

Evaluation of Trivalent and Hexavalent Chromium Retention on Ain Oussera Soil by the Batch Method and Radiotracer Technique.

Rebhi A.M.^{[1]*} Bouzidi A.^[2] Lahrech M. B.^[3] Mouhouche F.^[4] Ararem A.^[2]
Rebhi F.^[2] Lounici H.^[5]

Abstract Major toxicology studies have concluded that Cr (VI) is a highly toxic carcinogen to living organisms, and cause deaths if ingested in large doses. The trivalent form plays an important role in glucose and lipid metabolism for human and animal diets.

Industrial activities present in the study area investigated in this paper, such as tanning, production of paints, and cement, are the main sources of chromium in the soil and air, causing chromium pollution.

The aim of this study is to investigate the behavior of Cr (III) and Cr (VI) in soil samples from the Ain Oussera area, using the batch method and radiotracer technique. This assessment of chromium adsorption in the soil allows us to examine its impact. The pH effects of initial concentration, adsorbent dose and temperature were investigated. Particle size, X-ray diffraction and neutron activation analysis methods were used to characterize the soil samples. Results of the Freundlich, and Langmuir isotherm models were compared to the obtained experimental data. The thermodynamic parameters ΔH° , ΔS° and ΔG° for the adsorption were determined by using four temperatures, 10, 30, 40 and 60°C. The adsorption process was spontaneous and favoured at a low temperature.

The maximum adsorption percentage reached for Cr (III) and Cr (VI) in soil was 90 and 24, respectively, with a spontaneous reaction ($\Delta H^\circ < 0$). These results show that hexavalent chromium seeps through soil layers, and reaches the groundwater easily.

Keywords : _Heavy metals, chromium, batch sorption, gamma spectrometry, radiotracers.

Introduction

Metal pollution in soil has been mainly due to industrial or agricultural activities particulate emissions. This led to the pollution of the soil by dry deposition or by wet precipitation in scales different distances depending on the particle size and the atmospheric conditions (Hamadi et al., 2001). The use of fertilizers and pesticides can also contribute to the increase of metal pollution, and end up easily in the food chain of living beings including humans (Jose R. et al., 2009).

Metal pollution also has a negative effect on the molecular biology of living organisms by disrupting the metabolic functions in two ways: First, they accumulate and disrupt the function of organs and vital glands such as the heart, brain, kidney, liver, bone. Then, they also move essential nutrients that no longer fulfill their biological function (Jose R. et al., 2009). For example, enzymes those are catalysts for virtually all biochemical reactions in the metabolic process: Instead of the calcium in an enzymatic reaction, lead or cadmium can be found in its place, and not can fill the same role as the essential minerals, therefore, this disrupts the enzymatic activity (Selvaraju et al., 2009).

Chromium is one of toxic metal pollutants widely generated by industrial activity. Present in the environment predominantly in one of two valence states: trivalent chromium, an essential nutrient that occurs naturally, and is an essential nutrient that helps the use

of sugar, protein, and fat by the body (Romina et al., 2009) (Arunima S. and Krishna G., 2004).

Very soluble in water under the hexavalent form found in industrial waste, it is highly toxic and classified as carcinogenic for living organisms (Adel M. Z. and Norman T., 2003). This solubility gives a high mobility in ecosystems (Singh et al., 2009). The reduction of Cr (VI) to Cr (III) can limit its mobility and toxicity by reduce the potential ecotoxicological impacts (Abdelaziz et al., 2007).

The trivalent chromium state is present predominantly in most soils. The fate of soil chromium is partly dependent on the redox potential and the soil pH. Under reducing conditions, Cr (VI) is reduced to Cr (III) in soils involving aqueous inorganic species, electron transfers at mineral surfaces, reactions with non-silt substances such as carbohydrates and proteins, or reduction by soil silt substances (Yasar et al., 2009). The reduction of Cr (VI) to Cr (III) is pH dependent, increasing with lower pH values. In aerobic soils, the reduction is possible, even at slightly alkaline pH, if the soil contains appropriate organic energy sources to carry out the redox reaction (Avom et al., 1997).

