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

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Abstract. We used batch-type experiments to study Cr(VI) sorption/desorption on granitic material, forest soil, pyritic material, mussel shell, and on forest soil and granitic material amended with 12 t ha^{-1} (1.2 kg m^{-2}) 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 a 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. Sorption data were satisfactory adjusted to the Freundlich model. Regarding Cr(VI) fractionation, the soluble fraction (weakly bound) was dominant in mussel shell and in the unamended 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 not characterized by a 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 (Alves et al., 1993; Di et al., 2006). Cr(III) is the chemically most stable form of chromium, whereas Cr(VI) is highly toxic and more easily mobilized. Mobilization of Cr(VI), and then risks of water pollution and even of transfer to the food chain, are strongly related to retention processes affecting the pollutant (Lilli et al., 2015).

Different bio-adsorbents have 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) sorption on chitosan, with best results at pH 5. Blázquez et al. (2009) obtained Cr(VI) sorption $> 80\,\%$ on olive waste at pH < 2, although sorption clearly diminished when pH increased. Good Cr(VI) sorption 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 is necessary to increase the knowledge on Cr(VI) retention processes by sorbent materials. In this way, Fernández-Pazos et al. (2013) studied quantitative and kinetic aspects regarding Cr(VI) sorption/desorption on various solid media (fine and coarse mussel shell, unamended 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 in estimating the degree of stability of that retention.

Therefore, the main objectives of this work are (a) to determine Cr(VI) sorption/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} (1.2 kg m^{-2}) fine mussel shell; (b) to elucidate the influence of varying pH as regards Cr(VI) sorption on such materials; and, finally, (c) to determine the fractions where Cr(VI) is retained in the various solid materials investigated, which affect Cr(VI) release and thus overall risks of pollution.

2 Materials and methods

2.1 Materials

The materials used in this study are indicated in Table 1. The granitic material (GM) was sampled in Santa Cristina (Ribadavia, Ourense Province, Spain) and resulted 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. The forest soil (FS) was an A horizon, with dominance of *Eucalyptus globulus* as tree species, and it was sampled in the vicinity of the Alcoa aluminum factory (San Cibrao, Lugo Province, Spain). The pyritic material (PM) was from a copper mine spoil (Touro, A Coruña Province, Spain). The mussel shell (Sh) (< 1 mm) was from the factory Abonomar S.L. (Illa de Arousa, Pontevedra Province, Spain). The two mixtures (granitic material + 12 t ha^{-1} mussel shell – GM + Sh, and forest soil + 12 t ha^{-1} mussel shell – FS + Sh) were shaken for 48 h to achieve homogenization. The unity t ha^{-1} is widely used, but note that the dose 12 t ha^{-1} mussel shell is equivalent to 1.2 kg m^{-2}. The FS, PM, and Sh here used 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. Fernández-Pazos et al. (2013) found that the amendment of pyritic material with mussel shell had no positive effect on Cr(VI) retention, so this combination was discarded in the present study.

FS, PM, and GM were sampled in a zigzag manner (20 cm depth), with 10 subsamples taken to perform each of the composite FS, PM, and GM 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.

Table 1. Materials investigated and abbreviations used to designate them.

Granitic material	GM
Forest soil	FS
Pyritic material	PM
Mussel shell	Sh
Granitic material + 12 t ha^{-1} mussel shell	GM + Sh
Forest soil + 12 t ha^{-1} mussel shell	FS + Sh

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 KCl (solid : liquid ratio 1 : 2.5). Total C and N were quantified by means of the elemental Tru Spec CHNS autoanalyzer (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, and Mn, as well as As, Cd, Co, Cr, Cu, Ni, and Zn, were determined by means of inductively coupled plasma (ICP)–mass spectrometry (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}), and Al bound to organic matter in low-stability complexes (Al_{la}).

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

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

The adsorbents used were the materials previously mentioned (Table 1). Fernández-Pazos et al. (2013) found that the amendment of pyritic material with mussel shell had no 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 was 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 (6167× g) 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 spectrometry (Varian 800-NS, USA). All trials were performed by triplicate.

