

## Soils contaminated by heavy metals - study of the addition of carbon nanotubes and montmorillonite

A.A.S. Correia<sup>1</sup>, M.P. Matos<sup>2</sup>, A.R. Gomes<sup>3</sup> and M.G. Rasteiro<sup>4</sup>

<sup>1</sup>Univ Coimbra, CIEPQPF, Dep. Civil Engineering, Coimbra, Portugal, [aalberto@dec.uc.pt](mailto:aalberto@dec.uc.pt)

<sup>2</sup>Univ Coimbra, Dep. Civil Engineering, Coimbra, Portugal; [martim-matos@hotmail.com](mailto:martim-matos@hotmail.com)

<sup>3</sup>Univ Coimbra, Dep. Chemical Engineering, Coimbra, Portugal; [tita-1002@hotmail.com](mailto:tita-1002@hotmail.com)

<sup>4</sup>Univ Coimbra, CIEPQPF, Dep. Chemical Engineering, Coimbra, Portugal; [mgr@eq.uc.pt](mailto:mgr@eq.uc.pt)

### ABSTRACT

The "health" of soils is increasingly a concern of modern societies, considering its importance in the fields of food, water, biodiversity and even for climate change control. Anthropogenic activities accentuate this problem by inducing soil contamination. This experimental work studies the effect of two additives (carbon nanotubes versus natural clay) on the immobilization of heavy metals (lead, copper, nickel and zinc) in a contaminated soil. Suspension adsorption tests were carried out in order to provide preliminary information on the adsorption capacity of the soil for the different heavy metals tested, while percolation tests were carried out in order to evaluate the immobilization of heavy metals by different additives under conditions similar to a real soil contamination situation. The results showed that soil particles were able to retain considerable amounts of heavy metals (especially lead and copper), which is linked to their fine particle size and the high organic matter content of the soil. Under conditions of good dispersion of the additives, the addition of carbon nanotubes or natural clay can increase the adsorption of heavy metals, except for Zinc, due to its low electronegativity and high mobility. The results allow the conclusion that the additives, carbon nanotubes and natural clay, have the potential to minimize the mobility of heavy metals in contaminated soils when tested under conditions similar to a real on-site situation, minimizing their mobility to groundwater. The obtained results can help designers and decision makers in choosing the best materials to remediate heavy metal contaminated soils.

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

### 1 INTRODUCTION

The "health" of soils is increasingly a concern of modern societies, namely at the European level. The contamination of soils by heavy metals (HMs) can be a serious problem due to its impact on food, water and biodiversity. Heavy metal pollution can occur by natural (e.g. forest fires) or anthropogenic (use of pesticides and fertilizers, smelting, mining and emissions from industries) sources (Alloway 2013; Liu et al. 2018; Odigie and Flegal 2014). Heavy metals cannot be degraded and when present in soil they may leachate and threaten the quality of vegetables and cattle, water and ultimately human health (LI et al. 2016; Mulligan et al. 2001).

The mobility of the heavy metals in soils is very dependent of the soil characteristics, such as the organic matter content, grain size distribution and pH of the soil. Cationic heavy metals are more soluble and have more mobility in acidic environments (Wuana and Okieimen 2011). Fine grained soils, rich in silt and/or clay particles, show better capacity to immobilize heavy metals unlike coarse soils (Yao et al. 2015). The organic matter present in a soil contributes to the immobilization of HMs due to the complex interactions established between the constituents of the organic matter and the HM (Stevenson 1997; Mulligan et al. 2001).

The treatment of a heavy metal contaminated soil requires special precaution when compared to organic contaminants. Since heavy metal are not biodegradable and cannot be destroyed through high temperatures or the use of chemicals, organic-targeted soil remediation techniques are ineffective. The traditional method used to remediate HMs contaminated soils consists in excavation and relocation to a

landfill. The high costs, limited landfills availability (Scanferla et al. 2009) 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 (Liu et al. 2019). S/S consists in mixing additives with the soil with the objective to reduce the potential migration (mobility) of HMs and thus the risk of contaminating adjacent areas. Some of the mixing additives used in the S/S technique are binders, clay minerals, alkaline materials, organic compounds and recently, nanomaterials (Kumpiene et al. 2008; Mueller and Nowack 2010; Wang et al. 2016; Ma et al. 2017; Xia et al. 2017; Dai et al. 2018; Peng et al. 2018; Liu et al. 2019).

