Immobilization of mercury in contaminated soils through the use of new carbon foam amendments

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IMMOBILIZATION OF MERCURY IN CONTAMINATED SOILS
THROUGH THE USE OF NEW CARBON FOAM AMENDMENTS

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Abstract

Background: Mercury (Hg) is recognized as one of the 10 most toxic elements and is much more persistent in soils than in other environmental compartments. However, an effective, environmentally friendly, economical, and applicable at large-scale technology for the remediation of soils contaminated by Hg has not yet been established. This study evaluates the feasibility of a new carbon foam-based product for the remediation of three soils contaminated with Hg, and infers the mobilization or immobilization mechanism through a detailed study of Hg speciation.

Results: Soil treatment with the carbon foams, one of them impregnated with goethite, reduced Hg availability by between 75 and 100%. Mercury associated to humic acid (Hg-HA) determined the proportion of mobility and availability of Hg when soils were treated with carbon foams. When the pH dropped, the structure of HA changed causing the Hg-HA to become part of the unavailable fraction of the soil along with HgS. The carbon foam impregnated with goethite did not mobilize Fe as occurred with ZVI nanoparticles. The presence of acid groups on the surface of the foam (carboxyl, quinone and phenolic groups) can bind metal cations strongly improving Fe immobilization.

Conclusions: A novel carbon foam-based amendment was efficient in immobilizing Hg in all the soils studied. The carbon foam impregnated with goethite, in addition to not mobilizing Fe, had the additional advantage of its lesser effect on the electrical conductivity of the soil. This novel approach could be considered as a potential amendment for other sites contaminated with Hg and/or other metal(loid)s.

Keywords: Bioavailability; soil remediation; carbon foams; goethite; mercury speciation
1. Background

Mercury (Hg) is a recognized neurotoxic metal which can seriously impact health, especially in children and pregnant women. In 2017, an international agreement of expected compliance was finally reached in the UN Minamata Convention to permanently solve the problem of Hg pollution that considered aspects such as mercury waste, polluted sites and industrial emissions [1]. This agreement highlights the necessity of innovative approaches and technology transfer related to Hg management.

According to the United Nations Environment Programme (UNEP) [2], in 2015 approximately 2000 tons of Hg were emitted into the air from anthropogenic sources. Reemission from soils and oceans, which are acting as a reservoir, has led to higher levels of atmospheric Hg concentration. Moreover, Hg is much more persistent in soils than in other environmental compartments [3].

Technologies for remediation of Hg-contaminated soils include, but are not limited to, soil washing, stabilization/solidification, nanotechnology, thermal treatment, and biological treatments such as phytoremediation and bioremediation [4–6]. The effectiveness of each technology depends on various soil characteristics, so a thorough site assessment must be performed prior to application of any technique. Nowadays, there is an increasing interest in the development of low-cost, in-situ and environmentally friendly technologies to replace traditional remediation technologies, such as thermal treatment and soil washing [7]. Natural-based solutions (NBS) [8] require the use of effective and green technologies such as enhanced thermal treatment [9], application of Hg volatilizing bacteria [10] and certain amendments for Hg immobilization [11].

In-situ physico-chemical Hg immobilization techniques can minimize health risks by reducing the bioavailability of Hg [12], and can even improve soil properties [13]. For instance, the application of a sulfur-modified biochar reduced 99.3% of freely available
Hg in toxicity characterization leaching procedure (TCLP) leachates [14]. The use of nanoparticles has also been found to be effective for the immobilization of Hg and other heavy metal(loid)s [11, 15, 16]. A significant decrease in Hg and As availability was found after the application of zero valence iron nanoparticles (nZVI) to contaminated soils [11]. Column tests of sediment treatment with a 0.5 g/L FeS nanoparticles suspension showed a Hg reduction of >77% in the TCLP leachability [15]. Selenium nanoparticles turned out to be effective for Hg\(^0\) immobilization [16]. However, the fate and transport of nanoparticles in the environment and their effect on human health are not well established yet [17]. Although, as previously mentioned, different amendments showed high efficiency to immobilize Hg and immobilization technology has been recognized as the most economical and easily accessible method for the remediation of contaminated soils [18], this technology is still under development, new materials are emerging [19] and the mechanisms of Hg-immobilization are not fully understood.