Immediately after finalizing each batch experiment corresponding to the sorption trials, each sample was added with 30 mL of $NaNO_3$ 0.01 M solution to desorb Cr(VI) and then shaken for 24 h, centrifuged, and filtered as in the sorption trials (Arnesen and Krogstad, 1998). Desorbed Cr(VI), DOC, and pH were determined in all samples.

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

To study sorption, triplicate samples (1 g each) of the sorbent materials (Table 1) 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 a 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. All samples were shaken for 24 h, centrifuged for 15 min at 4000 rpm (6167× g), 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 as in the sorption trials, which were added with 10 mL of solutions containing 100 $mg\,L^{-1}$ Cr(VI), also including $NaNO_3$ 0.01 M as a background electrolyte. All samples were shaken for 24 h, centrifuged for 15 min at 4000 rpm (6167× g), and filtered 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. All samples were shaken for 24 h, centrifuged for 15 min at 4000 rpm (6167× g), and filtered through acid-washed 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 sorption 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

Samples corresponding to the sorbent materials (Table 1) were added with a $NaNO_3$ 0.01 M solution containing 100 $mg\,L^{-1}$ Cr(VI) (1 : 10 solid : solution ratio); then they were shaken for 24 h and filtered. The resulting liquid was analyzed for pH, DOC, and Cr(VI). Finally, fractionation of the adsorbed Cr(VI) was carried out using the European Community Bureau of Reference (BCR) procedure modified by Rauret et al. (1999). The fractionation was performed after 24 h, 1 week, and 1 month. The resulting fractions were acid-soluble fraction, reducible fraction, oxidizable fraction, and residual fraction (all of them measured, not estimated).

2.2.5 Data analysis

The statistical package SPSS 19.0 (IBM, USA) was used to check data for normality. Then, Pearson correlations were calculated.

Finally, Cr(VI) sorption data were fitted 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 sorption 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 sorption capacity, and n (dimensionless) is a constant related to the sorption intensity.

3 Results and discussion

3.1 Characterization of the solid materials used

Table 2 shows data of some basic characteristics of the solid materials used in this study.

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

3.2.1 Sorption

Figure 1 shows that Cr(VI) sorption increased with 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 sorption corresponded to the pyritic material (between 97.1 and 98.7 % of the initial amount added), significantly higher ($p < 0.005$) than that

Table 2. General characteristics of the solid materials (average values for three replicates, with coefficients of variation always < 5 %).

	Granitic material	Forest soil	Mussel shell	Pyritic material
Sand (%)	60.00	65.00	99.53	67.00
Silt (%)	17.00	20.00	0.34	14.00
Clay (%)	23.00	15.00	0.13	19.00
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
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 pyrophosphate; 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.

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 t ha^{-1}, equivalent to 1.2 kg m^{-2}) caused Cr(VI) sorption to reach values between 21 and 86 % on forest soil, whereas Cr(VI) sorption achieved up to 50 % on granitic material. In a previous work, Fernández-Pazos et al. (2013) found slightly lower Cr(VI) sorption on pyritic material and mussel shell, whereas sorption was very similar on their forest soil samples.

Significant correlations ($p < 0.005$) were found between the amounts of Cr(VI) sorbed (in mg kg^{-1}) and total Fe ($r = 0.995$), Fe extracted with ammonium oxalate ($r = 0.993$), non-crystalline inorganic Fe (r=0.992), and pH in water ($r = -0.900$), when chromium concentrations of 100 mg L^{-1} were added to the sorbent materials. Previously, Martin and Kempton (2000) observed that Cr(VI) sorption increased

