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Adsorption, desorption and fractionation of As(V) on untreated and mussel shell-treated granitic material

N. Seco-Reigosa[1], L. Cutillas-Barreiro[2], J. C. Nóvoa-Muñoz[2], M. Arias-Estévez[2], E. Álvarez-Rodríguez[1], M. J. Fernández-Sanjurjo[1], and A. Núñez-Delgado[1]

[1]Department Soil Science and Agricultural Chemistry, Engineering Polytechnic School, Campus Univ., 27002 Lugo, University Santiago de Compostela, Spain
[2]Department Plant Biology and Soil Science, Faculty of Sciences, Campus Univ., 32004 Ourense, University Vigo, Spain

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Correspondence to: A. Núñez-Delgado (avelino.nunez@usc.es)

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Abstract

As(V) adsorption and desorption were studied on granitic material, coarse and fine mussel shell, and granitic material amended with 12 and 24 t ha^{-1} fine shell, investigating the effect of different As(V) concentrations and different pH, as well as the fractions where the adsorbed As(V) was retained. As(V) adsorption was higher on fine than on coarse shell. Mussel shell amendment increased As(V) adsorption on granitic material. Adsorption data corresponding to the un-amended and shell-amended granitic material were satisfactory fitted to the Langmuir and Freundlich models. Desorption was always $< 19\,\%$ when the highest As(V) concentration (100 mg L^{-1}) was added. Regarding the effect of pH, the granitic material showed its highest adsorption (66 %) at pH < 6, and it was lower as pH increased. Fine shell presented notable adsorption in the whole pH range between 6 and 12, with a maximum of 83 %. The shell-amended granitic material showed high As(V) adsorption, with a maximum (99 %) at pH near 8, but decreasing as pH increased. Desorption varying pH was always $< 26\,\%$. In the granitic material, desorption increased progressively when pH increased from 4 to 6, contrary to what happened to mussel shell. Regarding the fractionation of the adsorbed As(V), most of it was in the soluble fraction (weakly bound). Globally, the granitic material did not show high As(V) retention capacity, which implies risks of water pollution and transfer to the food chain; however, the mussel shell amendment increased As(V) retention, making this practice recommendable.

1 Introduction

Igneous rocks, as granite, have low As concentrations (< 5 mg kg^{-1}), and background levels in soils are between 5 and 10 mg kg^{-1} (Smedley and Kinniburgh, 2002), although As levels are much higher in certain polluted soils. As pollution can be very relevant in mine sites where oxidation of sulfides such as pyrite takes place, as well as in areas treated with certain biocides and fertilizers (Matschullat, 2000). As is an element that can accumulate in living beings and may cause severe affectations, especially when it is in inorganic form (Smith et al., 2000; Ghimire et al., 2003), so having the potential to provoke environmental and public health issues.

When As-based products are spread on soils or spoils, with the aim of fertilizing, controlling plagues or promoting re-vegetation, risks of soil and water pollution, and subsequent transfer to the food chain, must be taken into account. In this way, it is interesting to determine As retention capacity corresponding to solid substrates receiving the spreading of the pollutant, both individually or treated with complementary materials that can affect As retention/release potential. At this regard, some previous works have investigated the effectiveness of mussel shell waste amendment to increase As retention on diverse solid materials (Seco-Reigosa et al., 2013a,b; Osorio-López et al., 2014), and this amendment could also be useful to increase As retention on granitic substrates (such as mine spoils or exposed C horizons), which has not been studied up to now.

As concentration in natural waters is mainly controlled by interactions between solids and solution, as adsorption/desorption, which are affected by pH and other environmental parameters. Clays, organic matter and Fe, Al and Mn oxy-hydroxides can protonate or deprotonate as a function of pH, facilitating retention of anions such as arsenate when they are positively charged, and promoting progressive anions release when pH go rising and surface charge becomes increasingly negative (Smith et al., 1999; Fitz and Wenzel, 2002); however, at high pH values and in the presence of sulfate and carbonate, co-precipitation of As with oxy-hydroxides and sulfates, or even as calcium arsenate, may occur (García et al., 2009). This could explain that certain soils show maximum As adsorption at pH near 10.5 (Goldberg and Glaubig, 1988). In this way, Zhang and Selim (2008) indicate that carbonate can play an important role in arsenate retention in solid substrates having high pH value. In fact, calcite has been related with As retention in calcareous soils and carbonate-rich environments, due to adsorption/precipitation of $CaCO_3$ and As forming inner sphere complexes (Alexandratos et al., 2007; Mehmood et al., 2009; Yolcubal and Akyol, 2008; Zhang and Selim, 2008), which could be relevant in granitic materials that were amended with mussel shell to promote As retention.

