Soils contaminated with hexavalent chromium and lead
Sorption, migration and remediation techniques
Bruna Catarina da Silva Fonseca

UMinho|2011

Universidade do Minho
Escola de Engenharia

Bruna Catarina da Silva Fonseca

Soils contaminated with hexavalent chromium and lead
Sorption, migration and remediation techniques

Maio de 2011

Universidade do Minho
Escola de Engenharia

Bruna Catarina da Silva Fonseca

Soils contaminated with hexavalent chromium and lead
Sorption, migration and remediation techniques

Tese de Doutoramento em Engenharia Química e Biológica

Trabalho efectuado sob a orientação da
Professora Doutora Maria Teresa de Jesus Simões Campos Tavares

Maio de 2011

|AUTOR:
Bruna Catarina da Silva Fonseca
E-mail: bfonseca@deb.uminho.pt
Telefone: +351 931 601 402
BI: 12412309

|SOILS CONTAMINATED WITH HEXAVALENT CHROMIUM AND LEAD SORPTION, MIGRATION AND REMEDIATION TECHNIQUES

|ORIENTADORA:
Professora Doutora Maria Teresa de Jesus Simões Campos Tavares

|ANO DE CONCLUSÃO
2011

|DOUTORAMENTO EM ENGENHARIA QUÍMICA E BIOLÓGICA

Universidade do Minho, 13 de Maio de 2011

To mammy

AGRADECIMENTO/AKNOWLEDGMENT

Obrigada a todos aqueles que compõem o meu feliz Universo!

The research work presented in this thesis was financially supported by Fundação para a Ciência e Tecnologia (FCT) and Fundo Social Europeu (FSE) through the research grant SFRH/BD/27780/2006.

“We know more about the movement of celestial bodies than about the soil underfoot”.

Leonardo Da Vinci

ABSTRACT

The interest in environmental soil science has been growing in the last years due to the continuous degradation of this major natural resource. With this in mind, and because chromium and lead are two of the most toxic heavy metals frequently detected as soil contaminants in the Portuguese territory, the study and development of few remediation techniques and the indissociable description of the sorption and migration of these two heavy metals in soils, were the main objectives of the research work described in this thesis.

Primarily, a representative sample of a typical loamy sand soil was collected in Porto, Portugal, in a zone of intense agriculture activity. This soil was used for a series of tests concerning the adsorption, transport and fate of the two targeted metals, as well as the main factors affecting it like pH, contaminant concentration and competition. The adsorption equilibrium of both metals was evaluated through the fitting of eight isotherm models to each experimental data set. The best fitting was observed for the Redlich-Peterson and Khan models for the adsorption of chromium and of lead, respectively. On its turn, the sorption kinetics was evaluated using three models - Elovich, pseudo first order and an empirical power function. The retention of lead was almost instantaneous and the empirical power function described better the sorption kinetics of chromium. Then, flow experiments were performed with effluents with both metals. Results revealed a high retention of chromium and a weak retention of lead, for low pH values. In consequence of the distinctive results obtained for chromium, a closer analysis was performed to the sorption and fate of this metal. It was observed that the sorption of hexavalent chromium decreased with increasing pH and that chromium retention increased with the increasing of its concentration in the influent solution. Also, the fitting of a continuous model - convection dispersion two site non-equilibrium - showed that isotherm models - Freundlich and Langmuir - tended to underestimate the adsorption parameters, even following the same trend when the pH of the contaminant solution was altered. Then, and because heavy metals are frequently identified as co-contaminants, the scenario of co-contamination was also evaluated for the focused soil. In order to do that the sorption and transport of five metals - Cr, Pb, Cd, Cu and Zn - was evaluated. The tests were undertaken in batch and continuous systems, using single- and multiple-metal acid solutions. In accordance to the type of assay - batch or continuous - proper theoretical models were once more fitted and, as expected, the influence of competition was observed either in batch and continuous systems, but with different tendencies. The FTIR spectra revealed always the notorious influence of clay minerals and organic matter in the metals sorption.

The application of a biological remediation technique was evaluated in the attenuation of the effects of hexavalent chromium on this soil. A bioleaching technique, using an *Acidithiobacillus thiooxidans* DSM504 pure culture was actually tested. Batch tests were performed to evaluate the effect of the operational temperature, the hexavalent chromium concentration and the pH of the contaminant solution. Removal values between 33.3% and 83.3% were obtained and the pH was identified as the major factor influencing the technique efficiency. Generally, high removal values were associated with acidic contaminations.

The cleaning of soils contaminated with lead was later approached, by the application of chemical washing to a highly contaminated soil. Batch desorption tests were performed applying single and composed desorption solutions to soil samples contaminated only with lead or co-contaminated with a polycyclic aromatic hydrocarbon, as these compounds are frequently found in sites contaminated with lead. Extraction levels around 100% were obtained by applying single or composed extraction solutions to the soil contaminated only with lead. Moreover, extractions of 48% and 55% were obtained for lead and phenanthrene, respectively, applying a composed solution to a co-contaminated soil.

The application of a novel technique comprising an electrochemical and a biological component was tested in the cleaning of soil contaminated with hexavalent chromium. In order to do that, biobarriers composed by *Arthrobacter viscosus* bacteria, supported either in activated carbon or zeolite, were placed before the anode chamber of the electrokinetic cells, aiming the reduction of the hexavalent chromium migrating in its direction. Removal values of 60% and 79% were obtained with zeolite and activated carbon biobarriers, respectively, for a test period of eighteen days.

Ultimately, this thesis 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 herein explored on such a valuable resource frequently forgotten and ignored: THE SOIL.

RESUMO

Ultimamente, o ramo de tecnologia ambiental da ciência do solo tem sido alvo de crescente interesse, dada a contínua degradação deste importante recurso natural. Posto isto, e porque tanto o crómio como o chumbo são metais pesados bastante tóxicos, frequentemente detectados em concentrações poluentes no território Português, o estudo do desenvolvimento de técnicas de remediação, e indissociavelmente, da sorção e migração destes dois metais no solo, foram os principais objetivos do trabalho de investigação descrito nesta tese.

Primeiramente, uma amostra representativa de um típico solo argilo - arenoso foi recolhida numa zona de grande atividade agrícola localizada no Porto, Portugal. Este solo foi utilizado para uma série de testes relacionados com a sorção e transporte dos dois metais pesados visados e com os principais fatores que influenciam estes fenómenos como o pH, a concentração dos metais e a presença de outros contaminantes. O equilíbrio de adsorção dos dois metais foi avaliado através do ajuste de oito modelos isotérmicos aos respectivos dados experimentais. Os melhores ajustes foram observados com os modelos de Redlich-Peterson e Khan, para o crómio e chumbo, respectivamente. Por sua vez, a cinética de sorção foi avaliada através do ajuste dos modelos de Elovich, de pseudo-primeira-ordem e de uma função exponencial empírica. Verificou-se que o chumbo foi instantaneamente retido e que a cinética de sorção de crómio é ajustada satisfatoriamente pela função exponencial empírica. Foram então realizados ensaios em contínuo, com efluentes com ambos os metais. Verificou-se uma alta retenção de crómio e uma fraca retenção de chumbo, para baixos valores de pH. Posteriormente, uma análise mais detalhada à sorção e transporte do crómio hexavalente confirmou a diminuição da adsorção de crómio hexavalente com o aumento do pH, e também um aumento da sua retenção fruto do aumento da concentração no afluente. O ajuste de um modelo contínuo, considerando o transporte em condições de não-equilíbrio, mostrou que os modelos isotérmicos - Freundlich e Langmuir – resultam na subestimação dos parâmetros de adsorção para o crómio hexavalente. Depois, e porque os metais pesados são frequentemente identificados como co-contaminantes, o cenário de co-contaminação foi avaliado através do estudo da sorção e transporte de cinco metais - Cr, Pb, Cd, Cu e Zn. Os testes foram realizados em sistema fechado e aberto, utilizando soluções ácidas mono- e multi-metálicas. De acordo com o tipo de ensaio - fechado ou

aberto - foram mais uma vez ajustados os modelos teóricos adequados, que traduziram a influência da competição, tanto em sistemas fechados como abertos, mas com diferentes tendências. Os espectros de FTIR revelaram sempre a grande influência dos argilominerais e da matéria orgânica na retenção de ambos os metais pelo solo.

Finalizados os testes de sorção e transporte, a aplicação da remediação biológica foi avaliada para atenuação dos efeitos de crómio hexavalente no solo, através da aplicação de uma técnica de biolixiviação, utilizando uma cultura pura de *Acidithiobacillus thiooxidans* DSM504. Realizaram-se ensaios em sistema fechado para avaliar o efeito da temperatura de operação, da concentração de crómio hexavalente e do pH da solução contaminante. Os valores de remoção registados, cuja variação dependeu essencialmente do pH, variaram entre 33,3% e 83,3%,. Geralmente, os valores de remoção mais altos estiveram associados com cenários de contaminação mais ácida.

A descontaminação de solos contendo chumbo foi abordada através da aplicação da lavagem química a um solo altamente contaminado. Foram realizados testes de dessorção em sistema fechado, aplicando soluções de extração simples e compostas a amostras contaminadas apenas com chumbo ou também com fenantreno, uma vez que este composto é encontrado frequentemente em áreas contaminadas com chumbo. Obtiveram-se remoções em torno de 100%, através da aplicação de soluções de extração simples ou compostas para o solo contaminado apenas com chumbo. Para o solo co-contaminado, registaram-se extrações de 48% e 55% para o chumbo e para o fenantreno, respectivamente, aquando da aplicação de uma solução composta.

A aplicação de uma nova técnica, conjugando uma componente eletroquímica e outra biológica, foi testada na descontaminação de solos com crómio hexavalente. Acoplaram-se biobarreiras compostas por *Arthrobacter viscosus* suportada em carvão ativado ou zeólito antes da câmara anódica das células eletrocinéticas, visando assim a redução do crómio hexavalente que migra nesta direção. Foram obtidos valores de remoção de 60% e 79%, utilizando biobarreiras de zeólito e carvão ativado, respectivamente, para um período dezoito dias.

Em última análise, esta tese pretende ser uma ferramenta para políticos e legisladores, através dos estudos de transporte, mas também para o setor industrial no que respeita ao desenvolvimento e aplicação das técnicas de descontaminação aqui exploradas a um recurso tão valioso: O SOLO.

TABLE OF CONTENTS

LIST OF ABBREVIATIONS

Abbreviation	Description
FAO	Food and Agriculture Organization of the United Nations
UNESCO	United Nations Educational, Scientific and Cultural Organization
SOM	Soil Organic Matter
US EPA	United States Environmental Protection Agency
CDE	Convection-dispersion equation
EEA	European Environment Agency
EIONET	European Environment Information and Observation Network
BIO-PRB	Permeable Reactive Biobarrier
GAC	Granular activated carbon
EK	Electrokinetic
CEC	Cationic exchange capacity
FAAS	Flame atomic absorption spectrometry
FTIR	Fourier transform infrared spectroscopy
OMC	Organic matter content
EC	Exchangeable cations
TSM	Two-site non-equilibrium model
BTC	Breakthrough curves
HSAB	Hard–soft acid–base
PHE	Phenanthrene
T80	Tween® 80
B35	Brij® 35 P
Na-EDTA	(Ethylenedinitrilo)-tetraacetic acid disodium salt
PAH	Polycyclic aromatic hydrocarbon
SEM	Scanning electron microscopy
EDAX	Electron-dispersive X-ray spectroscopy
EDS	Energy dispersive spectrometer
EBSD	Back-scattered electron detector
HPLC	High-performance liquid chromatography
EPS	Exopolysaccharides

LIST OF CHEMICAL SUBSTANCES AND IONS

Symbol	**Description**
Pb(II)	Divalent lead
Cr(III)	Trivalent chromium
Cr(VI)	Hexavalent chromium
$HCrO_4^-$	Hydrochromate anion
CrO_4^{2-}	Chromate anion
$Cr_2O_7^{2-}$	Dichromate anion
PO_4^{3-}	Phosphate
SO_4^{2-}	Sulfate
$PbCl_2$	Lead chloride
H_2CrO_4	Chromic acid
$K_2Cr_2O_7$	Potassium dichromate
$CaCl_2$	Calcium chloride
HNO_3	Nitric Acid
NaOH	Sodium hydroxide
$CaCO_3$	Calcium carbonate
KBr	Potassium bromide
NH_4Cl	Ammonium chloride
KH_2PO_4	Potassium dihydrogen phosphate
$MgCl_2{\cdot}6H_2O$	Magnesium chloride hexahydrate
$CaCl_2{\cdot}2H_2O$	Calcium chloride dihydrate

LIST OF SYMBOLS

Symbol	Description	SI units
q_e	Amount of metal adsorbed/desorbed per unit mass of soil at equilibrium	$\mathrm{kg\ kg^{-1}}$
C_e	Concentration of contaminant in the liquid phase at equilibrium	$\mathrm{kg\ m^{-3}}$
t	Time	s
q_t	Amount of contaminant sorbed per unit mass of soil at time t	$\mathrm{kg\ kg^{-1}}$
k_1	First order rate constant	$\mathrm{s^{-1}}$
α_E	Initial adsorption rate of the Elovich equation	$\mathrm{kg\ kg^{-1}\ s^{-1}}$
β_E	Desorption constant of the Elovich equation	$\mathrm{kg\ kg^{-1}}$
k_PF	Constant of the empirical power function	$\mathrm{kg\ kg^{-1}\ s}^{-\nu}$
ν_PF	Constant of the empirical power function	-
k_F	Freundlich distribution coefficient	$\mathrm{m}^{3/n}\ \mathrm{kg\ kg^{-1}\ kg}^{-1/n}$
n_F	Freundlich correction factor	-
q_max	Soil's maximum sorption capacity	$\mathrm{kg\ kg^{-1}}$
b_L	Langmuir constant related with the binding strength	$\mathrm{m^3\ kg^{-1}}$
q_D	Dubinin-Radushkevich maximum adsorption capacity	$\mathrm{kg\ kg^{-1}}$
B_D	Dubinin-Radushkevich activity coefficient	$\mathrm{mol^2\ J^{-2}}$
E	Mean sorption energy	$\mathrm{J\ mol^{-1}}$
R	Gas constant; Retardation factor or Removal	$\mathrm{J\ mol^{-1}\ K^{-1}}$
T	Absolute temperature	K
b_Te	Temkin constant related to the heat of sorption	$\mathrm{J\ mol^{-1}}$
a_Te	Temkin isotherm constant	$\mathrm{m^3\ kg^{-1}}$
k_RP	Redlich –Peterson model isotherm constant	$\mathrm{m^3\ kg^{-1}}$
a_RP	Redlich –Peterson model constant	$\mathrm{m}^{3\beta_\mathrm{RP}}\ \mathrm{kg}^{-\beta_\mathrm{RP}}$
β_RP	Redlich –Peterson model exponent	-
b_K	Khan model constant	$\mathrm{m^3\ kg^{-1}}$
a_K	Khan model exponent	-
k_S	Sips model isotherm constant	$\mathrm{m}^{3\beta_\mathrm{S}}\ \mathrm{kg}^{-\beta_\mathrm{S}}\ \mathrm{kg^{-1}}$
a_S	Sips model constant	$\mathrm{m}^{3\beta_\mathrm{S}}\ \mathrm{kg}^{-\beta_\mathrm{S}}$
β_S	Sips model exponent	-

Symbol	Description	SI units
k_T	Toth model constant	$kg^{n_T}\ m^{-3n_T}$
n_T	Toth model exponent	-
C_i	Initial concentration of the contaminant in the liquid phase	$kg\ m^{-3}$
V	Volume	m^3
W	Weight	kg
Q	Flow	$m^3\ s^{-1}$
v	Pore water velocity	$m\ s^{-1}$
D	Dispersion coefficient	$m^2\ s^{-1}$
C_0	Influent concentration	$kg\ m^{-3}$
θ	Water content	$m^3\ m^{-3}$
L	Soil bed length	m
q	Flux velocity	$m\ s^{-1}$
ρ_b	Soil bulk density	$kg\ m^{-3}$
C	Flux average or resident concentration or Conversion	$kg\ m^{-3}$
q_1	Solid phase concentration of the contaminant on equilibrium sites	$kg\ kg^{-1}$
q_2	Solid phase concentration of the contaminant on kinetic non-equilibrium sites	$kg\ kg^{-1}$
x	Distance	m
F	Fraction of the sites available for instantaneous adsorption	-
C_1	Relative concentration of contaminant in equilibrium sites scaled to the input concentration C_0	-
C_2	Relative concentration of contaminant in kinetic non-equilibrium sites scaled to the input concentration C_0	-
P	Peclet number	-
T	Dimensionless time	-
β	Partitioning coefficient	-
ω	Dimensionless mass transfer coefficient	-
k_L	Linear isotherm sorption coefficient	-
q_{Cr}	Mass of total chromium (de)sorbed per mass of soil	$kg\ kg^{-1}$
$C_{Cr(III)}$	Concentration of trivalent chromium in solution	$kg\ m^{-3}$
$C_{Cr(VI)}$	Concentration of hexavalent chromium in solution	$kg\ m^{-3}$
r^2	Coefficient of determination	-

Symbol	Description	SI units
C_{Cr}	Concentration of total chromium in solution	kg m^{-3}
k_2	Rate constants of the pseudo-second-order equation	kg kg^{-1} s^{-1}
C_{t}	Concentration of contaminant in the liquid phase at varying contact times	kg m^{-3}

LIST OF FIGURES

CHAPTER 1

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 5

CHAPTER 6

CHAPTER 7

LIST OF TABLES

CHAPTER 1

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 5

CHAPTER 6

CHAPTER 7

CHAPTER 1| Soils, Heavy Metals and Remediation Technologies

1. SOILS AND SOIL SCIENCE

The beginning of the exploitation and exploration of soil dates back to the Neolithic period, at 10 000 years ago, by the time of the Agricultural Revolution [1]. Since then, humans developed a very close relation with soils and in the beginning of the Renaissance several soil studies were attributed to European scientists. By that time, soil science was not yet an independent research field and its consolidation, as a worldwide scientific discipline, occurred later on in the second half of the nineteenth century [2,3]. Nowadays, soil science is widespread and it is beyond agricultural research: soil chemistry, physics, pedology, biology and mineralogy are already sub-disciplines of soil science. The milestones, characterizing the start up of each sub-discipline, can be consulted in Figure 1.1. Nonetheless, it should be noted that the research fields that actually present a faster development are related to environmental issues, like soil and groundwater contamination and its perniciousness to human health [2,4,5].

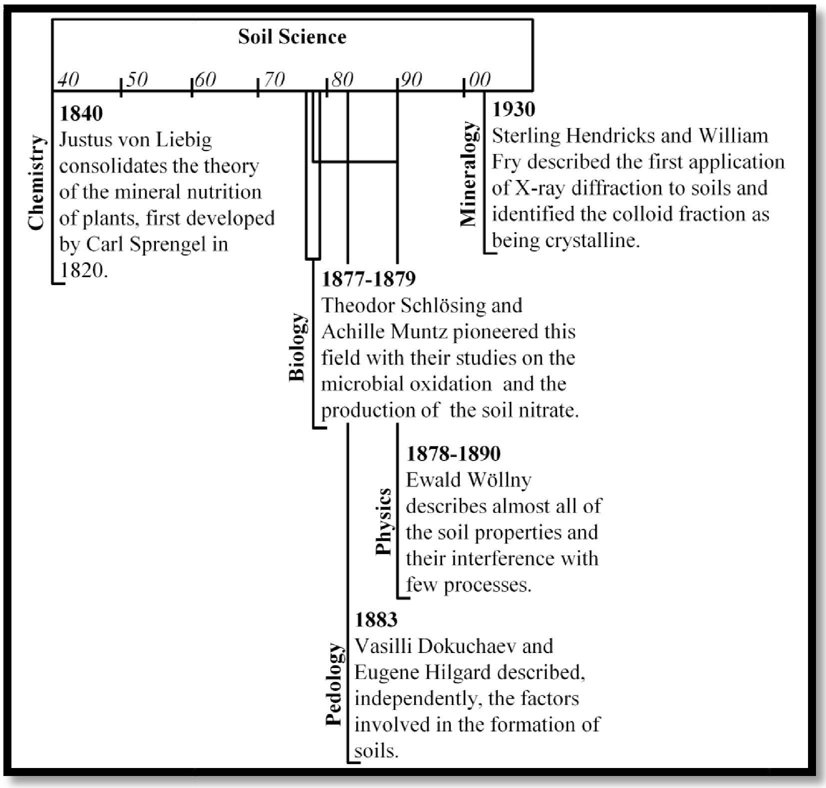


Figure 1.1. Remarkable milestones on the soil science development. The chronogram construction was based in the information collected by Churchman [5].

In the same way of its science, the understanding and definition of soil is in constant evolution, clearly depending on the type and level of knowledge. There are several soil concepts according with the activity and knowledge of who is studying it. However, its utmost importance as a habitat of living matter and as interface for water and nutrient distribution is unquestionable [6]. In this document, few environmental issues like the sorption and fate of pollutants in soils and its remediation will be tackled. Therefore, the most appropriated definition is the one adopted in the environmental soil chemistry, which describes soils as a heterogeneous open system composed by air, water, inorganic and organic solids, resultant from biological, geological and hydrologic weathering processes [7,8].

1.1. Soil

Actually, soil is succinctly described in the Thematic Strategy for Soil Protection of the European Commission "as the top layer of earth' crust, formed by mineral particles, organic matter, water, air and living organisms. It is the interface between earth, air and water and hosts most of the biosphere" [9]. However, this layer is different from site to site and depends essentially on the type of the parent material and its exposition to specific weathering processes. There are more than 320 major soil types in Europe, diverging on their depth, color, structure, texture, consistency, nutrients, acidity, mineralogy and organic matter, for example [6,9,10]. Attempting a detailed explanation of these phenomena and their results, the soil horizonation, composition and classification are issues briefly developed bellow.

1.2. Soil horizonation

As mentioned above, soils result primarily from the weathering of a parental rock. Then, the mineral weathered layer is gradually colonized by living organisms that bring an organic character to the soil. Finally, the accumulation and organization of the mineral and the organic materials results in a unique soil layer, known as the soil profile [6]. The soil profile corresponds to the vertical section comprehended between the soil surface and the parental material. Its observation allows the identification of seven horizontal layers differing between each other in their chemical, physical and biological characterization. These layers correspond to the soil horizons and result, essentially, from translocation processes of the mineral and organic materials by water and /or gravity [11,12]. According to the FAO/UNESCO designation, the seven master horizons of soils are denominated by the capital letters H, O, A, E, B. C and R [13]. Table 1.1 compiles a brief description of each horizon, considering the FAO directives.

Table 1.1. Soil horizon designations according to the FAO/UNESCO directives

	Horizon	Description
Surface		
	H	Composed essentially by organic material; saturated with water; located on top of mineral soils or buried at any depth beneath the surface.
	O	Composed essentially by organic matter and litter (leaves, needles, twigs, etc.); located on top of mineral or organic soils; not saturated with water; the mineral fraction generally presents less than half of its weigh.
	A	Mineral horizon located at the surface or below an O horizon; composed by humified organic matter mixed with mineral material; it usually presents a darker color.
	E	Mineral horizon with brighter colors due to the loss of silicate clays, aluminum and the consequently higher quantity of sand and silt particles; usually located near the surface, below an O or A horizon and above a B horizon.
	B	Mineral horizon formed below an A, E, O or H horizon; composed essentially by silicate clays, iron, aluminum and little organic matter; usually known as illuvial layer.
	C	Mineral horizon little affected by pedogenetic processes and lack properties of H, O, A, E or B horizons; the chemical, physical and mineralogical composition is usually very similar to the parental material.
	R	Hard bedrock underlying the soil; may correspond or not to the parental rock; granite, basalt, quartzite and indurate limestone or sandstone are examples of bedrock.
Bedrock		

It should be noted that soils may have several parental materials and that the origin of layering is actually explained by a panoply of simple and complex models.

Therefore, the horizons may diverge on their depth, color, texture, porosity, pH and nutrients among other characteristics. The transition between horizons can be fast and easily identified or be diffused, occurring gradually [12,14].

1.3. Soil composition

In the broad sense of the concept, soils are composed by the solid and porous phases. These phases vary in their proportion from soil to soil, and even in the same soil, from horizon to horizon. The solid phase is constituted by organic and inorganic particles whose aggregation permits the existence of void spaces, videlicet porous, that are filled with water (liquid phase) and air (gaseous phase) [6,8,15].

1.3.1. Solid phase

On its turn, the solid phase is composed by the organic and inorganic fractions. The inorganic fraction represents about 90% of the solid phase and is composed by primary and secondary minerals. The first ones, subjected to little chemical modification, include six silicates: quartz, feldspar, micas, amphiboles, pyroxenes and olivine. The secondary minerals respect to weathered primary minerals and include aluminosilicates, oxides, amorphous materials and sulfur and carbonate minerals. Within this mineral fraction, there are other fractions that can be grouped by their particle size [6-8]. Figure 1.2 resumes the classification system adopted by FAO/UNESCO in the *Guidelines for soil description* [16].

Clay	Silt		Sand					Gravel Cobles Stones
	Fine	Coarse	Very fine	Fine	Medium	Coarse	Very coarse	
2 μm	20 μm	63 μm	125 μm	200 μm	630 μm	1250 μm	2000 μm	

Figure 1.2. Particle size classes according to the FAO/UNESCO classification system

It is undoubtedly accepted, by the soil science community, that only particles with diameter bellow 2 mm can be designated as soil material [6,16]. The larger particles of soil material - sand - consist mainly of quartz, albeit feldspars, micas and heavy minerals can also be found, and are characterized by their almost spherical shape and abrasiveness. Following these particles in size is the silt fraction, which presents a mixture of sand and clay features. Finally, clay designates the colloidal fraction that comprises especially secondary minerals like clay minerals, oxides and carbonates, which greatly affect chemical reactions and processes. The clay minerals are aluminosilicates consisting in the layering of tetrahedral sheets of silica tetrahedron SiO_4^{4-}, or aluminum AlO_4^{5-}, linked to octahedral sheets formed from small cations, such as aluminum or magnesium, coordinated by six oxygen atoms. These structures may have permanent negative charges or be pH dependent. The kaolinite, illite, vermiculite, smectite and chlorite are the most common clay minerals in nature. On the other hand, even existing in lower concentration than the clay minerals, the oxides also affect the chemical properties of soil, and the most common are the iron, aluminum and manganese oxides [7,8,16,17]. The relative proportions of the soil fractions (sand, silt and clay) are used to classify the soil texture, through a triangular diagram. The diagram used by FAO/UNESCO is presented in the Figure 1.3.

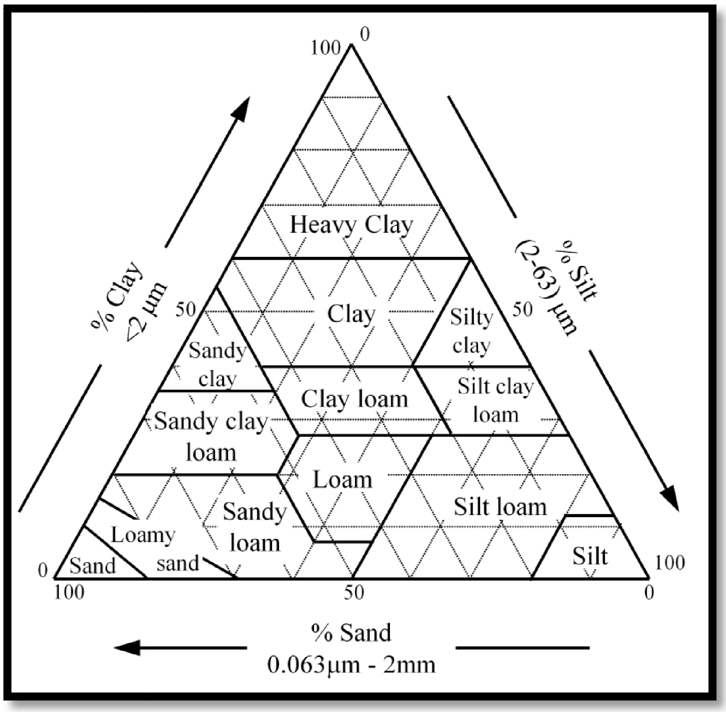


Figure 1.3. Relation of constituents of fine earth by size, defining textural classes, according to the FAO/UNESCO guidelines [16].

As mentioned above, besides the inorganic fraction, the solid phase is composed by organic matter as well, which also plays a significant role in affecting soil chemistry [8]. The SOM is generated through the decomposition of few organic materials and is constituted by litter, light fraction, microbial biomass, water-soluble organics - carbohydrates, aminoacids, lipids, resins and organic acids - and stabilized organic matter (humus). The humic substances constitute the higher fraction of SOM, and because of their reactivity participate in most of the soil chemical reactions. Moreover, these substances, with high molecular weight and refractory, which usually confer a darker color to soils, play a significant role in processes like aggregation, acidity control, cycling of nutrients and detoxification of hazardous compounds. The chemical fractionation of the humic substances, based on their solubility in acid or base, allows the subdivision of this class into humin (not separable of the mineral fraction), humic acids (soluble in alkaline medium) and fulvic acids (soluble in acidic media). Unlike the clay minerals, SOM only has pH dependent charges and its major reactions in soils involve cationic exchange, metal complexation, soil buffering, complexation with clay minerals and retention of organic molecules of natural or anthropogenic sources [7,8,18].

1.3.2. Soil solution

Soil solution can be defined as the liquid phase of the soil occupying the void spaces of the soil solid phase. This phase is mainly constituted by water, but also by gases and dissolved organic and inorganic substances. In fact, the proportion between the liquid and gaseous phases may differ due to climate conditions or soil activity. The organic/inorganic substances may be directly bounded to metal ions - inner-sphere complexes - or a molecule of water may be positioned in between - outer-sphere complexes. The soil solution is a very dynamic part of the soil and it is on the interface flanked by this part and the solid phase that processes of utmost importance for the various ecosystems occur. The scheme presented in the Figure 1.4 resumes the dynamic equilibria in soils [6,7,15,19].

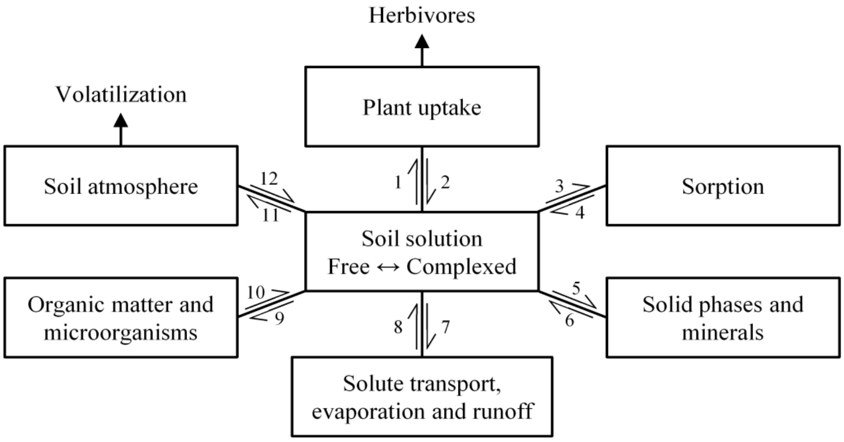


Figure 1.4. Diagram of the dynamic equilibria of soil reactions. Adapted from "Chemical Equilibria in Soils" [20].

The diagram presented above shows that, the soil solution is the media where the plants exude and uptake their residues and nutrients, respectively (1 and 2). The ions may complex with organic/inorganic compound or released (desorbed) and dissolved in soil solution (3 and 4). When saturation occurs, some minerals may precipitate till equilibrium is reached (5); but if the soil solution is under saturated, the minerals may be dissolved in order to re-establish the equilibrium (6). Several solutes may be leached or added to soil, either by natural or anthropogenic processes (7 and 8). The microorganisms and the organic matter may retain numerous ions, which can also be released when death or decomposition takes place, correspondingly (9 and 10). Finally, there is also a dynamic equilibrium between the atmosphere and the respective gaseous phase of soil solution (11 and 12). The composition of the soil solution varies through time and space and depends on the parental material, the pH, the oxidative conditions, the organic matter content and the addition of several compounds due to human activities. Some of the most important ions correspond to the trace metals, which are essential to plant growth like Fe, Zn, Mn, Cu, B, Mo and Ni. On the other hand, also elements like Co, Cr, Se and Sn, which are essential to animals and As, Cd, Hg and Pb, which are toxic to plants, animals and microorganisms, are regularly identified in soil solution. Beside the micronutrients, also the Al, C, N, P and S are elements extremely important in the cycles of soil, and therefore often identified in soil solution [8,21].

1.4. Worldwide soil groups: the FAO/UNESCO classification

According to the above sections it is obvious that soils may have different composition and organization levels, depending on several factors, namely its location. Therefore, the FAO/UNESCO adopted a classification system [13] that allows its distribution in 32 groups. A brief description of these groups and their regional distribution is presented in Table 1.2.

Table 1.2. Summary description of the soil groups recognized in the World reference base for soil resources published by FAO/UNESCO [13]

Group	Description	Regional distribution
Acrisols	Soils with low base saturation and low activity clays, with higher clay content in the subsoil.	These soils are found especially in humid tropical and subtropical and warm temperate regions, like Southeast Asia,, Southern fringes of the Amazon Basin, Southeast of the United States of America, East and West Africa.
Albeluvisols	Acid soils with a bleached horizon penetrating into a clay-rich subsurface horizon.	Northeast Europe; Northwest Asia; Southwest Canada; France; Central Belgium; Southeast of the Netherlands; West of Germany.
Alisols	Soil with higher clay content in the subsoil, low base saturation and high activity clays.	Latin America (Ecuador, Nicaragua, Venezuela, Colombia, Peru and Brazil); West Indies (Jamaica, Martinique and Saint Lucia); West Africa; Highlands of East Africa; Madagascar, Southeast Asia; Northern Australia; China; Japan; Southeast of the United States of America; Mediterranean Sea (Italy, France and Greece).
Andosols	Young soils with volcanic origin.	Typical from volcanic regions, like South America, Central America, Mexico, United States of America, Japan, Philippine Archipelago, Indonesia, Papua New Guinea, New Zealand, Fiji, Vanuatu, New Caledonia, Samoa, Hawaii, Africa (Rift Valley, Kenya, Rwanda, Ethiopia and Madagascar), Europe (Italy, France, Germany and Iceland).
Anthrosols	Soils modified due to anthropogenic activities.	These soils are found wherever agriculture has been practiced for a long time.
Arenosols	Sandy soils with low evolution.	Occur mainly in arid or semi arid regions, and correspond to the most extensive soil group in the world. The largest area is located in the Central Africa, near the equator.
Calcisols	Soils with substantial accumulation of secondary lime.	The major fraction of these soils can be found in arid and semi-arid tropics. However, its worldwide extension is difficult to quantify.

Table 1.2. Summary description of the soil groups recognized in the *World reference base for soil resource*, published by FAO/UNESCO (cont.)

Group	Description	Regional distribution
Cambisols	The horizons from subsoil are clearly divided through markedly alterations in color, clay content, structure or carbon content	Major areas can be found in temperate and boreal regions that were under the influence of glaciations. However, this soil can also characterize zones with active geologic erosion.
Chernozems	Black soils rich in organic matter. Among the best soils in the world.	Mainly identified in the middle latitude steppes of Eurasia and North America.
Cryosols	Mineral soils affected by frosting.	Located near the North and South Poles. Major areas comprising these soils are located in Russia, Canada, China, Alaska and Mongolia.
Durisols	Soils with accumulation of secondary silica.	Major occurrences were reported from Australia, South Africa, Namibia, and United States of America Also Central and South America and Kuwait are placed of minor occurrences.
Ferralsols	Red or yellow soils, strongly weathered, with low activity clays and high content of sesquioxides.	These soils are majorly concentrated in humid tropics on the continental shields of South America, like Brazil and Africa.
Fluvisols	Young soils in alluvial deposits.	Located essentially along rivers and lakes, in deltaic and marine deposit areas, these soils can be found in all continents and climates.
Gleysols	Soils greatly affected by elongated groundwater saturation.	Occurring from perhumid to arid climates, its major extents are located at subarctic areas like Russia, Canada and Alaska, and in humid temperate and subtropical lowlands, like China and Bangladesh.
Gypsisols	Soils with substantial accumulation of secondary calcium sulfate.	Only found in arid regions, like Mesopotamia, desert areas in the Near East and adjacent Central Asian republics, Libyan and Namib deserts, southeast and central Australia and of the United States of America.
Histosols	Soils comprising only organic materials.	These soils are essentially located in the boreal, subarctic and low arctic regions of the Northern Hemisphere. The rest is mostly located in temperate lowlands and cool mountain. Small areas can also be found in tropics
Kastanozems	Dark soils very rich in organic matter.	Occupies large areas of Eurasian short-grass steppe belt, Great Plains of the United States of America, Canada and Mexico, and, pampas and Chaco regions of northern Argentina, Paraguay and southern Bolivia.
Leptosols	Shallow soils	This is the most extensive soil group worldwide. Found almost everywhere, mountain areas of Asia, South America, Sahara, Arabian deserts, Ungava Peninsula, Canada and Alaska, are more prominent.

Table 1.2. Summary description of the soil groups recognized in the *World reference base for soil resource*, published by FAO/UNESCO (cont.)

Group	Description	Regional distribution
Lixisols	Soils with high clay content in the subsoil, low activity clays and high base saturation.	These soils can be found in seasonally dry tropical, subtropical and warm temperate regions like, sub-Sahelian, East Africa, South and Central America, Southeast Asia and Australia.
Luvisols	Soils with high clay content in the subsoil, high activity clays and high base saturation.	Located mainly in temperate regions like the west and centre of the Russia, the United States of America, Central Europe, Mediterranean region and southern Australia.
Nitisols	Deep, dark red, brown or yellow clayey soils having a pronounced shiny, nut-shaped structure.	More than a half is found in tropical Africa, (Ethiopia, Kenya, Congo and Cameroon). The rest is located at lower altitudes (Asia, South America, Central America, Southeast Africa and Australia)
Phaeozems	Soils with dark coloration due to the high content in organic matter.	The higher fraction is located in the humid and subhumid Central Lowlands and easternmost parts of the Great Plains of the United States of America, followed by the subtropical pampas of Argentina and Uruguay, China and Russia.
Planosols	Lighter soils with bleached topsoil, temporarily saturated with water.	These soils occur in subtropical and temperate regions with clear alternation of wet and dry seasons like Latin America, Africa, East United States of America, Southeast Asia and Australia.
Plinthosols	Wet soils, with subsoil very rich in a compound of humus, iron, clay and quartz.	Commonly found in wet tropics, markedly in the eastern Amazon basin, the central Congo basin and parts of Southeast Asia. Also found extensively in the Sudano-Sahelian zone.
Podzols	Acid soils with a subsurface accumulation of mixed compounds of iron, aluminum and organic matter.	Principally located at temperate and boreal regions of the Northern Hemisphere, these soils also occur along the Rio Negro, in French Guiana, Guyana and Suriname in South America, in the Malaysian region and in northern and southern Australia.
Regosols	Accommodates the weakly developed soils that do not fit in the other groups.	These soils are especially found in arid areas, like the mid-west of the United States of America, the northern Africa, the Near East and Australia.
Solonchaks	Saline soils	Principally located in arid zones of Northern Hemisphere, like northern Africa, the Near East, the former Soviet Union and Central Asia, but also in Australia and Americas.
Solonetz	Soils with subsurface clay accumulation and rich in Na and Mg.	Major areas are found in steppe climate zones like Ukraine, Russia, Kazakhstan, Hungary, Bulgaria, Romania, China, United States of America, Canada, South Africa, Argentina and Australia.

