Solid Earth
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Cr(VI) adsorption/desorption on untreated and mussel shell-treated soil materials: fractionation and effects of pH and chromium concentration

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Cr(VI) adsorption/desorption on untreated and mussel shell-treated soil materials

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Abstract

We used batch-type experiments to study Cr(VI) adsorption/desorption on granitic material, forest soil, pyritic material, mussel shell, and on forest soil and granitic material amended with $12\,t\,ha^{-1}$ shell, considering the effects of varying Cr(VI) concentration and pH. Sequential extractions were carried out to fractionate adsorbed Cr(VI) and to determine the stability of Cr(VI) retention. The pyritic material had the highest Cr(VI) retention capacity, whereas the granitic material showed the lowest retention potential. When high Cr concentrations were added, some saturation of the adsorbent surfaces became apparent, but Cr release remained low. The highest Cr retention was achieved at very acid pH value, with release progressively increasing as a function of increasing pH. The amendment with $12\,t\,ha^{-1}$ mussel shell did not cause marked changes in Cr(VI) retention. Adsorption data were satisfactory adjusted to the Freundlich model. Regarding Cr(VI) fractionation, the soluble fraction (weakly bound) was the dominant in mussel shell and in the un-amended and amended granitic material, whereas more stable fractions dominated in the pyritic material (residual fraction) and in the forest soil (oxidizable fraction). In conclusion, the pyritic material presented the highest Cr(VI) retention capacity, while the retention was low and weak on the granitic material; mussel shell was characterized by not marked Cr(VI) retention potential, and it did not cause remarkable increase in Cr(VI) retention when used to amend the granitic material or the forest soil.

1 Introduction

Mining, industrial and agricultural activities are the main sources of chromium pollution affecting the environment, notably the water and soil compartments. Cr(III) is the chemically most stable form of chromium, whereas Cr(VI) is highly toxic and more easily mobilized.

Different bio-adsorbent materials has been tried to remove Cr(VI) from polluted environments, as was the case for some microorganisms and other natural sorbents (Schiever and Volesky, 1995). Schmuhl et al. (2001) found high Cr(VI) adsorption on chitosan, with best results at pH 5. Blázquez et al. (2009) obtained Cr(VI) adsorption > 80 % on olive waste when pH was < 2, although adsorption clearly diminished when pH value increased. Good Cr(VI) adsorption results were achieved using algae and cyanobacteria (Park et al., 2006; Gupta and Rastogi, 2008a, b), as well as using waste from the coffee and tea industries (Fiol et al., 2008; Duran et al., 2011).

Globally, it would be of relevance increasing the knowledge on Cr(VI) retention processes when this pollutant interacts with sorbent materials. In this way, Fernández-Pazos et al. (2013) studied quantitative and kinetic aspects regarding Cr(VI) adsorption/desorption on various solid media (fine and coarse mussel shell, un-amended and mussel shell-amended forest and vineyard soils, slate processing fines and pyritic material). In addition to the kinetic characterization, it would be interesting to elucidate complementary aspects, such as the effects on Cr(VI) retention caused by changing pH, or the fractions where the retained Cr(VI) was bound, which can aid to estimate the degree of stability of that retention.

In view of that, the main objectives of this work are: (a) firstly to determine Cr(VI) adsorption/desorption when different Cr(VI) concentrations are added to a granitic material, a forest soil, a pyritic material, and fine mussel shell, as well as to the granitic material and the forest soil amended with $12\,t\,ha^{-1}$ fine mussel shell; (b) secondly, to elucidate the influence of varying pH as regards Cr(VI) adsorption on such materials; and (c) finally to determine the fractions where Cr(VI) is retained in the various solid materials investigated, affecting Cr(VI) release, as well as risks of water pollution and transfer to the food chain.

2 Materials and methods

2.1 Materials

The materials used in this study were: (a) a granitic material sampled in Santa Cristina (Ribadavia, Ourense Province, Spain) resulting from the evolution of a rocky substrate, similar to a C horizon, nowadays exposed to the atmosphere after the elimination of the upper horizons, then needing organic matter and nutrients to be restored, as happens with granitic mine spoils; (b) an A horizon corresponding to a forest soil with dominance of *Eucalyptus globulus* as tree species, sampled in the vicinity of the aluminum industry Alcoa (San Cibrao, Lugo Province, Spain); (c) pyritic material from a copper mine spoil (Touro, A Coruña Province, Spain); (d) finely crushed (< 1 mm) mussel shell from the factory Abonomar S.L. (Illa de Arousa, Pontevedra Province, Spain); (e) the following two mixtures: the granitic material $+12\,\mathrm{t\,ha^{-1}}$ mussel shell, and the forest soil $+12\,\mathrm{t\,ha^{-1}}$ mussel shell, shaking the mixtures for 48 h to achieve homogenization. The materials (b)–(d) were previously characterized by Fernández-Pazos et al. (2013) in a study focusing on kinetics of Cr(VI) retention, as well as in evaluating the effects of adding different concentrations of the pollutant to various sorbent materials.

