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Immobilization of heavy metals in contaminated soils with carbon nanotubes

Immobilisation de métaux lourds dans les sols contaminés avec des nanotubes de carbone

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ABSTRACT: This experimental work studies the performance of carbon nanotubes (CNTs) to immobilize heavy metals (HM) in contaminated soils. The soil was artificially contaminated with the heavy metals lead, copper, nickel and zinc. In order to avoid the formation of agglomerates of CNTs, which originates the loss of their beneficial properties, an aqueous suspension of CNTs was prepared using a non-ionic surfactant combined with ultrasonic energy. Then, the soil, with and without the addition of CNTs, was subjected to adsorption and permeability tests to evaluate the performance of CNTs in heavy metals immobilization. Permeability tests aims to reproduce conditions similar to a real situation of soil contamination. From the results it was possible to conclude that the addition of a small amount of dispersed carbon nanotubes can successfully increase the adsorption capacity of the soil and consequently improve the immobilization of heavy metals in the soil matrix. The immobilization percentage varies with the different heavy metals under study.

RÉSUMÉ: Ce travail expérimental étudie la performance des nanotubes de carbone (CNTs) pour immobiliser les métaux lourds (HM) dans les sols contaminés. Le sol a été artificiellement contaminé par les métaux lourds plomb, cuivre, nickel et zinc. Afin d'éviter la formation d'agglomérats de CNTs, entraînant la perte de leurs propriétés bénéfiques, une suspension aqueuse de CNTs a été préparée à l'aide d'un surfactant non-ionique associé à de l'énergie ultrasonique. Ensuite, le sol, avec et sans addition de CNTs, a été soumis à des tests d'adsorption et de perméabilité afin d'évaluer la performance des CNTs dans l'immobilisation de métaux lourds. Les tests de perméabilité visent à reproduire des conditions similaires à une situation réelle de contamination des sols. Les résultats ont permis de conclure que l'ajout d'une petite quantité de nanotubes de carbone dispersés peut augmenter efficacement la capacité d'absorption du sol et améliorer l'immobilisation des métaux lourds dans la matrice du sol. Le pourcentage d'immobilisation varie en fonction des différents métaux lourds étudiés.

Keywords: Stabilisation/solidification; carbon nanotubes; contaminated soils; adsorption tests; permeability tests

1 INTRODUCTION

The contamination of soils with heavy metals is a growing concern in modern societies. To avoid the spread of contamination, different techniques can be applied aiming to immobilize, degrade or even destroy the contaminants. However, heavy metals are not organic, thus, they can not be destroyed or degraded since they are not biodegradable (Kroopnick 1994; Lone et al. 2008). Soil stabilization/solidification (S/S) techniques can be applied mixing materials with the soil in order to partially immobilize heavy metals, as well as providing an improvement in the mechanical properties of the soil (Vaddoriya 2016; Matos et al. 2017). Materials like Portland cement, fly ash and clay are tradicionally applied in S/S (Lone et al. 2008; Vaddoriya 2016; Alvarez-Ayuso & García-Sánchez 2003). Due to their high surface area, the carbon nanotubes (CNTs) have the capacity to attrack and immobilize large quantities of heavy metals on their surface (adsorption). The potential use of CNTs in heavy metal contaminated water has been studied with very satisfactory results, however their application in contaminated soils is practically unexplored (Matos et al. 2017).

Although CNTs have high potential adsorption capacity, they exhibit a natural tendency to form aggregates with a strong negative impact on their adsorption capacity. Thus, it is important to develop strategies to assure an efficient CNTs dispersion, which may be done by mechanical methods (e.g., ultrasonic energy), combined or not with chemical methods (e.g., addition of polymers/surfactants that adsorb on the CNTs surface changing the outer structure of these nanoparticles and promoting their dispersion through steric or electrostatic interactions, Matos et al. 2017).

The properties of the soil have also a huge impact on the immobilization of heavy metals. In general, in soils with low pH (acid soils) the heavy metals exhibit higher mobility (Kumpiene et al. 2008). The organic matter present in the soil may also affect the mobility of the heavy metals,

since it has an impact on the physical and chemical interactions which lead to immobilizing the heavy metals (Kumpiene et al. 2008). The quantity of fine particles (silt and clay) in a soil is another important parameter since soils with high quantity of fine particles (which have high ionic exchange capacity) exhibit better capacity to immobilize heavy metals than coarse soils (Houben et al. 2012).