Table 1.2. Summary description of the soil groups recognized in the *World reference base for soil resource*, published by FAO/UNESCO (cont.)

Group	Description	Regional distribution
Stagnosols	Soils with mottles caused by the stagnant surface water.	Occur mainly in humid to perhumid temperate regions of West and Central Europe, North America, southeast Australia and Argentina.
Technosols	Soils with high content in anthropogenic material.	These soils are found wherever human activity occurs. It is mainly associated with waste sites like landfills, sludge, cinders, mine spoils and ashes, pavements and other soils made in human materials.
Umbrisols	Soils with dark coloration and with high organic content on the topsoil.	Located essentially in cool, humid, mountainous and with little or any soil moisture deficit, like the Andean ranges of Colombia, Ecuador, Venezuela, Bolivia and Peru, Brazil (Serra do Mar), South Africa (Drakensberg), North America, and also along the northwest Atlantic seaboard (British Isles, northwest Portugal and Spain), Asia (west of Lake Baikal, fringes of the Himalayas, India, Nepal, China and Myanmar) and Oceania (mountain ranges of Papua New Guinea, southeast Australia, eastern parts of South Island and New Zealand.
Vertisols	Heavy clay soils	The highest occurrence is reported to the semi-arid tropics, but these soils can also be found in wet tropics zones, like Trinidad. Other places, especially lowlands that are periodically wet in their natural state, were identified in Sudan, India, Ethiopia, South Africa, Australia, the southwest of the United States of America (Texas), Uruguay, Paraguay and Argentina.

The soil composition and characterization will be approached in all the following chapters as soil components and characteristics greatly influence the sorption and transport of metals through soils, and also their effect attenuation or elimination from contaminated land. From Chapter 2 to Chapter 5, a loamy sand soil from the north of Portugal was profoundly study in what concerns heavy metals fate and also their elimination through biological techniques. In Chapter 6, a highly and historically contaminated soil from Algeria was used in order to study the efficiency of a chemical process on the extraction of lead. Finally, and due to the novelty of the process, an artificial soil - kaolinite - contaminated with hexavalent chromium, was used to test a hybrid remediation technique - Chapter 7.

2. HEAVY METALS IN SOILS

2.1. Sorption and transport

Heavy metals occurring in the soil solution can be retained in the solid phase as well as they can be liberated from this phase to the soil solution. Therefore, it is evident the importance of the solid-solution interface not only in providing nutrients to plants but also in the dissemination of metals. Sorption is the term usually applied to describe any retention process onto a solid phase, like adsorption, precipitation and fixation. The terms sorbate, sorbent and sorptive, are generically applied to designate the material that accumulates on the interface, the solid surface where it is retained and the molecule or ion with the potential to be sorbed, correspondingly [7,8].

Adsorption is the major process affecting transport of metals, among those cited above, and will be here developed in more detail. During adsorption, the adsorbate accumulates in the interface soil-solution, interacting through three major mechanisms with the solid phase. The inner-sphere complexation occurs slowly, and often in an irreversible way, at the positive or negative charged oxides and clay minerals surface functional groups. The molecules or ions are either covalent or ionic bounded to one oxygen atom of the functional group -monodentate- or to two oxygen atoms - bidentate. Conversely, the outer-sphere complexes result from electrostatic interactions, between adsorbate and surfaces with opposite charge, being therefore weaker than inner-sphere complexes. This complexation occurs rapidly and is reversible and is also characterized by the interposition of a water molecule between the ion/molecule and the surface functional group. The other mechanisms are related with the solvated ions that are not adsorbed to surface functional group, moving freely in the soil solution and it is designated as diffuse-ion swarm. It should be noted that the mentioned functional groups are molecules bounded to various soil surfaces in contact with the liquid phase, like silanol, inorganic hydroxyl, or organic functional groups. These groups can be protonated or deprotonated, and therefore behave as Lewis basis, influencing greatly the adsorption of metal cations [7,8,19]. According to Sposito [7], it is correct to associate the specific adsorption to the inner-sphere complexation, and in contraposition, the diffuse-ion association and outer-sphere complexation to the nonspecific adsorption.

Surface precipitation is also a process of notorious importance. As the surface gets saturated in the metal cation or anion being sorbed, a new solid phase with a three dimensional structure, rises. Soil scientists called surface precipitate to this new structure, which gradually dominates the sorption processes as the surface loading increases. This process is very pH dependent, but is also greatly influenced by the ions concentration. In particular, metals can precipitate as oxides, hydroxides, carbonates, sulfides or phosphates onto soils [8,19].

2.1.1. Adsorption and kinetic models

Adsorption modeling can be approached by two different ways: empirical models, fitted after the experimental tests, or the molecular adsorption models that try to explain and describe the adsorption mechanisms by primarily defining the mathematical form. The constant capacitance model, the diffuse layer model and the triple layer model are important examples of molecular models. These models aim to describe adsorption considering the specific reaction occurring between ions and charged surfaces. The differences among them reside on the nature of the surface charge, the number and position of the potential planes and the position of the adsorbate [7,19]. Although the mechanistic models are of great importance for soil scientists, the empirical models will be herein described with more detail, as from the environmental engineering perspective these models reveal to be important tools supporting decisions on remediation processes and emergency plans, concerning heavy metal contamination.

Most of the investigations on heavy metal adsorption onto soil do not consider the kinetic behavior of metals retention. However, the time dependence has remarkable significance when describing heavy metals interaction with soils. Few kinetic models have been used to describe the adsorption process of contaminants onto soils, especially the Lagergren’s first order-rate equation, also known as pseudo-first-order equation, the pseudo-second-order equation and the Elovich equation, which are all based on the adsorption capacity, and the power function equation, that has a notable empirical character [8,22,23]. These four models will be approached later on and a thorough description will be exposed in Chapters 2, 3, 4 and 6. Moreover, several adsorption isotherm models will be extensively explained and used through this document, as these empirical models demonstrate great efficiency in describing the relation between the equilibrium concentrations of the heavy metals in the solid and liquid phases of soils, at a constant temperature [8,24,25]. Adsorption isotherms frequently used in describing the adsorption equilibrium of contaminant onto soils, like Freundlich and Langmuir equations, and also less consensual equations, like Dubinin-Radushkevich, Temkin, Redlich-Peterson, Khan, Sips and Toth, will be tackled in Chapters 2, 3, 4 and 6.

Adsorption isotherms characterizing the heavy metal adsorption equilibrium may have several shapes, which are properly represented in Figure 1.5. The S curve has a small initial slope that gradually increases with the metal concentration on solution, suggesting the high affinity of soil solution for the metal; the L-curve, which is frequently related with a high affinity of the soil for the metal as long as the surface is unsaturated, has a decreasing slope with the increasing of metal in solution; the H-curve is an extreme version of the L-curve; the C-curve has a constant slope independent from the metal concentration in solution, and is usually related with a constant partitioning of the metal between the interface and the liquid phase, or with a proportional increase between the adsorbing surface and the metal concentration. The L-curve, whose mathematical description involves frequently the Langmuir equation, is the most encountered in soil chemistry [7].

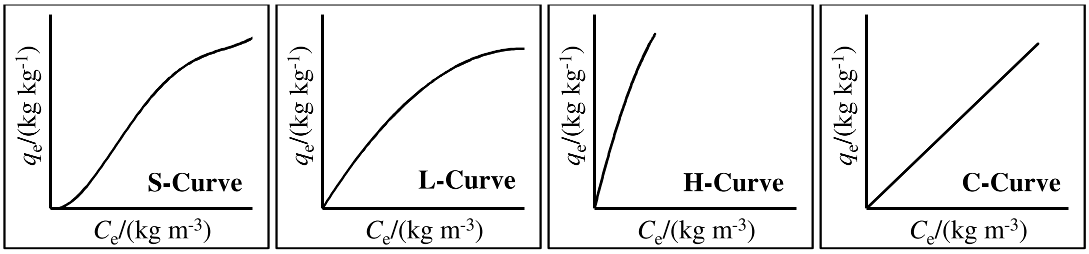


Figure 1.5. Representation of the four general categories of adsorption isotherms.

2.1.2. Transport and fate

Besides the adsorption, also desorption processes have great influence on the contaminants mobilization through soils and it is, therefore, an issue more and more approached in the environmental soil chemistry studies. The ease of desorption not also may improve the mobilization of contaminants through soils and groundwater, but can also be advantageous in the application of some remediation techniques. These processes can be described by adsorption kinetics or equilibrium models, resorting to batch systems. However, more realistic results are usually obtained through flow tests and the respective mathematical description [8,25]. Moreover, the fate and migration of heavy metals in soils and groundwater, for long spatial and temporal scales, can actually be predicted by sophisticated mathematical models, resorting to advanced software.

The convection-dispersion equation (CDE) has been successfully applied in the description of the transport of solutes through homogeneous soils, considering both the equilibrium and the nonequilibrium scenarios. Along the development of the present work, the STANMOD software and the code CXTFIT were used to obtain analytical solutions and consequent adjustment to experimental breakthrough curves of the CDE. Since steady one-dimensional flow is considered, the CXTFIT code can be used to fit the CDE, either to laboratorial or field solute transport data [26-28]. The description of the CDE equation and its fitting process, will be developed in detail in Chapter 3, but will also be approached in Chapters 4 and 7.

2.2. Chromium

Chromium occupies the seventh position concerning the most abundant elements in nature and most of it can be found in the core and in the mantle of earth. Chromium is a transition metal occupying the first position of the Group 6 of the periodic table, with a standard atomic weight of 51.9961 g mol^{-1}, a density of 7.14 g cm^{-3} and an atomic number of 24. In its crystalline form it is a steely-gray, lustrous, hard metal that takes a high polish and has a high melting point - 1907 °C [29]. Chromium exists in soils in two possible oxidation states: the trivalent chromium - Cr(III) - and the hexavalent chromium - Cr(VI). Due to its high oxidizing and corrosive character, Cr(VI) is highly toxic to plants and animals as it can easily penetrate biological membranes. In fact, this heavy metal is listed by EPA as a human carcinogen and also pointed in several countries as a priority pollutant. On the other hand, Cr(III) is a micronutrient essential to plants and also to animals nutrition, as it maintains the efficiency of glucose, lipid and protein metabolisms [30-33].

Most of the Cr found in nature results from anthropogenic activities, like the deposition of urban and industrial wastes, the elongated utilization of fertilizers and sewage sludge and also atmospheric deposition. However, the major sources concern industrial activities like electroplating, dying, photography and alloying. These activities essentially promote the accumulation of Cr(VI) as it is the major form used in industrial processes. The Cr (VI) exists in soils as a component of few complex anions, which are highly soluble in water, depending on the medium pH and reduction potential: the hydrochromate ions ($HCrO_4^-$) predominate for pHs lower than 6.5, the chromate ions (CrO_4^{2-}) predominate at pH 6.5 or higher, the dichromate ion ($Cr_2O_7^{2-}$) predominates at acidic pH's and high concentration levels, and the chromic acid (H_2CrO_4) that prevails at very low pH (pH<0.7) [31-34]. Due to its anionic nature, Cr(VI) adsorption occurs in positively charged sites, increasing with the pH decrease and consequent protonation of the soil surfaces, especially those with hydroxyl groups, like Fe, Mn and Al oxides, where the Cr(VI) is supposed to adsorb through inner-sphere complexation. On the other hand, Cr(VI) anions are repelled by the negative charged clay minerals, which improve its mobility compared with the Cr(III) cations [19,29,31,32].

Various species present on soils like organic material, sulfide and ferrous iron, are responsible for the reduction of Cr(VI) to Cr(III), which is a less hazardous form of Cr. Cr(III) is, as already mentioned, less mobile than Cr(VI) and therefore less bioavailable. Actually, Cr(III) can be readily adsorbed by soils or remain in soil solution as hydroxyl complexes, that quickly precipitate at relatively low pH values. In contrast, the organically complexed Cr(III) may be soluble for a long period, during which oxidation to Cr(VI) may occur, albeit Mn oxides are the only natural oxidants actually known [29,31,33]. This dichotomy between Cr(VI) and Cr(III) has been widely studied, and will also be approached on Chapters 2, 3 and 5 of this document.

2.3. Lead

In opposition with Cr, lead (Pb) is a rare metal on the earth´s crust. In its elemental form Pb is a bluish-gray, soft metal with an atomic weight of 207.19 g mol^{-1}, a density of 11.34 g cm^{-3}, a boiling point of 1749 °C, and with atomic number 82. It is not known any benefit or essential character of Pb to any living organism. Its accumulation by humans can occur through inhalation, ingestion, dermal absorption and placental transfer, resulting then in the poisoning of metabolic pathways and consequent affection of several systems, like hematopoietic, nervous or even reproductive. The exposition to high Pb concentrations may also result in stupor, convulsion, coma and death. Lead is also pernicious to plants and animals, inhibiting their growth and reproduction and leading therefore to their extinction [29].

In contraposition to its harmful effects, Pb is widely used by humans, bringing them great comfort through the production of several useful products. The deposition of old paints, batteries, pesticides, solder, glass, brass, bronze, pigments and ammunition, but also activities like industrial smelting, coal burning, mining and traffic exhaustion are examples of anthropogenic sources of Pb, greatly responsible for its excessive accumulation [21,29,34]. Once in soil, Pb, which occurs mainly in its divalent form, is one of the less mobile heavy metals. Its retention in soils is affected essentially by specific adsorption to solid phases, precipitation of lightly soluble or stable compounds and complexation or chelation with SOM [19,33,34]. Organic matter is the most important soil compound reacting with Pb. Its great affinity may increase sharply the mobility of the metal in soils, due to its complexation with dissolved organic matter or fulvic acids. Following the organic matter content also pH has proven to influence greatly the Pb adsorption, namely the pH rising results in higher partitioning coefficients. On the contrary, low pH values promote the hydrolysis of Pb by several ways, producing $Pb(OH)_2$ for pHs above 9 and $Pb(OH)^+$ for pH values amid 6 and 10 [19,35]. Finally, Mn, Fe and Al oxides were also reported as Pb binders, either through specific adsorption, through the formation of some specific minerals and through biphasic adsorption [19,36]. The sorption/desorption of lead will be approached in Chapters 4 and 6.

3. REMEDIATION TECHNOLOGIES

As previously mentioned, heavy metals and organic compounds are constantly being released in natural environments due to erosion processes. However, there are several anthropogenic sources of heavy metals and organic compounds, like commercial fertilizers, liming materials, sewage sludges, metal-smelting wastes, mining and fossil fuel combustion residues, among others, responsible for their excessive accumulation on soils and groundwater. Once exceeding acceptable limits, these contaminants may enter the food chain and cause serious damages in ecosystems and human health, as some of them are the most toxic pollutants occurring in natural environments [8,21,25]. Figure 1.6 shows the distribution of the main contaminants affecting soil in Europe and also the progress on decontamination, according to the latest available data of the European Environment Agency (EEA). Heavy metals represent 37.3% of the contaminants found in European soil and groundwater, while the organic substances complete almost the remaining 62.7%.

Considering the above-mentioned information and the data presented on Figure 1.7, contamination of soils and groundwater stills an issue of major concern to the European Commission, as great work is still missing in order to prevent it and remediate contaminated sites. Nowadays, most of the techniques applied across Europe are from chemical and physical nature, which sometimes result in negative impact on the ecosystems and also high costs for companies and countries. Therefore, the development of "green" and cost effective technologies is urgent. The sections bellow, present a brief resume of three important remediation techniques, investigated and applied in the last decades and also targeted during the research work here in described.

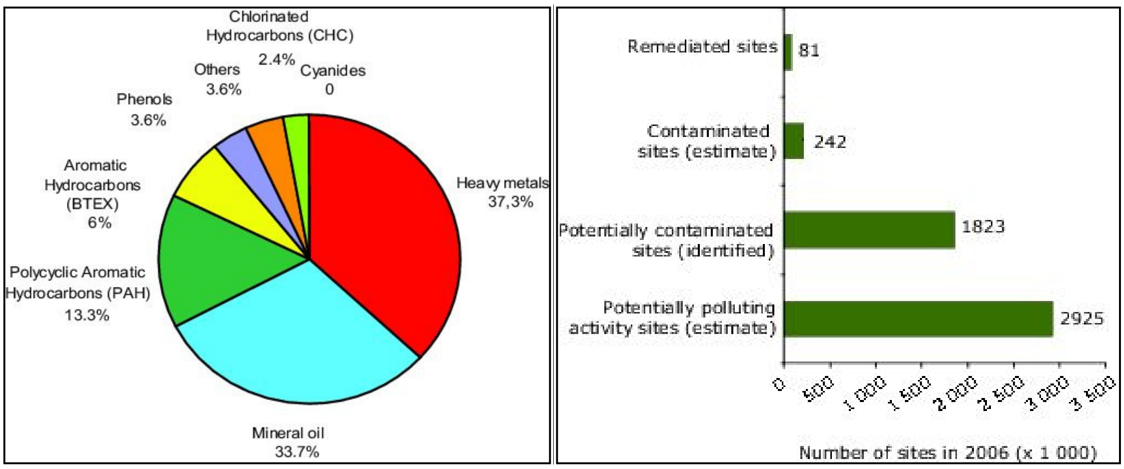


Figure 1.6. Overview of contaminants affecting soil and groundwater and the status of identification and clean-up of contaminated sites in Europe, as reported to the European Environment Agency through the EIONET priority data flows on contaminated sites [37,38].

3.1. Bioremediation

The bioremediation is fundamentally well known and also very attractive to scientists and the community in general, due to its "eco-friendly" and affordable nature and also due to the possibility to be applied *in situ*. The application of this cleaning technique has several branches that derive from the same principle: use of microorganisms or microbial processes to degrade, reduce or eliminate environmental contaminants. Techniques like bioattenuation, biostimulation, bioaugmentation, bioleaching, composting, bioreactors, bioventing and biosorption are actually under investigation and development. This thesis focuses two of those methods, and therefore only these are explored in more detail in the following subsections [39-41].

3.1.1. Bioleaching

Within the scope of this document, bioleaching can be defined as the mobilization of metals from soils due to the activity of chemolithotrophic bacteria, such as *Acidithiobacillus thiooxidans* that are able to oxidize elemental sulfur producing sulfuric acid, which can leach metal cations [42-44]. However, this is a natural process occurring since ever, that is responsible for the enrichment of metals in water. Besides the mentioned bacteria, also the *Acidithiobacillus ferrooxidans* and the *Leptospirillum ferrooxidans* are frequently related to the bioleaching. The bioleaching processes, either direct or indirect, are mainly described based on the action of these three species. The direct process assumes the attachment of the bacteria to specific sites of the contaminated surface, where the sulfur oxidation takes place through several steps catalyzed by enzymes, resulting in the solubilization of the metal due to electrochemical interactions [45-47]. On the other hand, during the indirect bioleaching the bacteria produce a lixiviate that will oxidize the sulfide minerals or will promote acidic conditions that favors metal solubilization [45]. Chapter 5 of this document will focus the indirect mechanism of sulfur oxidation by *Acidithiobacillus thiooxidans,* to remove Cr(VI) from soils. Therefore, other abilities of these bacteria were explored, as the reduction of Cr(VI) has to occur in order to leach Cr(III), since metal cations are very mobile in acidic media, in opposition to Cr(VI) anions.

3.1.2. Biosorption

Biosorption is widely known for being a cheap technique of decontamination: it can reduce total treatment costs by 28%, compared with conventional systems. Therefore, the application of this technique has attracted growing attention from the scientific community [48]. This type of bioremediation relies on sorption mechanisms like ion exchange, chelating, adsorption and diffusion through cell walls and membranes of microorganisms or other type of biomass, being therefore of great use in decontaminating heavy metal contaminated sites. During this bioremediation process metals are not destroyed by microorganisms, suffering instead changes on their chemical properties. It is accepted that van der Waals forces, covalent bonding, redox interactions, and extracellular precipitation, or their combination, are the mechanisms associated to the entrapment of the metals by the biomass [49,50]. Several studies have been made on the interactions between biomass and heavy metals, on the mathematical description of the kinetics and equilibrium of the processes and also on the optimization and scale up of the biosorption technique. However, all of them concern wastewater or liquid effluents and no applications are found in soils. [50-55]. Therefore, a novel application of this technique on the decontamination of soils, passing through the use of permeable reactive biobarriers (BIO-PRB) will be approached in the Chapter 7 of this thesis. The BIO-PRBs are composed by reactive biological materials that once in contact with the contaminated water plume, degrade, adsorb or precipitate the targeted contaminant(s) [56,57]. During this work, a culture of the *Arthrobacter viscosus* bacterium, supported either on activated carbon (GAC) or zeolite, was tested in a BIO-PRB as a downstream treatment of an electrokinetic (EK) cell, containing soil contaminated with Cr(VI).

3.2. Soil washing

Soil washing pretends, essentially, to separate the smaller-grained and most reactive soil material, where the great fraction of contaminants is adsorbed, from the larger-grained soil, using water. However, chelants, complexing agents and detergents are nowadays used, in order to improve the process efficiency. By using these substances, most of the contaminants can be readily transferred to the liquid phase, avoiding downstream treatments [58]. It can be therefore deduced that soil washing is an *ex situ* technique comprising more than one step and several operation units, which were greatly investigated [59,60]. Soil washing of heavy metal contaminated soils can have physical or chemical nature. The physical separation consists, essentially, in the reduction of the metal concentration, exploiting differences between the contaminant and the soil properties. On the other hand, the chemical extraction, which will be here in approached with more detail in Chapter 6, relies on the utilization of acids or chelating agents in order to solubilize the heavy metals. Several complexing/chelating agents have been successfully used in the treatment of single and mixed contaminated sites, with EDTA standing out for the heavy metals effects attenuation, along with other acids and detergents [61-67]. Soil washing has been catalogued as a relatively cheap technique that can be greatly controlled due to its *ex situ* character, but also as a risky technique as some of the chemical "washers" may bring hazardous effects to the environment. Moreover, factors such complexity of the mixture, humic acid content and the particle size distribution of soil material may influence negatively the yield of the process.

3.3. Electrokinetics

Electrokinetic remediation is an *in situ* technology that consists of the controlled application of low intensity direct current through the soil between appropriately distributed electrodes. The removal of heavy metals and organic compounds from soils by the electric field action has been widely studied in the last decade [68-71]. The main transport mechanisms are electromigration, migration of ions towards the opposite charged electrode and electro-osmosis, movement of liquid through the soil matrix relative to the charged particles. Thus, this technique promotes the electromigration of the metal ions to the electrode of opposite charge and the movement of organic compound (usually uncharged species) with the electro-osmotic flow. However, there are some problems concerning this method, like its elongation in time and the production of liquid effluents. As already mentioned, a hybrid decontamination method, complying this technique and a specific application of biosorption, the BIO-PRBs, was applied to a Cr(VI) contaminated soil during the research work. Therefore, a clear and more detailed description of the specific EK technique here in approached is presented at Chapter 7.

SCOPES AND AIMS

The present thesis aims to explore the behavior and fate of two of the most problematic heavy metals polluting soils worldwide, namely lead [Pb] and chromium [Cr]. In order to do that, few scenarios of contamination were explored by performing batch and flow tests that allowed the study of sorption and transport phenomena of the two metals. These particular studies were performed with a soil collected on the north of Portugal, near some agriculture fields, as this kind of data is lacking on the national panorama. Actually, Portugal is the country that less contributes to the European environment assessment, predicted by the *Thematic Strategy for Soil Protection* [9]. Besides these studies, and as the decontamination and attenuation of pollution is the great focus of actual studies on environmental soil science, three remediation techniques were used or developed during this research work. An agreement between the soil and the cleaning technique was obtained considering the type and level of contamination of the targeted soil and the novelty of the method. Therefore, bioleaching was tested in the decontamination of a soil artificially contaminated with Cr(VI), as this contaminant can be reduced to a less hazardous form and then be leached. Because good data was previously obtained on the transport and fate of the Cr(VI) with the soil collected at the north of Portugal, this was the selected soil for the bioleaching tests. The soil chemical washing was applied to decontaminate a historically contaminated soil, collected in Algeria, with a huge charge of Pb. Finally, and due to the novelty of the technique, a clay mineral very abundant in soils - kaolinite -was used as soil sample for the tests concerning the hybrid technique, which comprises EK cells and BIO-PRBs, in the removal of Cr(VI). In sum, this work aims to contribute for the clear description of the fate of heavy metals in Portuguese soils, the applicability of known techniques on the soil cleaning, but also and most importantly, to the development of new remediation techniques.

In order to expose the development of the research work, and the consequent accomplishment of the mentioned objectives, the thesis was outlined based on the author's original articles, as shown in the following subsection.

THESIS OUTLINE

CHAPTER 1: Soils, Heavy Metals and Remediation Technologies

[State of the Art, Scopus and Aims]

CHAPTER 2: Retention of Cr(VI) and Pb(II) on a loamy sand soil: Kinetics, equilibria and breakthrough

[Adapted from: *Chemical Engineering Journal* (2009) **152**: 212-219]

CHAPTER 3: Modelling of the Cr(VI) transport in typical soils of the North of Portugal

[Adapted from: *Journal of Hazardous Materials* (2009) **167**: 756-762]

CHAPTER 4: Mobility of Cr, Pb, Cd, Cu and Zn in a Loamy Sand Soil: a comparative study

[Adapted from: *Geoderma* (2011) Submitted]

CHAPTER 5: A combined remediation technology for the reduction and bioleaching of hexavalent chromium from soils using *Acidithiobacillus thiooxidans*

[Adapted from: *Journal of Biotechnology* (2011) Submitted]

CHAPTER 6: Desorption kinetics of phenanthrene and lead from historically contaminated soil

[Adapted from: *Chemical Engineering Journal* (2011) **167**: 84-90]

CHAPTER 7: An innovative hybrid technology - electrokinetic and biobarriers - applied to hexavalent chromium contaminated clays

[Adapted from: *Chemosphere* (2011) Submitted]

CHAPTER 8: Conclusions and perspectives

REFERENCES

[1] Chesworth, W. (2008) Encyclopedia of soil science, Springer, Dordrecht, The Netherlands.

[2] Brevik, E.C., Hartemink, A.E. (2010) Early soil knowledge and the birth and development of soil science, Catena 83, 23-33.

[3] Hartemink, A.E. (2009) The depiction of soil profiles since the late 1700s, Catena 79, 113-127.

[4] Hartemink, A.E. (2002) Soil science in tropical and temperate regions - Some differences and similarities, Adv. Agron. 77, 269-292.

[5] Churchman, G.J. (2010) The philosophical status of soil science, Geoderma 157, 214-221.

[6] Nortcliff, S. (2009) The Soil: Nature, Sustainable Use, Management, and Protection An Overview, GAIA-Ecol. Perspect. Sci. Soc. 18, 58-68.

[7] Sposito, G. (1989) The chemistry of soils, Oxford University Press, Inc., New York.

[8] Sparks, D.L. (1995) Environmental Soil Chemistry, Academic Press, San Diego.

[9] European Comission (2006) Thematic Strategy for Soil Protection, COM(2006)231 final, European Comisson, Brussels.

[10] Juma, N.G. (1999) What is Soil?, in: Pedosphere and its dynamics, Salman Productions Inc., Alberta, Canada. 1-22.

[11] Bockheim, J.G., Gennadiyev, A.N., Hammer, R.D., Tandarich, J.P. (2005) Historical development of key concepts in pedology, Geoderma 124, 23-36.

[12] Phillips, J.D., Lorz, C. (2008) Origins and implications of soil layering, Earth Sci. Rev. 89, 144-155.

[13] FAO (1998) World reference base for soil resources, World Soil Resources Reports 84, Food and Agriculture Organization of the United Nations, Rome, Italy.

[14] Phillips, J.D. (2001) Contingency and generalization in pedology, as exemplified by texture-contrast soils, Geoderma 102, 347-370.

[15] Snakin, V.V., Prisyazhnaya, A.A., Kovács-Láng, E. (2001) Soil Liquid Phase Composition, Elsevier B.V., Amsterdam, Netherlands.

[16] FAO (2006) Guidelines for soil description, Food and Agriculture Organization of the United Nations, Rome, Italy.

[17] Hillel, D. (2011) Introduction to Environmental Soil Physics, Elsevier, Department of Plant and Soil Sciences, University of Massachusetts, U.S.A.

[18] Stevenson, F.J. (1994) Humus Chemistry, John Wiley & Sons, Inc., New Yor.

[19] Bradl, H.B. (2004) Adsorption of heavy metal ions on soils and soils constituents, J. Colloid Interf. Sci. 277, 1-18.

[20] Lindsay, W.L. (1979) Chemical equilibria in soils, John Wiley & Sons, New York.

[21] Stevenson, F.J., Cole, M.A. (1999) Cycles of soil, John Wiley & Sons, Inc., New York.

[22] Serrano, S., Garrido, F., Campbell, C.G., Garcia-Gonzalez, M.T. (2005) Competitive sorption of cadmium and lead in acid soils of Central Spain, Geoderma 124, 91-104.

[23] Ho, Y.S. (2006) Review of second-order models for adsorption systems, J. Hazard. Mater. 136, 681-689.

[24] Alloway, B.J. (1995) Heavy metals in soils, Blackie, Glasgow.

[25] Impellitteri, C.A., Allen, H.E., Yin, Y., You, S., Saxe, J.K. (2001) Heavy metals release in soils, in: H.M. Selim, D.L. Sparks (Eds.), Lewis Publisher, Boca Raton. 149-165.

[26] Toride, N., Leij, F.J., van Genuchten, M.T. (1995) The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments, 137, U.S. Salinity Laboratory, U.S. Department of Agriculture, Riverside, California.

[27] Simunek, J., van Genuchten, M.T. (1999) The STANMOD computer software for evaluating solute transport in porous media using analytical solutions of Convection-Dispersion Equation, U.S. Salinity Laboratory, U.S. Department of Agriculture, Riverside, California.

[28] van Genuchten, M.T. (1981) Non equilibrium transport parameters from miscible displacement experiments, 119, U.S. Salinity Laboratory, U.S. Department of Agriculture, Riverside, California.

[29] Eisler, R. (2000) Handbook of chemical risk assessment: health hazards to humans, plants, and animals, CRC Press LLC, Boca Raton.

[30] Mishra, S., Jena, S. (2009) Bioreduction based bioremediation of hexavalent chromium Cr (VI) through potential indigenous microbes, Department of Chemical Engineering, National Institute of Technology, Rourkela, Orissa, India.

[31] Fendorf, S.E. (1995) Surface reactions of chromium in soils and waters, Geoderma 67, 55-71.

[32] Unceta, N., Séby, F., Malherbe, J., Donard, O. (2010) Chromium speciation in solid matrices and regulation: a review, Anal. Bional. Chem. 397, 1097-1111.

[33] McLean, J.E., Biedsoe, B.E. (1992) Behavior of Metals in Soils, EPA/540/S-92/018, Environmental Protection Agency, United States of America.

[34] Cameron, R.E. (2009) Guide to Site and Soil Description for Hazardous Waste Site Characterization, EPA/600/4-91/029, Environmental Protection Agency, United States of America.

[35] Lee, S.Z., Chang, L., Yang, H.H., Chen, C.M., Liu, M.C. (1998) Adsorption characteristics of lead onto soils, J. Hazard. Mater. 63, 37-49.

[36] Mckenzie, R.M. (1980) Adsorption of lead and other heavy-metals on oxides of manganese and iron, Aust. J. Soil Res. 18, 61-73.

[37] http://www.eea.europa.eu/data-and-maps/figures/ds_resolveuid/112E68F9-176D-4BD9-BC5F-BEE075A38F93 24/6/08

[38] http://www.eea.europa.eu/data-and-maps/figures/ds_resolveuid/236B1246-03BA-431D-AD3A-6D3A62F14241 16/8/07

[39] Iwamoto, T., Nasu, M. (2001) Current bioremediation practice and perspective, J.of Biosci. Bioeng. 92, 1-8.

[40] Boopathy, R. (2000) Factors limiting bioremediation technologies, Bioresour. Technol. 74, 63-67.

[41] Watanabe, K. (2001) Microorganisms relevant to bioremediation, Curr. Opin. Biotechno. 12, 237-241.

[42] Liu, Y.G., Zhou, M., Zeng, G.M., Li, X., Xu, W.H., Fan, T. (2007) Effect of solids concentration on removal of heavy metals from mine tailings via bioleaching, J. Hazard. Mater. 141, 202-208.

[43] Bosecker, K. (1997) Bioleaching: metal solubilization by microorganisms, FEMS Microbiol. Rev. 20, 591-604.

[44] Gomez, C., Bosecker, K. (1999) Leaching Heavy Metals from Contaminated Soil by Using *Thiobacillus ferrooxidans* or *Thiobacillus thiooxidans*, Geomicrobiol. J. 16, 233-244.

[45] Chen, S.Y., Lin, P.L. (2010) Optimization of operating parameters for the metal bioleaching process of contaminated soil, Sep. Purif. Technol. 71, 178-185.

[46] Bennett, J.C., Tributsch, H. (1978) Bacterial leaching patterns on pyrite crystal surfaces, J.Bacteriol. 134, 310-317.

[47] Rodriguez-Leiva, M., Tributsch, H. (1988) Morphology of bacterial leaching patterns by *Thiobacillus ferrooxidans* on synthetic pyrite, Arch. Microbiol. 149, 401-405.

[48] Volesky, B. (2001) Detoxification of metal-bearing effluents: biosorption for the next century, Hydrometallurgy 59, 203-216.

[49] Gavrilescu, M. (2004) Removal of heavy metals from the environment by biosorption, Eng. Life Sci. 4, 219-232.

[50] Volesky, B. (2007) Biosorption and me, Water Res. 41, 4017-4029.

[51] Loukidou, M.X., Zouboulis, A.I., Karapantsios, T.D., Matis, K.A. (2004) Equilibrium and kinetic modeling of chromium(VI) biosorption by *Aeromonas caviae*, Colloids Surf. A: Physicochem.Eng.Asp. 242, 93-104.

[52] Chojnacka, K., Chojnacki, A., Górecka, H. (2005) Biosorption of Cr^{3+}, Cd^{2+} and Cu^{2+} ions by blue-green algae Spirulina sp.: kinetics, equilibrium and the mechanism of the process, Chemosphere 59, 75-84.

[53] Pagnanelli, F., Beolchini, F., Di Biase, A., Vegliò, F. (2003) Effect of equilibrium models in the simulation of heavy metal biosorption in single and two-stage UF/MF membrane reactor systems, Biochem. Eng. J. 15, 27-35.

[54] Singha, B., Das, S.K. (2011) Biosorption of Cr(VI) ions from aqueous solutions: Kinetics, equilibrium, thermodynamics and desorption studies, Colloids Surf. B: Biointerfaces 84, 221-232.

[55] Blázquez, G., Martín-Lara, M.A., Tenorio, G., Calero, M. (2011) Batch biosorption of lead(II) from aqueous solutions by olive tree pruning waste: Equilibrium, kinetics and thermodynamic study, Chem. Eng. J. 168, 170-177.

[56] Boni, M.R., Sbaffoni, S. (2009) The potential of compost-based biobarriers for Cr(VI) removal from contaminated groundwater: Column test, J. Hazrd. Mat. 166, 1087-1095.

[57] Viamajala, S., Peyton, B.M., Gerlach, R., Sivaswamy, V., Apel, W.A., Petersen, J.N. (2008) Permeable reactive biobarriers for in situ Cr(VI) reduction: Bench scale tests using Cellulomonas sp. strain ES6, Biotechnol. Bioeng. 101, 1150-1162.

[58] USEPA (2001) A Citizen's Guide to Soil Washing, EPA/542-F-01-008, Office of Solid Waste and Emergency Response, United States Environmental Protection Agency, Washington DC, USA.

[59] Semer, R., Reddy, K.R. (1996) Evaluation of soil washing process to remove mixed contaminants from a sandy loam, J. Hazard. Mater. 45, 45-57.

[60] Kuhlman, M.I., Greenfield, T.M. (1999) Simplified soil washing processes for a variety of soils, J. Hazard. Mater. 66, 31-45.

[61] Dermont, G., Bergeron, M., Mercier, G., Richer-Laflèche, M. (2008) Soil washing for metal removal: A review of physical/chemical technologies and field applications, J. Hazard. Mater. 152, 1-31.

[62] Abumaizar, R.J., Smith, E.H. (1999) Heavy metal contaminants removal by soil washing, J. Hazard. Mater. 70, 71-86.

[63] Zhang, W., Tsang, D.C.W., Lo, I.M.C. (2007) Removal of Pb and MDF from contaminated soils by EDTA- and SDS-enhanced washing, Chemosphere 66, 2025-2034.

[64] Isoyama, M., Wada, S.I. (2007) Remediation of Pb-contaminated soils by washing with hydrochloric acid and subsequent immobilization with calcite and allophanic soil, J. Hazard. Mater. 143, 636-642.

[65] Andrade, M.D., Prasher, S.O., Hendershot, W.H. (2007) Optimizing the molarity of a EDTA washing solution for saturated-soil remediation of trace metal contaminated soils, Environ. Pollut. 147, 781-790.

[66] Torres, L.G., Lopez, R.B., Beltran, M. (2011) Removal of As, Cd, Cu, Ni, Pb, and Zn from a highly contaminated industrial soil using surfactant enhanced soil washing, J. Phys. Chem. Earth doi:10.1016/j.pce.2011.02.003.

[67] Zhang, W., Huang, H., Tan, F., Wang, H., Qiu, R. (2010) Influence of EDTA washing on the species and mobility of heavy metals residual in soils, J. Hazard. Mater. 173, 369-376.

[68] Page, M.M., Page, C.L. (2002) Electroremediation of contaminated soils, J. Environ. Eng. Asce 128, 208-219.

[69] Teutli-León, Oropeza, M.T., González, I., Soria, A. (2005) Mathematical modeling of a galvanostatic soil electroremediation process, AIChE J. 51, 1822-1833.

[70] Baraud, F., Tellier, S., Astruc, M. (1997) Ion velocity in soil solution during electrokinetic remediation, J. Hazard. Mater. 56, 315-332.