Forest soil, pyritic material and granitic material were sampled in a zigzag manner (20 cm depth), taken 10 subsamples to perform each of the final samples. These samples were transported to the laboratory to be air dried and sieved through 2 mm. Finally, chemical determinations and trials were carried out on the < 2 mm fraction.

2.2 Methods

2.2.1 Characterization of the solid materials used

The particle-size distribution of the materials was determined by using the Robinson pipette procedure. A pH-meter (model 2001, Crison, Spain) was used to measure pH in water and in 0.1 M KCl (solid : liquid relationship 1 : 2.5). C and N were quantified

by means of the elemental Tru Spec CHNS auto-analyzer (LECO, USA). Available P was determined according to Olsen and Sommers (1982). The exchangeable cations were displaced using NH_4Cl 1 M solution, then quantifying Ca, Mg and Al by atomic absorption spectroscopy, and Na and K by atomic emission spectroscopy (AAnalyst 200, Perkin Elmer, USA); the effective cationic exchange capacity (eCEC) was calculated as the sum of all these cations (Kamprath, 1970). Total concentrations of Na, K, Ca, Mg, Al, Fe, Mn, as well as As, Cd, Co, Cr, Cu, Ni and Zn, were determined by means of ICP-mass (820-NS, Varian, USA), after nitric acid (65 %) microwave assisted digestion. Different selective solutions were used to obtain the following Al and Fe fractions (Álvarez et al., 2013): total non-crystalline Al and Fe (Al_o, Fe_o), total Al and Fe bound to organic matter (Al_p, Fe_p), non-crystalline inorganic Al and Fe (Al_{op}, Fe_{op}), Al bound to organic matter in medium and low stability complexes (Al_{cu}), Al bound to organic matter in high stability complexes (Al_{pcu}), Al bound to organic matter in medium stability complexes (Al_{cula}), Al bound to organic matter in low stability complexes (Al_{la}).

2.2.2 Adsorption/desorption when different Cr(VI) concentrations are added

Cr(VI) adsorption and desorption as a function of the added concentration of the pollutant were studied as per Arnesen and Krogstrad (1998).

The adsorbents used were: granitic material, forest soil, mussel shell and pyritic material, as well as the forest soil and granitic material amended with $12\,t\,ha^{-1}$ mussel shell. Fernández-Pazos et al. (2013) found that the amendment of pyritic material with mussel shell had not positive effect on Cr(VI) retention, so this combination was discarded in the present study.

As in Fernández-Pazos et al. (2013), 3 g of each solid sample were added with 30 mL $NaNO_3$ 0.01 M dissolutions containing 0, 0.5, 5, 10, 25, 50 or $100\,mg\,L^{-1}$ of Cr(VI), prepared from analytical grade $K_2Cr_2O_7$ (Panreac, Spain). The resulting suspensions were shaken for 24 h, centrifuged at 4000 rpm for 15 min, and finally filtered using acid-washed paper. In the equilibrium dissolutions, pH was measured using a glass electrode (Crison, Spain), dissolved organic carbon (DOC) was determined by means

of UV-visible spectroscopy (UV-1201, Shimadzu, Japan), and Cr(VI) using ICP-mass (Varian 800-NS, USA). All trials were performed by triplicate.

Data were treated using the statistical package SPSS 19.0 (IBM, USA), fitting Cr(VI) adsorption data to the Freundlich model (Eq. 1). Fitting to the Langmuir model was not possible due to estimation errors being too high.

The formulation of the Freundlich equation is as follows:

$$q_e = K_f \cdot C_e n \tag{1}$$

where q_e (mg kg^{-1}) is the ion adsorption per unit of mass for the adsorbent, C_e (mg L^{-1}) is the equilibrium concentration of the dissolved Cr, K_f(L^n g^{-1} mg$^{(1-n)}$) is a constant related to the adsorption capacity, and n (dimensionless) is a constant related to the adsorption intensity.

After the ending of the adsorption trials, each sample was added with 30 mL of NaNO$_3$ 0.01 M solution to desorb Cr(VI), then shaking during 24 h, centrifuging and filtering as in the adsorption trials (Arnesen and Krogstad, 1998). Desorbed Cr(VI), DOC and pH were determined in all samples.

