Evaluation of Cr (VI) retention in soils of varying carbonate in arid land (Djelfa – Algeria).

Avaliação da retenção de Cr (VI) em solos de carbonato variável em terras áridas (Djelfa – Argélia).

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Abstract

Pollution by Chromium (Cr) presents a serious problem that may affect both health and the environment. This study aims to evaluate the contribution of carbonates to chromium sorption/desorption in soils with different concentrations of carbonates in the Djelfa region. The retention study was based on three soils with different total limestone concentrations. A physico-chemical analysis of the soils, followed by a sorption study by modifying some sorption parameters, and finally a comparison of chromium retention. According to the findings, sorption followed pseudo-second-order kinetics with a good regression value R². The activation energies were 12.85 and 16.44 kJ mol⁻¹, implying a physical sorption mechanism. The data agree with the Freundlich model.

Keywords: Sorption. Chromium. Freundlich. Retention. Arid region.

Resumo

A poluição por Cromo (Cr) apresenta um sério problema que pode afetar tanto a saúde quanto o meio ambiente. Este estudo tem como objetivo avaliar a contribuição dos carbonatos na sorção/dessorção de cromo em solos com diferentes concentrações de carbonatos na região de Djelfa. O estudo de retenção foi baseado em três solos com diferentes concentrações de calcário total. Uma análise físico-química dos solos, seguida de um estudo de sorção através da modificação de alguns parâmetros de sorção e, finalmente, uma comparação da retenção de cromo. De acordo com os resultados, a sorção seguiu uma cinética de pseudo-segunda ordem com um bom valor de regressão R². As energias de ativação foram 12.85 e 16.44 kJ mol⁻¹, implicando um mecanismo físico de sorção. Os dados estão de acordo com o modelo Freundlich.

Introduction

Human agricultural, urban, and industrial activities, which are constantly increasing, are at the origin of the contamination of our environment by metallic elements. Many organic molecules can be degraded; however, heavy metals cannot, and their concentrations are steadily increasing in soil, water, and food chains (ZORRIG, 2011).

Chromium is present in the environment mainly in two forms: Cr (III) (more stable) and Cr (VI), which is a powerful oxidant with a high solubility that gives it a high mobility in solution, making it the most toxic (ANDREWS et al., 2011).

Soil contamination by Cr (VI) is caused by a variety of anthropogenic activities, including mining, metallurgy, electroplating, pigment production, tanning, and wood preservation (ZAYED; TERRYL, 2003). Soils behave as reservoirs of pollutants, constituting a potential source of pollution as a result of changes in certain physico-chemical parameters of the environment (pH, redox potential, etc.). As a matter of fact, their leaching may be the reason why they accumulate along food chains and afterwards pose issues with public health (JEAN, 2007). Sorption refers to the displacement of metallic ions from the liquid phase to the solid phase. While desorption is the opposite of sorption, in which the sorbed molecules detach in solution, sorption and desorption are major factors controlling the behavior of metals in soils (NGUYEN, 2010).

Since soils in some areas of the Djelfa department have very high levels of carbonates, it is therefore useful to evaluate their contribution to the retention of metallic pollutants. Carbonates are known for their double role in soils: they partially control the pH by their dissolution balances, and a high content of carbonates makes the soil alkaline (LAMOUROUX, 1972). In addition, the surface of carbonates can be the site of metal retention phenomena, mainly according to two mechanisms: precipitation and/or co-precipitation, and adsorption (BOUZIDI et al., 2010).

This research intends to investigate the hexavalent chromium retention capacity in the soil of the Djelfa region, estimate the impacts of this harmful metal on the local environment and population, and assess the role of carbonates in the retention of the latter by soil particles. Therefore, an experimental approach was adopted for the study of the Cr (VI) ions adsorption on soil particles in the presence of carbonate. This study is interested in the effect of the different physico-chemical parameters, namely the velocity.

