

Article

Immobilization of Heavy Metals in Contaminated Soils—Performance Assessment in Conditions Similar to a Real Scenario

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Abstract: Soil “health” is becoming an increasing concern of modern societies, namely, at the European level, considering its importance to the fields of food, clean water, biodiversity, and even climate change control. On the other hand, human activities are contributing more and more to induce contamination in soils, especially in industrialized societies. This experimental work studies different additives (carbon nanotubes, clay, and Portland cement) with the aim to evaluate their effect on heavy metals, HMs (lead, copper, nickel, and zinc) immobilization in a contaminated soil in conditions similar to a real scenario. Suspension adsorption tests (fluid-like condition) were performed aiming to supply preliminary information about the adsorption capacity of the soil towards the different HMs tested, while percolation tests (solid-like conditions) were performed aiming to evaluate the HMs immobilization by different additives in conditions similar to a real situation of soil contamination. Results showed that soil particles alone were able to retain considerable amounts of HMs (especially Pb and Cu) which is linked to their fine grain size and the soil high organic matter content. In conditions of good dispersion of the additives, addition of carbon nanotubes or clay can rise the HMs adsorption, except in the case of Zn²⁺ due to its low electronegativity and high mobility. Moreover, the addition of cement to the soil showed a high capacity to immobilize the HMs which is due to the chemical fixation of the HMs to binder hydration products. In this case, HMs immobilization comes associated with a soil stabilization strategy. The results allow to conclude that the additives, carbon nanotubes and clay, have the potential to minimize HMs mobility in contaminated soils and can be a valid alternative to the usual additive, Portland cement, when tested in conditions similar to a real on-site situation, if the objective is not to induce also soil stabilization, for instance, to enable its use for construction purposes. The results obtained can help designers and decision-makers in the choice of the best materials to remediate HMs contaminated soils.

Keywords: contaminated soil; heavy metals; montmorillonite; carbon nanotubes; Portland cement; percolation tests

1. Introduction

Although soil is an essential asset to humans, its preservation is quite often not respected. Still, soil health is becoming an increasing concern, namely, at the European level. In this context,

the existence of heavy metals (HM) in contaminated soils can be a serious problem to soil health and thus to modern societies, affecting food and water sources and biodiversity. Heavy metal pollution can occur by natural or anthropogenic sources. Among the various anthropogenic activities, some must be highlighted due to their frequency and expressive way they contribute to the soil's contamination: the use of pesticides and fertilizers, smelting, mining, and emissions from industries [1,2]. Natural cases of soil contamination are unusual but can have severe effects, like, for example, forest fires that originate dusts rich in heavy metals, which deposit on the soil [3]. Heavy metals cannot be degraded and tend to contaminate the water and food chain, since, besides compromising the soil quality, they can leachate and threaten the quality of vegetables and cattle, and ultimately human health [4,5].

The mobility of the heavy metals in soils is very dependent on the soil characteristics, namely, the organic matter content, grain size distribution, and pH of the soil. In general, all heavy metals are more soluble and have more mobility in acidic environments, thus acidic soils tend to favor the spread of the contaminants, while more alkali soils tend to accumulate heavy metals [6]. Fine grained soils, with large quantities of silt and clay, show better capacity to retain heavy metals unlike coarse soils that allow the infiltration of water, being less capable to immobilize the heavy metals [7]. In general, the organic matter present in soil contributes to the retention of HM due to complex interactions established between the constituents of the organic matter and the HM [5,8].

Since heavy metals are not biodegradable and cannot be destroyed through high temperatures or the use of chemicals, ordinary soil remediation techniques are ineffective. The traditional method used to remediate HM-contaminated soils consists in excavation and relocation to a landfill. The high costs, limited landfills availability [9], and possibility of hazardous exposure of this traditional remediation method, led to the development of new methods that are more cost-effective and less harmful to the environment, like the solidification/stabilization (S/S) of soil [10]. S/S consists of mixing additives with the soil with the objective to reduce the potential migration of HM and thus the risk of contaminating adjacent areas. This technique has been supported by various associations due to its potentialities [11–14]. Some of the mixing additives used in the S/S technique are binders, clay minerals, alkaline materials, organic compounds, and more recently, nanomaterials [10,15–21].

Carbon nanotubes (CNTs) are materials with reduced size (nanoscale) and composed by cylindrical graphite sheets rolled up forming a tube. They can be single-walled (SWCNTs) or multi-walled carbon nanotubes (MWCNTs) depending on the number of layers of graphene sheets [22], being applied in a wide range of scientific areas [23–25]. Several studies have proven that CNTs possess high adsorption capacity [26–30], which means, in the present context, that this nanomaterial has the capacity to retain large quantities of heavy metals on its surface. Although studies, so far, were done on wastewaters [26–30], they raised the possibility of CNTs being added to a soil, potentially increasing its adsorption capacity and efficiently immobilizing contaminants, which was already validated in a previous study from the authors [31] and will be further explored in the present paper for different conditions.

Due to the high surface area, Van der Waals forces become important, which cause CNTs to form aggregates and lose part of their advantages [32]. Thus, to assure a good dispersion of the CNTs, two approaches may be used: mechanical and chemical methods. The mechanical methodology consists of applying ultrasonic energy, which overcomes the Van der Waals forces and promotes the dispersion of CNTs [33]. The non-covalent chemical method consists of the addition of surfactants which are long molecules that can promote the dispersion of the CNTs due to physical and chemical interactions [34]. Both methods can be combined in order to promote a more efficient dispersion of the CNTs [35].

The use of clay materials to immobilize heavy metals in contaminated soils has been documented by several authors [36–38]. Clay materials have the potential to immobilize heavy metals in soils through adsorption mechanisms, retaining them on their surface, since they have a considerable high surface area. Their use has obvious advantages when compared to other options, because they are an environmentally friendly material, widely available, and non-expensive [36]. The most important

properties to the potential adsorption capacity of a clay mineral are the specific area and cation exchange capacity (CEC). In general, higher values of CEC imply higher capacity to adsorb heavy metals. Clay minerals with higher surface area also have more adsorption potential, since they present more adsorption sites [39]. Korte et al. [40] showed that the adsorption potential is more closely tied to the specific surface of the clay than to CEC. Clay minerals are usually used in their natural state, but nowadays, some authors are focusing on the use of modified clay minerals [41–44]. The modification of clay minerals consists of adding chemicals or organic compounds to the clay minerals surface, attempting to improve their adsorption capacity.

Binders have been used in solidification/stabilization to immobilize heavy metal-contaminated soils and are an effective technique according to several authors [2,5,10,17–19,21,45–49]. In fact, they present the additional advantage of improving the mechanical properties of the soil while also immobilizing the contaminants [2,19,46,50]. In this case, there are complementary chemical and physical interactions that cause a decrease of the overall mobility of the contaminants and an effective fixation on site [9,10,51]. The principal mechanism causing the immobilization of the heavy metals is chemical fixation of the contaminants onto the binder components, as, for instance, onto calcium silicate hydrates (CSH), i.e., the HMs are immobilized by the soil/binder matrix [9,52]. The addition of binders to a soil has another beneficial effect on heavy metals immobilization: their addition can reduce the permeability of the soil which makes it harder for the heavy metals to migrate through the soil and contaminate adjacent areas [50]. They are an alkali material and mixing them with soil usually results in an increase of the pH [19,53,54], reducing the acidity of the soil and consequently reducing the mobility of the contaminants, since heavy metals show more mobility in acidic environments [6]. The combination of binders with different additives is a possibility recommended by some authors to more effectively immobilize contaminants [55]. However, the S/S technologies involving the use of binders, namely, Portland cement, limit the use of the soil for other purposes rather than construction.

