SOILS CONTAMINATED WITH HEXAVALENT CHROMIUM - SORPTION, MIGRATION AND REMEDIATION

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Soil, hexavalent chromium, sorption, migration, remediation.

ABSTRACT
The interest in environmental soil science has been growing in the last years due to the continuous degradation of this major natural resource. In this work, a representative sample of a typical loamy sand soil was collected in Porto, Portugal, in a zone of intensive agriculture activity. This soil was used for a series of tests concerning the adsorption, transport and fate of hexavalent chromium. The adsorption equilibrium and sorption kinetics were evaluated through the fitting of several mathematical models to the batch and flow experimental data. Generally, the results revealed a high retention of chromium for low pH values. Then, the application of a novel technique, comprising an electrochemical and a biological component was tested in the cleaning of soil contaminated with hexavalent chromium. Removal values of 60% and 79% were obtained with zeolite and activated carbon biobarriers, respectively. This work is integrated in a PhD thesis that pretends to be a tool for policies and decision makers, through the transport and fate studies, but also for the industrial sector aiming the development and application of the cleaning techniques explored.

INTRODUCTION
Soil is a key element in human survival and can be described by various definitions. 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 (Alloway 1995).

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 (Banks 2006; Proctor 1998). Therefore, Cr(VI) was the targeted metal of this study.

Sorption and Migration
Heavy metals sorption onto soils is highly affected by soil solution pH (Elzahabi 2001), 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 differently concentrated influents with three different pH values.

Electroremediation/Biobarriers
The application of electrokinetic cells promotes the electromigration of the Cr(VI) oxyanions towards the anode chamber, when a low voltage gradient is applied to the EK cell (Sanjay 2003). On the other hand, experiments using A. viscosus supported either in zeolites or activated carbon (GAC), showed great efficiency in the treatment of Cr(VI) effluents. The Cr(VI) is reduced by the bacteria to the trivalent form Cr(III), which is entrapped in the physical support by adsorption or ion exchange (Quintelas 2009; Silva 2008). Based on this knowledge, this work aims to evaluate the application of a system, which couples an EK cell with specific BIO-PRBs, in the cleaning of soils contaminated with Cr(VI).

RESULTS
Soil characterization
Table 1 resumes the characterization of the studied soil sample. It was classified as an acidic loamy sand soil,
with a high content in organic matter. The predominance in the clay minerals belongs to kaolinite, followed by illite, smectite and interstratified material.

Table 1: Chemical and physical properties of the soil collected at Póvoa de Varzim, Portugal

<table>
<thead>
<tr>
<th>Clay</th>
<th>2.58</th>
<th>[Cr] / (mg kg⁻¹)</th>
<th>0.17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silt</td>
<td>23.06</td>
<td>Kaolinite (%)</td>
<td>41</td>
</tr>
<tr>
<td>Sand</td>
<td>74.36</td>
<td>Illite (%)</td>
<td>31</td>
</tr>
<tr>
<td>pH (H₂O)</td>
<td>5.9</td>
<td>Esmectite (%)</td>
<td>18</td>
</tr>
<tr>
<td>CEC / (cmolc kg⁻¹)</td>
<td>12.52</td>
<td>Interstratified (%)</td>
<td>10</td>
</tr>
<tr>
<td>OMC / (%)</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Sorption and migration**

The sorption kinetics of Cr(VI) allowed the adjustment of a mathematical model, the empirical power function (Equation 1), whose rate constant increased with decreasing pH. On the other hand, the increase in the contaminant solution pH resulted in the “decrease” of the adsorption of Cr(VI) and therefore in its higher mobility (Figure 1).

\[ q_t = k t^v \]  

In these equation \( t \) is the contact time (h); \( q_t \) is the amount of metal sorbed per unit mass of soil at time \( t \) (mg kg⁻¹), \( k \) (mg kg⁻¹ h⁻ⁿ) and \( v \) are adjustment parameters of the power function equation.

**Electroremediation/Biobarriers**

The coupling of electrokinetic cells and permeable reactive biobarriers was performed either with activated carbon or zeolite, supporting a biofilm of *Arthrobacter viscosus*. The application of the system composed by activated carbon was more advantageous. Explicitly, its lower density, high specific area and capability to adsorb Cr(VI) oxyanions, resulted in higher uptake. The elevated porosity of activated carbon facilitated the transport of Cr(VI) towards the anode chamber of the electrokinetic cell, after the biobarrier saturation, improving therefore the total removal of the targeted contaminant - 79% vs 60%, as showed in Figure 2.

**REFERENCES**


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