Materials and methods

The Djelfa department is located in central Algeria, in the transition zone between the highlands and the Saharan Atlas. Climate data from the Djelfa station (1144 m above sea level) indicate that this pre-desert area has a semi-arid climate, hot and dry in summer and cold in winter. The average annual temperature is around 14.63°C and precipitation is irregular (the average annual precipitation cumulative is approximately 318 mm).

Stratified sampling was done on 31 soil depth samples (0–30 cm) of a limestone region (municipality of Djelfa) (Figure 1). Samples of soil were gathered by an auger, and the samples were collected in plastic bags labeled with the date, site number, and GPS coordinates W 84.

The soil samples were air-dried at room temperature for 48 hours and then sieved under a 2mm sieve. Calcium carbonate (CaCO₃) analysis was performed with Bernard’s Calcimeter on all samples to select 3 samples of high, medium, and low total limestone content.
The physico-chemical analysis and particle size characterization of the treated soil were carried out in accordance with the methods described by Aubert (1978). Additionally, pH (H$_2$O) and pH (KCl) were measured with a pH meter with a volume ratio of 1/5, and electrical conductivity (Ce) was analyzed by a conductivity meter with a volume ratio of 1/5 (NGUYEN, 2010).

![Figure 1 - Location of the Djelfa region on a map of Algeria.](image)

The grain size is based on sieving the sandy part of the soil using sieves of type AFNOR (20 µm, 50µm, 200µm, 2mm) and sedimentation of the fine part. The presence of organic matter is likely to prevent sedimentation; therefore, pre-treatment of samples with hydrogen peroxide was necessary (JUVIGNÉ, 1982; JULIEN; TESSIER, 2021).

Organic matter and carbonates were measured using the Walkely-Black method, which involves the oxidation of organic matter by chromic acid in the presence of sulfuric acid and then a chromic acid titration with a solution of ammonium ferrous sulfate, and the amount of oxidized substance is calculated from the reduced amount of dichromate. A 1.72 multiplication factor was used to convert organic carbon to organic matter (POUDEL, 2020; BOUZIDI et al., 2010). Moreover, Cationic exchange capacity (Metson CEC) was measured in buffered ammonium acetate at pH 7.

The adsorption study was done with 0.5 g of soil and 50 mL of a chromium solution of 1 mg/L. The mixture was agitated at a speed of 350 (rpm) for 1 hour (except for the kinetic study), then centrifuged at 3500 rpm using screw caps and filtered on a 0.45 µm. All experiments were conducted at room temperature (23°C), With the exception of the sorption to temperature experiments that were carried out at 10°C and 90°C.

The equilibrium distribution coefficient (Kd) was calculated using the following relation:

$$Kd = \frac{[CrVI]_s}{[CrVI]_l}$$

With [CrVI]$_s$ is amount of chromium (mg) sorbed by (g) soil and [Cr VI]$_l$ is concentration of chromium in the equilibrium solution (mg/mL). The retention rate was calculated by the equation:

$$R(\%) = \frac{C0 - Cf}{Cf} * 100$$
With C0 is initial chromium concentration (mg/L) and Cf is final chromium concentration (mg/L).

The kinetic was carried out at two temperatures of 23° and 100°C, with agitation durations varying from 1 minute to 10 hours. Further, the pH effect was estimated by the NaOH base and HNO3 acid for an interval of (2 to 12). The effect of agitation speed on sorption was (0 to 500) (min-1). Experiments on the effect of the initial concentration of Cr (VI) on retention ranged from 1 ppm to 1000 ppm.

