Modelling of the Cr(VI) transport in typical soils of the North of Portugal

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A B S T R A C T

Adsorption of hexavalent chromium [Cr(VI)] onto a loamy sand soil was studied using batch and steady flow tests with contaminant solutions at pH 2, 5 and 7. In all the cases the adsorption of Cr(VI) decreased with increasing pH. The hexavalent chromium speciation and its presence as different oxyanions, according to the solution pH, were the main variables affecting the adsorption process. The influence of the ratio soil/solution concentration was also studied in flow systems at pH 2. Chromium retention increased with the increasing of its concentration in the influent solution.

A two-site adsorption model was fitted to the breakthrough curves of hexavalent chromium solutions in order to estimate the Freundlich (k_f) and Langmuir (S_{max}) adsorption parameters, using CXTFIT code.

These values were compared to those determined by batch tests and it was concluded that batch tests tended to underestimate these parameters. Nevertheless, they followed the same trend as the parameters determined in opened system, even when the pH of the initial solution was modified.

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1. Introduction

Soil is a key element in human survival and can be described by various definitions according to its main utility. Nowadays, it is accepted that soil is a very complex heterogeneous medium which consists of solid phases containing minerals and organic matter, and soil solution, defined as the fluid phase where soil reactions, transport and adsorption occur [1]. The understanding of the contamination processes of this particular soil herein presented is fundamental for the recovery of extensive polluted areas, as this type of loamy sand soil is very common in industrialized regions.

Heavy metals are natural constituents of rocks and soils in concentrations that do not represent any risk to animal or plants. Some anthropogenic activities like the spreading of sewage sludge or fertilizers, the discharge of domestic and industrial effluents in land and also the atmospheric disposal, promoted the augmentation of these metals concentrations to toxic levels [2]. For example, electroplating, tannery and galvanization activities are important sources of chromium contamination [3].

The high aqueous solubility of hexavalent chromium is a public health concern since the anionic forms, chromate and dichromate, are considered hazardous and are highly mobile in soil and water environment. Exposure to Cr(VI) has been associated with allergic contact dermatitis in sensitive individuals and bronchial carcinomas and, at high concentrations, with skin ulcerations and perforation of the nasal septum [4–6].

Heavy metals sorption onto soils is highly affected by soil solution pH [7,8], but sorption studies are usually focused on the soil pH. However, spills near industries or direct discharge of high concentrated effluents occur in uncontrolled conditions of pH and a rapid intervention is mandatory. Therefore this piece of research intends to complement the knowledge about hexavalent chromium sorption onto soil by describing this process with three highly concentrated influents and at three different pH values.

Usually, batch experiments are used to obtain equilibrium adsorption isotherms and to evaluate the sorption capacity of soils for given metals present in fluid phases. Despite the importance of this information, those experiments present certain limitations because batch equilibrium models do not give any information about hydrodynamic parameters [9]. Thus, an accurate prediction of transport and adsorption of contaminants in soils can be obtained through flow experiments.

Specifically in this study, the adsorption of hexavalent chromium present in contaminant solutions with pH of 2, 5 and 7 was evaluated by batch and by flow methods. In order to do this, CXTFIT code [10] was used to estimate the parameters of the two-site non-equilibrium convection-dispersion equation (TSM/CDE) by adjusting the model to the experimental breakthrough curves (BTC). The batch equilibrium parameters were determined by the adjustment of Freundlich and Langmuir equations. In general, adsorption of chromium was higher in flow experiments and at low pH values. Consequently, to study the effect of the ratio soil/solution concentration, flow experiments with influents with 50, 75 and 100 mg.L⁻¹ of hexavalent chromium at pH 2 were performed. Concentrations were chosen in the range used to obtain the isotherm curves. Reten-
Chemical and physical properties of soil sample from Póvoa de Varzim, Portugal.

Table 1

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Texture (%)</td>
<td></td>
</tr>
<tr>
<td>Clay</td>
<td>2.58</td>
</tr>
<tr>
<td>Silt</td>
<td>23.06</td>
</tr>
<tr>
<td>Sand</td>
<td>74.36</td>
</tr>
<tr>
<td>pH (H2O)</td>
<td>5.9</td>
</tr>
<tr>
<td>Cationic exchange capacity (cmolc kg(^{-1}))</td>
<td>12.52</td>
</tr>
<tr>
<td>Organic matter content (%)</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Metal concentrations

| [Fe] (mg kg\(^{-1}\)) | 323   |
| [Mn] (mg kg\(^{-1}\))  | 14    |
| [Cr] (mg kg\(^{-1}\))  | 42.5  |

Carbonate content

| [CaCO3\(_3\)] (mg kg\(^{-1}\)) | 0.0    |

Apparent density\(^a\)

| \(\rho_s\) (kg m\(^{-3}\)) | 1320   |

\(^a\) Disturbed sample.