To reduce the impact of this pollution, several methods were tested in the world: The precipitation of heavy metals has long been the technique most used. Although this process is effective, it has drawbacks in that large amounts of sludge are produced which time

[1] Ecole Nationale Polytechnique d'Alger (Algérie)

[2] Centre de Recherche Nucléaire de Birine (Algérie)

[3] Laboratoire de Chimie Organique et des Substances Naturelles, Université de Djelfa (Algérie)

[4] Ecole Nationale Supérieure d'Agronomie (Algérie)

[5] Université de Bouira (Algérie)

* Corresponding Author. E-mail:rebghani@hotmail.com

the cup is very long (Reddy et al., 1997). The use of activated charcoal in the adsorption process is also much in demand, and has a high adsorption capacity mainly due to its large specific surface, but it is still very expensive (Xue Wen et al., 2009). Attention was focused on the use of new adsorbents based on natural materials and abundant. This is the case of soil and different parts that compose it (especially clays) (Weidong et al., 2009).

Previously conducted studies on adsorption of Trivalent and Hexavalent chromium have shown that the parameters of influence: pH, initial concentration, temperature, adsorbent dose and contact time greatly influences the effectiveness of retention. This influence has been verified from the results obtained in this and other studies (Abdelaziz et al., 2007).

Our main objective in this study was to evaluate the chromium retention capacity in Ain Oussera area soil, using the nuclear radiotracer technique. To achieve this objective, we first identified our sample points on the region map, taking as reference the site of Essalam nuclear reactor, while setting a radius of twenty miles with scanning of the four directions (North, South, East and West). We have taken every precaution necessary to extract the different layers of soil to fifty centimeters depth, in order to have a correct representation and simulate better the responses scale laboratory.

- East soil sample: Latitude = 35° 35' 23'' N ;
Longitude = 2° 55' 52'' E.
- North soil sample: Latitude = 35° 43' 49'' N ;
Longitude = 3° 5' 25'' E.
- West soil sample: Latitude = 35° 34' 23'' N ;
Longitude = 2° 55' 8'' E.
- South soil sample: Latitude = 35° 25' 59'' N ;
Longitude = 3° 6' 59'' E.

Materials and methods

1. Soil Sampling

The four samples were dried at room temperature for 48 hours, then mix on a 1 mm sieve. It took 10 g of each depth sampled (0 - 50 cm), and all gave the mixed soil sample simulated for a single region chosen.

The particle size was determined according to NF X 31-107 standard (Bouzidi et al., 2010) in CRNB chemistry laboratory. This standard allows a determination of the particle size distribution in five fractions: clays (0 to 2 µm), fine silt (2 to 20 µm), coarse silt (20 to 50 µm), fine sand (50 to 200 µm) and coarse sand (200 to 2000 µm).

2. Chromium radiotracer preparation

1 mg/l of Chromium radiotracer solutions were prepared by neutron irradiation (K_2CrO_4) for the Hexavalent; and metal chromium for trivalent) at a neutron flux of $6.8 \cdot 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$ during eight hours in the Algerian Essalam reactor. Irradiated salt was dissolved in deionised water to the desired concentration.

Cr^{51} was obtained from Cr^{50} (n, γ) Cr^{51} . Irradiated chromium was also dissolved in deionised water to the desired concentration.

3. Adsorption experiments

The batch experiments were carried out in 100 ml conical flasks, where 0.5 g of soil and 50 ml of 1 mg/l chromium solution was added. After equilibrium, the solution was filtered through a 0.45 µm membrane.

γ activity was measured with high purity germanium detector combined with a gamma spectrometry system. The removal percentage adsorption (R %) was calculated using the following equation (Bouzidi et al., 2010) :

$$R (\%) = \frac{A_i - A_f}{A_i} * 100 \quad (1)$$

The effect of pH, temperature and sorbent dose was studied. The pH was varied from 2 to 12, temperature from 5 to 60 °C and sorbent dose from 0 to 40 g/l, and initial concentration from 0 to 1000 mg/l.

Results and discussion

1. Characterization of soil sample

(1) Particle size analysis of soil

Table 1 Soil particle size

	East soil	West soil	North soil	South soil
Clays (%)	9.10	9.54	10.37	9.76
Fine silt (%)	11.35	7.80	7.46	8.89
Coarse silt (%)	1.22	1.57	1.19	1.34
Fine sand (%)	43.95	42.71	43.66	43.54
Coarse sand (%)	34.38	38.36	37.32	36.23

The soil type is major sandy loam for all samples. The Ain Oussera soil in the vicinity of the Es-Salam reactor has approximately the same physicochemical properties within a radius of 20 km. It is a sandy soil poor in organic substance with 10% of clay minerals, and 80 % of sand.