In view of that, the objectives of this work are: (a) to determine As(V) retention/release capacity corresponding to a granitic material, fine mussel shell, and coarse mussel shell, as well as to the granitic material amended with 12 or 24 $\mathrm{t\,ha^{-1}}$ fine mussel shell, for different As(V) concentrations and pH values; (b) to examine fitting of adsorption data to the Langmuir and Freundlich models; and (c) to determine the fractions where the adsorbed As(V) was retained, which is in relation with stability of retention.

2 Materials and methods

2.1 Materials

We used different solid materials: (a) granitic material from Santa Cristina (Ribadavia, Ourense Province, Spain), similar to a C horizon derived from the evolution of a rocky substrate, nowadays exposed to the atmosphere after the elimination of the upper horizons, then needing organic matter and nutrients to be restored, similarly to granitic mine spoils; (b) finely (< 1 mm), as well as coarsely (0.5–3 mm) crushed mussel shell, both from the factory Abonomar S.L. (Illa de Arousa, Pontevedra Province, Spain), that had been previously studied by Seco-Reigosa et al. (2013b); (c) mixtures of the granitic material +12 $\mathrm{t\,ha^{-1}}$ and 24 $\mathrm{t\,ha^{-1}}$ fine mussel shell (which showed higher adsorption potential than coarse shell in preliminary trials), shaking the mixtures for 48 h to achieve homogenization. The granitic material was sampled in a zigzag manner (20 cm depth), taken 10 subsamples to perform the final one. 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

The Robinson pipette procedure was used to characterize the particle-size distribution of the materials studied. A pH-meter (model 2001, Crison, Spain) was used to measure pH in water (solid : liquid relationship 1 : 2.5). C and N were measured using an elemental Tru Spec CHNS auto-analyzer (LECO, USA). Available P was determined as per Olsen and Sommers (1982). A NH_4Cl 1 M solution was used to displace the exchangeable cations, 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 using ICP-mass (820-NS, Varian, USA), after nitric acid (65 %) microwave assisted digestion. Different selective solutions were used to obtain 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 as a function of added As(V) concentration

The methodology of Arnesen and Krogstrad (1998) was used to study As(V) adsorption/desorption as a function of the added concentration of the pollutant.

The materials used were triplicate samples of the granitic material, coarse and fine mussel shell, and granitic material amended with 12 and 24 $t\,ha^{-1}$ fine mussel shell.

In the adsorption experiment, 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 As(V), prepared from analytical grade $Na_2HAsO_4 \cdot 7H_2O$ (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 As(V) using ICP-mass (Varian 800-NS, USA). Adsorbed As was calculated as the difference between added As(V) and As(V) remaining in the equilibrium solution.

Desorption studies were carried out at the end of the adsorption trials, adding 30 mL of a $NaNO_3$ 0.01 M solution to each sample, then shaking during 24 h, centrifuging at 4000 rpm for 15 min, and filtering through acid-washed paper. Desorbed As(V), DOC and pH were determined by triplicate in all samples.

Adsorption data were fitted to the Freundlich (Eq. 1) and Langmuir (Eq. 2) models.

The Freundlich equation can be formulated as follows:

$$q_e = K_F \cdot C_e n \qquad (1)$$

where q_e is the As(V) adsorption per unit of mass of the adsorbent, C_e is the equilibrium concentration of the dissolved As, K_F is a constant related to the adsorption capacity, and n is a constant related to the adsorption intensity.

The Langmuir equation formulation is formulated as follows:

$$q_e = X_m \cdot K_L \cdot C_e / (1 + K_L \cdot C_e) \qquad (2)$$

where X_m is the maximum adsorption capacity, and K_L is a constant related to the adsorption energy.

The statistical package SPSS 19.0 (IBM, USA) was used to perform the fitting of the adsorption experimental data to Freundlich and Langmuir models.

2.2.3 As(V) adsorption/desorption as a function of pH

Adsorption trials were performed using triplicate samples (1 g each) of fine mussel shell, and granitic material, as well as granitic material +12 t ha^{-1} fine mussel shell, that were added with 10 mL of solutions containing 5 mg L^{-1} As(V) and different concentrations of HNO$_3$ (0.0025 M, 0.0038 M, 0.005 M, 0.0075 M) or NaOH (0.0025 M, 0.0038 M, 0.005 M, 0.0075 M), including NaNO$_3$ 0.01 M as background electrolyte. To elaborate control samples, each of the solid materials were added with 10 mL of solutions containing NaNO$_3$ 0.01 M and 5 mg L^{-1} As(V), but without HNO$_3$ or NaOH. After 24 h of shaking, all samples were centrifuged for 15 min at 4000 rpm, then filtering through acid-washed paper. The resulting liquid phase was analyzed for pH, DOC and As(V), finally calculating adsorbed As(V) as the difference between added As(V) concentration and that remaining in the equilibrium solution.