In this work, the final objective is to evaluate the capacity of the additives CNTs and clay mineral as an alternative or complement to the traditional additive Portland cement to reduce the mobility of heavy metals (lead, copper, nickel, and zinc) in contaminated soil. Both CNTs and the clay mineral were previously treated applying ultrasonic energy and adding a surfactant to guarantee the good dispersion of the additives and an increase of the number of available adsorption sites. The soil was artificially contaminated with the heavy metals to be studied, and suspension adsorption tests were carried out to evaluate the adsorption capacity of the additives (CNTs and clay mineral). Percolation tests were then conducted to better evaluate the efficiency of CNTs, clay mineral, and binder to immobilize the heavy metals tested, in the soil, in conditions similar to a real on-site situation. Leaching tests were also performed in order to verify if CNTs (the nanomaterial used) are not being released in the environment.

2. Materials and Experimental Procedures

2.1. Materials

The soil selected for this study was collected in the region of Coimbra, in the center of Portugal. It is an organic fine-grained soil composed mainly of silt and clay particles, as stated in Table 1, exhibiting poor mechanical behavior [53,56]. The soft soil tested possesses a high organic matter content which combined with the particles composition induces potentially high adsorption capacity. However, since the soil is slightly acid, this may hinder the adsorption capacity of the soil, since all heavy metals present higher mobility in an acidic environment [15]. All tests were performed without modifying the pH of the natural soil or of any other material or suspension.

Table 1. Characteristics of the soil used in this work.

Soil Characteristics		
Grain size distribution	Clay (%) (<i>w/w</i>)	21
	Silt (%) (<i>w/w</i>)	59
	Sand (%) (<i>w/w</i>)	20
Specific gravity	G (-)	2.6
Natural water content	w (%) (<i>w/w</i>)	80.9
Liquid limit	w _L (%)	54.1 ^(a)
Plastic limit	w _P (%)	39.8
Organic matter content	OM (%) (<i>w/w</i>)	7.4
pH	pH (-)	5.4
Soil classification USCS ^(b)	(-)	OH

^(a) After drying; ^(b) Unified soil classification system [57].

In order to simulate real conditions, the soil was contaminated in the laboratory for the maximum HMs concentrations measured in contaminated soils found in Portugal (considered as the most challenging conditions) [58,59], and was stored in a temperature-controlled room (20 ± 2 °C) for 7 days, at least, to allow the HM to distribute evenly in the soil. Table 2 presents the maximum concentrations found in Portugal for the heavy metals under study (Pb, Cu, Ni, and Zn), and it is possible to verify that all the values are above the reference values recommended in the Ontario Soils Quality Guidelines [60], showing the presence in Portugal of highly contaminated soils. The values shown are referred to the dry weight of soil. The soil was contaminated in the laboratory by the following salts: lead nitrate ($\text{Pb}(\text{NO}_3)_2$ —supplied by Riedel-de-Haen), hydrated copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ —supplied by Merck), hydrated nickel sulphate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ —supplied by Fluka), and hydrated zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ —supplied by Sigma).

Table 2. Maximum values registered in Portuguese soils [59] and international guideline values [60] for the heavy metals studied in this work.

Heavy Metal	The Soil Geochemical Atlas of Portugal [59]	Ontario Soil Quality Guidelines [60]
	Maximum Value Registered (mg/kg)	Reference Values (mg/kg)
Lead	585	120
Copper	245	230
Nickel	880	270
Zinc	589	340

The carbon nanotubes used in this work were multi-walled carbon nanotubes (MWCNTs), with an indicative cost of 100 €/kg, supplied by Nanocyl, (MWCNTs CN7000), considering that they are up to ten times cheaper than the single-walled carbon nanotubes (SWCNTs). According to the supplier and Figueiredo et al. [35], the MWCNTs are characterized by a diameter of 9.5 nm (average), a length/diameter ratio of 158, a specific surface area of around 275,000 m²/kg, a specific density of 1.7 g/cm³ (on average), and zeta potential of around −25.2 mV.

Portland cement type I, mechanical strength class 42.5R, was the binder chosen for the present work. This binder, supplied by Cimpor Portugal, and with an indicative cost of 0.08 €/kg, is characterized by the chemical composition presented in Table 3.

Table 3. Chemical composition of the Portland CEM I 42.5R according to the supplier.

Components	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃
% (w/w)	63	19	5	3	3	3

The clay mineral selected for the laboratory work was montmorillonite (part of the smectite group), supplied by Vermeer Portugal, with an indicative cost of 0.56 €/kg. A summary of the chemical and mineral composition of the montmorillonite can be seen in Table 4. Montmorillonite is a clay mineral with a very high specific surface area (400–800 m²/g) due to its small dimensions (<2 µm), which gives to this clay mineral a higher cation exchange capacity (70–100 meq+/100 g) [36,38,54,55]. All of these characteristics indicate that the montmorillonite mineral has high potential adsorption capacity.

Table 4. Chemical and mineral composition of Montmorillonite according to the supplier.

Components	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	Mn ₃ O ₄	Fe ₂ O ₃
% (w/w)	2.03	2.26	19.16	58.6	0.05	0.9	0.55	1.26	0.17	0.02	3.69
Minerals	Diocahedral smectite			Quartz	Illite	Opal	Potassium feldspar				
%	85–90			5	2	2	trace				

The surfactant sodium dodecylbenzenesulfonate (SDBS), produced by Sigma Aldrich, was used to promote dispersion of the MWCNTs and montmorillonite. This anionic surfactant is a polymer of small dimensions with a hydrodynamic diameter of 81.02 nm and an average molecular weight of 363.02 kDa, and with a negative zeta potential of −66.97 mV. In the present study, it was chosen an anionic surfactant (SDBS) to guarantee the dispersion of each additive, instead of the non-ionic surfactant used earlier by the authors [31] to disperse MWCNTs, in order to evaluate the effect of combining, in one surfactant, both the dispersing potential towards the additives and the heavy metal trapping capacity, considering the opposite charge of both materials.