(2) Activation neutron analysis

Chromium concentration in the used soils was determined in order to characterise the soil by using neutron activation analysis given in table 2. Obtained results revealed that chromium concentration for all samples was comprised between around 3.3 and 6.8 mg/l.

Table 2 Soil composition result

	East soil	West soil	North soil	South soil
[Cr] (ppm)	4.4 ± 0.2	6.8 ± 0.3	5.6 ± 0.3	3.3 ± 0.2

(3) X. ray diffraction (XRD)

The composition of the sample taken from the north is identical to the one taken from the east in accordance with the X-ray diffraction spectrum. It is the same for the sample taken from the south.

According to the spectrums presented above, we note the sample taken from the east is composed of calcite, saponite at 17 Å, and silicon oxide of an alpha crystal structure.

The X-ray diffraction analysis of the soil sample in the western region shows that it is composed mainly of saponite and silicon oxide.

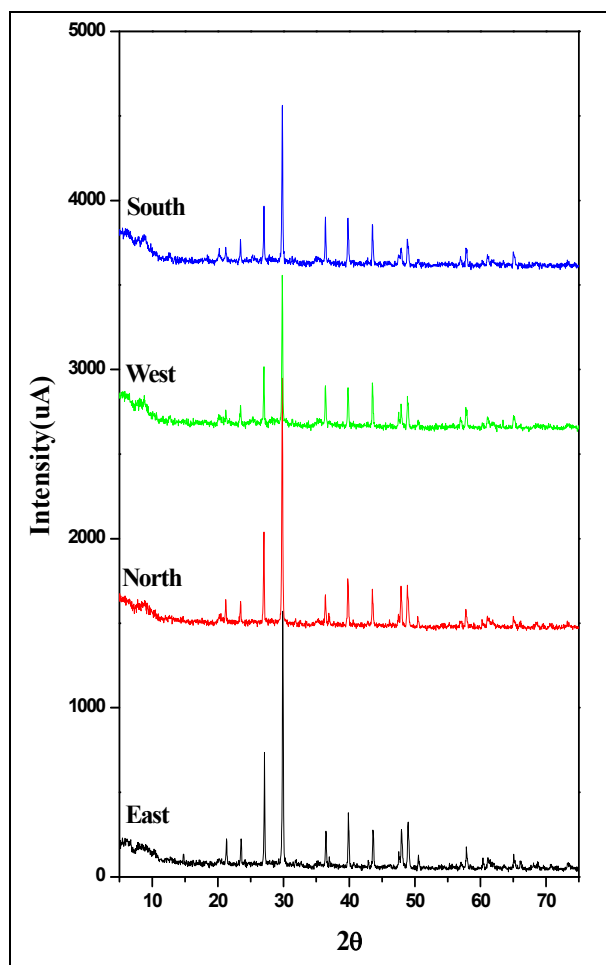


Fig.1 XRD spectra soil samples

These diffractions illustrate what is reported in the bibliography and what we have carried about XRD, focusing on the nature of the clay phases existing in the soil. Therefore, we will say that the smectite, the illite and the kaolinite are present in the soil of that region. We also note that the smectite is relatively high in fact, these two clays are generally the seat of irreversible sorption phenomena, illustrated by the migration of pollutants (cations) in the interfoliar spaces where they are trapped, especially heavy metals. Kaolinite clay which is a simple sheet presents a reversible adsorption at its edges.

2. Adsorption evaluation

(1) Chromium sorption kinetic

Chromium kinetic was studied during 6 hours as shown in figure 2, obtained results showed that Cr removal increase with increasing contact time, attains a value of about 70% for Cr (III) and 20% for Cr (VI) at around 20 minutes and does not change considerably for higher contact times values.

(2) Effect of pH

The effect of pH on the removal of chromium ions was investigated by testing values of pH ranging from 2.0 to 12. Results are shown in Figure 3 where it can be seen that the amount adsorbed for Cr (III) was found to increase with increasing pH. At Higher values of pH, a chromium hydroxide

could be formed as a solid phase precipitate which gives highest amount of adsorbed ions.

The Cr (VI) sorption was observed to increase with increasing pH attains a maximum at around pH 6 and decrease after 6.5 pH values, which exists predominantly as HCrO_4^- in aqueous solution below pH 6. The elimination of chromium in its two forms is low for acidic pH values of soil. The same phenomenon has been clearly observed by Bouzidi et al., and Yasar et al. in soil.