Carbon Nanotubes (CNTs) are very small materials (nanoscale) composed by cylindrical graphite sheets rolled up forming a single-wall or multi-walls tubes (Khan et al. 2015). Several studies have proven that CNTs possess high adsorption capacity (Thakur and Thakur 2015; Zhao et al. 2010; Li et al. 2003; Gadhave and Waghmare 2014; Yang et al. 2009), which means this nanomaterial has the capacity to immobilize heavy metals on its surface (Thakur and Thakur 2015; Zhao et al. 2010; Li et al. 2003; Gadhave and Waghmare 2014; Yang et al. 2009; Matos et al. 2017; Correia et al. 2020; Oliveira et al. 2021).

Natural clays (particle's diameter  $< 2 \mu\text{m}$ ) have the potential to immobilize heavy metals in soils through adsorption mechanisms, retaining them on their surface, since they have considerable high specific surface area (Zhang et al. 2011; Alvarez-Ayuso and García-Sánchez 2003; Garcia-Sanches et al. 2012). The most important properties to the potential adsorption capacity of a clay mineral are the specific surface area and cation exchange capacity (CEC) (Sposito, 1984; Stumm, 1992). In general, higher values of CEC imply higher capacity to adsorb heavy metals. Clay minerals with higher specific surface area also have more adsorption potential, since they present more adsorption sites (Aydinalp and Marinova 2003). Korte et al. (1976) showed that the adsorption potential is more closely tied to the specific surface area of the clay than to the CEC. The use of natural clays has obvious advantages since they are an environmental friendly material, widely available and non-expensive (Zhang et al. 2011).

The main goal of the present work is to evaluate the capacity of two additives (carbon nanotubes versus natural clay) on the immobilization of heavy metals (lead, copper, nickel and zinc) in a contaminated soil. Both additives were previously treated applying ultrasonic energy and adding a surfactant, to guarantee the adequate dispersion of the additives and increase the number of available adsorption sites. The soil was artificially contaminated with the heavy metals under study, and suspension adsorption tests were carried out to evaluate the adsorption capacity of the two additives (CNTs and clay mineral). Percolation tests were then conducted to better evaluate the efficiency of additives to immobilize the heavy metals tested, in the soil, in conditions similar to a real on-site situation.

## 2 MATERIALS AND TESTING

### 2.1 Materials

The soil selected for this study is an organic fine grained soil composed mainly by silt (59%) and clay (21%) particles, Table 1. The soil studied exhibit a high organic matter content (7.4%) which combined with the particles composition induces a high potential adsorption capacity. However, since the soil is slightly acid ( $\text{pH} = 5.4$ ), this may be detrimental for the adsorption capacity of the soil, since all heavy metals present higher mobility in acidic environment (Kumpiene et al. 2008).

This soil was contaminated in the laboratory for the maximum heavy metals concentrations measured in contaminated soils found in Portugal (Costa and Jesus-Rydyń 2001; Inácio et al. 2008), simulating in this way a real scenario. The soil was contaminated in laboratory using salts containing the heavy metal ions under study, more precisely, lead nitrate  $\text{Pb}(\text{NO}_3)_2$ , hydrated copper chloride  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , hydrated nickel sulfate  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , and hydrated zinc sulfate  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ . Table 2 presents the maximum concentrations found in Portugal for the heavy metals under study (lead, copper, nickel and zinc), and it is possible to verify that all the values are above the reference values recommended in the Ontario Soils Quality Guidelines (Ministry of the Environment 2011), showing the presence in Portugal of highly contaminated soils. After the soil being contaminated it was stored in a temperature-controlled room ( $20 \pm 2^\circ\text{C}$ ) during 7 days, at least, to allow the HMs to distribute evenly in the soil.

