



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

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ABSTRACT

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

A two-site adsorption model was fitted to the breakthrough curves of hexavalent chromium solutions in order to estimate the Freundlich (k_F) and Langmuir (S_{max}) adsorption parameters, using CXTFIT code. These values were compared to those determined by batch tests and it was concluded that batch tests tended to underestimate these parameters. Nevertheless, they followed the same trend as the parameters determined in opened system, even when the pH of the initial solution was modified.

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1. Introduction

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

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

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

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

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

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

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Table 1
Chemical and physical properties of soil sample from Póvoa de Varzim, Portugal.

Characteristics	
Texture (%)	
Clay	2.58
Silt	23.06
Sand	74.36
pH (H ₂ O)	5.9
Cationic exchange capacity (cmol _c kg ⁻¹)	12.52
Organic matter content (%)	3.5
Metal concentrations	
[Fe] (mg kg ⁻¹)	323
[Mn] (mg kg ⁻¹)	14
[Cr] (mg kg ⁻¹)	42.5
Carbonate content	
[CaCO ₃] (mg kg ⁻¹)	0.0
Apparent density ^a	
ρ _b (kg m ⁻³)	1320

^a Disturbed sample.

tion was about three times higher for the concentration of 100 mg L⁻¹.

Functional groups present in the soil that may have some role in the sorption process were evaluated by FTIR.

2. Material and methods

2.1. Soil characterization

A sample of a loamy sand soil collected in a zone of great agricultural activity at Póvoa de Varzim, Oporto, Portugal (41°25'15.58"N and 8°45'58.27"O), was used in this study. The soil was collected from the O-horizon and from the A-horizon (0–30 cm) and stored in plastic bags. The mixed sample was passed through a 2 mm stainless steel sieve after being air dried. Particle size distribution was determined in a laser granulometer (Beckman-Coulter 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 are summarized in Table 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 CaCl₂ solution containing graded levels of hexavalent chromium concentration, i.e. 50, 75, 100, 125, 150, 175 and 200 mg L⁻¹ as K₂Cr₂O₇ solution. Sorption sets were made for pH values of 2, 5 and 7, and each of them was duplicated. Blanks and

Table 2
Experimental conditions of flow experiments.

Influent pH	2	5	7	2	2
C ₀ (mg L ⁻¹) ^a	48.6	48.6	44.7	80.8	110
θ (m ³ m ⁻³) ^b	0.42	0.41	0.45	0.39	0.38
L (cm) ^c	15.3	15.0	14.1	15.3	15.5
q (cm h ⁻¹) ^d	20	20	18	20	20
ρ _b (kg m ⁻³) ^e	1300	1243	1322	1324	1293

^a Influent concentration.

^b Water content.

^c Soil bed length.

^d Flux velocity.

^e Soil bulk density.

quality control were also made. The soil suspensions were equilibrated for 240 h at room temperature (25 °C) 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% HNO₃), after pH measuring, stored at 4 °C 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, α (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% HNO₃) and stored for posterior analyses by FAAS. Breakthrough curves were fitted by two-site adsorption model (TSM) using CXTFIT code [10]. The Freundlich adsorption parameter, k_F, and the Langmuir adsorption parameter, S_{max}, were obtained from the fitting. Table 2 summarises the experimental conditions for all flow experiments.

Previously to the flow tests with the hexavalent chromium, a flow experiment using CaCl₂ (0.01 M) as a tracer was also conducted to evaluate independently the average pore water velocity (ν) 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 AAS. Samples were also characterized with transmission FTIR (FTIR BOMEM MB 104) on KBr pressed pellets (100 mg of KBr and 1 mg of sample). Background correction for atmospheric air was used for each spectrum. Spec-

Table 3
Freundlich, Langmuir and pseudo-first order parameters of batch experiments at pH 2.

Influent pH	Freundlich isotherm parameters			Langmuir isotherm parameters			Pseudo-first order equation	
	k _F	n	r ²	S _{max}	b	r ²	α	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

Table 4
Physical parameters obtained by fitting the equilibrium CDE to the BTC of CaCl₂ tracer.

C ₀ (mg L ⁻¹)	Influent pH	Physical parameters (R = 1)			Two-site adsorption model parameters				Freundlich	Langmuir	Pseudo-first order
		D	ν	r ²	R	β	ω	r ²	k _F	S _{max}	α
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	

TSM model parameters fitted to the BTC of the hexavalent chromium influents and isotherm models parameters.

tra were obtained in the range 500–4000 wavenumbers, with a minimum of 10 scans and a resolution of 4 cm⁻¹.

