasticity. These properties make them particularly suitable as low-cost natural sorbents for the treatment of industrial and processing waters and wastewater.

Our aim is a contribution to provide further support that could be a promising agent in the fight against heavy metal pollutants in wastewater.

In this work we investigate the characteristics of Cr(III) and Fe(III) adsorption from aqueous solution by the smectite-rich clay (JK). Then we evaluate in terms of kinetics the equilibrium time and the rate constant of the process.

EXPERIMENTAL

Materials

The natural clay was taken from Jebel Kebir (North of Tunisia). It was powdered in an agate mortar and sieved through 63 μm mesh to obtain finer grains. Powdered clay was dried at 60 °C, before the experiments. The less than 63 μm fraction was purified by repeated cation exchange with NaCl solution (1 M) followed by washing, sedimentation and dialysis^[15]. We will specify as Jkb the raw sample, before purification, and as JKp the purified and sodium exchanged product. The TEM (Figure 1, 2) is used to observe their morphology with a Tecnai G2 ultra Twin Instruments

Methods

All the reagents used in this study were analytical grade. A $CrCl_3$ and $FeCl_3$ solution was used in the batch

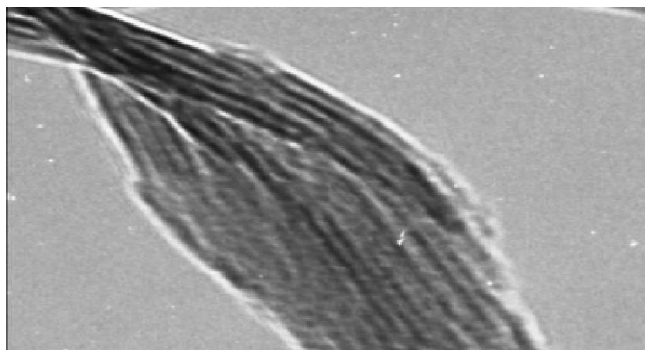


Figure 1 : Morphology of JKb observed with TEM

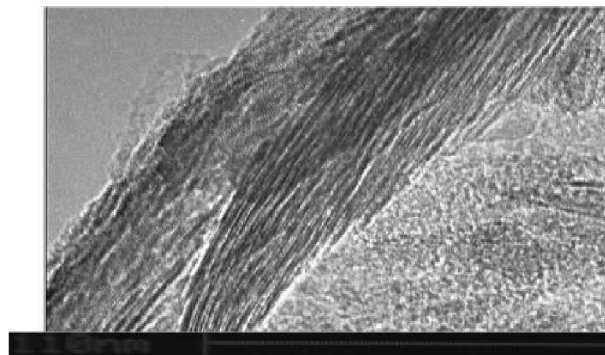


Figure 2 : Morphology of JKp observed with TEM

experiments. A volume of 50 cm³ of solutions with various amounts of clays (JKb, JKp) was placed in an Erlenmeyer flask to start the experiments. The initial metal ion concentration used in the tests ranged between 1 and 4 mmol.L⁻¹ for both clays and the slurry concentrations 1g.L⁻¹ of clays. The batch adsorption experiments were also conducted at fixed pH 3. The pH of the solutions was adjusted by adding diluted NaOH and HCl solutions. The stirring speed was constant and fixed at 130 rpm during the test at room temperature (about 20 °C). The experiments were terminated at a contact time of 2 h. After centrifugation, the supernatant liquid was used for measurements. A quantitative analysis of chromium and iron in solution was made by inductively coupled plasma atomic emission spectroscopy.

RESULTS AND DISCUSSION

Original properties of Jebel Kebir clay

The mineralogical and chemical compositions of the materials were determined by a series of techniques, including x-ray diffraction (XRD), infrared spectroscopy (IR) and inductively coupled plasma (ICP).