The mobility of Hg depends on its chemical speciation, which is a function of several soil parameters and their interactions. In addition, information on mercury species in soils is essential to establish the remediation methodology. Mercury speciation analysis requires very sensitive techniques that preserve the integrity of the species during the sampling and the whole analytical procedure. The most common methods to determine Hg species in solids can be classified as: i) indirect methods, which are sequential chemical extraction methods [20] and ii) direct methods, such as X-ray absorption spectroscopy (EXAFS or XANES) [21] and the programmed thermal desorption [22]. The main drawback of sequential extraction is that it is not possible to differentiate between all Hg species because they are selectively separated into groups. EXAFS and XANES techniques present the disadvantage of high detection limits that make them useful only for the most contaminated samples. In addition, they require complex
equipment and in most cases difficult to access. The thermal desorption technique does not require the use of reagents, it is direct and fast and it presents very low detection limits. However, in some cases, its selectivity is limited by an overlap of peaks that prevents a reliable identification of some Hg species. In the present work, direct and indirect methods are used in a complementary way to identify mercury species before and after being treated in-situ with amendments.

Carbon foams are a new generation of materials with enormous application potential [23]. They are ultralight carbonaceous materials with high adsorption capacity and, thanks to some characteristics such as microporosity, they can favor the nanodispersion of iron species on their surface. Furthermore, these materials can be modified to improve their performance. For example, loading with goethite, which has a freer structure to complex with cations than other Fe compounds [24], could lead to a more efficient immobilization of other contaminants such as As [25] reducing the risks associated with the application of alternative Fe-based amendments [17].

This study provides demonstration that carbon foams impregnated with goethite can be used as soil amendment for Hg immobilization. Three contaminated soils from industrial areas were tested to evaluate the effects of the new carbon foam amendments on pH, electrical conductivity (EC) and the availability of Fe, and to understand the mobility of Hg in soils through an in-depth study of the Hg speciation in the untreated and treated soils.

2. Experimental

2.1 Soil samples

Three samples of mercury contaminated soils were chosen for this study. The locations and the different characteristics of these soils have been previously reported
[26–28]. In brief, they were taken from: 1) two old Hg mining-metallurgy sites (S and T soils). In particular, mercury mining and processing activities are commonly of environmental concern because of the abundance of this element in the emissions and waste generated and 2) an industrial area (A soil). These lands contain metallurgical dust, slag, and other wastes that have a dramatic effect on soil quality, as well as ground and surface waters.

2.2 Soil amendments

The following materials were used as amendments:

- ZVI nanoparticles (nZVI). These nanoparticles were supplied by NANO IRON s.r.o (Czech Republic) as NANOFER 25S. The suspension contains 14-18% of Fe(0) and 2-6% of iron oxide. The suspension is alkaline with a pH of 9.5-11.5.
- Carbon foam (CF). The methodology followed to prepare CF using a carbon as precursor has been described elsewhere [29]. In brief, the green carbon foam was synthetized from a mixture of coal and an activation agent (ZnCl$_2$) in a closed reactor, at the temperature of maximum fluidity of the coal (450 °C), and in an inert (Ar) atmosphere. The resulting green foam was carbonized under an Ar flow of 100 mL min$^{-1}$, at 500°C and washed to remove inorganic salts. The CF was ground and sieved to between 0.2-0.5 mm.
- Carbon foam impregnated with goethite (CFGo). The CF previously obtained was impregnated with a solution of FeSO$_4$·7H$_2$O and CH$_3$COONa in water in proportions 1.5 g CF / 0.28 g FeSO$_4$ /0.4 g CH$_3$COONa / 5 mL H$_2$O. The suspension of CF was shacked in an ultrasound bath for 1 hour at 40 kHz and then heated under reflux for 2 hours. After cooling to room temperature, the solution was filtered and the solid dried at 60 °C for 4 h. This treatment results in the formation of goethite (FeO(OH)) on the surface of the support.
2.3 Soil analysis and characterization

