



Universidade do Minho
Escola de Engenharia

Semana da Escola de Engenharia October 24 - 27, 2011

SOILS CONTAMINATED WITH HEXAVALENT CHROMIUM - SORPTION, MIGRATION AND REMEDIATION

Bruna Fonseca
Department of Biological Engineering
E-mail: bfonseca@deb.uminho.pt

KEYWORDS

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,



Semana da Escola de Engenharia October 24 - 27, 2011

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

Clay	2.58	[Cr] / (mg kg ⁻¹)	0.17
Silt	23.06	Kaolinite (%)	41
Sand	74.36	Illite (%)	31
pH (H ₂ O)	5.9	Esmectite (%)	18
CEC/ (cmol _c kg ⁻¹)	12.52	Interstratified (%)	10
OMC/ (%)	3.5		

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).

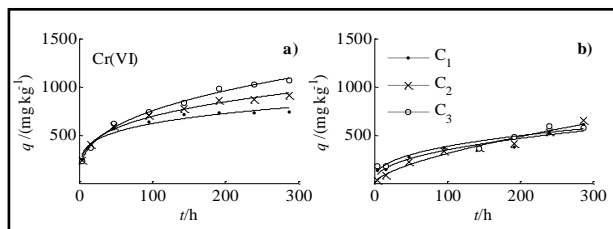


Figure 1: Variation of mass of Cr(VI) adsorbed per mass of soil, for different initial solutions, at pH 2 (a) and pH 5 (b). ($C_1=75 \text{ mg L}^{-1}$; $C_2=92 \text{ mg L}^{-1}$; $C_3=128 \text{ mg L}^{-1}$).

$$q_t = kt^v \quad (1)$$

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^{-v}) and v are adjustment parameters of the power function equation.

Electroremediation/Bio barriers

The coupling of electrokinetic cells and permeable reactive bio barriers 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 bio barrier saturation, improving therefore the total removal of the targeted contaminant - 79% vs 60%, as showed in Figure 2.

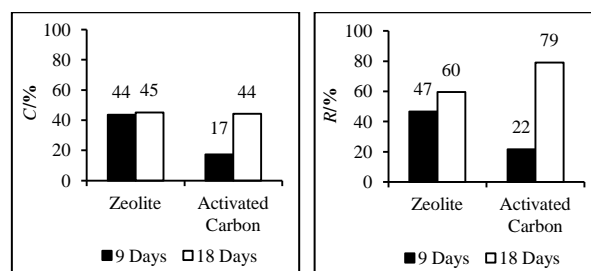


Figure 2: Fraction of hexavalent chromium reduced to the trivalent form - $C/\%$ - and total removal of the hexavalent chromium - $R/\%$ - determined for the assays regarding the both types of bio barriers.

REFERENCES

- Alloway B.J. 1995. “Heavy metals in soils”. Blackie, Glasgow.
- Banks M.K., Schwab A.P., Henderson C. 2006. “Leaching and reduction of chromium in soil as affected by soil organic content and plants”. *Chemosphere*, No. 62, 255-264.
- Elzahabi M., Yong R.N. 2001. “pH influence on sorption characteristics of heavy metal in the vadose zone” *Engineering Geology*, No. 60, 61-68.
- Proctor D.M., Fredrick M.M., Scott P.K., Paustenbach D.J., Finley B.L. 1998. “The prevalence of chromium allergy in the United States and its implications for setting soil cleanup: A cost-effectiveness case study”. *Regulatory Toxicology and Pharmacology*, No. 28, 27-37.
- Quintelas C., Fonseca B., Silva B., Figueiredo H., Tavares T. 2009. “Treatment of chromium(VI) solutions in a pilot-scale bioreactor through a biofilm of *Arthrobacter viscosus* supported on GAC”. *Bioresource Technology*, No. 100, 220-226.
- Sanjay K., Arora A., Shekhar R., Das, R.P. 2003. Electroremediation of Cr(VI) contaminated soils: kinetics and energy efficiency, *Colloids and Surfaces A*, No. 222, 253-259.
- Silva B., Figueiredo H., Quintelas C., Neves I.C., Tavares T. 2008. “Zeolites as supports for the biorecovery of hexavalent and trivalent chromium”. *Microporous and Mesoporous Materials*, No. 116, 555-560.

ACKNOWLEDGMENT

The author gratefully acknowledge the Fundação para a Ciência e Tecnologia, Ministério da Ciência e tecnologia, Portugal by her PhD grant (SFRH/BD/27780/2006).