The present work studies the use of carbon nanotubes (CNTs) in soil remediation, with the main goal to evaluate performance of CNTs to immobilize the heavy metals lead, copper, nickel and zinc. The experimental work started with the dispersion of CNTs in an aqueous suspension prepared using a non-ionic surfactant combined with ultrasonic energy. The soil was artificially contaminated with the heavy metals under study, and adsorption tests in suspension conditions were done in order to evaluate the adsorption capacity of the soil, with and without the addition of CNTs. To validate the adsorption test results, permeability tests were executed, simulating the conditions of a real case scenario.

2 MATERIALS AND EXPERIMENTAL PROCEDURE

2.1 Materials

The present work is based on the Coimbra soft soil (located in a region known as "Baixo Mondego" near Coimbra city, Portugal) collected at a depth of 2.5m. Table 1 summarizes the main geotechnical and chemical properties of the soil. In general, the soil is predominantly clayey-silt (clay+silt = 80%) with a high organic matter content (7.41%), exhibiting pH (5.34) of a slightly acid soil, characteristics that may have a strong influence on the adsorption capacity of the soil. Indeed, its organic matter content and grain size composition suggest that the soil may have high potential adsorption capacity, although the soil's pH value indicates a slight decrease of the potential adsorption capacity.

Table 1. Principal properties of the Coimbra soft soil

Natural water content, w_{nat} (%)	80
Unit weight, γ_{sat} (kN/m^3)	14.6
Natural void ratio, e_{nat} (-)	2.1
Clay fraction (%)	21
Silt fraction (%)	59
Sand fraction (%)	20
Density, G (-)	2.61
Organic matter content, OM (%)	7.41
Liquid limit, w_L (%)	54
Plastic limit, w_P (%)	40
Undrained shear strength, c_u (kPa)	< 25
CaO (%)	0.74
SiO$_2$ (%)	62
Al$_2$O$_3$ (%)	16
Fe$_2$O$_3$ (%)	4.8
MgO (%)	1.1
pH (-)	5.34

The carbon nanotubes selected were multiwall carbon nanotubes (MWCNTs) which is justified by its cost (100.000€/ton) lower than that of the single-wall carbon nanotubes. The MWCNTs were produced by Nanocyl and, according to producer's data, they have an average diameter of 9.5 nm, average length of 1 500 nm and a specific surface of 275 000 m^2/kg. MWCNTs are composed essentially of pure carbon (90%), with some metal oxides (10%). Further characterization of the MWCNTs was conducted with the assessment of the mass density (1.7 g/cm3) and zeta potential (-25.2 mV) (Figueiredo et al. 2015).

A non-ionic surfactant was used to promote the dispersion of the MWCNTs. The surfactant selected was Pluronic F-127 produced by Sigma-Aldrich. It has a low molecular weight (9.49 kDa), an hydrodynamic diameter of 6.92 nm and an almost null zeta potential (-0.43 mV).

The amount of heavy metals used to contaminate the soil was the maximum values referred in the "The Soil Geochemical Atlas of Portugal: Overview and applications" (Inácio et al. 2008), thus, simulating real conditions (Table 2). The soil was artificially contaminated using salts containing the heavy metals ions under study. The salts used were lead nitrate Pb(NO$_3$)$_2$,

hydrated copper chloride, CuCl22H$_2$O, hydrated nickel sulfate, NiSO$_4$6H$_2$O and hydrated zinc sulfate, ZnSO$_4$7H$_2$O.

Table 2. Maximum values registered by Inácio et al. (2008) in portuguese soils for the heavy metals studied in this work (expressed in mg per kg of dry soil)

Lead (mg/Kg)	585
Copper (mg/Kg)	245
Nickel (mg/Kg)	880
Zinc (mg/Kg)	589

2.2 Experimental procedure

The experimental procedure adopted is based in two types of tests: adsorption and permeability tests.

The adsorption tests aim to evaluate the adsoprtion capacity of the soil with no addition (reference tests) and with the addition of MWCNTs, assessing the potential benefit of adding MWCNTs. Tests with olny MWCNTs in aqueous suspension were also conducted in order to determine their adsorption capacity. The laboratory procedure adopted was the following:

1) the soil was artificially contaminated with each of the 4 heavy metals under study. An ultrapure water suspension containing the soil and the heavy metal salt was added to a beaker until 50 ml were reached. The heavy metal under study was dissolved using a magnetic stirrer at 150 rpm. It was used a quantity of 60g soil, with a water content of 66.9%, corresponding to a dry weight of 36g of soil.