2.2. Experimental Procedures

2.2.1. Adsorption Tests

In this work, the main objective of the adsorption tests was to supply preliminary information about the adsorption capacity of the soil towards the different heavy metals tested, and to preliminary evaluate if the addition of MWCNTs or montmorillonite could improve the adsorption capacity of the soil. As referred, both MWCNTs and montmorillonite were subjected to a previous treatment to guarantee an adequate dispersion of these additives. The pre-dispersing procedure consisted in the application of ultrasonic energy (20 kHz, 500 W, amplitude 75% during 15 min, using a sonicator probe Sonics Vibracell 501) to the aqueous suspension of MWCNTs or montmorillonite enriched with the surfactant SDBS (used in a concentration of 0.03%, w/w) which, besides enabling dispersion of the particles, can contribute to the adsorption of the heavy metals due to its charge. It must be noticed that in the present study, it was possible to guarantee a good dispersion of the MWCNTs using a much lower concentration of the anionic surfactant than in the previous work [31] where a different surfactant was used (Pluronic F-127, non-ionic type) with a concentration of 2%. This strategy proved to be efficient for the dispersion of the additives.

The quality of the MWCNTs dispersion was evaluated by measuring the size distribution of the aqueous MWCNTs suspensions, additivated with SDBS, prepared in the above-mentioned conditions. The Z average diameter (D_z) of the optimized MWCNTs suspension was 216.9 nm (measured by the Dynamic Light Scattering technique, Malvern Instruments Nanosizer ZN [61]).

Three different tests were performed:

1. Adsorption tests with soil alone contaminated with the heavy metals (reference test) with the objective to evaluate the adsorption capacity of the soil particles by themselves to be used as reference for the remaining studies;
2. Adsorption tests using a suspension of MWCNTs or montmorillonite (applied independently) dispersed in an aqueous solution of heavy metals, and pre-treated with ultrasounds and surfactant, with the objective to evaluate the adsorption capacity of these additives by themselves;
3. Adsorption tests using soil contaminated with heavy metals combined with carbon nanotubes or clay mineral (montmorillonite), and pre-treated with ultrasounds and surfactant, with the objective to evaluate the benefits in the adsorption capacity of using the two dual systems (soil + MWCNTs or soil + montmorillonite).

Figure 1 supplies a scheme of the adsorption tests conducted.

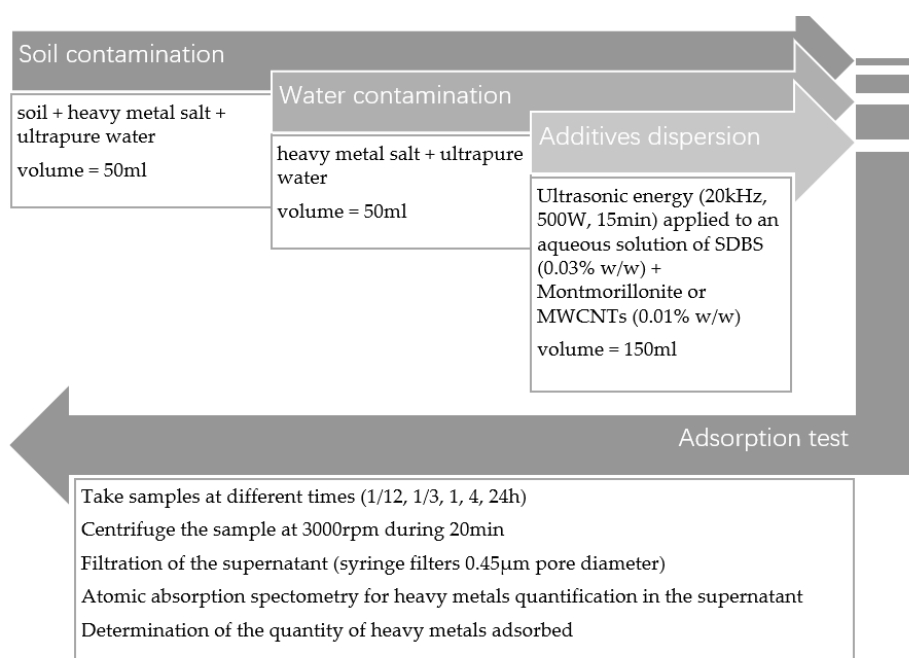


Figure 1. Procedure adopted for the adsorption tests in suspension conditions for the different types of tests: only soil, only MWCNTs/Montmorillonite in water and soil with the addition of MWCNTs/Montmorillonite.

2.2.2. Percolation Tests

To evaluate the effectiveness of the different additives to immobilize heavy metals in conditions closer to a real on-site situation, percolation tests were conducted in four different situations: using only the soil (reference tests) and also using the soil additivated with MWCNTs or montmorillonite or mixing the soil with Portland cement. The tests consisted of using small samples of contaminated soil (37.6 cm³), additivated or not, and to percolate water through them, using an hydraulic charge of 5 m (≈50 kPa). The heavy metal concentration in the leachate liquid was measured using atomic absorption spectrometry (Perkin Elmer atomic absorption spectrometer 3300). The procedure adopted for the percolation tests started with the laboratory contamination of the soil (stage 1), followed by the addition of the additive materials (stage 2) and ended with the percolation tests followed by the measurement of the heavy metals that percolated through the contaminated sample which allowed calculation of the amount of heavy metals immobilized (stage 3). In stage 1, four equal soil portions (5 kg each) were taken from the natural soil, air dried, and carefully mixed with a solution of lead, copper, nickel, or zinc, so that after mixing with the soil, all four portions possessed the original water content (80.9%). Each contaminated soil portion was stored for 7 days to ensure a uniform distribution of the HMs. In stage 2, for each of the four soil portions, a representative small sample was collected and mixed

with a suspension of MWCNTs (in the same way as described for the adsorption tests), or mixed with montmorillonite in its natural state or in suspension, or still mixed with a slurry of Portland cement (corresponding to a binder quantity of 25 kg per cubic meter of soil, i.e., a small amount of binder was chosen, smaller than the amount usually used for soil stabilization (100 to 250 kg/m³ [54]), because the main goal is the soil's remediation only [2,46] and not its mechanical improvement). The samples with Portland cement were stored submerged in water in a temperature-controlled room (20 ± 2 °C) during a curing time of 7 days. For the samples additivated with montmorillonite, a quantity of 25 kg of montmorillonite was used, in its natural state, per cubic meter of soil (equal to the binder amount to allow direct comparison), or, alternatively, a suspension of montmorillonite was prepared, as described for the adsorption tests, and added to the soil. In the third stage, the samples contaminated with the different heavy metals, additivated or not, were introduced in PVC tubes with 35 mm of height and 37 mm of diameter. The samples were protected from solid particles loss by a paper filter placed on the top plus two perforated PVC discs (on the top and bottom of the samples) to allow water to flow through the cell. After sealing the tubes, the percolation tests started with a flow of water under an hydraulic charge of 5 m, and the leachate was collected in a beaker. When the leachate volume was at least equal to the sample's volume, the percolation test ended. After filtering the leachate, atomic absorption spectrometry tests were performed to evaluate the amount of heavy metals in the leachate, using the same methodology described for the adsorption tests. A schematic of the percolation tests arrangement is shown in Figure 2. The arrangement constructed allowed for different samples to be tested simultaneously, either of soil contaminated with the same HM or testing the soil's samples contaminated with different HMs.