Electrical conductivity (EC) and pH were measured to evaluate the influence of the amendments application on soil properties in a suspension of soil (1g) and Milli-Q water (2.5 mL). The functionalized groups present on the surface of the carbon foams were identified by Temperature Programmed Desorption (TPD). The distribution and particle size of iron on the surface of the carbon foam were studied by Scanning Electron Microscopy (SEM) whereas the crystalline structure was examined by X-ray diffraction (XRD). The analysis of Hg in all solid and liquid samples was determined directly using an automatic mercury analyzer AMA 254.

2.4 Soil treatment

Subsamples of polluted soils (20 g) were treated in 50 mL vials maintaining the proportion of 20% of amendment with 80% of soil. In the case of nZVI suspension the proportion was 2% (w/w), a cost-effective dose according to previous studies carried by the authors [25, 30]. Deionized water was added to the vials to achieve water holding capacity of the soil. The vials were shaken on an orbital shaker at 170 rpm for 72 h. After this, the treated soils were air dried.

2.5 Leaching test

The mobility of Hg in the raw and treated soils was determined by TCLP tests following the USEPA Method 1311 (1992). The leaching tests were carried out in 50 mL vials using 1 g of sample and 20 mL of CH₃COOH/ NaOH at pH 4.93±0.05. The samples were placed on an orbital shaker at 170 rpm for 18 h. Then, the liquid was separated from the solid by centrifugation (4000 rpm for 15 min), filtered and preserved at 4ºC. The liquids were then analyzed for Hg as described in Section 2.3.

2.6 Hg speciation and sequential extraction
The potential mobility and availability of Hg in soil samples were also evaluated by two sequential extraction procedures: the Tessier method [31] and a simplified USEPA Method 3200 [32] that is specific for mercury species. The Tessier and USEPA 3200 methods consist of five and three sequential extraction steps, respectively, which yield five and three Hg fractions as a function of each species solubility in different solvents. The following fractions were obtained with Tessier method: exchangeable (EX); bound to carbonates (CB); bound to Fe-Mn oxides (OX); bound to organic matter (OM) and residual (RS), whereas with USEPA Method 3200 were obtained: mobile Hg (M), semi-mobile Hg (SM) and no-mobile Hg (NM). Hg concentrations were measured in the extracts by AMA 254.

The study was completed with the identification of mercury species in the untreated and treated soils directly by desorption at programmed temperature using a mercury temperature programmed desorption (HgTPD) device [33]. The device previously described [34] consists of a temperature-programed furnace coupled to a PYRO 915 furnace from LUMEX and a continuous mercury analyzer (RA-915). Desorption profiles are obtained by heating the sample at a rate of 50 °C min⁻¹. The different desorption peaks obtained are assigned to each mercury species using the reference database made with mercury compounds. The compounds used in this work as reference were mercury bound to humic acids (Hg-HA) and HgS, as they are the most likely species to be present in soil samples, as well as other species that can possibly be present, such as Hg⁰, HgO and HgCl₂.

2.7 Statistical analysis

Statistical analyses were carried out using the SPSS 24.0 program. Analysis of variance (ANOVA) and test of homogeneity of variance were performed using LSD’s and Dunnett’s T3 tests.
3. Results and discussion

3.1 Soil and carbon foam characterization

The electrical conductivity (EC), pH and Hg content in the soils (A, S and T) and carbon foams (CF and CFGo) are shown in Table 1. The three soils showed pH values ranging from 6.8 to 7.8. It is remarkable the high concentrations of Hg in S and T soils which exceed the maximum levels permitted by regional [35] and international regulations [36, 37]. In the case of the A soil, the mercury concentration is lower than the limit set for industrial soils, although it is higher than that for soils reserved for recreational purposes, residential or for other uses. Therefore, these soils pose a high environmental risk.