2) dispersion of MWCNTs: i) 3g of the surfactant Pluronic F-127 were added to 150 ml of ultrapure water, corresponding to a concentration of 2% (w/w) of surfactant, as previously optimized (Matos 2016). The dissolution of the surfactant was promoted using a magentic stirrer at the speed of 150 rpm during 12h; ii) to this solution 0.015g of MWCNTs were added, corresponding to a concentration of 0.01% (w/w) of MWCNTs; iii) The resulting suspension (ultrapure water + MWCNTs + surfactant) was

then subjected to ultrasonic energy (Sonics Vibracell 501), applied during 15 min with a frequency of 20 kHz and power of 500W (these values were based on the optimal values for MWNCTs dispersion previously determined, Matos 2016); iv) This suspension was then added to the contaminated soil previously prepared, resulting in the final 200 ml of suspension (Soil + ultrapure water + MWCNTs + surfactant), kept under agitation (150 rpm) inside a goblet.

3) representative samples of 15 ml of suspension were taken (with a syringe from the middle of the goblet at middle height) at 5min, 20min, 1h, 4h and 24h. Every sample was centrifugated at 3000 rpm during 20 min in order to separate the liquid (supernatant) and solid phase. The liquid was then collected and filtered using hydrophilic syringe filters (made of nylon) with 0.45µm pore diameter. The filtered liquid was then analysed using atomic absorption spectometry (atomic spectrometer 3300, Perkin Elmer), in order to determine the concentration of heavy metals in the samples: knowing the initial concentration of heavy metals, the quantity adsorbed by the solid particles was determined by the diference between the initial concentration and the concentration after the time considered.

The permeability tests aim to corroborate the results from the adsorption tests in conditions similar to a real situation of soil contamination. Permeability tests were done using only the soil contaminated with the different heavy metals (reference tests), and contaminated soil enriched with MWCNTs. The heavy metals concentration in the leachate liquid was evaluted using again atomic absortion spectrometry. The procedure adopted was as follows:

1) a sample of soil with a natural water content of 80.9% was dryed until the water content was 66.9%. The soil was divided in 4 portions and each portion was mixed with a solution of lead, copper, nickel or zinc. The solutions of soil + heavy metals had at the end the original water content (80.9%).

2) the soil was first homogeneized and a portion 100g was taken. 150ml of MWCNTs

suspension were prepared, in the same way as described in the adsorption tests. The soil and the suspension of MWCNTs were mixed reaching a water content of 115%. The soil was then carefully placed in PVC tubes with 35mm of height and 37mm of diameter. The PVC tubes were sealed with two PVC caps sustained by a metalic support and o-rings to avoid water leaks. Two perforated PVC discs were placed on the top and bottom to allow the percolation of water while confining the soil sample. A schematic of the permeability cell is shown in Figure 1.

3) the samples were subjeted to percolation of water with a hydraulic charge of 5 m, the leachate being collected in a beaker. The test was finished when the leachate volume was equal to the sample volume (~37.6 cm^3). The leachate was then filtered (as specified for the adsorption tests) and subjected to atomic absorption spectrometry to quantify the heavy metals in the aqueous phase, in a similar way as presented for the adsorption tests.
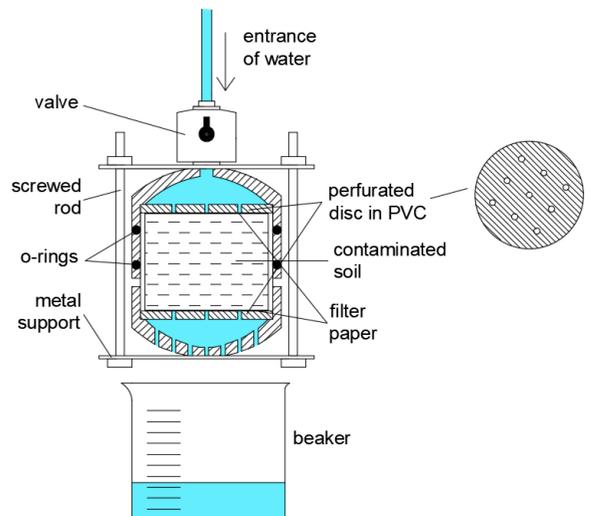