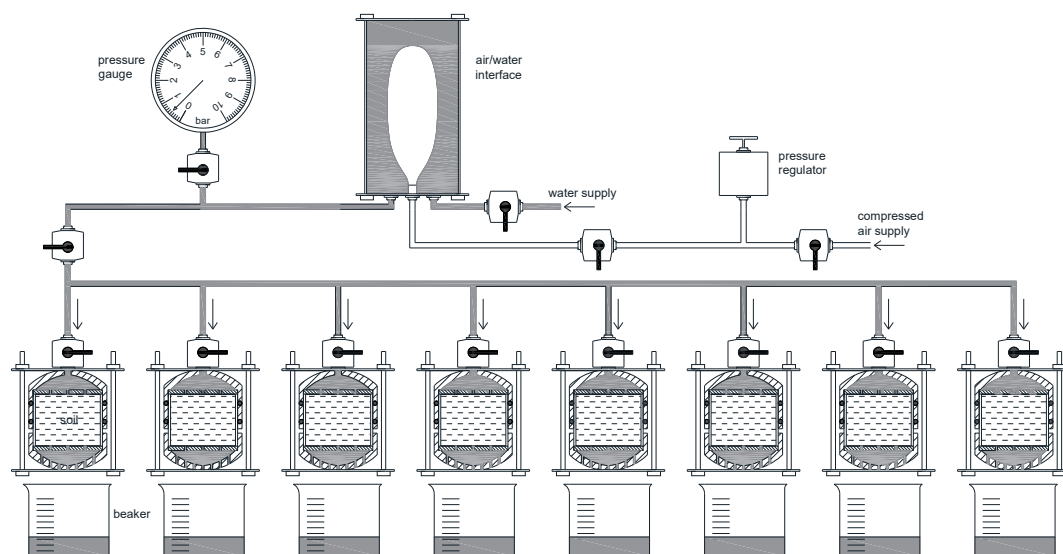


Figure 2. Schematics of the percolation tests: soil cells, beakers and injection system composed by a pressure regulator, air compressor and interface air/water.

In all percolation tests, the samples were always saturated with water.

2.2.3. Leaching Tests

In order to assess the possible release of the MWCNTs to groundwater aquifers once applied on-site, further leaching tests were performed. These tests were conducted for both contaminated soil with and without MWCNTs, with a concentration of 0.01% (*w/w*) of MWCNTs in the last case. The samples were prepared in the same way as described for the percolation tests. The leaching tests were performed in accordance with the standard NEN 7345 [62] with some adaptations as follows: (i) the contaminated soil samples were wrapped in a 5 µm mesh nylon tissue and submerged in ultrapure water at least 2 cm below the water surface; (ii) the leaching test was done under constant temperature

(22 °C) and immediately after each leachate collection (at 1, 3, 7, and 14 days), the ultrapure water was renewed; (iii) for each leachate sample, the pH was measured and the presence of carbon nanotubes was verified through SEM images of the powder obtained after drying the leachate samples. The equipment used to acquire the SEM images was a JEOL JSM-5310 model, from the Instituto Pedro Nunes in Coimbra, Portugal.

3. Results and Discussion

3.1. Adsorption Tests

The adsorption tests performed in the present study had the objective to pre-evaluate how the addition of MWCNTs (0.01% *w/w*) or montmorillonite (0.01% *w/w*) to the soil can contribute to improve the adsorption capacity of the soil. Tests using only aqueous suspensions of MWCNTs or montmorillonite were also conducted to assess the adsorption capacity of these materials on their own. Knowing the initial concentration of heavy metals added to the soil, the quantities adsorbed by the solid particles (soil alone or soil and MWCNTs/montmorillonite) was calculated based on the difference between the initial concentration and the measured concentration in collected water samples at different times (5 min, 20 min, 1 h, 4 h, and 24 h).

3.1.1. Addition of MWCNTs

Figure 3 and Table S1 in Supplementary Materials present the evolution of the heavy metals adsorption with time by the soil alone (reference), suspension of MWCNTs, and for the suspension of the soil enriched with MWCNTs. It is apparent from the results obtained that adsorption of the heavy metals is initially very rapid, tending quickly to equilibrium which is reached at the end of 5 min. Thus, after this initial period, no significant changes on the amount of adsorbed material were detected for all the situations and HMs tested.

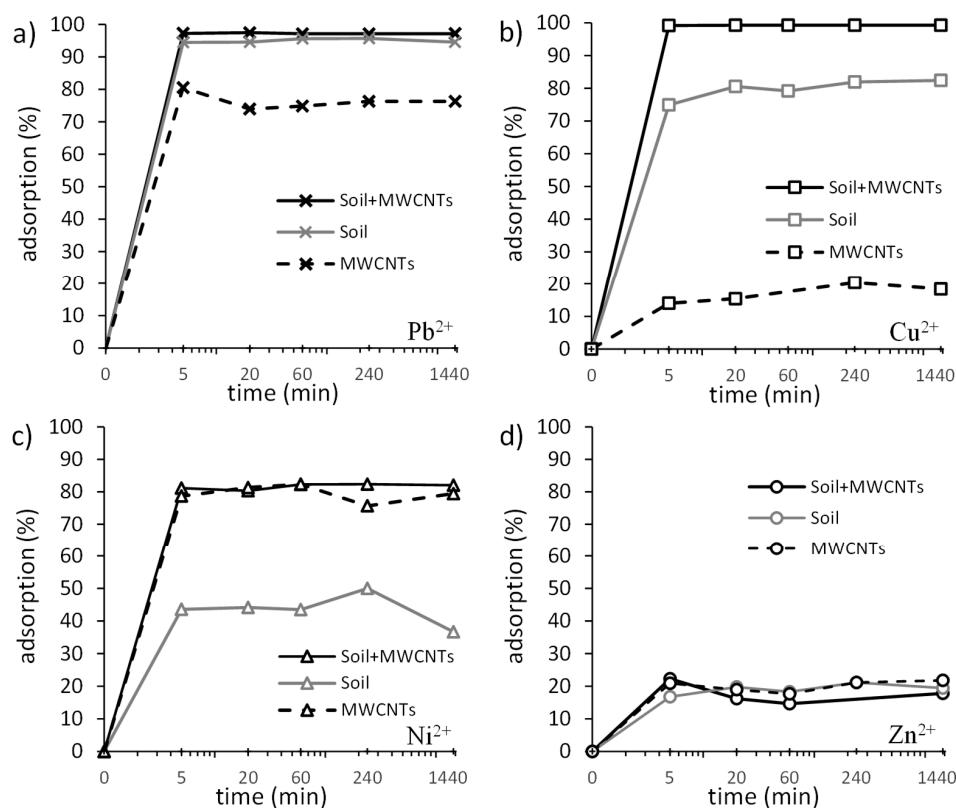


Figure 3. Results from the adsorption tests. Individual adsorption of lead (a), copper (b), nickel (c) and zinc (d) by the soil, MWCNTs and suspension of soil with the addition of MWCNTs.

