Interactions between natural materials and inorganic pollutants

Mohamed Salah Medjram¹, Nassira Ferroudj²

Abstract — The heavy metal pollution poses a threat to groundwater resources, soils and sub-soils. In contrast to most organic contamination, the metallic elements are not biodegradable and potentially toxic. Clays play a significant role in a wide range of environmental problems, and their applications are increasing steadily, particularly in trapping heavy metals and reducing their toxic effects. In our work we have conducted tests adsorption of chromium on a clay-like bentonite.

Keywords — pollution, environment, water, chromium VI, adsorption, clay-like, bentonite.

1 Introduction

The adsorption of inorganic compounds onto solides hydrous is an electrostatic process where specific interactions between the ionic species and the surface of the solid are established. In this process, activated carbon has been widely used in wastewater treatment to remove heavy metals, they are one of the most important pollutants in surface and groundwater [1-2]. The removal of heavy metals from wastewater is important, as (i) most of them pose a threat to the environment due to their nondegradability and their toxicity to the aquatic organisms when discharged to receiving waters [3], and (ii) because of the stringent regulations imposed on effluent quality and solid wastes from industries. One of the most heavy pollutants metals which has a great toxic effect in wastewater is chromium, especially hexavalent chromium, it is considred as a second toxic metal after mercury, pollution by Chromium causes serious intoxications (foetal malformations, neural troubles) and pose serious health hazards [4-5]. Extensive studies have been published on the removal of heavy metals by activated carbons [6-7]. The main objective of this present investigation were to(i) determine, the effectiveness degree of the adsorption process onto a clay-like bentonite, in relation to the depollution of a water highly contaminated by chromium, and (ii) to study the effect of important factors such as pH, temperature, stirring velocity, impact of contact time, impact of mass ratio solid/liquid, onto the process, in order to obtain maximum removal efficiency.

2 MATERIAL AND METHODS

2.1. Apparatus

Batch mode adsorption experiments were carried out using 1000 ml (fluid volume) discontinuous reactor perfectly agitated, closed and thermostated as shown in figure 1. The reactor is a glass cylinder of 25 cm height and internal diameter 15 cm. The agitation is carried out using a mechanical agitator. The sliding part used is a stem with four blades inclined with 45 degrees, 5 cm in diameter. The temperature is recorded in various phases. The reactor is plunged in a thermostated bath.

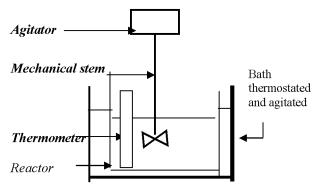


Figure 1: Scheme of the experiment set-up for adsorption in batch mode.

2.2. Analysis of hexavalent chromium

Cr VI was proportioned by the spectrometer UV-Visble (Lambda 11). The wavelength resolution was 540 nm [8]. Dilution of the samples prior to analysis was necessary.

2.3. Reagents and bentonite

As raw material, the bentonite is a mixture of clay minerals and crystalline impurities in the form of rock [9]. Study of clays is justified by their abundance in nature, the importance of surfaces which they develop, the presence of electrical

^{1.} M.S. Medjram G.C.E.S. Laboratory, Faculty of Technology - , PO Box 26, University of Skikda. 21000 Skikda Algeria E-mail: medjram ms@yahoo.fr

^{2.} N. Ferroudj GC.E.S. Laboratory, Faculty of Technology - , PO Box 26, University of Skikda. 21000 Skikda Algeria E-mail: medjram ms@yahoo.fr

charges on the surface and above all the exchangeability of interlayer cations [10]. The bentonite used in the experiment comes from the deposit of M'zila, district of Mostaganem Algeria. Its chemical composition is given in Table 1.

Table 1. Chemical composition of bentonite

Element	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaCO ₃	CaO	LOI
%	60,92	14,62	4,28	5,76	3,79	11

A stock solution of 1000 mg Γ^1 was prepared by dissolving $K_2Cr_2O_7$ with Purity greater than 99,8 % in distilled water. Distilled water have pH between 6,5 to 6,8 and a conductivity of 0,2 to 0,6 μ s/cm. A solution from 100 to 900 mg Γ^1 was prepared from stock solution.

2.4. Procedure of Cr VI elimination

A typical batch mode experiment was carried out as follows: 1000 ml of 100, 200, 400 and 800 mg l⁻¹ Cr VI at an initial pH 2 and 2g of adsorbent (clay) were taken in the reactor (fig.1) and agitated at 200 rpm and 18°C. 1 ml of the supernatant solution are carried out with intervals of time in order to measure the reduction in the concentration of the solution in metal in the course of time until having a constant metal concentration. The analyses of the supernatant solution were achieved as previously described [8]. In order to determine the isotherm of Cr VI onto bentonite, 100 ml of chromium aqueous solutions, at different concentrations (100 to 1000 mg 1⁻¹), and a fixed concentration of adsorbent (2g), were continuously stirred at 25°C. The stirring rate was 200 rpm. Equilibrium was reached after a contact time of 15 minutes (determined during preliminary evaluations). The amount of Cr VI adsorbed q = x/m $(mg g^{-1})$ can be obtained as follows:

$$q = (C_0 - C_e) V/m$$
 (1)

where C_0 and C_e are the initial and equilibrium solution concentrations (mg Γ^1), V is the volume of solution (l), and m is the amount of bentonite used (g). The isotherm of metal adsorption considered is obtained by tracing q vs C_e [11]. pH effect was studied by adjusting chromium solution pH to different values between 1,5 and 7,0 with dilute NaOH and HCl solutions. The temperature effect on Cr VI elimination onto bentonite was also studied. Cr VI concentrations in the solution used were from 100 to 1000 mg Γ^1 , pH 2 and 2g of bentonite.