TABLE 1 : Chemical Composition of Jebel Kebir clays

W%	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	Na ₂ O	MnO	P ₂ O ₅	TiO ₂	Total
JK b	31.29	11.13	50.24	3.48	0.27	2.95	0.13	0.03	0.18	0.32	100.00
JK p	52.98	19.17	12.53	7.74	0.43	4.99	0.55	0.03	0.27	1.33	100.00

Chemical composition

The element materials by weight composition (TABLE 1) were determined by ICP (Inductively Coupled Plasma) after solubilisation by acid digestion according to the standard^[16].

Cation exchange capacities (CEC)

The total internal plus external surface areas (SSA) are measured by the absorption isotherm of methylene blue (MB) from the aqueous solutions where the amounts of MB are represented as a function of the amount Figure 3. ^[17, 18].

The cation exchange capacities (CEC) of clay minerals are determined by adsorption of the copper ethylene diamine complexes^[19, 20, 21]. The results are presented in TABLE 2.

TABLE 2 : Physical characteristics of Jebel Kebir clays

Materials	SSA (m ² /g)	CEC (meq /100 g)
Natural clay (JK b)	206	25.4
purified clay (JK p)	403	49.6

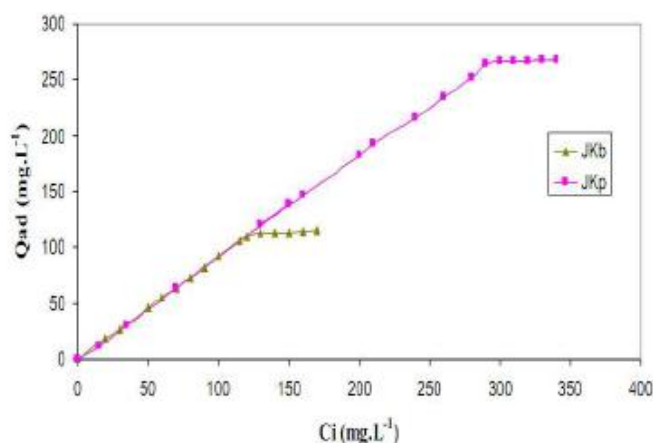


Figure 3 : Methylene blue absorption by JKb and JKp.

Infrared spectroscopy

The infrared spectra (Figure 4a and Figure 4b) are in the frequency range 4000–400 cm⁻¹. The distinct increase of infrared absorbance at 3611–911 cm⁻¹ confirms the dominant presence of dioctahedral smectite with [Al, Al-OH] stretching and bending bands^[22, 23].

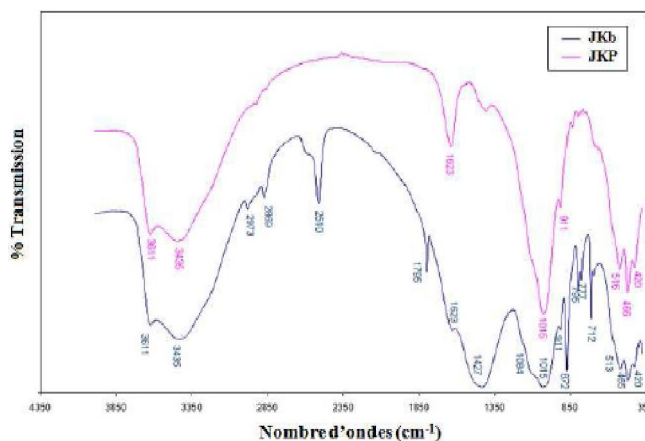


Figure 4a : IR absorption spectra of natural and purified sample (JK).