2.2.3 Cr(VI) adsorption/desorption as a function of pH

To study adsorption, triplicate samples (1 g each) of mussel shell, granitic material, forest soil and pyritic material, as well as granitic material $+12$ t ha^{-1} mussel shell and forest soil $+12$ t ha^{-1} mussel shell, were added with 10 mL of solutions containing 5 mg L^{-1} Cr(VI) and different concentrations of HNO$_3$ (0.0025, 0.0038, 0.005, 0.0075 M) or NaOH (0.0025, 0.0038, 0.005, 0.0075 M), also including NaNO$_3$ 0.01 M as background electrolyte. Control samples were constituted by each of the solid materials added with 10 mL of solutions containing NaNO$_3$ 0.01 M and 5 mg L^{-1} Cr(VI), but without HNO$_3$ or NaOH. After shaking for 24 h, all samples were centrifuged for 15 min at 4000 rpm, and filtered through acid-washed paper. The resulting liquid was analyzed for pH, DOC and Cr(VI). Adsorbed Cr(VI) was calculated as the difference between added Cr(VI) concentration and that remaining in the equilibrium solution.

Desorption was studied using triplicate samples (1 g each) of the same solid materials than in the adsorption trials, that were added with 10 mL of solutions containing 100 mg L^{-1} Cr(VI), also including NaNO$_3$ 0.01 M as background electrolyte. After shaking for 24 h, all samples were centrifuged for 15 min at 4000 rpm, and filtered

5 through acid-washed paper, discarding the liquid phase. The remaining solid phase was then subjected to a desorption procedure, adding 30 mL of solutions containing NaNO$_3$ 0.01 M and diverse HNO$_3$ or NaOH concentrations aiming to provide a wide pH range, then being different for the various solid samples. After shaking for 24 h, all samples were centrifuged for 15 min at 4000 rpm, and filtered through acid-washed

10 paper. The resulting liquid was analyzed for pH, DOC and Cr(VI). Desorbed Cr(VI) was calculated as the difference between the amount retained in the adsorption phase and that released to the equilibrium solution in the desorption phase, and it was expressed as percentage of the total amount adsorbed.

2.2.4 Fractionation of the Cr(VI) adsorbed at three different incubation times

15 Samples corresponding to granitic material, forest soil, mussel shell, pyritic material, as well as granitic material +12 t ha^{-1} mussel shell, and forest soil +12 t ha^{-1} mussel shell, were added with a NaNO$_3$ 0.01 M solution containing 100 mg L^{-1} Cr(VI) (1 : 10 solid : solution ratio), then shaking for 24 h and filtering. The resulting liquid was analyzed for pH, DOC and Cr(VI). Finally, fractionation of the adsorbed Cr(VI) was carried

20 out using the BCR procedure modified by Rauret et al. (1999). The fractionation was performed for three different incubation times: 24 h, 1 week and 1 month. The resulting fractions were: acid soluble fraction, reducible fraction, oxidizable fraction, and residual fraction.

3 Results and discussion

3.1 Characterization of the solid materials used

Table 1 shows data referred to the basic characteristics of the solid materials used in this study. Additionally, particle size percentages (sand, silt and clay) were as follows: granitic material (60, 17, 23 %); forest soil (65, 20, 15 %); mussel shell (99.53, 0.34, 0.13 %); pyritic material (67, 14, 19 %).

3.2 Adsorption/desorption when different Cr(VI) concentrations were added

3.2.1 Adsorption

Figure 1 shows that Cr(VI) adsorption increased as a function of increasing Cr(VI) concentration in the equilibrium solution, which was directly related to the increase in the Cr(VI) concentration added. The same behavior was observed by Fernández-Pazos et al. (2013) using mussel shell, pyritic material, forest soil and slate processing fines, by Rawajfih and Nsour (2008) using *Phragmites australis* biomass, and by Vinodhini and Nilanjana (2009) using various bio-adsorbent materials. In the present work, the maximum adsorption corresponded to the pyritic material (between 97.1 and 98.7 %), significantly higher than that achieved by forest soil (between 22.1 and 86 %), mussel shell (between 20.9 and 31.2 %), and the granitic material (between 19.5 and 31.2 %). The mussel shell amendment ($12\,\mathrm{t\,ha^{-1}}$) caused a slight decrease in Cr(VI) adsorption on forest soil (reaching values between 21 and 86 %), whereas it provoked a slight increase in Cr(VI) adsorption on granitic material (achieving up to 50 %). In a previous work, Fernández-Pazos et al. (2013) found slightly lower Cr(VI) adsorption on pyritic material and mussel shell, whereas adsorption was very similar on their forest soil samples.