For the present study Multi-Wall Carbon Nanotubes (MWCNTs CN7000) were selected due to their reduced cost when compared with Single Wall Carbon Nanotubes. According to the supplier (Nanocyl) and Figueiredo et al. (2015), 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 m<sup>2</sup>/kg, a specific density of 1.7 g/cm<sup>3</sup> (in average) and a zeta potential of around -25.2 mV. The MWCNTs selected for this studied have an indicative cost of 100 €/kg.

**Table 1.** Characteristics of the soil used in this work (Correia 2011; Coelho 2000)

<b>Clay (%)</b>	21
<b>Silt (%)</b>	59
<b>Sand (%)</b>	20
<b>G (-)</b>	2.6
<b>w (%)</b>	80.9
<b>w<sub>L</sub> (%)</b>	54.1 <sup>(a)</sup>
<b>w<sub>P</sub> (%)</b>	39.8
<b>OM (%)</b>	7.4
<b>pH (-)</b>	5.4
<b>Soil classification USCS<sup>(b)</sup></b>	OH

(a) after drying

(b) Unified soil classification system (ASTM D2487, 1998)

**Table 2.** Maximum values registered in Portuguese soils and international reference values for the heavy metals studied in this work.

<b>Heavy Metal</b>	<b>Maximum value registered in Portuguese soils (mg/Kg)* (Inácio et al. 2008)</b>	<b>Ontario soil reference values (mg/Kg)* (Ministry of the Environment 2011)</b>
<b>Lead, Pb</b>	585	120
<b>Copper, Cu</b>	245	230
<b>Nickel, Ni</b>	880	270
<b>Zinc, Zn</b>	589	340

\* The values shown are referred to the dry weight of soil

The natural clay selected for the present work was montmorillonite, supplied by Vermeer Portugal, presenting the chemical and mineral composition shown in Table 3. Montmorillonite is a clay mineral with a very high specific surface (400–800 m<sup>2</sup>/g), which gives to this clay mineral a higher cation exchange capacity (70-100 meq+/100g) (Kitazume and Terashi 2013; Goyal and Chauhan 2015). All of these characteristics indicate that the montmorillonite mineral has a high potential adsorption capacity. The montmorillonite selected for this studied has an indicative cost of 0.56 €/kg.

**Table 3.** Bulk chemistry and mineral composition of Montmorillonite according to the supplier.

<b>Components (%)</b>	<b>Minerals (%)</b>
<b>Na<sub>2</sub>O</b>	<b>Diocahedral smectite</b> 85-90
<b>MgO</b>	<b>Quartz</b> 5
<b>Al<sub>2</sub>O<sub>3</sub></b>	<b>Illite</b> 2
<b>SiO<sub>2</sub></b>	<b>Opal</b> 2
<b>P<sub>2</sub>O<sub>5</sub></b>	<b>Potassium feldspar</b> trace
<b>SO<sub>3</sub></b>	
<b>K<sub>2</sub>O</b>	
<b>CaO</b>	
<b>TiO<sub>2</sub></b>	
<b>Mn<sub>3</sub>O<sub>4</sub></b>	
<b>Fe<sub>2</sub>O<sub>3</sub></b>	

## 2.2 Adsorption Tests

Adsorption tests were performed with the aim to study the adsorption capacity of the soil towards the different heavy metals tested, and to evaluate if the additives (MWCNTs or montmorillonite) could improve the adsorption capacity of the soil.

Before adding the MWCNTs or the natural clay to the soil it is important to guarantee an adequate dispersion of these additives, avoiding losing part of their advantages. For such, the application of ultrasonic energy to the aqueous suspension of MWCNTs or montmorillonite enriched with an anionic surfactant SDBS (used in a concentration of 0.03%, w/w) was used.