2.4. Evaluation of batch sorption parameters

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

Freundlich equation:

$$S_e = k_F C_e^n \quad (1)$$

Langmuir equation:

$$S_e = \frac{S_{\max} C_e b}{1 + b C_e} \quad (2)$$

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

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

$$S_t = S_e [1 - \exp(-\alpha t)] \quad (3)$$

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

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

2.5.1. Two-site non-equilibrium adsorption

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

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

$$\frac{\partial C}{\partial t} + \left(\frac{\rho}{\theta}\right) \left(\frac{\partial S_1}{\partial t} + \frac{\partial S_2}{\partial t}\right) = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (4)$$

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 (m³ m⁻³), t is time (h), S_1 is the solid phase concentration on equilibrium sites (mg kg⁻¹), S_2 is the solid phase concentration on kinetic non-equilibrium sites (mg kg⁻¹), D is the dispersion coefficient (cm² h⁻¹), x is distance (cm) and v is the average pore water velocity (cm h⁻¹).

The non-equilibrium adsorption process is defined by:

$$\frac{\partial S_2}{\partial t} = \alpha [(1 - F)f(C) - S_2] \quad (5)$$

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

$$S_1 = Ff(C) \quad (6)$$

and

$$S_{2e} = (1 - F)f(C) \quad (7)$$

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

$$\beta R \frac{\partial C_1}{\partial T} = \left(\frac{1}{P}\right) \left(\frac{\partial^2 C_1}{\partial X^2}\right) - \frac{\partial C_1}{\partial X} - \omega(C_1 - C_2) \quad (8)$$

$$(1 - \beta)R \frac{\partial C_2}{\partial T} = \omega(C_1 - C_2) \quad (9)$$

where the dimensionless parameters are defined as follows

$$C_1 = \frac{C}{C_0} \quad (10)$$

$$C_2 = \frac{S_2}{[(1 - F)k_L C_0]} \quad (11)$$

$$T = \frac{vt}{L} \quad (12)$$

$$X = \frac{x}{L} \quad (13)$$

$$R = 1 + \frac{\rho k_L}{\theta} \quad (14)$$

$$P = \frac{vL}{D} \quad (15)$$

$$\beta = \frac{(\theta + F\rho k_L)}{(\theta + \rho k_L)} \quad (16)$$

$$\omega = \frac{\alpha(1 - \beta)RL}{v} \quad (17)$$

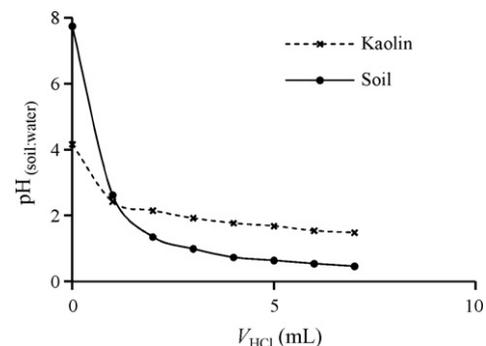


Fig. 1. Buffering capacity test results.