Desorption trials consisted of triplicate samples (1 g each) of fine mussel shell and granitic material, that were added with 10 mL of solutions containing 100 mg L^{-1} As(V), including NaNO$_3$ 0.01 M as background electrolyte. After a shaking period of 24 h, all samples were centrifuged for 15 min at 4000 rpm, then filtering through acid-washed paper, this time discarding the liquid phase. The remaining solid phase was added with 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 this to achieve desorption for different pH values. 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 As(V), finally calculating desorbed As(V) as the difference between the amount retained in the adsorption phase and that released to the equilibrium solution in this desorption phase, and it was expressed as percentage of the total amount adsorbed.

2.2.4 Fractionation of the As(V) adsorbed at three different incubation times

Granitic material, fine mussel shell, and granitic material +12 t ha^{-1} fine mussel shell samples were added with a NaNO$_3$ 0.01 M solution containing 100 mg L^{-1} As(V) (1 : 10 solid : solution ratio), shaking for 24 h and filtering through acid-washed paper. The resulting liquid phase was analyzed for pH, DOC and As(V). Finally, the adsorbed As(V) was fractionated using the BCR procedure modified by Rauret et al. (1999), using the four steps indicated by Nóvoa-Muñoz et al. (2007), finally obtaining an acid soluble fraction, a reducible fraction, an oxidizable fraction, and a residual fraction. The fractionation was performed for three different incubation times: 24 h, 1 week and 1 month.

3 Results and discussion

3.1 Characterization of the solid materials

Table 1 shows that the granitic material had low C and N percentages (indicating low organic matter content), and acid pH (5.7), whereas pH was alkaline for fine and coarse mussel shell (9.4 and 9.1, respectively). Total Ca and Na contents were higher for fine and coarse mussel shell, whereas the granitic material presented the lowest effective cation exchange capacity (eCEC $< 4\,\mathrm{cmol\,kg^{-1}}$), as well as high Al saturation (64.5 %) and total Al concentrations. Regarding Al forms, amorphous $\mathrm{Al_o}$ compounds were clearly more abundant in the granitic material, whereas those bound to organic matter ($\mathrm{Al_p}$) had low presence in all of the studied materials, with most of the amorphous Al being in inorganic form ($\mathrm{Al_{op}}$). Similarly, the low organic-C content of the granitic material and coarse and fine mussel shells justified that most Fe was bound to inorganic forms ($\mathrm{Fe_{op}}$). Furthermore to that showed in Table 1, the particle size distribution of the granitic material was 60 % sand, 23 % clay and 17 % silt.

3.2 Adsorption/desorption as a function of added As(V) concentration

Figure 1a shows that As(V) adsorption was equivalent on granitic material and fine mussel shell, and higher than on coarse mussel shell. The different behavior for both mussel shell materials can be in relation with the higher surface area of fine shell ($1.4\,\mathrm{m^2\,g^{-1}}$) than that of coarse shell ($1\,\mathrm{m^2\,g^{-1}}$), as previously stated by Peña-Rodríguez et al. (2013). Figure 1b indicates that As(V) adsorption increased when granitic material was amended with mussel shell. Adsorption curves in Fig. 1 show type C layout (Giles et al., 1960) for granitic material and fine and coarse mussel shell (Fig. 1a), exhibiting a rather constant slope when the added arsenic concentration was increased. This kind of adsorption curve is generally associated to the existence of a constant partition between the adsorbent surface and the equilibrium solution in the contacting layer, or to a proportional increase of the adsorbent surface taking place when the amount of adsorbed arsenic increases, as indicated by Seco-Reigosa et al. (2013b), who found the same type of adsorption curve studying arsenic retention on pine sawdust and on fine mussel shell. The granitic material treated with mussel shell shows adsorption curves that are near C type (Fig. 1b).

Figure 2 shows that adsorption progressively decreased on granitic material when the As(V) concentration added was $> 10\,\mathrm{mg\,L^{-1}}$. The $24\,\mathrm{t\,ha^{-1}}$ mussel shell amendment caused slightly increase in adsorption, whereas the $12\,\mathrm{t\,ha^{-1}}$ amendment did not result in systematic increased adsorption.

Regarding desorption, Table 2 shows released As(V) concentrations and percentages (referred to the amounts previously adsorbed). The highest desorption percentage (49 %) corresponded to coarse mussel shell when $25\,\mathrm{mg\,L^{-1}}$ As(V) were added. When $100\,\mathrm{mg\,L^{-1}}$ As(V) were added, percentage desorption was always $< 19\,\%$. Mussel shell amendment (12 and $24\,\mathrm{t\,ha^{-1}}$) increased As(V) desorption, which could be in relation with the fact that arsenate bind strongly to the surface of oxides and hydroxides in clearly acid environments (pH between 3.5 and 5.5; Silva et al., 2010), whereas increased pH values favor desorption (Golberg and Glaubig, 1988). Any case, most of the adsorbed As(V) did not desorb, indicating notable irreversibility of the process.

