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# Environmental Science

*An Indian Journal**Current Research Paper*

ESAIJ, 3(2), 2008 [224-228]

## Adsorption of chromium Cr(III) and Cr(VI) from aqueous solutions by common abundant moroccan natural clay

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*Received: 9<sup>th</sup> October, 2007 ; Accepted: 14<sup>th</sup> October, 2007*

### ABSTRACT

The objective of the present study was to investigate the adsorption of the heavy metals Cr(III) and Cr(VI) from aqueous solutions, onto on abundant Moroccan natural clay, (AMN). The adsorption experiments were studied in batch reactor at room temperature. The adsorption equilibrium time for both of Cr(VI) and Cr(III) was found to be 10min and 4h respectively. The influence of the pH solution on the Cr(VI) and Cr(III) adsorption was studied in the pH range of 2-7, the optimum pH for the Cr(VI) adsorption is 2, while that of Cr(III) is at the pH values above 4. Equilibrium isotherms for the adsorption of Cr(VI) and Cr, (III) on AMN were analyzed by Freundlich, and Langmuir adsorption isotherms and they showed good fits to describe the adsorption equilibrium of Cr(VI) and Cr(III) on the natural clay, (AMN). The adsorption capacities for this natural clay, (AMN) for Cr(III) and Cr(VI) were found to be 512 and 0.15 mg/g, respectively.

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### KEYWORDS

Natural clay;  
Removal;  
Adsorption;  
Chromium.

### INTRODUCTION

Rapid growth in industry and population has resulted in environmental degradation. Heavy metals like mercury, lead, cadmium, copper, chromium and nickel are toxic even in extremely minute quantities. Chromium is widely used in electroplating, leather tanning, metal finishing and chromate preparation. Chromium exists in two stable oxidation states Cr(III) and Cr(VI). The Cr(VI) state is of particular concern because of its toxicity. The recommended limit of chromium in potable water is 0.05 mg l<sup>-1</sup>[17]. Chromium, (III) occurs naturally

and is an essential nutrient that helps the body to use sugar, protein and fat. Although Cr(III) is an essential oligoelement for animal life, its oxidation to toxic Cr(VI) can lead to ecological problems<sup>[10]</sup>. Chromium, (VI) rarely occurs naturally, but is usually produced from anthropogenic sources. The International Agency for Research on Cancer, (IARC) has determined that chromium, (VI) is carcinogenic to humans. The remediation of chromium, (VI) contaminated industrial effluents is gaining great interest due to limitations on potable water supplies<sup>[8]</sup>.

The permissible limit of Cr(VI) for industrial

wastewater to be discharged to surface water is 0.1 mg l<sup>-1</sup>. Hence, it becomes imperative to remove Cr(VI) from wastewaters before discharging them into aquatic systems or onto land. Different methods, such as reduction and precipitation<sup>[14]</sup>, ion exchange<sup>[5]</sup>, electro dialysis, reverse osmosis, solvent extraction<sup>[13]</sup>, electrochemical precipitation<sup>[6]</sup> and adsorption<sup>[4]</sup> have been suggested for the removal of hexavalent chromium.

Among these, adsorption is the most promising technique. Several authors have reported studies on various low cost adsorbents. Activated carbon prepared by carbonization of rice husk<sup>[16]</sup>, groundnut husk<sup>[16]</sup> and coconut sawdust<sup>[21]</sup> have been reported.

In recent years, considerable attention has been devoted to study the use of industrial wastes as adsorbents. Fly ash from a thermal power plant<sup>[11]</sup>, waste slurry from a fertilizer plant<sup>[25]</sup>, Fe(III)/Cr(III) hydroxide obtained from the petrochemical industry<sup>[9]</sup>, blast furnace fluedust<sup>[12]</sup> and photo film waste sludge<sup>[20]</sup> have been examined for removal of hexavalent chromium. The adsorption of Cr(VI) on bituminous coal<sup>[22]</sup>, sphagnum peat moss<sup>[26]</sup>, coconut husks and palm pressed fibbers<sup>[23]</sup>, sawdust, sugarcane bagasse, sugarbeet pulp and maizecob<sup>[2]</sup> has been reported.

In this present study, we propose the removal of Cr(III) and Cr(VI) by adsorption on one abundant Moroccan common clay, (AMN). The adsorption experiments will be carried out in the batch reactors and will have as objectives: (i) the study of pH influence on the amount of Cr(III) and Cr(VI), and, (ii) the study of the kinetics and the adsorption isotherms of Cr(III) and Cr(VI).