Three different adsorption tests were performed:

- 1 –tests with soil alone contaminated with the heavy metals (control test) with the objective to evaluate the adsorption capacity of the soil particles;
- 2 –tests using a suspension of MWCNTs or montmorillonite (applied in a concentration of 0.01% w/w) dispersed in an aqueous solution of heavy metals, pretreated with ultrasounds and surfactant as described above, with the objective to evaluate the adsorption capacity of these additives applied alone;
- 3 –tests using soil contaminated with heavy metals combined with MWCNTs or montmorillonite (applied in a concentration of 0.01% w/w), pretreated with ultrasounds and surfactant as described above, with the objective to evaluate the benefits in the adsorption capacity of combining soil with additives.

Knowing the initial concentration of heavy metals added to the soil, the quantities adsorbed by the solid particles (soil, 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, 1h, 4h and 24h). The heavy metal concentration in the water samples was measured using atomic absorption spectrometry.

## 2.3 Percolation tests

Percolation tests were performed with the aim to study the adsorption capacity of the two additives (MWCNTs or montmorillonite) towards the different heavy metals tested in conditions closer to a real scenario. For such, two different percolation tests were performed:

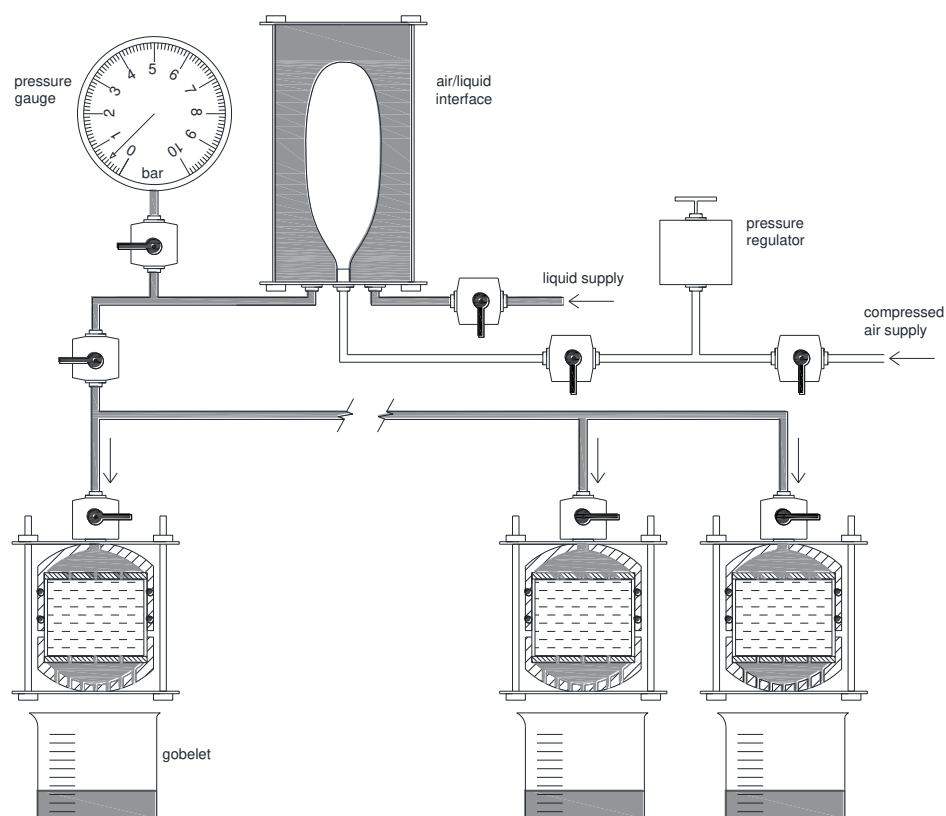
- 1 –tests with soil alone contaminated with the heavy metals (control test);
- 2 –tests using soil contaminated with heavy metals combined with MWCNTs (applied in a concentration of 0.01% and 0.05% w/w) or montmorillonite (applied in a concentration of 0.01%, 1% and 1.14% w/w).