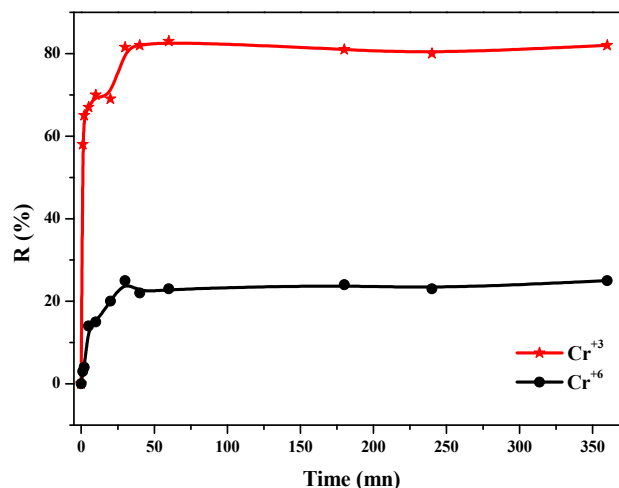


Fig.2 Chromium sorption kinetic

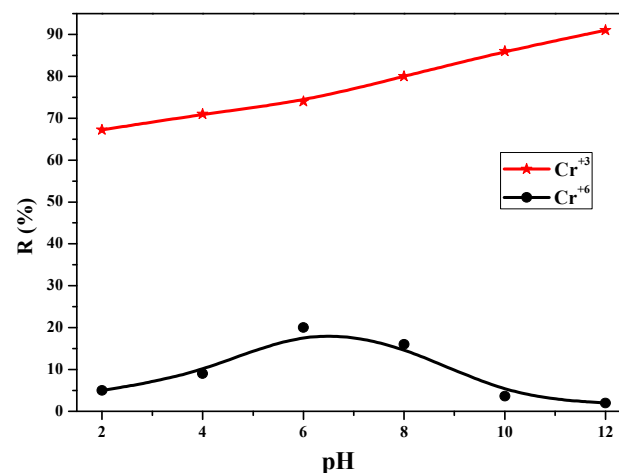


Fig.3 Influence of solution pH on chromium sorption

(3) Effect of adsorbent dose

Adsorbent dose effect on Chromium adsorption was studied by using six doses 1, 2, 10, 16, 20, and 40 g/l.

As shown in Figure 4, the sorption percentage increase with increasing dose. Such performance on the adsorbent may be attributed to the fact that some of the adsorption sites remain unsaturated during the adsorption process. However, the results also showed that the percentage of adsorption increased with increasing concentration of the solid because of the increase in the number of reaction sites available to the metal ions. When all of the available adsorption sites are occupied, increase in the sorbent dose does not change the uptake rate considerably.

(4) Effect of temperature

With temperature varying between 10°C and 40°C, the

chromium adsorption is maximum like shown on Figure 5.

The temperature effect study shows a slight variation of the adsorption rate for the five selected temperatures. Then, the environment temperature changes lightly affect the Chromium retention efficiency in this soil.