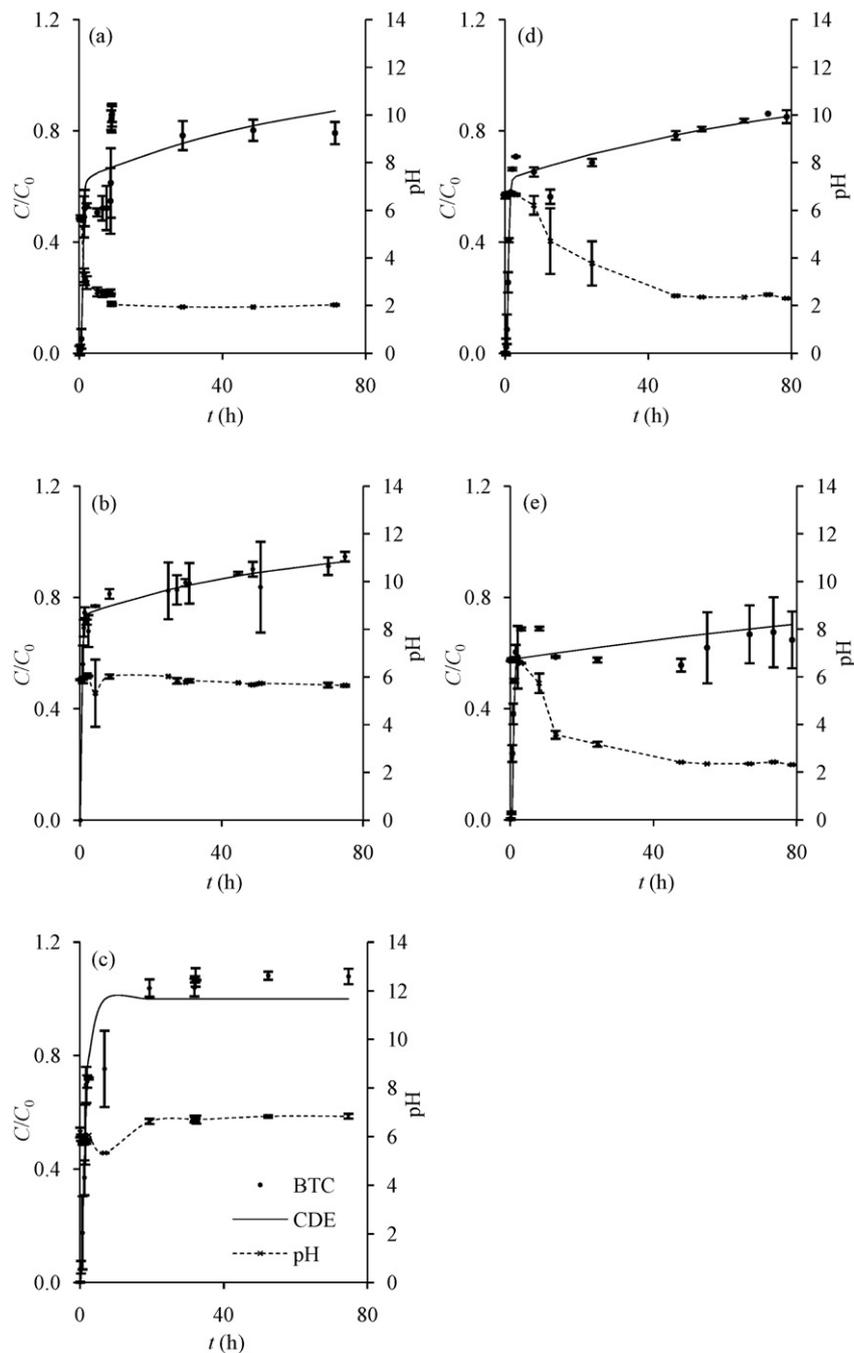


Fig. 2. Experimental and fitted BTCs with the two-site model (TSM), for soil columns contaminated with different hexavalent chromium influents: (a) $C_0 = 50 \text{ mg L}^{-1}$ and pH 2; (b) $C_0 = 50 \text{ mg L}^{-1}$ and pH 5; (c) $C_0 = 50 \text{ mg L}^{-1}$ and pH 7; (d) $C_0 = 75 \text{ mg L}^{-1}$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

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 nonlinear adsorption parameters of Freundlich and Langmuir isotherm models it was assumed that [24]:

$$k_L = k_F n C^{n-1} \quad (18)$$

or

$$k_L = \frac{b S_{\max}}{(1 + bC)^2} \quad (19)$$

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]:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (20)$$

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

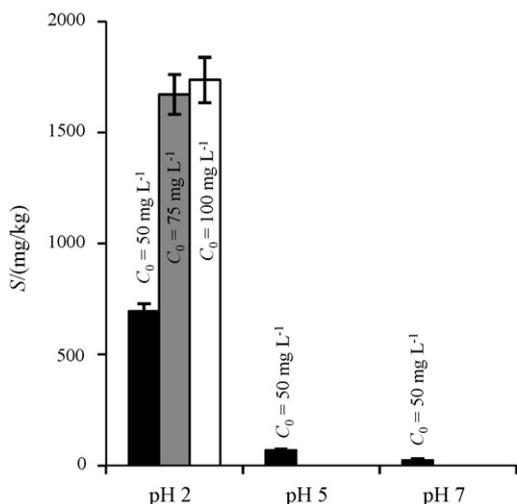


Fig. 3. Mass of chromium adsorbed per mass of soil during the contamination with influents with 50 mg L^{-1} of concentration and different pH values – 2, 5 and 7 – and with influents at pH 2 with different concentrations – 50, 75, 100 mg L^{-1} .