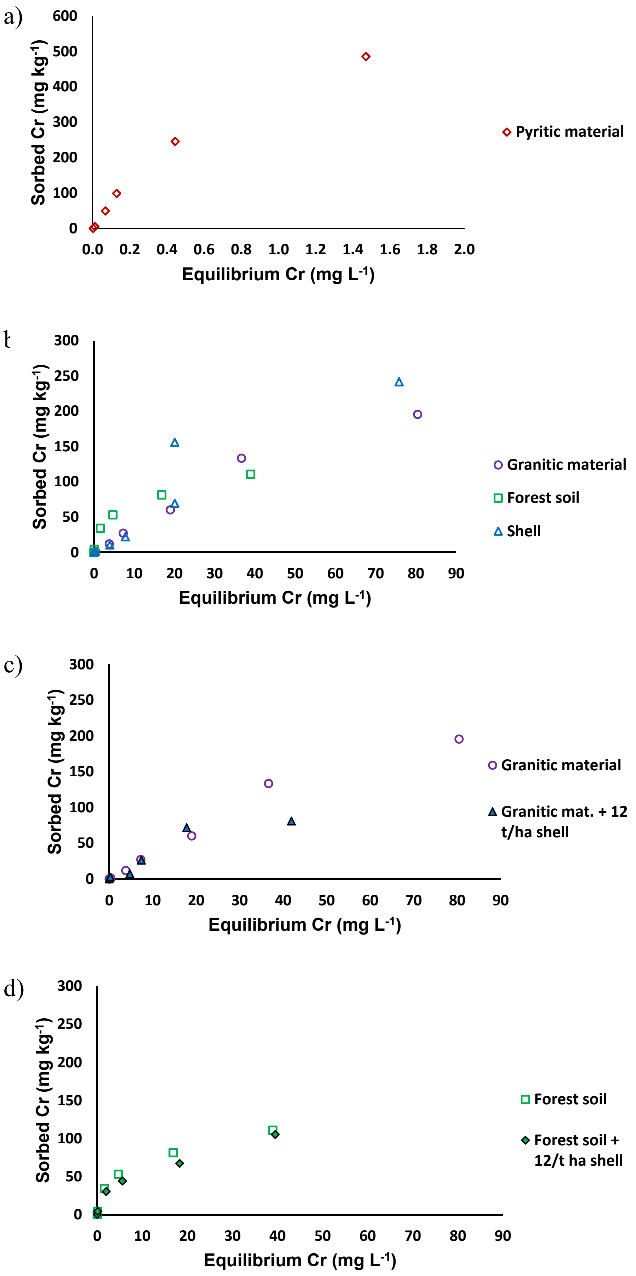

Figure 1. Sorption points corresponding to the pyritic material **(a)**; granitic material, forest soil, and mussel shell **(b)**; granitic material with or without mussel shell **(c)**; and forest soil with or without mussel shell **(d)**. Mean values; triplicate samples with coefficient of variation < 5 %.

Table 3. Fitting of the various materials to the Freundlich model.

	Freundlich		
	K_F ($L^n\ g^{-1}\ mg^{(1-n)}$)	n	R^2
GM	7.5 ± 2.5	0.75 ± 0.08	0.980
FS	28.1 ± 2.0	0.38 ± 0.02	0.995
Sh	10.7 ± 7.1	0.73 ± 0.17	0.895
PM	381.6 ± 11.7	0.66 ± 0.04	0.994
GM + Sh	8.3 ± 5.2	0.63 ± 0.19	0.891
FS + Sh	19.9 ± 2.1	0.45 ± 0.03	0.993

$p < 0.005$; GM: granitic material; FS: forest soil; Sh: mussel shell; PM: pyritic material.

as a function of Fe oxide 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 relation to the high sorption capacity of our pyritic material, characterized by having high Fe contents and very acid pH; furthermore, a stepwise regression test corroborated the importance of the total Fe content in Cr(VI) sorption, explicating 99 % of the variance. In our study, the pyritic material was the one with the highest Cr(VI) sorption capacity, as well as the lowest pH (2.97), and a high concentration of amorphous 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) sorption, which could be related to its low total and non-crystalline Fe contents (Table 2). Correlations ($p < 0.005$) between adsorbed Cr(VI) and pH of the solution were positive for unamended ($r = 0.701$) and shell-amended granitic material ($r = 0.770$), and for unamended ($r = 0.672$) 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) sorption takes place on the various materials: electrostatic bindings, then including the possibility of OH^- release and consequent pH increase when chromium anions adsorb (Arnesen and Krogstad, 1998; 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 ($p < 0.005$) for 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 could be related to the release of organic ions when Cr(VI) sorption takes place. When added Cr(VI) concentrations increased, both granitic material and forest soil showed decreasing sorption percentages, thus suggesting progressive saturation of the adsorbent surfaces (Nameni et al., 2008). Maximum sorption was clearly higher for forest soil (86 % of the initial amount added) than for granitic material (31 %), which could be due to the higher content of organic matter, organo-aluminum complexes, and Alo and Feo in the forest soil. In this respect, Kantar et al. (2008) indicate that

Table 4. Desorbed Cr ($\mathrm{mg\,kg^{-1}}$ and % of the amount previously retained) when 0, 0.5, 5, 10, 25, 50, or $100\,\mathrm{mg\,L^{-1}}$ Cr was previously added to the various materials.