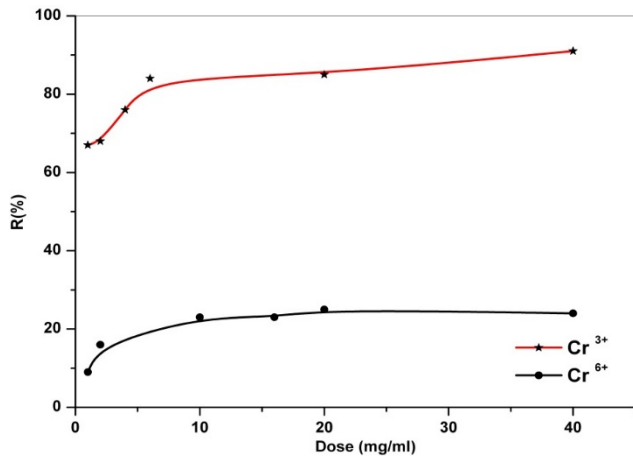


Fig.4 Effect of adsorbent dose

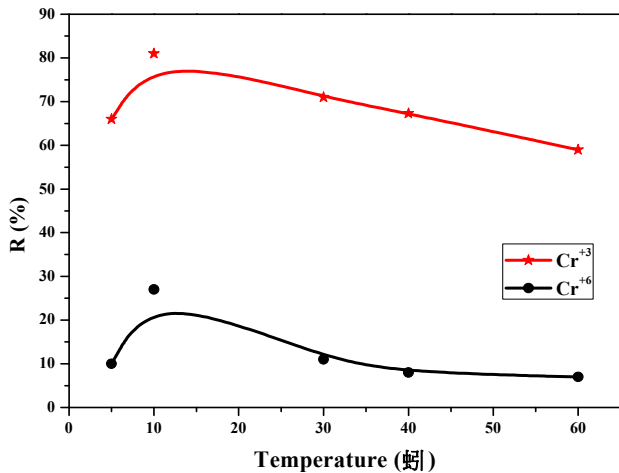


Fig.5 Influence of temperature

(5) Effect of initial concentration

The effect of initial concentration on chromium adsorption is visualized in Figure 6, implied a considerable effect on Cr (VI) removal.

As shown in figure 6, adsorption decreases with the increase of initial concentration for constant pH and adsorbent dose levels.

These results showed that if the initial concentration increases, the available adsorption sites become occupied and consequently the Chromium ions uptake depends closely to the initial concentration.

3. Adsorption isotherm

The adsorption data were fitted using the Freundlich equation, linearized form of this isotherm can be represented in the following:

$$\log q = \log K_F + \frac{1}{n} \log C \quad (2)$$

Where q is the amount of solute adsorbed per unit weight of solid (mol.g⁻¹), K_F and 1/n are Freundlich constants related to sorption capacity and intensity of adsorption, respectively. (Abdelaziz B. et al.,2007).

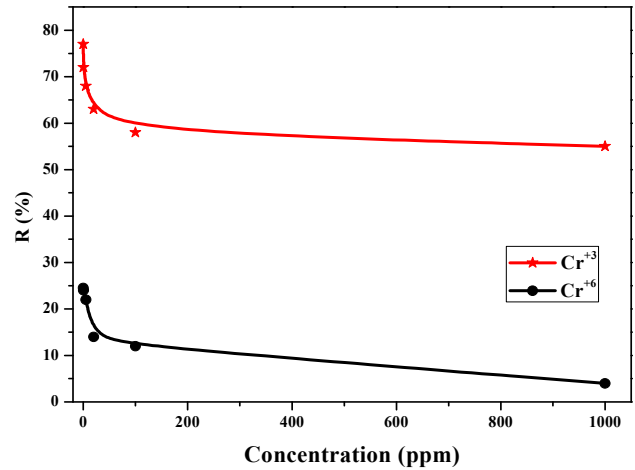


Fig.6 Effect of initial concentration

The validity of isotherm model is tested by comparing the experimental and calculated data in figure 7.

Calculated Freundlich parameters K_F and n are provided in Figure 8 and 9. The Freundlich equation (3) is well suited to describe the equilibrium aqueous phase. Its empirical formula is:

$$q = K_F * C_n^{\frac{1}{n}} \quad (3)$$

(K_F) and (n) are Freundlich constants, indicative of the intensity and adsorption capacity (Mohammad Saied Hosseini et al. 2009). This formula was used in its linear form.