Table 2

Experimental conditions of flow experiments.

<table>
<thead>
<tr>
<th>Influent pH</th>
<th>2</th>
<th>5</th>
<th>7</th>
<th>2</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(c_0) (mg L(^{-1}))(^a)</td>
<td>48.6</td>
<td>48.6</td>
<td>44.7</td>
<td>80.8</td>
<td>110</td>
</tr>
<tr>
<td>(\theta) (m(^3) m(^{-1}))(^b)</td>
<td>0.42</td>
<td>0.41</td>
<td>0.45</td>
<td>0.39</td>
<td>0.38</td>
</tr>
<tr>
<td>(L) (cm(^3))</td>
<td>15.3</td>
<td>15.0</td>
<td>14.1</td>
<td>15.3</td>
<td>15.5</td>
</tr>
<tr>
<td>(q) (cm h(^{-1}))(^d)</td>
<td>20</td>
<td>20</td>
<td>18</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>(\rho_b) (kg m(^{-3}))(^e)</td>
<td>1300</td>
<td>1243</td>
<td>1322</td>
<td>1324</td>
<td>1293</td>
</tr>
</tbody>
</table>

\(^a\) Influent concentration.  
\(^b\) Water content.  
\(^c\) Soil bed length.  
\(^d\) Flux velocity.  
\(^e\) Soil bulk density.

The sorption process was about three times higher for the concentration of 100 mg L\(^{-1}\). Functional groups present in the soil that may have some role in the sorption process were evaluated by FTIR.

2. Material and methods

2.1. Soil characterization

A sample of a loamy sand soil collected in a zone of great agricultural activity at Póvoa de Varzim, Oporto, Portugal (41° 25' 15.58" N and 8° 45' 58.27" O), was used in this study. The soil was collected from the O-horizon and from the A-horizon (0–30 cm) and stored in plastic bags. The mixed sample was passed through a 2 mm stainless steel sieve after being air dried. Particle size distribution was determined in a laser granulometer (Beckman-Coulter LS230). Carbonate content was determined with a Scheibler calcimeter (Scheibler). Cationic exchange capacity was quantified using ammonium acetate at pH 7 [11]. The metal concentrations in soil were determined by flame atomic absorption spectrometry (FAAS). Freundlich and Langmuir isotherm models were fitted to the equilibrium data.

Kinetic assays were very similar. However, they were only performed for Cr(VI) concentration equal to 50 mg L\(^{-1}\), for different contact times—4, 16, 48, 92, 142, 192 and 240 h. The pseudo-first order equation was adjusted to kinetic data in order to determine the first order kinetic rate coefficient, \(\alpha\) (h\(^{-1}\)).

2.3. Continuous flow experiments

All column experiments were conducted in duplicate, in two columns of acrylic (25 cm × 3.2 cm). The air-dried soil samples were packed into the column under vibration and progressively saturated with distilled water to prevent air entrapment. The influent Cr(VI) solutions of 50, 75 and 100 mg L\(^{-1}\) at pH 2, 5 or 7, were introduced from the bottom of the column to ensure saturation flow conditions [15]. Effluent samples were collected for about 80 h in 50 mL propylene tubes at the top of the column. After the pH measurement, the samples were acidified (2% HNO\(_3\)) and stored for posterior analyses by FAAS. Breakthrough curves were fitted by two-site adsorption model (TSM) using CXTFIT code [10]. The Freundlich adsorption parameter, \(k_F\), and the Langmuir adsorption parameter, \(S_{\text{max}}\), were obtained from the fitting. Table 2 summarises the experimental conditions for all flow experiments.

Previously to the flow tests with the hexavalent chromium, a flow experiment using CaCl\(_2\) (0.01 M) as a tracer was also conducted to evaluate independently the average pore water velocity \((\nu)\) and the dispersion coefficient \((D)\), by measuring the conductivity of 25 mL samples and fitting the breakthrough curve with CXTFIT code to the equilibrium convection-dispersion equation (CDE). These two parameters were kept constant for the fitting of Cr(VI) breakthrough curves.