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 in Table 3.

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 (Fig. 1). Hexavalent chromium form exists mainly as oxyanions and these can be adsorbed in the positively charged sites. So, for lower pH values adsorption is higher [4,14].

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

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

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

3.2. Flow experiments

3.2.1. Tracer experiments

The BTC curve obtained for the nonreactive tracer (CaCl_2) was fitted by Eq. (14), using the CXTFIT code, Table 4. The dispersion coefficients obtained for the columns used in the flow tests at

pH 2 were smaller than the other two, indicating that the axial dispersion was lower in these columns, probably due to unsaturated conditions [10]. However, the values of the pore water velocity, v , are quite similar to the values of the experimental flux, q (Table 2). This could be indicative that all the water is mobile.

3.2.2. Two-site non-equilibrium model

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

3.2.3. Effects of initial solution pH

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

Despite of the above considerations, a notable decrease of the retardation factor, R , and of the sorption parameters is observed when the pH is raised to 7, a value very close to the $\text{p}K_{\text{a}2}$ (6.49) of the chromic acid ($\text{HCrO}_4^-/\text{CrO}_4^{2-}$) [31]. The adsorption of anions of polyprotic conjugate acids decreases with increased pH, with a more pronounced decrease above the $\text{p}K_{\text{a}2}$, explaining the drastic decrease of the retardation factor for pH 7. For pH values higher than $\text{p}K_{\text{a}2}$ 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 4. The desorption of chromium oxyanions due to the elevated pH of the influent may explain the unexpected values of relative concentration [27].

3.2.4. Effects of soil/solution ratio

The analysis of Fig. 2e reveals very low relative concentrations in the effluents of the soil bed contaminated with the most concentrated solution. In fact, the retardation factor is about three times higher than those found for the two lower concentrations. Du and Hayashi [33] reported similar results with cadmium (Cd^{2+}), verifying that adsorption increased with the increase in soil/solution ratio. Aksu [34] also found the same behavior in the biosorption of Ni^{2+} , 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 4), maybe due to diffusivity of the chromium adsorbed onto clay minerals and metal oxides into the lattice structures of these minerals. Then, hexavalent chromium become strongly fixed into the pore spaces, not

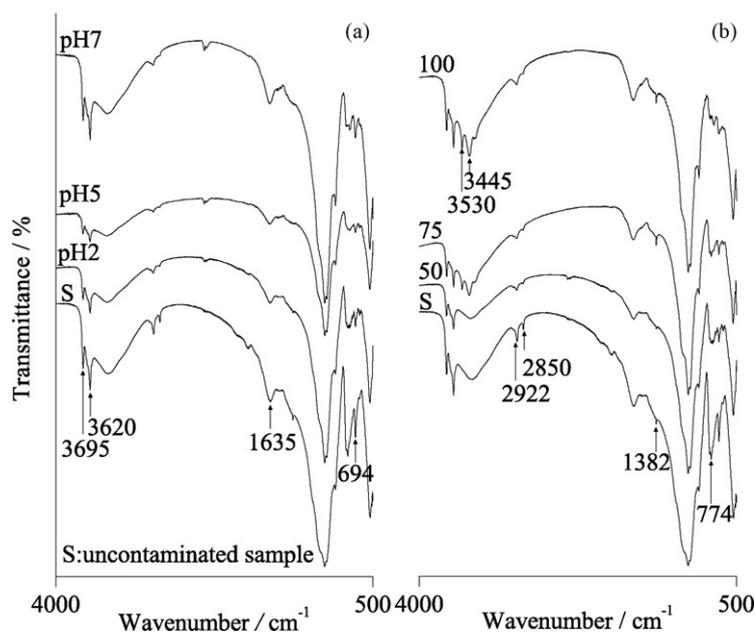


Fig. 4. Infrared spectra of soil bed samples before and after flow experiments with chromium influents with 50 mg L^{-1} , at pH 2, 5 and 7. Spectra of soil beds contaminated with chromium influents with 50, 75 and 100 mg L^{-1} , at pH 2.

being easily desorbed to the liquid phase [26]. Fig. 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^{2+} 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

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

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

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

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

Specifically, in the spectra of the soil sample contaminated with the influents at pH 2 (Fig. 4b) it is evident the appearance of two

peaks around 3530 and 3445 cm^{-1} in the samples contaminated with the most concentrated influents. These peaks are located in a region characterized by intense OH absorption ($3300\text{--}3800 \text{ cm}^{-1}$). 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 and 2922 cm^{-1} that tend to overlap for the contaminated samples. These bands result from the extensive transformation of simpler aliphatic moieties from the mineral wax, for example. Also the small peak around 1380 cm^{-1} is attributed to CH deformations from aliphatic structures [40–42].