## EXPERIMENTAL

### Materials

The clay material used in this work came from Dhar El Mahraz quarry in Fez. The chemical analysis, (wt.%) of this clay was: SiO<sub>2</sub>, 50.32; Al<sub>2</sub>O<sub>3</sub>, 15.94; Fe<sub>2</sub>O<sub>3</sub>, 5.91; CaO, 13.89; MgO, 3.77 and K<sub>2</sub>O, 2.08, this clay has been studied by several authors [sahraoui et al., and lahsini...] who found that it is constituted of a mixture of kaolin and the illite. This clay is crushed and sieved beforehand to a size lower than 500µm. It was then washed by distilled water until stabilization of the

pH of the suspension in order to eliminate the metallic salts, it is filtered in continuation dried at the steam room in 110°C and is stocked in closed small bottle safe from light. The synthetic solution of Cr(III) and Cr(VI) were prepared by dissolution of the appropriate mass of Cr(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O, (Riedel-deHaën) and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, (Riedel-deHaën) in distilled water.

### Adsorption procedure

The adsorption experiments of chromium(III) and, (VI) by AMN clay, were carried out in a series of Erlenmeyer flasks containing the desired dose of the adsorbent and the 50mL of chromium aqueous solution at the desired concentration and initial pH (adjusted with diluted hydrochloric(0.1N) acid, or sodium hydroxide (0.1N) solution) measured by LP115-pH meter) in a constant temperature bath. After shaking for a fixed time, the flasks were removed and the suspensions were filtered by 0.45µm cellulose membrane. the concentrations of Cr(III) and Cr(VI) in the filtrate were determined by PYE UNICAM SP9 Atomic Absorption Spectrometer(SAA) in air acetylene.

The amount of adsorbed chromium was calculated using the following equation:

$$Q = \frac{(C_0 - C_1) \times V}{m}$$

Where Q is the amount of absorbed chromium(mg/g); C<sub>0</sub> and C<sub>1</sub> are the initial and residual concentration, (mg/L), respectively; V is the volume of chromium aqueous solution(L); m is the dose of AMN clay, (g).

## RESULTS AND DISCUSSIONS

### Effect of pH

Since pH is an important parameter, the effect of initial pH of solution on the Cr(VI)/Cr(III) adsorption onto AMN clay was studied, in order to find out the optimum pH for maximum removal efficiency, experiments were conducted with 50ml of 1.g l<sup>-1</sup> chromium solution with adsorbent doses 1,5g of AMN clay over a pH range 2-7, pH adjustments were made either with 0.1 N HCl or 0.1 N NaOH.

Figure 1 and 2 presents the effect of initial pH on the removal of Cr(VI) and Cr(III), by AMN clay, it seems that the amount adsorbed of Cr(III) increases with increasing of pH from 2 to 5. This can be explained

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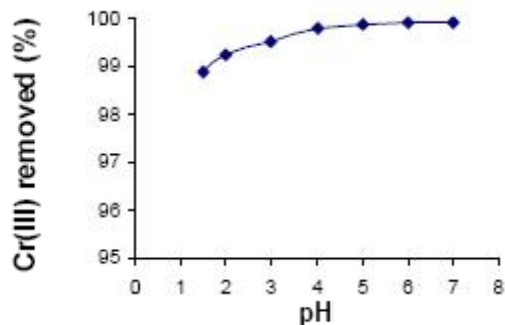


Figure 1: Effect of pH on Chromium removed, (%) Cr(III)

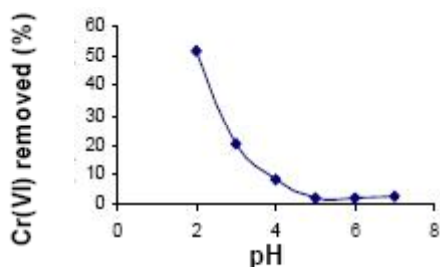


Figure 2: Effect of pH on Chromium removed, (%) Cr(VI)

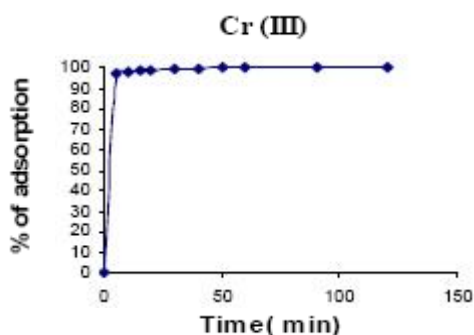


Figure 3: The effects of contact time on the Cr, (III) adsorption by AMN clay, (1g/l Cr(VI) solutions; adsorbent masse 1.5g, pH no adjusted, temperature: 20°C)