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 immobilized (stage 3). In stage 1, four equal soil portions (5 kg each) were taken from the natural soil, air dried, and 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%). 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. For the samples additivated with montmorillonite, it was used a quantity of 25Kg of montmorillonite (equivalent to a concentration of 1.14% w/w), in its natural state, per cubic meter of soil, or, alternatively, a suspension of montmorillonite (concentration of 0.01% or 1% w/w) 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 35mm of height and 37mm of diameter (37.6cm<sup>3</sup>). 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 the water to flow. After sealing the tubes, the percolation tests started with a flow of water under a hydraulic charge of 5 m, and the leachate was collected in a beaker. When the leachate volume equaled the sample's volume (37.6ml) the percolation test ended. After filtering the leachate atomic absorption spectrometry tests were performed to evaluate the amount of heavy metals immobilized (based on the amount released which was measured) in the soil sample. The heavy metals quantity adsorbed by the solid particles (soil+additive) was determined by comparing the known initial concentration of each heavy metal on the soil samples and the final concentration of the heavy metals present in the collected leachate liquid after the percolation tests. A schematic of the percolation tests arrangement is shown in Figure 1. In all percolation tests the samples were in a saturated condition.

### 3 RESULTS

#### 3.1 Adsorption Tests

Figure 2 present the evolution of the heavy metals adsorption with time by the soil alone (control), suspension of MWCNTs or montmorillonite and for the soil enriched with MWCNTs or montmorillonite. It is clear 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 minutes. Thus, after this initial period no significant changes on the amount of adsorbed material were detected.



**Figure 1.** Schematic of the percolation tests: soil samples, beakers and injection system composed by a pressure regulator, air compressor and interface air/water.