Adsorption data were adjusted to the Freundlich and Langmuir models (Table 3), finding that the un-amended and shell-amended granitic material fitted well to both models, whereas fine and coarse mussel shell can be fitted only to the Freundlich model. Maji et al. (2007) found satisfactory adjustment to both Freundlich and Langmuir models studying As(V) adsorption on lateritic substrates, while Yolcubal and Akyol (2008) obtained better fitting to the Freundlich model using carbonate-rich solid substrates.

3.3 As(V) adsorption/desorption as a function of pH

3.3.1 Adsorption

Figure 3 shows the repercussion on As(V) adsorption of adding different HNO_3 and NaOH molar concentrations to fine mussel shell and to the un-amended and shell-amended granitic material. The acid concentrations added to fine shell did not permit to reach pH < 7 (Fig. 3a), whereas the addition of alkaline solutions allowed to achieve pH values near 12 for this material. The granitic material exhibited the lowest buffer potential (possibly related to its low colloids content), presenting pH values between 2 and 10. Mussel shell amendment increased the buffer potential of this granitic material, especially when the 24 t ha^{-1} dose was used.

Figure 3b shows that As(V) adsorption on the granitic material (expressed in mg kg^{-1}) progressively decreased from pH 4 as a function of increasing pH value, whereas the mussel shell amendment increased As(V) adsorption. The granitic material contains variable charge compounds (such as Fe and Al oxy-hydroxides, kaolinite-type clays and organic matter), positively charged at acid pH, facilitating retention of $H_2AsO_4^-$ and $HAsO_4^{2-}$ (Smedley and Kinniburgh, 2002; Xu et al., 2002; Yan et al., 2000), but suffering progressive de-protonation and increase of negative charge as pH increases, which can lower As(V) adsorption (Fitz and Wenzel, 2002). However, the effect of lowering As(V) adsorption due to pH increase did not occur when granitic material was amended with mussel shell, which must be in relation with the additional As(V) adsorption capacity associated to calcium carbonate present in mussel shell, establishing cationic bridges when pH values are higher (Alexandratos et al., 2007). Our granitic material suffered just slight changes in As(V) adsorption in the pH range 3.5 to 6.9, which can be in relation with the effective adsorption that As(V) experience in a wide range (4–11) (Stanic et al., 2009).

Expressing As(V) adsorption as percentage with respect to the amount added, the maximum for the un-amended granitic material (66 %) took place at pH < 6, progressively decreasing from that point as a function of increasing pH value. Fine mussel shell adsorbed As(V) notably on the pH range 6–12, with maximum value of 83 %. When the granitic material was amended with fine mussel shell, As(V) adsorption reached 99 % at pH near 8, then progressively decreasing as pH increased.

In the case of the shell-amended granitic material, significant statistical correlations existed between adsorbed As(V) and pH ($r = 0.926$ and $r = 0.880$ for the 12 and 24 t ha^{-1} mussel shell doses, respectively), whereas no correlation was found between both parameters in the case of mussel shell by itself. The latter can be due to the absence of anionic exchange with OH^- groups when As(V) anions adsorb on mussel shell, contrary to that happening to other anions on different adsorbent materials (Arnesen and Krogstad, 1998; Bower and Hatcher, 1967; Gago et al., 2012; Huang and Jackson, 1965). However, other anions than OH^- can be released, as is the case for SO_4^{2-}, PO_4^{3-} or organic anions, which is in concordance with the correlations found between adsorbed As(V) and DOC ($r = 0.810$, for fine shell, and $r = 0.919$ and $r = 0.913$, for the granitic material amended with 12 and 24 t ha^{-1} mussel shell, respectively). Moreover, other mechanisms that can be responsible of anion retention (as retention on calcite, or H and van der Waals bindings) do not implicate OH^- release (Boddu et al., 2003). Different authors remark the influence of pH on As(V) adsorption (Maji et al., 2007; Partey et al., 2008; Stanic et al., 2009), but in the case of our granitic material, Al, Fe, Al_o, Fe_o, organic matter and organo-aluminum complexes contents must be also relevant.

Fine and coarse mussel shell presented alkaline pH (9.39 and 9.11, respectively, Table 1), causing that the dominant As species is $HAsO_4^{2-}$ (Yan et al., 2000), which can bind to the surface of carbonates such as calcite by means of inner sphere complexes with octahedral Ca (Alexandratos et al., 2007).