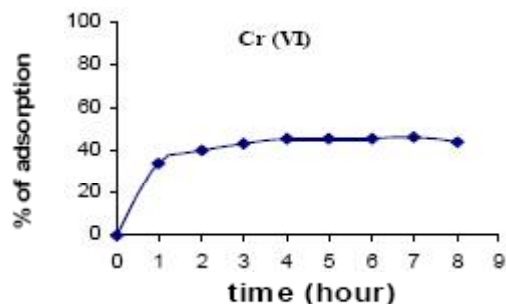


Figure 4: The effects of contact time on the Cr, (VI) and Cr, (III) adsorption by AMN clay, (1g/l Cr(VI) solutions; adsorbent masse 1.5g, initial pH: 2, temperature: 20°C)

by the diminution of competition between  $H^+$  protons

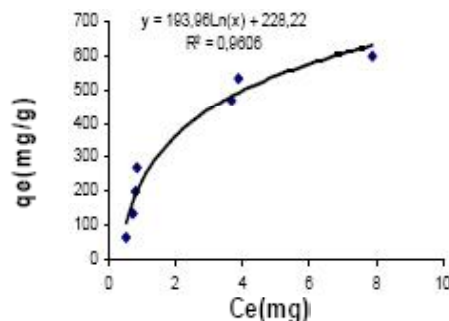


Figure 5: Experimental isotherms of Cr(III) adsorbed by AMN clay at pH 2

and Cr(III) cations towards the adsorption sites and the deprotonation of the particle edges. At pH values above 5, the Cr(III) adsorption was not significantly affected by the solution pH. This is because at the pH range of 5-7, the predominant specie is  $Cr_3(OH)_4^{5+}$ .

We note that the Cr(VI) adsorption is optimal in the pH 2 and decreases with increasing pH may also be attributed to the surface complexation<sup>[2]</sup>. Therefore, the adsorption of Cr(VI) anions decreases with an increase in pH. Previous studies have shown that Cr(VI) exists predominally in solution as  $HCrO_4^-$  at low values and  $CrO_4^{2-}$  at high pH values<sup>[18]</sup>. The adsorption of these species on the particle edges, ( $S-OH^{2+}$ ) can be described by the following complexation reactions:



### Kinetics adsorption

The experimental results of the adsorption kinetics of Cr(III) and Cr(VI) are illustrated in figure 3 and 4. The rate of adsorption of Cr(III) and Cr(VI) was followed by looking at the increase in the adsorption as a function of time until the adsorption remained constant, implying equilibrium was reached.

As seen in figure 3 and 4, the adsorption of Cr(III) is rapid in the first minutes and the equilibrium is then attained within 10min, whereas the adsorption of Cr(VI) is slow compared at the one observed of Cr(III). It found that equilibrium was attained at about 4h. Therefore, an agitation period of 1 and 4h was selected to establish the adsorption isotherms of Cr, (III) and Cr, (VI), respectively.

### Adsorption isotherms

Figure 5 and 6 Shows the experimental data for

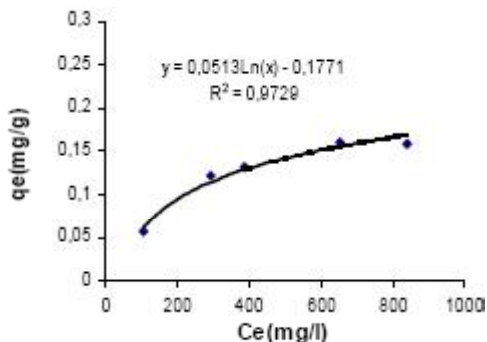


Figure 6: Experimental isotherms of Cr(VI) adsorbed by AMN clay at pH 2

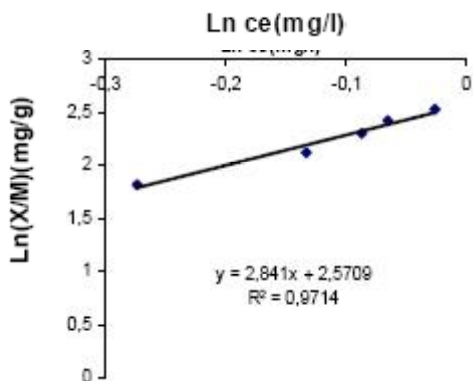


Figure 7 : Freundlich adsorption isotherm for Cr, (III) adsorption on the AMN clay, (pH: 2, T: 25°C)

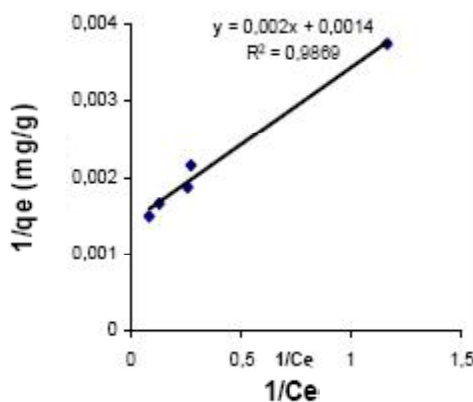


Figure 8 : Langmuir adsorption isotherm for Cr(VI) adsorption on the AMN clay, (pH:2, T:25°C)

Cr(III) and Cr(VI) ion adsorption isotherm for the AMN clay. These figure show that the AMN clay exhibits a marked affinity for Cr(III) ions in aqueous solution. The ultimate capacities of adsorption of Cr(III) and Cr(VI) are 512 and 0.15 mg/g respectively.