Significant correlations were found between Cr(VI) adsorption and total Fe ($r = 0.995$), Fe extracted with ammonium oxalate ($r = 0.993$), non-crystalline inorganic Fe

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($r = 0.992$), and pH in water ($r = -0.900$). Previously, Martin and Kempton (2000) observed that Cr(VI) adsorption increased as a function of Fe oxides content, whereas Mesuere and Fish (1992) and Weerasooriya and Tobschall (2000) indicated that Cr(VI) has slow to moderate affinity for Fe and Al oxy-hydroxides. These facts are in rela-
5   tion with the high adsorption capacity of our pyritic material, characterized by having high Fe contents and very acid pH; furthermore, a step-wise regression test corroborated the importance of the total Fe content on Cr(VI) adsorption, explicating 99 % of the variance. In our study, the pyritic material was the one with the highest Cr(VI) adsorption capacity, as well as the lowest pH (2.97), and high concentration of amor-
10 phous minerals. It is remarkable that this pyritic material had high specific surface and pH-dependent exchange capacity, developing positive charge at acid pH, while chromium was in anionic form ($HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$). The granitic material showed the lowest Cr(VI) adsorption, which can be in relation with its low total and non-crystalline Fe contents (Table 1). Correlations between adsorbed Cr(VI) and pH
15 of the solution were positive for un-amended ($r = 0.701$) and shell-amended granitic material ($r = 0.770$), and for un-amended ($r = 0.672$) and shell-amended forest soil ($r = 0.819$), whereas correlations were negative for mussel shell by itself ($r = -0.994$) and for pyritic material ($r = -0.424$). These differences could be due to different mechanisms acting when Cr(VI) adsorption takes place on the various materials: electrostatic
20 bindings, then including the possibility of OH^- release and consequent pH increase when chromium anions adsorb (Arnesen and Krogstad, 1998; Bower and Hatcher, 1967; Gago et al., 2012), or other mechanisms not including OH^- release, such as Van der Waals and H bindings (Boddu et al., 2003). Furthermore, in the present study DOC values increased as a function of adsorbed Cr(VI), with significant correlations for
25 granitic material by itself ($r = 0.978$) or mussel shell-treated ($r = 0.983$), forest soil by itself ($r = 0.905$) or mussel shell-treated ($r = 0.984$), mussel shell ($r = 0.978$), and pyritic material ($r = 0.973$), which can be in relation with release of organic ions when Cr(VI) adsorption takes place. When added Cr(VI) concentrations increased, both granitic material and forest soil showed decreasing adsorption percentages, then suggesting

progressive saturation of the adsorbent surfaces (Nameni et al., 2008). Maximum adsorption was clearly higher for forest soil (86 %) than for granitic material (31 %), which can be due to the higher organic matter, organo-aluminum complexes, and Al_o and Fe_o contents in the forest soil. At this respect, Kantar et al. (2008) indicate that some ferric organic compounds facilitate the stabilization of Cr(VI) in acid to slightly alkaline soils due to the catalytic reduction of Cr(VI) to Cr(III).

Adsorption data were satisfactory fitted to the Freundlich model (Table 2), as other authors found for various bio-sorbents (Cetinkaya-Donmez et al., 1999; Prakasham et al., 1999), meaning that adsorption maximum would not be easily predictable for these materials.

Significant correlations were found between the Freundlich constant K_f and Fe_T ($r = 1$), Fe_{op} ($r = 1$), and Fe_o ($r = 0.999$), making evident the importance of amorphous minerals in Cr(VI) adsorption.

3.2.2 Desorption

Table 3 shows that the lowest Cr(VI) desorption corresponded to the pyritic material (0.4–0.8 %), whereas mussel shell by itself released between 17 and 26 % of the amounts previously adsorbed. When $12\,t\,ha^{-1}$ mussel shell were added to forest soil, Cr(VI) desorption increased to between 8 and 44 %, however desorption decreased to between 29 and 40 % when the granitic material was amended.

3.3 Cr(VI) adsorption/desorption as a function of pH

3.3.1 Adsorption

Figure 2 shows an overall increase in Cr(VI) adsorption as a function of decreasing pH values in the equilibrium solutions. Similarly, different authors indicated that optimum pH values for Cr(VI) adsorption are between 1 and 2.5 (Huang and Wu, 1977; Boddu et al., 2003; Mohanty et al., 2006; Rawajfih and Nsour, 2008; Vinodhini and Nilanjana,