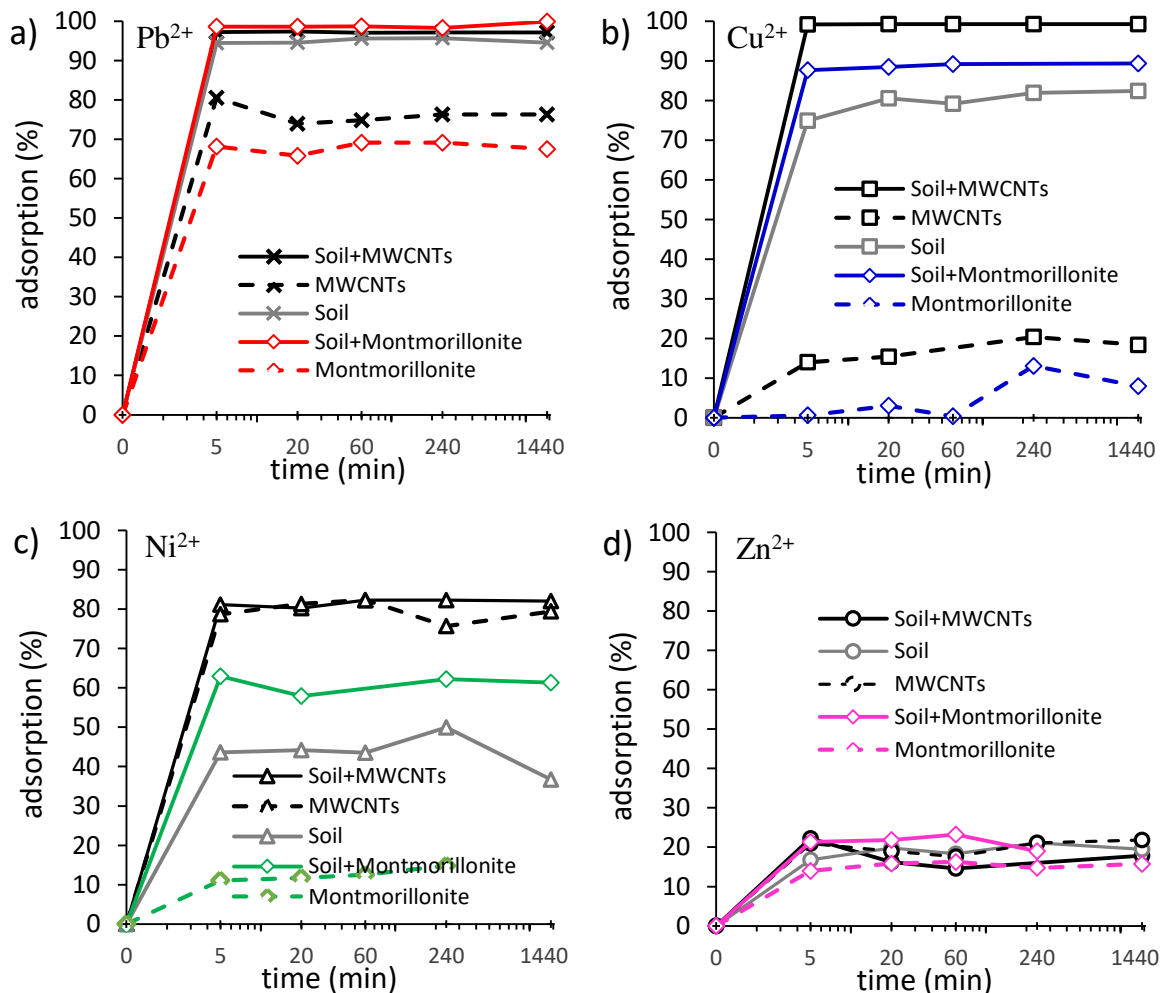
Looking at the results of the tests (Figure 2) where only suspensions of additives were used (aqueous suspension of MWCNTs or montmorillonite), it is possible to conclude that the heavy metals lead ( $Pb^{2+}$ ) and nickel ( $Ni^{2+}$ ) were adsorbed by the MWCNTs in large amounts while montmorillonite exhibits a similar adsorption capacity only for the heavy metal lead ( $Pb^{2+}$ ). For the other heavy metals tested, the adsorption capacity of the additives was very low. Regarding the MWCNTs, it is known that certain metals show higher affinity to MWCNTs than others (Gao et al., 2009), with the adsorption being directly related to the electronegativity of the heavy metals, i.e., 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) (Kinraide and Yermiyahu 2007). Regarding the poor results exhibited by the montmorillonite alone, such results may be explained by its lower specific surface area due to the larger particle size, when compared with MWCNTs.

Examining the results of adsorption by soil particles alone (Figure 2), it may be concluded that the soil can capture a significant quantity of heavy metals, possibly as a result of the fine grain size (rich in silt and clay particles) and high content of organic matter, Table 1. The heavy metal exhibiting a higher degree of adsorption was lead, followed by copper, nickel and zinc. Lead was the heavy metal most adsorbed by the soil particles alone due to its high electronegativity, which decreases its mobility. The second most adsorbed heavy metal by soil particles was copper, which can be related to the high content of organic matter in the soil tested. As it was shown by Gomes and Fontes (2001) the interaction organic matter/heavy metals is stronger towards copper than for other heavy metals. When comparing the

results of adsorption by soil particles alone with the adsorption by additives alone (MWCNTs or montmorillonite), with the exception of nickel all other heavy metals showed a higher tendency to be adsorbed by the natural soil.

The addition of MWCNTs or montmorillonite to the soil increased the adsorption capacity of the soil, except in the case of  $Zn^{2+}$ . This increase is more significant in the case of  $Cu^{2+}$  and  $Ni^{2+}$ , where a higher enhancement was achieved by adding MWCNTs than by adding montmorillonite. For all the situations studied the adsorption of zinc was always very poor, which can be related to the low electronegativity and higher mobility of this metal compared to the other heavy metals tested.