The Langmuir and Freundlich adsorption isotherm models were examined in this study to describe the adsorption equilibrium. Isotherm studies were

conducted at the effective initial pH of 2 of Cr(VI) and no adjusted pH of Cr(III), Agitation constant, and an equilibrium time 20 min and 4 h for Cr(III) and Cr(VI) respectively. TABLE 1. presents the constants of regression equations and constants of adsorption models for Cr(III) and Cr(VI) removal.

According to Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent, and once adsorbate occupies a site, no further adsorption can take place at this site. Thus, the Langmuir model is given by Eq. (1).

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{bQ} \times \frac{1}{C_e} \tag{1}$$

Where Q and b, the Langmuir constants, are the saturated monolayer adsorption capacity, and the adsorption equilibrium constant, respectively. Ce is the equilibrium solution concentration; q<sub>e</sub> is the amount of chromium adsorbed at the equilibrium.

The Langmuir parameters can be used to predict affinity between the adsorbate and adsorbent using the dimensionless separation factor, RL, defined by Hall and al and others<sup>[1,22,17]</sup> as.

$$R_L = \frac{1}{1 + bC_0}$$

The adsorption capacity Q and energy of adsorption b were calculated from the slope and intercept of the Langmuir plot and found to be in the TABLE 1. The equilibrium parameter R<sub>L</sub>. Values between 0 and 1 for all the concentration of chromium indicating favourable adsorption

On the other hand, the Freundlich isotherm is an empirical model that is based on adsorption on heterogeneous surface and is given by Eq. (2).

$$\text{Ln}q_e = \text{Ln}K_f + \frac{1}{n} \text{Ln}C_e \tag{2}$$

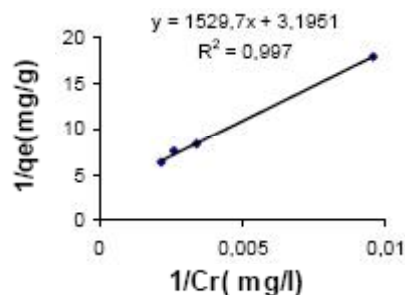


Figure 9: Langmuir adsorption isotherm for Cr, (III) adsorption on the AMN clay at, (pH:2, T:25°C)



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TABLE 1: Isotherm constants and values of R<sup>2</sup>

	Langmuir isotherm			Freundlich isotherm		
	Q(mg/g <sup>-1</sup> )	b(lmg <sup>-1</sup> )	R <sup>2</sup>	K <sub>f</sub> (mgg <sup>-1</sup> )	n	R <sup>2</sup>
Cr(III)	500	0.7	0.98	0.41	0.35	0.97
Cr(VI)	0.3129	0.002	0.99	0.0023	1.4513	0.99

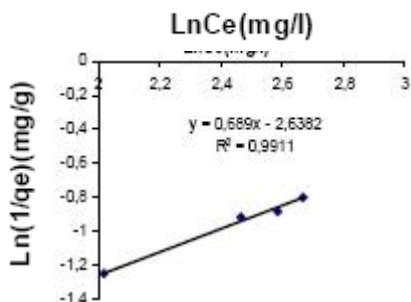


Figure 10: Freundlich adsorption isotherm for Cr(VI) adsorption on the AMN clay, (pH:2, T:25°C)

Where  $K_f$  and  $n$  are the Freundlich constants, which represent adsorption capacity and adsorption intensity, respectively,  $K_f$  and  $n$  calculated from the intercept and slope of the plot were given in the TABLE1.

## CONCLUSION

Natural clay was studied as low-cost alternative adsorbent for removal of chromium species, (Cr(III) and Cr(VI)). The results showed that this Moroccan natural clay AMN can be a suitable adsorbent for the removal of Cr(III) from aqueous solution, as both kinetics and capacity are highly favourable. Study the influence of pH on the adsorption shows that the amount of Cr(III) adsorbed increases with pH and becomes insignificant for a value of pH above 4, well that of Cr(VI) adsorbed decreases with pH, the suitable condition for the adsorption are acid pH 2. The adsorption kinetics study of the Cr(III) and Cr(VI) reveals a rapid adsorption of Cr(III) compared with Cr(VI). Concerning the adsorption isotherms study, the maximal adsorption capacity of AMN clay is higher for Cr(III) with a value 512 and low for Cr(VI) with a value 0.15 mg/g.

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