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

4. Conclusions

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

It was also showed that the two-site adsorption model describes quite well the mobility of hexavalent chromium in soils. Nevertheless, since at high pH values desorption of the studied heavy

metal may occur, this dynamic model seems to be inappropriate to describe the transport of Cr(VI) in these situations.

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

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References

- [1] B.J. Alloway, *Heavy Metals in Soils*, Blackie, Glasgow, 1995.
- [2] S. Serrano, F. Garrido, C.G. Campbell, M.T. Garcia-Gonzalez, Competitive sorption of cadmium and lead in acid soils of Central Spain, *Geoderma* 124 (2005) 91–104.
- [3] P.R. Wittbrodt, C.D. Palmer, Reduction of Cr(VI) in the presence of excess soil fulvic-acid, *Environ. Sci. Technol.* 29 (1995) 255–263.
- [4] M.K. Banks, A.P. Schwab, C. Henderson, Leaching and reduction of chromium in soil as affected by soil organic content and plants, *Chemosphere* 62 (2006) 255–264.
- [5] M. Panssar-Kallio, S.P. Reinikainen, M. Oksanen, Interactions of soil components and their effects on speciation of chromium in soils, *Anal. Chim. Acta* 439 (2001) 9–17.
- [6] D.M. Proctor, M.M. Fredrick, P.K. Scott, D.J. Paustenbach, B.L. Finley, 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 (1998) 27–37.
- [7] R.N. Yong, W.Z.W. Yaacob, S.P. Bentley, C. Harris, B.K. Tan, Partitioning of heavy metals on soil samples from column tests, *Eng. Geol.* 60 (2001) 307–322.
- [8] M. Elzahabi, R.N. Yong, pH influence on sorption characteristics of heavy metal in the vadose zone, *Eng. Geol.* 60 (2001) 61–68.
- [9] Y.T. Tran, K. Bajracharya, D.A. Barry, Anomalous cadmium adsorption in flow interruption experiments, *Geoderma* 84 (1998) 169–184.
- [10] N. Toride, F.J. Leij, M.T. van Genuchten, The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments, U.S. Salinity Laboratory, U.S. Department of Agriculture, Riverside, California, 137 (1995).
- [11] W.H. Hendershot, H. Lalonde, M. Duquette, Ion exchange and exchangeable cations, *Soil Sampling Methods Anal.* (1993) 197–206.
- [12] USEPA, *Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils*, 3051A, Environmental Protection Agency, United States of America, 2007.
- [13] J. Tinsley, The determination of organic carbon in soils by dichromate mixture, in: IV International Congress of Soil Science, 1950, pp. 161–164.
- [14] K.R. Reddy, M. Donahue, R.E. Saichek, R. Sasaoka, Preliminary assessment of electrokinetic remediation of soil and sludge contaminated with mixed waste, *J. Air Water Manage.* 49 (1999) 823–830.
- [15] C. Papeis, W. Um, 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, 1999.
- [16] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1403.
- [17] R. Sips, On the structure of a catalyst surface, *J. Chem. Phys.* 16 (1948) 490–495.
- [18] T.V.N. Padmesh, K. Vijayaraghavan, G. Sekaran, M. Velan, Application of two- and three-parameter isotherm models: biosorption of Acid Red 88 onto *Azolla microphylla*, *Biorem. J.* 10 (2006) 37–44.
- [19] Y.S. Ho, Review of second-order models for adsorption systems, *J. Hazard. Mater.* 136 (2006) 681–689.
- [20] M.T. van Genuchten, Non equilibrium transport parameters from miscible displacement experiments, U.S. Salinity Laboratory, U.S. Department of Agriculture, Riverside, California, 119 (1981).
- [21] K. Bajracharya, D.A. Barry, MCMFIT—efficient optimal fitting of a generalized nonlinear advection-dispersion model to experimental-data, *Comput. Geosci.* 21 (1995) 61–76.
