






Communication

Cadmium and Lead Sorption/Desorption on Non-Amended and By-Product-Amended Soil Samples and Pyritic Material

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Abstract: Batch-type experiments were used to study cadmium (Cd) and lead (Pb) sorption/desorption on forest soil, vineyard soil and pyritic material samples, on the by-products mussel shell, oak ash, pine bark and hemp waste, and on forest soil, vineyard soil and pyritic material amended with 48 t ha⁻¹ of oak ash, mussel shell, and hemp waste. The main results were that the forest soil showed higher Cd and Pb retention than the vineyard soil and the pyritic material. Regarding the byproducts, sorption was in the following order: oak ash > mussel shell > hemp waste > pine bark, with desorption following an inverse sequence. The pH was the parameter that most influenced Cd and Pb sorption. Cd and Pb sorption curves showed better fitting to the Freundlich than to the Langmuir model, indicating the dominance of multilayer interactions. Oak ash and mussel shell were the amendments causing higher increase in Cd and Pb sorption on both soils and the pyritic material (close to 100% with the oak ash amendment), as well as more a pronounced decrease in desorption. These results could be used to favor an effective management of the by-products studied, which could retain Cd and Pb in soils and degraded areas, preventing water pollution.

Keywords: by-products; Cd pollution; Pb pollution; release; retention

1. Introduction

Heavy metals pollution is recognized as a global concern [1–4]. Specifically, Cd and Pb are heavy metal pollutants associated to relevant environmental and health issues, even at low concentrations [5–9].

Biosorption is considered an efficient and low-cost alternative to fight heavy metals pollution [10–15]. In fact, Fu and Wang [1] reviewed the sorption capacities of agricultural and industrial waste and by-products, as well as of various types of natural substances, finding promising results. In this regard, in the last years we have studied several sorbents for the removal or retention of cationic heavy metals (Cd, Cu, Hg, Ni, Pb, Zn) [16–20], and anionic pollutants (Cr(VI) and As(V)) [21–28]. However, as far as we know, no previous study has dealt with Cd and Pb retention on forest soil, vineyard soil, and pyritic material samples, as well as on fine mussel shell, oak ash, hemp waste and pine bark samples, differentiating between results corresponding to the individual materials and those corresponding to the soils and pyritic material amended with the by-products.

In view of that, in this work we studied individual Cd and Pb sorption/desorption on various soils and by-products, as well as on soils and pyritic material amended with the three by-products that showed the highest Cd and Pb sorption capacities. The results of this work could be of relevance to promote the recycling of the by-products studied, as well as to facilitate the correct management of soils or degraded areas where Cd and Pb pollution is a concern.

2. Materials and Methods

2.1. Materials

We used a forest soil, a vineyard soil, pyritic material, finely ground mussel shell, pine bark, oak ash and hemp waste.

In addition, after processing in the laboratory (drying and sieving through 2 mm mesh, see details in Supplementary Material), representative samples of forest soil, vineyard soil and pyritic material were individually amended with 48 t ha^{-1} of the by-products oak ash, fine shell, and hemp waste. The amounts (g) of each soil and pyritic material required were calculated taking into account the bulk densities (g cm^{-3}) of each one, as well as a vertical depth of 20 cm, which makes it possible to know the amount of soil or pyritic material (g) present in $10,000 \text{ m}^2$ (1 ha), then transforming the corresponding doses to t ha^{-1} . These mixtures were stirred for 48 h to facilitate homogenization. Thus, apart from the seven individual materials, there were nine additional mixtures of materials (i.e., forest soil, vineyard soil and pyritic material amended with each of three by-products).

2.2. Methods

2.2.1. Characterization of the Materials

All details corresponding to analytical methods [29–51] and to chemical characteristics of each material were previously published [52] and are included in the Supplementary Material (see Table S1, as well as Figures S1–S7). Specifically, determined parameters were: total C and N contents, pH in distilled water, pH of the point of zero charge (pH_{pzc}), exchangeable Na, K, Ca, Mg and Al, effective cationic exchange capacity (eCEC), total P, total concentrations of Na, K, Ca, Mg, Al, Fe, Mn, as well as As, Cd, Cr, Cu, Ni, Pb, and Zn, total non-crystalline Al and Fe (Al_0 , Fe_0), particle-size distribution of forest and vineyard soil samples. In addition, the main functional groups were determined by infrared spectroscopy (FTIR).

2.2.2. Cd and Pb Sorption/Desorption Experiments

Similarly to findings in Coelho et al. [16], to perform individual sorption experiments, 3.0 g of each material (both individual materials and the amended soils and pyritic material) was weighed and added with 30 mL of a 0.01 M NaNO_3 solution, with increasing concentrations (0, 0.5, 1.5, 3.0 and 6.0 mmol L^{-1}) of Cd or Pb, respectively, prepared from $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich, St. Louis, MO, USA), and $\text{Pb}(\text{NO}_3)_2$ (Scharlau, Cham, Germany).

The resulting suspensions were stirred for 24 h, centrifuged at 4000 rpm ($6167 \times g$) for 15 min, and filtered through acid washed paper (pore size $2.5 \mu\text{m}$). Cadmium, Pb, dissolved organic carbon (DOC), and pH values were quantified in the filtrated liquid using ICP Mass (model 820-NS, Varian, Palo Alto, CA, USA), UV-visible spectroscopy (model UV-1201, Shimadzu, Kyoto, Japan), and pH meter (model 2001, Crison, Barcelona, Spain) equipment. Certified materials used for accuracy were from Sigma-Aldrich (St. Louis, MO, USA) and from Scharlau (Cham, Germany), for Cd and Pb. Detection limits were $<0.00001 \text{ mg L}^{-1}$ for Cd and Pb.

To determine desorption, after ending the sorption experiments each sample was added with 30 mL of 0.01 M NaNO_3 , then the samples were stirred for 24 h, centrifuged at 4000 rpm ($6167 \times g$) for 15 min, and filtered through acid washed paper (pore size $2.5 \mu\text{m}$).