Figure 1. Schematic of the permeability tests

3 RESULTS

3.1 Adsorption tests

Figure 2 summarizes the results obtained from the adsorption tests, exhibiting the time evolution of the heavy metals adsorption by the MWCNTs alone, the soil alone (reference) and the soil enriched with MWCNTs. All the results show that the adsorption of the heavy metals is characterized by an initial rapid adsorption, with equilibrium reached within the first 5 minutes. After that there were no significant changes on the adsorption values.
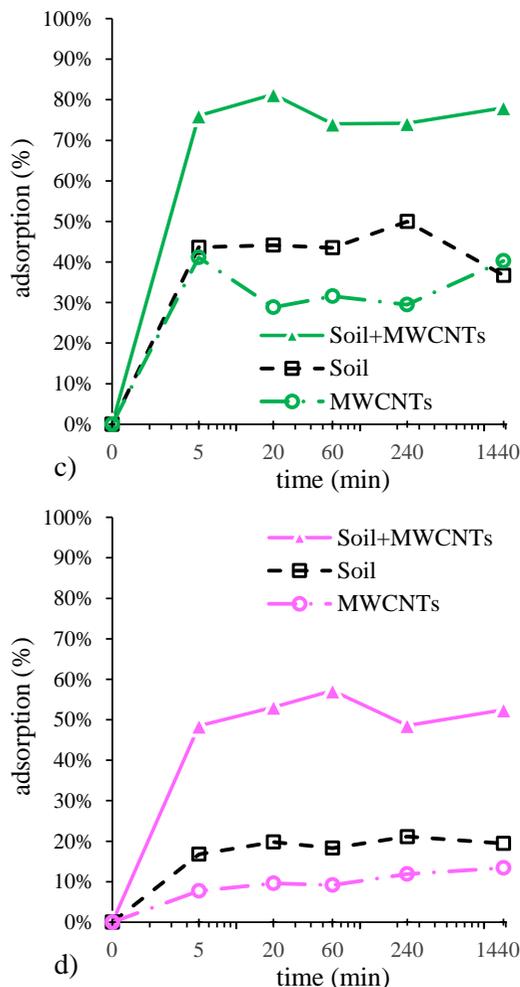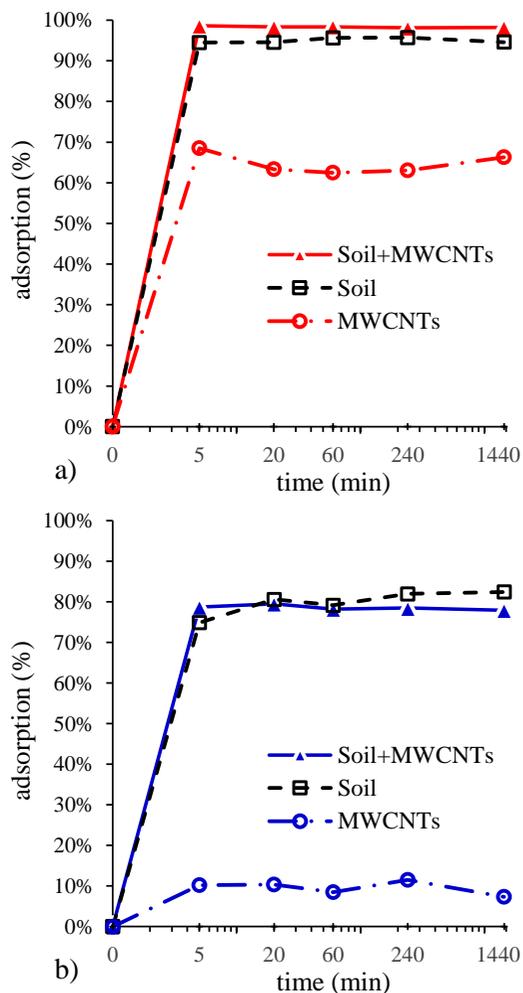

Figure 2. Results from the adsorption tests: lead (a), copper (b), nickel (c) and zinc (d) by the MWCNTs, soil and soil with the addition of MWCNTs

The results show clearly that the heavy metals studied in this work were adsorbed in different quantities, being the lead the heavy metal adsorbed in larger quantities and zinc the heavy metal that showed the lowest adsorption. The affinity order (Pb>Cu>Ni>Zn) can be explained by the different electronegativity of the heavy metals (Pb^{2+}: 2.33; Cu^{2+}: 1.90; Ni^{2+}: 1.91; Zn^{2+}: 1.65, Kinraide & Yermiyahu 2007) and the properties of the soil used, more precisely the organic matter content (Gomes & Fontes 2001).