Studies were also conducted to examine the change in the adsorption behavior of Cr VI onto bentonite. The determination of the effect stirring speed on the process, we varies this one between 200 and 1200 rpm. All these tests were carried out as follows: after agitation of mixtures (100 ml of chromium solution at 200 mg I⁻¹ with 0,5 g of GAC) during 15 minutes,

Samples of 1ml were withdrawn for analysis using the spectrometer UV-Visble to determine Cr VI concentration remaining in the fluid phase, and therefore the amounts of Cr VI adsorbed onto bentonite.

For the kinetic studies, 2g of bentonite was continuously stirred with 1l of aqueous Cr VI solution (800 mg l⁻¹) at 25°C. The analyses of the supernatant solution were achieved as previously described.

3. Results and discussion

3.1. Effect of shaking time

Figure 2 shows the variation in the percentage adsorption of Cr VI onto clay with shaking time, using distilled water as the sorptive medium. This figure indicates that Cr VI adsorption is quite rapid, equilibrium time reached after 20 minutes.

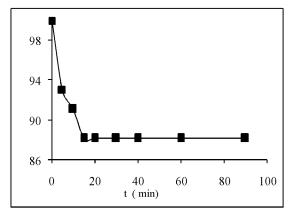


Fig 2. Shaking time Effect of on Cr (VI) adsorption onto bentonite.

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Figure 2 shows the variation in the percentage adsorption of Cr VI onto bentonite with shaking speed.

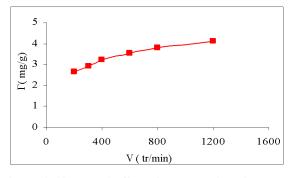


Fig 2. Shaking speed effect of Cr (VI) adsorption onto bentonite.

The results clearly show that increasing the shaking speed leads to increased retention capacity of chromium by bentonite. This phenomenon is explained by the fact that increasing the shaking

speed increases the likelihood of contact between the substrate and the metal solution and therefore favors the retention of chromium by bentonite.

3.3. Effect of temperature

The temperature used was varied from 25 to 50 °C. The Comparison between the isotherms Cr VI onto bentonite obtained at different temperature (figure 3) reveal that the amount adsorbed decreased with increase of the temperature from 25, 40 and 50 °C. The process of chromium ion adsorption onto bentonite is exothermic.

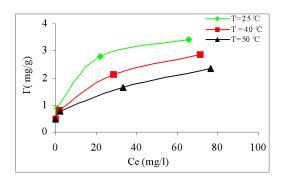


Fig 3: Temperature Effect on the adsorption of Cr VI ions from bentonite.

3.4. Effect of pH

An attempt was then made to find the optimal pH range from chromium solution that gives a maximum adsorption capacity. The decrease in pH supports the disappearance of metal as shown in figure 4. The highest rate of fixation of chromium is obtained at pH 1.5, Therefore it would be preferable to acidify the medium.

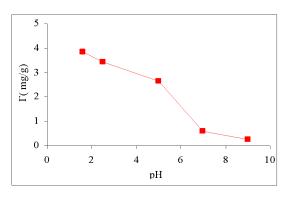


Fig 4: Effect of pH on the adsorption of Cr VI ions from bentonite.

3.5. Effect of the solid / liquid ratio (S / L)

Figure 6 presents the effect of the solid/liquid ratio on the removal of Cr VI. Results show that Increasing of the mass Support involves an increase in surface area responsible for the fixation of chromium, and therefore the probability of contact between the adsorbate and the adsorbent becomes more important.

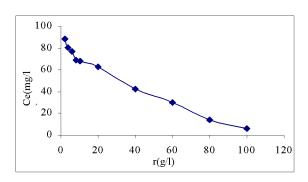


Figure 6: Effect of the solid / liquid ratio.

4. Adsorption isotherms.

The application of the linearization of the three classic models of adsorption (those of Langmuir, Freundlich and Temkin) to our experimental results gives the following results, which show that the chromium adsorption follows the Freundlich model-

Métal	T (°C)	Langmiur Model	Freundlich Model	Temkin Model
		K _L (l/mg)	K_{F}	ΔQ (kJ/mol)
Cr ⁺⁶	25	0,06	0,93	20,642

Figure 7: The amount of Cr VI adsorbed on to activated carbon as a function of time.

Where K is the first-order rate constant of adsorption (min $^{-1}$). ΔQ is the adsorption energie and K_F is the constant in Freunlich isotherm.

5. Conclusion

The possibility of depollution of water contaminated by Cr ⁶⁺ by using the process of adsorption on bentonite was studied. The different test generated several results. The process of chromium ion adsorption onto bentonite is exothermic. Chromium elimination decreases with pH; therefore it would be preferable to acidify the medium. Chromium removal is affected by Shaking speed until 1200 tr/min.

Adsorption isotherms results show that the chromium adsorption follows the Freundlich model.

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