Cadmium, Pb, DOC, and pH were quantified in the filtrated liquid as indicated above. Percentage desorption was calculated after determining concentrations released to the equilibrium solution, referring to those previously retained by sorption. All determinations were performed by triplicate.

2.3. Data Analyses

The statistical package SPSS 21 (IBM, North Castle, NY, USA) was used to perform basic statistical treatment (descriptive statistics, stepwise linear regression, and correlation analysis) and fitting to adsorption models.

Data from sorption experiments were adjusted to the Langmuir and Freundlich models.

In the Langmuir model, a maximum adsorption value (Q_m) can be calculated from Equation (1):

$$Q_{eq} = Q_m K_L C_e / (1 + K_L C_e) \quad (1)$$

where Q_{eq} is the quantity of each heavy metal adsorbed (mmol kg^{-1}), Q_m is the maximum adsorption capacity (mmol kg^{-1}), K_L is the Langmuir constant related to the adsorption energy (L mmol^{-1}), and C_e is the concentration of each heavy metal in the equilibrium solution (mmol L^{-1}).

The Freundlich model can be expressed by means of Equation (2):

$$Q_{eq} = K_F C_e^{1/n} \quad (2)$$

where Q_{eq} is the quantity adsorbed of each heavy metal (mmol kg^{-1}), K_F is the Freundlich constant related to the energy of adsorption ($\text{L}^n \text{kg}^{-1} \text{mmol}^{(1-n)}$), C_e is the concentration of each metal in the equilibrium (mmol L^{-1}), and n is a constant related to the adsorption intensity.

3. Results

3.1. Cd Sorption on the Individual Materials

As shown in Figure 1a, Cd sorption was clearly higher on the forest soil sample (with a maximum of $32.4 \text{ mmol kg}^{-1}$) than on the vineyard soil sample and pyritic material. Expressed as percentage of Cd retained (referred to the concentration added), the amount sorbed decreased gradually with the increase of added Cd: from 92 to 54% for forest soil, from 67 to 39% for vineyard soil, and from 26 to 12% for the pyritic material.

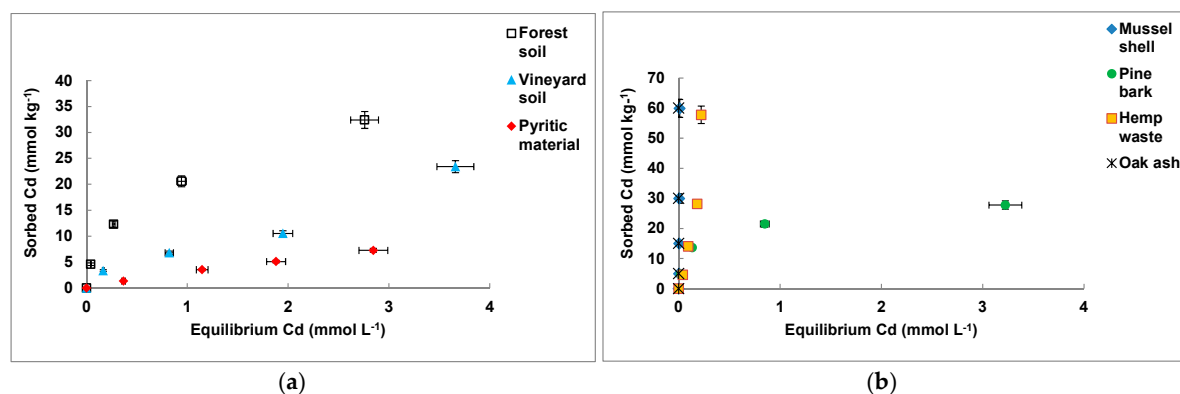


Figure 1. Cd sorption curves for forest soil, vineyard soil, and pyritic material (a), and for the by-products studied (b). Average values (with error bars) for three replicates, with coefficients of variation always <5%.

Regarding by-products, Figure 1b shows that the highest Cd sorption corresponded to oak ash, mussel shell, and hemp waste (maximum sorption close to 60 mmol kg^{-1}), whereas it was clearly

lower for pine bark. Expressed as percentage, sorption was always >99% for oak ash and mussel shell, between 92 and 96% for hemp waste, and between 46 and 96% for pine bark.

Overall, the values of the sorption curves were better adjusted to the Freundlich than to the Langmuir model (Table 1), meaning that Cd saturation would be hardly reached. Mussel shell, hemp waste and oak ash cannot be fitted to either model due to too high errors of estimation, which is frequent when sorption values are as high as those found for Cd on these materials.

Table 1. Freundlich and Langmuir constants and R^2 (coefficients of determination) values corresponding to Cd sorption on the soils and by-products studied. -: error values too high for fitting.

Sorbent Material	Freundlich			Langmuir		
	K_F ($L^n \text{ kg}^{-1} \text{ mmol}^{(1-n)}$)	n	R^2	K_L ($L \text{ mmol}^{-1}$)	Q_m (mmol kg^{-1})	R^2
Forest soil	21.0 ± 0.4	0.43 ± 0.02	0.998	1.5 ± 0.6	39.2 ± 5.3	0.971
Vineyard soil	6.9 ± 1.7	0.92 ± 0.21	0.955	-	-	-
Pyritic material	3.0 ± 0.3	0.54 ± 0.06	0.983	0.4 ± 0.1	10.5 ± 0.7	0.996
Mussel shell	-	-	-	-	-	-
Pine bark	21.0 ± 1.4	0.27 ± 0.05	0.960	7.3 ± 2.4	27.3 ± 1.9	0.973
Hemp waste	-	-	-	-	-	-
Oak ash	-	-	-	-	-	-

In the present study, the lowest Cd sorption corresponded to three of the materials having the lowest pH values in the equilibrium solutions: pyritic material (pH between 3.21 and 3.39), vineyard soil (between 3.45 and 3.72), and pine bark (between 3.61 and 4.0), although forest soil sorbed remarkable Cd concentrations even if it had clearly acidic pH values in the equilibrium solutions (between 3.42 and 3.62). However, the pH values were much higher for the remaining materials: between 6.45 and 6.61 for mussel shell, between 8.09 and 8.48 for hemp waste, and between 12.83 and 13.01 for oak ash. It is obvious that those high pH values facilitate precipitation, which is considered within the sorption processes, although it is not adsorption.