To study the adsorption mechanisms of heavy metals, several authors have applied models of kinetic analysis of systems (adsorbent-adsorbate) (HACHI, 2007; SU et al., 2019; UME et al., 2022), it is a modeling of soils by linear equations of pseudo-first order and pseudo-second order; these models are determined:

First second order: \( \frac{dq}{dt} = K_1(q_e - q_t) \)

Pseudo second order: \( t = \left( \frac{1}{K_2q_e^2} \right) + \left( \frac{1}{q_e} \right) t \)

With qt: adsorption capacity (mg/g) at time t, qe: equilibrium adsorbed Cr(VI) concentration (mg L-1), k1: first order pseudo speed constant (min-1), K2: -second-order pseudo-speed constant (min-1) and t is contact time.

The thermodynamic equilibrium of adsorption is related to the variation of the Gibbs standard free energy (G0), the variation of the standard enthalpy (H°), and the variation of the standard entropy (S°). The equations were used to determine the different thermodynamic parameters (PATHANIA et al., 2020; BARAD et al., 2022; AL-SAIDI et al., 2021):

\[ \Delta G^0 = -RT \ln(K_d) \]

With \( \Delta G^0 \): variation d’enthalpie libre standard (J mol\(^{-1}\)), R: constant des gaz parfait (8,314 J mol K\(^{-1}\)), T: temperature absolute (K) and Kd is coefficient de distribution:

\[ \ln(K_d) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \]

\[ K_d = \frac{Ci - Ce}{Ce} \times \frac{V}{m} \]

\[ \Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \]

With \( \Delta S^0 \) is entropie standard, \( \Delta H^0 \) is enthalpie standard and \( \Delta G^0 \) is standard Gibbs free energy.

The Freundlich model is based on the amount of Cr (VI) adsorbed at equilibrium \( q_e \) (mg g\(^{-1}\)), and the concentration at equilibrium in solution \( C_e \) (mg L\(^{-1}\)). K is the adsorption coefficient, and n is the Freundlich coefficient.

The Freundlich equation is described as follows: \( \log q = \log KF + 1/n \log C_e \).

The linear correlation coefficient was applied to calculate the relationship between various physicochemical parameters.
Results and discussion

The main characteristics of a soil are its texture, structure, pH, electrical conductivity, and mineral content (REBHI et al., 2016). Our experiments were limited to three soils containing different concentrations of carbonates. The results are presented in Table 1.

Table 1 - Soil physico-chemical parameters.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Soil 1</th>
<th>Soil 2</th>
<th>Soil 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.80</td>
<td>7.73</td>
<td>7.99</td>
</tr>
<tr>
<td>Ce (µs/cm)</td>
<td>187</td>
<td>111</td>
<td>206</td>
</tr>
<tr>
<td>CEC (meston) (cmol+/kg)</td>
<td>10.02</td>
<td>9.89</td>
<td>11.41</td>
</tr>
<tr>
<td>Organic matter %</td>
<td>1.37</td>
<td>1.32</td>
<td>1.29</td>
</tr>
<tr>
<td>Total carbonate %</td>
<td>18.1</td>
<td>9.6</td>
<td>27.46</td>
</tr>
<tr>
<td>Bicarbonates (meq/100g)</td>
<td>2.4</td>
<td>2.6</td>
<td>1.7</td>
</tr>
<tr>
<td>Active limestone %</td>
<td>5.2</td>
<td>3.81</td>
<td>8.59</td>
</tr>
<tr>
<td>Grain-size</td>
<td>Sandy clay</td>
<td>Sandy loam</td>
<td>Sandy loam</td>
</tr>
<tr>
<td>Cr hexavalent (mg/kg)</td>
<td>17.1</td>
<td>14.86</td>
<td>16.32</td>
</tr>
</tbody>
</table>

The evolution of adsorption rate as a function of contact time for the three soils is shown in Figure 2. The kinetics was studied for 10 hours, as shown in Figure 3, and the findings demonstrated that sorption increases with time. For the three soils, equilibrium is reached after 1 hour of agitation, which is called "equilibrium time", and no change is noted after that point. Soil 3 has the maximum sorption, followed by Soil 1, and in the end, Soil 2 has the lowest sorption.