$$1/n = 3,638 ; K_F = 12,884 ; R^2 = 0,956$$

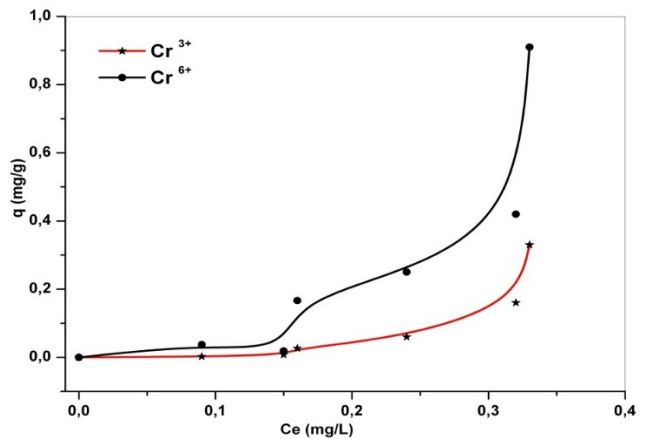


Fig.7 Adsorption isotherms

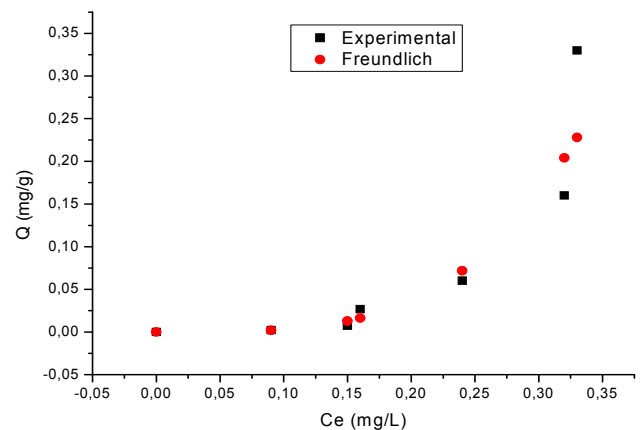


Fig.8 Freundlich isotherm

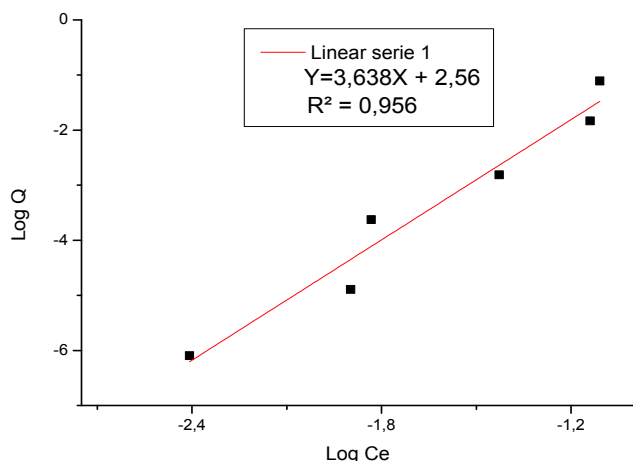


Fig.9 Freundlich isotherm linearization

4. Thermodynamic parameters

The thermodynamic parameters calculate, allow us to show the influence of temperature on the adsorption and to compare the results with those from the literature. These results were obtained from the Van't Hoff law (Yasar A. et al., 2009).

- The distribution coefficient: $K_d = \frac{[Cr]_s}{[Cr]_l}$ (5)

- The enthalpy change: $\Delta H^0 = R \frac{T_1 T_2}{T_2 - T_1} \ln \frac{K_d(T_2)}{K_d(T_1)}$ (KJ/mole) (6)

- The Gibb's free energy change: $\Delta G^0 = -RT \ln K_d$ (KJ/mole) (7)

- The entropy change: $\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}$ (KJ/mole) (8)

The calculated values of ΔH , ΔG and ΔS are given in Table 3.

In this study, the Gibbs free energy change values were found to be negative, which indicated what has encouraged the feasibility and spontaneity of the chromium adsorption (Yasar Aydın A. et al. 2009). The enthalpy change was $-48.254 \text{ kJ.mol}^{-1}$ for Cr (III) and $-26,728 \text{ kJ.mol}^{-1}$ for Cr (VI), which indicated the exothermic nature of adsorption process.

Table 3 Thermodynamic parameters result

[Cr]	K_d (L/g) (5°C / 60°C)	ΔH (KJ/mole)	ΔG (KJ/mole) (5°C / 60°C)	ΔS (KJ/mole K) (5°C / 60°C)
1 ppm (Cr ³⁺)	0,194 / 0,144	-48,254	-3,790 / -5,365	-0,187 / -0,160
1 ppm (Cr ⁶⁺)	0,011 / 0,075	-26,728	-10,423 / -7,171	-0,0586 / - 0,0587

Conclusion

The present study shows us the composition of Ain Oussera soil which can be useful as an adsorbent to immobilize toxic pollutants from water. This immobilization has been tested in this work, and has been found to be very effective for Cr (III), and insufficient for Cr (VI).

In this study, the adsorption of chromium on Ain Oussera soil has been monitored in batch methods. Biosorption efficiency was shown to be affected by various experimental parameters including solution pH, temperature, and initial concentration.

Thermodynamic analysis confirmed the spontaneous and exothermic character of adsorption process. The decrease in randomness of species resulted with negative entropy.

The use of radiotracer technique to evaluate adsorption of soil has enabled us to know the quantity of chromium retained.

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