[71] Sumbarda-Ramos, E., Guerrero-Gutierrez, O., Murillo-Rivera, B., González, I., Oropeza-Guzman, M. (2010) Electrokinetic treatment for clayed and sandy soils, J. Appl. Electrochem. 40, 1255-1261.

CHAPTER 2| Retention of Cr(VI) and Pb(II) on a loamy sand soil: Kinetics, equilibria and breakthrough

Adapted from: *B. Fonseca, H. Maio, C. Quintelas, A. Teixeira, T. Tavares*

Chemical Engineering Journal

2009

***152:** 212-219*

1. INTRODUCTION

Release of heavy metals into soils, as a result of anthropogenic activities like disposal of industrial effluents and spreading of sewage sludge, has raised the concentration of heavy metals in soils to toxic levels [1-3]. Therefore, the study of sorption processes is of utmost importance to understand how the contaminants are transferred from the liquid phase to the solid phase and retained therein [4,5]. Moreover the understanding of the contamination processes of this particular loamy sand soil is fundamental for the recovery of extensive polluted areas, as this type of soil is very common in industrialized regions.

Chromium and lead are among the most toxic heavy metals present in some industrial effluents, which are sometimes directly discharged in soils. Chromium has been widely used among various industries, such as metal plating and leather tanning. The most stable oxidation states of chromium commonly found in nature are Cr(III) and Cr(VI) [6-9]. While Cr(III) is essential for metabolic processes, Cr(VI) is toxic and carcinogenic. Moreover, as an oxyanion, is highly mobile in soil and water [10-12]. On the other hand, lead has a low mobility and is strongly retained by soil constituents. Lead occurs mainly as a divalent cation - Pb (II) - which, being not essential to plants or animals, is known to be hazardous to health [13,14]. Exogenous sources of lead in soil include fossil fuels, mining and smelting operations, and road runoff water [15,16].

The retention on soils of both metals is controlled mainly by redox reactions, precipitation, nucleation and adsorption/desorption processes [13,17]. These sorption processes are affected by many factors (e.g. organic matter, cationic exchange capacity, pH of soil). Many studies have focused on the sorption of chromium and lead under different experimental conditions, but always at the equilibrium pH of the soil and/or with low concentrations of those metals [1,18-21]. However, acid spills of high contaminated industrial effluents occur sporadically, and a different behaviour of those contaminants could be expected.

Therefore, the aim of this study is to evaluate the sorption processes of Cr(VI) and Pb(II) present in acid solutions highly concentrated. Specifically, batch equilibrium experiments to generate sorption isotherms and kinetic data using single metal solutions at initial pH of 2 and 5, were undertaken. In addition, to obtain better and more realistic means of evaluating soil performance at the tested pH values, column experiments were also performed. The retardation factor - R - was determined by the method used previously by the authors [22]. Batch tests data were analyzed and fitted by eight sorption isotherms - Freundlich, Langmuir, Dubinin-Radushkevich, Temkin, Redlich-Peterson, Khan, Sips and Toth - and three kinetic models - Lagergren, Elovich and Power Function Equation – since some of these models have been successfully used to predict and compare sorption performance of various soils and heavy metals [1-3,13,20,23,24].

FTIR spectra analyses performed on different samples of contaminated soils indicate that clays play an important role in the overall retention process and the presence of surface groups usually responsible for metal ions adsorption was confirmed

2. THEORY

2.1. Sorption kinetics

Lagergren's first-order rate equation is the oldest known one describing the adsorption rate based on the adsorption capacity. It assumes that the reaction rate is limited by only one process or mechanism on a single class of sorbing sites and that all sites are of the time dependent type [3,25]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}$$

Elovich's equation is useful to describe sorption reactions without desorption of products. The adsorption rate decreases with time due to the increased surface coverage [26]:

$$\frac{dq_t}{dt} = \alpha_E \exp(-\beta_E q_t) \tag{2}$$

In this study the power function equation was also used. Besides its empirical character, this equation provides a good method to compare experimental results [1,5]:

$$q_{\mathrm{t}} = k_{PF} t^{v_{\mathrm{PF}}} \tag{3}$$

In these equations 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_1 is the first order rate constant (h^{-1}); q_{e} is the amount of metal sorbed per unit mass of soil at equilibrium (mg kg^{-1}); α_{F} is the initial adsorption rate [mg kg^{-1} h^{-1}] and β is the desorption constant (kg mg^{-1}) of Elovich equation; k_{PF} (mg kg^{-1} h^{-v}) and v_{PF} are adjustment parameters of the power function equation.

2.2. *Equilibrium models*

Four isotherm models with two adjustable parameters and four models with three adjustable parameters were used to describe the experimental data:

2.2.1. *Two parameters isotherms*

Freundlich equation assumes that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation. It is described as:

$$q_{\mathrm{e}} = k_{\mathrm{F}} C_{\mathrm{e}}^{1/n} \tag{4}$$

where q_{e} is defined earlier, C_{e} is the concentration of metal in the solution at equilibrium (mg L^{-1}); k_{F} is the distribution coefficient (L$^{1/n}$ mg kg^{-1} mg $^{-1/n}$) and n is a correction factor [5,27].

A form of Langmuir isotherm is commonly applied to adsorption of heavy metal ions onto soil. It assumes that adsorption occurs until the solid surface is completely covered by a layer of molecules/atoms:

$$q_{\mathrm{e}} = \frac{q_{\max} b_{\mathrm{L}} C_{\mathrm{e}}}{1 + b_{\mathrm{L}} C_{\mathrm{e}}} \tag{5}$$

where $q_{\max}$ is the maximum amount of metal that can be adsorbed (mg kg^{-1}) and b_{L} is a constant related to the binding strength (L mg^{-1}) [5,28].

Dubinin-Radushkevich equation is used to describe systems where the dispersion forces are the dominant component of the adsorption interaction:

$$q_{\mathrm{e}} = q_D \exp\left[-B_D\left[RT\ln\left(1+\frac{1}{C_{\mathrm{e}}}\right)\right]^2\right] \tag{6}$$

where q_{D} is the maximum adsorption capacity (mg kg^{-1}); B_{D} is the activity coefficient (mol^2 J^{-2}) related to mean sorption energy - E - (J mol^{-1}), which may be calculated by [29-31]:

$$E = \frac{1}{\sqrt{2B_{\mathrm{D}}}} \tag{7}$$

The Temkin isotherm considers that the heat of adsorption of all the molecules on the layer decreases linearly with coverage:

$$q_e = \frac{RT}{b_{\mathrm{Te}}}\ln\left(a_{\mathrm{Te}}C_{\mathrm{e}}\right) \tag{8}$$

where R is the gas constant (J mol^{-1} K^{-1}), T is the absolute temperature (K), b_{Te} is the constant related to the heat of sorption (J mol^{-1}) and a_{Te} is the Temkin isotherm constant (L mg^{-1}) [30,32].

2.2.2. Three parameters isotherms

The Redlich Peterson equation was proposed to improve the fit by the Langmuir or the Freundlich equation:

$$q_e = \frac{k_{\mathrm{RP}} C_e}{1 + a_{\mathrm{RP}} {C_e}^{\beta_{\mathrm{RP}}}} \tag{9}$$

where k_{RP} is the Redlich - Peterson model isotherm constant (L kg^{-1}), a_{RP} is the model constant (L$^{\beta_{\mathrm{RP}}}$ mg$^{-\beta_{\mathrm{RP}}}$) and β_{RP} is the model exponent [33].

Khan proposed a simple expression for a generalized model for a single solute that can cover extreme cases of Langmuir and Freundlich type isotherms:

$$q_e = \frac{q_{\max} b_{\mathrm{K}} C_{\mathrm{e}}}{(1 + b_{\mathrm{K}} C_{\mathrm{e}})^{a_{\mathrm{K}}}} \tag{10}$$

where $q_{\max}$ was defined earlier, b_{K} is the Khan model constant (L mg^{-1}) and a_{K} is the model exponent [34].

The Sips equation predicts a monolayer sorption capacity for high sorbate concentrations and reduces to Freundlich equation for lower sorbate concentrations:

$$q_{\mathrm{e}} = \frac{k_{\mathrm{S}} {C_{\mathrm{e}}}^{\beta_{\mathrm{S}}}}{1 + a_{\mathrm{S}} {C_{\mathrm{e}}}^{\beta_{\mathrm{S}}}} \tag{11}$$

where k_{S} is the Sips model isotherm constant (mg L$^{\beta_{\mathrm{S}}}$ mg$^{-\beta_{\mathrm{S}}}$ kg^{-1}), a_{S} is the model constant (L$^{\beta_{\mathrm{S}}}$ mg$^{-\beta_{\mathrm{S}}}$) and β_{S} is the model exponent [30,35].

The Toth's model derived from the potential theory and applies to heterogeneous adsorption:

$$q_{\mathrm{e}} = \frac{q_{\max} C_{\mathrm{e}}}{\left(k_{\mathrm{T}} + {C_{\mathrm{e}}}^{n_{\mathrm{T}}}\right)^{1/n_{\mathrm{T}}}} \tag{12}$$

where k_T is the Toth model constant ($mg^{n_T}\ L^{-n_T}$) and n_T is the model exponent [30,36].

3. MATERIAL AND METHODS

3.1. Soil characterization

A bulk soil sample was collected in Póvoa de Varzim, Porto, Portugal at depth of 0 cm - 50 cm, near EN 13 road (41º25'15.58''N and 8º45'58.27''O). The soil was air-dried, homogenized and sifted through a 2.0 mm stainless steel sieve.

The Cr and Pb concentrations in soil were determined by flame atomic absorption spectrometry (Varian SpectraAA-400), after microwave (Aurora Instruments MW600) digestion with nitric acid using US EPA method 3051A [37]. Soil pH was determined with 1:1 soil/water suspension. Particle distribution was determined by laser granulometry (Beckman-Coulter mod. LS230), the cationic exchange capacity and exchangeable cations were quantified using ammonium acetate at pH 7 [38] and the Mehlich methods [39], respectively. Organic matter content was determined by the Tinsley method [40]. The major mineral composition was determined by X-ray diffraction analysis (Philips PW3710).

3.2. Batch experiments

Batch experiments with Cr and Pb were performed by adding 20 mL of single - metal solution, to 2 g of soil samples in 50 mL polypropylene tubes. Solutions with varying concentrations were prepared from $PbCl_2$ and $K_2Cr_2O_7$, in 0.01 M $CaCl_2$. The initial pH of each solution was adjusted to a desire value - 2 or 5 - by addition of concentrated HNO_3 (65%) and diluted NaOH (0.1M). The real concentration of each solution was determined by flame atomic absorption. The concentrations for both metals, varied from about 50 mg L^{-1} to 200 mg L^{-1}. Suspensions were agitated in an orbital mixer at room temperature for different contact lengths of time, at 100 rpm - (1, 2, 4, 8, 12, 16, 24 and 48 h) for the Pb solutions and (4, 8, 12, 24, 48, 96, 144, 192, 240 and 288 h) for the Cr solutions. After shaking, the solutions were centrifuged at 10000 rpm for 10 min. The supernatants were collected in eppendorfs with 2% ($^v/_v$) of HNO_3 after pH measuring, stored at 4 ºC and analyzed by flame atomic absorption spectrometry. Proper blanks, without the soil sample, and duplicates, were made for each solution concentration and time. The amount of metal adsorbed on the soil is calculated by:

$$q_{\mathrm{t}} = \frac{(C_{\mathrm{i}} - C_{\mathrm{e}})V}{W} \tag{13}$$

where C_e was defined earlier, C_i is the initial concentration of metal in the liquid phase, (mg L^{-1}); V is the volume of metal solution (L) and W is the weight of the soil sample (kg).

3.3. Column tests

For the continuous flow experiments, 160 g of soil were manually packed into a column of Perspex (25 cm × 3.2 cm) forming a soil bed with 17 cm and a porosity of about 0.32. Deionised water was initially passed at a slow and steady rate to saturate the column.

Then, 20 litters each of $PbCl_2$ and $K_2Cr_2O_7$ solutions were prepared with 50 mg L^{-1} of Pb or Cr, respectively. The pH was adjusted to values of 2 or 5, with HNO_3 and NaOH. The solutions were passed upwards through the columns via a peristaltic pump ($Q \approx 2.6$ mL min^{-1}) to ensure saturated flow conditions. Samples of the column effluent were collected, acidified after pH measurement, and analyzed by flame atomic absorption spectrometry. All experiments were made in duplicate.

After the assays, soil beds were sliced in three samples that were properly homogenized. Then, a sample was digested, with nitric acid, in microwave, according US EPA method 3051A [37] and analyzed by flame atomic absorption spectrometry. Soil samples were also characterized, in duplicate, with transmission FTIR (*BOMEM MB104)* on KBr pressed pellets. Background correction for atmospheric air was used for each spectrum. The resolution was 4 cm^{-1} with minimum of 10 scans for each spectrum and the range was 500 - 4000 wavenumbers. Spectra were analyzed by comparing the absorption bands of the samples with known absorption frequencies for different types of bonds.

4. RESULTS AND DISCUSSION

4.1. Soil characterization

Table 2.1 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 cationic exchange capacity is low. The predominance in the clay minerals belongs to kaolinite, followed by illite, smectite and interstratified material.

Table 2.1. Chemical and physical properties of the soil collected at Póvoa de Varzim, Portugal

Texture (%)		Heavy metals concentration/ (mmol kg^{-1})	
Clay	2.58	[Cr]	0.17
Silt	23.06	[Pb]	0.58
Sand	74.36	[Zn]	4.21
pH (H_2O)	5.9	[Cd]	0.01
CEC/ ($cmol_c$ kg^{-1})	12.52	[Cu]	0.54
OMC/ (%)	3.5	$CaCO_3$/(mg kg^{-1})	
EC/ ($cmol_c$ kg^{-1})		Clay Minerals (%)	
[Ca^{2+}]	7.20	Kaolinite	41
[Mg^{2+}]	0. 81	Illite	31
[K^+]	0. 37	Esmectite	18
[Na^+]	0. 52	Interstratified	10
Apparent Density		[PO_4^{3-}]/(mg kg^{-1})	7.2 ± 0.8
ρ_b/(kg m^{-3})	1320		

4.2. Batch experiments

4.2.1. Sorption kinetics

Table 2.2 shows the adjusted parameters of the kinetic equations for experiments with Cr. According to the correlation coefficient values *(r^2)*, better adjustment was achieved with the empirical power function, represented in Figure 2.1 a) and Figure 2.1 b) for each data set. The initial concentration did affect the estimated apparent sorption rate (ν_{PF}), which increases with the initial metal concentration in liquid phase (Table 2.2). This is indicative that the rate limiting factor is affected by metal initial concentration [41]. Figure 2.1 a) and Figure 2.1 b) shows that for similar initial concentrations of Cr, lower values of metal adsorbed per mass of soil were obtained for pH 5. Actually, the rate constants of the empirical power function are smaller than those obtained at pH 2 (Table 2.2). According to Impellitteri [42], soil with pH-dependent charge tends to deprotonate with increasing pH. However, Cr adsorption is favored if surfaces are positively charged, increasing with reduced pH, since the most common species are in the anionic form ($\mathrm{HCrO_4^-, CrO_4^{2-}, Cr_2O_7^{2-}}$). This may explain the higher rate constants values for pH 2 [10]. In fact, the pH of the liquid phase tends to increase along the batch experiments revealing the protonation of soil surface.

The correlation coefficients obtained for the adjustment of the Elovich equation to Cr adsorption kinetics revealed a good fitting (Table 2.2). In fact, the graphs of Figure 2.1 a) and Figure 2.1 b) show the typical behavior described by this model. There is a high rate adsorption at the beginning which decreases along time [43]. The initial higher rate of metal sorption has been attributed to adsorption on high affinity surface sites or on sites with higher bonding strength with the metal. Once these sites are exhausted, the uptake may be controlled by diffusion, precipitation and/or sorption reactions on sites with higher activation energy [44].

During the assays on Pb, with the initial solutions at pH 5, precipitation was noticed. In fact, in Figure 2.1 d) it is obvious that the whole Pb was retained in the solid phase. On the other hand, at pH 2, the adsorption occurs rapidly, Figure 2.1 c). Consequently, the tested models did not adjust the adsorption kinetics of Pb in the same conditions tested for Cr.

Table 2.2. Parameters and correlation coefficients (r^2) of the kinetic equations adjusted to experimental data with initial solution of chromium at pH 2 and pH 5. The CI column respects to the parameters interval for a confidence level of 95%

pH	C_i	Pseudo first-order			Elovich model				
		k_1	*CI*	r^2	α_E	*CI*	β_E	*CI*	r^2
2	75	0.103	0.048	0.862	15.29	7.11	0.008	0.001	0.988
	92	0.052	0.024	0.989	12.13	1.90	0.006	0.000	0.992
	128	0.035	0.009	0.893	10.34	2.86	0.005	0.001	0.964
	154	0.030	0.010	0.908	9.02	2.46	0.005	0.001	0.963
	172	0.032	0.011	0.903	9.97	2.17	0.005	0.001	0.977
	189	0.025	0.008	0.913	8.17	2.19	0.005	0.001	0.960
	204	0.027	0.007	0.939	7.93	2.80	0.006	0.002	0.931
5	78	0.010	0.008	0.806	5.73	3.12	0.011	0.004	0.849
	98	0.008	0.001	0.963	4.50	1.54	0.008	0.003	0.892
	131	0.006	0.002	0.652	6.95	5.65	0.011	0.006	0.826

pH	C_i	Empirical power function				
		k_{PF}	*CI*	v_{PF}	*CI*	r^2
2	75	217.6	66.2	0.226	0.061	0.893
	92	185.7	36.6	0.285	0.039	0.989
	128	146.4	30.1	0.354	0.040	0.993
	154	115.6	36.1	0.377	0.061	0.987
	172	142.5	28.0	0.364	0.038	0.994
	189	94.3	35.4	0.405	0.073	0.985
	204	78.6	22.8	0.435	0.056	0.991
5	78	36.1	32.6	0.461	0.174	0.935
	98	13.7	11.8	0.663	0.161	0.979
	131	53.8	69.6	0.388	0.247	0.880

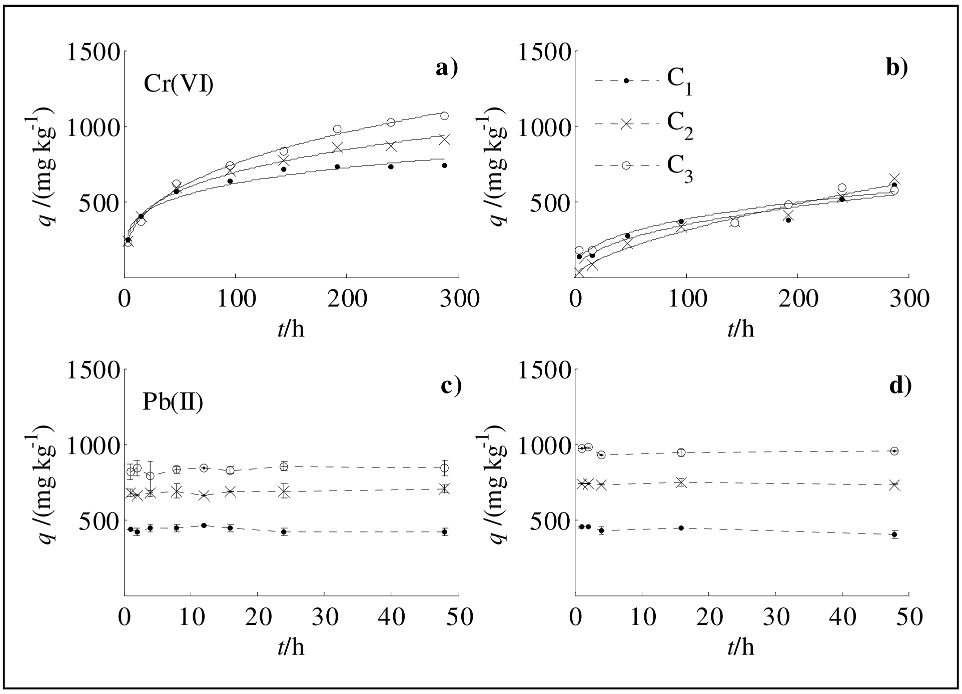


Figure 2.1. a) b) Variation of mass o Cr(VI) adsorbed per mass of soil, for different initial solutions, at pH 2 and pH 5 respectively (C_1=75 mg L^{-1};C_2=92 mg L^{-1};C_3= 128 mg L^{-1}) . Lines represent the empirical power function, adjusted to each kinetic data; c) d) Variation of mass o Pb(II) adsorbed per mass of soil for different initial solutions, at pH 2 and pH 5 respectively (C_1=78 mg L^{-1};C_2=98 mg L^{-1};C_3= 131 mg L^{-1}). The error bars depict the confidence interval for a level of confidence of 95%.

4.2.2. Equilibrium models

Once more it was not possible to obtain a good fitting with any of the tested isotherm models in the case of Pb adsorption at pH 5. Therefore, Table 2.3 shows the results obtained with initial solutions of both metals at pH 2. An overall analysis reveals that almost all isotherm equations fit better the experimental data obtained in batch test with Pb, compared to Cr. Besides, among the two parameters models, Langmuir equation presents the best fitting for Pb (Figure 2.2), meaning that these cations are strongly adsorbed as a monolayer covering the solid surface. According to this model, Cr shows more affinity to this soil, since the parameter b_L found is higher. However, the tested soil showed a higher maximum adsorption capacity - q_{max} - for Pb, as it can be seen in Table 2.3. This can be explained by the hard - soft acid - base principle. The sorption capacity increases with increasing polarizability and ionic radii and decreasing electronegativity, thus decreasing hardness [45]. According to Ghosh and Biswas [46], the global hardness of Pb is lower than the global hardness of Cr, explaining the lower value of the Langmuir constant - $q_{\max}$ - founded for this metal. For Cr, the best fit was obtained with the Dubinin-Radushkevich equation (Figure 2.2) and the value obtained for the mean energy sorption is lower than 8 kJ mol^{-1}, which indicates that adsorption is mainly physical due to weak Van der Waals forces [47].

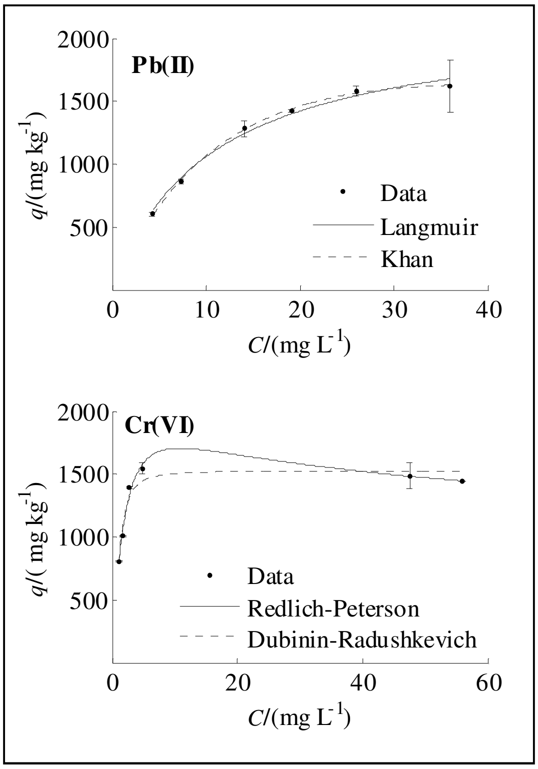


Figure 2.2. Sorption isotherms obtained for Cr(VI) and Pb(II) for high equilibrium concentrations. Two parameters models are represented by solid lines and three parameters models by the dash lines. The error bars depict the confidence interval for a level of confidence of 95%.

From the three-parameter models fitting, the best correlation coefficients were found for Redlich-Peterson isotherm applied to Cr adsorption and for Khan equation applied to Pb(II) adsorption (Table 2.3). Redlich-Peterson and Khan equations, properly represented in Figure 2.2, covers Langmuir and Freundlich isotherms, suggesting the existence of a monolayer strongly adsorbed on the solid surfaces, and, eventually, one or more layers weakly adsorbed due to distance to soil surface [28,30,34].

Table 2.3. Isotherms constants and correlation coefficients (r^2) obtained for the two and three parameter models, for Cr(VI) and Pb(II) sorption onto soil, for initial pH of 2. Confidence intervals - *CI* - determined for a 95% confidence level

			Cr(VI)	Pb(II)
Two Parameter Models	Freundlich	k_F	1078	387.1
		CI	409	202.5
		n_F	11.33	2.38
		CI	17.46	0.96
		r^2	0.460	0.940
	Langmuir	q_{max}	1570	2168
		CI	304	255
		b_L	1.32	0.095
		CI	1.36	0.030
		r^2	0.783	0.990
	Dubinin-Radushkevich	q_D	1525	1563
		CI	96	200
		B_D	2.55E-7	4.46E-6
		CI	-	2.39E-6
		E	1400	335
		r^2	0.933	0.929
	Temkin	a_{Te}	4443	0.785
		CI	6.448E4	0.366
		b_{Te}	19.84	4.855
		CI	27.78	0.901
		r^2	0.496	0.982

			Cr(VI)	Pb(II)
Three Parameter Models	Redlich-Peterson	k_{RP}	975	1584
		CI	271	29
		a_{RP}	0.304	0.025
		CI	0.197	0.027
		β_{RP}	1.191	1.285
		CI	0.100	0.247
		r^2	0.987	0.998
	Khan	q_{max}	3306	6087
		CI	1334	5365
		a_K	1.262	0.028
		CI	0.190	0.028
		b_K	0.327	1.904
		CI	0.220	1.230
		r^2	0.985	0.999
	Sips	k_S	1199	125.6
		CI	1000	98.9
		a_S	0.796	0.067
		CI	0.662	0.044
		β_S	2.360	1.307
		CI	2.183	0.465
		r^2	0.949	0.996
	Toth	q_{max}	1496	1786
		CI	134	258
		k_T	23.44	66.35
		CI	128.15	152.86
		n_T	4.05	1.69
		CI	5.90	0.86
		r^2	0.970	0.997

4.3. Column Tests

Variations of Cr and Pb concentration in the effluents [C/(mg L^{-1})] relative to the influent [C_i/(mg L^{-1})] are shown as breakthrough curves (C/C_i *vs* t) in Fig. 3. As it was mentioned before the Cr oxyanions ($HCrO_4^-$,CrO_4^{2-},$Cr_2O_7^{2-}$) are weakly sorbed by soils under alkaline to slightly acidic conditions leading to high mobility in the subsurface [11]. Thus, Cr appears in higher concentrations in the leachate of the column fed with dichromate solution at pH 5, Figure 2.3 a).

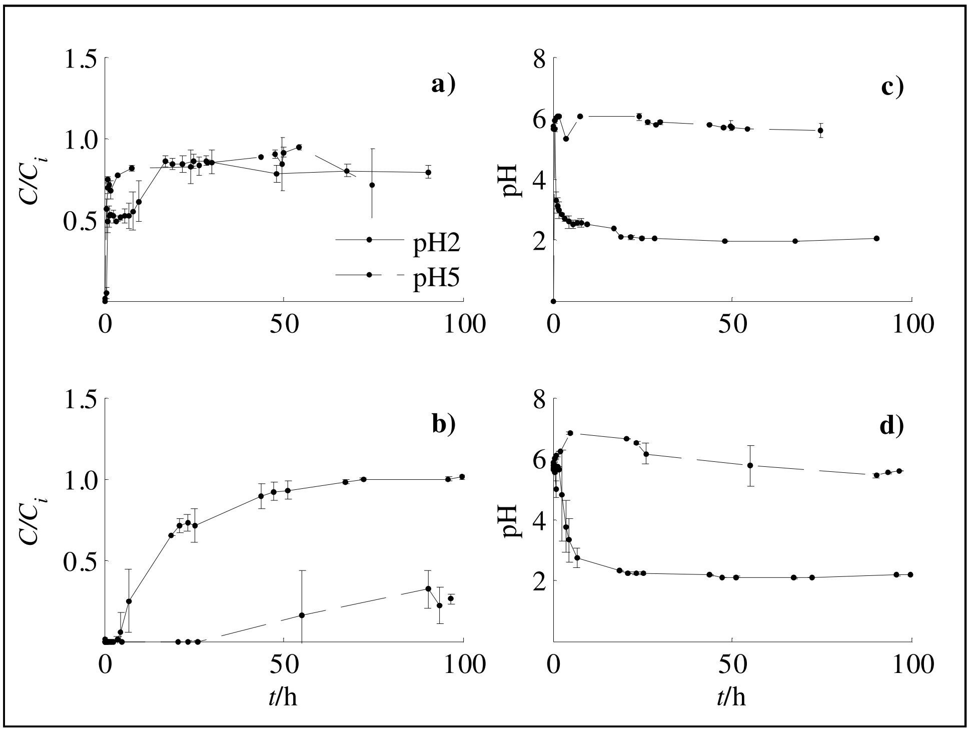


Figure 2.3. a) Effect of influent pH on the Cr(VI) breakthrough curves; b) Effect of influent pH on the Pb(II) breakthrough curves ($C_i \approx 50$ mg L^{-1}); c) Variation of the pH on Cr(VI) effluents d) Variation of the pH on Pb(II) effluents.

As it can be seen in Figure 2.3 c), pH values of the column fed with Cr solution at pH 2 decreased fast. This may be due to the high concentration of protons in this influent that are rapidly sorbed by soil, which has a low buffering capacity, implying a large number of positively charged sites that can retain Cr oxyanions [22]. On the other hand, the lowest concentration of protons in the influent at pH 5 leads to a slower protonation of the solid surfaces. However, these differences can also result from Cr(VI) reduction to Cr(III) that is less mobile due its stronger adsorption and complexation. Other researchers [48,49] showed that organic compounds do not directly reduce Cr(VI) at pH values greater than 2, which can explain the higher retention of Cr in the soil column at pH 2, as it can be seen in Figure 2.4 by the higher values of metal concentration in the three soil bed sections. Also, the determination of the retardation factor, by the method used elsewhere by the authors [22], confirmed the higher retention of Cr at pH 2, Table 2.4.

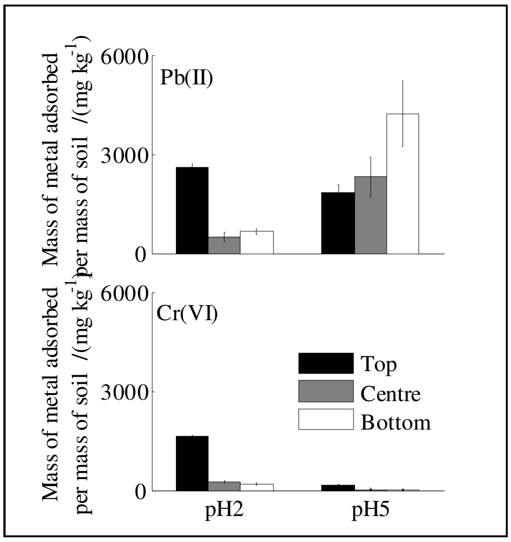


Figure 2.4. Mass of metal retained per mass of soil in three different zones of the soil bed, for column test with Pb and Cr. The error bars depict the confidence interval for a level of confidence of 95%.

Table 2.4. Retardation factors determined for the tested metals and pH values

C_0/(mg/L)	Influent pH	R
47	2	27
	5	23
54	2	18
	5	339

The breakthrough curve shown in Figure 2.3 b) for the assay with Pb influent at pH 5, indicates that no saturation occurred in this column. On the other hand, at pH 2, Pb showed higher mobility. In fact, the retardation factor obtained for this influent is about 19 times higher than the retardation factor obtained for the influent at pH 2 containing the same concentration of Pb (Table 2.4). This behavior is due to the high pH values of the effluent along the experiment at pH 5, as it can be seen in Figure 2.3 d), which promotes the Pb precipitation. Accordingly, Figure 2.4 shows a higher retention at the bottom of the column where the influent is feed, for the tests at pH 5, implying a promptly high immobilization. In contrast, the effluent pH along the experiment at pH 2 tends to decrease due to the already mentioned lower buffering capacity of the soil, avoiding precipitation phenomena.

4.4. FTIR spectral analysis

Figure 2.5 shows the FTIR spectra of the soil samples of the bottom, centre and top of the columns bed after the sorption tests with the influent at pH 2 and of an uncontaminated soil sample. Clay minerals represented by the SiO-H stretch at 3695 cm^{-1}, 3620 cm^{-1}, Si-O-Si stretch at 1030 cm^{-1} and a small weak band at 694 cm^{-1} appear to play an important role in the sorption process of both metals, especially of Pb, since these bands tend to overlap for the contaminated samples [5,50,51]. In fact, heavy metals are sorbed by a variety of soil phases with hydroxyl groups on their surfaces and edges including the clay minerals, where sorption reactions are often more rapid.

FTIR spectra of the soil used in Pb experiment shows a variation of O-H bend of adsorbed water (~1635 cm^{-1}), suggesting the formation of $PbOH^+$ in the surface. The soil sample contains some natural organic matter that greatly adsorbs trace metals resulting in the overlapping of the C-H stretch band (2920 cm^{-1}, 2850 cm^{-1}) in both spectrums. As already mentioned in previous sections, in the case of Cr this phenomenon can also result from the reduction of Cr(VI) to Cr(III) by natural organic matter [11,50,52,53].

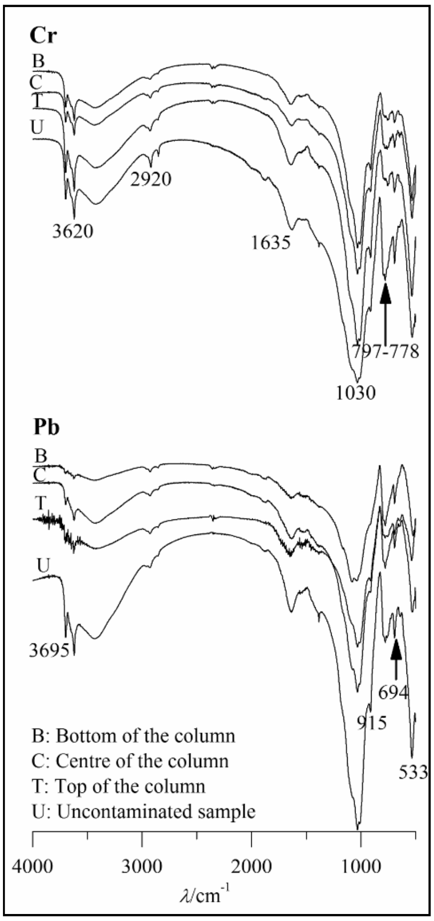


Figure 2.5. FTIR spectra of columns soil samples, before and after the flow experiments with Cr(VI) and Pb(II) influents at pH 2.

REFERENCES

[1] Serrano, S., Garrido, F., Campbell, C.G., Garcia-Gonzalez, M.T. (2005) Competitive sorption of cadmium and lead in acid soils of Central Spain, Geoderma 124, 91-104.

[2] Chaturvedi, P.K., Seth, C.S., Misra, V. (2006) Sorption kinetics and leachability of heavy metal from the contaminated soil amended with immobilizing agent (humus soil and hydroxyapatite), Chemosphere 64, 1109-1114.

[3] Covelo, E.F., Andrade, M.L., Vega, F.A. (2004) Heavy metal adsorption by humic umbrisols: selectivity sequences and competitive sorption kinetics, J. Colloid Interface Sci. 280, 1-8.

[4] Usman, A.R.A. (2008) The relative adsorption selectivities of Pb, Cu, Zn, Cd and Ni by soils developed on shale in New Valley, Egypt, Geoderma 144, 334-343.

[5] Sparks, D.L. (1995) Environmental Soil Chemistry, Academic Press, San Diego.

[6] Quintelas, C., Sousa, E., Silva, F., Neto, S., Tavares, T. (2006) Competitive biosorption of ortho-cresol, phenol, chlorophenol and chromium(VI) from aqueous solution by a bacterial biofilm supported on granular activated carbon, Process. Biochem. 41, 2087-2091.

[7] Jiang, J., Xu, R., Wang, Y., Zhao, A. (2008) The mechanism of chromate sorption by three variable charge soils, Chemosphere 71, 1469-1475.

[8] Fendorf, S.E. (1995) Surface reactions of chromium in soils and waters, Geoderma 67, 55-71.

[9] Lee, S.Z., Chang, L.Z., Chen, C.M., Yang, H.H., Hu, P.Y. (2001) The effect of hydration on adsorption and desorption of heavy metals in soils, J. Environ. Sci. Health, Part A 36, 63-74.

[10] Pantsar-Kallio, M., Reinikainen, S.P., Oksanen, M. (2001) Interactions of soil components and their effects on speciation of chromium in soils, Anal. Chim. Acta 439, 9-17.

[11] Wittbrodt, P.R., Palmer, C.D. (1995) Reduction of Cr(VI) in the presence of excess soil fulvic-acid, Environ. Sci. Technol. 29, 255-263.

[12] Narukawa, T., Riley, K.W., French, D.H., Chiba, K. (2007) Speciation of chromium in Australian fly ash, Talanta 73, 178-184.

[13] Martinez-Villegas, N., Flores-Velez, L.M., Dominguez, O. (2004) Sorption of lead in soil as a function of pH: a study case in Mexico, Chemosphere 57, 1537-1542.

[14] Srivastava, P., Singh, B., Angove, M. (2005) Competitive adsorption behavior of heavy metals on kaolinite, J. Colloid Interface Sci. 290, 28-38.

[15] Stevenson, F.J., Cole, M.A. (1999) Cycles of soil, John Wiley & Sons, Inc., New York.

[16] Barbosa, A.E., Hvitved-Jacobsen, T. (1999) Highway runoff and potential for removal of heavy metals in an infiltration pond in Portugal, Sci. Total Environ. 235, 151-159.

[17] Bradl, H.B. (2004) Adsorption of heavy metal ions on soils and soils constituents, J. Colloid Interface Sci. 277, 1-18.

[18] Hooda, P.S., Alloway, B.J. (1998) Cadmium and lead sorption behaviour of selected English and Indian soils, Geoderma 84, 121-134.

[19] Adhikari, T., Singh, M.V. (2003) Sorption characteristics of lead and cadmium in some soils of India, Geoderma 114, 81-92.

[20] Markiewiez-Patkowska, J., Hursthouse, A., Przybyla-Kij, H. (2005) The interaction of heavy metals with urban soils: sorption behaviour of Cd, Cu, Cr, Pb and Zn with a typical mixed brownfield deposit, Environ. Int. 31, 513-521.

[21] Yolcubal, I., Akyol, N.H. (2007) Retention and Transport of Hexavalent Chromium in Calcareous Karst Soils, Turk. J. Earth Sci. 16, 363-379.

[22] Fonseca, B., Teixeira, A., Figueiredo, H., Tavares, T. (2009) Modelling of the Cr(VI) transport in typical soils of the North of Portugal, J. Hazard. Mater. 167, 756-762.

[23] Bhattacharyya, K.G., Sen Gupta, S. (2007) Adsorptive accumulation of Cd(II), Co(II), Cu(II), Pb(II), and Ni(II) from water on montmorillonite: Influence of acid activation, J. Colloid Interface Sci. 310, 411-424.