Table 1. Electrical conductivity, pH and Hg content in the soils and carbon foams studied.

|     | pH    | EC (dS m\(^{-1}\)) | Hg (mg kg\(^{-1}\)) |
|-----|-------|---------------------|---------------------|
| A   | 7.8±0.0 | 0.18±0.00          | 18.0±0.9            |
| S   | 7.7±0.0 | 0.46±0.00          | 1251±5              |
| T   | 6.8±0.0 | 0.15±0.00          | 1361±94             |
| CF  | 2.7±0.0 | 1.17±0.02          | <DL                 |
| CFGo| 4.2±0.0 | 0.76±0.00          | <DL                 |

DL: detection limit

Figure 1 shows two SEM images of the carbon foam before and after impregnation with goethite (FeO(OH)). The analysis of CFGo by SEM (Figure 1b) and XRD (Figure S1) revealed the presence of FeO(OH) in the form of nanoneedles homogeneously distributed on the surface of the carbon foam. The impregnation with FeO(OH) moderated the CF original pH and EC values (Table 1).
Figure 1. SEM images of a) CF and b) CFGo.

The analysis by TPD showed a greater number of phenol and/or ethers groups, represented by the peak between 600-800 °C in the CO curve and carbonyl and quinone groups (desorption peak around 800-900 °C) in CFGo than non-impregnated CF foam (Figure S2). The presence of carboxylic acid-type groups was also observed according to the desorption of CO$_2$ around 200-400 °C (Figure S2).

3.2 Evaluation of Hg mobility

Figure 2 shows the results of TCLP tests for soils before and after treatment with nZVI, CF and CFGo. The three treatments reduced Hg leachability except for A soil treated with nZVI. This exception is likely due to the pH increase after nZVI treatment (Figure 2a), since it is well known that pH is one of the most important factors affecting the Hg mobility [38, 39].
Figure 2. Mercury concentration and pH in TCLP extracts with the three treatments applied to a) A soil, b) S soil and c) T soil.

It is generally supposed that the retention of Hg by nZVI is due to its chemical reduction and precipitation. The interaction between Hg and Fe has been observed within the nanoparticles and suggest an underlying mechanism for Hg$^{2+}$ reduction of to Hg$^0$ [40]. This process would be favored by the different standard redox potential of Hg (E$^{0} =$ 0.86V) and Fe (E$^{0} =$ $-$0.44 V), which makes Hg reduction thermodynamically favorable ($\Delta E(0) =$ 1.30 V) [40]. In the case of the treatments with carbon foams, even in the absence of goethite, the leachability of Hg is reduced in all soils and the Hg concentration drops below the detection limits of the technique of analysis in the case of soil A. With the aim to understand the retention of Hg by both carbon foams a detailed study of Hg speciation has been carried out with these materials.

3.3 Evaluation of Hg speciation.
The analysis of Hg speciation by HgTPD (Figure 3) revealed that the main mercury species present before and after treatment with both carbon foams were Hg-HA and HgS, whose range of decomposition is from 100 to 300°C according to mercury standard profiles (Figure 3d). However, some differences are observed in the profiles depending on the soil and amendment.

**Figure 3.** Mercury thermal profiles of soils before and after treatment with the carbon foams for (a) A soil, (b) S soil and (c) T soil, and (d) mercury pure compounds (Hg\(^0\), HgCl\(_2\), HgS, Hg-HA and HgO).