According to Appel and Ma [53], and to Kim et al. [54], the main factors influencing Cd retention in soils are total Cd concentration and pH, which affects hydrolysis of the elements, organic matter solubility, and surface charge of the variable charge compounds [55]. In acid soils, Cd is easily exchanged and available to plants, whereas, as pH increases, Cd retention is favored by sorption on variable charge compounds, by inner-sphere complexes formation, and by hydroxide precipitation [56,57]. In this way, Memon et al. [58] obtained maximum Cd adsorption on sawdust at $\text{pH} > 4$ because at those pH carboxyl groups are deprotonated and negatively charged, being able to electrostatically bind Cd (which at those pH, and up to pH 8, is found as Cd^{2+}), while at $\text{pH} > 9$ adsorption decreases due to hydrolysis of the metal, appearing CdOH^+ , with lower affinity for sorbent surfaces. At $\text{pH} < 3$, variable charge surfaces tend to be positively charged, decreasing adsorption of cationic metals. In fact, Cd is mainly found as Cd^{2+} in the soil solution, although it can form complex ions, such as CdCl^+ , CdCl_3^- , CdCl_4^{2-} , CdOH^+ , CdHCO_3^+ , $\text{Cd}(\text{OH})_3^-$ or $\text{Cd}(\text{OH})_4^{2-}$ [59], and in contaminated soils the predominant soluble Cd species are the free Cd^{2+} ion and neutral species, such as CdSO_4 or CdCl_2 , present in increasing quantities at $\text{pH} > 6.5$ [60].

In the present study, correlation between pH in the equilibrium solution and sorbed Cd was significant only in the case of pine bark (coefficient of correlation $r = -0.930$, $p < 0.05$). The fact that the variation of pH with the addition of Cd depends on the type of sorbent may be related to the sorption of the metal taking place by different mechanisms. When the dominant mechanism is the electrostatic attraction between the surface of the negatively charged bio-sorbent and Cd^{2+} , an exchange with H^+ can take place, decreasing solution pH [61]. According to Memon et al. [58], the ion exchange mechanism could be the most frequent in Cd adsorption on organic materials (such as the hemp waste and pine bark in the present study), since its cell walls are formed by cellulose and lignin, with many hydroxyl groups present in tannins and other phenols (see Supplementary Material), which are active ion exchangers. However, Taty-Costodes et al. [61] and Pagnanelli et al. [62], also indicate the presence of mechanisms other than cation exchange, such as specific adsorption and complexation processes, as

well as physical adsorption, and probable micro-precipitations, which would explain the differences found in the present study in relation to pH change, since these processes do not imply H^+ release.

Regarding dissolved organic carbon (DOC) levels in equilibrium solutions, in the present study there was a tendency for DOC to decrease as the added Cd concentration increased, although it was only significant for forest soil ($r = -0.969$, $p < 0.01$), vineyard soil ($r = -0.879$, $p < 0.05$), and pine bark ($r = -0.992$, $p < 0.01$). These DOC decreases may be due to the high affinity of cationic metals to form organic complexes [63] and their subsequent precipitation. According to Park et al. [64], the availability of metals is reduced due to their adsorption on solid surfaces, and to the formation of stable complexes with humic substances. In this sense, several studies identify organic matter as one of the main components controlling Cd distribution in soils [65,66], indicating that Cd adsorption decreases when soil organic matter content is reduced. Furthermore, organic Cd complexes are not very stable, and dissociate when pH is <6 [67].

On the other hand, the forest and vineyard soils in the present study had a 15% clay fraction, and they both (as well as the other materials studied) had relevant concentrations of non-crystalline oxides (especially oak ash, the pyritic material, and both soils, see Supplementary Material). The clay minerals represent an important contribution of negatively charged surfaces, which can retain cations through electrostatic adsorption, as demonstrated by Shaheen et al. [56] for vermiculites, smectites, imogolites and allophanes, while Chen et al. [68] indicated that montmorillonites present high Cd removal capacity from aqueous solutions. Specifically, Serrano et al. [69] indicate that soils with high pH and clay content have the highest Cd sorption capacities, taking into account that Cd retention would occur through precipitation reactions at high pH, while exchange reactions would dominate at low pH values.

In addition to that, Fe hydroxides play an important role in the retention of metals through a high specificity adsorption mechanism, often by direct coordination with surface oxygen, and trace elements adsorbed on these oxides could be exchanged only by other cationic metals having similar affinity for the surface, or by protons [70]. Retention may also include isomorphic substitution and cation exchange mechanisms [56].

Furthermore, total Ca content is very high in some of the materials here studied, especially in fine mussel shell, oak ash and hemp waste (see Supplementary Material). In relation to this, Shaheen et al. [56] indicated that the presence of free $CaCO_3$ reduces the solubility of trace elements, which is attributed to a direct effect due to surface interactions, and to an indirect effect related to its repercussion on pH. Carbonated surfaces have a high affinity for Cd, and $CdCO_3$ precipitates have been found on such surfaces [66,71]. In fact, divalent metal cations have a tendency to associate with calcite, initially through surface adsorption reactions, and subsequently as precipitates within the calcite layers by recrystallization, giving a specific sorption with little tendency to desorption [72]. On the other hand, the presence of carbonates in soils implies lower solubility of metallic elements, as a consequence of high pH values, which favors its precipitation (which can be considered within global sorption), although adsorption decreases at very high pH values [56].