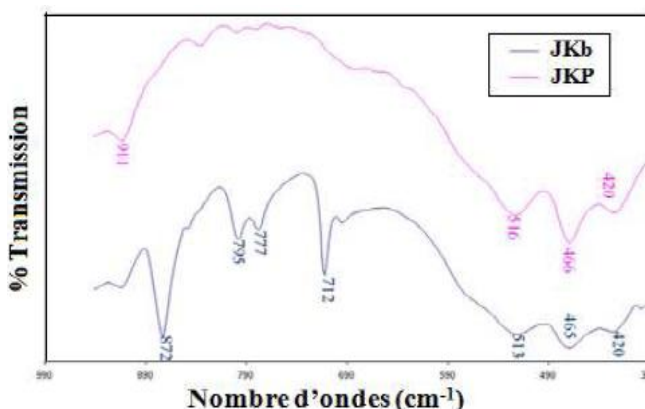


Figure 4b : IR adsorption spectra of the clay Jebel Kebir (expansion)

The absorption bands at 3435 cm⁻¹ and at 1630 cm⁻¹ may be attributed to the OH frequencies for the water molecule adsorbed on the clay surface^[24].

The adsorption bands at 420,466–516 cm⁻¹ can be assigned respectively to [Si-O-Fe], [Si-O-Mg] and [Si-O-Al].H^[25].

The (Si-O) bands are strongly evident in the silicate structure and can be readily recognized in the infrared spectrum by the very strong absorption bands in the 1015 cm⁻¹^[26].

The calcite or calcium carbonate (CaCO₃) is characterized by the band at 1433 cm⁻¹. The latter band appears for JKb, as an intense broad band. This band disappears in the spectra of the purified clay JKp. The frequency vibrations of purified samples obtained by

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IR are given in TABLE 3.

TABLE 3 : IR vibration frequency of the Jebel Kebir Na-purified clay (JKp)

Frequency (cm ⁻¹)	Allocation
3611	ν (Al-Al-OH)
3435	ν (OH _{im}) de l'hydratation
1630	ν (OH) de l'hydratation
1015	ν (Si-O) ou δ (Si-O-Si)
911	ν (Al-Al-OH)
795-777	δ (Fe-OH)
516	δ (Si-O-Al)
466	δ (Si-O-Mg) ou δ (Si-O)
420	δ (Si-O-Fe)
516	δ (Si-O-Al)

X-ray diffraction

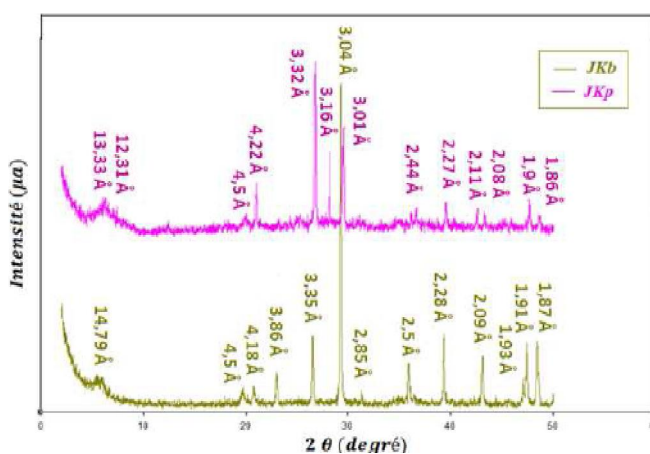


Figure 5 : X-ray diffractograms of raw and purified clay powder (JK).

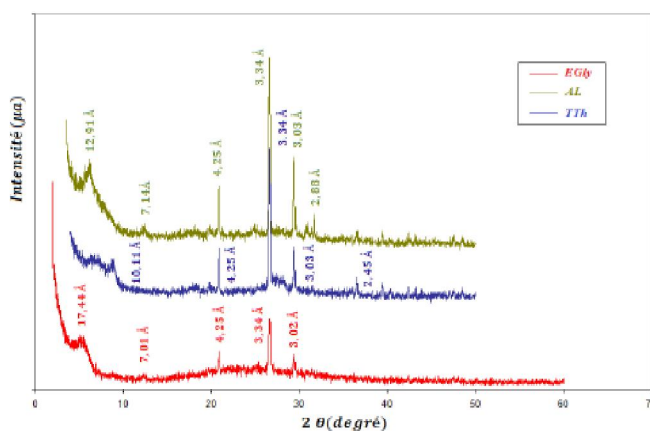


Figure 6 : X-ray diffractograms of Na-purified JK samples; AL: untreated; TTh heated for 3 hours at 823K. Egly: ethylene glycol treated.