At the end of the experiment, a homogeneous sample of each column was digested [12] and analyzed by AAS. Samples were also characterized with transmission FTIR (FTIR BOMEM MB 104) on KBr pressed pellets (100 mg of KBr and 1 mg of sample). Background correction for atmospheric air was used for each spectrum. Spec-

Table 3

Freundlich, Langmuir and pseudo-first order parameters of batch experiments at pH 2.

<table>
<thead>
<tr>
<th>Influent pH</th>
<th>2</th>
<th>5</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich isotherm parameters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(k_F)</td>
<td>62</td>
<td>58</td>
<td>28</td>
</tr>
<tr>
<td>(n)</td>
<td>0.36</td>
<td>0.34</td>
<td>0.47</td>
</tr>
<tr>
<td>(r^2)</td>
<td>0.965</td>
<td>0.584</td>
<td>0.715</td>
</tr>
<tr>
<td>Langmuir isotherm parameters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(S_{\text{max}})</td>
<td>452</td>
<td>389</td>
<td>431</td>
</tr>
<tr>
<td>(b)</td>
<td>0.03</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>(r^2)</td>
<td>0.930</td>
<td>0.509</td>
<td>0.650</td>
</tr>
<tr>
<td>Pseudo-first order equation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha)</td>
<td>0.003</td>
<td>0.003</td>
<td>0.002</td>
</tr>
<tr>
<td>(r^2)</td>
<td>0.757</td>
<td>0.929</td>
<td>0.882</td>
</tr>
</tbody>
</table>
tra were obtained in the range 500–4000 wavenumbers, with a minimum of 10 scans and a resolution of 4 cm⁻¹.

### 2.4. Evaluation of batch sorption parameters

For the evaluation of the equilibrium data two isotherm models were used:

**Freundlich equation:**

\[ S_e = k_F C^\theta_e \]  

**Langmuir equation:**

\[ S_e = \frac{S_{max} C_e}{1 + b C_e} \]  

where \( S_e \) is the mass of metal adsorbed per mass of soil (mg kg⁻¹), in equilibrium with the concentration of the metal in the liquid phase, \( C_e \) (mg L⁻¹), \( k_F \) is the Freundlich constant (L¹⁽¹⁾⁻¹⁽¹⁾⁻¹ mg⁻¹), \( \theta \) is the Freundlich exponent, \( S_{max} \) is the maximum adsorption of the metal (mg kg⁻¹) and \( b \) is the Langmuir equilibrium constant (L mg⁻¹) [16, 17, 18].

To evaluate the adsorption kinetics, the pseudo-first order equation was adjusted to the kinetics data sets (\( S_t \) vs \( t \)) of the three pH values:

\[ S_t = S_0 [1 - \exp(\alpha t)] \]  

where \( S_0 \) and \( S_t \) are the amount of metal sorbed in soil (mg kg⁻¹) at the equilibrium and at the time \( t \) (h), respectively, and \( \alpha \) is the first order kinetic rate coefficient (h⁻¹) [19].

### 2.5. Evaluation of transport and sorption parameters by the convection-dispersion equation

#### 2.5.1. Two-site non-equilibrium adsorption

Heavy metals can be sorbed by different constituents of soils, like minerals or organic matter, at different rates and intensities while being transported through a packed column. Therefore, the two-site adsorption model assumes that the adsorption can occur instantaneously (equilibrium) or be time dependent (first-order kinetic) [20, 21].

If there is no production or degradation of the solute, the two-site non-equilibrium model can be written as:

\[ \frac{\partial C}{\partial t} + \left( \frac{\rho}{\theta} \right) \left( \frac{\partial S_1}{\partial t} + \frac{\partial S_2}{\partial t} \right) = D \frac{\partial^2 C}{\partial x^2} - \nu \frac{\partial C}{\partial x} \]  

where \( C \) is the flux average or resident concentration (mg L⁻¹), \( \rho \) is the soil bulk density (kg m⁻³), \( \theta \) is the volumetric water content (m³ m⁻³), \( t \) is time (h), \( S_1 \) is the solid phase concentration on equilibrium sites (mg kg⁻¹), \( S_2 \) is the solid phase concentration on kinetic non-equilibrium sites (mg kg⁻¹), \( D \) is the dispersion coefficient (cm² h⁻¹), \( x \) is distance (cm) and \( \nu \) is the average pore water velocity (cm h⁻¹).