In the present study, when 6 mmol L^{-1} of Cd were added, and all the studied sorbent materials were considered, bivariate correlations analysis showed significant correlations between Cd sorption and pH ($r = 0.933$, $p < 0.01$), exchangeable Al ($r = -0.781$, $p < 0.05$), and exchangeable Ca ($r = 0.754$, $p > 0.05$). These results reflect the influence of pH on Cd sorption, since Cd sorption increases at higher pH due to the appearance of negative charges in variable charge compounds, and under these conditions there is less Al and more Ca in the exchange complex.

3.2. Pb Sorption on the Individual Materials

As shown in Figure 2a, Pb sorption was clearly higher on the forest soil samples (maximum $51.4 \text{ mmol kg}^{-1}$, corresponding to 86% of 6 mmol L^{-1} added) than on the vineyard soil samples (maximum $36.6 \text{ mmol kg}^{-1}$, corresponding to 61% sorption), and pyritic material (maximum $35.7 \text{ mmol kg}^{-1}$, 60% sorption). When low Pb concentrations were added, the percentage sorption

was between 97.7% and 99.9% for forest soil, between 77% and 99% for vineyard soil, and between 66% and 87% for pyritic material.

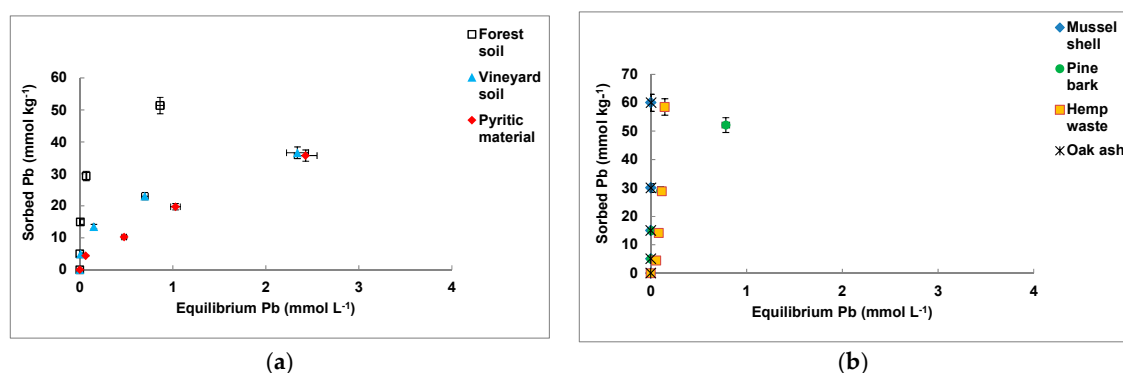


Figure 2. Pb sorption curves for the forest soil, vineyard soil, and pyritic material (a), and for the by-products studied (b). Average values (with error bars) for three replicates, with coefficients of variation always <5%.

The higher Pb sorption on the forest soil compared to the pyritic material could be attributed to the higher organic matter content of the former. It could also explain the higher Cd sorption on the forest soil with respect to the vineyard soil, in conjunction with the Al_o and Fe_o contents in the forest soil sample (See Supplementary Material), as previously pointed out by Fernández-Pazos et al. [22] and Seco-Reigosa et al. [26].

Regarding the effect of pH, Irani et al. [73] indicated that Pb adsorption on different sorbent materials increased from pH 2 to 6, attributing it to a gradual increase in the negative charges on the sorbents, whereas at pH > 6 the formation of Pb hydroxides would lead to difficult adsorption. On the other hand, Petruzelli et al. [74] demonstrated that Pb has great affinity for the formation of organic complexes, which remain stable till low pH values (pH 4). In acid media, usual Pb concentrations in the soil solution are between 0.003 and 0.046 mg L⁻¹, and under these conditions chemical speciation indicates that Pb is preferably in free form or as PbSO₄, whereas soluble organometallic complexes dominate when pH is neutral [75]. Furthermore, according to McKenzie [76], Fe oxides preferentially absorb Pb, in comparison with Cd.

As shown in Figure 2b, Pb sorption was high on all by-products. Percentage sorption was always >99.8% for mussel shell and oak ash, >89% for hemp waste, and >86.9% for pine bark.

In previous works, Tofan et al. [77] obtained 96% retention for Pb in hemp waste, with added concentrations similar to those in the present study. As for pine bark, Paradelo et al. [18] demonstrated the high efficacy of this bio-sorbent to retain metals, especially Pb, in stable forms of low mobility, finding 100% retention when 2 mmol L⁻¹ of Pb were added. The high tannin and lignin content of pine bark, as well as its functional groups (see Supplementary Material), would be the cause of this great affinity for metals. High Pb adsorption capacity was also highlighted for oak ash by Papandreou et al. [78], which found retention close to 100% at 48 h after adding 1 mmol L⁻¹ of Pb.

Table 2 shows that Pb sorption was better adjusted to the Freundlich model in most of the materials here studied. As in the case of Cd, mussel shell, hemp waste, and oak ash cannot be fitted to either model, which is frequent when sorption is as high as that of Pb in these materials. Reddy et al. [79] also found a better fit for the Freundlich model using different biosorbents for Pb.

Table 2. Freundlich and Langmuir constants and R^2 values corresponding to Pb sorption on the soils and by-products studied. -: error values too high for fitting.