As shown in Figure 5 Quartz (reflection at 3.35 Å) and calcite (reflection at 3.04 Å) are the major impurities. The positions of (001) reflections of the smectite appear at 14.79 Å for the sample, suggesting that the fraction might be in the Ca-exchange form^[27].

The purified sample with Na-exchange shows the position of the 001 reflection ($d = 12.31 \text{ \AA}$) characteristic of a sodium smectite^[28].

The main reflections produced in the X-ray diffractograms by the lamellar sheets of JCKp are summarized in TABLE 4, which describes the characteristic reflections and their behaviour after a heat treatment as well as treatment with ethylene glycol. (Figure 4) Heating the sample above 823 K collapses the interlayer spacing at 7.14 Å^[29].

The diffractograms of JK purified sample show the 001 and 002 reflection of kaolinite respectively at 7.10–4.22- 3.5 Å^[30].

These reflections 7.14 Å disappear by heating at 823 K^[31].

TABLE 4 : Distances of reticular planes characteristics JKp

Distances of the characteristic reticular planes (d. Å) of JKp			
Na-exchanged	Untreated heated at 823K	EGlycolate treated	Characteristic band
12.91	10.11	17.44	Smectite
7.14	disappears	7.01	Kaolinite
4.25	4.25	4.25	Smectite
3.34	3.34	3.34	Kaolinite
2.88	2.45	disappears	Kaolinite

Conclusions

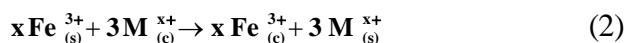
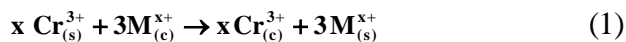
Taking the results of the different techniques into account, we deduce that Jebel Kebir material is constituted by smectite, kaolinite, calcite and quartz. The mineralogical compositions of the purified samples are given in TABLE 5.

TABLE 5 : Mineralogical composition (w %) of Na- purified Jebel Kebir clay.

Sample	smectite	Kaolinite	Calcite	Quartz	feldspar
JKp	80	20	Nd*	Nd*	Nd*

Amount of adsorbed chromium ions on clays

The equilibrium that may describe the interaction between the iron and chromium ions and clay is:



Where x, 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 the clay can be expressed like:

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

Where, Qe, Ci, Ce and S are respectively the adsorbed metallic ion onto the clays (mmol.g⁻¹), the initial concentration (mmol.L⁻¹), the equilibrium concentration of metallic ion (mmol.L⁻¹), and the slurry concentration.

The ionic 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 pH solution increases and is readjusted.