		Desorbed	Added Cr ($\mathrm{mg\,L^{-1}}$)					
		Cr	0.5	5	10	25	50	100
GM	$\mathrm{mg\,kg^{-1}}$	0.003	0.943	10.249	16.893	37.799	68.150	128.289
	%	0	61	92	65.5	66	55	67
FS	$\mathrm{mg\,kg^{-1}}$	0.000	0.634	0.905	1.314	4.773	17.711	45.115
	%	0	15	2.6	2.5	6	16	21
PM	$\mathrm{mg\,kg^{-1}}$	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
Sh	$\mathrm{mg\,kg^{-1}}$	0.038	0.178	2.301	4.565	11.784	29.580	52.747
	%	0	17	23	26	22	20	23
GM + $12\,\mathrm{t\,ha^{-1}}$ Sh	$\mathrm{mg\,kg^{-1}}$	0.000	0.787	2.943	9.093	21.312	30.976	61.636
	%	0	31	41	35	33	40	29
FS + $12\,\mathrm{t\,ha^{-1}}$ Sh	$\mathrm{mg\,kg^{-1}}$	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; PM: pyritic material; Sh: mussel shell.

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).

Sorption data were satisfactory fitted to the Freundlich model through nonlinear regression (Table 3), as other authors found for various bio-sorbents (Cetinkaya-Donmez et al., 1999; Prakasham et al., 1999). Due to the fact that the Freunlich model considers that, theoretically, sorption could be infinite, the fitting to this equation means that sorption maximum would not be easily predictable for these materials.

Significant correlations ($p < 0.005$) were found between the Freundlich constant K_F and $\mathrm{Fe_T}$ ($r = 1$), $\mathrm{Fe_{op}}$ ($r = 1$), and $\mathrm{Fe_o}$ ($r = 0.999$), making evident the importance of amorphous minerals in Cr(VI) sorption.

3.2.2 Desorption

Table 4 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 $12\,\mathrm{t\,ha^{-1}}$ mussel shell was 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) sorption/desorption as a function of pH

3.3.1 Sorption

With the exception of panel a, Fig. 2 shows an overall increase in Cr(VI) sorption as a function of decreasing pH values in the equilibrium solutions. Similarly, different authors have indicated that optimum pH values for Cr(VI) sorption 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, thus facilitating the binding to chromium anions that dominate at these very acid pH values ($\mathrm{HCrO_4^-}$, $\mathrm{CrO_4^{2-}}$, and $\mathrm{Cr_2O_7^{2-}}$) (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 increasing pH values cause competition between chromium oxyanions and $\mathrm{OH^-}$, thus decreasing Cr(VI) sorption. The pyritic material showed the maximum Cr(VI) sorption, concretely $50\,\mathrm{mg\,kg^{-1}}$ (equivalent to 99 % of the initial amount added) at pH 3.3 (Fig. 2a), remaining high for the whole pH range. The mussel shell retained around 50 % of the initial amount of Cr(VI) added when it was treated with acid and the solution pH approached 7; however, the addition of base caused sorption to diminish to $2.3\,\mathrm{mg\,kg^{-1}}$ (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 $45.7\,\mathrm{mg\,kg^{-1}}$ Cr(VI) (equivalent to 91 % of initial amount added) 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 charge surfaces can explain maximum Cr(VI) sorption when pH < 3, the fact that the pyritic material showed high sorption even when the pH value was increased could be related to its abundant oxy-hydroxides content, some of them with elevated point of zero charge (Bradl, 2004), as well as related to Cr(VI) reduction to Cr(III) in the presence of $\mathrm{S^{2-}}$ and $\mathrm{Fe^{2+}}$, given that Cr(III) may be precipitated at pH values between 6 and 11 (Eary and Rai, 1988; Sass and Rai, 1987; Weng et al., 1994). Mussel shell amendment did not cause great changes in the sorbent behavior of the amended materials (Fig. 1); however it provoked a slight pH increase and slight lowering in Cr(VI)