Looking at the results of the tests where only MWCNTs were used (aqueous suspension of MWCNTs), it can be concluded that the heavy metals lead (Pb^{2+}) and nickel (Ni^{2+}) were adsorbed in larger amounts than the heavy metals copper (Cu^{2+}) and zinc (Zn^{2+}). It is known that certain metals show higher affinity to CNTs than others as reported by [63]. In the present study, the amount of each individual heavy metal adsorbed is clearly related to its electronegativity and atomic radius. According to the Pauling scale, the electronegativity of Pb^{2+} and Ni^{2+} are respectively 2.33 and 1.91, higher than those of Cu^{2+} (1.90) and Zn^{2+} (1.65), while the atomic radius follows the sequence $\text{Pb} > \text{Ni} > \text{Cu} > \text{Zn}$ [64], explaining, in this way, the higher adsorption of lead and nickel by the MWCNTs, both having higher electronegativity and atomic radius (the higher the atomic radius the lower the mobility of the heavy metal). For these tests, adsorption percentages of 82.3 and 76.4 were obtained for Ni^{2+} and Pb^{2+} , respectively, while for Cu^{2+} and Zn^{2+} , the maximum values were 20.4 and 21.8, respectively. These results are in agreement with the findings of Matos et al. [31], but in the present study, the MWCNTs showed a higher adsorption capacity which can be explained by the combined effect of the surfactant selected (SDBS) that promotes the dispersion of the MWCNTs and further trapping of the heavy metals, considering the opposite charge of both materials.

Examining the results of adsorption by soil particles alone, it may be concluded that the soil alone can capture a significant quantity of heavy metals, possibly as a result of the fine grain size and high content of organic matter. The heavy metal exhibiting a higher degree of adsorption was lead, followed by copper, nickel, and zinc. When comparing with the adsorption by MWCNTs alone, all metals, except nickel, presented a higher tendency to be adsorbed by the natural soil. Copper was the HM where this tendency was clearer, with 82.5% of adsorption in soil compared to the 18.4% obtained when only a dispersion of MWCNTs was used. This can be attributed to the high content of organic matter in the soil tested, which had a particularly strong effect on the adsorption of copper. The organic matter present in soils can help retaining heavy metals through both physical and chemical interactions. It has been proved previously [65] that this interaction (organic matter/heavy metals) is stronger towards copper than to other heavy metals. Considering that the soil tested has a high organic matter content, copper adsorption by the soil alone was higher than in the case of Ni^{2+} and Zn^{2+} adsorption. Pb^{2+} maintained a high adsorbing tendency, as already observed when using the MWCNTs alone, due to its high electronegativity, which decreases its mobility.

When comparing adsorption by soil alone with adsorption by the soil additivated with MWCNTs (0.01% *w/w*), an increase of the adsorption capacity of the additivated soil is always observed, except in the case of Zn^{2+} . This trend is particularly evident in the case of Cu^{2+} and Ni^{2+} , where a significant enhancement was achieved by adding the MWCNTs. The low adsorption perceived in the case of Zn^{2+} can be related to the low electronegativity and higher mobility of this metal compared to the other heavy metals tested. Furthermore, the combination of soil with MWCNTs resulted in higher adsorption capacity when compared to the MWCNTs alone, except, again, in the case of zinc for which very similar values were obtained in the three situations tested. In general, the results reported in this study lead us to conclude that mixing MWCNTs with soil can effectively increase the amount of HMs immobilized. Thus, it is possible to say that this strategy can be a valid option to be used in the remediation of contaminated soils, as well as in stabilization processes, especially taking into consideration the very low amounts of MWCNTs required. When comparing the results with the authors' previous work [31], where it was used a non-ionic surfactant, the results are in general better, except in the case of zinc for which similar results were obtained. This shows once again that the anionic surfactant (SDBS) has a positive impact in the immobilization process, even when applied in a lower concentration than the non-ionic one (almost 100 times smaller).

3.1.2. Addition of Montmorillonite

In Figure 4 and Table S2 in Supplementary Materials, the results of the adsorption of the heavy metals by the soil (reference, Figure 3 and Table S1), montmorillonite, and the soil additivated with montmorillonite are presented. As was observed when the additive was the MWCNTs, the adsorption

by montmorillonite is characterized by an initial rapid adsorption, equilibrium being reached in the first 5 min.

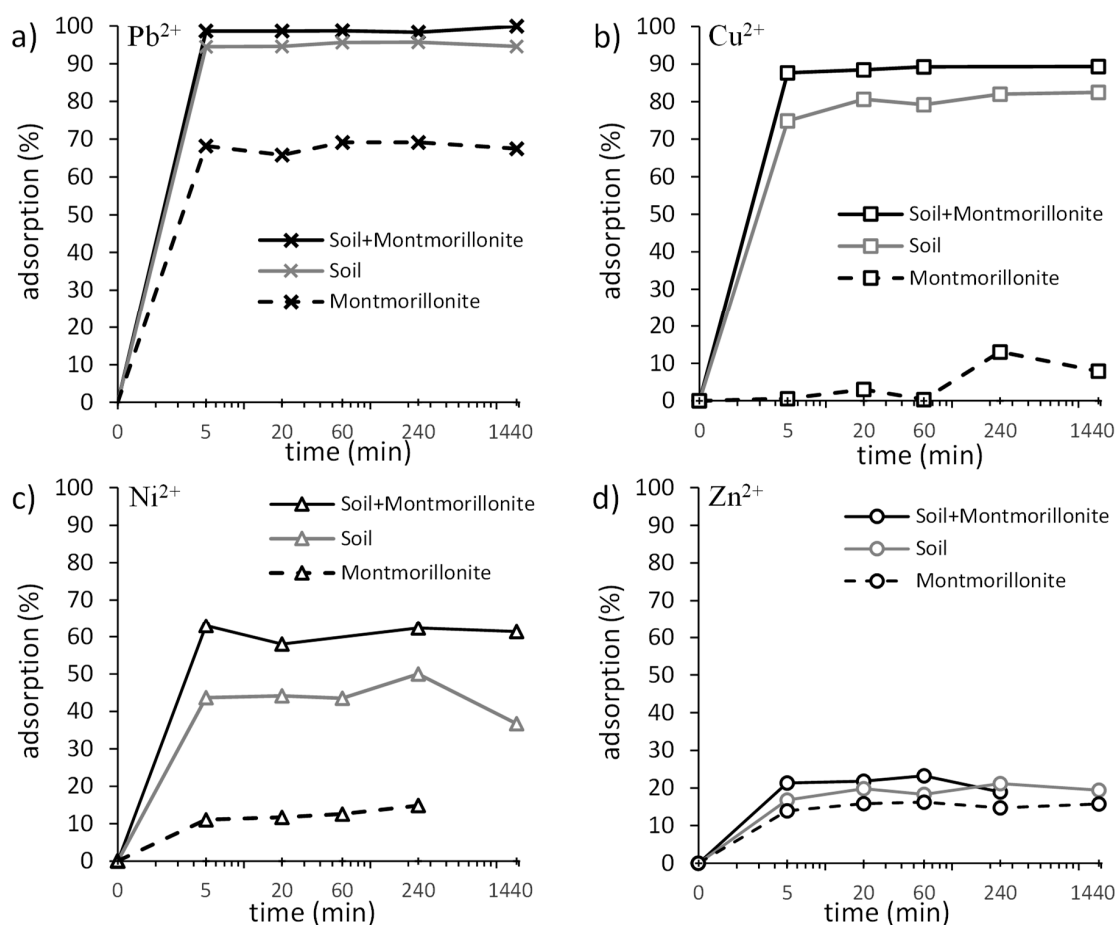


Figure 4. Results from the adsorption tests. Individual adsorption of lead (a), copper (b), nickel (c) and zinc (d) by the soil, Montmorillonite and suspension of soil with the addition of Montmorillonite.