- [22] A. Kreft, A. Zuber, Physical meaning of Dispersion-Equation and its solutions for different initial and boundary-conditions, *Chem. Eng. Sci.* 33 (1978) 1471–1480.
- [23] L. Candela, J. varez-Benedi, M.T.C. de Melo, P.S.C. Rao, Laboratory studies on glyphosate transport in soils of the Maresme area near Barcelona, Spain: transport model parameter estimation, *Geoderma* 140 (2007) 8–16.
- [24] L.Z. Zhou, H.M. Selim, Solute transport in layered soils: nonlinear and kinetic reactivity, *Soil Sci. Soc. Am. J.* 65 (2001) 1056–1064.
- [25] M.T. van Genuchten, A closed-form equation for predicting the hydraulic conductivity of unsaturated soils, *Soil Sci. Soc. Am. J.* 44 (1980) 892–898.
- [26] H.B. Bradl, Adsorption of heavy metal ions on soils and soil constituents, *J. Colloid Interface Sci.* 277 (2004) 1–18.
- [27] D.L. Sparks, *Environmental Soil Chemistry*, Academic Press, San Diego, 1995.
- [28] J. Sastre, G. Rauret, M. Vidal, Effect of the cationic composition of sorption solution on the quantification of sorption-desorption parameters of heavy metals in soils, *Environ. Pollut.* 140 (2006) 322–339.
- [29] E.F. Covelto, M.L. Andrade, F.A. Vega, Heavy metal adsorption by humic umbrilsols: selectivity sequences and competitive sorption kinetics, *J. Colloid Interface Sci.* 280 (2004) 1–8.
- [30] D.M. Miller, M.E. Sumner, W.P. Miller, A comparison of batch-generated and flow-generated anion adsorption-isotherms, *Soil Sci. Soc. Am. J.* 53 (1989) 373–380.
- [31] N. Bailey, A. Carrington, K.A.K. Lott, M.C.R. Symons, Structure and reactivity of the oxyanions of transition metals. Acidities and spectra of protonated oxyanions, *J. Chem. Soc.* (1960) 290–297.
- [32] J.M. Zachara, D.C. Girvin, R.L. Schmidt, C.T. Resch, Chromate adsorption on amorphous iron oxyhydroxide in the presence of major groundwater ions, *Environ. Sci. Technol.* 21 (1987) 589–594.
- [33] Y.J. Du, S. Hayashi, A study on sorption properties of Cd²⁺ on Ariake clay for evaluating its potential use as a landfill barrier material, *Appl. Clay Sci.* 32 (2006) 14–24.
- [34] Z. Aksu, Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel(II) ions onto *Chlorella vulgaris*, *Process. Biochem.* 38 (2002) 89–99.
- [35] P. Miretzky, C. Munoz, A. Carrillo-Chavez, Experimental Zn(II) retention in a sandy loam soil by very small columns, *Chemosphere* 65 (2006) 2082–2089.
- [36] S. Ghorai, K.K. Pant, Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina, *Sep. Purif. Technol.* 42 (2005) 265–271.
- [37] R. Alvarez, L.A. Evans, P.J. Milham, M.A. Wilson, Effects of humic material on the precipitation of calcium phosphate, *Geoderma* 118 (2004) 245–260.
- [38] E. Smidt, K. Meissl, The applicability of Fourier transform infrared (FT-IR) spectroscopy in waste management, *Waste Manage.* 27 (2007) 268–276.
- [39] G. Sposito, *The Chemistry of Soils*, Oxford University Press, Inc., New York, 1989.
- [40] R.R.E. Artz, S.J. Chapman, A.H. Jean Robertson, J.M. Potts, F. Laggoun-Défarge, S. Gogo, L. Comont, J.R. Disnar, A.J. Francez, FTIR spectroscopy can be used as a screening tool for organic matter quality in regenerating cutover peatlands, *Soil Biol. Biochem.* 40 (2008) 515–527.
- [41] C. Cocozza, V. D'Orazio, T.M. Miano, W. Shoty, 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 (2003) 49–60.
- [42] S.J. Chapman, C.D. Campbell, A.R. Fraser, G. Puri, FTIR spectroscopy of peat in and bordering Scots pine woodland: relationship with chemical and biological properties, *Soil Biol. Biochem.* 33 (2001) 1193–1200.