When the soils are treated with the carbon foams the profiles are wider and have maximum desorption peaks at temperatures slightly higher than the untreated soils, suggesting a change of mercury speciation due to treatment. Figure S3 shows the deconvolution of the thermal profiles for the original soils and after be treated with the carbon foam impregnated with goethite. The overlapping of peaks corresponding to the
main mercury species present in the raw soils, HgS and Hg-HA, is clearly observed. However, the distribution of these mercury species is different in the soils treated with the CFGo (Figure S3). Humic acids, one of the main components of soil organic matter, contain different functional groups. The complex structure of HA is dynamic depending on environmental conditions such as pH or ionic strength, which determine the mobility of certain contaminants and trace metals. HA contains different size fractions with different mobility that affects the bioavailability of pollutants in different ways [39, 41]. Alkaline conditions were found to promote the disaggregation of HA particles, causing greater mobility of pollutants [39]. This suggests that the very low Hg leachability observed when soils are treated with carbon foam (Figure 2) is the consequence of the decrease in pH values (Figure 2), which leads to a change in the HA structure and that, in turn, affects Hg-HA mobility.

In order to further test this proposed mechanism, a speciation study was carried out in soils using two sequential extraction methods. Figure 4 shows the results obtained by the USEPA Method 3200 (left column) and the Tessier method (right column), in the untreated and treated soils.
Figure 4. Mercury fractionation following the USEPA Method 3200 (M: Mobile Hg, SM: Semi-mobile Hg, NM: Non-mobile Hg) (left column) and the Tessier Method (EX: Exchangeable Hg, CB: Hg bound to carbonates, OX: Hg bound to Fe-Mn oxides, OM: Hg bound to organic matter, RS: residual Hg) (right column) in soils before and after treatment with the carbon foams for (a) A soil, (b) S soil and (c) T soil.

Most of the mercury in the original and treated soils was extracted from the SM fraction (Figure 4), which is consistent with the occurrence of mercury in Hg$^{2+}$ complexes or amalgamates [31]. Mercury is also found in the NM fraction in the form of mercury stable compounds like HgS in all the soils. It is notable that semi-mobile Hg decreased in soils after being treated with carbon foams while non-mobile Hg increased, which would lead to lower leachability in treated soils (Figure 2). These results agree with those
inferred by the study carried out by HgTPD, which reflected a change in the thermal profiles in the soils after being treated with carbon foams (Figure 3).

Similar conclusions were drawn from Tessier sequential extraction results (Figure 4). A common pattern of Hg distribution was observed in the three soils after the treatment with the carbon foams, decreasing the mercury bound to organic matter, notably humic and fulvic acids (OM fraction), and increasing the mercury residual (RS fraction). The concentration of Hg in the non-available RS fraction was significantly increased after treatment with both carbon foams, especially in the case of A and T soils, reaching 80 and 65%, respectively.

The results obtained by both methods and HgTPD procedure show good agreement for the untreated and treated soils. The occurrence of HgS in all the soils, identified by the peak between 100-200°C in the desorption thermograms, was confirmed by the mercury extracted in the NM and RS fractions. The presence of mercury complexed by humid acids identified by thermal desorption at 100-300°C was confirmed by the extraction of mercury from the SM and OM fractions. The lower mobility of Hg after treatment with carbon foams (Figure 2) was also confirmed by the higher concentration of Hg extracted in the NM and RS fractions and the thermal profiles that are wider and with a maximum desorption peak at slightly higher temperatures as a consequence of the change in the HA structure, which leads to a lower availability of Hg-HA species (Figure 3).

3.4 Impact on the pH, EC and Fe availability.

To determine the impact of carbon foams on soil properties and compare it with the effects of nZVI, pH, EC and Fe concentration were measured (Figure 2 and 5). As was previously mentioned, the application of nZVI hardly affected the pH of the soils with the exception of A soil in which the pH increased. However, the treatment with the carbon
foams led to a pH decrease, especially in the case of CF (Figure 2). A lower pH enhances the immobilization of Hg.