Kinetic study

- Equilibrium contact time

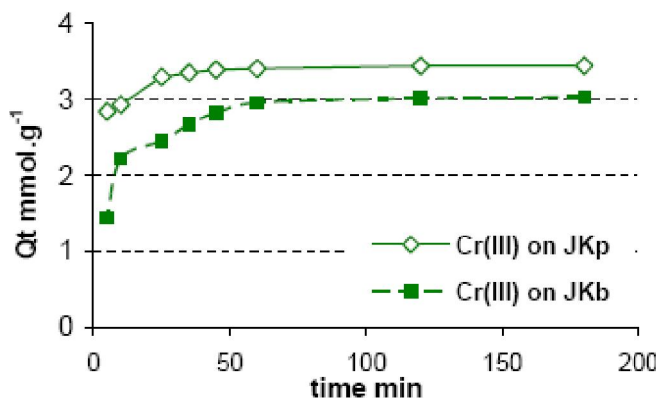


Figure 7 : Effect of shaking time on adsorption of Cr (III) on JKb and JKp

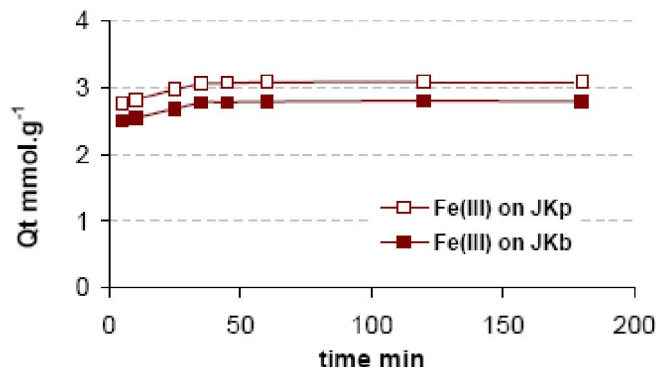


Figure 8 : Effect of shaking time on adsorption of Fe (III) on JKb and JKp

The sorption of Cr(III) on JKb and JKp was studied as a function of shaking at pH 3 and an initial Cr(III) concentration of 4 mol.L⁻¹. The equilibrium was reached when the quantity removed from solution attain a maximum value and did not change with time (Figure).

However, the uptake of Fe (III) is more rapid. The rapid equilibrium on smectic clay can be attributed to its expanded lattice, which made all exchange sites equally available and permitted exchange readily. Similar results have been reported for the adsorption of chromium(III) on Jebel Chakir clay^[32, 33].

On the basis of these results a shaking period of 2 h was used for all further studies so that all analysis, for both JKp and JKb, were made at the same time.

TABLE 6 : Equilibrium time and adsorbed quantity

Metal cation	Adsorbant	Equilibrium time min	Qe mmol.g ⁻¹
Cr(III)	JKb	60	3.13
	JKp	60	3.45
Fe(III)	JKb	35	3.13
	JKp	35	2.78

-Kinetic models

In order to investigate the mechanism of sorption kinetic models have been used to test experimental data. Three kinetic models were used to fit the experimental data at initial concentration 4mmol.L⁻¹, temperatures at 22 °C, pH 3.0

The first and pseudo-first-order equation^[34] does not well fitted for the whole range of contact time. Comparing with linear correlation coefficient R², kinetics data for the adsorption of iron and chromium from aqueous solution were in good agreement with pseudo-second-order equation.

The pseudo-second-order kinetic model^[35] is expressed as:

$$\frac{t}{Q_t} = \frac{1}{Q_e K} + \frac{1}{Q_e} t$$

where K is the rate constant of second-order adsorption, Qt is the sorption capacity at time t (mmol.g⁻¹) and qe is the sorption capacity at equilibrium (mmol.g⁻¹). Thus, the constants can be obtained from the slope and the intercept of a straight line plot of t / Qt against t

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The pseudo-second-order kinetic model includes

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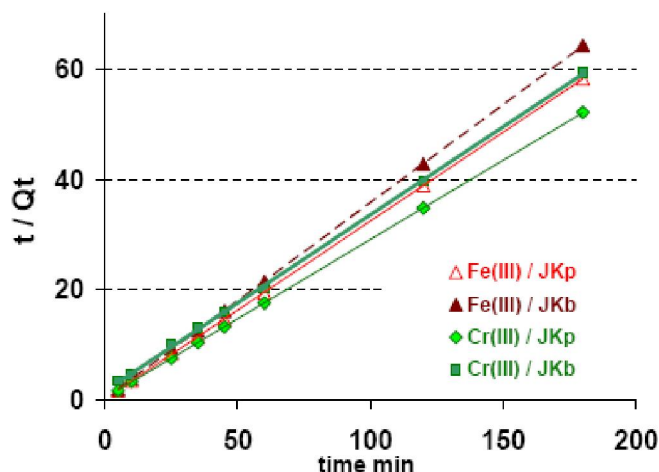