3.3.2 Desorption

Figure 4 shows that, when a concentration of 100 mg L^{-1} As(V) was added, As(V) desorption from fine shell and granitic material was always < 26 % of the amount previously adsorbed, considering the whole pH range studied (2–12). Two different behaviors took place: (a) As(V) desorption from granitic material clearly increased as pH increased between 4 and 6, and (b) As(V) desorption from mussel shell clearly decreased as pH increased between 4 and 6. Moreover, As(V) desorption from mussel shell continued to be low at pH > 6, slowly decreasing, whereas release from the granitic material further increased when pH > 6.

As(V) desorption from mussel shell clearly increased at pH < 6, in accordance with that signaled by Goldberg and Glaubig (1988), who found that As adsorption on calcite increased from pH 6 to 10 (then decreasing release), attaining maximum adsorption at pH between 10 and 12, then decreasing at higher pH values. Di Benedetto et al. (2006) indicated that As(V) can be incorporated to calcite in alkaline conditions, then preventing its mobilization even in situations where oxy-hydroxides do not exhibit adsorption potential. Alexandratos et al. (2007) signaled that arsenate anions have great affinity for calcite at pH around 8, establishing strong bindings due to inner sphere complexes, with AsO_4^{3-} binding to the mineral surface through Ca cationic bridges. All these facts are in accordance with the low As(V) release suffered by our mussel shell samples at pH > 6 (Fig. 4).

3.4 Fractionation of the As(V) adsorbed at three different incubation times

Figure 5 shows that the As(V) soluble fraction (exchangeable and bound to carbonates) is quantitatively the most important in all samples (especially in the un-amended and shell-amended granitic material), representing at 24 h of incubation contents that ranged between a minimum of 69 % in fine mussel shell, and a maximum of 88 % in the 12 t ha^{-1} shell-amended granitic material. The soluble fraction corresponds to the most mobile As(V), which is weakly retained mainly due to anionic exchange mechanisms (Keon et al., 2001), and which is associated to high risks of toxicity. Moreover, Taggart et al. (2004) indicate that As(V) derived from anthropogenic pollution incorporates to the most mobile fractions of solid substrates in great percentage. In our materials, the As(V) reducible fraction (associated to Al and Fe oxides and oxy-hydroxides), represented between 9 and 19 % of the As(V) adsorbed at 24 h of incubation (Fig. 5), whereas the As(V) residual fraction (that incorporated to the structure of minerals) constituted always $< 16\,\%$ of the amount adsorbed. Finally, the As(V) oxidizable fraction (associated to organic matter and as sulfides) was always $< 2.6\,\%$ (Fig. 5), attributable to the low organic content of the solid materials here studied. The increase of incubation time from 24 h to 1 week and to 1 month, as well as the $12\,\mathrm{t\,ha^{-1}}$ shell amendment of the granitic material, did not cause relevant modifications in the percentage content of each fraction of the adsorbed As(V) (Fig. 5).

The As(V) reducible fraction (bound to Al and Fe oxides and oxy-hydroxides) correlated positively with DOC ($r = 0.957$ at 24 h, and $r = 0.954$ at 1 week incubation time), suggesting that arsenate compete with organic groups to bind on oxides and oxy-hydroxides. Additionally, the As(V) residual fraction correlated with total Fe ($r = 0.980$ at 24 h, and $r = 0.973$ at 1 month incubation time), suggesting the existence of re-adsorption and co-precipitation processes with Fe minerals.

4 Conclusions

The granitic material here studied presented lower As(V) adsorption capacity than the fine and coarse mussel shells used. Furthermore, As(V) retention on the granitic material was weak, then implying scarce capacity to attenuate acute toxic effects of an eventual As(V) pollution episode, with remarkable risk of mobilization and transfer to water, plants and the food chain. Fine shell showed moderate As(V) retention potential (higher than that of coarse shell). The amendment of 12 and $24\,\mathrm{t\,ha^{-1}}$ fine mussel shell on the granitic material increased As(V) retention, thus justifying this management practice. Most of the adsorbed As(V) did not desorb in a wide range of pH, with higher risk corresponding to the granitic material when pH increased from pH value 6. The adsorbed As(V) was retained mainly on the soluble fraction, with weak bindings, also facilitating release, mobilization and eventual pollution of waters and transfer to the food chain.