Examining the adsorption by montmorillonite alone, it is obvious that only lead was adsorbed in high quantity, while for the other HMs, adsorption was very low. Confronting these results with the ones obtained for MWCNTs alone (Figure 3 and Table S1), it is seen that montmorillonite has a lower adsorption capacity, which can be related to its lower specific surface area due to the larger size.

The addition of montmorillonite to the soil increased the adsorption capacity of the soil tested for all HMs considered. In the case of Zn²⁺, adsorption was always very poor for all the situations considered, which, as referred, is certainly related to the higher mobility of this metal. The results for the soil additivated with montmorillonite show again that the affinity order of the heavy metals studied is Pb > Cu > Ni > Zn, in-line with the one registered in the tests with soil and MWCNTs (Cu > Pb > Ni > Zn), since the adsorption results for Pb²⁺ and Cu²⁺ are very similar in the latter case. Moreover, as discussed previously for the case of the MWCNTs, the combination of soil with montmorillonite allowed increasing substantially the heavy metals adsorption efficiency, when compared to adsorption by montmorillonite alone and even to the tests where soil alone was used, especially for the HMs Cu²⁺ and Ni²⁺.

If we compare the addition of montmorillonite (Figure 4 and Table S2) with the addition of MWCNTs to the soil (Figure 3 and Table S1), it may be verified that adding MWCNTs leads to a better performance, especially for Cu²⁺ and Ni²⁺, since in the case of Pb²⁺ adsorption is already very high using the soil alone, as previously discussed. Still, even if montmorillonite presents a slightly lower adsorption capacity for Cu²⁺ and Ni²⁺, the cost can be substantially lower. Therefore, the final choice

of the additive to remediate a soil contaminated with HMs should take into consideration these two factors (efficiency and cost), at least for the cases where montmorillonite presented also a high immobilization capacity.

3.2. Percolation Tests

The percolation tests performed in the present study aim to reproduce in the laboratory a real situation of contaminated soil, allowing the comparative performance of three different additives, MWCNTs, montmorillonite, and Portland cement. The heavy metals quantity adsorbed by the solid particles (soil + additive) was determined by comparing the initial concentration of each HM on the soil samples and the final concentration of the HMs present in the collected leachate liquid after the percolation tests.

3.2.1. Addition of MWCNTs

Figure 5 and Table S3 in Supplementary Materials present the results of the adsorption of the HMs by the soil alone (reference) and by the soil enriched with MWCNTs (two different concentrations of MWCNTs were tested: 0.01 and 0.05%, *w/w*). Evaluating the results, it is possible to see that in the percolation tests, the amount of heavy metals immobilized by only the soil particles is much higher when compared to the suspension adsorption tests. In this case, the heavy metals Pb^{2+} and Cu^{2+} are almost totally immobilized by the soil particles alone without the need of any additive. Regarding Ni^{2+} and Zn^{2+} , the amount of these HMs immobilized increases also when compared to the suspension adsorption tests. However, these two heavy metals still show potential to contaminate adjacent areas, when only soil is used, due to their higher mobility. The main difference between the adsorption and percolation tests are the initial conditions of the soil: for the first case, fluid-like conditions (without any soil structure) are present, while in the second case, the conditions are solid-like (with a soil structure, characterized by a low hydraulic conductivity coefficient of the order of 10^{-9} m/s [53]). Thus, in the percolation tests, the soil properties have more influence on the immobilization of the HMs, mimicking closer what may happen in a real situation.

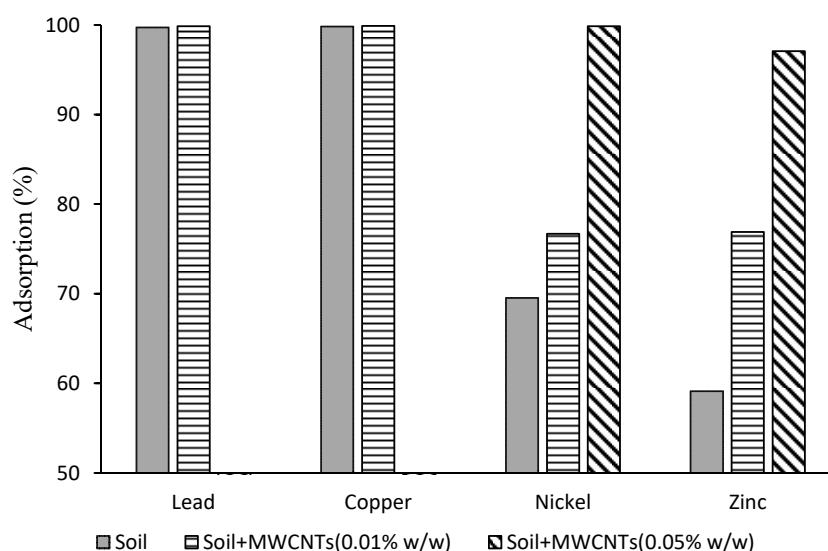


Figure 5. Results from the percolation tests. Immobilization of heavy metals by the soil with or without the addition of MWCNTs (two concentrations: 0.01 and 0.05% *w/w*).

A careful look at the results of the tests where the soil was contaminated with nickel and zinc, leads to the conclusion that the additive MWCNTs in a concentration of 0.01% (*w/w*) produced the increase of the adsorption of Ni^{2+} and Zn^{2+} , as it was observed in [31] for a different surfactant type and concentration. This increase is more significant when a higher concentration of MWCNTs

is used (0.05%, *w/w*). For this last MWCNTs concentration, it was possible to achieve almost total immobilization of these heavy metals (99.86 and 97.06 retention percentage for Ni²⁺ and Zn²⁺, respectively). The results reported lead us to conclude that mixing a small quantity of MWCNTs with the soil studied can efficiently decrease the mobility of the HMs, in situations similar to field conditions, indicating that this may be a valid option to be used in the immobilization of contaminated soils with similar properties to the soil studied here.

3.2.2. Addition of Montmorillonite

The addition of montmorillonite to the soil was studied in two distinct ways: montmorillonite on its natural state was added to the soil in a dosage of 25 kg of montmorillonite per cubic meter of soil (to compare directly with the additive Portland cement alone); modified montmorillonite (previously dispersed with ultrasounds in aqueous solution enriched with the surfactant SDBS) was applied in a concentration of 0.01% *w/w* (corresponding to 0.2 kg of montmorillonite per cubic meter of soil) and 1% *w/w* (corresponding to 22 kg of montmorillonite per cubic meter of soil). In Figure 6 and Table S4 in Supplementary Materials, the results of the addition of montmorillonite to the soil are presented.