[24] Echeverria, J.C., Morera, M.T., Mazkiaran, C., Garrido, J.J. (1998) Competitive sorption of heavy metal by soils. Isotherms and fractional factorial experiments, Environ. Pollut. 101, 275-284.

[25] Ho, Y.S. (2006) Review of second-order models for adsorption systems, J. Hazard. Mater. 136, 681-689.

[26] Gunay, A., Arslankaya, E., Tosun, I. (2007) Lead removal from aqueous solution by natural and pretreated clinoptilolite: Adsorption equilibrium and kinetics, J. Hazard. Mater. 146, 362-371.

[27] Freundlich, H. (1906) Concerning adsorption in solutions, Zeitschrift fur Physikalische Chemie--Stochiometrie und Verwandtschaftslehre 57, 385-470.

[28] Langmuir, I. (1918) The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40, 1361-1403.

[29] Dubinin, M.M. (1960) The potential theory of adsorption of gases and vapors for adsorbents with energetically nonuniform surfaces, Chem. Rev. 60, 235-241.

[30] Padmesh, T.V.N., Vijayaraghavan, K., Sekaran, G., Velan, M. (2006) Application of two-and three-parameter isotherm models: Biosorption of Acid Red 88 onto *Azolla microphylla*, Biorem. J. 10, 37-44.

[31] SarI, A., Tuzen, M. (2008) Biosorption of cadmium(II) from aqueous solution by red algae (Ceramium virgatum): Equilibrium, kinetic and thermodynamic studies, J. Hazard. Mater. 157, 448-454.

[32] Srihari, V., Das, A. (2008) Comparative studies on adsorptive removal of phenol by three agro-based carbons: Equilibrium and isotherm studies, Ecotoxicol. Environ. Saf. 71, 274-283.

[33] Aksu, Z. (2002) Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel(II) ions onto *Chlorella vulgaris*, Process. Biochem. 38, 89-99.

[34] Khan, A.R., Ataullah, R., AlHaddad, A. (1997) Equilibrium adsorption studies of some aromatic pollutants from dilute aqueous solutions on activated carbon at different temperatures, J. Colloid Interface Sci. 194, 154-165.

[35] Sips, R. (1948) On the structure of a catalyst surface, J. Chem. Phys. 16, 490-495.

[36] Toth, J. (1971) State Equations of Solid-Gas Interface Layers, Acta Chim. Academ. Sci. Hung. 69, 311-&.

[37] USEPA (2007) Microwave assisted acid digestion of sediments, sludges, soils, and oils, 3051, Environmental Protection Agency, United States of America.

[38] Hendershot, W.H., Lalande, H., Duquette, M. (1993) Ion exchange and exchangeable cations, in: M.R.Carter, E.G.Gregorich (Eds.), Soil Sampling and Methods of Analysis, 197-206.

[39] Mehlich, A. (1953) Rapid determination of cation and anion exchange properties and pH of soils, J. Assoc. Ana. Chem. 36, 445-457.

[40] Tinsley, J. (1950) The determination of organic carbon in soils by dichromate mixture, IV International Congress of Soil Science, IV International Congress of Soil Science , 161-164, IV International Congress of Soil Science.

[41] Chen, J.P., Wang, L. (2004) Characterization of metal adsorption kinetic properties in batch and fixed-bed reactors, Chemosphere 54, 397-404.

[42] Impellitteri, C.A., Allen, H.E., Yin, Y., You, S., Saxe, J.K. (2001) Heavy metals release in soils, in: H.M. Selim, D.L. Sparks (Eds.), Lewis Publisher, Boca Raton. 149-165.

[43] Teng, H., Hsieh, C.T. (1999) Activation energy for oxygen chemisorption oil carbon at low temperatures, Ind. Eng. Chem. Res. 38, 292-297.

[44] Strawn, D.G., Sparks, D.L. (2000) Effects of soil organic matter on the kinetics and mechanisms of Pb(II) sorption and desorption in soil, Soil Sci. Soc. Am. J. 64, 144-156.

[45] Liu, C.L., Chang, T.W., Wang, M.K., Huang, C.H. (2006) Transport of cadmium, nickel, and zinc in Taoyuan red soil using one-dimensional convective-dispersive model, Geoderma 131, 181-189.

[46] Ghosh, D.C., Biswas, R. (2003) Theoretical calculation of absolute radii of atoms and ions. Part 2. The ionic radii, Int. J. Mol. Sci. 4, 379-407.

[47] Bekci, Z., Seki, Y., Yurdakoc, M.K. (2006) Equilibrium studies for trimethoprim adsorption on montmorillonite KSF, J. Hazard. Mater. 133, 233-242.

[48] Connett, P.H., Wetterhahn, K.E. (1986) Reaction of chromium(VI) with thiols - pH-Dependence of chromium(VI) thio ester formation, J. Am. Chem. Soc. 108, 1842-1847.

[49] Anderson, L.D., Kent, D.B., Davis, J.A. (1994) Batch experiments characterizing the Reduction of Cr(VI) using suboxic material from a mildly reducing sand and gravel aquifer, Environ. Sci. Technol. 28, 178-185.

[50] Alvarez-Puebla, R.A., Valenzuela-Calahorro, C., Garrido, J.J. (2004) Modeling the adsorption and precipitation processes of Cu(II) on humin, J. Colloid Interface Sci. 277, 55-61.

[51] Smidt, E., Meissl, K. (2007) The applicability of Fourier transform infrared (FT-IR) spectroscopy in waste management, Waste Manage. 27, 268-276.

[52] Jardine, P.M., Fendorf, S.E., Mayes, M.A., Larsen, I.L., Brooks, S.C., Bailey, W.B. (1999) Fate and transport of hexavalent chromium in undisturbed heterogeneous soil, Environ. Sci. Technol. 33, 2939-2944.

[53] 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 62, 255-264.

CHAPTER 3| Modelling of the Cr(VI) transport in typical soils of the North of Portugal

Adapted from: *B. Fonseca, A. Teixeira, H. Figueiredo, T. Tavares*

Journal of Hazardous Materials

2009

167: *756-762*

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 concentration 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 presents 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. Retention 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, Porto, Portugal (41º25’15.58’’N and 8º45’58.27’’O), was used in this study. The soil was collected from the O-horizon and from the A-horizon (0 cm - 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 mod. LS230). Carbonate content was determined with a Scheibler calcimeter (Scheibler). Cationic exchange capacity was quantified using ammonium acetate at pH 7 [11]. The metals concentrations in soil were determined by flame atomic absorption spectrometry (Varian SpectraAA-400), after microwave (Aurora Instruments MW600) digestion with nitric acid using US EPA method 3051A [12]. Soil pH was determined with 1:1 soil/water suspension and organic matter content was determined by the Tinsley method [13]. These characteristics were already summarized in Table 2.1. Titration analyses were performed to assess the acid buffering capacities of the soil as described by Reddy *et al.* [14].

2.2. *Batch experiments*

To obtain sorption isotherms of Cr(VI), 2 g of soil samples were placed in 50 mL polypropylene tubes and equilibrated with 20 mL of 0.01 M $CaCl_2$ solution containing graded levels of hexavalent chromium concentration, i.e. 50, 75, 100, 125, 150, 175 and 200 mg L^{-1} as $K_2Cr_2O_7$ solution. Sorption sets were made for pH values of 2, 5 and 7, and each of them was duplicated. Blanks and quality control were also made. The soil suspensions were equilibrated for 240 h at room temperature (25 ºC) in an orbital mixer (Certomat® S), at 100 rpm. After shaking, the solutions were centrifuged at 5000 rpm for 5 min. The supernatant was collected in pre-acidified eppendorfs (2% HNO_3), after pH measuring, stored at 4 ºC and analyzed 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, 144, 192 and 240 h. The pseudo-first order equation was adjusted to kinetic data in order to determine the first order kinetic rate coefficient, k_1 (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, q_{max}, were obtained from the fitting. Table 3.1 summarizes the experimental conditions for all flow experiments.

Table 3.1. Experimental conditions of flow experiments

Influent pH	2	5	7	2	2
C_0 (mg L^{-1})	48.6	48.6	44.7	80.8	110
θ (m^3 m^{-3})	0.42	0.41	0.45	0.39	0.38
L (cm)	15.3	15.0	14.1	15.3	15.5
q (cm h^{-1})	20	20	18	20	20
ρ_b (kg m^{-3})	1300	1243	1322	1324	1293

Previously to the flow tests with the hexavalent chromium, a flow experiment using $CaCl_2$ (0.01M) as a tracer was also conducted to evaluate independently the average pore water velocity (v) 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 experience, a homogeneous sample of each column was digested [12] and analyzed by FAAS. 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. Spectra 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:

$$q_{\mathrm{e}} = k_{\mathrm{F}} C_{\mathrm{e}}^{\mathrm{n_F}} \tag{14}$$

Langmuir equation:

$$q_{\mathrm{e}} = \frac{\left(q_{\max} C_{\mathrm{e}} b_{\mathrm{L}}\right)}{\left(1 + b_{\mathrm{L}} C_{\mathrm{e}}\right)} \tag{15}$$

where q_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 (L$^{1/n}$ mg $^{(1-1/n)}$ kg^{-1}), n_F is the Freundlich exponent, q_{max} is the maximum adsorption of the metal (mg kg^{-1}) and b_L is the Langmuir equilibrium constant (L mg^{-1}) [16-18].

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

$$q_t = q_e\left[1-\exp(k_1 t)\right] \tag{16}$$

where q_t and q_e are the amount of metal sorbed in soil (mg kg^{-1}) at the equilibrium and at the time t (h), respectively, and k_1 is the first order kinetic rate coefficient (h^{-1}) [19].

2.5. Evaluation of transport and sorption parameters by the convection-dispersion equation (CDE)

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:

$$\frac{\partial C}{\partial t}+\frac{\rho}{\theta}\left(\frac{\partial q_1}{\partial t}+\frac{\partial q_2}{\partial t}\right)=D\frac{\partial^2 C}{\partial x^2}-v\frac{\partial C}{\partial x} \tag{17}$$

where C is the flux average or resident concentration (mg L^{-1}), ρ is the soil bulk density (kg m^{-3}), θ is the volumetric water content (m^3 m^{-3}), t is time (h), q_1 is the solid phase concentration on equilibrium sites (mg kg^{-1}), q_2 is the solid phase concentration on kinetic non-equilibrium sites (mg kg^{-1}), D is the dispersion coefficient (cm^2 h^{-1}), x is distance (cm) and v is the average pore water velocity (cm h^{-1}).

The non-equilibrium adsorption process is defined by:

$$\frac{\partial q_2}{\partial t} = k_1[(1-F)f(C)-q_2] \tag{18}$$

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]:

$$q_1 = Ff(C) \tag{19}$$

and

$$q_{2e} = (1-F)f(C) \tag{20}$$

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:

$$\beta R\frac{\partial C_1}{\partial T} = \frac{1}{P}\left(\frac{\partial^2 C_1}{\partial X^2}\right) - \frac{\partial C_1}{\partial X} - \omega(C_1 - C_2) \tag{21}$$

$$(1-\beta)R\frac{\partial C_2}{\partial T} = \omega(C_1 - C_2) \tag{22}$$

where the dimensionless parameters are defined as follows

$$C_1 = \frac{C}{C_0} \tag{23}$$

$$C_2 = \frac{q_2}{(1-F)k_{\mathrm{L}}C_0} \tag{24}$$

$$T = \frac{vt}{L} \tag{25}$$

$$X = \frac{x}{L} \tag{26}$$

$$R = 1 + \frac{\rho k_{\mathrm{L}}}{\theta} \tag{27}$$

$$P = \frac{vL}{D} \tag{28}$$

$$\beta = \frac{(\theta + F\rho k_{\mathrm{L}})}{(\theta + \rho k_{\mathrm{L}})} \tag{29}$$

$$\omega = \frac{k_1(1-\beta)RL}{v} \tag{30}$$

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; β is a partitioning coefficient, ω is a dimensionless mass transfer coefficient and k_{L} is the linear isotherm sorption coefficient [10,23]. To calculate the non linear adsorption parameters of Freundlich and Langmuir isotherm models it was assumed that [24]:

$$k_{\mathrm{L}} = k_{\mathrm{F}} n_F C^{n_F - 1} \tag{31}$$

or

$$k_{\mathrm{L}} = \frac{b_L q_{\max}}{(1 + b_L C)^2} \tag{32}$$

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]:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \tag{33}$$

The flow regime can then be characterized by applying the tracer Cl^- at the same flow rate as the contaminant influent.

3. RESULTS AND DISCUSSION

3.1. Batch Experiments

The Freundlich, Langmuir and linear isotherm models were fitted to the batch equilibrium data. However, the fitting of the linear model was always very poor ($0.0 < r^2 < 0.2$) and these results were discarded of discussion. Values of the Freundlich and Langmuir parameters and also of the pseudo-first order kinetics equation are listed on Table 3.2.

Table 3.2. Freundlich, Langmuir and pseudo-first order parameters of batch experiments

Influent pH	Freundlich isotherm parameters			Langmuir isotherm parameters			Pseudo-first order equation	
	k_F	n_F	r^2	q_{max}	b	r^2	k_1	r^2
2	62	0.36	0.965	452	0.03	0.930	0.003	0.757
5	58	0.34	0.584	389	0.03	0.509	0.003	0.929
7	28	0.47	0.715	431	0.01	0.650	0.002	0.882

Analyzing the Freundlich isotherm coefficient, k_F, it may be concluded that raising the liquid phase pH from 2 to 5 resulted in a moderate 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 (Figure 3.1). 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, q_{max}, is quite constant for the three batch equilibrium data sets (Table 3.2). 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_F, also the Langmuir parameter, b_L, remained practically constant, as expected since these parameters are constants of the models.

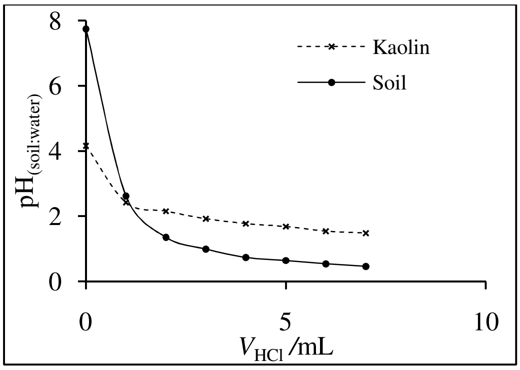


Figure 3.1. Buffering capacity test results.

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, k_1, show that adsorption occur rapidly at lower pH values, due to the protonation of soil surface as referred previously.

3.2. Flow experiments

3.2.1. Tracer experiments

The BTC curve obtained for the nonreactive tracer ($CaCl_2$) was fitted by Equation (33), using the CXTFIT code, Table 3.3. 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 3.1). This could be indicative that all the water is mobile.

Table 3.3. Physical parameters obtained by fitting the equilibrium CDE to the BTC of $CaCl_2$ tracer. TSM model parameters fitted to the BTC of the hexavalent chromium influents and isotherm models parameters

C_0/(mg L^{-1})	Influent pH	Physical parameters (R=1)			Two site adsorption model parameters				Freundlich	Langmuir	Pseudo-first order
		D	v	r^2	R	β	ω	r^2	k_F	q_{max}	k_1
47.3	2	15	16	0.992	27	0.05	0.03	0.837	280	1738	0.001
	5	49	22	0.994	23	0.04	0.02	0.938	284	1560	0.001
	7	32	18	0.993	2.2	0.46	0.20	0.952	7.1	85	0.217
80.8	2	15	14	0.991	30	0.03	0.03	0.980	280	1738	-
110	2	15	16	0.986	95	0.01	0.04	0.838	918	5697	-

3.2.2. Two-site non equilibrium model

The curves of the adjusted two-site adsorption model can be observed in Figure 3.2 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 3.3). A prior analysis of these results shows that sorption parameters, k_F and q_{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_F and b_L, were kept constant, since they did not vary significantly for batch tests experiments.

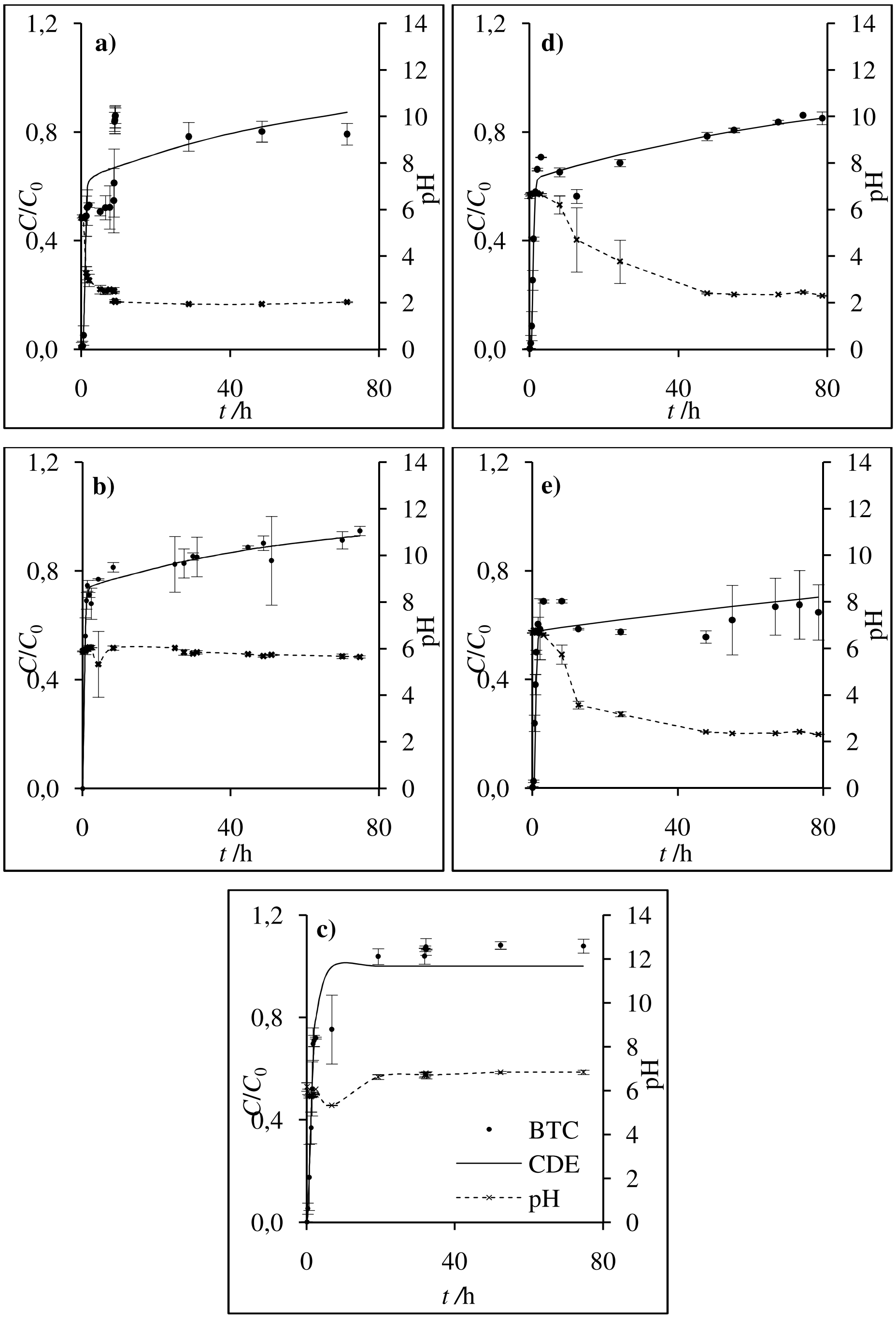


Figure 3.2. Experimental and fitted BTCs with the two-site model (TSM), for soil columns contaminated with different hexavalent chromium influents: a) C_0 = 50 mg L^{-1} and pH = 2; b) C_0 = 50 mg L^{-1} and pH = 5; c) C_0 = 50 mg L^{-1} and pH = 7; d) C_0 = 75 mg L^{-1} and pH = 2; e) C_0 = 100 mg L^{-1} and pH = 2.

3.2.3. Effects of initial solution pH

A decrease in the retardation factor (Table 3.3) and in the total mass of metal retained per mass of soil (Figure 3.3) 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].

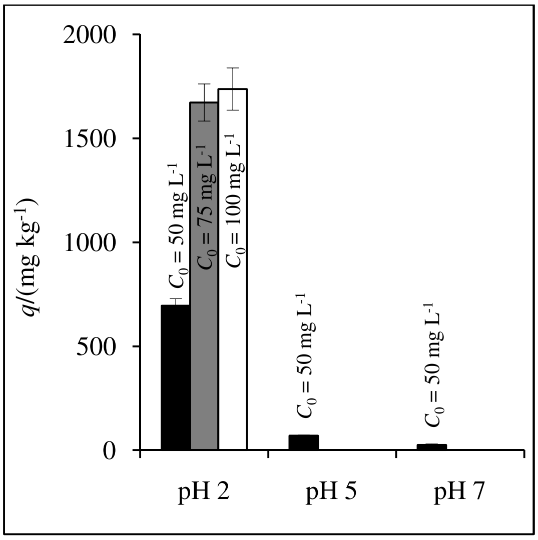


Figure 3.3. Mass of chromium adsorbed per mass of soil during the contamination with influents with 50 mg L^{-1} of concentration and different pH values – 2, 5 and 7 – and with influents at pH 2 with different concentrations – 50, 75, 100 mg L^{-1}.

Despite of the above considerations, a notable decrease of the retardation factor, *R*, and of the sorption parameters was observed when the pH was raised to 7, a value very close to the pK_{a2} (6.49) of the chromic acid (CrO_4^-/CrO_4^{2-}) [31]. The adsorption of anions of polyprotic conjugate acids decreases with increased pH, with a more pronounced decrease above the pK_{a2}, explaining the drastic decrease of the retardation factor for pH 7. For pH values higher than pK_{a2} the predominant specie is CrO_4^{2-}, 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 CrO_4^{2-} for the positive charged sites may explain the large decrease of the retardation factor [26,32]. On the other hand, at low pH values $HCrO^{4-}$ 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 3.3. 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 Figure 3.2 e) 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 *et al.* [33] reported similar results with cadmium [Cd(II)], verifying that adsorption increased with the increase in soil/solution ratio. Aksu [34] also found the same behavior in the biosorption of Ni(II), and attributed the phenomenon to the diminution of the mass transfer resistance between the aqueous and solid phase. In fact, the mass transfer coefficient, ω, also increased (Table 3.3), maybe due to diffusivity of the chromium adsorbed onto clay minerals and metal oxides into the lattice structures of these minerals. Then, hexavalent chromium becomes strongly fixed into the pore spaces, not being easily desorbed to the liquid phase [26]. Figure 3.3 shows no big difference between the mass of metal retained per mass of soil, in the columns contaminated with the highest concentrated solutions. Although it confirms that the retention in the assay with the influent with 100 mg L^{-1} of chromium was elevated.

In opposition to the results obtained by Miretzky *et al.* [35] with Zn(II) in similar conditions, the BTC does not shift to the left when the concentration of the influent solution increases. Which means that breakthrough occurs at the same time for all the tested concentrations. Therefore, and since break occurs very rapidly in all the cases, adsorption is mainly controlled by mass transfer in the columns contaminated with the influents at pH 2 [36].

3.2.5. FTIR spectral analysis

Figure 3.4 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 Figure 3.3 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 (~1635 cm^{-1}), for pH 2 and 5 [27,38].

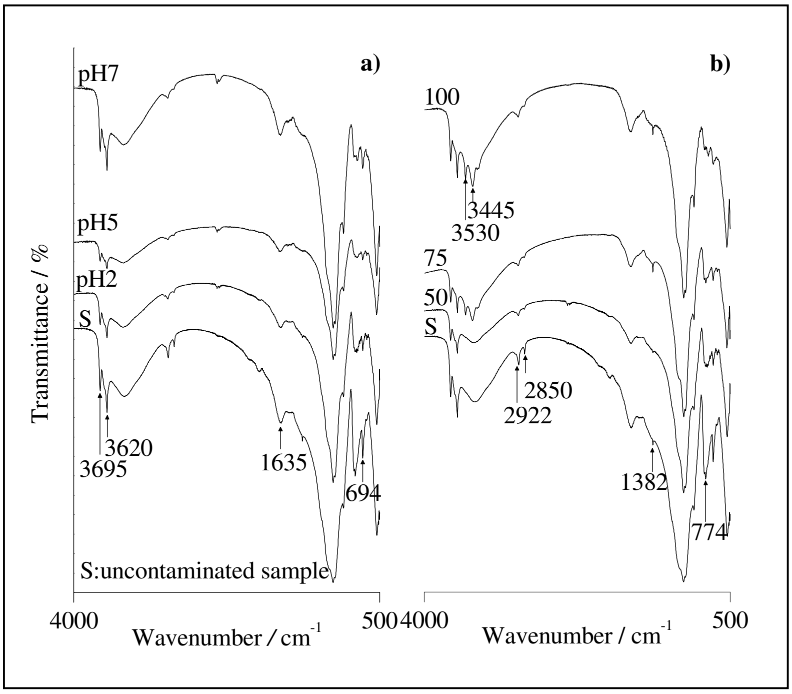


Figure 3.4. Infrared spectra of soil bed samples before and after flow experiments with chromium influents with 50 mg L^{-1}, at pH 2, 5 and 7. Spectra of soil beds contaminated with chromium influents with 50, 75 and 100 mg L^{-1}, at pH 2.

There are singly coordinated OH groups on the edges of clay mineral. They can be coordinated for example with Al(III) forming the aluminol edge groups, whose characteristic band (~ 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 (Figure 3.4 b) it is evident the appearance of two peaks around 3530 cm^{-1} 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 cm^{-1} - 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 hydroxyls groups can be protonated and complex metal anions [39].

In both spectra, there are well resolved peaks around 2850 cm^{-1} 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 1380cm^{-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.

REFERENCES

[1] Alloway, B.J. (1995) Heavy metals in soils, Blackie, Glasgow.

[2] Serrano, S., Garrido, F., Campbell, C.G., Garcia-Gonzalez, M.T. (2005) Competitive sorption of cadmium and lead in acid soils of Central Spain, Geoderma 124, 91-104.

[3] Wittbrodt, P.R., Palmer, C.D. (1995) Reduction of Cr(VI) in the presence of excess soil fulvic-acid, Environ. Sci. Technol. 29, 255-263.

[4] 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 62, 255-264.

[5] Pantsar-Kallio, M., Reinikainen, S.P., Oksanen, M. (2001) Interactions of soil components and their effects on speciation of chromium in soils, Anal. Chim. Acta 439, 9-17.

[6] 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, Regul. Toxicol. Pharm. 28, 27-37.

[7] Yong, R.N., Yaacob, W.Z.W., Bentley, S.P., Harris, C., Tan, B.K. (2001) Partitioning of heavy metals on soil samples from column tests, Eng. Geol. 60, 307-322.

[8] Elzahabi, M., Yong, R.N. (2001) pH influence on sorption characteristics of heavy metal in the vadose zone, Eng. Geol. 60, 61-68.

[9] Tran, Y.T., Bajracharya, K., Barry, D.A. (1998) Anomalous cadmium adsorption in flow interruption experiments, Geoderma 84, 169-184.

[10] Toride, N., Leij, F.J., van Genuchten, M.T. (1995) The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments, 137, U.S. Salinity Laboratory, U.S. Department of Agriculture, Riverside, California.

[11] Hendershot, W.H., Lalande, H., Duquette, M. (1993) Ion exchange and exchangeable cations, in: M.R.Carter, E.G.Gregorich (Eds.), Soil Sampling and Methods of Analysis, 197-206.

[12] USEPA (2007) Microwave assisted acid digestion of sediments, sludges, soils, and oils, 3051, Environmental Protection Agency, United States of America.

[13] Tinsley, J. (1950) The determination of organic carbon in soils by dichromate mixture, IV International Congress of Soil Science, IV International Congress of Soil Science , 161-164, IV International Congress of Soil Science.

[14] Reddy, K.R., Donahue, M., Saichek, R.E., Sasaoka, R. (1999) Preliminary assessment of electrokinetic remediation of soil and sludge contaminated with mixed waste, J. Air Wate. Manage. 49, 823-830.

[15] Papelis, C., Um, W. (1999) Anion and cation transport in zeolitized tuffs from the Nevada test site: Effects of ion type, pH, and ionic strength, in: H.M. Selim, D.L. Sparks (Eds.), Heavy metals release in soils, Lewis Publisher, Boca Raton. 31-54.

[16] Langmuir, I. (1918) The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40, 1361-1403.

[17] Sips, R. (1948) On the structure of a catalyst surface, J. Chem. Phys. 16, 490-495.

[18] Padmesh, T.V.N., Vijayaraghavan, K., Sekaran, G., Velan, M. (2006) Application of two-and three-parameter isotherm models: Biosorption of Acid Red 88 onto *Azolla microphylla*, Biorem. J. 10, 37-44.

[19] Ho, Y.S. (2006) Review of second-order models for adsorption systems, J. Hazard. Mater. 136, 681-689.

[20] van Genuchten, M.T. (1981) Non equilibrium transport parameters from miscible displacement experiments, 119, U.S. Salinity Laboratory, U.S. Department of Agriculture, Riverside, California.

[21] Bajracharya, K., Barry, D.A. (1995) MCMFIT - efficient optimal fitting of a generalized nonlinear advection-dispersion model to experimental-data, Comput. Gesosci. 21, 61-76.

[22] Kreft, A., Zuber, A. (1978) Physical meaning of Dispersion-Equation and its solutions for different initial and boundary-conditions, Chem. Eng. Sci. 33, 1471-1480.

[23] Candela, L., varez-Benedi, J., de Melo, M.T.C., Rao, P.S.C. (2007) Laboratory studies on glyphosate transport in soils of the Maresme area near Barcelona, Spain: Transport model parameter estimation, Geoderma 140, 8-16.

[24] Zhou, L.Z., Selim, H.M. (2001) Solute transport in layered soils: Nonlinear and kinetic reactivity, Soil Sci. Soc. Am. J. 65, 1056-1064.

[25] van Genuchten, M.T. (1980) A closed-form equation for predicting the hydraulic conductivity of unsaturated soils, Soil Sci. Soc. Am. J. 44, 892-898.

[26] Bradl, H.B. (2004) Adsorption of heavy metal ions on soils and soils constituents, J. Colloid Interface Sci. 277, 1-18.

[27] Sparks, D.L. (1995) Environmental soil chemistry, Academic Press, San Diego.

[28] Sastre, J., Rauret, G., Vidal, M. (2006) Effect of the cationic composition of sorption solution on the quantification of sorption-desorption parameters of heavy metals in soils, Environ. Pollut. 140, 322-339.

[29] Covelo, E.F., Andrade, M.L., Vega, F.A. (2004) Heavy metal adsorption by humic umbrisols: selectivity sequences and competitive sorption kinetics, J. Colloid Interface Sci. 280, 1-8.

[30] Miller, D.M., Sumner, M.E., Miller, W.P. (1989) A comparison of batch-generated and flow-generated anion adsorption-isotherms, Soil Sci. Soc. Am. J. 53, 373-380.

[31] Bailey, N., Carrington, A., Lott, K.A.K., Symons, M.C.R. (1960) Structure and reactivity of the oxyanions of transition metals .Acidities and spectra of protonated oxyanions, J. Chem. Soc., 290-297.

[32] Zachara, J.M., Girvin, D.C., Schmidt, R.L., Resch, C.T. (1987) Chromate adsorption on amorphous iron oxyhydroxide in the presence of major groundwater ions, Environ. Sci. Technol. 21, 589-594.

[33] Du, Y.J., Hayashi, S. (2006) A study on sorption properties of Cd^{2+} on Ariake clay for evaluating its potential use as a landfill barrier material, Appl. Clay Sci. 32, 14-24.

[34] Aksu, Z. (2002) Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel(II) ions onto *Chlorella vulgaris*, Process. Biochem. 38, 89-99.

[35] Miretzky, P., Munoz, C., Carrillo-Chavez, A. (2006) Experimental Zn(II) retention in a sandy loam soil by very small columns, Chemosphere 65, 2082-2089.

[36] Ghorai, S., Pant, K.K. (2005) Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina, Sep. Purif. Technol. 42, 265-271.

[37] Alvarez, R., Evans, L.A., Milham, P.J., Wilson, M.A. (2004) Effects of humic material on the precipitation of calcium phosphate, Geoderma 118, 245-260.

[38] Smidt, E., Meissl, K. (2007) The applicability of Fourier transform infrared (FT-IR) spectroscopy in waste management, Waste Manage. 27, 268-276.

[39] Sposito, G. (1989) The chemistry of soils, Oxford University Press, Inc., New York.

[40] Artz, R.R.E., Chapman, S.J., Jean Robertson, A.H., Potts, J.M., Laggoun-Défarge, F., Gogo, S., Comont, L., Disnar, J.R., Francez, A.J. (2008) FTIR spectroscopy can be

used as a screening tool for organic matter quality in regenerating cutover peatlands, Soil Biol. Biochem. 40, 515-527.

[41] Cocozza, C., D'Orazio, V., Miano, T.M., Shotyk, W. (2003) Characterization of solid and aqueous phases of a peat bog profile using molecular fluorescence spectroscopy, ESR and FT-IR, and comparison with physical properties, Org. Geochem. 34, 49-60.

[42] Chapman, S.J., Campbell, C.D., Fraser, A.R., Puri, G. (2001) FTIR spectroscopy of peat in and bordering Scots pine woodland: relationship with chemical and biological properties, Soil Biol. Biochem. 33, 1193-1200.

CHAPTER 4| Mobility of Cr, Pb, Cd, Cu and Zn in a Loamy Sand Soil: a comparative study

Adapted from: *B. Fonseca, H. Figueiredo, J. Rodrigues, A. Queiroz, T. Tavares*

Submitted to Geoderma

2011

1. INTRODUCTION

The release and disposal of heavy metals from anthropogenic activities have been responsible for the increasing concentrations of these contaminants in soil environments. The high loading of metals in soils may affect the growth of plants and the health of animals, thereby representing a significant threat to public health [1]. Consequently, the development of effective strategies to manage heavy metal pollution is of great importance [2] but requires extensive knowledge of the sorption and transport behaviors of heavy metals and of the diverse variables affecting these processes. Several studies have been performed in order to establish the influence of different parameters on heavy metal sorption/desorption [3-9]. Most of these studies primarily reported the results of batch tests, giving detailed information on the sorption process but little on the transport of the heavy metals. Therefore, because the simultaneous presence of competing metals is known to affect sorption processes and leaching potentials through soil profiles, this study sought to evaluate the retention of heavy metals using either batch or flow tests, simulating single- and multi-metal contamination, in order to obtain more realistic results [10]. However, it is also important to perform these types of studies for different regions and soils, as the composition of the soil matrix may result in unexpected behavior.

Some heavy metals such as cadmium (Cd), zinc (Zn) and copper (Cu) can be found in fertilizers used on agricultural lands [11,12]. In addition, Zn and Cu are also present in high concentrations, along with lead (Pb), in roadside soils [13]. These four metals, together with chromium (Cr), are frequently identified in wastes from several industrial activities including electroplating, car manufacturing, and metallurgy [12,14,15]. Thus, these five metals can be readily found as co-contaminants in agricultural lands as well as near roads and/or automotive facilities. For this reason, a soil sample collected in a location of great agricultural activity near an automotive facility was used to study the competitive and noncompetitive sorption and transport of Cr, Pb, Cd, Zn and Cu.

Batch tests were undertaken using single- and multiple-metal solutions with equimolar concentrations of the aforementioned heavy metals in order to study their sorption equilibria. The Langmuir isotherm model was adjusted to experimental data, allowing the determination of the soil's maximum sorption capacity for each metal, with and without competition. To evaluate the retention of each metal in single- and multiple-metal flow systems, the respective solutions were pumped through soil columns. Finally, the CXTFIT code was used to fit the dimensionless two-site nonequilibrium convection-dispersion equation to the breakthrough curves [16,17] in order to determine the retardation factor for each metal under the tested conditions. Functional groups present in the soil that may have some role in the sorption process were identified by FTIR.

2. MATERIAL AND METHODS

2.1. Soil characterization

Several representative soil samples of a loamy sand soil were collected at Póvoa de Varzim, Porto, Portugal (41º25'15.58''N and 8º45'58.27''O), homogenized and characterized as described elsewhere [9,18]. The particle distribution was determined by means of laser granulometry (Beckman-Coulter mod.LS230). The soil pH was determined according to US EPA method 9045D [19]. The ammonium acetate [20] and the Tinsley [21] methods were used to quantify the cationic exchange capacity and the organic matter content of the soil, respectively. Moreover, the concentration of each element - Cr, Cd, Pb, Zn, Cu - was determined by flame atomic absorption (Varian SpectraAA-400), after microwave digestion (Aurora Instruments MW600) with nitric acid using US EPA method 3051A [22]. Iron and manganese oxides were determined by the dithionite-citrate method [23]. Finally, the carbonate content and mineral composition were determined with a Scheibler calcimeter and by X-ray diffraction analysis (Philips PW3710), correspondingly. Table 2.1 summarizes the physical and chemical characterization performed for the studied soil.

2.2. Batch experiments

Sorption isotherm assays for Cr, Pb, Cd, Zn and Cu, with either single or mixed solutions, were performed using the batch equilibrium technique. The experiments were conducted by adding 20 mL of each metal solution or an equimolar solution of the five metals to 2 g of soil in 50 mL polypropylene centrifuge tubes. The experiments were performed using seven different solutions, prepared on a molar concentration basis, in order to prevent mass effects [24]. The heavy metal concentration range [0.05 mM - 0.48 mM] was selected considering the legislated limit for Pb, as this was the heaviest metal tested. Except for the Cr solutions, which were prepared from potassium dichromate salt, the solutions were prepared using nitrate salts of the desired heavy metals in a background of 0.01 M of $CaCl_2$. This background was used to improve centrifugation and minimize cation exchange [25]. The solutions were acidified with concentrated HNO_3 (65 %), in order to avoid the precipitation of metal cations ($pH \leq 2$). It should be noted that the initial concentration of every metal was determined by flame atomic absorption spectroscopy after the preparation of the solutions.

Preliminary studies showed that over the concentration range tested, Cr reached sorption equilibrium after 192 h, the longest equilibration time of the five metals studied [10,18,26,27]. Therefore, all the batch equilibrium tests, including blanks, were undertaken in an orbital mixer (Certomat® S) for 192 h at room temperature (25 ± 0.5 ºC) and at a shaking speed of 100 rpm. The polypropylene tubes containing the soil-solution mixtures were then centrifuged at 5000 rpm for 5 min, and an aliquot of the supernatant was collected in pre-acidified sample tubes (2 % HNO_3). These samples were stored at 4ºC for future analysis by flame atomic absorption spectroscopy. The pH of the supernatant was measured and was always approximately 6 ± 0.5.