The non-equilibrium adsorption process is defined by:

\[ \frac{\partial S_2}{\partial t} = \alpha [(1 - F) f(C) - S_2] \]  

where \( F \) represents the fraction of the sites available for instantaneous adsorption and at equilibrium adsorption on both sites is described by a nonlinear isotherm [9, 21]:

\[ S_1 = F f(C) \]  

and

\[ S_{2e} = (1 - F) f(C) \]  

The CXTFIT code was used in this work under flux-type boundary conditions as described by Kreft [22]. This code adjusts the following dimensionless form of the two-site non-equilibrium model to the breakthrough curves in order to estimate the transport and sorption parameters:

\[ \beta R \frac{\partial C_1}{\partial t} = \left( \frac{1}{P} \right) \left( \frac{\partial^2 C_1}{\partial X^2} - \frac{\partial C_1}{\partial X} - \alpha (C_1 - C_2) \right) \]  

\[ (1 - \beta) R \frac{\partial C_2}{\partial t} = \alpha (C_1 - C_2) \]  

where the dimensionless parameters are defined as follows:

\[ C_1 = \frac{C}{C_0} \]  

\[ C_2 = \frac{S_2}{[(1 - F) k_F C_0]} \]  

\[ T = \frac{\nu t}{L} \]  

\[ X = \frac{x}{L} \]  

\[ R = 1 + \frac{\rho k_1}{\theta} \]  

\[ P = \frac{\nu L}{D} \]  

\[ \beta = \frac{(\theta + F \rho k_1)}{(\theta + \rho k_1)} \]  

\[ \omega = \frac{\alpha (1 - F) R L}{\nu} \]  

### Table 4

<table>
<thead>
<tr>
<th>C₀ (mg L⁻¹)</th>
<th>Influent pH</th>
<th>Physical parameters (R = 1)</th>
<th>Two-site adsorption model parameters</th>
<th>Freundlich</th>
<th>Langmuir</th>
<th>Pseudo-first order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>D</td>
<td>v</td>
<td>r²</td>
<td>R</td>
<td>β</td>
</tr>
<tr>
<td>47.3</td>
<td>5</td>
<td>15</td>
<td>16</td>
<td>0.992</td>
<td>27</td>
<td>0.05</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>49</td>
<td>22</td>
<td>0.994</td>
<td>23</td>
<td>0.04</td>
</tr>
<tr>
<td>7</td>
<td>80.8</td>
<td>32</td>
<td>18</td>
<td>0.993</td>
<td>2.2</td>
<td>0.46</td>
</tr>
<tr>
<td>110</td>
<td>2</td>
<td>15</td>
<td>16</td>
<td>0.986</td>
<td>30</td>
<td>0.03</td>
</tr>
</tbody>
</table>

TSM model parameters fitted to the BTC of the hexavalent chromium influents and isotherm models parameters.
In the above equation $C_1$ and $C_2$ are the relative concentration of chromium in equilibrium (1) and kinetic (2) sites scales to the input concentration $C_0$; $P$ is the Peclet number; $T$ is the dimensionless time; $L$ is column length; $R$ is the retardation factor; $\beta$ is a partitioning coefficient, $\omega$ is a dimensionless mass transfer coefficient and $k_L$ is the linear isotherm sorption coefficient [10,23]. To calculate the nonlinear adsorption parameters of Freundlich and Langmuir isotherm models it was assumed that [24]:

$$k_L = k_F n C^{n-1}$$

or

$$k_L = \frac{b S_{\text{max}}}{(1 + b C)^2}$$

Transport of reactive solutes in soils may also be affected by physical non-equilibrium processes. To discard this hypothesis, a saturated flow regime was kept through a homogeneous soil bed [10,21].

### 2.5.2 Equilibrium model parameters

For nonreactive tracers, like the CaCl$_2$ used to characterize the hydraulic conditions in this study, the CDE can be reduced to [21,25]:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x}$$

The flow regime can then be characterized by applying the tracer Cl$^-$ at the same flow rate as the contaminant influent.
coefficients obtained for the columns used in the flow tests at model was always very poor (0.0 < 
cluded that raising the liquid phase pH from 2 to 5 resulted in a decrease in adsorption. However, when the pH was elevated to 7 the decrease in adsorption is considerable.