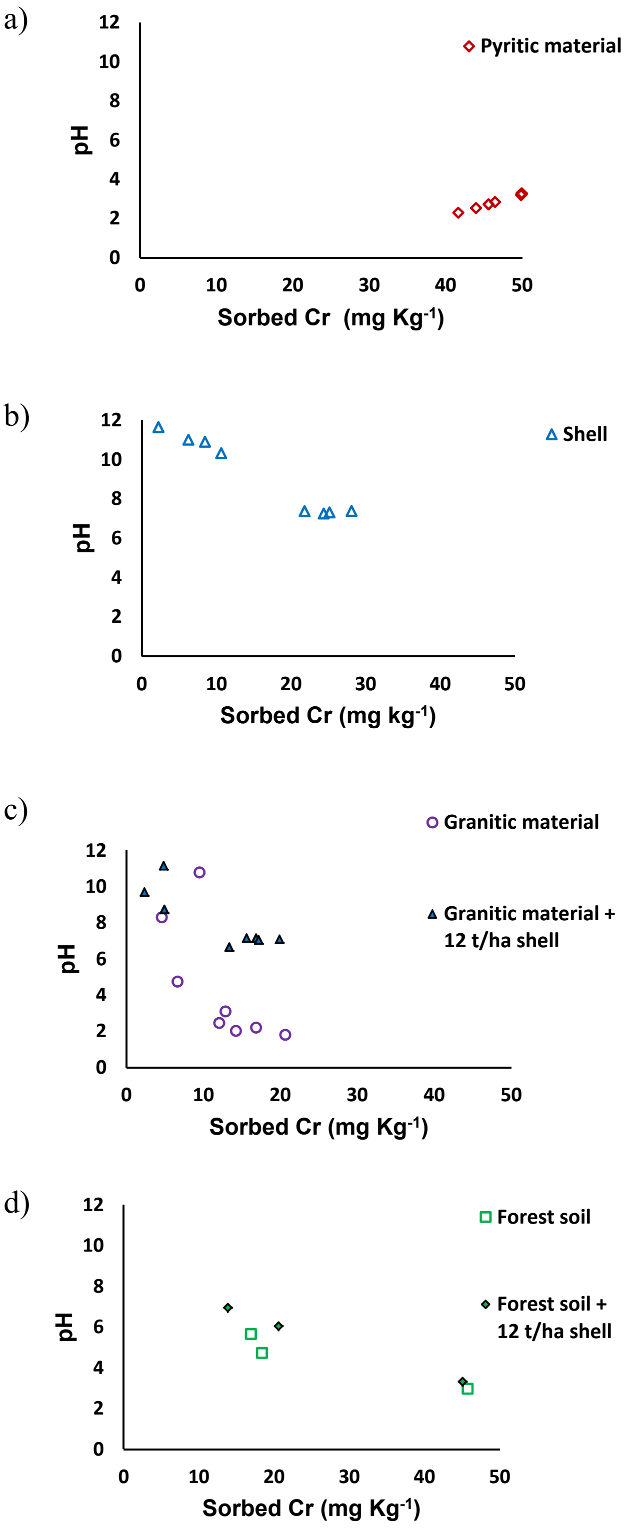

Figure 2. Relation between pH and sorbed Cr (mg kg^{-1}) for pyritic material **(a)**, mussel shell **(b)**, amended and unamended granitic material **(c)**, and amended and unamended forest soil **(d)**, after being added with 100 mg L^{-1} Cr. Mean values; triplicate samples with coefficient of variation < 5 %.