Figure 9 : Pseudo-second order curves of heavy metals adsorption by JKb and JKp in aqueous solution at 22°C

TABLE 7 : Parameters for adsorption kinetic model

Metal	Adsorbant	Q_e mmol.g ⁻¹	K g.mmol ⁻¹ .min ⁻¹	R^2
Cr(III)	JKb	3.125	0.062	0.9996
	JKp	3.448	0.216	1.000
Fe(III)	JKb	3.125	0.465	1.000
	JKp	2.778	0.518	1.000

all courses of adsorption, such as diffusion of external liquid membrane, surface adsorption, intra-particle diffusion^[36], Adsorption of tannic acid, humic acid, and dyes from water using the composite of chitosan and activated clay, J. Colloid Interface Sci. 278 (2004) 18–25.], which can provide real, complete and reliability adsorption mechanism for iron and chromium adsorption onto JKb and JKp adsorbents. Pseudo-second-order kinetic model predicts the behavior over the whole range of studies and is in agreement with chemisorptions being the rate-controlling step.

Sorption isotherms

The isotherms (Figure 10, 11) were obtained as in the preceding section, by using a variation in cation concentration interval [0-10] mmol.L⁻¹, while keeping all other parameters as temperature (22°C), solution to solid ratio (1g.L⁻¹), shaking time (2hours) and pH 3 constant.

The chosen pH value for which the ion adsorption was performed was 3 where free cations of iron and chromium (Fe³⁺ and Cr³⁺) are the predominant species in solutions.

The capacity of metal adsorbed onto JKb clay

varied in the following order Fe (III) = Cr (III) and Cr (III) > Fe (III) onto JKp clay.