A decrease in the pH of the liquid phase results in the fast protonation of the soil surface due to the low acid buffering capacity of the soil compared with a simpler soil, kaolin (Fig. 1). Hexavalent chromium form exists mainly as oxyanions and these can be adsorbed in the positively charged sites. So, for lower pH values adsorption is higher [4,14].

The Langmuir sorption parameter, S_max, is quite constant for the three batch equilibrium data sets (Table 3). This would be expected since the tested soil was the same in all the experiments, and this parameter measures the maximum adsorption capacity of the adsorbent [26,27]. Like the Freundlich parameter, n, also the Langmuir parameter, b, remained practically constant, as expected since these parameters are constants of the models.

It should be noticed that both models described well the adsorption for the low pH value. The non-saturation of all adsorption sites may be the explanation of this scenario [28].

The pseudo-first order equation fits quite well the Cr(VI) adsorption kinetics for all the tested pH values. Covelo et al. [29] also obtained good fitting of this model for a quite similar soil. The higher values of the coefficient rate, α, show that adsorption occur rapidly at lower pH values, due to the protonation of soil surface as referred previously.

3. Flow experiments

3.2. Tracer experiments

The BTC curve obtained for the nonreactive tracer (CaCl₂) was fitted by Eq. (14), using the CXTFIT code, Table 4. The dispersion coefficients obtained for the columns used in the flow tests at pH 2 were smaller than the other two, indicating that the axial dispersion was lower in these columns, probably due to unsaturated conditions [10]. However, the values of the pore water velocity, v, are quite similar to the values of the experimental flux, q (Table 2). This could be indicative that all the water is mobile.

3.2.2. Two-site non-equilibrium model

The curves of the adjusted two-site adsorption model can be observed in Fig. 2 for all the influent pH values. A good fit was obtained for all pH values and concentrations, denoting that this model describes well the transport and adsorption processes (Table 4). A prior analysis of these results shows that sorption parameters, K_F and S_max, determined for the lower pH values and concentrations are similar. However, these values are about four/five times higher than those observed for the batch equilibrium data. According to Miller [30] this appears to be due to the removal of competitive anions in flow systems effluent. To determine these parameters the other two constants, n and b, were kept constant, since they did not vary significantly for batch tests experiments.

3.2.3. Effects of initial solution pH

A decrease in the retardation factor (Table 4) and in the total mass of metal retained per mass of soil (Fig. 3) is noticed when the influent pH is increased. The protonation of soil surface may also occur in the flow tests. However, also the reduction, at low pH values, of hexavalent chromium to the trivalent form, that is less mobile and strongly adsorbed, may explain this behavior [5].

Despite of the above considerations, a notable decrease of the retardation factor, R, and of the sorption parameters is observed when the pH is raised to 7, a value very close to the pKₐ2 (6.49) of the chromic acid (HCrO₄⁻/CrO₄²⁻) [31] The adsorption of anions of polyprotic conjugate acids decreases with increased pH, with a more pronounced decrease above the pKₐ2, explaining the drastic decrease of the retardation factor for pH 7. For pH values higher than pKₐ2, the predominant species is CrO₄²⁻, which can be adsorbed by formation of inner sphere bidentate complexes, releasing two OH⁻ anions from the surface. This factor, coupled with the higher concentration of OH⁻ at higher pH values that compete with the CrO₄²⁻ for the positive charged sites may explain the large decrease of the retardation factor [26,32]. On the other hand, at low pH values HCrO₄⁻ can be easily adsorbed at positive charged sites without competition or releasing only one OH⁻ anion [27].

At pH 7, values of relative concentration higher than 1 were achieved, which are related to the under estimation of the isotherm models sorption parameters and the upper estimation of first-order rate coefficient presented at Table 4. The desorption of chromium oxyanions due to the elevated pH of the influent may explain the unexpected values of relative concentration [27].