The concentration of metal adsorbed onto the soil at equilibrium - q_e/(mmol kg^{-1}) - was calculated as:

$$q_{\mathrm{e}} = \frac{(C_{\mathrm{i}} - C_e)V}{W} \tag{34}$$

Where C_e is the concentration of metal in the solution at equilibrium (mM); C_i is the initial concentration of metal in the liquid phase (mM); V is the volume of metal solution (L) and W is the weight of the soil sample (kg). The results were plotted in a graph of q_e versus C_e and the Langmuir isotherm model was fitted to data:

$$q_{\mathrm{e}} = \frac{q_{\max} b_{\mathrm{L}} C_{\mathrm{e}}}{1 + b_{\mathrm{L}} C_{\mathrm{e}}} \tag{35}$$

q_{max} is the maximum mass of metal that can be sorbed by the sample (mg kg^{-1}); b_L is a constant related to the binding strength (L mg^{-1}) [18,28,29].

2.3. *Continuous flow experiments*

All column experiments, including duplicates, were conducted at room temperature - 25 ± 1 ºC - in acrylic columns 2.5 cm in diameter by 25 cm deep. The packed soil in the columns had a mean bulk density of (2.3 ± 0.3) g cm^{-3} and a bed height of (22 ± 1) cm. Single-metal solutions with 0.05 mM of each metal - Cr, Pb, Cd, Zn and Cu - and also a mixed solution with equimolar concentrations of the five metals, each with a pH lower than 2, were passed through the columns for approximately 35 h at an average flow rate of (15 ± 0.2) mL min^{-1}. To ensure saturation flow conditions and, consequently, the absence of immobile regions, the columns were operated in an upward flow mode [30]. The samples were collected in 50 mL polypropylene tubes, and an aliquot was acidified with 2% ($^{v}/_{v}$) of concentrated HNO_3 (65 %) for final analyses by flame atomic absorption spectroscopy. The pH of the effluent samples was also measured. The dimensionless two-site nonequilibrium convection-dispersion equation (TSM) was then fitted to the obtained experimental breakthrough curves (C/C_0 *vs* t) using the CXTFIT model [16], in order to determine the retardation factor - R - the coefficient of partitioning between the equilibrium and nonequilibrium phases - β - and the mass transfer coefficient for transfer between the two phases - ω The hydraulic parameters, namely the dispersion coefficient - $D/(cm^2\ h^{-1})$ - and the pore water velocity - $v/(cm\ h^{-1})$ - were determined independently for each column. Specifically, the equilibrium convection-dispersion equation (CDE) was fitted to the breakthrough curves of a nonreactive tracer - $CaCl_2$ (0.01 M). Consequently, a residence time of approximately 50 min was estimated for the flow experiments. The detailed procedure has been described elsewhere by Fonseca *et al.* [9].

After each displacement experiment, the soil bed was collected and homogenized, three samples of each column were digested [9,22], and the metal concentration in each sample was determined through flame atomic absorption spectroscopy. These samples were also analyzed by transmission FTIR (FTIR BOMEM MB 104) on pressed KBr pellets (100 mg of KBr and 1 mg of sample). Background correction for atmospheric air was used for each spectrum. Spectra were obtained in the range 500-4000 wavenumbers with a minimum of 10 scans and a resolution of 4 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1. Soil characterization

According to the data compiled in Table 2.1, it can be inferred that the studied soil is slightly acidic loamy sand. It has considerable organic matter content, but low cationic exchange capacity and no carbonate [18]. Kaolinite was found to be the predominant mineral composing the clay fraction of the soil sample. Finally, all the heavy metals were found in concentrations below the national legislated limit for soils with pH between 5.5 and 7.

3.2. Batch Experiments

Figure 4.1 shows the isotherm curves obtained for each metal in competitive (multiple-metal) and noncompetitive (single-metal) systems. Generally, the isotherm curves have the shape of an L-curve isotherm, resulting from the relatively high affinity of the soil particles for the metal at low surface coverage, an affinity that decreased as the surface became saturated [24,31]. For the noncompetitive sorption of Pb and the competitive sorption of Cr, the isotherms obtained took the form of nearly vertical lines, or H-type isotherms. These are usually produced by inner-sphere surface complexation or by significant van der Waals interactions in the adsorption process [31]. Finally, the curves obtained for the non-competitive sorption of Cu and Zn revealed an S-type curve. This is related to the low affinity between the soil particles and the metal at low concentrations due to the interference of other substances, such as soluble organic matter, that can compete with soil particles for the metal cations [31]. Except for Cr, all the other equilibria were reached more slowly in the case of competitive sorption (Figure 4.1) as the ions competed for sorption sites [32]. Nevertheless, the higher sorption density of Cu may also be due to the formation of Cu-Cr precipitates, since the soil solution at the end of the experiment had a pH of approximately 6 [33]. This could also explain the higher retention of Cr when in competition with Cu and other metals [34].

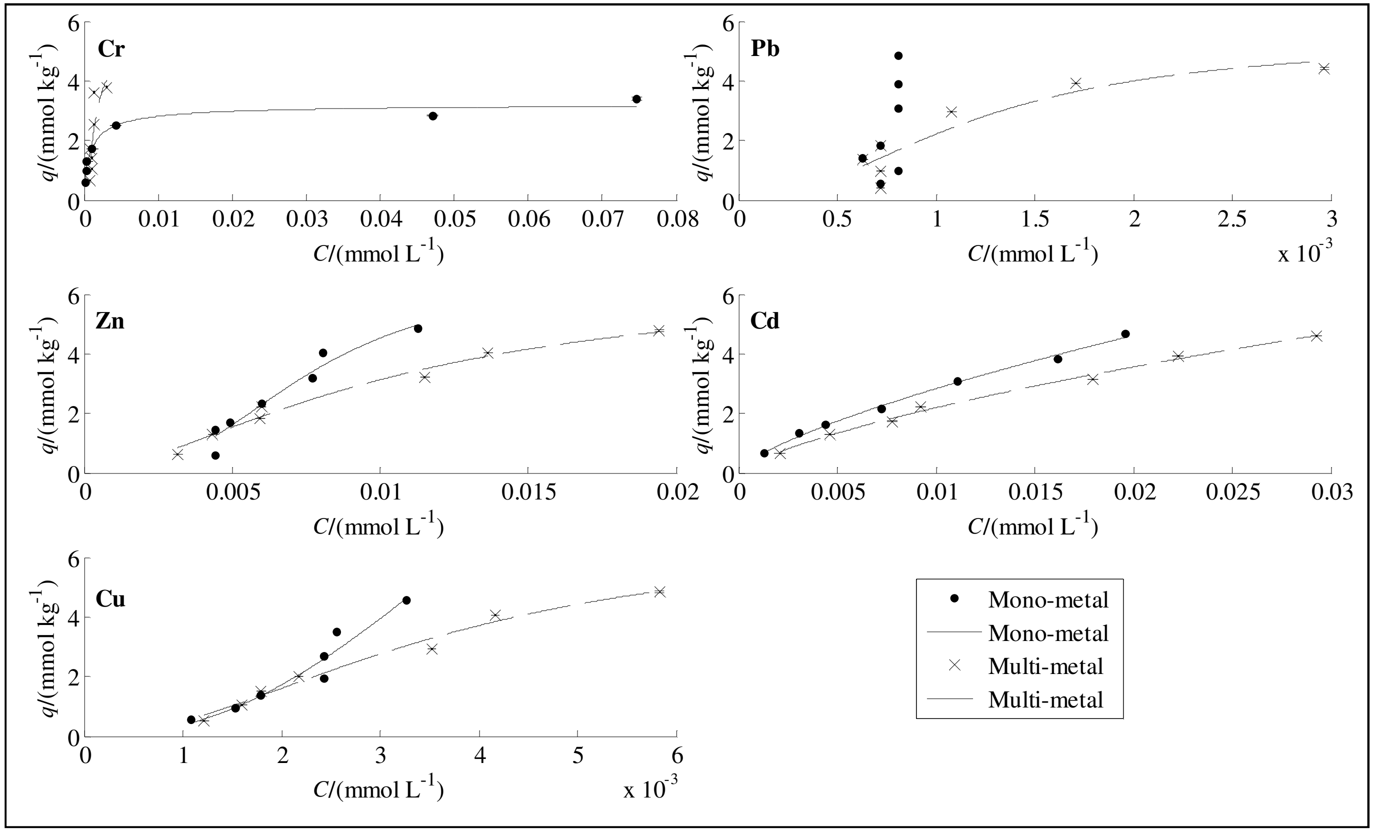


Figure 4.1. Adsorption isotherms obtained for the tested metals in competitive and non competitive systems. Lines represent the adjusted Langmuir model. The error bars depict the confidence interval for a level of confidence of 95%.

As mentioned before, the experimental isotherm obtained for the sorption of Pb in the absence of competition was a nearly vertical line (Figure 4.1), revealing its total sorption and its high affinity for the soil despite the variation in the solution concentration. Given this observation and the values of the Langmuir affinity constant - b_L - determined for each metal in both systems (Table 4.1), a sorption trend can be defined as: Cr > Pb > Cd > Cu > Zn. This trend can be mainly explained by the conventional hard–soft acid–base (HSAB) principle and the nature of the ions studied. The "hard" ions are those with high electronegativity, low polarizability and small ionic size. These ions prefer hard ligands but form weak complexes with them. However, the "soft" ions have greater affinity for "soft" sites and are more strongly bounded [4,29,35,36]. It should be noted that, at low pH values, Cr(VI) exists mainly as an oxyanion, which is adsorbed at positively charged sites. In fact, the equilibrium pH values of the sorption experiments, including the blank, were between 5.5 and 6.5, indicating the degree of protonation of the soil surface. Furthermore, oxyanions are "soft" bases and, according to the Pearson concept, can react strongly with Lewis acid sites created by inner-sphere surface complexation [9,31,37-39].

Table 4.1. Values of Langmuir and Sips equations parameters determined in the mono- and multi-metal batch systems, for each tested metal. The standard deviations were under 10%

Langmuir	Mono-metal	Multi-metal
	Cr	
q_{max}	3.10	-
b_L	1364	-
r^2	0.964	-
	Pb	
q_{max}	-	14.0
b_L	-	183
r^2	-	0.793
	Zn	
q_{max}	9879	17.0
b_L	0.04	21.0
r^2	0.831	0.971

Langmuir	Mono-metal	Multi-metal
	Cd	
q_{max}	10	10
b_L	41	30
r^2	0.988	0.991
	Cu	
q_{max}	9977	8531
b_L	0.1	0.1
r^2	0.735	0.956

As the working concentration range is very narrow in these studies, the experimental maximum sorption capacities observed (Figure 4.1) differ largely from the estimated values (Table 4.1), because the trend of the isotherm curves for higher concentrations is unpredictable. However, it is clear from the experimental data (Figure 4.1) that all the metals at the tested concentration range were totally sorbed in this soil, in either noncompetitive or competitive scenarios.

3.2. Flow experiments

In Figure 4.2, the breakthrough curves obtained for each metal in competitive and noncompetitive flow tests are shown. The respective adjusted two-site adsorption models are also presented. Generally, the fit provided by the two-site adsorption model was good, as demonstrated by the correlation coefficient values in Table 4.2. However, the breakthrough curve of Zn in the competitive sorption experiment could not be fit using this model. Values of relative concentration much higher than 1 were obtained for this assay, with more expression in the first 5 h before the breakthrough point of the other metals (Figure 4.2). The Zn cations can be easily exchanged when competing with other metal cations [40]. Therefore, it can be assumed that a fraction of the highly concentrated native Zn (Table 2.1) was washed out from the column, increasing its concentration in the effluent, especially before the saturation of the exchangeable surfaces.

Examining the single-metal systems, it is evident that the highest retardation factor - R - was obtained for Cr, whose affinity for the soil was already shown to be the highest among the metals studied (Table 4.2). Cr oxyanions were specifically sorbed to sites with high dissociation constants, making them less vulnerable to leaching. However, the batch tests revealed that the other metals were sorbed at less energetic sites, making them more susceptible to acid leaching. A trend in relative metal mobility under the conditions studied can be defined as: Zn > Cd > Pb > Cu > Cr, which is slightly different from what would be expected after the analysis of the affinity constants (b_L) obtained in the batch tests (Table 4.1), although it is known that the sorption and transportation of heavy metals in dynamic environments do not always occur under equilibrium conditions [31]. In fact, compared with Cd and Cu, the values of the partitioning coefficient between the equilibrium and nonequilibrium phases - β - obtained for Cr and Zn were significantly lower (Table 4.2). This suggests that the sorption of these metals occurs instantaneously at equilibrium sites but is time-dependent at the remaining sites, with higher sorption energy [16]. However, the values found for the mass transfer coefficients ($\omega > 1$) suggest that not only Cd and Cu cations but also Zn cations are promptly sorbed at equilibrium sites. The results with respect to Pb transport and sorption are less conclusive. The mass transfer coefficient points to a nonequilibrium process ($\omega < 1$), but the value of β reveals that a larger amount of these cations are sorbed at equilibrium sites than at nonequilibrium sites [17,41,42]. According to the batch experiment results, both Cr and Pb cations were retained at sites with high sorption energies; therefore, sorption at nonequilibrium sites seems to be predominant, as this reaction is kinetically controlled. When in competition, the mass transfer coefficient did not vary significantly for Cr and Pb, as these metals seemed to be sorbed more specifically. By contrast, the value of this variable decreases for the Cd and Cu cations, probably because competition stimulates the specific sorption of these ions.

The values obtained for the retardation factor - R - estimated for Cr and Cu transport in the competitive system were much higher than the values obtained for the other metals. This strengthens the aforementioned hypothesis of the precipitation of a Cu-Cr solid in the column, which is especially reasonable given that the pH of the effluent in the first five hours was above 6 (Figure 4.3), due to the low acid-buffering capacity of the soil [9,33]. It should be noted that the hydroxides of the tested metals do not precipitate in the pH range at which experiments were conducted [43]. Finally, as expected, the Cd retardation factor decreased when Cd was in competition with other cations for sorption sites [10,26,32]. Pb ions experienced a slightly higher retardation in the competitive scenario, as this metal is adsorbed specifically on sites with high dissociation constants. As can be observed, the curve correspondent to the competitive scenario in Figure 4.2 grew more slowly, suggesting increasing sorption density at high-energy sites [31,44].

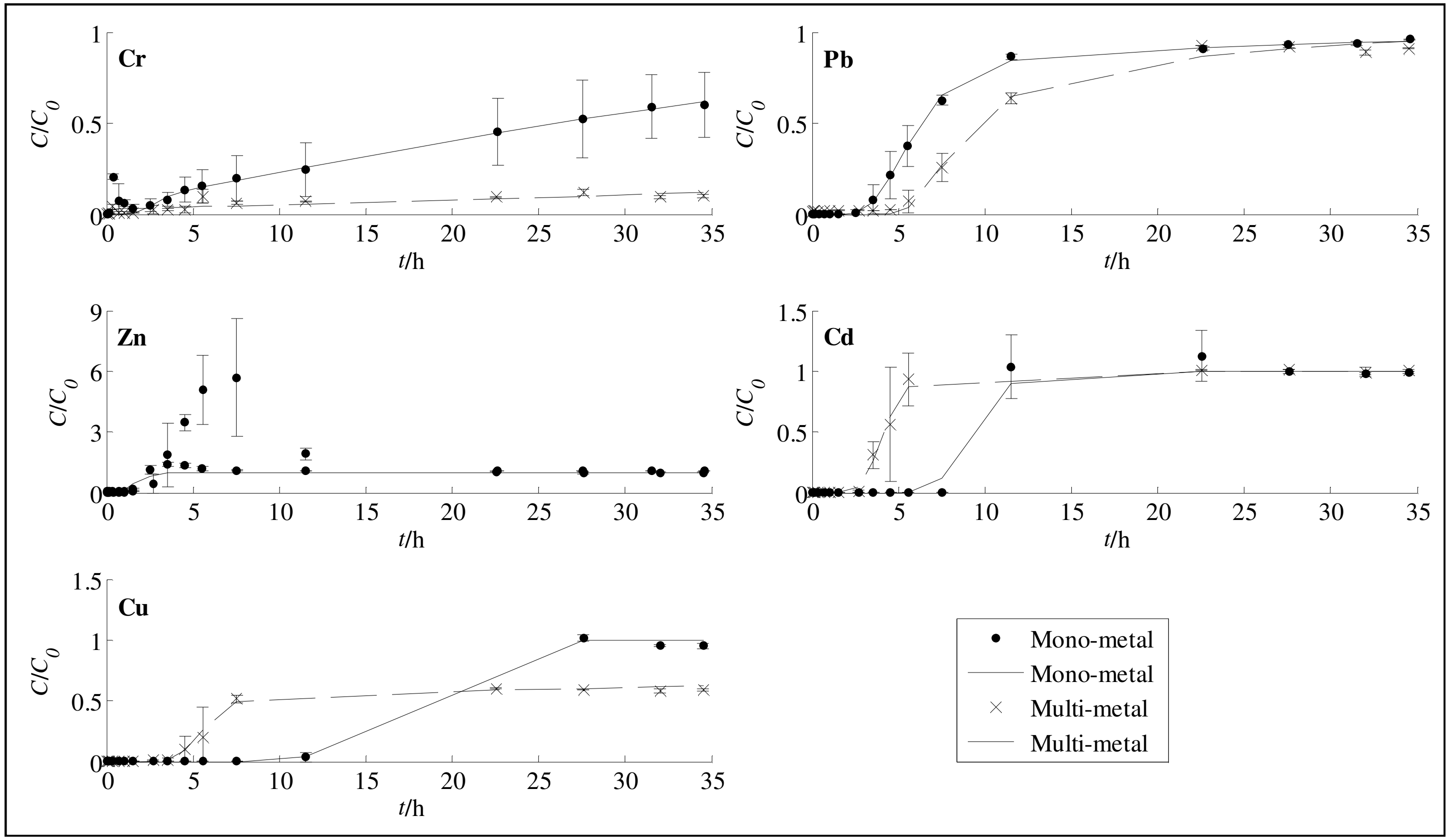


Figure 4.2. Experimental breakthrough curves obtained for each metal in competitive and non competitive scenarios. Lines represent the adjusted two-site model. The error bars depict the confidence interval for a level of confidence of 95%.

Table 4.2. Quality of fit and parameter estimates based on the two site chemical nonequilibrium convective dispersion equation, for mono- and multi-metal flow systems. The standard deviations were under 10%

Parameters	Mono-metal	Multi-metal	Parameters	Mono-metal	Multi-metal
	Cr			**Cd**	
R	107	502	R	27	13
β	0.11	0.00	β	0.99	0.72
ω	0.13	0.17	ω	100	0.58
r^2	0.924	0.73	r^2	0.987	0.996
	Pb			**Cu**	
R	34	39	R	49	198
β	0.63	0.62	β	0.99	0.09
ω	0.01	0.02	ω	60	0.03
r^2	0.999	0.995	r^2	0.998	0.993
	Zn				
R	6	-			
β	0.18	-			
ω	100	-			
r^2	0.887	0.030			

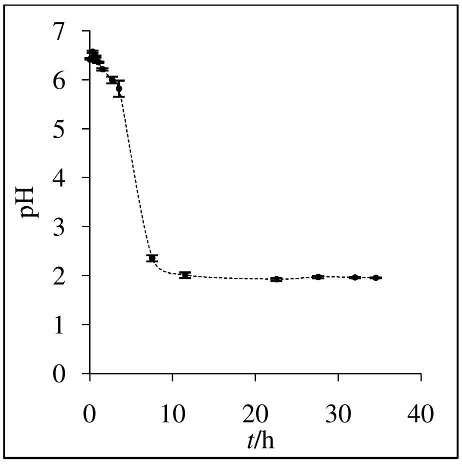


Figure 4.3. Variation of the effluent pH along the competitive flow test. The experiment was performed in duplicate being the standard deviation less than 10%.

3.2.1. FTIR spectral analysis

Figure 4.4 shows the FTIR spectra obtained for an uncontaminated soil sample and from the single-metal contaminated and co-contaminated soil samples collected from the soil bed columns. The bands of clay minerals represented by the SiO–H stretches at 3706 cm^{-1} and 3622 cm^{-1} (kaolin) and the Si–O–Si stretch at 1030 cm^{-1} were slightly different from the spectra of the contaminated samples [45]. The authors have reported similar results previously, when studying the noncompetitive sorption of chromium, and attributed these to the sorption of metals at the edges of the clay minerals [9,46]. However, the acidic character of the inlet solutions may have enhanced the dissolution of silicates, as these peaks decreased for the contaminated sample. However, the peaks do not overlap, revealing the persistence of these edges, even if they are less concentrated. There are two bands at approximately 2900 cm^{-1}, attributed to the C-H stretch of aliphatic structures, and a band at approximately 1634 cm^{-1} that change in all spectra [47]. However, the change is more evident in the cases of Pb and Cr. Pb forms strong complexes with soil organic matter and can compete with most other metals for sorption sites [44]. Cr transport can also be significantly retarded by the presence of organic matter, as this material has been reported to reduce Cr(VI) to Cr(III) under acidic conditions or to complex chromium oxyanions, as mentioned previously [37,48]. In this particular case, the bands assigned at 1634 cm^{-1} and 1384 cm^{-1} may also be related to the interactions with the free water and the organic matter fractions [49]. The bands at 692 cm^{-1} and 797 cm^{-1} commonly associated with inorganic materials tended to overlap for the contaminated samples, probably due to the presence of heavy metal complexes [50].

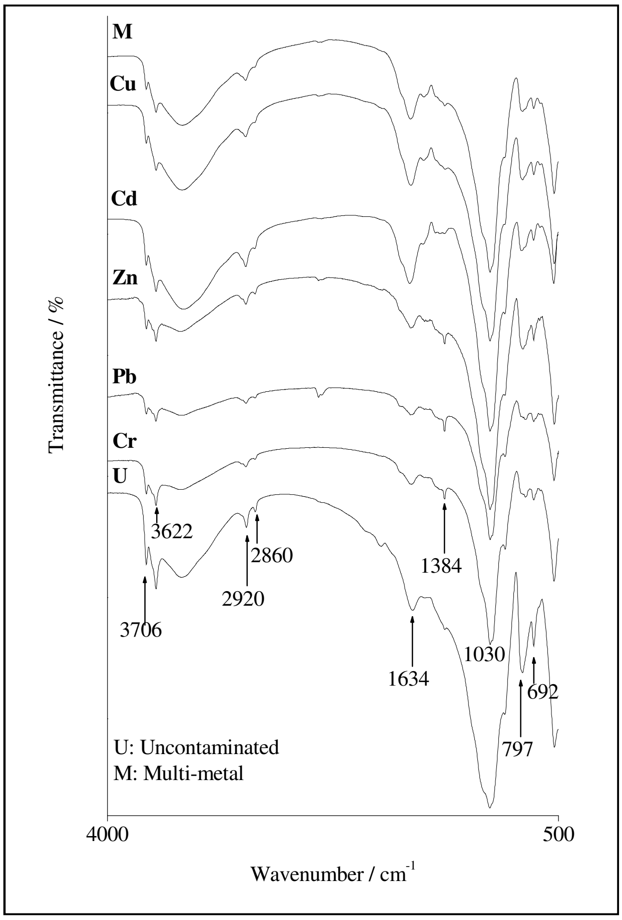


Figure 4.4. FTIR spectra of an uncontaminated and contaminated soil samples collected in each column after the flow tests.

REFERENCES

[1] Berti, W.R., Jacobs, L.W. (1996) Chemistry and phytotoxicity of soil trace elements from repeated sewage sludge applications, J. Environ. Qual. 25, 1025-1032.

[2] Adhikari, T., Singh, M.V. (2003) Sorption characteristics of lead and cadmium in some soils of India, Geoderma 114, 81-92.

[3] Hanna, K., Lassabatere, L., Bechet, B. (2009) Zinc and lead transfer in a contaminated roadside soil: Experimental study and modeling, J. Hazard. Mater. 161, 1499-1505.

[4] Liu, C.L., Chang, T.W., Wang, M.K., Huang, C.H. (2006) Transport of cadmium, nickel, and zinc in Taoyuan red soil using one-dimensional convective-dispersive model, Geoderma 131, 181-189.

[5] Fontes, M.P.F., de Matos, A.T., da Costa, L.M., Neves, J.C.L. (2000) Competitive adsorption of zinc, cadmium, copper, and lead in three highly-weathered Brazilian soils, Commun. Soil Sci. Plant Anal. 31, 2939-2958.

[6] Appel, C., Ma, L. (2002) Concentration, pH, and surface charge effects on cadmium and lead sorption in three tropical soils, J. Environ. Qual. 31, 581-589.

[7] Lee, S.Z., Chang, L.Z., Chen, C.M., Yang, H.H., Hu, P.Y. (2001) The effect of hydration on adsorption and desorption of heavy metals in soils, J. Environ. Sci. Health, Part A 36, 63-74.

[8] Sipos, P., Németh, T., Kis, V.K., Mohai, I. (2008) Sorption of copper, zinc and lead on soil mineral phases, Chemosphere 73, 461-469.

[9] Fonseca, B., Teixeira, A., Figueiredo, H., Tavares, T. (2009) Modelling of the Cr(VI) transport in typical soils of the North of Portugal, J. Hazard. Mater. 167, 756-762.

[10] Serrano, S., Garrido, F., Campbell, C.G., Garcia-Gonzalez, M.T. (2005) Competitive sorption of cadmium and lead in acid soils of Central Spain, Geoderma 124, 91-104.

[11] Tran, Y.T., Bajracharya, K., Barry, D.A. (1998) Anomalous cadmium adsorption in flow interruption experiments, Geoderma 84, 169-184.

[12] USEPA (2009) Guide to Site and Soil Description for Hazardous Waste Site Characterization, Cameron, R. E, 600/4-91/029, Environmental Protection Agency, United States of America.

[13] Miller, D.M., Sumner, M.E., Miller, W.P. (1989) A comparison of batch-generated and flow-generated anion adsorption-isotherms, Soil Sci. Soc. Am. J. 53, 373-380.

[14] Lau, S.L., Stenstrom, M.K. (2005) Metals and PAHs adsorbed to street particles, Water Res. 39, 4083-4092.

[15] Covelo, E.F., Vega, F.A., Andrade, M.L. (2008) Sorption and desorption of Cd, Cr, Cu, Ni, Pb and Zn by a Fibric Histosol and its organo-mineral fraction, J. Hazard. Mater. 159, 342-347.

[16] Toride, N., Leij, F.J., van Genuchten, M.T. (1995) The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments, 137, U.S. Salinity Laboratory, U.S. Department of Agriculture, Riverside, California.

[17] van Genuchten, M.T. (1981) Non equilibrium transport parameters from miscible displacement experiments, 119, U.S. Salinity Laboratory, U.S. Department of Agriculture, Riverside, California.

[18] Fonseca, B., Maio, H., Quintelas, C., Teixeira, A., Tavares, T. (2009) Retention of Cr(VI) and Pb(II) on a loamy sand soil: Kinetics, equilibria and breakthrough, Chem. Eng. J. 152, 212-219.

[19] USEPA (2004) Soil and waste pH, Method 9045D, Environmental Protection Agency, United States of America.

[20] Hendershot, W.H., Lalande, H., Duquette, M. (1993) Ion exchange and exchangeable cations, in: M.R.Carter, E.G.Gregorich (Eds.), Soil Sampling and Methods of Analysis, 197-206.

[21] Tinsley, J. (1950) The determination of organic carbon in soils by dichromate mixture, IV International Congress of Soil Science, IV International Congress of Soil Science , 161-164, IV International Congress of Soil Science.

[22] USEPA (2007) Microwave assisted acid digestion of sediments, sludges, soils, and oils, 3051, Environmental Protection Agency, United States of America.

[23] Mehra, O.P., Jackson, M.L. (1958) Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate, Clays and Clay Minerals 7, 317-327.

[24] Echeverria, J.C., Morera, M.T., Mazkiaran, C., Garrido, J.J. (1998) Competitive sorption of heavy metal by soils. Isotherms and fractional factorial experiments, Environ. Pollut. 101, 275-284.

[25] OECD (2000) OECD Guideline 106. Guideline for the testing of chemicals: Adsorption-desorption using a batch equilibrium method.

[26] Vega, F.A., Covelo, E.F., Andrade, M.L. (2006) Competitive sorption and desorption of heavy metals in mine soils: Influence of mine soil characteristics, J. Colloid Interface Sci. 298, 582-592.

[27] Usman, A.R.A. (2008) The relative adsorption selectivities of Pb, Cu, Zn, Cd and Ni by soils developed on shale in New Valley, Egypt, Geoderma 144, 334-343.

[28] Langmuir, I. (1918) The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40, 1361-1403.

[29] Sparks, D.L. (1995) Environmental Soil Chemistry, Academic Press, San Diego.

[30] Papelis, C., Um, W. (1999) Anion and cation transport in zeolitized tuffs from the Nevada test site: Effects of ion type, pH, and ionic strength, in: H.M. Selim, D.L. Sparks (Eds.), Heavy metals release in soils, Lewis Publisher, Boca Raton. 31-54.

[31] Sposito, G. (1989) The chemistry of soils, Oxford University Press, Inc., New York.

[32] Markiewiez-Patkowska, J., Hursthouse, A., Przybyla-Kij, H. (2005) The interaction of heavy metals with urban soils: sorption behaviour of Cd, Cu, Cr, Pb and Zn with a typical mixed brownfield deposit, Environ. Int. 31, 513-521.

[33] Sun, J.M., Zhu, W.T., Huang, J.C. (2006) Characterization of primary precipitate composition formed during co-removal of Cr(VI) with Cu(II) in synthetic wastewater, Environ. Sci. Pollut. Res. 13, 379-385.

[34] Yolcubal, I., Akyol, N.H. (2007) Retention and Transport of Hexavalent Chromium in Calcareous Karst Soils, Turk. J. Earth Sci. 16, 363-379.

[35] Puls, R.W., Bohn, H.L. (1988) Sorption of Cadmium, Nickel, and Zinc by Kaolinite and Montmorillonite Suspensions, Soil Sci. Soc. Am. J. 52, 1289-1292.

[36] Ghosh, D.C., Biswas, R. (2003) Theoretical calculation of absolute radii of atoms and ions. Part 2. The ionic radii, Int. J. Mol. Sci. 4, 379-407.

[37] 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 62, 255-264.

[38] Bailey, N., Carrington, A., Lott, K.A.K., Symons, M.C.R. (1960) Structure and reactivity of the oxyanions of transition metals. Acidities and spectra of protonated oxyanions, J. Chem. Soc., 290-297.

[39] Pearson, R.G. (1963) Hard and soft acids and bases, J. Am. Chem. Soc. 85, 3533-3539.

[40] Covelo, E.F., Andrade, M.L., Vega, F.A. (2004) Heavy metal adsorption by humic umbrisols: selectivity sequences and competitive sorption kinetics, J. Colloid Interface Sci. 280, 1-8.

[41] Seuntjens, P., Tirez, K., Simunek, J., van Genuchten, M.T., Cornelis, C., Geuzens, P. (2001) Aging effects on cadmium transport in undisturbed contaminated sandy soil columns, J. Environ. Qual. 30, 1040-1050.

[42] Candela, L., varez-Benedi, J., de Melo, M.T.C., Rao, P.S.C. (2007) Laboratory studies on glyphosate transport in soils of the Maresme area near Barcelona, Spain: Transport model parameter estimation, Geoderma 140, 8-16.

[43] Cherry, K.F. (1982) Plating waste treatment, Ann Arbor Science, Michigan.

[44] Strawn, D.G., Sparks, D.L. (2000) Effects of soil organic matter on the kinetics and mechanisms of Pb(II) sorption and desorption in soil, Soil Sci. Soc. Am. J. 64, 144-156.

[45] Smidt, E., Meissl, K. (2007) The applicability of Fourier transform infrared (FT-IR) spectroscopy in waste management, Waste Manage. 27, 268-276.

[46] Alvarez, R., Evans, L.A., Milham, P.J., Wilson, M.A. (2004) Effects of humic material on the precipitation of calcium phosphate, Geoderma 118, 245-260.

[47] Carballo, T., Gil, M.V., Gomez, X., Gonzalez-Andres, F., Moran, A. (2008) Characterization of different compost extracts using Fourier-transform infrared spectroscopy (FTIR) and thermal analysis, Biodegradation 19, 815-830.

[48] Jardine, P.M., Fendorf, S.E., Mayes, M.A., Larsen, I.L., Brooks, S.C., Bailey, W.B. (1999) Fate and transport of hexavalent chromium in undisturbed heterogeneous soil, Environ. Sci. Technol. 33, 2939-2944.

[49] Haberhauer, G., Gerzabek, M.H. (1999) Drift and transmission FT-IR spectroscopy of forest soils: an approach to determine decomposition processes of forest litter, Vib. Spectrosc. 19, 413-417.

[50] Du, C.W., Linker, R., Shaviv, A. (2007) Characterization of soils using photoacoustic mid-infrared spectroscopy, Appl. Spectrosc. 61, 1063-1067.

CHAPTER 5| A combined remediation technology for the reduction and bioleaching of hexavalent chromium from soils using *Acidithiobacillus thiooxidans*

Adapted from: *B. Fonseca, J. Rodrigues, T. Mendes, A. Queiroz, T. Tavares*

Submitted to Journal of Biotechnology

2011

1. INTRODUCTION

The release of hexavalent chromium - Cr(VI) - into soils, due to several anthropogenic activities, is more and more a matter of major concern, as this is an highly mobile, toxic and carcinogenic compound, also designated as a priority pollutant in various countries. Consequently, the development of cleaning technologies aiming its attenuation/elimination has been a challenge for scientific researchers. Several physico-chemical techniques are already being used to decontaminate Cr(VI) polluted soils, but the "green" ones are an increasingly focus of attention, mostly because of their cost effectiveness. It is estimated that bioremediation using microorganisms can reduce total treatment costs in 28%, compared with conventional systems [1-8].

Bioleaching is a bioremediation technique usually applied to heavy metals contaminated soils, sediments and sludges. Its application, using iron and sulfur oxidizing bacteria, either indigenous or laboratorial, has been fairly studied [8-19]. However, there is a lack of specific studies on Cr(VI) bioleaching, as the metal is basically quantified concerning its total concentration. In 1922, Waksman *et al.* [20] isolated acidophilic and chemoautotrophic bacteria - *Acidithiobacillus thiooxidans* - that can use elemental sulfur as its source of energy, and consequently acidify the media, due to the production of sulfuric acid:

$$S_2 + 3O_2 + 2H_2O \xrightarrow{Acidithiobacillus\ thiooxidans} 2H_2SO_4 \qquad (36)$$

Later, Allegretti *et al.* [21] proved that Cr(VI) can be reduced to a less toxic, less mobile and non carcinogenic cation - trivalent chromium, Cr(III) - by the action of higher polythionates, which are intermediate compounds of the oxidation process of elemental sulfur, catalyzed by *Acidithiobacillus thiooxidans*. Furthermore, it is also known that, due to its high *redox* potential ($E^o \geq 1.3V$), the Cr(VI) oxyanions can be easily reduced to Cr(III) by some biomaterials, especially in acidic media [22]:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \leftrightarrow 2Cr^{3+} + 7H_2O \qquad (37)$$

$$CrO_4^{2-} + 8H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O \qquad (38)$$

$$HCrO_4^- + 7H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O \qquad (39)$$

$$H_2CrO_4 + 6H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O \qquad (40)$$

In consequence of the above mentioned reasons, this study aims to be a contribution on the characterization and optimization of bioleaching operational parameters, using *Acidithiobacillus thiooxidans* DSM504, to clean soils contaminated with Cr(VI). With this purpose, and based on previous tests performed with a typical loamy sand soil from the north of Portugal [6,23], two values of the Cr(VI) contaminant solution - pH 2 and pH_{free} - of the Cr(VI) concentration in soil - 50 mg kg^{-1} and 100 mg kg^{-1} - and of the operational temperature - 26°C and T_{room} - were evaluated by means of batch tests. Considering that each of the three parameters - n - could assume two values - L - eight experiments were performed - L^n [24].

2. MATERIAL AND METHODS

2.1. Material

Soil: Various soil samples of the loamy sand soil were collected in Póvoa de Varzim, Porto, Portugal (41°25'15.58''N and 8°45'58.27''O), homogenized, and characterized over again as described elsewhere [6,7,23]. Table 2.1 resumes the main characteristics of this soil sample.

Contaminant: The potassium dichromate ($K_2Cr_2O_7$) used to contaminate the soil was 99.5% pure and was purchased from Panreac.

Inoculum: The bacteria used for leaching experiments were the *Acidithiobacillus thiooxidans* DSM 504, obtained from the German Collection of Microorganisms and Cell Cultures. The bacteria was revived form frozen cultures (-80 C in 20% glycerol) by growing cells in DSMZ 35 medium: 0.10 g of NH_4Cl, 3.00 g of KH_2PO_4, 0.10 g of $MgCl_2 \cdot 6H_2O$, 0.14 g of $CaCl_2 \cdot 2H_2O$ and 10 g of elemental sulfur, per liter of distilled water. The inoculum for the bioleaching assays resulted from a six day incubation of 500 mL of culture media in a rotary shaker at 150 rpm and 26°C. The absorbance of the inoculum at 620 nm was averagely 0.034, corresponding to the beginning of the exponential phase of the growth curve.

2.2. *Soil preparation and analysis*

Four sub-samples of the collected soil were spiked with solutions of $K_2Cr_2O_7$, in order to obtain two contamination levels of Cr(VI): 50 mg kg^{-1} and 100 mg kg^{-1}. The pH of two contaminant solutions, with different concentrations, was adjusted to 2 using concentrated HNO_3 (65%). The pH of the two remaining solutions was kept unadjusted (pH $\simeq$7.7). The mixtures were stirred frequently till they were dry (2/3 days). For each sample, including the original soil, the real concentration of Cr(VI) was determined by Flame Atomic Absorption (FAA), after an acid digestion of the soil, according to the US EPA method 3051 [25]. The concentration of phosphates - $[PO_4^{3-}]$/(mg kg^{-1}) - was determined using the stannous chloride method, described in standard methods [26], after the extraction with sodium bicarbonate as described by Olsen *et al.* [27]. And, the pH was determined according to the US EPA method 9045D [28]. The analyses were made in triplicate. Table 5.1 compiles the main characteristics of the four contaminated samples.