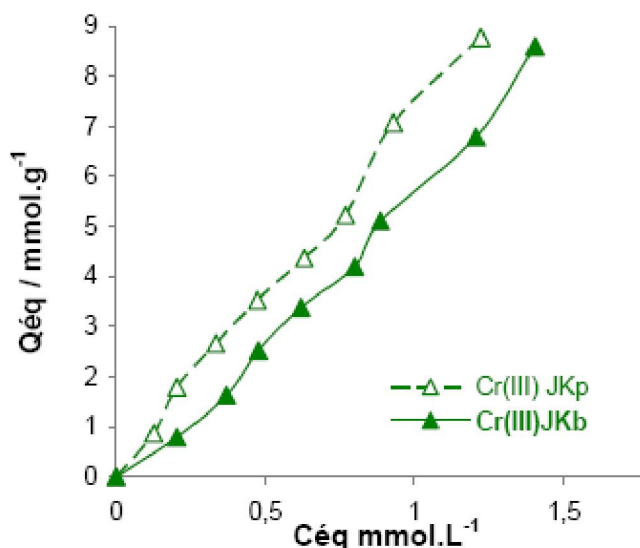


Figure 10 : Adsorption isotherms of Cr (III) on JKp and JKb

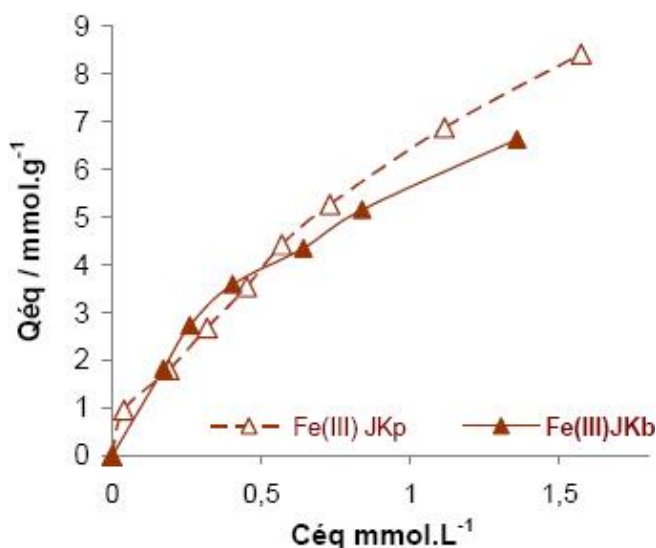


Figure 11 : Adsorption isotherms of Fe (III) on JKp and JKb

The adsorption isotherms for Cr (III) and Fe (III) on JKb and JKp were obtained at various metal concentrations from 0 to 10 mmol.L⁻¹, while keeping all other parameters as solution to solid ratio, shaking time and pH constant and shows these results for Cr(III) and Fe(III) respectively.

After adding the natural clays, the pH of the suspension increased and was readjusted to a value of 4. All other parameters, such as the solution to sorbent ratio, the shaking time and the temperature were kept constant.

The adsorbed chromium ion Q_e , onto the clays (mg.g^{-1}) is expressed as:

$$Q_e = \frac{K_L C_e}{1 + aC_e} \quad (3)$$

$$Q_e = K_F C_e^n \quad (4)$$

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

The sorption data were analysed in terms of Langmuir (3) and Freundlich (4) isotherms^[37,38]. Figure 6. Shows the adsorption isotherms of trivalent chromium on two substrates, at room temperature (22°C).