2009; Wang et al., 2009), due to a higher density of positive charges on the adsorbent surface, then facilitating the binding to chromium anions that dominate at these very acid pH values ($HCrO_4^-$, CrO_4^{2-}, $Cr_2O_7^{2-}$) (Boddu et al., 2003; Gupta et al., 2001; Ucun et al., 2002). Rawajfih and Nsour (2008), as well as Wang et al. (2009), found that
5 increasing pH values cause competition between chromium oxyanions and OH^-, then decreasing Cr(VI) adsorption. In the present study, the pyritic material was the one reaching the maximum Cr(VI) adsorption, concretely $50\,mg\,kg^{-1}$ (equivalent to 99 %) at pH 3.3 (Fig. 2a), remaining high for the whole pH range. The mussel shell retained around 50 % of Cr(VI) when it was treated with acid and the solution pH approached 7;
10 however, the addition of base caused that adsorption diminished to $2.3\,mg\,kg^{-1}$ (equivalent to 4.5 %) when pH increased to 10–12 (Fig. 2b). The granitic material showed increased Cr(VI) retention at pH < 3 (Fig. 2c). The forest soil adsorbed $45.7\,mg\,kg^{-1}$ Cr(VI) (equivalent to 91 %) at pH 2.97, but it decreased to 19.7 (39 %) after being treated with base, reaching pH 5.7 (Fig. 2d). Although positive charges on variable
15 charge surfaces can explain maximum Cr(VI) adsorption when pH < 3, the fact that the pyritic material showed high adsorption even when pH value was increased can be in relation with its abundant oxy-hydroxides content, some of them with elevated point of zero charge (Bradl, 2004), as well as in relation with Cr(VI) reduction to Cr(III) in presence of S^{2-} and Fe^{2+}, gave that Cr(III) may be precipitated at pH values between 6 and
20 11 (Eary and Rai, 1988; Sass and Rai, 1987; Weng et al., 1994). Mussel shell amendment did not cause great changes in the adsorbent behavior of the amended materials, however it provoked an slight pH increase, and slight lowering in Cr(VI) adsorption. But, in the case of the forest soil and the granitic material, this amendment increased Cr(VI) adsorption if compared with samples having similar pH values, which can be attributed
25 to precipitation with carbonates, as signaled by Aziz et al. (2008) studying chromium retention on limestone.

3.3.2 Desorption

Figure 3 shows chromium desorption percentage for the various materials after being added with $100 \, \text{mg L}^{-1}$ Cr(VI). Desorption from the pyritic material was very low at pH < 4 (Fig. 3a), increasing with pH up to $478.8 \, \text{mg kg}^{-1}$ (51.7 % of the amount previ-
5 ously adsorbed) at pH 11, similarly to that found by Muthukrishnan and Guha (2008). Low crystallinity Fe and Al oxy-hydroxides can be positively charged at pH < 7 (Parfitt, 1978; Richard and Bourg, 1991), then retaining CrO_4^{2-} (Rai et al., 1989). As pH decrease, $HCrO_4^-$ concentration increases, and this anion adsorbs strongly both to low crystallinity Fe and Al oxy-hydroxides and to crystalline Fe and Al oxides (Zachara
10 et al., 1989). Cr(VI) desorption from mussel shell was very low at pH close to 5.5, clearly increasing at higher and (mainly) at lower pH values. Cr(VI) released from the granitic material hardly changed as a function of pH (Fig. 3c), and was always lower than 15 % of the amount previously adsorbed. Cr(VI) was strongly retained in forest soil at pH < 7 (Fig. 3d), increasing release with pH up to a maximum attained at pH
15 10.8. Chrysochoou et al. (2010) indicate that the presence of organic matter (as in forest soil) or sulfides (as in pyritic material) can facilitate Cr(VI) reduction to Cr(III), which can precipitate at pH > 5. Avundainayagam et al. (2001) signal that Ca^{2+} can favor Cr(VI) retention in calcareous soils, acting as cationic bridge on negatively charged surfaces, or by means of $CaCrO_4$ formation (Perkins and Palmer, 2000). The mussel
20 shell amendment increased Cr(VI) desorption from the granitic material (Fig. 3c), similarly to that found by Yolcubal et al. (2007) in a calcareous soil. However, the shell amendment had not effect on Cr(VI) release from our forest soil (Fig. 3d).

3.4 Fractionation of the Cr(VI) adsorbed at three different incubation times

Figure 4 shows the results corresponding to the fractionation of the adsorbed Cr(VI),
25 after 24 h (Fig. 4a), 1 week (Fig. 4b), and 1 month of incubation (Fig. 4c). The soluble fraction (the most labile – Gleyzes et al., 2002 – constituted by exchangeable and carbonate-bound forms) was 95 % of the adsorbed Cr in mussel shell, and 80 % in