sorption. But in the case of the forest soil and the granitic material, this amendment increased Cr(VI) sorption as compared with samples having similar pH values, which can be attributed 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 mg L^{-1} Cr(VI). Desorption from the pyritic material was very low at pH < 4 (Fig. 3a), increasing with pH up to 51.7 % (478.8 mg kg^{-1}) at pH 11, similar to the findings of 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 decreases, $HCrO_4^-$ concentration increases, and this anion adsorbs strongly both to low-crystallinity Fe and Al oxy-hydroxides and to crystalline Fe and Al oxides (Zachara et al., 1989). Cr(VI) desorption from mussel shell was minimum at pH close to 5.5 (Fig. 3b), clearly increasing at higher and (largely) at lower pH values. Cr(VI) released from the granitic material hardly changed as a function of pH (Fig. 3c), and it was always lower than 15 %. Cr(VI) was almost completely retained in forest soil at pH < 7 (Fig. 3d), increasing release with pH up to a maximum attained at pH 10.8. Chrysochoou et al. (2010) indicated that the presence of organic matter (as in forest soil) or sulfides (as in pyritic material) facilitates Cr(VI) reduction to Cr(III), which can precipitate at pH > 5. Avundainayagam et al. (2001) found that Ca^{2+} can favor Cr(VI) retention in calcareous soils, acting as a cationic bridge on negatively charged surfaces, or by means of $CaCrO_4$ formation (Perkins and Palmer, 2000). Although without statistical significance, the mussel shell amendment increased Cr(VI) desorption from the granitic material (Fig. 3c), similarly to the findings of Yolcubal et al. (2007) in a calcareous soil. However, the shell amendment had no 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), 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 the soluble fraction in the granitic material to increase 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 (unamended or amended) did not show relevant modifications in the percentage of the solu-