![Figure 2 - Cr (VI) adsorption kinetics in the three soils (C₀=1 mg/L, pH= 6.8, T= 23°C).](image)

The first stage of retention would correspond to the easily accessible fixation sites from the first moment of agitation of the soil suspension, followed by a second longer stage of occupation of the less accessible sites in the ground. The equilibrium is finally reached within one hour of contact, indicating that the adsorption sites are practically saturated (BAYARD; 1997). The application of the pseudo-first-order equation has proven to be incompatible with our data. On the other hand, our results are very well presented by the pseudo-second order equation, with correlation coefficients R² of the curves t/q as a function of t that are all close to unity. The results are presented in Figures 3, 4, and 5.
The results of linear correlation coefficients R2, K2 constants, and adsorbed quantities at equilibrium qe are grouped in Table 2.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Soil 1</th>
<th>Soil 2</th>
<th>Soil 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>T °C</td>
<td>23</td>
<td>60</td>
<td>23°C</td>
</tr>
<tr>
<td>qe (mg g⁻¹)</td>
<td>0,250</td>
<td>0,12</td>
<td>0,182</td>
</tr>
<tr>
<td>K2 (g mg⁻¹ min⁻¹)</td>
<td>1,06</td>
<td>1,69</td>
<td>0,61</td>
</tr>
<tr>
<td>R²</td>
<td>0,9997</td>
<td>0,997</td>
<td>0,9984</td>
</tr>
</tbody>
</table>

The findings demonstrate that the equilibrium concentration corresponds approximately to the kinetic results, and the K2 constant is more important in soil 3 compared to the other two soils, which means that the adsorption rate in this soil is higher. The correlation coefficients are all close to 1, which confirms the correspondence of this model with our results.

In order to assess the impacts of the sorption experimental technique conditions, some parameters have been chosen to evaluate their effects on the sorption of chromium VI on three soils containing different concentrations of carbonates.
The effect of pH on chromium VI adsorption was studied at 23°C, testing pH values from 2 to 12. The results are shown in Figure 6. The data demonstrated that the amount of chromium adsorption increases with an increasing in pH to approximately 4 to 6, which will be the pH of the maximum adsorption (peak), and then there is a decrease in retention in the basic medium from 6 to 12. Also, a strong retention of soil 3 was noted compared to other soils at all pH ranges. The same behavior was reported by (REBHI et al., 2016) in a study evaluating the behavior of chromium III and chromium VI in the soils of Ain Ouessara.

In pH ranges from 2.0 to 6.0, Cr (VI) is mainly found in HCrO$_4$, H$_2$CrO$_4$ and CrO$_4$, with HCrO$_4$ dominating. Hence, greater retention at acidic pH was due to electrostatic attraction between HCrO$_4^-$ and the positively charged absorbent surface. The least adsorption of Cr (V1) in the pH range above 6.0 may be explained by the competition between anionic species such as ions and OH for the same adsorption sites on the surface of the adsorbent (PATHANIA et al., 2020).

The effect of temperature on the adsorption of chromium VI was studied over a temperature range of 5°C to 100°C on the three soils; the results are presented in Figure 7. The results show that the three soils behave in the same way, with a higher retention on soil 3, followed by soil 1, and finally soil 2. Fixation of Cr VI increased with the decrement of the temperature, contrary to high temperatures. This behavior is explained by the improvement of Cr (V) ions mobility with the increment of the solid temperature (SABER-SAMANDARI et al., 2014), which means that our adsorption system is exothermic in nature.

The effect of the initial concentration on the adsorption of Cr (VI) was studied with different concentrations from 1ppm up to 1000 ppm on the three soils; the results are presented in Figure 8. At low concentrations, the metal ions interact with the binding sites and cause maximum adsorption. Because at low concentrations, the ratio of the available surface area to the initial Cr (VI)
concentrations is more important, we note that soil 3 has a strong retention compared to other soils, which may be due to its cationic exchange capacity. However, in the case of increased concentration, metal ions begin to look for free binding sites, and due to a lack of binding sites for complexation, adsorption decreases (TIMBO et al., 2017).