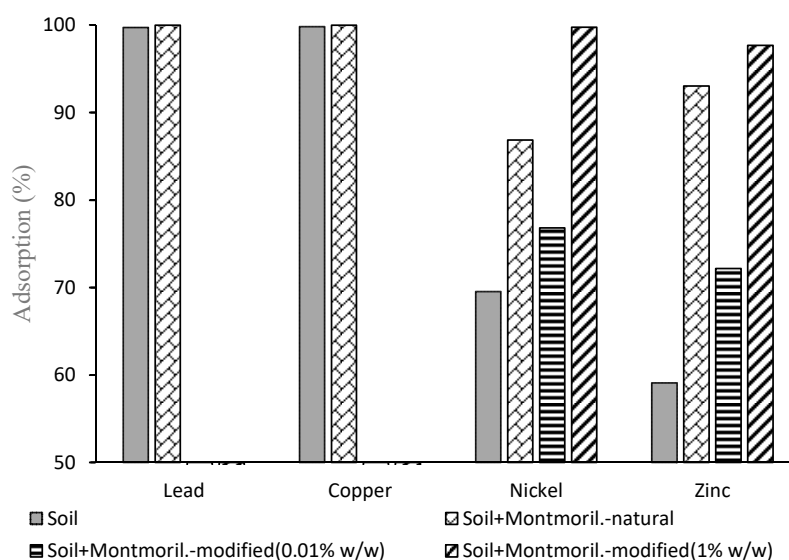


Figure 6. Results from the percolation tests. Immobilization of heavy metals by the soil and the soil with the addition of different quantities of montmorillonite (natural state or modified).

The results show that mixing the soil with montmorillonite on its natural state does have a positive effect on the retention of some of the heavy metals. The addition of montmorillonite has almost no effect on the retention of the heavy metals Pb²⁺ and Cu²⁺ when compared with the adsorption by soil alone (Table S3), mainly due to the high affinity of lead and copper to the soil used in this work. The results for Ni²⁺ and Zn²⁺ show that the addition of montmorillonite on its natural state led to an increase in the amount of these HMs adsorbed compared to adsorption on soil alone; however, the adsorption values are far from satisfactory (what justifies the study, for these two heavy metals, with montmorillonite previously dispersed by ultrasounds and surfactant addition).

The addition of modified montmorillonite resulted, in general, in an increase of the adsorption capacity of the soil for the heavy metals nickel and zinc (compare Tables S3 and S4). However, the montmorillonite concentration of 0.01% (*w/w*), equal to the one used for the MWCNTs, is too low, and a concentration of 1% (*w/w*) has to be used to immobilize Ni²⁺ and Zn²⁺ almost completely (even in the case of Zn²⁺ in spite of its high mobility), corresponding to an increase of the adsorption efficiency, when compared with the use of montmorillonite in its natural state, especially for

Ni^{2+} . Additionally, the amount of montmorillonite corresponding to this concentration is still slightly lower than the one used for montmorillonite in its natural state.

The results here reported lead to the conclusion that clay particles chemically modified, in this case with the application of ultrasounds to an aqueous solution enriched with the surfactant SDBS, have a higher capacity to retain heavy metals, even when lower amounts of clay are used (1% *w/w*). This can be related to the fact that the ultrasounds and surfactant promote the dispersion of the montmorillonite particles, increasing the surface area and consequently its adsorption capacity. The adsorption efficiency obtained using dispersed montmorillonite (1% *w/w*) is similar to the one obtained using MWCNTs (0.05% *w/w*), for conditions similar to the ones found in a real ground.

3.2.3. Portland Cement

Figure 7 and Table S5 in Supplementary Materials present the results obtained from the percolation tests using Portland cement alone and enriched with MWCNTs or montmorillonite, both dispersed with ultrasounds and the surfactant SDBS. The results showed that the use of Portland cement without any other additive is effective in the retention of all heavy metals studied, as was already expected [10,19,48,49,51]. This high capacity to immobilize heavy metals is related to the chemical fixation of the HMs to binder hydration products, as calcium silicate hydrated (CSH). Portland cement is mainly composed of silicates and calcium elements (Table 3). When the cement is hydrated, the calcium and silicates react with water forming calcium silicate hydrated (CSH). CSH is a cementitious gel, which tends to react with the heavy metals, immobilizing these on the binder matrix while releasing calcium ions [52]: Equation (1), where M^{2+} represents the heavy metal ion and $\text{C}_3\text{S}_2\text{H}_3$ represents the calcium silicate hydrated.

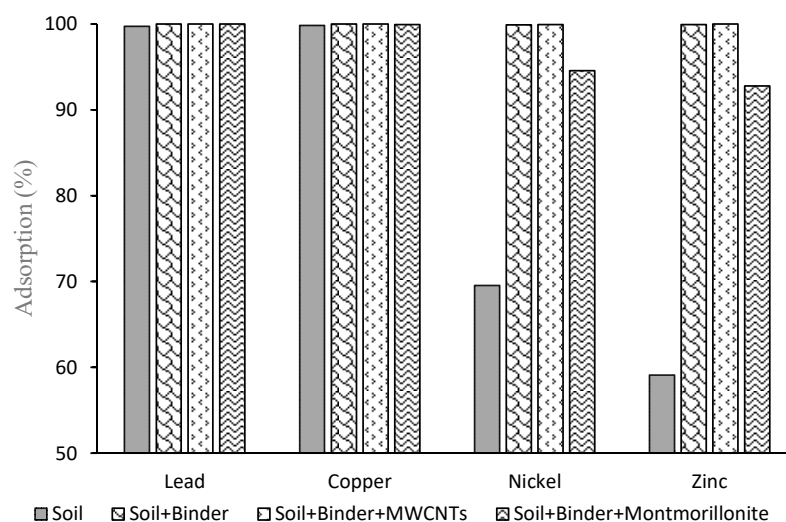
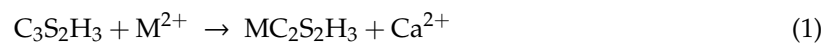


Figure 7. Results from the percolation tests. Immobilization of heavy metals by the soil, the soil with Portland cement and the soil with Portland cement with MWCNTs/montmorillonite.

The combination of Portland cement with MWCNTs had almost no impact on the amount of HMs immobilized. The combination of Portland cement with montmorillonite has a slight negative effect, resulting in a slightly lesser adsorption of Ni^{2+} and Zn^{2+} . This suggests that the CSH are reacting with the montmorillonite particles, preventing some reactions between CSH and the HMs to occur due to a smaller number of adsorption sites.

From the results obtained from the percolation tests, it is possible to conclude that Portland cement in a small dosage (25 kg of cement per cubic meter of soil compared to the usual amount of 100 to 250 kg/m^3 used for stabilization purposes [54]), is very effective without the need of any other additive. The addition of MWCNTs to the binder results in an additional cost without any significant advantage,

except the eventual increase of the mechanical properties of the soil [35,66], while the addition of montmorillonite to the binder has a negative effect.