2.3. *Bioleaching experiments*

The batch bioleaching tests were performed in 250 mL Erlenmeyer flasks. The working volume, of 150 mL, was constituted by 10 % ($^v/_v$) of inoculum, 1% ($^w/_v$) of elemental sulfur, 3% ($^w/_v$) of contaminated soil and 90% of DSMZ 35 medium. The absorbance of the inoculum was 0.034 ± 0.022. For each set of experiments, eighteen flasks, sealed with solid silicone caps, were incubated in a rotary shaker, at 150 rpm, for seventy days. A pair of flasks - duplicates - was removed, each five days during the first twenty days, and each ten days for the remaining period, in order to keep the chemical equilibrium undisturbed. The liquid and solid phases were separated by centrifugation (5000 rpm, 10 min) and properly stored for future analyses. Eight sets of experiments were prepared, by varying the contamination level - 50 mg kg^{-1} and 100 mg kg^{-1} - the pH of contaminant solution - pH 2 and pH_{free} - and the operation temperature - 26°C and T_{room}. A different code was ascribed to each experimental set, according to the studied variable (Table 5.1). Three sets of blank experiments were undertaken. In Set I (chemical control) the soil was autoclaved, in Set II (biological control) the elemental sulfur was annulled, and in Set III (biological control) the flasks were not inoculated with *Acidithiobacillus thiooxidans*.

Table 5.1. References ascribed to each assay, according to the variable parameters. Chemical properties of the soil samples contaminated with hexavalent chromium

Code		Characteristics of the soil samples		
T = 26°C	$T = T_{\text{room}}$	[Cr]/(mg kg^{-1})	pH (H_2O)	[PO_4^{3-}]/(mg kg^{-1})
C50pH2T26	C50pH2T	46 ± 0	5.9 ± 0.0	7.8 ± 1.2
C50pHT26	C50pHT	51 ± 2	6.7 ± 0.1	10.8 ± 0.7
C100pH2T26	C100pH2T	120 ± 2	6.1 ± 0.1	5.5 ± 0.3
C100pHT26	C100pHT	118 ± 0	7.0 ± 0.0	16.9 ± 2.0

2.3.1. *Chemical analyses*

The liquid phase was analyzed for total chromium by FAA and for Cr(VI) by US EPA method 7196A [29]. The concentration of the Cr(III) in solution - $C_{\text{Cr(III)}}$/(mg L^{-1}) - and the mass of total chromium desorbed per mass of soil - q_{Cr}/(mg kg^{-1}) - were determined by the expressions:

$$C_{\text{Cr(III)}} = C_{\text{Cr}} - C_{\text{Cr(VI)}} \tag{41}$$

$$q_{\text{Cr}} = \frac{C_{\text{Cr}} V}{W} \tag{42}$$

where C_{Cr} and $C_{\text{Cr(VI)}}$ are, respectively, the concentrations of total and hexavalent chromium in solution (mg L^{-1}), V is the batch working volume (L) and W is the mass of soil sample (kg). In order to follow the production of sulfuric acid, the sulfates - [SO_4^{2-}]/(mg L^{-1}) - were quantified in the liquid phase according to the modified turbidimetric method described by Kolmert *et al.* [30]. The variation of phosphates -

[PO_4^{3-}]/(mg L^{-1}) - in solution was also evaluated applying the stannous chloride method to the liquid samples.

3. RESULTS AND DISCUSSION

3.1. Soil characterization

As mentioned before, the soil used to perform the tests here in described, was already characterized [6,23]. However, and to ensure the soil steadiness, some of its characteristics were reevaluated. As expected, physical characteristics like the particle size distribution did not reveal significant discrepancy, and the loamy sand soil designation stills fitting. Values concerning the pH, organic matter content and metal oxides concentration were kept almost equal. However, the total chromium concentration did decreased in the meanwhile. This can be explained, by the time interval between sampling: the atmospheric conditions, especially the rain, may have drained the chromium sorbed at the superficial layers - A- horizon and O-horizon. This phenomenon greatly justifies the need of this study. Finally, the phosphates concentration was also determined, as this element was followed during the bioleaching assays, in order to evaluate the dissolution of insoluble rock phosphate [31]. However, the found concentration was very low.

3.2. Total chromium removal: influence of concentration, pH and temperature

First and foremost, it is essential to refer that sulfur oxidation to sulfuric acid was recorded for some of the blank tests. Concretely, either for the sterilized and unsterilized soil - Set I and III - the oxidation was not very extent, but sporadic values of 30% were achieved for the Cr(VI) removal. Fact that is in accordance with what was stated by Waksman *et al*. [31]: when sulfur is added to soil, it is slowly oxidized to sulfuric acid, depending on the substances present in the sample. However, for the Set II, where no sulfur was added, maximum values of 2% were achieved for the removal of Cr(VI). This may correspond to the fraction that was weakly sorbed to the soil matrix through van der Waals forces [7].

Even so, the main gold of this study was to test the ability of the *Acidithiobacillus thiooxidans* DSM504 bacterium to catalyze, and consequently accelerate the sulfur oxidation, while it is reducing and leaching Cr(VI) from a contaminated soil, in different scenarios. Figure 5.1 resumes the main results obtained. The removal values, concerning total chromium, were represented according to the tested parameter, for the eight experimental sets.

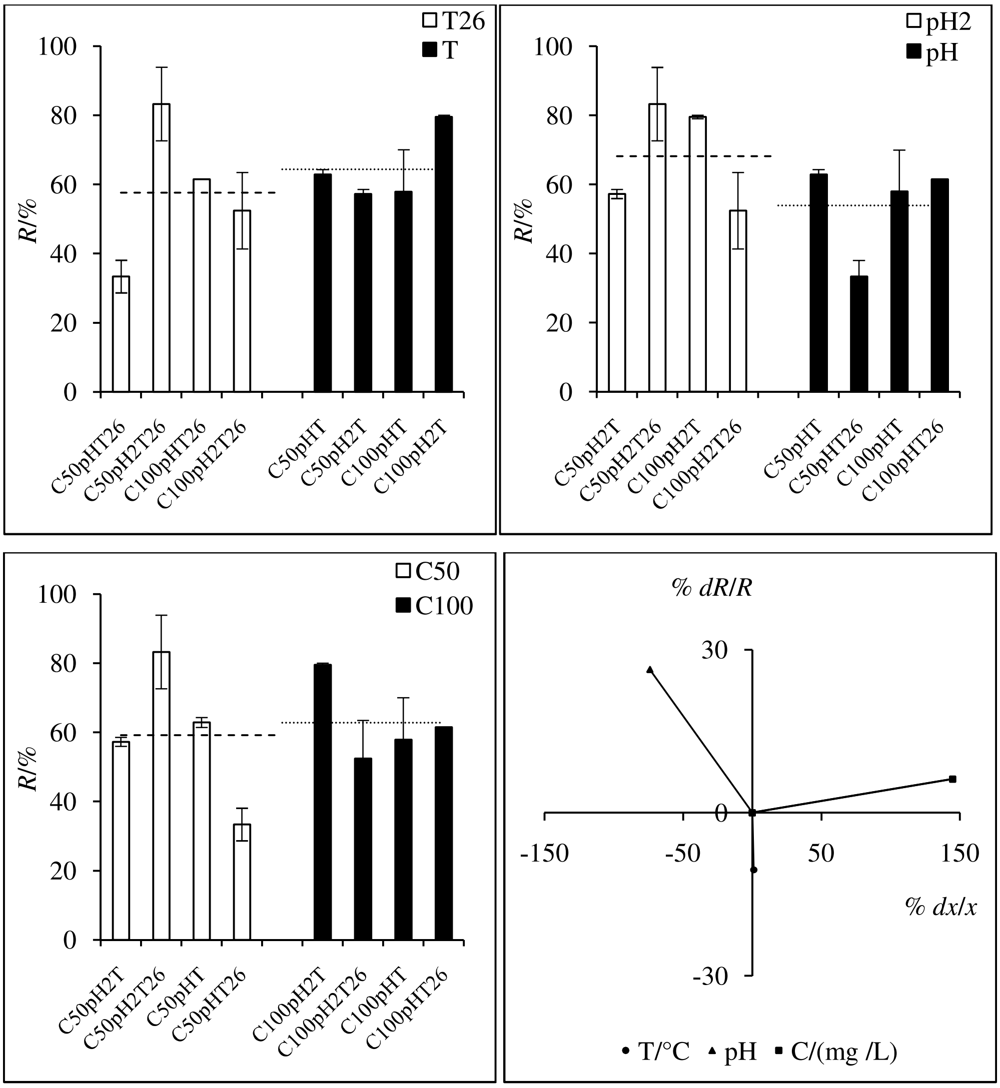


Figure 5.1. Cr(VI) removal, obtained for the variation of each parameter. Dot lines represent the removals mean values, concerning each parameter variation.

The lowest removal values - 33.3% and 53.4% - were obtained for the tests at 26 °C, using the soil contaminated with 50 mg kg^{-1} and 100 mg kg^{-1}, and with solutions of free pH and equal to 2, respectively. The higher removal values - 83.3% and 79.5% -

were obtained for the tests respecting the contaminant solutions with pH 2, performed at 26 °C and at room temperature, with either 50 mg kg^{-1} or 100 mg kg^{-1} of Cr(VI), correspondingly. Here in appears the first evidence of the great influence of soil pH in the efficiency of the chromium dissolution process. It should be noted that the contamination using the solutions with pH 2 resulted in the acidification of the soil samples - Table 5.1. According to the adopted sensitive analysis method, described by Hatzikioseyian *et al.* [32] and presented in Figure 5.1, the relative change of the contamination pH resulted in a higher relative change of the Cr(VI) removal, compared with the other two variables - T/°C and q_{Cr}/(mg kg^{-1}). This method was applied considering the mean values of free contamination pH, room temperature and contamination level of 50 mg kg^{-1}, as the base point. Still focusing on this graphic, a relative lower interference of the operation temperature and of the contaminant concentration was observed. Strengthening these results are the removal mean values - Figure 5.1 - concerning the variation of temperature and concentration parameters, that dist very little from each other, compared with the results obtained due to pH variation. However, it is important to refer that, averagely an increasing removal was observed for the increase in the contaminant loading, as reported by Jeyasingh *et al.* [2] for indigenous microorganisms. And also, that the expected enhancement of the contaminant removal for increasing temperatures, frequently associated to biological treatments, was not observed at such minor variation [5].

During similar studies with contaminated sludge, Villar and Garcia [13] did not note a significant discrepancy between removals for an initial pH of 4 and 7. On the other hand, but in longer assays, Kumar and Nagendran [18] observed a difference of 18% between bioleaching efficiencies, on soil systems at initial pH of 3 and 7, but with opposite trend, and registered a maximum removal - 90% - for the assay with an initial pH of 5. Although, besides the shorter contact time and the lower variation on pH in the first case, only total chromium was determined in both studies. And, as it is well known, trivalent chromium cations and hexavalent oxyanions have different mobility in acid/basic media [6]. Therefore, these removal values may be essentially related with one of the forms present in the contaminated sludge or soil, but also with the ideal pH for the bacteria growth. In order to clarify this, a closer approach was made through the evaluation of important parameters like media pH, Cr(VI) dissolution and sulfate production, along the most efficient assays for each contaminant concentration - C50pH2T26 and C100pH2T.

3.3. *Sulfur oxidation, pH variation and Cr(VI) dissolution*

As properly introduced, the *Acidithiobacillus thiooxidans* bacteria have the ability to oxidize elemental sulfur and produce sulfuric acid. Therefore, the sulfates production was followed, in all assays, and a representative result is shown on Figure 5.2, for the assays C50pH2T26 and C100pH2T.

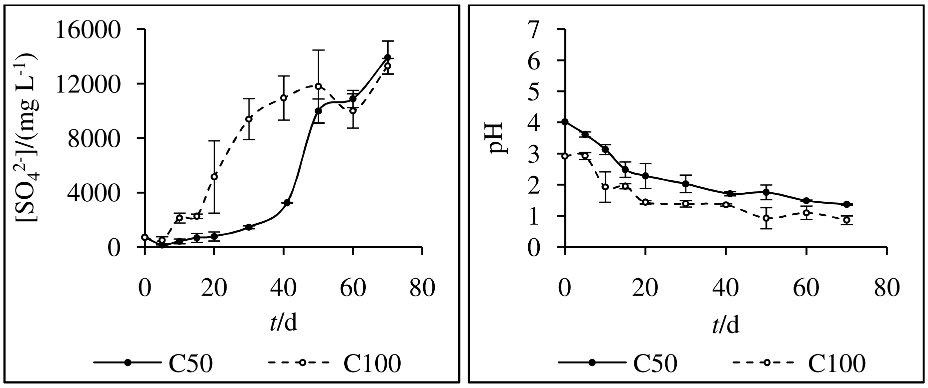


Figure 5.2. Sulfates concentration and pH in the liquid phase, registered along the most successful assays, performed with the soil samples contaminated at 50 mg kg^{-1} (C50) and 100 mg kg^{-1}(C100).

The maximum sulfate production is in accordance with the concentration range reported by other authors in similar studies [11,16,18]. An exponential increasing of the sulfate concentration is clear between the days 6 and 60. According to Liu *et al.* [16], this is an evidence of positive correlation between the exponential growth phase of the bacteria and the oxidation of elemental sulfur. However, the production of sulfuric acid kept growing after 60 days, meaning that other mechanisms than the bacteria metabolism may be involved in its production [16]. Therefore a decreasing pH was noted during the all experiment due to the constant production of sulfuric acid, as it can be seen on Figure 5.2. As expected, a higher total production of sulfuric acid, during the test with the soil contaminated with 100 mg kg^{-1} of Cr(VI), resulted in lower pH values, and consequently in a highly oxidizing environment [8]. Most of the heavy metal cations are then easily removed from soil matrices, except the Cr(VI) that exists mainly as oxyanions in natural environments, being less mobile in such acidic media [6,23]. Even though, dissolution of total chromium was recorded along the bioleaching batch tests - Figure 5.3.

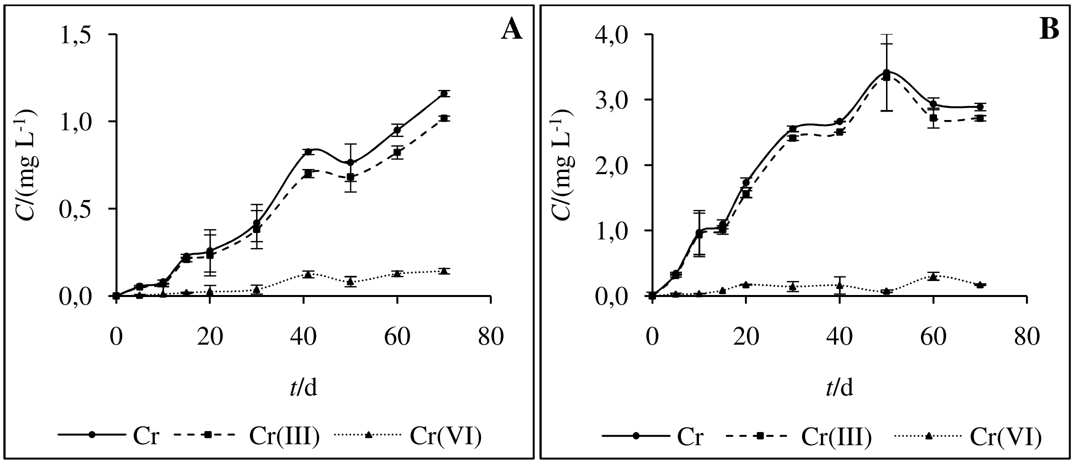


Figure 5.3. Cr, Cr(III) and Cr(VI) concentrations in the liquid phase, along the batch tests. A) Test undertaken at 26°C with the soil contaminated with 50 mg kg^{-1} of Cr(VI), at pH2 (C50pH2T26). B) Test undertaken at room temperature with the soil contaminated with 100 mg kg^{-1} of Cr(VI), at pH2 (C100pH2T).

A closer analysis to Figure 5.3 reveals that almost the whole chromium in solution is in the trivalent form, which means that the Cr(VI) was reduced and then leached. As mentioned previously, Allegretti *el al.* [21] proved that the oxidation of elemental sulfur generates a few sulfur compounds - polythionates, $S_x(SO_3)_2H_2{\cdot}wH_2O$ - which may be responsible for Cr(VI) reduction. Actually, these polythionates are known to be oxidized by substances with less reduction potential than Cr(VI) oxyanions. Steudel [33] proposed the spherical unilamellar and multilamellar vesicles model action: elemental sulfur is dissolved in a hydrophobic membrane - polythionates - that constrains an aqueous internal cavity. When the environment is acid these vesicles lose stability and the polythionates are slowly oxidized and released to the media. Therefore, given the high oxidizing environment during the bioleaching tests, the polythionates were responsible for the Cr(VI) reduction, and consequently for the bioleaching of Cr(III) cations, also favored by the acidic conditions. It is evident that higher levels of sulfur oxidation, expressed by the high concentration of sulfuric acid, in Figure 5.2, resulted in higher Cr(VI) reduction, explaining the elevated removal values - Figure 5.1.

The importance of the pH on the all process may also explain the lower removal values, obtained for the scenarios where a pH non adjusted contaminant solution was used - Figure 5.1. The low pH registered for these soils - Table 5.1 - resulted in a faster decrease of the media pH, due to the soil buffering capacity, favoring the Cr(VI) removal. Some authors reported the remnant chromium as bounded to the organic and residual fractions, and also noted an increasing on bioleaching efficiency with contact time. From the author's perspective, and because only total chromium was determined, it is plausible to attribute the non removed chromium to the hexavalent fraction. On the other hand, the same authors refer consistently the exchangeable and Fe/Mn oxide-bound fractions as the more mobile and bioavailable, which may justify the presence of few dissolved Cr(VI) - Figure 5.2 [11,12,18].

3.4. Phosphates dissolution

The digestion of soil organic matter and erosion of the original rock, and the consequent release of bounded nutrients, are often attributed to the highly oxidizing environment and the low pH, registered during the bioleaching experiments [8,34].

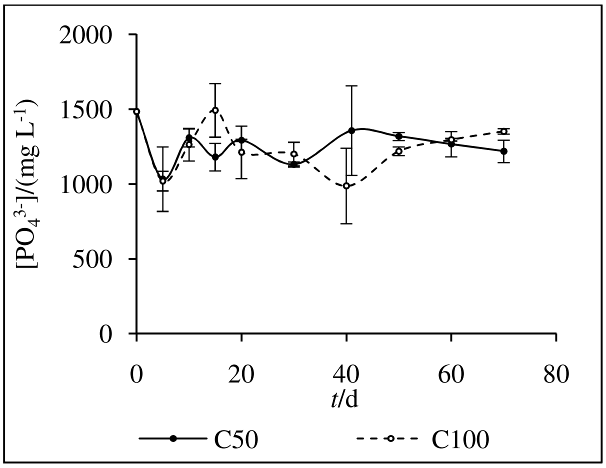


Figure 5.4. Phosphates concentration in the liquid phase, along the batch tests with soil contaminated at 50 mg kg^{-1} (C50) and 100 mg kg^{-1} (C100), concerning the higher removal values.

Therefore, this may represent a clear disadvantage on the application of this technique, as nutrients such phosphorus and nitrogen may be lost during the process. Even the low phosphate concentration found in the soil, an evaluation of its flotation in the liquid phase was performed, and a relatively constant behavior was observed - Figure 5.4. The slight decrease at the beginning was clearly related with phosphorus consumption during bacteria growth. Therefore, either if the soil is poor or not in phosphorus, the adding of this nutrient is mandatory for the success of the operation.

REFERENCES

[1] Loukidou, M.X., Zouboulis, A.I., Karapantsios, T.D., Matis, K.A. (2004) Equilibrium and kinetic modeling of chromium(VI) biosorption by *Aeromonas caviae*, Colloids Surf. A: Physicochem.Eng.Asp. 242, 93-104.

[2] Jeyasingh, J., Philip, L. (2005) Bioremediation of chromium contaminated soil: optimization of operating parameters under laboratory conditions, J. Hazard. Mater. 118, 113-120.

[3] Ore, S., Grennberg, K. (2000) The effect of metal pollutants leaching from the road constructed with bottom ash. Proceedings from: 7th International Conference on the Biogeochemistry of Trace Elements, Uppsala, Sweden.

[4] Mishra, S., Jena, S. (2009) Bioreduction based bioremediation of hexavalent chromium Cr (VI) through potential indigenous microbes, Department of Chemical Engineering, National Institute of Technology, Rourkela, Orissa, India.

[5] Umrania, V. (2006) Bioremediation of toxic heavy metals using acidothermophilic autotrophes, Bioresour. Technol. 97, 1237-1242.

[6] Fonseca, B., Teixeira, A., Figueiredo, H., Tavares, T. (2009) Modelling of the Cr(VI) transport in typical soils of the North of Portugal, J. Hazard. Mater. 167, 756-762.

[7] Krishna, K.R., Philip, L. (2005) Bioremediation of Cr(VI) in contaminated soils, J. Hazard. Mater. 121, 109-117.

[8] NareshKumar, R., Nagendran, R. (2008) Changes in nutrient profile of soil subjected to bioleaching for removal of heavy metals using *Acidithiobacillus thiooxidans*, J. Hazard. Mater. 156, 102-107.

[9] Gomez, C., Bosecker, K. (1999) Leaching Heavy Metals from Contaminated Soil by Using *Thiobacillus ferrooxidans* or *Thiobacillus thiooxidans*, Geomicrobiol. J. 16, 233-244.

[10] Lombardi, A.T., Garcia, O. (2002) Biological leaching of Mn, Al, Zn, Cu and Ti in an anaerobic sewage sludge effectuated by Thiobacillus ferrooxidans and its effect on metal partitioning, Water Res. 36, 3193-3202.

[11] Kumar, N.R., Nagendran, R., Parvathi, K. (2008) Bioleaching of heavy metals from contaminated soil using *Acidithiobacillus thiooxidans*: effect of sulfur/soil ratio, World J. Microbiol. Biotechnol. 24[8], 1539-1546.

[12] Liu, Y.G., Zhou, M., Zeng, G.M., Li, X., Xu, W.H., Fan, T. (2007) Effect of solids concentration on removal of heavy metals from mine tailings via bioleaching, J. Hazard. Mater. 141, 202-208.

[13] Villar, L.D., Garcia, J. (2006) Effect of Anaerobic Digestion and Initial pH on Metal Bioleaching from Sewage Sludge, J. Environ. Sci Health, Part A: Toxic/Hazard. Subst. Environ. Eng. 41, 211-222.

[14] Zagury, G.J., Narasiah, K.S., Tyagi, R.D. (2001) Bioleaching of metal-contaminated soil in semicontinuous reactor, J. Environ. Eng. 127, 812.

[15] Park, H.S., Lee, J.U., Ahn, J.W. (2007) The effects of Acidithiobacillus ferrooxidans on the leaching of cobalt and strontium adsorbed onto soil particles, Environ. Geochem. Health 29, 303-312.

[16] Liu, H.L., Chiu, C.W., Cheng, Y.C. (2003) The effects of metabolites from the indigenous *Acidithiobacillus thiooxidans* and temperature on the bioleaching of cadmium from soil, Biotechnol. Bioeng. 83, 638-645.

[17] Kumar, N.R., Nagendran, R. (2009) Fractionation behavior of heavy metals in soil during bioleaching with *Acidithiobacillus thiooxidans*, J. Hazard. Mater. 169, 1119-1126.

[18] Kumar, R.N., Nagendran, R. (2007) Influence of initial pH on bioleaching of heavy metals from contaminated soil employing indigenous *Acidithiobacillus thiooxidans*, Chemosphere 66, 1775-1781.

[19] Ishigaki, T., Nakanishi, A., Tateda, M., Ike, M., Fujita, M. (2005) Bioleaching of metal from municipal waste incineration fly ash using a mixed culture of sulfur-oxidizing and iron-oxidizing bacteria, Chemosphere 60, 1087-1094.

[20] Waksman, S.A. (1922) Microorganisms concerned in the oxidation of sulfur in the soil V. Bacteria oxidizing sulfur under acid and alkaline conditions, J. Bacteriol. 7, 609-616.

[21] Allegretti, P., Furlong, J., Donati, E. (2006) The role of higher polythionates in the reduction of chromium(VI) by *Acidithiobacillus* and *Thiobacillus* cultures, J. Biotechnol. 122, 55-61.

[22] B.Silva, H.Figueiredo, I.C.Neves, T.Tavares (2009) The role of pH on Cr(VI) reduction and removal by *Arthrobacter viscosus*, Int. J. Chem. Biol. Eng. 2, 100-103.

[23] Fonseca, B., Maio, H., Quintelas, C., Teixeira, A., Tavares, T. (2009) Retention of Cr(VI) and Pb(II) on a loamy sand soil: Kinetics, equilibria and breakthrough, Chem. Eng. J. 152, 212-219.

[24] Plackett, R.L., Burman, J.P. (1946) The design of optimum multifactorial experiments, Biometrika 33, 305-325.

[25] USEPA (2007) Microwave assisted acid digestion of sediments, sludges, soils, and oils, 3051, Environmental Protection Agency, United States of America.

[26] American Public Health Association (APHA) (1998) Standard methods for the examination of water and wastewater, American Public Health Association Publications, Washington.

[27] Olsen, S.R., C.V.Cole, F.S.Watanabe, L.A.Dean (1954) Estimation of available phosphorus in soils by extraction with sodium bicarbonate, Circ. 939, U. S. Department Of Agricultural.

[28] USEPA (2004) Soil and waste pH, Method 9045D, Environmental Protection Agency, United States of America.

[29] USEPA (1992) Chromium, hexavalent (colorimetric), 7196A, Environmental Protection Agency, United States of America.

[30] Kolmert, A., Wikstrom, P., Hallberg, K.B. (2000) A fast and simple turbidimetric method for the determination of sulfate in sulfate-reducing bacterial cultures, J. Microbiol. Methods 41, 179-184.

[31] Waksman, S.A., Joffe, J.S. (1922) The chemistry of the oxidation of sulfur by microorganisms to sulfuric acid and transformation of insoluble phosphates into soluble forms, J. Biol. Chem. 50, 35-45.

[32] Hatzikioseyian, A., Tsezos, M., Mavituna, F. (2001) Application of simplified rapid equilibrium models in simulating experimental breakthrough curves from fixed bed biosorption reactors, Hydrometallurgy 59, 395-406.

[33] Steudel, R. (1989) On the Nature of the Elemental Sulfur Produced by Sulfur-oxidizing Bacteria, in: Schlegel H.G., B. Bowien (Eds.), Biology of Autotrophic Bacteria, Science Tech. Publ., Madison, WI. 289-303.

[34] Waksman, S.A., Joffe, J.S. (1922) Microorganisms concerned in the oxidation of sulfur in the soil II. *Thiobacillus thiooxidans*, a new sulfur-oxidizing organism isolated from the soil, J. Bacteriol. 7, 239-256.

CHAPTER 6| Desorption kinetics of phenanthrene and lead from historically contaminated soil

Adapted from: *B. Fonseca, M. Pazos, H. Figueiredo, T. Tavares, M.A. Sanromán*

Chemical Engineering Journal

2011

***167:** 84-90*

1. INTRODUCTION

In the last decade, the decontamination of soils containing heavy metals and polycyclic aromatic hydrocarbons (PAHs) has been intensely investigated [1-6]. This type of soil contamination has been increasing, especially in urban areas, near gas stations or major roads and metalliferous mines, due to several human activities.

A set of cleaning technologies have been proposed and used effectively, including bioremediation, soil flushing, soil washing, electrokinetics and enhanced phytoextraction [4,7-12]. However, the success of these techniques depends on the availability of the contaminants in the aqueous phase of the soil/solution system. Several chelants and surfactants have been tested to determine if they are capable of enhancing the extraction/solubilisation of heavy metals and PAHs, respectively. Notably, the efficacies of (ethylenedinitrilo)-tetraacetic acid disodium salt (Na-EDTA) as a chelant and of polyethylene glycol sorbitan monooleate (Tween® 80/T80) and polyethylene glycol dodecyl ether (Brij® 35 P/ B35) as surfactants have been incontestably proven by several studies [4,5,8,12-18].

Despite all of the attention paid to this subject, to our knowledge, there are few reports that describe the desorption kinetics of contaminated sites polluted with both heavy metals and PAHs [12].

This study pretends to explore the application of composed solutions containing both a chelant and a surfactant (EDTA and/or T80 and B35) in the remediation of a soil contaminated with pollutants mixtures. It also pretends to evaluate and describe the desorption kinetics through mathematical modelling, providing therefore an useful tool to predict pollutants behaviour, during the decontamination process. Phenanthrene (PHE) and lead (Pb) were chosen as representative contaminants from each class, as both are in the priority pollutants list of the Environmental Protection Agency and are commonly found at high concentrations in environmental samples. Further, Pb is a positive charged ionic contaminant and PHE is a neutrally charged non-ionic contaminant [1,6,19].

The data obtained in batch desorption, of single and composed solutions containing EDTA and/or T80 and B35, were fitted to two kinetic models: the pseudo-second-order equation and the empirical power function. Moreover, scanning electron microscopy was used to characterise the soil before and after decontamination and to identify the role of some of its constituents during the sorption/desorption processes.

2. MATERIAL AND METHODS

2.1. Material

Contaminant: The phenanthrene used to contaminate the soil was > 97% pure and purchased from Sigma-Aldrich.

Extractants: The surfactants utilised were Brij® 35 P/ B35 (Fluka) and Tween® 80/T80 (Panreac), and the chelant agent used was EDTA (Panreac).

Original Soil: Typical samples of soil contaminated with approximately 5000 mg kg^{-1} of Pb were collected near an industrial waste site located at 12 km east of Algiers, Algeria (36°46'34.68''N and 3°3'30.6''E). The soil samples were previously characterised as described elsewhere by Amrate *et al.* [20].

2.2. Soil preparation

The co-contaminated soil samples were prepared by mixing the collected soil with a PHE solution (completely dissolved in hexane) to obtain an initial concentration of 500 mg kg^{-1}, which is the typical PAH concentration found near source zones of contaminated sites [21] Then the mixture was placed in a ventilation hood for 7-9 days until the hexane was completely evaporated.

2.3. Batch experiments

A series of batch experiments were conducted in order to evaluate the extraction of Pb and PHE under different operational conditions. Based on our previous studies [6,18,22], the nonionic surfactants T80 and 1% ($^{w}/_{v}$) B35 were chosen; EDTA (0.01 M) was chosen as the complexing agent. The EDTA concentration was selected based on its stability constants, the optimal molar ratio range and the type of complexation reactions being performed [4,16].

Then, 2 g of co-contaminated soil were mixed with each of the extraction solutions at three different soil:solution ratios (1:2.5, 1:5 and 1:10) in 100 mL Erlenmeyer flasks on a horizontal shaker (150 rpm) at room temperature. During the subsequent 24 h period, each experimental set was stopped at varying contact time in order to not disturb the equilibrium. The supernatant was collected, centrifuged at 10,000 rpm for 5 min and analysed for Pb and PHE content.

Then, an extraction process was tested by employing a 24 h contact time between the co-contaminated soil and one solution at a time. The pH was monitored in all experimental sets. A blank test using deionised water was properly performed, and no desorption was observed. The experiments were performed in duplicate being the standard deviation less than 10%.

2.3.1. Evaluation of the batch data

For the evaluation of the resultant kinetic data from the assays with composed extraction solutions and soils contaminated with Pb or with Pb and PHE, two kinetic models were selected:

Pseudo-second-order equation:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{43}$$

Empirical power function:

$$q_t = k_{PF} t^{v_{PF}} \tag{44}$$

where q_t (mg kg^{-1}) is the amount of contaminant desorbed from soil at time t (h); k_{PF} (kg mg^{-1} h^{-v}) and k_2 (kg mg^{-1} h^{-1}) are the rate constants of the respective equations; q_e (mg kg^{-1}) is the amount of contaminant desorbed per mass of soil at equilibrium and v is the constant of the empirical power function. The amount of each contaminant desorbed from the soil for each reaction time was calculated by

$$q_t = \frac{C_t V}{W} \tag{45}$$

where C_t (mg L^{-1}) is the concentration of contaminant in the liquid phase at varying contact times and V (L) is the volume of the liquid phase [23,24].

2.4. Analytical methods

Samples were taken from the soil and solutions, before and after the extraction assays, for chemical analysis. All analytical determinations were performed in triplicate with an experimental error below 3%.

2.4.1. PHE extraction and concentration

The PHE was extracted from the soil samples by a pressurised solvent extraction system using an OnePSE instrument (Applied Separations Inc.). The dry sample was thoroughly mixed with pelletized diatomaceous earth. When a free-flowing powder was obtained, it was placed into an extraction vessel inside of the instrument. The extraction solution was composed of acetone/hexane (1:1 $^{v}/_{v}$). After four cycles of 5 min at 110°C and 100 bar of pressure, the extraction was complete, and the PHE concentration in the collected sample was determined. Pressurised solvent extraction has been approved for use following EPA Method 3545A and can replace Soxhlet and sonication techniques.

The PHE concentration was determined by an HPLC (Agilent 1100) equipped with an XDB-C8 reverse-phase column (150×4.6 mm i.d., 5 µm). Prior to injection, the samples were filtered through a 0.45-µm Teflon filter. The injection volume was set at 5 µL and the isocratic eluent (60:40 acetonitrile/water) was pumped at a rate of 1 mL min^{-1} for 10 min. Detection was performed with a diode array detector from 200 to 400 nm, as the detection wavelength of phenanthrene is 252 nm, and, the column temperature was maintained at 20°C.

2.4.2. Pb extraction and concentration

The protocols used for the chemical extraction and analysis of metals were performed in accordance with EPA Methods 3010 and 3050B [25]. Flame atomic absorption spectrometry (FAAS) was performed using a Varian SpectrAA-250 Plus to determine the Pb concentration.

2.5. *SEM analysis*

The morphology and chemistry of samples, in the same conditions mentioned in the previous section, were analysed by scanning electron microscopy (SEM). The microscope used was a Nova™ 200 NanoSEM with an integrated electron-dispersive X-ray spectroscopy (EDAX) system (Pegasus X4M). The integrated system enabled simultaneous collection of data by an energy dispersive spectrometer (EDS) and a back-scattered electron detector (EBSD).

3. RESULTS AND DISCUSSION

3.1. *Soil characterization*

As mentioned previously, the soil samples used in the present work correspond to those used by Amrate *et al.* [20]. The chemical soil properties are listed in Table 6.1. These soil samples are poor in organic matter, have a pH close to neutral and are contaminated with high concentrations of Pb (approximately 5000 mg kg^{-1}). In the co-contaminated soil, the PHE concentration was around 500 mg kg^{-1}.

Table 6.1. Chemical properties of soil [1]

Parameter	Data	Parameter	Data
pH (only with Pb)	7.30 ± 0.02	Quartz (%)	45.0
pH (Pb and PHE)	6.18 ± 0.13	Calcite (%)	24.5
Ignition loss at 550 °C (%)	5.0±0.9	Dolomite (%)	1.6
Active calcareous (%)	4.9±0.7	Gypse (%)	1.4
C.E.C. (meq/100 g)	4.82±0.17	Albite (%)	8.3
Organic matter (%)	1.26±0.11	Chlorite (%)	7.3
Lead (mg kg $^{-1}$)	5489±383	Kaolinite	6.3
Nickel (mg kg^{-1})	139±13	Illite (%)	2.4
Cadmium (mg kg $^{-1}$)	22±8	Orthoclase (%)	3.2
Phenantrene (mg kg $^{-1}$)	455.0±0.5		

[1] Adapted from Amrate *et al.* [20]

3.2. Batch experiments

The effects of surfactants and complexing agents on the removal of PHE and Pb polluted soil were observed. According to previous research, EDTA may improve Pb solubility [22,26,27]. To enhance PHE removal, nonionic surfactants were selected because of their higher solubilisation capacities and lower cost when compared to cationic and anionic surfactants. Specifically, the nonionic surfactants T80 and B35 were chosen based on our previous studies [18].

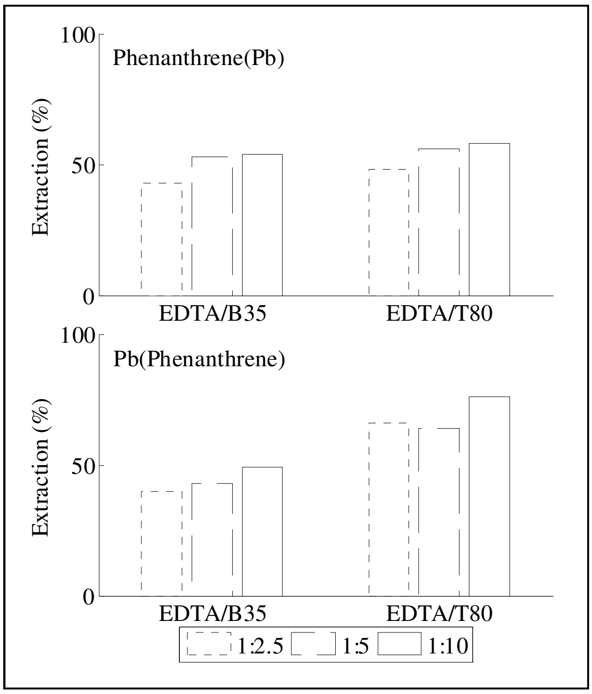


Figure 6.1. Percentage of extraction obtained after 24 h of contact between soil samples contaminated with Pb (~5000 mg kg^{-1}) and PHE (~500 mg kg^{-1}) and the composed solutions EDTA/B35 or EDTA/T80 for varying soil:solution ratios. (A) Values obtained for the PHE extraction. (B) Values obtained for the Pb extraction.

At first, batch experiments were performed to examine the extraction behaviour of PHE and Pb from co-contaminated soil using an extraction solution that contained a mixture of T80 (1% $^{w}/_{v}$) or B35 (1% $^{w}/_{v}$) and 0.01 M EDTA. Initially, the optimal soil: solution ratio was determined. The extraction levels of PHE and Pb, obtained with three different soil: solution ratios via application of the EDTA/T80 and EDTA/B35 solutions to 2 g of co-contaminated soil, are shown in Figure 6.1. In contrast to results reported previously by other authors [28], we found that generally a decreasing soil:solution ratio resulted in a higher extraction efficiency, with a higher efficiency of extraction especially noted when the ratio was reduced from 1:2.5 to 1:5 or 1:10. However, there was no remarkable difference between the two lower soil: solution ratios. Therefore, to avoid unnecessary costs and waste production, the subsequent tests were carried out at the soil: solution ratio of 1:5, which also enabled measurement of adequate kinetic profiles.

3.2.1. Single and composed solutions

As with the previous extraction assays, the efficiency and kinetic behaviour of the two composed solutions in the remediation of co-contaminated soil (containing both Pb and PHE contaminants) and of the soil containing only the original Pb contamination were tested using the soil: solution ratio 1:5.

The kinetics profiles of Pb desorption in the original and co-contaminated soil with both of the extraction solutions (EDTA/B35 and EDTA/T80) are illustrated in Figure 6.2. The maximum extraction of Pb was obtained using the soil contaminated only with Pb; this result was verified when single extraction solutions comprised solely of EDTA, B35 or T80 were tested in both contamination scenarios (Figure 6.3). The main difference between these soils samples, most likely resulting from the type of contamination, was the pH value (Table 6.1). Several authors have demonstrated that, to obtain high extraction values, the pH of the soil-solution system must be maintained as slightly alkaline or higher than the pK_{a2} (6.16) of EDTA [4,13,20,29,30]. These conditions guarantee predomination of the $EDTA^{4-}$ ion, which coordinates with Pb via four acetate groups and two nitrogen atoms with four electron pairs, making a highly stable Pb complex [15,20]. In this study, pH values lower than the pK_{a2} were reported at the initiation of the assays performed with the soil co-contaminated with Pb and PHE, resulting in a decreased Pb extraction efficiency. Also, according to recent studies, at high concentrations phenanthrene is sorbed mainly through non-specific hydrophobic forces and therefore can form cation-π bond with Pb to eventually enhance its sorption [31].