Sorbent Material	Freundlich			Langmuir		
	K_F ($L^n \text{ kg}^{-1} \text{ mmol}^{(1-n)}$)	n	R^2	K_L ($L \text{ mmol}^{-1}$)	Q_m (mmol kg^{-1})	R^2
Forest soil	54.0 ± 2.3	0.25 ± 0.02	0.99	29.6 ± 19.3	51.1 ± 7.1	0.93
Vineyard soil	26.8 ± 0.3	0.36 ± 0.01	1.00	2.5 ± 1.2	41.2 ± 6.0	0.96
Pyritic material	19.1 ± 0.7	0.70 ± 0.05	1.00	0.3 ± 0.1	84.7 ± 21.5	0.99
Mussel shell	-	-	-	-	-	-
Pine bark	56.8 ± 2.1	0.31 ± 0.02	0.99	15.9 ± 8.4	54.3 ± 7.1	0.95
Hemp waste	-	-	-	-	-	-
Oak ash	-	-	-	-	-	-

As for Cd, Pb sorption is highly pH-dependent, since this parameter affects the solubility of the metal ions, and also the ionization state of the functional groups in variable charge compounds of the sorbent surfaces [80]. In the present work, the materials with higher pH showed clearly higher Pb sorption capacities, which is indicative of the influence of the acid-base conditions on metal retention. Lead adsorption processes on different types of biosorbents probably include various types of mechanisms, such as surface complexation, electrostatic attraction and ion exchange [80]. According to these authors, when the exchange processes prevail, a decrease in pH in the equilibrium solutions is frequently observed, caused by an H^+ increase in the solution after being exchanged with Pb^{2+} on the sorbent surfaces. In the present study, a decrease in pH at equilibrium with increasing Pb concentration added was also observed (except in oak ash and hemp waste); however, pH/sorbed-Pb correlations were only significant in the vineyard soil ($r = -0.997$, $p < 0.01$) and pine bark ($r = -0.995$, $p < 0.01$). This probably indicates the existence of ion exchange on these sorbent surfaces.

In the present study, DOC values undergo small variations in most materials when increasing Pb concentrations were added, with a DOC decrease observed in both soils, pine bark and hemp waste. DOC levels were significantly correlated with sorbed Pb just for forest soil ($r = -0.897$, $p < 0.05$). A possible precipitation of organometallic complexes could explain DOC decreases. On the other hand, a DOC increase associated to Pb adsorption was pointed out by Karami et al. [81] using biochar as sorbent, which would provide soluble organic compounds.

In the present study, when 6 mmol L^{-1} of Pb were added, and considering all the studied sorbent materials, Pb sorption showed a significant ($p < 0.05$) and negative correlation with exchangeable Al ($r = -0.69$) and with Al saturation ($r = -0.757$). There was also a significant ($p < 0.01$) and positive correlation with pH ($r = 0.827$). Pb sorption increases as pH grows due to the rise in negative charges, and both exchangeable Al and Al saturation decrease when pH increases.

3.3. Cd and Pb Desorption from the Individual Materials

Table 3 shows desorbed Cd and Pb concentrations and percentages, with low Pb desorption rates for all materials (always $<9.8\%$, and in most cases $<5.6\%$), lower than those obtained for Cd (except in the case of hemp waste and oak ash), which indicates that Pb remains more strongly sorbed on most of the studied materials. Mohapatra et al. [82] also found higher Pb adsorption with respect to Cd, which attributed to the higher ionic radius of the first, since Pb retention tends to occur through inner-sphere complexes, while it occurs through outer-sphere complexes in the case of Cd.

Mussel shell and oak ash showed the lowest Pb desorption, with percentages $<0.26\%$. These two by-products can be considered as the most suitable for Pb retention or removal among those here studied, presenting high Pb sorption and low desorption. In the opposite side, the pyritic material had Pb desorption between 7.9 and 9.7%.

Considering these results, oak ash and mussel shell would be the most appropriate materials to be used as Cd sorbents, since they have high Cd sorption and very low desorption potential ($<0.63\%$ in all cases). In the opposite side would be the pyritic material, with desorption values between 54.7 and 75.5% for all Cd concentrations added. Papandreou et al. [83] also found high Cd adsorption and

low desorption capacity for oak ash, attributed to its high pH, giving negative surface charges from pH 6, with subsequent high affinity for Cd²⁺ and formation of very stable complexes.

Table 3. Cd and Pb desorption (mmol kg⁻¹ and %) from the forest soil, vineyard soil, pyritic material and by-products studied. Average values for three replicates, with coefficients of variation always <5%.

Sorbent Material	Added Cd or Pb (mmol L ⁻¹)	Cd Desorption (mmol kg ⁻¹)	Cd Desorption (%)	Pb Desorption (mmol kg ⁻¹)	Pb Desorption (%)
Forest soil	0.5	0.10	2	0.01	0.2
	1.5	0.57	5	0.02	0.1
	3.0	1.68	8	0.01	0.3
	6.0	4.11	13	0.93	1.8
Vineyard soil	0.5	0.52	15	0.02	0.3
	1.5	1.50	22	0.17	1.2
	3.0	2.86	27	0.79	3.4
	6.0	4.56	19	2.03	5.5
Pyritic material	0.5	0.72	54	0.34	7.9
	1.5	1.91	54	0.99	9.7
	3.0	3.79	74	1.80	9.1
	6.0	5.47	76	3.00	8.4
Mussel shell	0.5	0.03	0.62	0.01	0.25
	1.5	0.04	0.27	0.02	0.13
	3.0	0.04	0.13	0.02	0.05
	6.0	0.05	0.08	0.03	0.04
Pine bark	0.5	0.07	1.4	0.01	0.26
	1.5	0.40	2.9	0.04	0.26
	3.0	2.05	9.5	0.25	0.87
	6.0	3.95	14.2	2.32	4.45
Hemp waste	0.5	0.08	1.72	0.16	3.7
	1.5	0.24	1.69	0.41	2.9
	3.0	0.47	1.68	0.50	1.7
	6.0	0.84	1.46	0.89	1.5
Oak ash	0.5	0.001	0.013	0.008	0.16
	1.5	0.001	0.004	0.009	0.06
	3.0	0.001	0.002	0.010	0.03
	6.0	0.001	0.001	0.011	0.02

3.4. Cd and Pb Sorption on the Amended Materials

Once the sorption and desorption of each material were analyzed separately, amendments were applied to both soils and the pyritic material, namely adding the three by-products that had given better results in the previous phases: mussel shell, hemp waste and oak ash, with individual doses of 48 t ha⁻¹.

As shown in Figure 3, the amendments allowed an overall increase in Cd sorbed on both soils and pyritic material, although this effect was not observed in the sorption curve corresponding to hemp waste applied on the forest soil (Figure 3a). Oak ash was the most effective amendment in all three cases, and the smallest effect was that due to hemp waste.