granitic material, after 24 h of incubation. The mussel shell amendment caused that the soluble fraction in the granitic material increased to 95 %, with parallel diminution of other more stable fractions, probably due to Cr binding to carbonates present in the shell. Mussel shell and the granitic material (un-amended or amended) did not show
5 relevant modifications in the percentage of the soluble fraction for more extended periods of incubation (1 week and 1 month). At 24 h of incubation, the soluble fraction was 35 % for forest soil, and 7 % for the pyritic material. The value did not suffer relevant changes with time for the latter, but in the case of forest soil it decreased to 17 and to 11 % when incubation time was 1 week and 1 month, respectively, due to the
10 increase of a more stable fraction (the oxidizable one, related with organic matter). The mussel shell amendment did not cause remarkable changes in the content of the soluble fraction of forest soil. At 24 h of incubation, the reducible fraction (Cr bound to Fe and Al oxides and oxy-hydroxides) represented less than 12 % in mussel shell, as well as in amended and un-amended forest soil and granitic material, but more
15 than 35 % in the pyritic material, which can be due to its Fe_T and amorphous Fe contents (Reddy et al., 1997; Nieto et al., 2008). In fact, in the present study significant correlations were found between Cr(VI) in the reducible fraction and Fe_{op} ($r = 0.999$), Fe_T ($r = 0.998$), Fe_o ($r = 0.997$), $Fe_T + Mn_T$ ($r = 0.997$), and Mn_T ($r = 0.964$). When the incubation time increased to 1 week and 1 month, the reducible fraction decreased
20 in the pyritic material, increasing in parallel the residual fraction (that corresponding to Cr incorporated to minerals). The mussel shell amendment did not cause relevant changes in the reducible fraction contents. At 24 h of incubation, the oxidizable fraction (Cr bound to organic matter) represented between 3 and 15 % in mussel shell and the pyritic and granitic materials, however it was 55 % in forest soil, which had higher or-
25 ganic matter content. When incubation time increased, Cr(VI) in the oxidizable fraction also increased in the forest soil, reaching 80 %, whereas that in the soluble fraction (the most labile one) decreased. At 24 h of incubation, the residual fraction was quantitatively the most important in the pyritic material, representing 40 % of the adsorbed Cr(VI), and it increased to 50 % when incubation lapsed 1 week.

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4   Conclusions

The pyritic material showed the highest Cr(VI) retention capacity among the solid substrates studied, while the lowest corresponded to the granitic material. The forest soil presented high adsorption potential when pH was acid and the Cr(VI) concentration added was $< 10\,\text{mg}\,\text{L}^{-1}$. When the concentrations added were high (50–$100\,\text{mg}\,\text{L}^{-1}$), certain saturation of the adsorbent surfaces became apparent, although Cr(VI) release was low in the wide pH range studied. Cr(VI) retention was more pronounced at very acid pH, while increasing pH values favored its release. Mussel shell showed limited Cr(VI) retention capacity, and it did not cause marked changes in Cr(VI) adsorption when used as amendment on forest soil and granitic material. Adsorption curves fitted satisfactorily to the Freundlich model. The soluble Cr(VI) fraction was the dominant in the mussel shell and in the un-amended and amended granitic material, whereas more stable fractions dominate in the pyritic material (residual fraction), and in the forest soil (oxidizable fraction). Globally, the pyritic material showed the highest and strongest Cr(VI) retention capacity, whereas the lowest and weakest corresponded to the granitic material.

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Cr(VI) adsorption/desorption on untreated and mussel shell-treated soil materials

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Table 1. General characteristics of the solid materials (average values for 3 replicates, with coefficients of variation always < 5 %).

	Granitic material	Forest soil	Mussel shell	Pyritic material
Sand (%)	60	65	99.53	67
Silt (%)	17	20	0.34	14
Clay (%)	23	15	0.13	19
C (%)	0.11	4.22	11.43	0.26
N (%)	0.04	0.33	0.21	0.04
pH_{H_2O}	5.72	5.65	9.39	2.97
pH_{KCl}	3.69	4.70	9.04	2.58
Ca_c (cmol kg^{-1})	0.18	4.37	24.75	0.36
Mg_c (cmol kg^{-1})	0.13	0.66	0.72	0.29
Na_c (cmol kg^{-1})	0.27	0.33	4.37	0.14
K_c (cmol kg^{-1})	0.31	0.60	0.38	0.24
Al_c (cmol kg^{-1})	1.63	1.92	0.03	2.86
e-CEC (cmol kg^{-1})	2.53	7.88	30.26	3.89
Al-saturation (%)	64.55	24.41	0.11	73.68
P_{Olsen} (mg kg^{-1})	2.56	28.80	54.17	8.80
Ca_T (mg kg^{-1})	< 0.01	709	280 168	603
Mg_T (mg kg^{-1})	355	831	981	8384
Na_T (mg kg^{-1})	102	515	5174	412
K_T (mg kg^{-1})	1434	1544	202	3186
Mn_T (mg kg^{-1})	24	93	34	296
Cu_T (mg kg^{-1})	7	16	7	773
Zn_T (mg kg^{-1})	18	37	8	58
Ni_T (mg kg^{-1})	1	11	8	5
Cd_T (mg kg^{-1})	< 0.001	0.43	0.07	0.08
Cr_T (mg kg^{-1})	3	18	5	99
Co_T (mg kg^{-1})	0.4	1.4	1.0	3.1
As_T (mg kg^{-1})	3	4	1	7
Al_T (mg kg^{-1})	5981	19 660	433	9624
Fe_T (mg kg^{-1})	3505	9486	3535	135 157

Cr(VI) adsorption/desorption on untreated and mussel shell-treated soil materials

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Table 1. Continued.