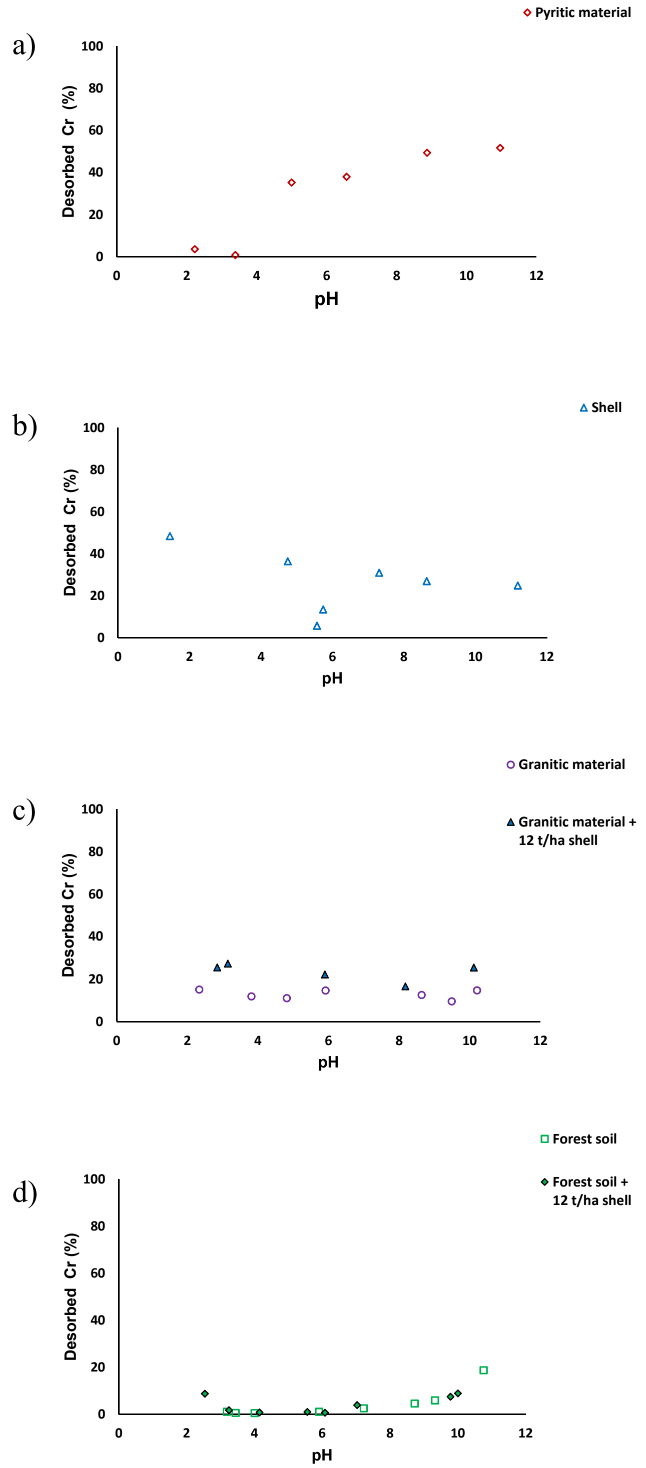

Figure 3. Relation between desorbed Cr(VI) (%) and pH for pyritic material **(a)**, mussel shell **(b)**, amended and unamended granitic material **(c)**, and amended and unamended forest soil **(d)**, after being added with 100 mg L^{-1} Cr. Mean values; triplicate samples with coefficient of variation < 5 %.

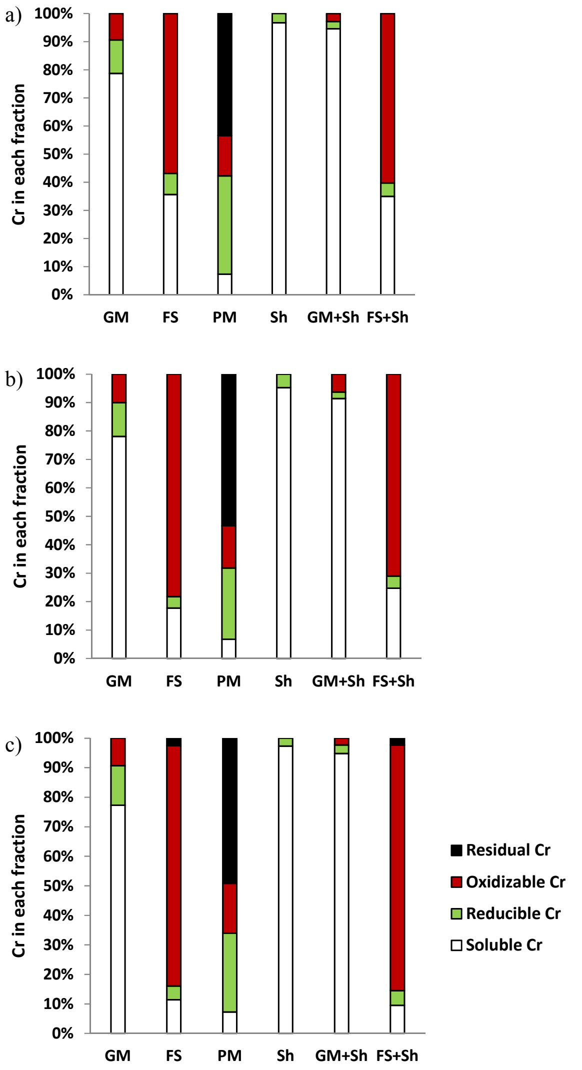

Figure 4. Percentages of the various fractions of chromium sorbed after the addition of 100 mg L^{-1} Cr at time 0, and taken after 24 h **(a)**, 1 week **(b)**, and 1 month **(c)** of incubation. GM: granitic material; FS: forest soil; PM: pyritic material; Sh: mussel shell. Mean values; triplicate samples with coefficient of variation < 5 %.

ble 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 increase of a more stable fraction (the oxidizable one, related to 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 unamended forest soil and granitic material, but more 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, considering all values, significant ($p < 0.005$) partial correlations were found between Cr(VI) in the reducible fraction and Fe_{op} ($r = 0.999$), Fe_T ($r = 0.998$), Fe_o ($r = 0.997$), and Mn_T ($r = 0.964$). When the incubation time increased to 1 week and 1 month, the reducible fraction decreased 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 organic 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.

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 sorption potential when pH was acid and the Cr(VI) concentration added was < 10 mg L^{-1}. When the concentrations added were high (50–100 mg 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) sorption when used as an amendment on forest soil and granitic material. Sorption curves fitted satisfactory to the Freundlich model. The soluble Cr(VI) fraction was dominant in the mussel shell and in the unamended and amended granitic material, whereas more stable fractions dominate in the pyritic material (residual fraction) and in the forest soil (oxidizable fraction).

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