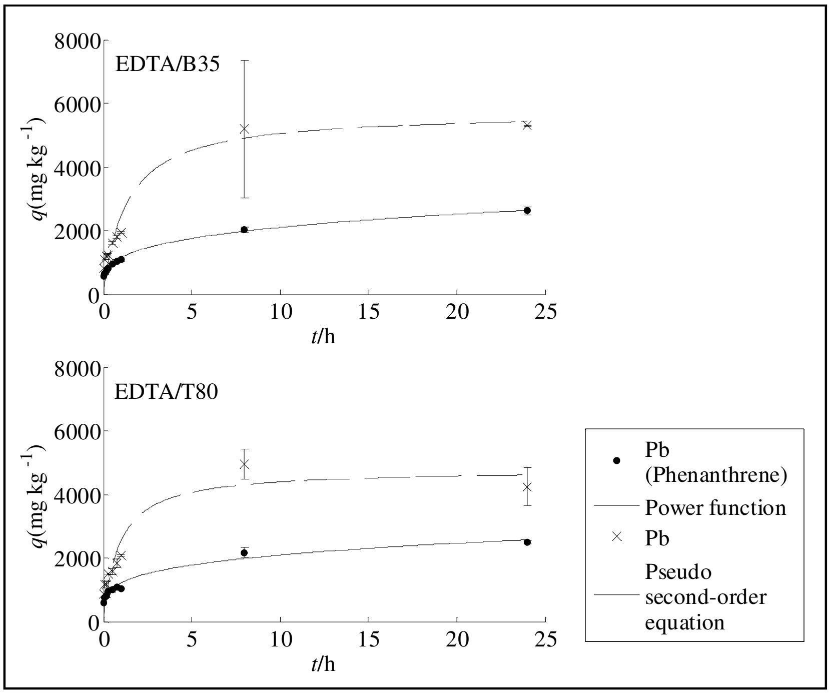


Figure 6.2. Kinetic profiles for lead extraction obtained for the composed solutions, EDTA/T80 and EDTA/B35, applied to soil samples contaminated with Pb [× Pb] or with Pb and PHE [· Pb (Phenanthrene)]. The lines represent the kinetic model with the best fit.

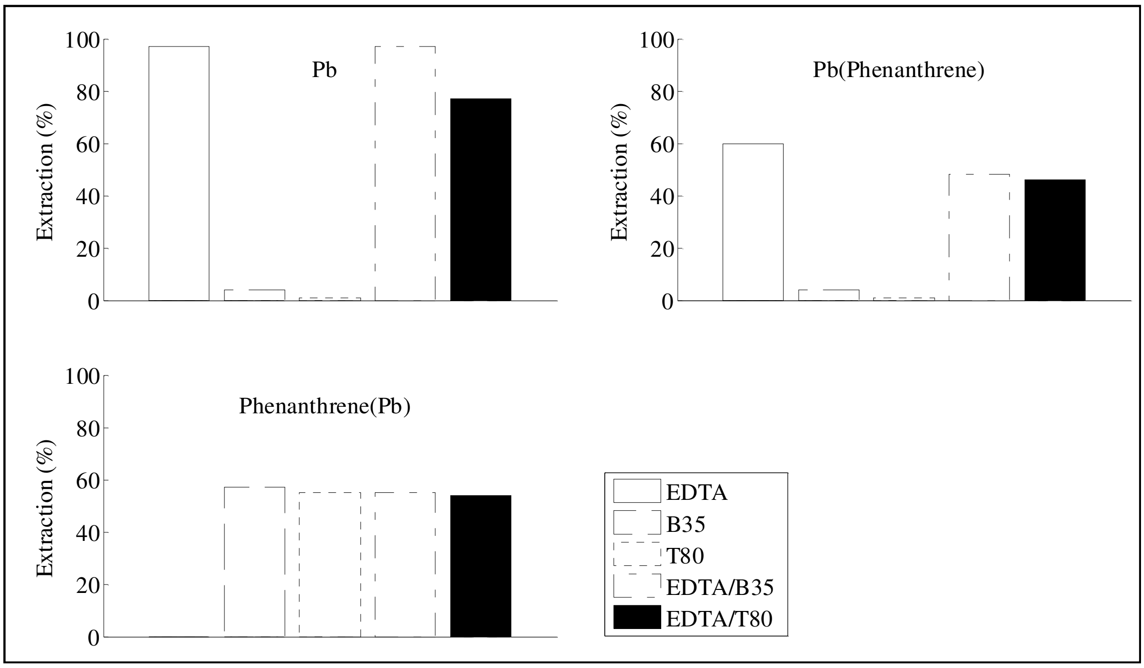


Figure 6.3. Percentages of Pb and PHE extraction from soil contaminated with PHE and Pb [Pb(Phenanthrene); Phenanthrene (Pb)] and soil contaminated only with Pb after 24 h of contact with single and composed solutions comprised of EDTA and/or EDTA with B35 or T80.

The PHE extraction appeared to be independent from the type of solution, single or composed, employed to remediate the co-contaminated soil (Figure 6.3). As shown in Figure 6.3, the application of the chelant agent EDTA as a single solution or as a component of a composed solution did not improve the extraction efficiency of the contaminant.

3.2.2. Kinetics modelling of extractions with composed solutions

The desorption profiles of Pb and PHE from co-contaminated soil are shown in Figures 6.2 and 6.4. The rapid desorption of both contaminants during the first eight hours was followed by a plateau that corresponded to a decrease in desorption velocity. According to a recent report by Labib *et al.* [32], when the adsorption energy is considerably high, the desorption process is limited by the transport rate of contaminants that move from the surface layer to the sub-layer. Therefore, the contaminants sorbed in the low energy sites are easily and quickly desorbed compared to the fraction that is strongly sorbed. On the other hand, other authors believe that in the slower phase, the desorption of PHE is mainly controlled by intraparticle diffusion [33].

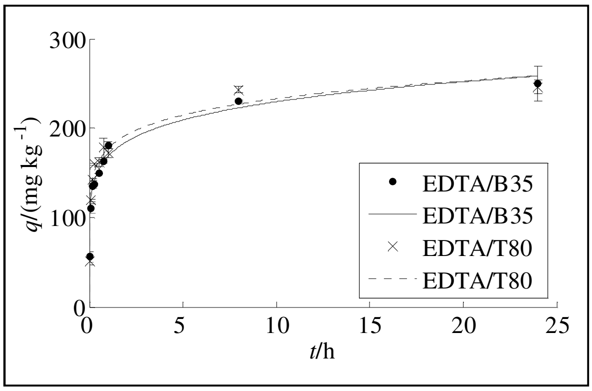


Figure 6.4. Kinetic profile of PHE extraction obtained for systems of a composed solution, EDTA/T80 or EDTA/B35, and co-contaminated soil samples. The lines represent the empirical power function, adjusted to the experimental data.

The desorption process was enhanced by the use of composed solutions that contained a surfactant (T80 or B35) and a chelant (EDTA). Although several kinetic models were tested, the experimental data were well fitted by the empirical power function and also by the pseudo-second-order equation, for both contaminants (Table 6.2). It should be noticed that, besides its empirical character, the first model provides a good method to compare experimental results [23]. Given this, the values derived for the empirical power function constant, *k*, suggest a higher efficiency in the simultaneous extraction of Pb and PHE with the EDTA/T80 solution. Use of this solution resulted in extraction of 46% of the Pb and 54% of the PHE after 24 h, whereas 48% and 55% of Pb and PHE were extracted with the EDTA/B35 solution, respectively. These findings are in accordance with results reported by Cheng and Wong [5] and Alcantara *et al.* [18]. These previous studies demonstrated that T80 has a higher capacity for PHE extraction in the soil-water systems than B35. Nevertheless, the percent of the total PHE extracted with the EDTA/B35 and the B35 solutions in this study were higher than the values obtained in these previous studies (< 40%). This discrepancy between the percents of extraction may have occurred mainly due to differences in soil composition, as clay minerals or organic matter strongly bind PAHs [34], but the equilibrium between the soil:solution ratio and the concentration of the extracting solution may also have contributed. It should be noted that in all studies conducted, the concentration of surfactants was higher than their respective critical micelle concentrations in order to enhance PHE solubilisation via micelle and microemulsion formation [5,17,18].

The values estimated through the adjustment of the pseudo-second-order equation for the mass of PHE and Pb desorbed from the contaminated soil - q_e, Table 6.2 - were very similar to the correspondent experimental values obtained - Figure 6.2 and 6.4. Therefore, and as recently reported by Wang *et al.* [35], the pseudo-second-order equation is suitable for desorption process of phenanthrene and lead, from a contaminated soil. Focusing now the soil contaminated only with Pb, a significantly higher maximum (de)sorption capacity value, q_e, was found for the EDTA/B35 solution. In fact, Figure 6.3 demonstrates that when used alone, B35 promoted a higher desorption of Pb than T80; however, EDTA used alone still resulted in a more efficient extraction. The EDTA concentration in the single or composed solutions was 0.01 M in order to use an EDTA:Pb molar ratio of two, which is within the optimal range identified by Zhang and Lo [4]. Though others have reported results similar to those obtained in this study [4,36], the values obtained for Pb extraction from the original soil were high (~100%) compared to values obtained with soils that had a longer period of contamination [13,29]. Once again, the soil and/or the contamination characteristics may have affected the success of the remediation enhanced by composed solutions.

Table 6.2. Parameters and correlation coefficients (r^2) obtained for the adjustment of two kinetic desorption equations. The values correspond to four data sets – desorption of Pb from the mono and co-contaminated soils, using the composed solutions of EDTA/B35 and EDTA/T80. Desorption of phenanthrene, using the same composed solutions, from the co-contaminated soil

Soil contaminated with lead (Pb) and phenanthrene (PHE)

	(Solution) Contaminant Kinetic parameters	(EDTA/B35) Pb	(EDTA/B35) PHE	(EDTA/T80) Pb	(EDTA/T80) PHE
Power Function	k/(mg kg^{-1} h^{-v})	1150 ± 204	168 ± 20	1217 ± 232	177 ± 19
	v	0.261 ± 0.073	0.135 ± 0.055	0.236 ± 0.081	0.118 ± 0.052
	r^2	0.917	0.873	0.877	0.882
Second-order rate equation	k_2/(kg mg^{-1} h^{-1})	0.001 ± 0.001	0.031 ± 0.034	0.001 ± 0.001	0.042 ± 0.045
	q_e/(mg kg^{-1})	2422 ± 684	223 ± 45	2357 ± 715	224 ± 41
	r^2	0.783	0.770	0.720	0.795

Soil contaminated with lead (Pb)

	(Solution) Contaminant Kinetic parameters	(EDTA/B35) Pb	(EDTA/T80) Pb
Power Function	k/(mg kg^{-1} h^{-v})	2179 ± 547	2179 ± 610
	v	0.309 ± 0.099	0.256 ± 0.116
	r^2	0.911	0.826
Second-order rate equation	k_2/(kg mg^{-1} h^{-1})	0.0001 ± 0.0001	0.0002 ± 0.0002
	q_e/(mg kg^{-1})	5718 ± 1202	4781 ± 1242
	r^2	0.914	0.842

3.3. SEM analysis

The images obtained by scanning electron microscopy with a back-scattered electron (BSE) detector are shown in Figure 6.5 (A and B). These images correspond to co-contaminated samples before and after decontamination. The "brighter" BSE intensity (Figure 6.5, A, Z1) suggested the presence of atoms with higher atomic numbers, which was confirmed by the respective energy dispersive spectroscopy data (Z1). Pb was detected as the major element present, followed by oxygen (O) and iron

(Fe), which suggested that Pb was mainly sorbed by iron oxides, as suggested by Amrate *et al*. [20] with the procedure of Tessier [37]. In the second analyzed zone (Figure 6.5, A, Z2), and also in the image of the decontaminated sample (Figure 6.5, B), “dark” areas are predominant, and only residual Pb was detected by the energy dispersive spectroscopy. Once more, atoms of Fe and O were detected as well as atoms of silica (Si) and aluminum (Al), which indicated the presence of aluminosilicates that are characteristic of clay minerals. Several images were acquired, and a decreased BSE or “bright” intensity was detected in all of the decontaminated samples.

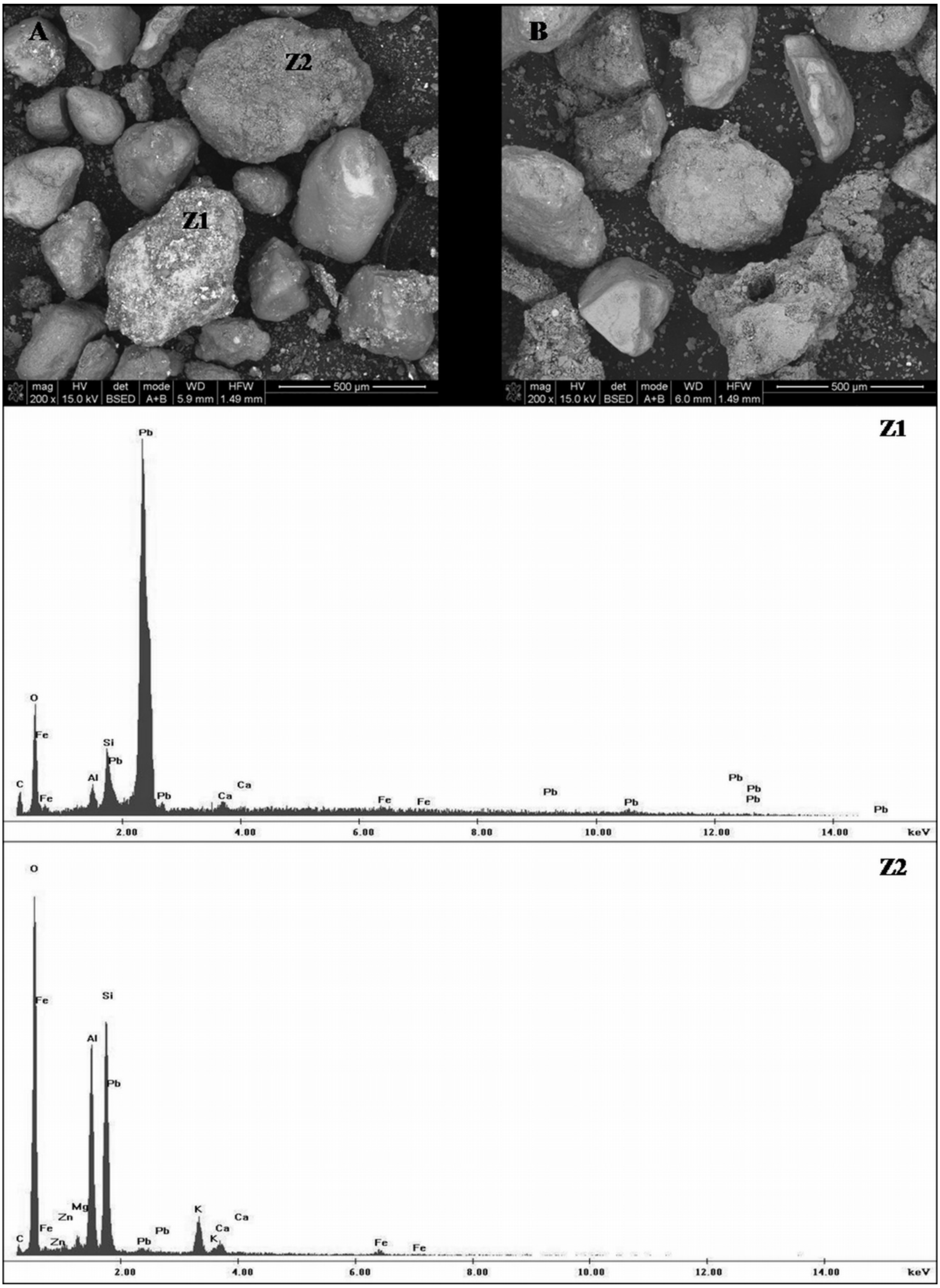


Figure 6.5. SEM images of a soil sample contaminated with Pb (A) and of a decontaminated soil sample (B) obtained with the EBSD detector. The lower graphs shows the EDS results for a zone highly concentrated with Pb (Z1) and for a non-taminated zone (Z2).

REFERENCES

[1] Ik Chung, H., Kamon, M. (2005) Ultrasonically enhanced electrokinetic remediation for removal of Pb and phenanthrene in contaminated soils, Eng. Geol. 77, 233-242.

[2] Glover, L.J., Eick, M.J., Brady, P.V. (2002) Desorption Kinetics of Cadmium^{2+} and Lead^{2+} from Goethite: Influence of Time and Organic Acids, Soil Sci Soc Am J 66, 797-804.

[3] Bamforth, S.M., Singleton, I. (2005) Bioremediation of polycyclic aromatic hydrocarbons: current knowledge and future directions, J. Chem. Technol. Biotechnol. 80, 723-736.

[4] Zhang, W.H., Lo, I.M.C. (2006) EDTA-enhanced washing for remediation of Pb- and/or Zn-contaminated soils, J. Environ. Eng. Asce 132, 1282-1288.

[5] Cheng, K.Y., Wong, J.W.C. (2006) Effect of synthetic surfactants on the solubilization and distribution of PAHs in water/soil-water systems, Environ. Technol. 27, 835-844.

[6] Alcantara, T., Pazos, M., Cameselle, C., Sanromán, M.A. (2008) Electrochemical remediation of phenanthrene from contaminated kaolinite, Environ. Geochem. Health 30, 89-94.

[7] Kirkham, M.B. (2000) EDTA-Facilitated Phytoremediation of Soil with Heavy Metals from Sewage Sludge, Int. J. Phytoremediat. 2, 159-172.

[8] Peters, R.W. (1999) Chelant extraction of heavy metals from contaminated soils, J. Hazard. Mater. 66, 151-210.

[9] Zagury, G.J., Narasiah, K.S., Tyagi, R.D. (2001) Bioleaching of metal-contaminated soil in semicontinuous reactor, J. Environ. Eng. 127, 812.

[10] Sekhar, K.C., Kamala, C.T., Chary, N.S., Balaram, V., Garcia, G. (2005) Potential of Hemidesmus indicus for phytoextraction of lead from industrially contaminated soils, Chemosphere 58, 507-514.

[11] Tao, X.Q., Lu, G.N., Dang, Z., Yang, C., Yi, X.Y. (2007) A phenanthrene-degrading strain Sphingomonas sp GY2B isolated from contaminated soils, Process Biochem 42, 401-408.

[12] Lestan, D., Luo, C.l., Li, X.d. (2008) The use of chelating agents in the remediation of metal-contaminated soils: A review, Environ. Pollut. 153, 3-13.

[13] Heil, D., Hanson, A., Samani, Z. (1996) The competitive binding of lead by EDTA in soils and implications for heap leaching remediation, Radioact. Waste. Manag. Environ. Restor. 20, 111-127.

[14] Darban, A.K., Foriero, A., Yong, R.N. (2000) Concentration effects of EDTA and chloride on the retention of trace metals in clays, Eng. Geol. 57, 81-94.

[15] Yuan, S.H., Xi, Z.M., Jiang, Y., Wan, J.Z., Wu, C., Zheng, Z.H., Lu, X.H. (2007) Desorption of copper and cadmium from soils enhanced by organic acids, Chemosphere 68, 1289-1297.

[16] Wong, J.S.H., Hicks, R.E., Probstein, R.F. (1997) EDTA-enhanced electroremediation of metal-contaminated soils, J. Hazard. Mater. 55, 61-79.

[17] Wong, J.W.C., Fang, M., Zhao, Z.Y., Xing, B.S. (2004) Effect of surfactants on solubilization and degradation of phenanthrene under thermophilic conditions, J. Environ. Qual. 33, 2015-2025.

[18] Alcantara, M.T., Gomez, J., Pazos, M., Sanromán, M.A. (2008) Combined treatment of PAHs contaminated soils using the sequence extraction with surfactant-electrochemical degradation, Chemosphere 70, 1438-1444.

[19] Saifullah, Meers, E., Qadir, M., de Caritat, P., Tack, F.M.G., Du Laing, G., Zia, M.H. (2009) EDTA-assisted Pb phytoextraction, Chemosphere 74, 1279-1291.

[20] Amrate, S., Akretche, D.E., Innocent, C., Seta, P. (2005) Removal of Pb from a calcareous soil during EDTA-enhanced electrokinetic extraction, Sci. Total. Environ. 349, 56-66.

[21] Gómez, J., Alcántara, M.T., Pazos, M., Sanromán, M.A. (2010) Remediation of polluted soil by a two-stage treatment system: Desorption of phenanthrene in soil and electrochemical treatment to recover the extraction agent, J. Hazard. Mater. 173, 794-798.

[22] Pazos, M., Alcantara, M.T., Cameselle, C., Sanromán, M.A. (2009) Evaluation of Electrokinetic Technique for Industrial Waste Decontamination, Sep. Sci. Technol. 44, 2304-2321.

[23] Fonseca, B., Maio, H., Quintelas, C., Teixeira, A., Tavares, T. (2009) Retention of Cr(VI) and Pb(II) on a loamy sand soil: Kinetics, equilibria and breakthrough, Chem. Eng. J. 152, 212-219.

[24] Sparks, D.L. (1995) Environmental Soil Chemistry, Academic Press, San Diego.

[25] USEPA (2008) Acid digestion of sediments, sludges, and soils., 3050B, Environmental Protection Agency, United States of America.

[26] Reddy, K.R., Ala, P.R. (2005) Electrokinetic remediation of metal-contaminated field soil, Sep. Sci. Technol. 40, 1701-1720.

[27] Jensen, P.E., Ahring, B.K., Ottosen, L.M. (2007) Organic acid enhanced electrodialytic extraction of lead from contaminated soil fines in suspension, J. Chem. Technol. Biotechnol. 82, 920-928.

[28] Kim, C., Lee, Y., Ong, S.K. (2003) Factors affecting EDTA extraction of lead from lead-contaminated soils, Chemosphere 51, 845-853.

[29] Hong, P.K.A., Li, C., Banerji, S.K., Regmi, T. (1999) Extraction, Recovery, and Biostability of EDTA for Remediation of Heavy Metal-Contaminated Soil, J. Soil Contam. 8, 81-103.

[30] Soltan, M.E. (2006) Remobilization of selected metal ions from Nile sediment (Egypt) according to sequential extraction and metal-EDTA complex, Chem. Ecol. 22, 359-378.

[31] Zhang, W., Cao, J., Huang, H., Zhang, R. (2010) Effect of Coexisting Lead and Phenanthrene on Their Individual Sorption on a Clayish Soil, Soil and Sediment Contam. An Int. J. 19, 322-337.

[32] Labib, M., Dukhin, S.S., Tabani, Y. (2010) Desorption kinetics during capillary flow, Colloids Surf. A: Physicochem. Eng. Asp. 354, 45-50.

[33] Wang, G.H., Grathwohl, P. (2009) Activation energies of phenanthrene desorption from carbonaceous materials: Column studies, J. Hydrol. 369, 234-240.

[34] Luthy, R.G., Aiken, G.R., Brusseau, M.L., Cunningham, S.D., Gschwend, P.M., Pignatello, J.J., Reinhard, M., Traina, S.J., Weber, W.J., Westall, J.C. (1997) Sequestration of hydrophobic organic contaminants by geosorbents, Environ. Sci. Technol. 31, 3341-3347.

[35] Wang, G., Zhou, Y., Wang, X., Chai, X., Huang, L., Deng, N. (2010) Simultaneous removal of phenanthrene and lead from artificially contaminated soils with glycine-[beta]-cyclodextrin, J. Hazard. Mater. 184, 690-695.

[36] Pichtel, J., Pichtel, T.M. (1997) Comparison of solvents for ex situ removal of chromium and lead from contaminated soil, Environ. Eng. Sci. 14, 97-104.

[37] Tessier, A., Campbell, P.G.C., Bisson, M. (1979) Sequential extraction procedure for the speciation of particulate trace metals, Anal. Chem. 51, 844-851.

CHAPTER 7| An innovative hybrid technology - electrokinetic and biobarriers - applied to hexavalent chromium contaminated clays

Adapted from: *B. Fonseca, M. Pazos, T. Tavares, M.A. Sanromán*

Submitted to Chemosphere

2011

1. INTRODUCTION

Hexavalent chromium - Cr(VI) - is extensively used in a wide range of industrial activities, like manufacturing of stainless steel, chrome leather tanning, ceramics, pyrotechnics and electronics. It is frequently released to waters and soils, due to accidental spills, storm water run-off and uncontrolled leaching from storage ponds or dumps. Moreover, it is known as one of the most toxic heavy metals, being in evidence in the EPA list of human carcinogens and designated as a priority pollutant in many countries [1-3].

Several techniques have been developed and actually used to treat soils contaminated with Cr(VI), like flushing, phytoremediation, excavation and landfill disposal. However, for over a decade, the removal of Cr(VI) from soils through the operation of electrokinetic (EK) cells has attracted significant attention, as they can be applied, either *in* or *ex situ*, with cost effectiveness. Basically, this technique promotes the electromigration of the Cr(VI) oxyanions towards the anode chamber, when a low voltage gradient is applied to the EK cell [4-12]. However, there are some problems concerning this method, like its elongation in time and the production of liquid effluents [13,14].

On the other hand, the use of permeable reactive barriers (PRBs) has gained popularity in the groundwater cleaning field, due to its high efficiency, low cost and simple operation procedures. These barriers are composed by reactive materials that once in contact with the contaminated water plume, can degrade, adsorb or precipitate the targeted contaminant(s) [15,16]. Due to the evolution of biotechnology, biologic materials are being successfully used in these PRBs. Previous experiments using *Arthrobacter viscosus* supported either in zeolites or activated carbon (GAC), showed great efficiency in the treatment of Cr(VI) effluents. Succinctly, when these systems are applied, 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 [3,17-22]. This biosorption mechanism is known as the "adsorption coupled reduction". The Cr(III) is a less soluble, mobile and toxic form of chromium, and above all this, it is an essential micronutrient [1,23,24]. Furthermore, these biobarriers (BIO-PRBs) containing the immobilized chromium can then be used as catalysts. [25].

Based on the above-mentioned 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). In order to perform it, reactive biobarriers consisting of *Arthrobacter viscosus* supported on zeolite 13X or on GAC, were placed before the anode chambers of EK cells, packed with contaminated soil. This system was tested using kaolin which is a model sample representative of low permeability soil with low buffering capacity.

2. MATERIAL AND METHODS

2.1. Material

Contaminant: The potassium dichromate ($K_2Cr_2O_7$) used to contaminate the soil was purchased from Normapur AR.

Soil: The soil selected for this research was the clay mineral kaolin, since it represents a low permeability soil, with consistent and uniform mineralogy and low cation exchange and buffer capacities. The composition and properties of this soil were summarized elsewhere [26]

Bacteria: Arthrobacter viscosus was obtained from the Spanish Type Culture Collection of the University of Valencia. It was maintained at 4ºC on 15 g L^{-1} agar slants and plates with culture medium containing 10 g L^{-1} of glucose, 5 g L^{-1} of peptone, 3 g L^{-1} of malt extract and 3 g L^{-1} of yeast extract.

Supports: GAC was purchased from MERCK. It was characterized by an average particle size of 2.5 mm, a Langmuir area of 1270 m^2 g^{-1} and an average pore diameter of 2 nm [27]. The Zeolite 13X was provided by Xiamen Zhongzhao Imp.&Exp. Co., Ltd. The pellets size was 5-8 mm and normal pore diameter 13 Å. Both supports were macerated with the purpose of working with their powder.

2.2. Soil preparation

The soil was spiked with $K_2Cr_2O_7$ solution, in order to obtain a concentration of Cr(VI) around 50 mg kg^{-1}. The quantity required to obtain the desired concentration, was dissolved in a volume of water. The mixture was placed in a fume hood and stirred every day, till complete dryness (2-3 days). Then, the soil was mixed with water to obtain a moisture content of 30 % ($^{w}/_{w}$). The mixture was performed in a glass vat with stirring rod. At the end, a sample was collected to determine the initial concentration of Cr(VI).

2.3 Biobarriers preparation

A volume of 500 mL of culture medium for *Arthrobacter viscosus* previously prepared. Then, the zeolite or the activated carbon, were added in order to obtain the same ratio of solid:solution ($^{v}/_{v}$) for both supports (1:12.5). This decision was supported by previous tests performed with the same supports [17,22,27-29]. Each set was sterilized at 121 °C for 20 min, cooled to room temperature, inoculated with bacteria and kept at 28 °C for 48 h. Half of the volume of the growth culture, together with the support, was filtered by using a mechanical vacuum system with cellulose filters (Whatman, Ø 32 mm). The pairing of two filters, containing biomass supported on zeolite or carbon, constituted a "biobarrier".

2.4. Experimental setup

The experiments correspondent to the blank assays were performed in glass cells with 13.5 cm of length and 32 mm of diameter [30], filled with the contaminated kaolin. Then, a cathode and anode electrode chambers (with 300 mL working volume) were coupled at the ends of the column, isolated from the matrix with filter papers and porous stones. Graphite electrodes were used for both chambers and three auxiliary electrodes allowed the measurement of the electric field through the column. The electrode chambers were filled with distilled water and the liquid was recirculated, by peristaltic pumps, to prevent the development of concentration gradients. The pH in both chambers was controlled in order to maintain it around 5, which is a value that represents a commitment between the optimum pH for the bacteria and the optimum pH for the Cr(III) adsorption by each support [20,23,31,32]. The adjustment was made with NaOH (0.1 M) and HNO_3 (0.1 M). A potential difference of 10 V was applied to the horizontal column. Readings of voltage drop and current intensity were made periodically. Since the dichromate anions migrate towards the anode chamber, as proved by the blank assays results, the tests with biobarriers were performed by inserting the biobarrier, comprised between two filter papers and two porous stones, before this compartment. All the tests, either blank or with carbon or zeolite biobarriers, were performed for two time intervals - 9 and 18 days - aiming the optimization of the decontamination process. Table 7.1 resumes the various experimental setups.

After each experiment, the soil column was divided in five sections (S1 to S5). These soil samples, the biobarrier and the liquid from the electrode chambers were analyzed for total and hexavalent chromium, after pH determination. Consequently, trivalent chromium was determined through the numerical difference between these two forms. All samples were processed in duplicate.

Table 7.1. Experimental conditions

			Current	**pH control**	
Assay interval	**Assay**	**Biobarrier**	**Voltage**	**Anode chamber**	**Cathode chamber**
9 d	1	Blank	10 V	NaOH 0.1M	HNO_3 2M
	2	Activated carbon			
	3	Zeolite			
			Intensity		
18 d	4	Blank	0.5 mA		
	5	Activated carbon			
	6	Zeolite			

2.5. Analytical methods

The analytical methods used to determine the total and the hexavalent chromium concentrations, on the liquid and solid phases are listed below.

Total chromium: The soil samples were digested in a microwave (CEM MDS-2000) with HNO_3 (65%), according to the US EPA method 3051 [33]. The determination of total chromium was made by flame atomic absorption (Varian SpectrAA-250 Plus).

Hexavalent chromium: Prior to the Cr(VI) determination on soil samples, an alkaline digestion was performed as described on US EPA method 3060A [34]. The quantification of Cr(VI) was made by the US EPA colorimetric method 7196A. The absorbance was measured using a Thermo Heλios β spectrophotometer [35].

pH: The pH of liquid samples was directly measured with a Jenway 3520 pH meter, and the pH of soil samples was determined following the US EPA method 9045D [36].

2.6. SEM analysis and bioviability

The morphology and chemistry of the biobarrier after each test were analysed by scanning electron microscopy (SEM). The microscope used was a Nova™ 200 NanoSEM with an integrated electron-dispersive X-ray spectroscopy (EDAX) system (Pegasus X4M). The integrated system enabled simultaneous collection of data by an energy dispersive spectrometer (EDS) and a back-scattered electron detector (EBSD).

The bioviability of the *Arthrobacter viscosus* was also tested at the end of the assays, by streaking in an agar plate containing the growth medium.

3. RESULTS AND DISCUSSION

3.1. Blank assay: evaluation of hexavalent chromium mobility

In order to evaluate the mobility of the Cr(VI) in an electrokinetic cell, under the applied current, two blank assays were performed. The first one lasted 9 days, but no satisfactory removal was achieved. Therefore, the time interval was elongated to the double - 18 days - and better results were achieved. The analysis of the Figure 7.1 reveals that the higher percentage of Cr(VI) - 76.9% - was found in the anode chamber, which means that the Cr(VI) oxyanions migrated toward this compartment. Consequently, the contaminant remaining on the kaolinite was gradually concentrated in the anode chamber direction. It should be noted that 100% of the initial charged Cr(VI) was recovered, from the different section of the electrokinetic cell, after the test.

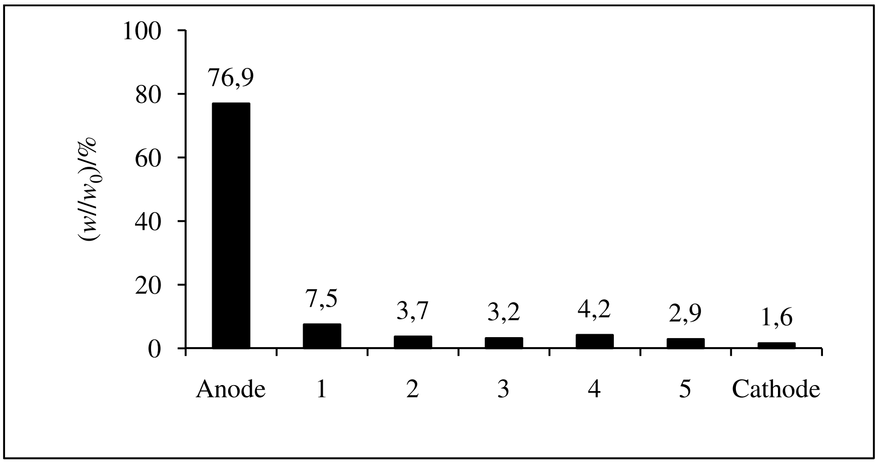


Figure 7.1. Distribution of the hexavalent chromium across the electrokinetic cell - soil and electrode chambers - recorded for the blank assay.

The regular analysis of the anode chamber liquid revealed a growing concentration of the Cr(VI) in this compartment, enabling therefore the construction of an experimental breakthrough curve (BTC). Then, by approximating the system to the transport of a solute in a homogeneous saturated porous media, the equilibrium convection dispersion equation (CDE) was successfully adjusted to the obtained BTC - Figure 7.2 - using the CXTFIT code [2,37,38]:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \tag{46}$$

and

$$P = \frac{vL}{D} \tag{47}$$

R is the retardation factor, C is the Cr(VI) concentration (mg L^{-1}), t is the elapsed time (d), D is the dispersion coefficient (cm^2 d^{-1}), x is the distance along the direction of flow (cm) and v is the average pore water velocity (cm d^{-1}) and P is the Peclet number [39,40]. The values obtained for the estimated parameters - R, D and v - the BTC and the adjusted CDE are presented in Figure 7.2. The R values relatively higher than 1 express the occurrence of the Cr(VI) adsorption onto the kaolinite [41]. On the other hand, the low value of the pore water velocity reflects the low nonequilibrium effects, which strength the applicability of the equilibrium selected model to the transport of the Cr(VI) through the electrokinetic cell [42]. Finally, the Peclet number obtained for the studied system - 0.315 - expresses the predominance of dispersion in the transport of Cr(VI) through the kinetic cell, which is in accordance with the distribution of the contaminant after the electrokinetic treatment - Figure 7.1 - and may result from the counter osmotic flow of water: towards the cathode [43].

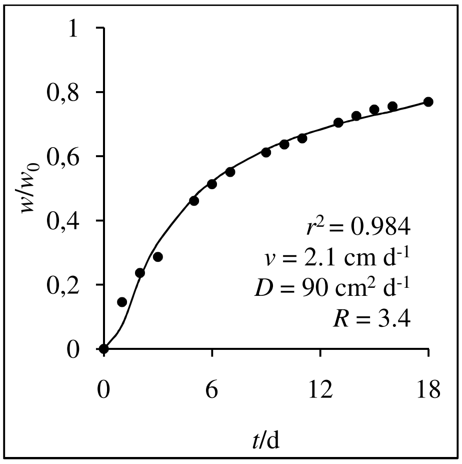


Figure 7.2. Equilibrium convection dispersion equation adjusted to the experimental breakthrough curve of the hexavalent chromium, concerning the liquid collected at the anode chamber during the blank assay.

3.2. Application of a biobarrier

As mentioned previously, blank assays were performed for periods of 9 and 18 days. In the same way, the tests with biobarriers, composed by *Arthrobacter viscosus* supported either by activated carbon or zeolite, were undertaken for 9 and 18 days.

3.2.1. Removal and conversion of hexavalent chromium

On a first approach, overall results concerning the reduction of the Cr(VI) to Cr(III) - conversion - and the full amount of Cr(VI) eliminated from the kaolinite - removal - were generated. Figure 7.3 shows two graphics, where the percent values of conversion - *C* - and removal - *R* - can be consulted.

Focusing on the results regarding the assays of 9 days, the small difference between the removal and the conversion of the hexavalent chromium stands out for both experimental setups. It appears that almost all the hexavalent chromium eliminated from the soil was reduced to the trivalent form. By extending the test period, high removal values were generally recorded. Nevertheless, the reduction of the contaminant, in the system that contains the biobarrier with zeolite, did not vary significantly. So, we assume that the rest of the hexavalent chromium was mobilized, due to the electric current applied. On the other hand, a different behavior was observed for the system containing the biobarrier with activated carbon. Both values increased greatly. The conversion come up to values similar to the ones obtained with the zeolite and the removal values were the higher recorded in the all experiment. Nevertheless, the removal was once more superior to the conversion, denoting that other processes contributed to the decontamination of the soil. In order to clarify these considerations, a closer study was made by analyzing the Cr(VI) mass distribution through the various sections of the electrokinetic cells regarding the most successful assays - 18 days.