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

		Coarse mussel shell	Fine mussel shell	Granitic material
C	%	12.67	11.43	0.11
N	%	0.36	0.21	0.04
C/N		35.00	55.65	2.80
pH_{H_2O}		9.11	9.39	5.72
Ca_e	cmol kg^{-1}	12.64	24.75	0.18
Mg_e	cmol kg^{-1}	0.58	0.72	0.13
Na_e	cmol kg^{-1}	5.24	4.37	0.27
K_e	cmol kg^{-1}	0.31	0.38	0.31
Al_e	cmol kg^{-1}	0.04	0.03	1.63
eCEC	cmol kg^{-1}	18.82	30.25	2.53
Al saturation	%	0.21	0.11	64.55
P_{Olsen}	mg kg^{-1}	23.21	54.17	2.56
Ca_T	mg kg^{-1}	298 085	280 168	< 0.01
Mg_T	mg kg^{-1}	1020	980.6	355.16
Na_T	mg kg^{-1}	5508	5173	102.38
K_T	mg kg^{-1}	80.57	202.1	1434.00
Al_T	mg kg^{-1}	93.89	433.24	5980.68
Fe_T	mg kg^{-1}	3534	1855	3505.09
Mn_T	mg kg^{-1}	5.70	33.75	23.96
Cu_T	mg kg^{-1}	3.20	6.72	7.15
Zn_T	mg kg^{-1}	7.71	7.66	18.10
Cd_T	mg kg^{-1}	0.02	0.07	0.00
Ni_T	mg kg^{-1}	5.64	8.16	0.97
Cr_T	mg kg^{-1}	1.32	4.51	2.71
Co_T	mg kg^{-1}	0.68	1.02	0.41
As_T	mg kg^{-1}	0.48	1.12	2.94

Table 1. Continued.

		Coarse mussel shell	Fine mussel shell	Granitic material
Al_o	$mg\,kg^{-1}$	85.00	178.33	1425.00
Al_p	$mg\,kg^{-1}$	62.67	78.67	462.67
Al_{cu}	$mg\,kg^{-1}$	7.57	22.87	150.18
Al_{la}	$mg\,kg^{-1}$	2.47	2.60	137.43
Al_{op}	$mg\,kg^{-1}$	22.33	99.67	962.33
Al_{pcu}	$mg\,kg^{-1}$	55.10	55.80	312.49
Al_{cula}	$mg\,kg^{-1}$	5.10	20.27	12.75
Fe_o	$mg\,kg^{-1}$	42.67	171.00	224.33
Fe_p	$mg\,kg^{-1}$	7.67	37.67	54.33
Fe_{op}	$mg\,kg^{-1}$	35.00	133.33	170.00

X_e: exchangeable concentration of the element; X_T: total concentration of the element; Al_o, Fe_o: Al and Fe extracted with ammonium oxalate; Al_p, Fe_p: Al and Fe extracted with sodium piro-phosphate; Al_{cu}: Al extracted with copper chloride; Al_{la}: Al 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. Desorption results (mg kg^{-1} and %) corresponding to fine and coarse mussel shell, and to the un-amended and shell-amended (12 and 24 t ha^{-1}) granitic material (average values of 3 replicates, with coefficients of variation always < 5 %).

Added As	Fine shell		Coarse shell		GM		GM + 12 t ha^{-1}		GM + 24 t ha^{-1}	
(mg L^{-1})	(mg kg^{-1})	(%)	(mg kg^{-1})	(%)	(mg kg^{-1})	(%)	(mg kg^{-1})	(%)	(mg kg^{-1})	(%)
0	0.02	0.0	0.04	0.0	0.01	0.0	0.02	0.0	0.07	0.0
0.5	0.25	6.9	0.22	7.6	0.10	2.3	0.38	9.9	0.51	10.7
5	2.68	7.5	2.22	7.9	0.90	2.0	3.24	6.6	5.72	12.3
10	6.18	9.0	3.49	6.2	2.98	3.8	9.85	10.2	12.58	14.2
25	12.96	8.2	17.71	49.4	10.09	6.4	34.76	16.6	29.08	15.0
50	25.81	9.9	37.20	46.4	25.82	9.5	65.38	25.1	33.62	10.1
100	45.57	8.4	39.01	7.0	54.65	10.7	98.17	18.9	72.67	12.3

GM: granitic material.

Table 3. Fitting of the adsorption results to the Freundlich and Langmuir models

	Freundlich			Langmuir		
	K_F(L^n kg^{-1} $mmol^{(1-n)}$)	n (dimensionless)	R^2	K_L(L $mmol^{-1}$)	X_m(mmol kg^{-1})	R^2
Fine shell	10.8 ± 0.8	0.86 ± 0.08	0.987	–	–	
Coarse shell	38.7 ± 11.4	3.14 ± 0.55	0.991	–	–	
GM	9.0 ± 0.5	0.68 ± 0.06	0.991	1.0 ± 0.6	16.7 ± 6.0	0.978
GM + 12 t ha^{-1}	7.7 ± 0.9	0.41 ± 0.09	0.938	9.2 ± 8.0	6.9 ± 1.6	0.866
GM + 24 t ha^{-1}	10.8 ± 1.0	0.61 ± 0.08	0.977	1.6 ± 1.3	16.1 ± 7.5	0.951

GM: granitic material; 12 and 24 t ha^{-1}: doses of the fine mussel shell amendments; – fitting was not possible due to estimation errors being too high.