The linear forms of these equations are,

$$\frac{C_e}{Q_e} = \frac{1}{K_L} + \frac{a}{K_L} C_e \quad (5)$$

$$\log Q_e = \log K_F + n \log C_e \quad (6)$$

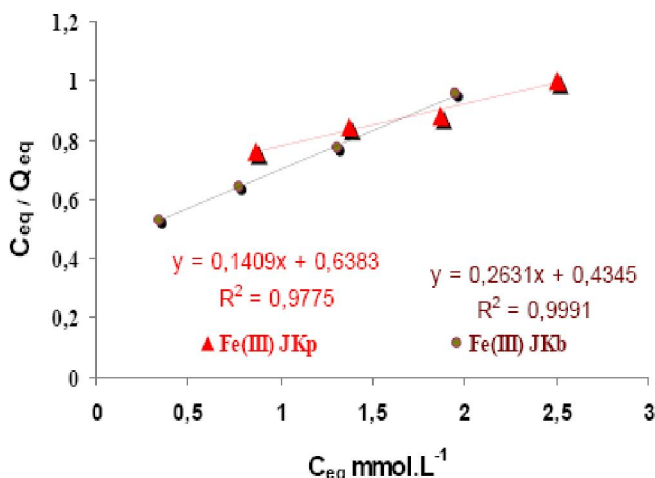


Figure 12 : Linearised Langmuir Adsorption Isotherm of Fe (III) on JKp and JKb

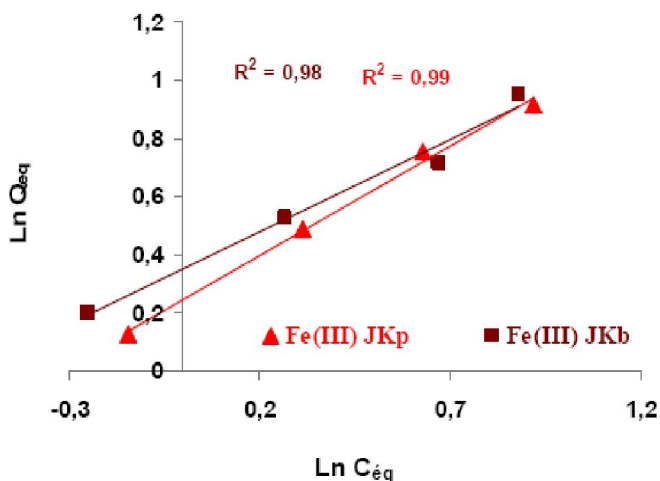


Figure 13 : Linearised Freundlich adsorption Isotherm of Fe (III) on JKp and JKb

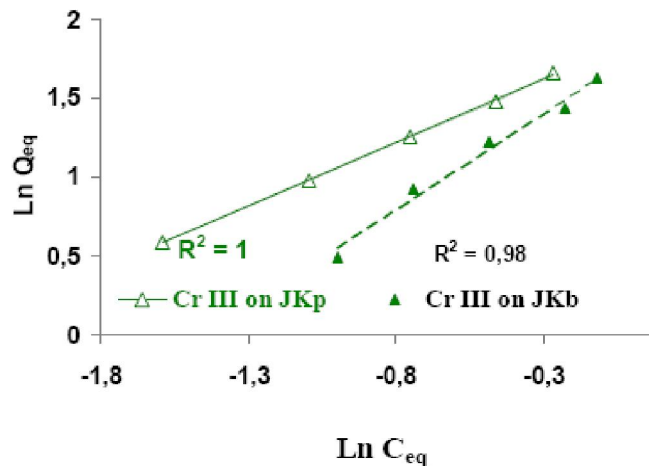


Figure 14 : Linearised Freundlich Adsorption Isotherm of Cr (III) on JKp and JKb

TABLE 8 : Freundlich and Langmuir parameters

Parameters Freundlich				
Clay	Metal	n	K_F	R^2
JKp	Cr(III)	0.799	6.39	1.00
	Fe(III)	0.76	1.28	0.98
JKb	Cr(III)	1.23	5.86	0.98
	Fe(III)	0.63	1.42	1.00

Parameters Langmuir					
Clay	Metal	$K_L(\text{g}^{-1}.\text{L})$	$a(\text{g}^{-1}.\text{L})$	$Q_{\max} \text{mmol.g}^{-1}$	R^2
JKb	Fe(III)	2.30	8.75	3.80	1.00

The plots respectively of C_e / Q_e against C_e and $\log Q_e$ against $\log C_e$ give straight lines.

Comparing with linear correlation coefficient R^2

In the case of iron the experimental data are well fitted to the linearised Langmuir isotherm for natural clay (Figure 12) and Freundlich model for purified clay (Figure 13), whereas the chromium adsorption data are in good agreement with Freundlich equation (Figure 14).

CONCLUSION

Jebel Kebir Clay has been evaluated for their purifying qualities since they are thought to act as a filter and purifier for pollutants.

The original clay was characterized, the results show that the material is a smectite (80%) with a small proportion of kaolinite(20%). The CEC and SSA values for the raw clay sample (JKb) are respectively 25 meq /100 g, 206 m^2/g of fired clay; and 50 meq /100 g and 403 m^2/g of fired clay for Na-purified clay.

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The adsorption equilibrium time of Cr (III) and Fe (III) by both raw and the Na-purified clay were determined. The results prove that the uptake of Fe (III) is the most rapid.

Kinetics data for the adsorption of iron and chromium on JKb and JKp from aqueous solution are in good agreement with pseudo-second-order model. This model predicts the behavior in agreement with chemisorptions.

The adsorption isotherms for Cr (III) and Fe (III) on JKb and JKp were obtained at various metal concentrations from 0 to 10 mmol.L⁻¹, while keeping all other parameters as solution to solid ratio, shaking time and pH constant

The capacity of metal adsorbed onto JKb clay varied in the following order Fe (III) = Cr (III) and Cr (III) > Fe (III) onto JKp clay.

The sorption data were analysed in terms of Langmuir and Freundlich isotherms.

In the case of iron the experimental data are well fitted to the linearised Langmuir isotherm for natural clay and Freundlich model for purified clay, whereas the chromium adsorption data are in good agreement with Freundlich equation.

Consequently, The Jebel Kebir clay may be an effective adsorbent for the removal of metal in wastewater

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