The amended forest soil presented the highest sorption for all Cd concentrations added, in some cases close to 100% with the oak ash and mussel shell amendments, and always being >76% with both by-products. The oak ash amendment caused very similar effects on the vineyard soil. Cd sorption rates were always >54% with the oak ash and mussel shell amendments, and >42% with the hemp waste amendment. The oak ash amendment clearly increased Cd sorption on the pyritic material, reaching values of >97% when the lowest Cd concentration was added, and being >46% with the highest Cd concentration. The effects of the other two amendments on the pyritic material were clearly

lower, with maximum Cd sorption of 75% (and minimum 40%) due to mussel shell, and between 64% and 42% when adding hemp waste.

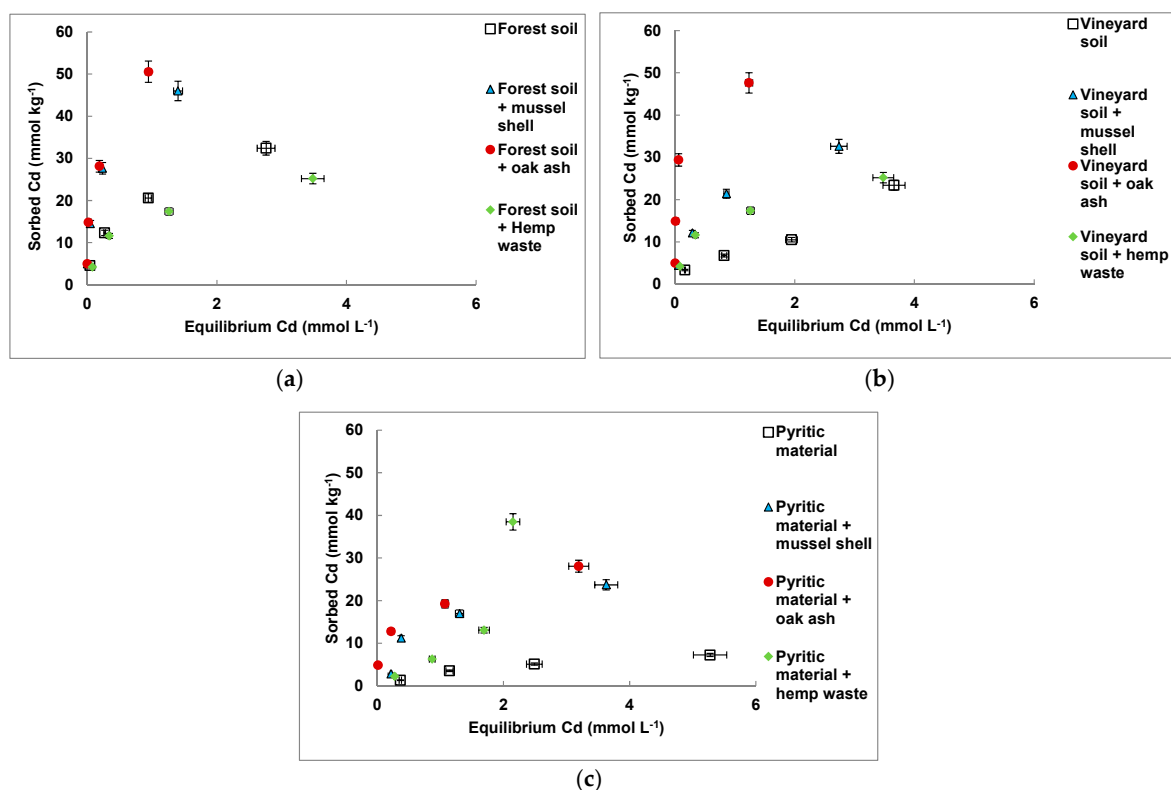


Figure 3. Cd sorption curves for the non-amended and amended forest soil (a), vineyard soil (b), and pyritic material (c). Average values (with error bars) for three replicates, with coefficients of variation always <5%.

The increased sorption after the addition of the amendments was consistent with that previously commented regarding the high Cd sorption capacity of oak ash and mussel shell, and followed the same order obtained individually for each of the materials used as amendment, that is, oak ash \approx mussel shell > hemp waste. This took place even if the ranges of pH values in the equilibrium solutions corresponding to the amended materials were shorter than those previously found for the individual materials, all of them being <7, and, specifically: 4.24–6.25 for forest soil + mussel shell, 3.81–6.73 for forest soil + oak ash, 3.8–5.8 for forest soil + hemp waste; 3.55–4.02 for vineyard soil + mussel shell, 5.21–6.49 for vineyard soil + oak ash, 3.6–3.7 for vineyard soil + hemp waste; 3.74–4.08 for pyritic material + mussel shell, 4.05–6.51 for pyritic material + oak ash, 3.69–3.75 for pyritic material + hemp waste.

Figure 4 shows that the amendments increased Pb sorption as compared to the non-amended forest soil, vineyard soil and pyritic material. Oak ash was the amendment causing the highest increase in Pb sorption, always reaching >99% for any of the Pb concentrations added. Mussel shell caused a somehow lower, but similar, increase: Pb sorption >97% in forest soil and pyritic material, and >80% in vineyard soil. The hemp waste amendment gave Pb sorption >91% in the forest soil, >82% in the material pyritic, and >74% in the vineyard soil.

As in the case of Cd, the degree of enhancement in Pb sorption was consistent with that previously commented for the individual materials, and followed the same order obtained for each individual amendment, that is, oak ash = mussel shell > hemp waste. Again, the ranges of pH values in the equilibrium solutions corresponding to the amended materials were also shorter than those previously found for the individual materials, once again all of them being <7.