In general, the results for the soil additivated with MWCNTs or montmorillonite showed that the affinity order of the heavy metals studied is  $Cu \approx Pb > Ni > Zn$  and  $Pb > Cu > Ni > Zn$ , for MWCNTs and montmorillonite, respectively. When comparing the addition of MWCNTs with the addition of montmorillonite to the soil (Figure 2), it may be concluded that in general MWCNTs promotes higher adsorption. However, it is important to highlight that even if montmorillonite presents a slightly lower adsorption capacity, the cost of montmorillonite ( $\approx 0.56 \text{ €/kg}$ ) can be substantially lower than MWCNTs ( $\approx 100 \text{ €/kg}$ ). Therefore, the final choice of the additive to remediate a soil contaminated with heavy metals should take into consideration these two factors (efficiency and cost).



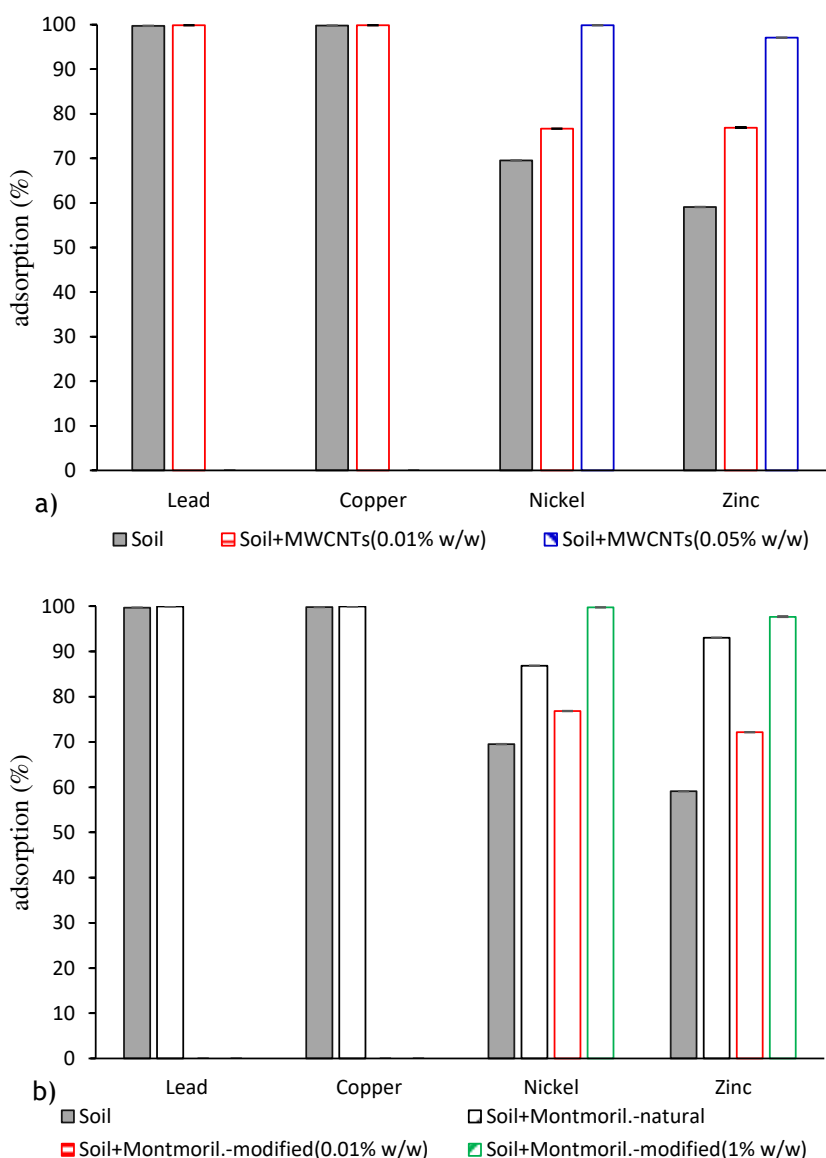
**Figure 2.** Results from the suspension adsorption tests. Individual adsorption of lead (a), copper (b), nickel (c) and zinc (d) by the soil additivated or not with MWCNTs or Montmorillonite (applied in a concentration of 0.01% w/w).