All the amendments increased soil EC values (Figure 5), but CF induced the highest change, ranging from 0.2, 0.4 and 0.1 to 1.9, 2.9 and 2.2 dS m\(^{-1}\) in A, S and T soils, respectively. It is noteworthy that when this CF is impregnated with goethite there is a more moderate increase in the EC values. This fact should be taken into account in relation to soil functionality and the possible damage to its biological activity and plant development.

**Figure 5.** Iron concentration and EC value in TCLP extracts after application of the three treatments to a) A soil, b) S soil and c) T soil.

When treatment impact on Fe availability was studied (Figure 5), it was observed that the application of nZVI led to an increase in Fe leaching while the treatment with both carbon foams favored Fe immobility. The application of nZVI and the subsequent increase in Fe availability was found as due to the diffusion of nZVI that are not retained
in the soil, forming complexes with other elements [25]. However, the presence of certain
surface groups in the foams could favor the decrease of available Fe [42]. It was observed
that functional groups such as carboxylic and phenol groups, which are negatively
charged in a pH range of 4 to 8 and were identified in the carbon foams by TPD (Figure
S2), can bind metal cations strongly [43].

4. Conclusions

A novel carbon foam-based amendment was efficient in immobilizing Hg in all the
soils studied. The main species present in soils were HgS and Hg-HA, the latter being the
one that determined the percentage of mobility and availability of Hg when soils were
treated with the carbon foams. When the pH dropped, the structure of humic acid changed
causing the Hg-HA species to become part of the unavailable fraction of the soil along
with HgS. These results were confirmed by mercury desorption technique at programmed
temperature and sequential extraction. The carbon foam impregnated with goethite, in
addition to not mobilizing Fe, presented the additional advantage of its lesser effect on
the soil’s electrical conductivity. Furthermore, this type of amendment could also be used
for the remediation of soils contaminated with other metals.

Abbreviations

AMA; Advanced Mercury Analyzer.

°C; Celsius degrees.

CB; Fraction bound to carbonates.

CSIC; Consejo Superior de Investigaciones Científicas. (Spanish National Research
Council).

DL; Detection limit
dS; DeciSiemens
EC; Electrical conductivity
EX; Fraction exchangeable.
EXAFS; Extended X-ray Absorption Fine Structure
g; Grams
h; Hour
Hg⁰; Elemental gaseous mercury.
Hg²⁺; Oxidized mercury
HA; Humic acid
HgTPD; Mercury Temperature Programmed Desorption.
INDUROT; Institute of natural Resources and Territorial Planning (University of Oviedo).
kg; Kilogram
kHz; KiloHertz
L; Liter
µg; Microgram.
m; Meter
M; Mobile
mg; Miligram
min; Minutes.
ml; Milliliter.
mm; Millimeter.
NBS; Natural-based solutions
NM; No mobile
nZVI; Zero valence iron nanoparticles
OM: Fraction bound to organic-matter.

OX: Fraction bound to Fe and Mn oxides.

rpm: Revolutions per minute

RS: Residual fraction

SEM: Scanning Electron Microscope

SM: Semi-mobile

T: Temperature

TPD: Temperature Programmed Desorption.

TCLP: Toxicity characterization leaching procedure

UNEP: United Nations Environmental Program.

USEPA: United States Environmental Protection Agency

V: Volt

% w/w: Weigh percentage.

XANES: X-ray Absorption Near Edge Structure

XRD: X-ray diffraction.

Declarations

Ethics approval and consent to participate
Not applicable

Consent for publication
Not applicable

Availability of data and material
The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests
The authors declare that they have no competing interests

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**Authors' contributions**

IJ-T: Conceptualization, Investigation. MAL-A: Writing (original draft)- Review & Editing, Supervision. Project administration. DB: Resources, statistical analysis and interpretation. CA-N: Investigation. ER: Investigation. AIP: Writing - Review & Editing, Supervision. JRG: Writing - Review & Editing, funding acquisition. MRM-T Writing - Review & Editing, funding acquisition

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