Vega et al. [84] found that amending a mine soil with sludge and barley straw resulted in a great increase in Pb and Cd sorption capacity, mostly through Ca^{2+} displacement, although it also involved the displacement of other various exchangeable cations. Ramírez-Pérez et al. [20] found high Cd sorption capacity for a mussel shell amended soil; in particular, the non-amended soil retained 15% Cd, rising to 87% when amended with mussel shell. Mussel shell amendment increased pH, and its high content in aragonite might be another important parameter in Cd retention, mainly due to $(\text{Cd,Ca})\text{CO}_3$ precipitation mechanisms [85]. Furthermore, Shaheen and Rinklebe [86] studied the effects of different emerging and low cost amendments on Cd and Pb retention in a contaminated floodplain soil, finding that most amendments decreased soluble + exchangeable Cd and Pb, whereas Fernández-Calviño et al. [87] found high Cd and Pb sorption on mussel shell amended soils, attributed to the mineralogy of the mussel shell, since calcite and aragonite can effectively sorb these cationic metals.

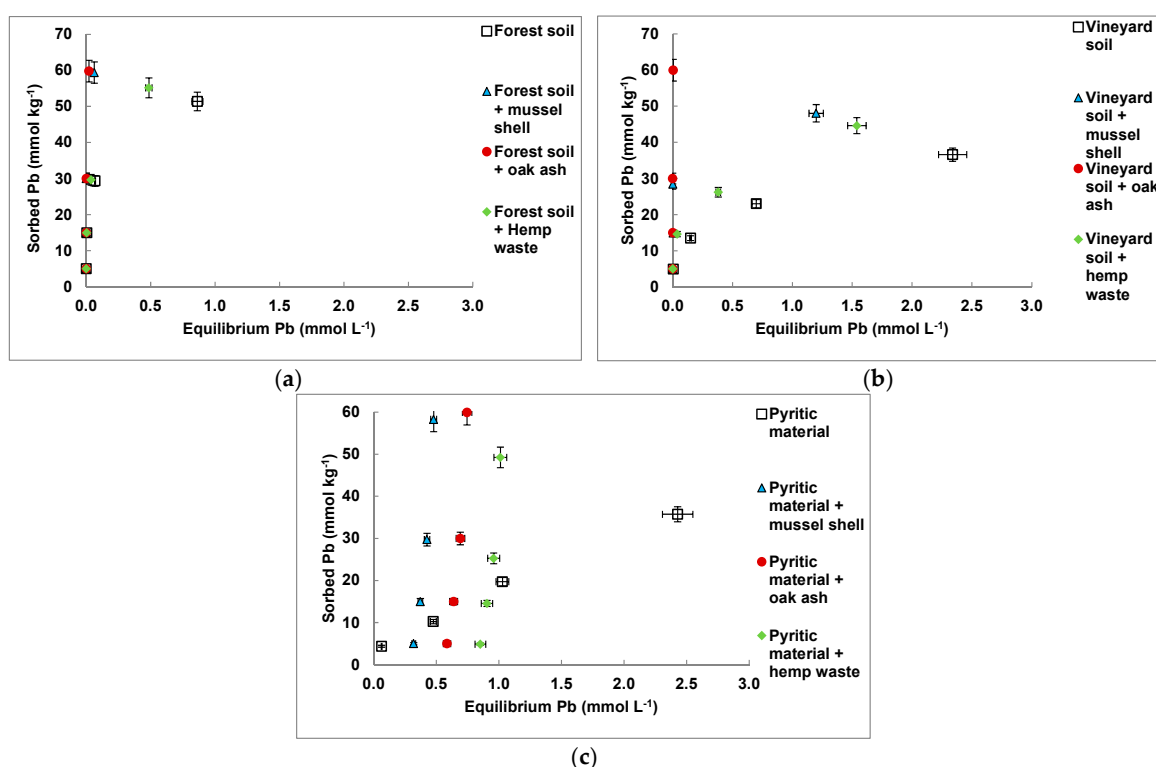


Figure 4. Pb sorption curves for the non-amended and amended forest soil (a), vineyard soil (b), and pyritic material (c). Average values (with error bars) for three replicates, with coefficients of variation always <5%.

3.5. Cd and Pb Desorption from the Amended Materials

Comparing data presented in Table 4 with that included in Table 3, it is clear that the amendments decreased Cd and Pb desorption in all cases, with oak ash and mussel shell being the most effective.

It is interesting to note the Cd desorption decrease attained in the pyritic material, since desorption was between 54% and 76% before amendment. These results, together with those obtained for sorption, highlight the usefulness of mussel shell and oak ash as effective sorbents in Cd-polluted media. The hemp waste amendment also caused a decrease in desorption from all materials, with the lowest desorption corresponding to the forest soil sample (always <7.2%). Considering both sorption and desorption results, it is clear that the by-products used as amendments would be appropriate to reduce Cd mobility in contaminated soils, thereby reducing toxicity risks.

With regard to Pb, the amendments decreased desorption from all materials. In addition, desorption was lower for Pb than for Cd. Oak ash and mussel shell were the amendments causing greater decrease in Pb desorption, with desorption percentages being <1% for any Pb concentration added. As in the case of Cd, Pb sorption and desorption results could encourage the use of the tested amendments (especially oak ash and mussel shell) for the stabilization of these heavy metals in contaminated soils, reducing their mobility and thereby decreasing their potential toxicity.

Fernández-Calviño et al. [87,88] detected a clear decrease in Cd and Pb desorption after amending pyritic mine soil samples with mussel shell or pine bark (respectively), which was related to a reduction in soluble fractions, and to an increase in less mobile fractions of both metals.

Table 4. Cd and Pb desorption (mmol kg^{-1} and %) from the non-amended and waste-amended forest soil, vineyard soil, and pyritic material. Average values for three replicates, with coefficients of variation always <5%.