The effect of agitation was studied from 0 (rpm) to 500 (rpm) on the three soils; the results are shown in Figure 9.

The retention capacity increases over the range of 0 to 300 rpm, which is the optimum agitation speed for the three soils. The highest retention was noted in soil 3 in all the ranges from 0 to 500 (rpm) followed by soil 2, and at the end, soil 1. Regarding the range of 0 to 300 rpm, increased sorption could be explained by the fact that soil particles initially aggregate at the bottom of the conical flask, limiting the availability of their active sites for metal inputs. Increased agitation velocity at this stage promotes dispersal of soil particles, leading to more adsorption spaces, to some extent (300 rpm for this study), the increase in agitation velocity begins to exceed electrostatic interaction, the force of the metal ions adsorbed to the surface of the soil particles. From this point on, retention becomes light and desorption begins to occur simultaneously (UME et al., 2022).

In order to evaluate the effect of temperature on the adsorption of Cr (VI) at a concentration of 1 ppm, thermodynamic analysis was applied in a temperature range from 23°C to 60°C. The results of ΔH°, ΔG° and ΔS° are grouped in Table 3.

Based on the ΔH° and ΔG° values, the sorption reactions of Cr (VI) on the three studied soils are exothermic and spontaneous. The value of Kd on soil 3 indicates intense sorption on this soil when compared to soil 2 and Soil 1.
The negative value of $\Delta S^\circ$ expresses a decrease in the disorder of the system after adsorption, as a result of the adsorbate/adsorbent fixation that leads to a decrease in the degree of freedom of the system (MOHAMMED-AZIZI; BOUFATIT, 2018).

Table 3 - Thermodynamic parameters of Cr (VI) sorption.

<table>
<thead>
<tr>
<th>T °C</th>
<th>Soil 1</th>
<th>Soil 2</th>
<th>Soil 3</th>
<th>Soil 4</th>
<th>Soil 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_d (ml g(^{-1}))</td>
<td>42.57</td>
<td>21.43</td>
<td>26.98</td>
<td>14.54</td>
<td>47.23</td>
</tr>
<tr>
<td>$\Delta H^\circ$ (kJ mol(^{-1}))</td>
<td>-15.23</td>
<td>-14.07</td>
<td>-15.54</td>
<td>-15.45</td>
<td>-15.45</td>
</tr>
<tr>
<td>$\Delta G^\circ$ (kJ mol(^{-1}))</td>
<td>-9.23</td>
<td>-8.48</td>
<td>-8.11</td>
<td>-7.4</td>
<td>-9.49</td>
</tr>
<tr>
<td>$\Delta S^\circ$ (kJ mol(^{-1}) K(^{-1}))</td>
<td>-0.0202</td>
<td>-0.0202</td>
<td>-0.0201</td>
<td>-0.0201</td>
<td>-0.0204</td>
</tr>
</tbody>
</table>

The Freundlich model is among the models that many researchers most frequently employ in adsorption isotherm modeling (BELAID; KACHA, 2011; FAYOUD et al., 2015; TIMBO et al., 2017; IFGUISS et al., 2022); it is established for heterogeneous surfaces, while Langmuir is established for single-ply adsorption on homogeneous surfaces (ANTONIADIS et al., 2018). We noted that the correlation coefficients are all close to the unit; the highest K-coefficient corresponds to the most important adsorption in our study (Figure 10), soil 3. 1/n is an exponent whose value is less than (JAMET, 1988).

According to the classification of the International Union of Pure and Applied Chemistry (IUPAC), our results could be classified in class II (Figure 10), which is the class most commonly encountered. It is a multilayer adsorption on open surfaces (BABAA, 2004).