3.2.4. Effects of soil/solution ratio

The analysis of Fig. 2e reveals very low relative concentrations in the effluents of the soil bed contaminated with the most concentrated solution. In fact, the retardation factor is about three times higher than those found for the two lower concentrations. Du and Hayashi [33] reported similar results with cadmium (Cd²⁺), verifying that adsorption increased with the increase in soil/solution ratio. Aksu [34] also found the same behavior in the biosorption of Ni²⁺, and attributed the phenomenon to the diminution of the mass transfer resistance between the aqueous and solid phase. In fact, the mass transfer coefficient, u₀, also increased (Table 4), maybe due to diffusivity of the chromium adsorbed onto clay minerals and metal oxides into the lattice structures of these minerals. Then, hexavalent chromium become strongly fixed into the pore spaces, not
Fig. 4. Infrared spectra of soil bed samples before and after flow experiments with chromium influents with 50 mg L\(^{-1}\), at pH 2, 5 and 7. Spectra of soil beds contaminated with chromium influents with 50, 75 and 100 mg L\(^{-1}\), at pH 2.

Fig. 4 shows the FTIR transmittance spectra of the soil samples of the columns bed after the sorption tests and of an uncontaminated soil sample.

The main evidence of these spectra is the similarity between the spectrum of the sample contaminated with the solution of 50 mg L\(^{-1}\) at pH 7 and the uncontaminated sample. In fact, like the Fig. 3 demonstrates, the quantity of hexavalent chromium adsorbed at this pH was very small.

The kaolinitic OH vibrations are represented mainly by two bands at 3695 and 3620 cm\(^{-1}\). This band clearly decreases for the lower pH values when the adsorption is higher, denoting that the oxyanions may be adsorbed at the edge of this clay mineral [37]. The water molecule is unstable and can be exchanged by an inorganic anion, what may explain the decrease of the band correspondent to the OH bend of adsorbed water (\(\sim\)1635 cm\(^{-1}\)), for pH 2 and 5 [27,38].

There are singly coordinated OH groups on the edges of clay mineral. They can be coordinated for example with Al\(^{3+}\) forming the aluminol edge groups, whose characteristic band (\(\sim\)694 cm\(^{-1}\)) decreases in the spectra of the contaminated samples, because these groups can dissociate and bind protons. Thus it is evident the intervention of these groups in the adsorption of the chromium oxyanions [27,37].

Specifically, in the spectra of the soil sample contaminated with the influents at pH 2 (Fig. 4b) it is evident the appearance of two peaks around 3530 and 3445 cm\(^{-1}\) in the samples contaminated with the most concentrated influents. These peaks are located in a region characterized by intense OH absorption (3300–3800 cm\(^{-1}\)). This means that this surface functional group, found also in metal oxides, has an important function in chromium adsorption. In fact some metal oxides are known to great adsorbed metals, because their hydroxys groups can be protonated and complex metal anions [39].

In both spectra, there are well resolved peaks around 2850 and 2922 cm\(^{-1}\) that tend to overlap for the contaminated samples. These bands result from the extensive transformation of simpler aliphatic moieties from the mineral wax, for example. Also the small peak around 1380 cm\(^{-1}\) is attributed to CH deformations from aliphatic structures [40–42].

Since the soil was collected in a zone of agricultural activity it would be expected the presence of primary amine groups characteristic from fertilizers and sludges. That was corroborated by a sharp peak at 774 cm\(^{-1}\), in the spectrum of the uncontaminated sample, which almost overlapped in the spectra of the contaminated ones. This may happen due to the reaction/sorption of the hexavalent chromium with these compounds.

4. Conclusions

This study was designed to evaluate the influence of a hexavalent chromium solution pH and concentration in the transport and fate of this heavy metal in typical soils of the North of Portugal, very similar to many found in industrialized areas all over the planet. The increase in the contaminant solution pH resulted in the decrease of the adsorption of Cr(VI) and therefore in its higher mobility. Adsorption was markedly dependent on chromium speciation and on the type of oxyanions present at each solution pH. It was also reported the increase of the hexavalent chromium retention with the influent concentration increasing. Adsorption can be followed by absorption due to the concentration gradient. The presence of surface groups that are usually responsible for these sorption phenomena was confirmed by FTIR.

It was also showed that the two-site adsorption model describes quite well the mobility of hexavalent chromium in soils. Nevertheless, since at high pH values desorption of the studied heavy
metal may occur, this dynamic model seems to be inappropriate to describe the transport of Cr(VI) in these situations.

It was proved that batch adsorption parameters are frequently underestimated, but they can be used to compare the adsorption process at different scenarios, since they vary in accordance with those parameters determined from flow tests.

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