	Granitic material	Forest soil	Mussel shell	Pyritic material
Al_o (mg kg^{-1})	1425	4275	178	563
Al_p (mg kg^{-1})	463	4163	78.7	229
Al_{op} (mg kg^{-1})	963	112	99.7	335
Al_{cu} (mg kg^{-1})	150	868	22.9	186
Al_{pcu} (mg kg^{-1})	312	3295	55.8	42.7
Al_{la} (mg kg^{-1})	137	146	2.6	91.1
Al_{cula} (mg kg^{-1})	12.8	722	20.3	134
Fe_o (mg kg^{-1})	224	2333	171	41 860
Fe_p (mg kg^{-1})	54.3	2246	37.7	625
Fe_{op} (mg kg^{-1})	170	86.9	133	41 235

$Element_c$: concentration in the exchange complex; $Element_T$: total concentration; Al_o, Fe_o: extracted with ammonium oxalate; Al_p, Fe_p: extracted with sodium piro-phosphate; Al_{cu}: extracted with copper chloride; Al_{la}: extracted with lanthanum chloride; Al_{op}: Al_o-Al_p; Al_{pcu}: Al_p-Al_{cu}; Al_{cula}: Al_{cu}-Al_{la}; Fe_{op}: Fe_o-Fe_p.

Table 2. Fitting of the various materials to the Freundlich model.

	Freundlich		
	K_f ($L^n g^{-1} mg^{(1-n)}$)	n (dimensionless)	R^2
Granitic material	7.5 ± 2.5	0.75 ± 0.08	0.98
Forest soil	28.1 ± 2.0	0.38 ± 0.02	0.995
Mussel shell	10.7 ± 7.1	0.73 ± 0.17	0.895
Pyritic material	381.6 ± 11.7	0.66 ± 0.04	0.994
Granitic material + shell	8.3 ± 5.2	0.63 ± 0.19	0.891
Forest soil + shell	19.9 ± 2.1	0.45 ± 0.03	0.993

Table 3. Desorbed Cr ($mg\,kg^{-1}$ and %) when 0, 0.5, 5, 10, 25, 50 or 100 $mg\,L^{-1}$ Cr were previously added to the various materials.

	Desorbed Cr	Added Cr ($mg\,L^{-1}$)						
		0	0.5	5	10	25	50	100
GM	$mg\,kg^{-1}$	0.003	0.943	10.249	16.893	37.799	68.150	128.289
	%	0	61	92	65.5	66	55	67
FS	$mg\,kg^{-1}$	0.000	0.634	0.905	1.314	4.773	17.711	45.115
	%	0	15	2.6	2.5	6	16	21
Pyritic material	$mg\,kg^{-1}$	0.018	0.040	0.213	0.401	1.335	4.015	4.722
	%	0	0.8	0.4	0.4	0.5	0.8	0.5
Fine shell	$mg\,kg^{-1}$	0.038	0.178	2.301	4.565	11.784	29.580	52.747
	%	0	17	23	26	22	20	23
GM+12 $t\,ha^{-1}$ shell	$mg\,kg^{-1}$	0.000	0.787	2.943	9.093	21.312	30.976	61.636
	%	0	31	41	35	33	40	29
FS+12 $t\,ha^{-1}$ shell	$mg\,kg^{-1}$	0.000	0.626	2.276	4.560	16.198	37.978	85.178
	%	0	15	8	10	24	36	44

GM: granitic material, FS: forest soil.