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀| |▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

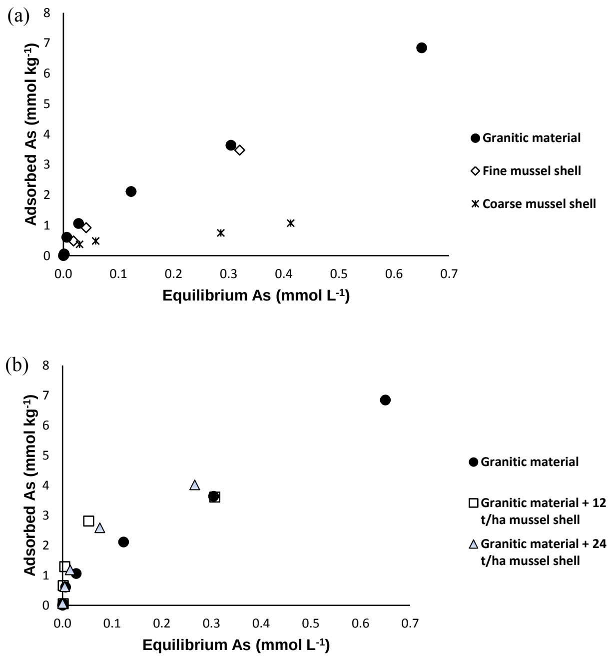

Figure 1. Adsorption curves for the individual materials **(a)** and for the un-amended and shell-amended (12 or 24 t ha^{-1}) granitic material **(b)**. Average values of 3 replicates, with coefficients of variation always < 5 %.

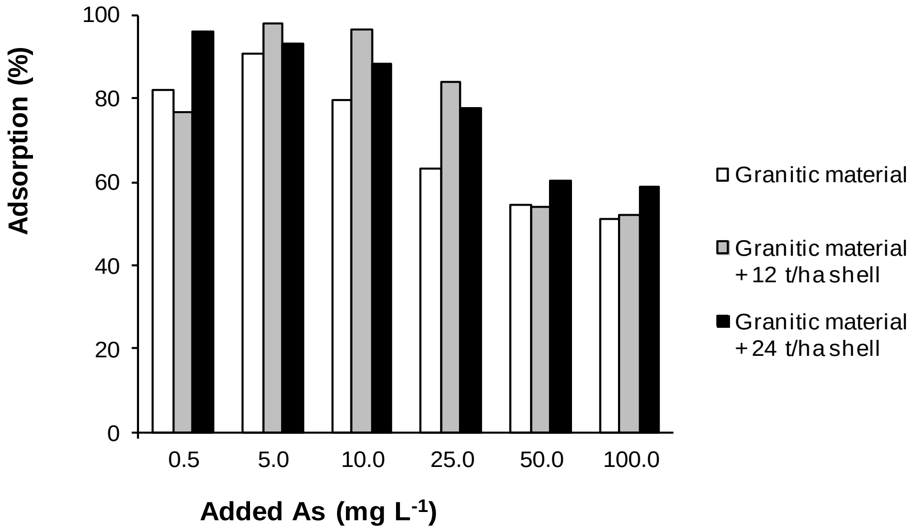

Figure 2. Relationship between added As(V) ($\mathrm{mg\,L^{-1}}$) and As(V) percentage adsorption for the un-amended and shell-amended (12 or 24 $\mathrm{t\,ha^{-1}}$) granitic material. Average values for 3 replicates, with coefficients of variation always $< 5\,\%$.