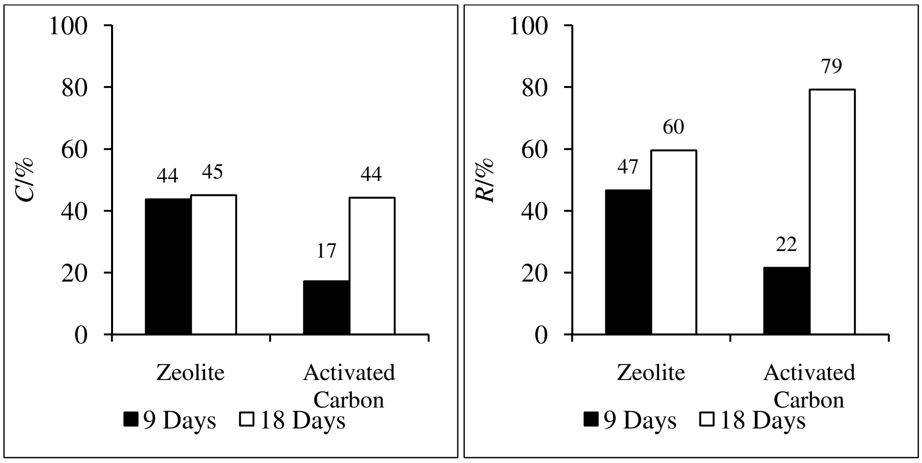


Figure 7.3. Fraction of hexavalent chromium reduced to the trivalent form - C/% - and total removal of the hexavalent chromium - R/% - determined for the assays regarding the both types of biobarriers.

3.2.2. Distribution of the hexavalent and trivalent chromium through the soil columns: pH dependence

Figure 7.4 shows the mass distribution of Cr(VI) and Cr(III) according to the type of biobarrier coupled to the electrokinetic cell - zeolite (A) or activated carbon (B). First and foremost it is important to point and discuss the concentration of Cr(III) in both biobarriers. It is well known that the *Arthrobacter viscosus* are great producers of exopolysaccharides (EPS), which confers to the bacteria the ability for adhesion to a support and also enhances its metal retention capacity. On the other hand, these bacteria are recognized reducers of Cr(VI) to Cr(III). Therefore, and according to the "adsorption coupled reduction" theory, the trivalent cations were effectively entrapped in both supports after de Cr(VI) reduction, explaining the high levels of this cation in both biobarriers [17,19,20]. Nevertheless, the mass of Cr(III) decreased from the biobarrier to the cathode, highlighting the release and consequent movement of these cations towards this section as a result of the electric field applied.

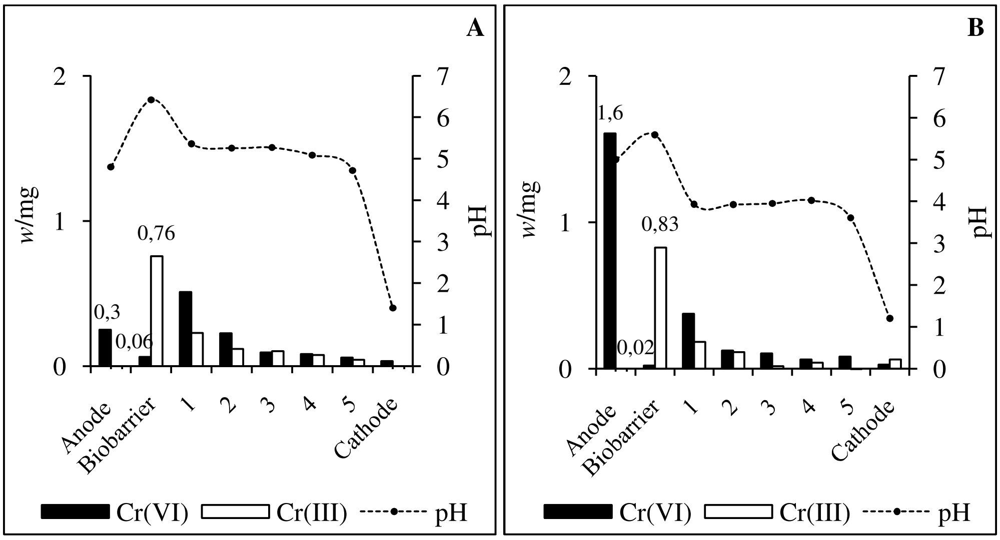


Figure 7.4. Mass and pH distribution observed for the assays with both type of biobarriers. A) Zeolite supported biobarrier. B) Activated carbon supported biobarrier.

Consistently with what was mentioned in the previous section, the quantity of Cr(VI) determined in the anode chamber was higher for the assay of 18 days, with the biobarrier containing activated carbon (1.6 mg *vs* 0.3 mg). This probably occurred due to the saturation of the biobarrier with Cr(III) and consequent transport of Cr(VI) across it, having more expression in this biobarrier due to its higher porosity and specific area. It is important to focus that for this system in particular, the increasing of the test period enhanced the conversion, as more Cr(VI) reached the biobarrier being effectively dispersed on it. In fact, observing Figure 7.4, it is evident that the highest mass of trivalent chromium (0.83 mg *vs* 0.76 mg) was determined for the biobarrier composed with activated carbon. In opposition, the higher compaction of the biobarrier with zeolite probably interfered with the ionic migration of the Cr(VI) oxyanions, but also with its dispersion through the biobarrier, affecting negatively the conversion, even for the elongated test period. However, the difference between the mass of Cr(III) determined in both biobarriers has not such expression as the difference between the quantities of Cr(VI) determined in the anodes chambers. Therefore, it is reliable to infer that the conversion efficiency is very close for both types of biobarriers, but due to its highest porosity, the activated carbon biobarrier promotes an higher removal of Cr(VI), after the saturation of the barrier matrix with Cr(III).

The pH determined across the EK cell showed the same tendency for both tests, and varied between 3.9 and 5.4, for the soil sections. The slight increasing pH in the direction of the anode chamber may also explain the increasing quantities of Cr(VI) in the same direction, as its mobility tends to increase with the pH [2,44]. However, as the system is under an electrical current, it is difficult to infer the level of correlation between these two variables. Comprehensively, the pH determined in the anode chamber was 5 ± 0.2 for both experiments. As mentioned before, the pH was controlled in both chambers in order to be kept around 5, which is the pH reported to increase Cr(III) biosorption, by several authors [18,23,45-47]. On the other hand, the pH determined in the cathode chambers was 1.2 ± 0.2. The typical basic environment of this chamber created by the reduction of water, implied its regular acidification in order to avoid the migration of a base front towards the biobarrier [48]. Therefore, punctually low values of pH are reliable. Finally, the highest pH values determined in the biobarriers - 6.4 for the zeolite and 5.6 for the activated carbon - are clearly related with the supports nature, as both increase the pH in the medium, with more expression for the zeolite [23,49]. The pH range (4-6) was reported by Mohan *et al.* [32] as the optimum for the adsorption of Cr(III) on carbon surface, as this presented a negative charge and all the Cr(III) species were cationic. Therefore, the adsorption process was classified as an electrostatic attraction between the ionized acid sites of the activated carbon and the Cr(III) cations. Wu *et al.* [31] studied the sorption of Cr(III) onto a zeolite in the pH range (2.5 - 9.0) and noted an increase tendency till a pH of 6.5. As zeolites have permanent negative charge, the sorption of Cr(III) above its solubility limit (pH = 4.71) was attributed to the precipitation of the metal hydroxides on the surface of the zeolite [19]. In fact, this phenomenon may have occurred in both supports used in this study.

3.2.3. Biobarriers uptake and microorganisms viability

It was above-mentioned that the mass of Cr(III) retained in the biobarrier with activated carbon was superior to the mass of Cr(III) retained by the zeolite biobarrier. Even the low significant difference between the total mass of Cr(III) retained by both biobarriers - 0.07 mg - the value of uptake, relative to the total chromium, was considerably higher for the activated carbon biobarrier - 0.074 mg g^{-1} *vs* 0.048 mg g^{-1}. This is clearly related with the difference between the bulk densities and specific areas of the supports, as the activated carbon has a lower density and a higher specific area. Nevertheless, the pointed uptake respects to the total chromium and consequently the difference between the Cr(VI) retained in each biobarrier - Figure 7.4 - should also influence their values. In fact, the activated carbon has more ability to retain the Cr(VI) oxyanions on its positive charged sites, generated by the liberation of OH^- ions during the reaction with water [49]:

$$C_xO_2 + H_2O = [C_xO]^{2+} + 2OH^- \tag{48}$$

Finally, the biobarriers were positively tested for the adhesion and bioviability of the *Arthrobacter viscosus*, by means of SEM analysis and growth on solid media, respectively. The microorganism did growth on the agar plates, revealing a high resistance to the Cr(VI) tested levels. During the SEM/EDS analysis, elements like N, C and O were detected punctually in noticeable reasons, allowing the caption of images of biomass adsorbed to each support - Figure 7.5.

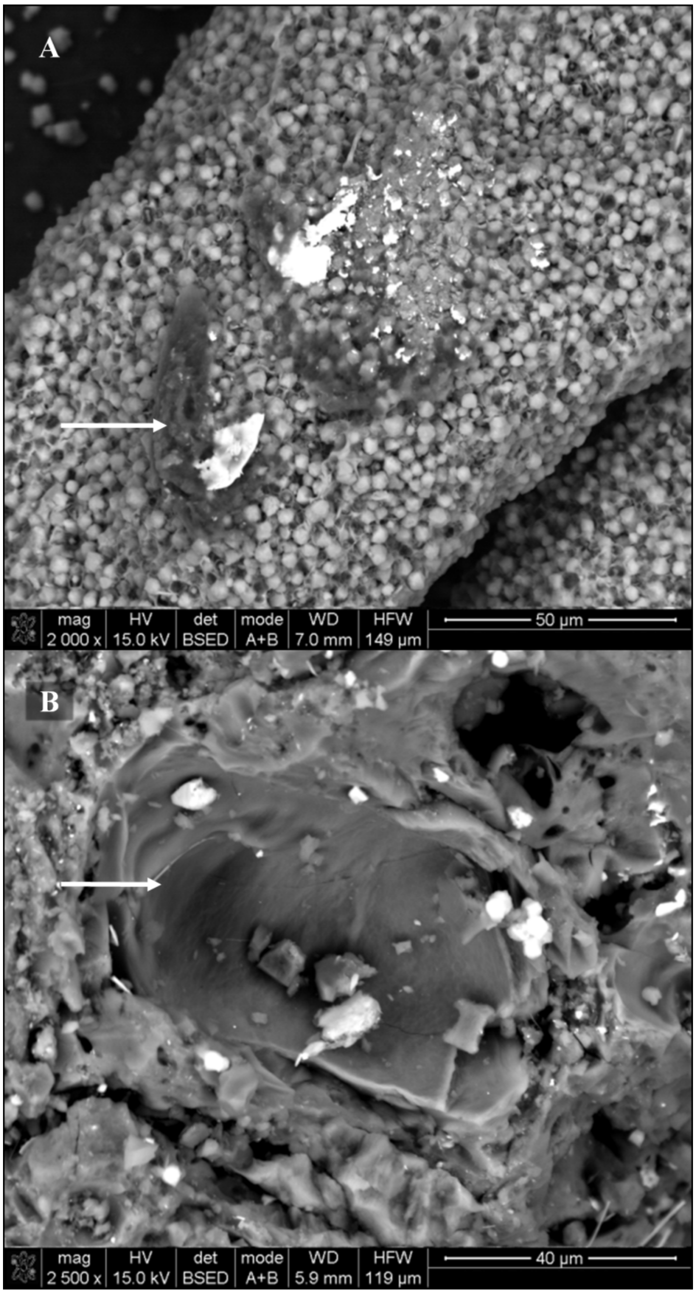


Figure 7.5. SEM images of the biobarriers after the combined treatment. The arrows are pointing the biomass adhered to each support. A) Zeolite supported biobarrier. B) Activated carbon supported biobarrier.

REFERENCES

[1] Unceta, N., Séby, F., Malherbe, J., Donard, O. (2010) Chromium speciation in solid matrices and regulation: a review, Anal. Bional. Chem. 397, 1097-1111.

[2] Fonseca, B., Teixeira, A., Figueiredo, H., Tavares, T. (2009) Modelling of the Cr(VI) transport in typical soils of the North of Portugal, J. Hazard. Mater. 167, 756-762.

[3] Mishra, S., Jena, S. (2009) Bioreduction based bioremediation of hexavalent chromium Cr (VI) through potential indigenous microbes, Department of Chemical Engineering, National Institute of Technology, Rourkela, Orissa, India.

[4] Sanjay, K., Arora, A., Shekhar, R., Das, R.P. (2003) Electroremediation of Cr(VI) contaminated soils: kinetics and energy efficiency, Colloids Surf. , A 222, 253-259.

[5] Hanay, O., Hasar, H., Kocer, N.N. (2009) Effect of EDTA as washing solution on removing of heavy metals from sewage sludge by electrokinetic, J. Hazard. Mater. 169, 703-710.

[6] Zhang, P., Jin, C.J., Zhao, Z.H., Tian, G.B. (2010) 2D crossed electric field for electrokinetic remediation of chromium contaminated soil, J. Hazard. Mater. 177, 1126-1133.

[7] Reddy, K.R., Chinthamreddy, S. (2003) Effects of initial form of chromium on electrokinetic remediation in clays, Adv. Environ. Res. 7, 353-365.

[8] Merdoud, O., Akretche, D.E. (2008) Electroremediation of an industrial area contaminated by chromium, J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng. 43, 866-870.

[9] Manna, M., Sanjay, K., Shekhar, R. (2003) Electrochemical cleaning of soil contaminated with a dichromate lixiviant, Int. J. Miner. Process. 72, 401-406.

[10] Mascia, M., Palmas, S., Polcaro, A.M., Vacca, A., Muntoni, A. (2007) Experimental study and mathematical model on remediation of Cd spiked kaolinite by electrokinetics, Electrochim. Acta 52, 3360-3365.

[11] Ricart, M.T., Pazos, M., Gouveia, S., Cameselle, C., Sanroman, M.A. (2008) Removal of organic pollutants and heavy metals in soils by electrokinetic remediation, J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng. 43, 871-875.

[12] Pazos, M., Alcantara, M.T., Cameselle, C., Sanroman, M.A. (2009) Evaluation of Electrokinetic Technique for Industrial Waste Decontamination, Sep. Sci. Technol. 44, 2304-2321.

[13] Teutli-León, Oropeza, M.T., González, I., Soria, A. (2005) Mathematical modeling of a galvanostatic soil electroremediation process, AIChE J. 51, 1822-1833.

[14] Baraud, F., Tellier, S., Astruc, M. (1997) Ion velocity in soil solution during electrokinetic remediation, J. Hazard. Mater. 56, 315-332.

[15] Boni, M.R., Sbaffoni, S. (2009) The potential of compost-based biobarriers for Cr(VI) removal from contaminated groundwater: Column test, J. Hazard. Mater. 166, 1087-1095.

[16] Viamajala, S., Peyton, B.M., Gerlach, R., Sivaswamy, V., Apel, W.A., Petersen, J.N. (2008) Permeable reactive biobarriers for in situ Cr(VI) reduction: Bench scale tests using Cellulomonas sp. strain ES6, Biotechnol. Bioeng. 101, 1150-1162.

[17] Figueiredo, H., Silva, B., Quintelas, C., Neves, I.C., Tavares, T. (2010) Effect of the supporting zeolite structure on Cr biosorption: Performance of a single-step reactor and of a sequential batch reactor-A comparison study, Chem. Eng. J. 163, 22-27.

[18] 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, Bioresour. Technol. 100, 220-226.

[19] Tavares, M.T., Quintelas, C., Figueiredo, H., Neves, I. (2006) Comparative study between natural and artificial zeolites as supports for biosorption systems, 1294-1298, Trans Tech Publications Ltd, Zurich-Uetikon.

[20] Silva, B., Figueiredo, H., Quintelas, C., Neves, I.C., Tavares, T. (2008) Zeolites as supports for the biorecovery of hexavalent and trivalent chromium, Microporous Mesoporous Mater. 116, 555-560.

[21] Pazos, M., Branco, M., Neves, I.C., Sanromán, M.A., Tavares, T. (2010) Removal of Cr(VI) from Aqueous Solutions by a Bacterial Biofilm Supported on Zeolite: Optimisation of the Operational Conditions and Scale-Up of the Bioreactor, Chem. Eng. Technol. 33, 2008-2014.

[22] Quintelas, C., Tavares, T. (2001) Removal of chromium(VI) and cadmium(II) from aqueous solution by a bacterial biofilm supported on granular activated carbon, Biotechnol. Lett. 23, 1349-1353.

[23] Silva, B., Figueiredo, H., Neves, I.C., Tavares, T. (2009) The role of pH on Cr(VI) reduction and removal by *Arthrobacter viscosus*, Int. J. Chem. Biol. Eng. 2, 100-103.

[24] Fendorf, S.E. (1995) Surface reactions of chromium in soils and waters, Geoderma 67, 55-71.

[25] Figueiredo, H., Silva, B., Quintelas, C., Raposo, M.M.M., Parpot, P., Fonseca, A.M., Lewandowska, A.E., Bañares, M.A., Neves, I.C., Tavares, T. (2010) Immobilization of chromium complexes in zeolite Y obtained from biosorbents: Synthesis, characterization and catalytic behaviour, Appl. Catal. , B 94, 1-7.

[26] Alcantara, M.T., Gomez, J., Pazos, M., Sanromán, M.A. (2008) Combined treatment of PAHs contaminated soils using the sequence extraction with surfactant-electrochemical degradation, Chemosphere 70, 1438-1444.

[27] Quintelas, C., Fernandes, B., Castro, J., Figueiredo, H., Tavares, T. (2008) Biosorption of Cr(VI) by three different bacterial species supported on granular activated carbon-A comparative study, J. Hazard. Mater. 153, 799-809.

[28] Lameiras, S., Quintelas, C., Tavares, T. (2008) Biosorption of Cr (VI) using a bacterial biofilm supported on granular activated carbon and on zeolite, Bioresour. Technol. 99, 801-806.

[29] Figueiredo, H., Silva, B., Quintelas, C., Pereira, M.F.R., Neves, I.C., Tavares, T. (2010) Biosorption of Hexavalent Chromium Based on Modified y Zeolites Obtained by Alkali-Treatment, Environ. Eng. Manage. J. 9, 305-311.

[30] Pazos, M., Gouveia, S., Sanroman, M.A., Cameselle, C. (2008) Electromigration of Mn, Fe, Cu and Zn with citric acid in contaminated clay, J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng. 43, 823-831.

[31] Wu, D., Sui, Y., He, S., Wang, X., Li, C., Kong, H. (2008) Removal of trivalent chromium from aqueous solution by zeolite synthesized from coal fly ash, J. Hazard. Mater. 155, 415-423.

[32] Mohan, D., Singh, K.P., Singh, V.K. (2006) Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth, J. Hazard. Mater. 135, 280-295.

[33] USEPA (2007) Microwave assisted acid digestion of sediments, sludges, soils, and oils, 3051, Environmental Protection Agency, United States of America.

[34] USEPA (1996) Alkaline digestion for hexavalent chromium, 3060A, Environmental Protection Agency, United States of America.

[35] USEPA (1992) Chromium, hexavalent (colorimetric), 7196A, Environmental Protection Agency, United States of America.

[36] USEPA (2004) Soil and waste pH, Method 9045D, Environmental Protection Agency, United States of America.

[37] Simunek, J., van Genuchten, M.T. (1999) The STANMOD computer software for evaluating solute transport in porous media using analytical solutions of Convection-Dispersion Equation, U.S. Salinity Laboratory, U.S. Department of Agriculture, Riverside, California.

[38] Toride, N., Leij, F.J., van Genuchten, M.T. (1995) The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments, 137, U.S. Salinity Laboratory, U.S. Department of Agriculture, Riverside, California.

[39] Hossain, M.A. (1999) Modeling advective-dispersive transport with reaction: An accurate explicit finite difference model, Appl. Math. Comput. 102, 101-108.

[40] Wang, H. (2002) Describing and Predicting Breakthrough Curves for non-Reactive Solute Transport in Statistically Homogeneous Porous Media, Faculty of the Virginia Polytechnic Institute and State University, Blacksburg, Virginia.

[41] van Genuchten, M.T. (1981) Non equilibrium transport parameters from miscible displacement experiments, 119, U.S. Salinity Laboratory, U.S. Department of Agriculture, Riverside, California.

[42] Candela, L., varez-Benedi, J., de Melo, M.T.C., Rao, P.S.C. (2007) Laboratory studies on glyphosate transport in soils of the Maresme area near Barcelona, Spain: Transport model parameter estimation, Geoderma 140, 8-16.

[43] Baraud, F., Fourcade, M.C., Tellier, S., Astruc, M. (1997) Modelling of decontamination rate in an electrokinetic soil processing, Int. J. Environ. Anal. Chem. 68, 105-121.

[44] Fonseca, B., Maio, H., Quintelas, C., Teixeira, A., Tavares, T. (2009) Retention of Cr(VI) and Pb(II) on a loamy sand soil: Kinetics, equilibria and breakthrough, Chem. Eng. J. 152, 212-219.

[45] Uluozlu, O.D., Sari, A., Tuzen, M., Soylak, M. (2008) Biosorption of Pb(II) and Cr(III) from aqueous solution by lichen (Parmelina tiliaceae) biomass, Bioresour. Technol. 99, 2972-2980.

[46] Chojnacka, K. (2005) Biosorption of Cr(III) ions by eggshells, J. Hazard. Mater. 121, 167-173.

[47] Yan, G.Y., Viraraghavan, T. (2003) Heavy-metal removal from aqueous solution by fungus Mucor rouxii, Water Res. 37, 4486-4496.

[48] Acar, Y.B., Alshawabkeh, A.N. (1993) Principles of electrokinetic remediation, Environ. Sci. Technol. 27, 2638-2647.

[49] Ouki, S.K., Neufeld, R.D. (1997) Use of activated carbon for the recovery of chromium from industrial wastewaters, J. Chem. Technol. Biotechnol. 70, 3-8.

CHAPTER 8| Conclusions and Perspectives

CONCLUSIONS AND PERSPECTIVES

This thesis focused two main subjects: the transport and fate of chromium and lead in Portuguese soils and the application or development of few remediation techniques, according to the contamination scenario, to clean soils contaminated with these two heavy metals.

On a first approach, the retention of Cr oxyanions and Pb cations onto a common Portuguese loamy sand soil was studied at low different pHs -2 and 5 - and high initial concentrations of the contaminant solutions - (50 to 200) mg L^{-1} [Chapter 2]. Despite the solution pH used in the batch tests, the cations of Pb were always rapidly retained, in opposition to Cr whose sorption occurred slowly. Consequently, only the sorption kinetics of Cr allowed the adjustment of a mathematical model, the empirical power function, whose rate constant increased with decreasing pH. On the other hand, the equilibrium studies showed that Pb adsorption was well described by the Langmuir monolayer theory and that Cr was mainly retained by physical adsorption, described by Dubinin-Radushkevich model. On their turn, the performed continuous tests confirmed the high retention of Pb that increased with pH due to precipitation. It was also showed that the reduction of Cr(VI), suggested by FTIR results, and the protonation of soil groups at low pH values, may be responsible for the high retention of Cr onto soils. Finally, and according to FTIR results, both metals adsorb mainly on the hydroxyl groups at the edge of the clay minerals. So, both metals have great mobility in acid environments threatening the quality of groundwater near industrial environments.

Due to its distinct behavior in nature, and also due to the fact that it is associated with several Portuguese industrial sectors, Cr was object of a more detailed study in what concerns its sorption and transport [Chapter 3]. In order to do that, few factors affecting its fate in soils were evaluated, namely the influence of the contaminant solution pH and its Cr(VI) concentration, which is the most pernicious form of Cr. 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. The existence of marked concentration gradients may result in absorption processes, following adsorption phenomena, which may explain the increase of the hexavalent chromium retention recorded for the influent concentration increase. The presence of OH groups, usually responsible for sorption phenomena, was once more confirmed by

FTIR. It was also shown that the two site adsorption model - TSM - describes quite well the mobility of Cr(VI) in soils. Nevertheless, since at high pH values the desorption of the targeted heavy metal may occur, this dynamic model seems to be inappropriate to describe the transport of Cr(VI) in these situations. Finally and remarkably, it was proved that batch adsorption parameters are frequently underestimated; even though they can be used to compare the adsorption process at different scenarios, since they vary in accordance with the correspondent parameters determined from flow tests.

As mentioned, the release and disposal of heavy metals may occur by single or mixed wastes. Therefore, Cr and Pb may be found as isolated pollutants, but also, and most likely, in sites co-contaminated with other heavy metals like Cd, Cu and Zn. For that reason, the effect of competition in the sorption and transport of the two targeted heavy metals was approached in Chapter 4. The batch and continuous tests showed that this type of soil - loamy sand - has a high affinity for all the tested metals but a different maximum sorption capacity for each one. An affinity trend was defined as: Cr > Pb > Cd > Cu > Zn, according to the respective Langmuir constant – b_L. Similarly, a trend of the maximum sorption capacities of the soil - q_{max} values - was described as: Cu ≈ Zn > Cd > Pb > Cr. The results of the flow tests showed that in dynamic systems, reactions were not in equilibrium, and therefore, the trend of the retardation factor was different: Zn>Cd>Pb>Cu>Cr. Generally, in competitive situations, the heavy metals were less strongly sorbed by soil, due to the competition for sorption sites. However, Cr and Cu seemed to precipitate as a Cu-Cr solid, due to the increase in the soil pH. Also, Zn is less effectively retained in flow systems, mainly due to the acid leaching of Zn ions, which were highly concentrated in this soil. The existence of competition among heavy metals does not always reduce their retention in soil, depending on the concentration, pH and types of metals involved. Other processes besides adsorption may also occur, thereby influencing the selection of decontamination techniques.

During this research work, three decontamination techniques were applied. The applicability of the bioleaching, using *Acidithiobacillus thiooxidans* DSM 504, on the decontamination of soils polluted with Cr(VI), was explored in Chapter 5. Parameters such operation temperature, contamination pH and contaminant concentration were evaluated and a maximum removal of 83% was obtained for the bioleaching test concerning the soil contaminated with 50 mg kg^{-1} of Cr(VI), at pH 2, and operated at 26 °C. The parameter that most influenced the efficiency of the process was the contamination pH, whose decrease improved the removal of Cr(VI). On the other hand, at the temperature range tested no significant changes were observed in the yield of the method. Finally, the increased contaminant concentration affected positively the same factor. It was also proved that, during the oxidation of sulfur, Cr(VI) was reduced to Cr(III) that was easily leached in the acidic environment. In sum, the laboratory scale study proofs that bioleaching of Cr(VI) contaminated soils can be economically performed, using *Acidithiobacillus thiooxidans*: no temperature control is needed in temperate climate; high Cr(VI) charges favor its reduction rate to Cr(III); stream treatments can be eliminated as Cr(III), less toxic and less mobile; and finally, due to the acidic character of most Cr(VI) contamination, that was proved to enhance the efficiency of the bioleaching process. Even though, larger scale work is needed to fully assess this technology.

In Chapter 6, another cleaning technique was evaluated: the desorption process of PHE and Pb from a contaminated soil via application of composed solutions comprised of a surfactant (T80 or B35) and the chelant EDTA. The extraction of PHE was not influenced by the presence of the chelant EDTA, but the opposite occurred for the extraction of Pb, which was negatively affected by the presence of EDTA. Therefore, the usage of a composed solution in the extraction of Pb from soils contaminated only with this metal is not advisable. Further, the extraction of Pb from the contaminated soil samples was considerably affected by the presence of the co-contaminant PHE, which suggested that the presence of this co-contaminant may prolong the residence time of Pb in soils. Succinctly, the use of composed solutions enhanced the solubilization of a mixture of organic and inorganic contaminants. Moreover, the desorption kinetics of PHE and Pb from soil with those solutions can be described by the empirical power function and the pseudo-second-order equation. Consequently, composed solutions could be employed to enhance remediation of co-contaminated soils using other techniques, such as electrokinetic remediation or phytoremediation. As the concentration of two pollutants can be reduced in the same time interval, it may be cost effective to use composed solutions for the remediation of heavy metals and hydrocarbons mixtures.

The last tested technique was exposed and discussed on Chapter 7 and concerns the applicability of a novel technique on the remediation of soils contaminated with hexavalent chromium. The described technique consists in the coupling of two well known and successfully tested set-ups - electrokinetic cells and permeable reactive biobarriers. Two types of barriers were tested, either with activated carbon or zeolite, supporting a biofilm of *Arthrobacter viscosus*. For an eighteen days period, the systems showed similar conversion of Cr(VI) to Cr(III) - 45% and 44 % - and also similar retention of Cr(III) - 0.76 mg and 0.83 mg - for the systems composed by the biobarrier with zeolite and activated carbon, respectively. However, 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 values - 0.074 mg g^{-1} vs 0.048 mg g^{-1}. 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%. In sum, these laboratory scale tests demonstrated the efficiency of this novel remediation technique. However, futures tests concerning its optimization and application on real soils are required in order to validate it as a large scale solution.

In sum, the transport, sorption and fate of chromium and lead in a typical soil from the north of Portugal were herein described and explored in detail. It was essentially proved that an acidic media promotes an high retention of hexavalent chromium and low retention of divalent lead, and that competitive scenarios may improve the retention of hexavalent chromium due to mineral precipitation, but influences negatively the lead sorption equilibrium. On the other hand, the bioleaching technique proved its efficiency in the attenuation of moderate charges of hexavalent chromium in this soil. On its turn, the chemical washing/extraction was successfully used in a soil highly and historically contaminated with lead, either solely or co-contaminated with a polycyclic hydrocarbon. Finally, the development of a hybrid and novel technique for the cleaning of soils contaminated with hexavalent chromium was herein successfully approached.

Besides the encouraging results obtained by the application of the targeted remediation techniques, a lot of work work is still required. The implementation of each technique at the pilot scale is of utmost importance and appears as the next step on this line of research. On the other hand, deep knowledge and characterization of the Portuguese soils and its contamination urges, as Portugal is a very poor contributor to the Soil Thematic Strategy, proposed by the European Commission in 2006.

CHAPTER 9| Quality criteria of the publications

The evaluation of the publications included on this thesis are based on the *Journal Citation Reports ® of the ISI Web of Knowledge*

9.1. Retention of Cr(VI) and Pb(II) on a loamy sand soil: Kinetics, equilibria and breakthrough

JOURNAL: Chemical Engineering Journal

VOLUME: 152

PAGES: 212-219

YEAR: 2009

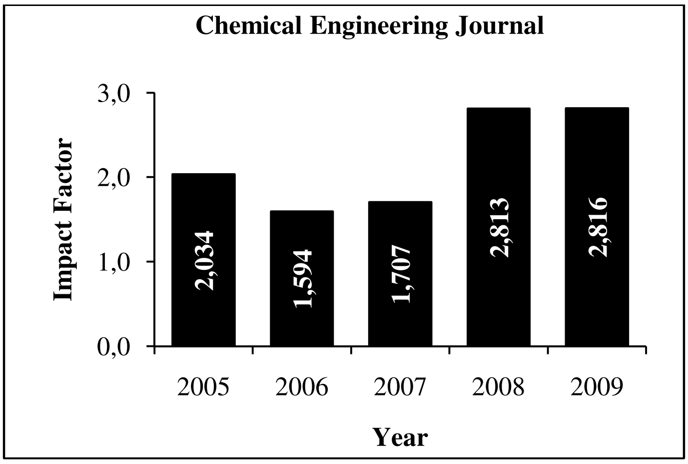
ISSN: 1385-8947

COUNTRY: Switzerland

PUBLISHER: Elsevier Science SA

IMPACT FACTOR IN THE PUBLICATION YEAR: 2.816

RANKING OF THE JOURNAL IN ITS SUBJECT CATEGORIES BASED ON IMPACT FACTOR IN 2009: Occupies the 13th position, in a total of 128, of the Chemical Engineering category - Quartile 1 (Q1).



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

JOURNAL: Journal of Hazardous Materials

VOLUME: 167

PAGES: 756-762

YEAR: 2009

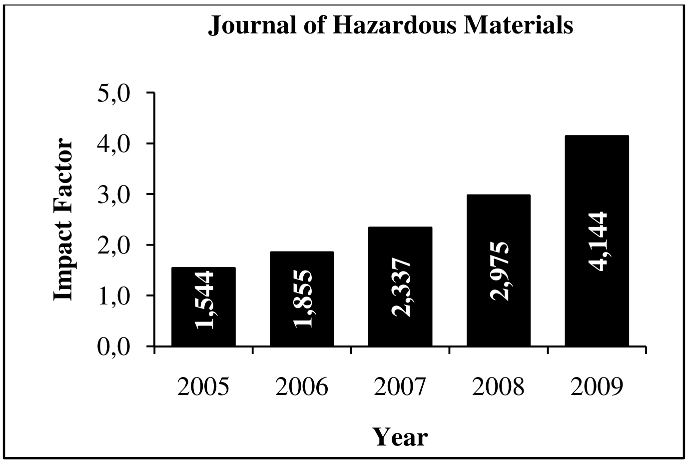
ISSN: 0304-3894

COUNTRY: Netherlands

PUBLISHER: Elsevier Science BV

IMPACT FACTOR IN THE PUBLICATION YEAR: 4.144

RANKING OF THE JOURNAL IN ITS SUBJECT CATEGORIES BASED ON IMPACT FACTOR IN 2009: Occupies the 1st position, in a total of 106, of the Civil Engineering category - Quartile 1 (Q1); the 4th position, in a total of 42, of the Environmental Engineering category - Quartile 1 (Q1); the 11th position, in a total of 181, of the Environmental Sciences category - Quartile 1 (Q1).



9.3. Mobility of Cr, Pb, Cd, Cu and Zn in a Loamy Sand Soil: a comparative study

JOURNAL: Geoderma

STATUS: Submitted

YEAR: 2011

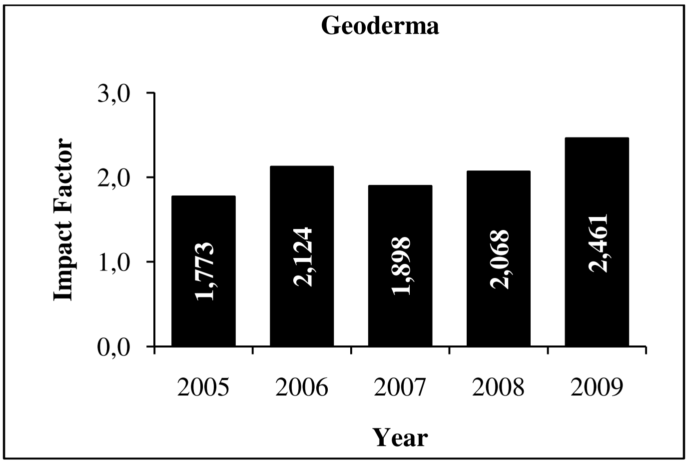
ISSN: 0016-7061

COUNTRY: Netherlands

PUBLISHER: Elsevier Science BV

IMPACT FACTOR IN THE PUBLICATION YEAR: 2.461

RANKING OF THE JOURNAL IN ITS SUBJECT CATEGORIES BASED ON IMPACT FACTOR IN 2009: Occupies the 5th position, in a total of 31, of the Soil Science category - Quartile 1 (Q1).



9.4. A combined remediation technology for the reduction and bioleaching of hexavalent chromium from soils using *Acidithiobacillus thiooxidans*

JOURNAL: Journal of Biotechnology

STATUS: Submitted

YEAR: 2011

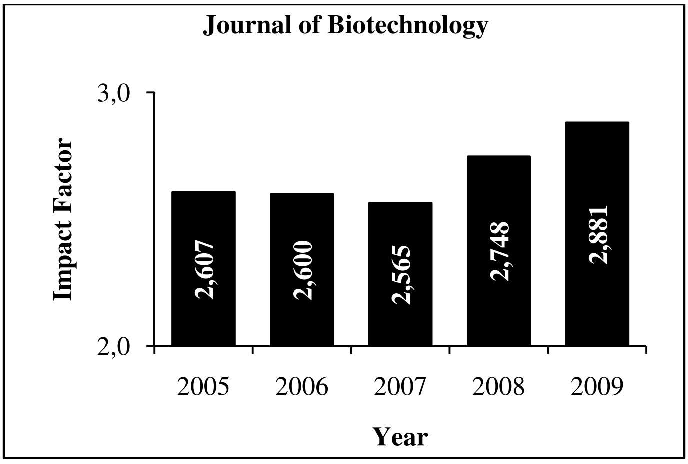
ISSN: 0168-1656

COUNTRY: Netherlands

PUBLISHER: Elsevier Science BV

IMPACT FACTOR IN THE PUBLICATION YEAR: 2.881

RANKING OF THE JOURNAL IN ITS SUBJECT CATEGORIES BASED ON IMPACT FACTOR IN 2009: Occupies the 48th position, in a total of 152, of the Biotechnology & Applied Microbiology category - Quartile 2 (Q2).



9.5. Desorption kinetics of phenanthrene and lead from historically contaminated soil

JOURNAL: Chemical Engineering Journal

VOLUME: 167

PAGES: 84-90

YEAR OF PUBLICATION: 2011

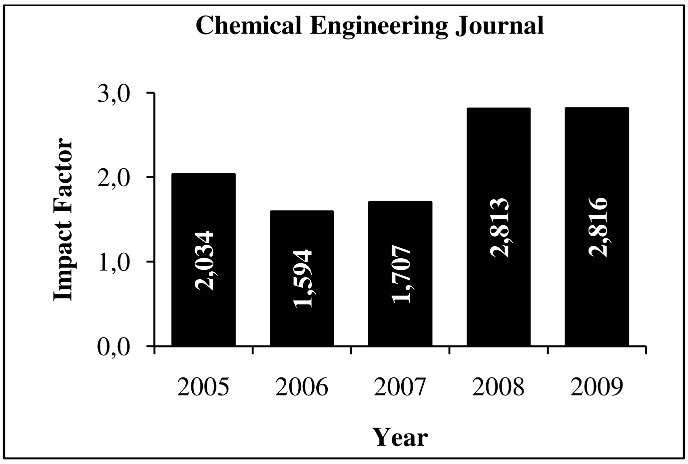
ISSN: 1385-8947

COUNTRY: Switzerland

PUBLISHER: Elsevier Science SA

IMPACT FACTOR IN THE PUBLICATION YEAR: 2.816

RANKING OF THE JOURNAL IN ITS SUBJECT CATEGORIES BASED ON IMPACT FACTOR IN 2009: Occupies the 13th position, in a total of 128, of the Chemical Engineering category - Quartile 1 (Q1).



9.6. An innovative hybrid technology - electrokinetic and biobarriers - applied to hexavalent chromium contaminated clays

JOURNAL: Chemosphere

STATUS: Submitted

YEAR OF PUBLICATION: 2011

ISSN: 0045-6535

COUNTRY: England

PUBLISHER: Pergamon-Elsevier Science Ltd

IMPACT FACTOR IN THE PUBLICATION YEAR: 3.253

RANKING OF THE JOURNAL IN ITS SUBJECT CATEGORIES BASED ON IMPACT FACTOR IN 2009: Occupies the 23rd position, in a total of 181, of the Environmental Sciences category - Quartile 1 (Q1).