Lead has very high electronegativity (2.33), which means it has high attraction to the surface of the particles and therefore is easily adsorbed by the soil particles alone. The addition of MWCNTs increases only ~4% the adsorption capacity, which was mainly due to the high adsorption capacity provided by the soil particles. So, in this case, the advantage of adding MWCNTs is negligible.

In the case of the heavy metal copper (Figure 2b), the adsorption capacity by the soil was also very high, around 80%. This value can be explained by its medium electronegativity (1.90) and by the organic matter present in the soil. Indeed, the organic matter has the capacity to attrack heavy metals, and it has been shown by Gomes & Fontes (2001) it shows high tendency to retain the metals lead and copper and low affinity towards nickel and zinc. When MWCNTs were added to the soil, the adsorption capacity showed no increase, which may be explained due the high affinity of copper to the soil itself. Thus, again, the advantage of using MWCNTs in this case is negligible. The adsorption of copper by only MWCNTs was very low, showing that this metal has, provably, strong attraction to the organic matter present in the soil and not to the surface of MWCNTs.

For the heavy metals nickel (Figure 2c) and zinc (Figure 2d), the results showed that the soil particles alone have low adsorption capacity, which can be related with the low electronegativity and less affinity to organic matter. The addition of MWCNTs resulted in a substantial increase of the adsorption capacity, which is mainly due to the MWCNTs adsorption capacity.

3.2 Permeability tests

Figure 3 summarizes the results obtained from the permeability tests, exhibiting the heavy metals adsorption by the soil alone (reference) and the soil enriched with MWCNTs. The main difference between the adsorption and permeability tests were the initial conditions of the samples: in the adsorption tests, the samples did not have any soil structure, while in the permeability tests the samples exhibit a soil structure, so, it is expected a major influence of the soil characteristics on the permeability tests, as must occur in a real situation.
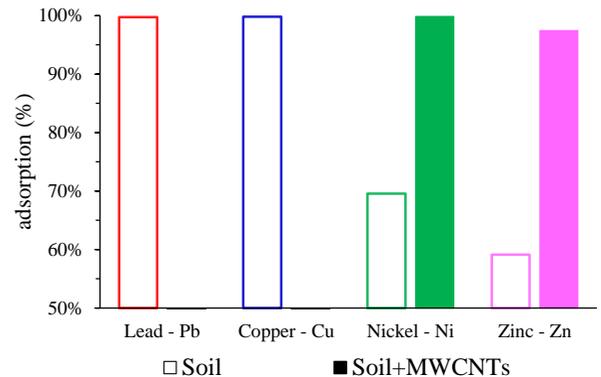

Figure 3. Results from the permeability tests (only Ni^{2+} and Zn^{2+} were tested with MWCNTs)

The results of the permeability tests are in accordance with the adsorption tests, but now the soil with no addition of MWCNTs can retain a higher amount of heavy metals, more notorious in the case of nickel and zinc. This may be justified by the "structure" of the permeability samples, with a stronger influence of the soil properties (organic matter and fine particles).

While lead and copper were almost completely adsorbed only by the soil, showing no need of improvement, the heavy metals nickel (70% adsorved) and zinc (60% adsorved) showed a considerable potential to migrate through the soil alone, having higher risk to contaminate adjacent areas. Thus, the addition of MWCNTs were only studied for the heavy metals nickel and zinc. The addition of MWCNTs increases the adsorption capacity of ~30% and ~37% for nickel and zinc, respectively. From the results it is possible to conclude that addition of MWCNTs properly dispersed can be an effective material to immobilize these heavy metals in soils.

4 CONCLUSIONS

From the experimental work performed it is possible to conclude that depending on the heavy metal under study, the addition of MWCNTs to the soil can have a beneficial effect, improving its adsorption capacity. Although there was little or no increase in the adsorption of lead and copper, the adsorption of nickel and zinc was substantially improved when the MWCNTs were present, as showed by the adsorption and permeability tests. It should be pointed out that the heavy metals nickel and zinc present a bigger risk to contaminate adjacent areas due to their higher mobility. The results indicate that MWCNTs can be used in the Stabilization/Solidification of soil to immobilize heavy metals in soils, justifying further research on this topic.

5 ACKNOWLEDGEMENTS

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