### 3.2 Percolation Tests

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, Correia (2011)). Thus, in the percolation tests the soil properties have more influence on the immobilization of the heavy metals, mimicking closer what may happen in a real situation.

Figure 3 presents the results of the percolation tests performed, expressing the adsorption capacity by the soil alone (control) and for the soil enriched with MWCNTs (concentration of 0.01 and 0.05% w/w) or montmorillonite (concentration of 0.01%, 1% and 1.14% w/w). The results showed that the heavy metals immobilized by the soil alone is much higher when compared to the suspension adsorption tests (Figure 2), especially for copper and zinc. The results clearly show that the heavy metals lead and copper are almost totally immobilized by the soil particles without the need of any additive. However, the heavy metals nickel and zinc showed potential to contaminate adjacent areas, when only soil is used, due to their higher mobility. Thus, for these two heavy metals the addition of MWCNTs or montmorillonite may enhance the adsorption capacity, contributing to immobilize such heavy metals.



**Figure 3.** Results from the percolation tests. Immobilization of heavy metals by the soil with or without the addition of: a) MWCNTs, b) Montmorillonite.

A careful look to the tests where the soil was contaminated with nickel and zinc, leads to the conclusion that the adsorption capacity of these heavy metals increases with the concentration of MWCNTs (Figure 3 a)). For a concentration of 0.05% (w/w) of MWCNTs, it was possible to achieve almost total immobilization of these heavy metals. However, when the soil was enriched with montmorillonite on its natural state (without surfactant) the adsorption values for the heavy metals nickel and zinc were far

from satisfactory, justifying the study with montmorillonite previously dispersed in a surfactant solution (identified in Figure 3 as montmorillonite modified). Indeed, 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, effect that is larger the higher the concentration of montmorillonite. Indeed, the application of ultrasounds and surfactant promotes the dispersion of the montmorillonite particles, increasing the specific surface area and consequently its adsorption capacity. For a concentration of 1% (w/w) of modified montmorillonite it was possible to achieve almost total immobilization of these heavy metals.

#### 4 CONCLUSIONS

Adsorption and percolation tests were performed with the aim to evaluate the efficiency of different additives (MWCNTs and montmorillonite) to immobilize the heavy metals lead, copper, nickel and zinc in a soil in conditions similar to a real case scenario. The study revealed that even if the adsorption tests are a valid tool to evaluate the performance of the additives, only the percolation tests can take in consideration the influence of the soil's properties, reproducing in a better way the conditions of a real site situation.

The results obtained allow to conclude that the different heavy metals have different affinities to the present soil, with a high organic matter content, and it was identified the order of affinity of the metals studied:  $Pb > Cu > Ni > Zn$ . The addition of MWCNTs to the contaminated soil revealed to be efficient for the immobilization of the heavy metals studied. The use of montmorillonite allowed an increase in the immobilization of the heavy metals studied in this work, when compared with the soil alone. The use of modified montmorillonite (pretreated with ultrasounds and surfactant) was more efficient than the use of montmorillonite without any previous treatment, when nickel and zinc are considered, even when lower amounts of modified montmorillonite were used. The results reported lead us to conclude that mixing a small quantity of MWCNTs (0.05% w/w) or modified montmorillonite (1% w/w) with soil can efficiently decrease the mobility of the heavy metals in soils, indicating that this may be a valid option to be used in the inertization/remediation of contaminated soils.

Since both additives (MWCNTs and montmorillonite) studied in this work revealed to be technically efficient in the immobilization of heavy metals in soils, the designers' and decision-makers' choice of the best additive will depend mainly on the environmental-economic compromise.

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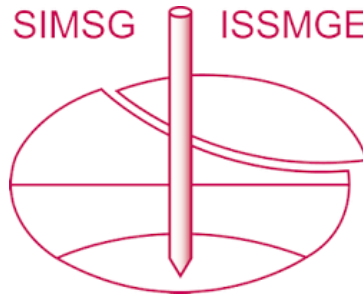
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