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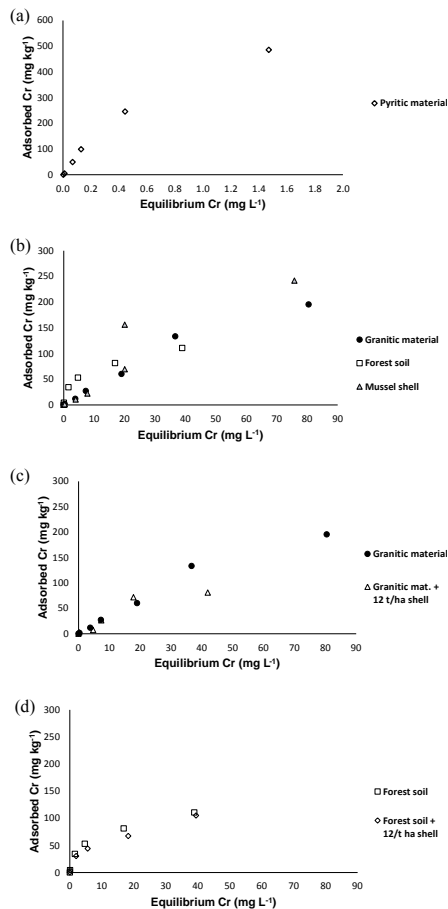
Figure 1. Adsorption curves corresponding to the pyritic material **(a)**, granitic material, forest soil and mussel shell **(b)**, granitic material with or without mussel shell **(c)**, and forest soil with or without mussel shell **(d)**.
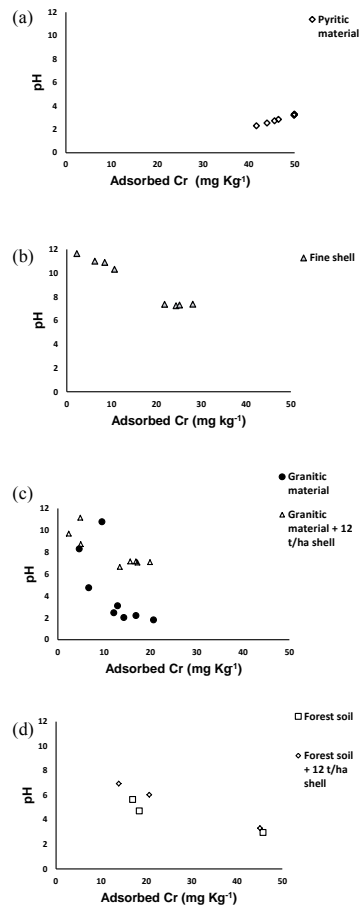
Figure 2. Relationship between pH and adsorbed Cr ($mg\,kg^{-1}$) for pyritic material **(a)**, mussel shell **(b)**, amended and un-amended granitic material **(c)**, and amended and un-amended forest soil **(d)**.
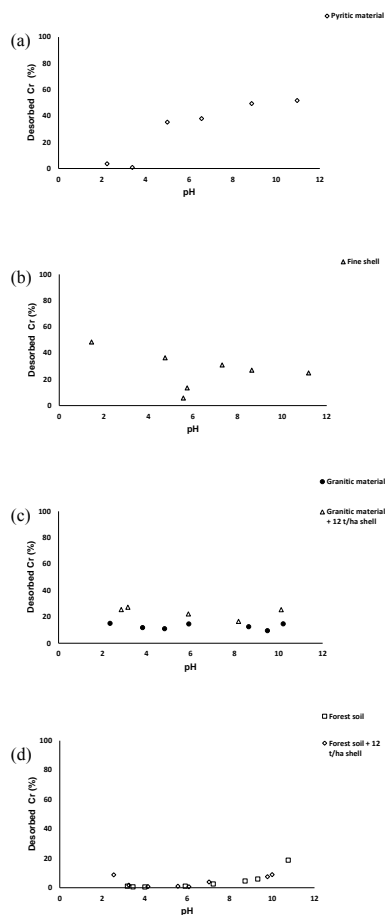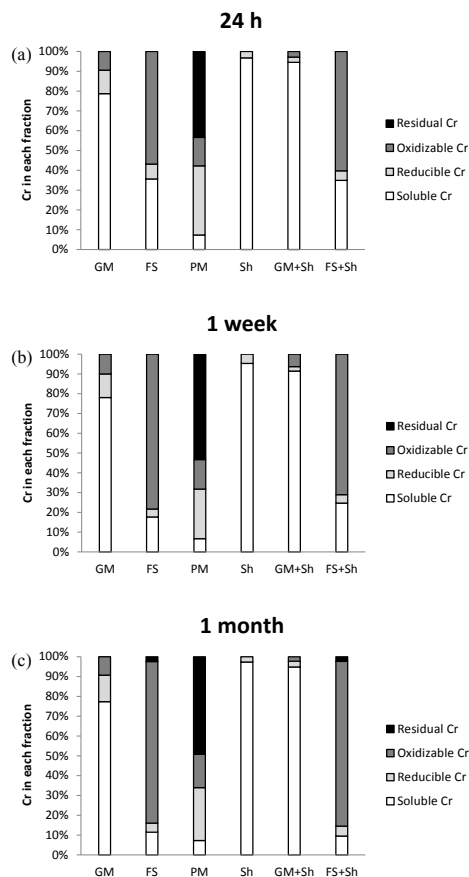
Figure 3. Cr(VI) desorbed (%) as a function of pH, for pyritic material **(a)**, mussel shell **(b)**, amended and un-amended granitic material **(c)**, and amended and un-amended forest soil **(d)**.

Figure 4. Percentages of the various fractions of chromium adsorbed after 24 h **(a)**, 1 week **(b)** and 1 month **(c)** of incubation. GM: granitic material; FS: forest soil; PM: pyritic material; Sh: mussel shell.