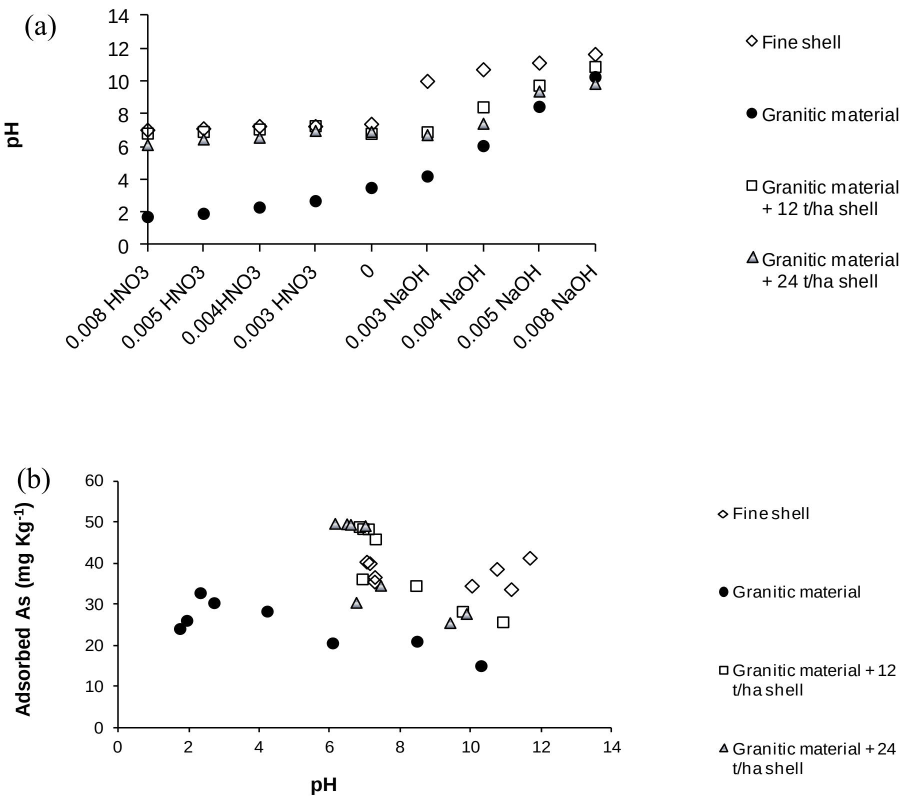

Figure 3. (a) Time-course evolution of pH for the solid materials as a function of the various molar concentrations of added HNO_3 and NaOH; **(b)** Relationship between adsorption ($mg\,kg^{-1}$) and pH value for fine shell, and the un-amended and shell-amended granitic material. Average values for 3 replicates, with coefficients of variation always < 5 %.

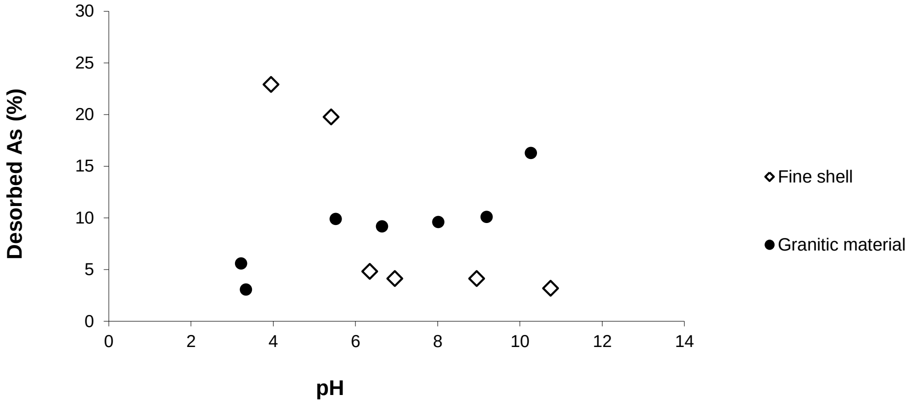

Figure 4. Relationship between As(V) desorption (%) and pH value for fine shell, and for the granitic material (average values for 3 replicates, with coefficients of variation always < 5 %), when 100 mg L^{-1} As(V) were added to the adsorbents.

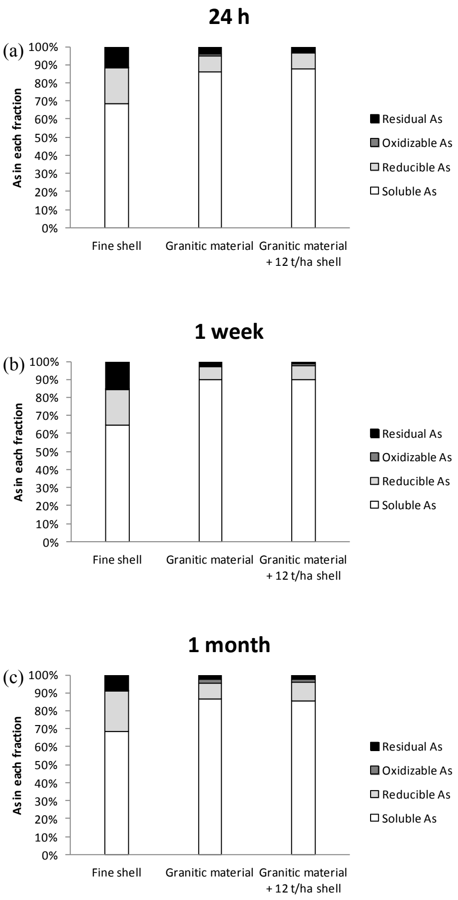

Figure 5. Percentages of the various fractions of As(V) adsorbed after 24 h **(a)**, 1 week **(b)** and 1 month **(c)** of incubation. Average values for 3 replicates, with coefficients of variation always < 5 %.