3.3. Leaching Tests

Leaching tests and acquisition of SEM images of the leachate were performed in order to assure that MWCNTs were not being released from the soil matrix into the environment, considering the eventual negative environmental impacts of the presence of these nanoparticles in water bodies. For each of the leachate samples, collected after 1, 3, 7, and 14 days, SEM images of the dry powder samples were acquired (an example is presented in Figure 8) and the presence of MWCNTs particles (diameter of 9.5 nm, length of 1500 nm) was never observed. The images of the samples obtained from leachates resulting from soil alone without MWCNTs were always similar to the ones obtained for leachates coming from soil additivated with MWCNTs. Therefore, the presence of nanoparticles MWCNTs was never detected in the leachates. In the future, the possibility of leaching of the surfactant will also be checked.

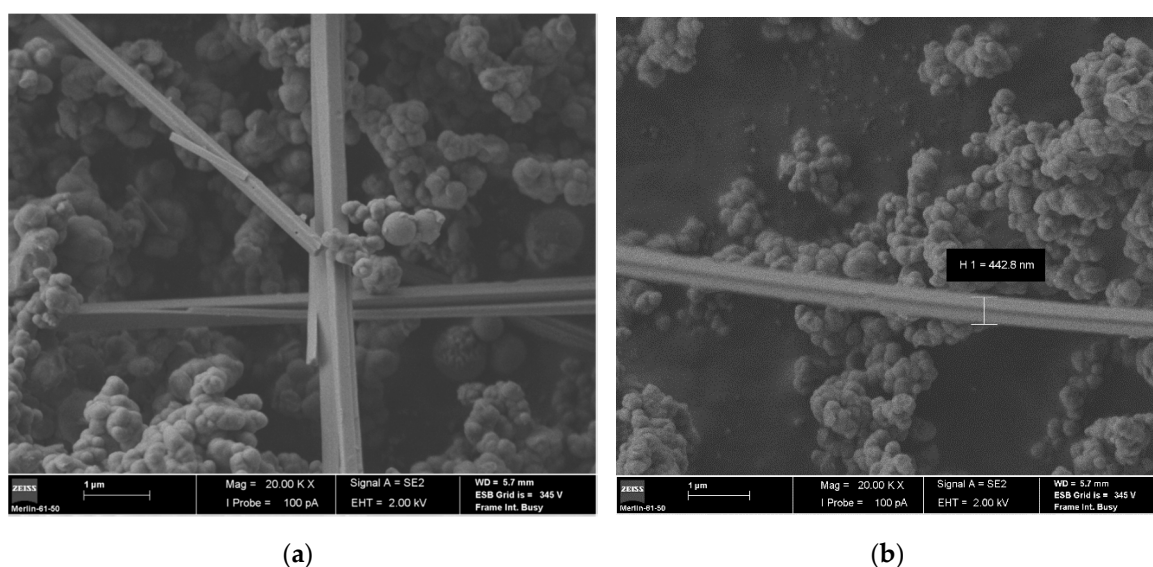


Figure 8. SEM images of the powder obtained from a leachate sample collected at 3 days: (a) contaminated soil with heavy metals; (b) contaminated soil with heavy metals enriched with MWCNTs.

4. Conclusions

This experimental work assessed the efficiency of different additives (MWCNTs, montmorillonite, and Portland cement) to immobilize the heavy metals lead, copper, nickel, and zinc in soil in conditions similar to a real case scenario. The choice of the HMs tested took into consideration the existent contamination scenario in Portugal, aiming also at testing HMs with different degrees of mobility. The study revealed that even if the adsorption tests are a valid tool to evaluate the performance of the additives, only percolation tests can take into consideration the influence of the soil's properties, reproducing the conditions of a real field situation in a better way.

The results obtained allow to conclude that the different HMs have different affinities to the soil studied, with a high organic matter content; the affinity order identified was $Pb > Cu > Ni > Zn$. The use of Portland cement in a low dosage (25 kg of cement per cubic meter of soil), without any other additive, proved to be very efficient to immobilize the HMs studied with the advantage of the mechanical enhancement of the soil. The combination of Portland cement with other additives is not advised, since the addition of MWCNTs results in an increase of the cost without significant technical benefits regarding HMs immobilization, and the combination of Portland cement with montmorillonite is counterproductive. If the aim is not the mechanical enhancement of the soil, then the

use of montmorillonite as a single additive allowed an increase in the immobilization of the HMs studied in this work, when compared with the soil alone adsorption capacity. The use of chemically modified and well-dispersed montmorillonite was more efficient than the use of montmorillonite without any previous treatment, when nickel and zinc are considered, even when lower amounts of montmorillonite are used. The addition of MWCNTs in a concentration of 0.05% (*w/w*), as a single additive to the contaminated soil, revealed to be efficient for the immobilization of the HMs studied, presenting results similar to the ones obtained with montmorillonite for Ni²⁺ and Zn²⁺, but using a much lower concentration of MWCNTs. Moreover, it was verified that the nanoparticles were not released into the water when the soil with MWCNTs was put in contact with water up to 14 days.

Since all the options studied in this work revealed to be technically efficient in the immobilization of heavy metals in soils, it may be concluded that MWCNTs and clay mineral are a valid alternative to the traditional addition of Portland cement even when tested in conditions similar to a real case scenario, unless stabilization of the soil is also required. The designers' and decision-makers' choice of the best additive will depend mainly on the environmental/economic compromise.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2076-3417/10/22/7950/s1>, Table S1: Results of the individual adsorption tests—Adsorption of the heavy metals under study by the Soil, suspension of MWCNTs in water, and suspension of Soil with addition of MWCNTs (MWCNTs = 0.01%, *w/w*). Table S2: Results of the individual adsorption tests—Adsorption of the heavy metals under study by a suspension of Montmorillonite in water and suspension of Soil with addition of Montmorillonite (montmorillonite = 0.01%, *w/w*) (results for soil alone as reference are given in Table S1). Table S3: Results of the percolation tests—adsorption of the heavy metals under study by soil with or without the addition of MWCNTs. Table S4: Results of the percolation tests—adsorption of the heavy metals under study by soil with or without the addition of Montmorillonite. Table S5: Results of the percolation tests—adsorption of the heavy metals under study by soil with the addition of Portland cement without or with addition of a second additive (MWCNTs or Montmorillonite).

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Conflicts of Interest: On behalf of all authors, the corresponding author states that there is no conflict of interest.

Abbreviations

The following symbols are used in this paper:

C	concentration [mg/L]
Ca ²⁺	calcium ion
CNTs	carbon nanotubes
CSH	calcium silicate hydrated
Cu ²⁺	copper ion
G	specific gravity
M ²⁺	heavy metal ion
MWCNTs	multi-walled carbon nanotubes
Ni ²⁺	nickel ion
OM	organic matter
Pb ²⁺	lead ion
S/S	solidification/stabilization
SDBS	sodium dodecylbenzenesulfonate
SWCNTs	single-walled carbon nanotubes
w	natural water content
Zn ²⁺	zinc ion

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