We opted for a sequential extraction of the carbonate phase of soils to see the carbonate-free retention rate at an equilibrium time of 1 h and 23°C and compare it to the total retention of whole soils under the same conditions (Table 4). The extraction was done by mixing sodium acetate and acetic acid (25% each) at pH 4 and ambient temperature; this is the most suitable extraction for the attack of carbonates only (BELAID, KACHA, 2011). This comparison will extract the role of carbonates in the retention of Cr (VI) in our soil samples.
Table 4 - Freundlich model parameters.

<table>
<thead>
<tr>
<th>Freundlich Parameters</th>
<th>n</th>
<th>K</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil 1</td>
<td>0.262</td>
<td>4.57</td>
<td>0.9517</td>
</tr>
<tr>
<td>Soil 2</td>
<td>0.33</td>
<td>3.45</td>
<td>0.9699</td>
</tr>
<tr>
<td>Soil 3</td>
<td>0.23</td>
<td>5.37</td>
<td>0.9681</td>
</tr>
</tbody>
</table>

With the exception of Soil 1, which has a higher percentage of clay than other soils, our samples are not significantly different from one another when it comes to some essential parameters that affect the retention of heavy metals, such as CEC and organic matter.

The analyses in Table 5 demonstrate that the higher the rate of carbonates in the soil, the higher the retention of Cr (VI), with soil 3 having the highest retention of Cr (VI) at 17.65% with a rate of 27.46 carbonates, followed by soil 1 with a retention rate of 10.83% and 18.1 carbonates, while soil 2 presented the lowest carbonate content at 9.6% and a lower retention of Cr (VI) at 6.96%.

Table 5- Comparison of Cr (VI) retention on whole soil and soil after carbonate extraction.

<table>
<thead>
<tr>
<th>Retention of Cr (VI)</th>
<th>Soil retention with carbonate extraction</th>
<th>Cr (VI) retention on carbonates only</th>
<th>Carbonate levels %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole soil %</td>
<td>Soil %</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Soil 1</td>
<td>29.86</td>
<td>19.03</td>
<td>10.83</td>
</tr>
<tr>
<td>Soil 2</td>
<td>21.77</td>
<td>14.81</td>
<td>6.96</td>
</tr>
<tr>
<td>Soil 3</td>
<td>32.8</td>
<td>15.15</td>
<td>17.65</td>
</tr>
</tbody>
</table>

It is noted that other differences in chromium retention rates may be due to the distribution of chromium over several fractions in the soil. As an example, soil 1, which has the highest proportion of clay, has the highest retention without carbonates, knowing that clay minerals have physico-chemical characteristics that give them a high adsorption capacity (IFGUIIS et al., 2022).

Finally, it was concluded that carbonates play a role in the retention of Cr (VI), and the calcareous soils, specifically calcite, have an affinity for the adsorption of heavy metals on their surface (ZACHARA et al., 1991). This is consistent with previous studies that confirmed the affinity of Cr (VI) with carbonates (GUREN et al., 2020; ZHANG; LIU, 2022).

**Conclusion**

In the studied soils, the retention of Cr (VI) chromium is more remarkable than the soil's carbonate richness is high. The soil sorption parameters such as pH, temperature, frequency of agitation, initial concentration did not influence chromium retention by carbonates. Still the soil richest in carbonate has the highest retention values in Cr (VI) respectively soil 3, soil 1 and soil 2. The test with pure carbonates compared with carbonated soils confirms that the retention of chromium Cr (VI) is proportional only in the presence of carbonates.

**Conflicts of interest**

There were no conflicts of interest for the authors.

**Authors’ contribution**

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Amira Kessab – execution of the experiment and writing; Kamel Guimer – field prospecting and execution of the experiment; Mohamed Hachi – execution of the experiment; Belkacem Boumaraf – work corrections; Fateh Mimeche – corrections and revision of the text.

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