Amended Material	Added Cd or Pb (mmol L^{-1})	Cd Desorption (mmol kg^{-1})	Cd Desorption (%)	Pb Desorption (mmol kg^{-1})	Pb Desorption (%)
FS + MS	0.5	0.01	0.3	0.01	0.16
	1.5	0.09	0.6	0.01	0.09
	3.0	0.27	1.0	0.02	0.06
	6.0	1.19	2.6	0.04	0.06
FS + OA	0.5	0.01	0.2	0.01	0.24
	1.5	0.08	0.5	0.03	0.17
	3.0	0.27	0.9	0.02	0.08
	6.0	1.19	2.4	0.03	0.04
FS + HW	0.5	0.08	1.7	0.01	0.24
	1.5	0.33	2.6	0.02	0.12
	3.0	1.21	5.4	0.05	0.17
	6.0	2.46	7.1	0.57	1.04
VS + MS	0.5	0.08	1.8	0.01	0.17
	1.5	0.26	2.1	0.01	0.08
	3.0	0.73	3.4	0.05	0.17
	6.0	1.69	5.2	0.24	0.50
VS + OA	0.5	0.03	0.5	0.02	0.31
	1.5	0.09	0.6	0.04	0.23
	3.0	0.23	0.8	0.04	0.14
	6.0	0.77	1.6	0.03	0.06
VS + HW	0.5	0.21	5.1	0.02	0.33
	1.5	0.86	7.4	0.04	0.29
	3.0	1.93	11.1	0.22	0.84
	6.0	3.67	14.6	1.54	3.45
PM + MS	0.5	0.22	8.0	0.00	0.09
	1.5	0.85	7.6	0.01	0.06
	3.0	1.23	7.2	0.07	0.23
	6.0	3.83	16.1	0.12	0.21
PM + OA	0.5	0.04	0.7	0.01	0.10
	1.5	0.18	1.4	0.01	0.05
	3.0	4.02	20.9	0.02	0.07
	6.0	1.86	6.6	0.13	0.22
PM + HW	0.5	0.56	25.2	0.07	1.44
	1.5	1.57	25.0	0.47	3.26
	3.0	4.03	30.8	1.04	4.11
	6.0	3.01	7.8	2.75	5.58

FS + MS = Forest soil + mussel shell; FS + OA = Forest soil + oak ash; FS + HW = Forest soil + hemp waste; VS + MS = Vineyard soil + mussel shell; VS + OA = Vineyard soil + oak ash; VS + HW = Vineyard soil + hemp waste; PM + MS = Pyritic material + mussel shell; PM + OA = Pyritic material + oak ash; PM + HW = Pyritic material + hemp waste.

3.6. Implications of the Research

In some cases, Cd and Pb concentrations in the environment can reach very high values. As examples, Madejón et al. [89] reported up to 2300 mg kg⁻¹ of Pb as well as high Cd concentrations in soils covered with sludge from the Aznalcollar (SW Spain) mine spill, more than one year after the accident. Cui et al. [90] reported up to 992 mg kg⁻¹ for Pb, and up to 22 mg kg⁻¹ for Cd as mean values in soils near a smelter in China, with estimated daily intakes up to 2.83 mg day⁻¹ for Pb and 0.22 mg day⁻¹ for Cd. High Cd and Pb concentrations in soils and crops affected by a spill were also detected by Liu et al. [91]. All these works take into account heavy metals transfer to water, plants and overall to the food chain, finding high levels and very high risks for public health in some cases. Due to that, researching on the efficacy of low cost sorbent materials that could retain Cd and Pb concentrations as high as 6 mmol L⁻¹ (674 and 1243 mg L⁻¹, respectively) can be of relevance. In this way, the results of the present study indicate that doses of 48 t ha⁻¹ of oak ash and mussel shell amendments gave Cd and Pb sorption close to 100% on forest soil, vineyard soil and pyritic material samples, as well as pronounced decrease in desorption. This research should be complemented with additional future investigation on multiple aspects, in order to finally attain enough knowledge to facilitate practical implementation of measures that could aid to protect the environment (including natural waters) from heavy metals contamination.

4. Conclusions

Among the materials here studied, the forest soil sample sorbed more and desorbed less Cd and Pb than the vineyard soil and the pyritic material. The pyritic material presented the worst sorption results among these three materials, especially for Cd, with sorption not exceeding 30%, and desorption reaching >70% with the highest concentrations of Cd added. With respect to the by-products used, the best sorbents were oak ash, mussel shell, hemp waste, and pine bark (in that order). The desorption capacity of the different materials followed an inverse sequence. Within the parameters that characterize the different sorbents, pH was the one that most strongly influenced Cd and Pb sorption. Cadmium and Pb sorption curves were better adjusted to the Freundlich than to the Langmuir model. The oak ash, mussel shell and hemp waste amendments increased Cd and Pb sorption and decreased desorption on the forest soil, vineyard soil and pyritic material, with oak ash being the most effective, giving sorption values close to 100% in all cases, as well as reduced desorption. These results were especially relevant in the pyritic material, since it presented low Cd sorption, and high desorption, with the higher concentration of Cd added. The overall results of this research could be useful to promote the recycling of the by-products studied, and could aid in the management of soils and degraded areas affected by Cd and Pb contamination, thus contributing to prevent water pollution. Future additional research could be performed in order to complement the present study, both to extend it in broader aspects, and to deepen the understanding of mechanisms and other relevant matters which are not fully covered in this work. In this way, additional experiments on sorption capacity versus sorbent dose, as well as varying pH values in a wide range (even including simulation of acid rains), speciation, repercussion of natural colloids and natural organic matter, or using spectroscopic and surface analysis to increase knowledge on adsorption-desorption mechanism, could be some of the complementary research tasks to be carried out.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4441/9/11/886/s1, Table S1: General characteristics of the sorbent materials (average values for 3 replicates, with coefficients of variation always <5%), Figure S1: Infrared spectrum of forest soil, Figure S2: Infrared spectrum of vineyard soil, Figure S3: Infrared spectrum of pyritic material, Figure S4: Infrared spectrum of fine mussel shell, Figure S5: Infrared spectrum of pine bark, Figure S6: Infrared spectrum of oak ash, Figure S7: Infrared spectrum of hemp waste.

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