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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 in nature and is much more persistent in soils than in other environmental compartments. However, an effective, environmentally friendly, economical, and large-scale applicable 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 carbon foams, one of them impregnated with goethite, reduced Hg availability by 75–100%. The proportion of mercury associated to humic acids (Hg–HA) determined the mobility and the availability of Hg when soils were treated with carbon foams. The drop of pH promotes changes in the structure of HA, a consequence of which is that Hg–HA becomes part of the unavailable fraction of the soil along with HgS. The carbon foam impregnated with goethite did not mobilize Fe as occurred with zero valence iron nanoparticles. The presence of acidic groups on the surface of the foam (carboxyl, quinone and phenolic groups) can strongly improve the binding of metal cations, enhancing 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 low effect on the electrical conductivity of the soil. This novel approach could be considered as a potential amendment for other industrial and/or abandoned mining areas contaminated with Hg and/or other metal(loid)s.

Keywords: Bioavailability, Soil remediation, Carbon foams, Goethite, Mercury speciation

Background

Mercury is a recognized neurotoxic metal that can seriously affect 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, which considers aspects such as mercury waste, polluted sites and industrial emissions

[1]. This agreement highlights the necessity of innovative approaches and technology transfer in relation 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 reservoirs, 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/

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solidification, nanotechnology, thermal treatment, and biological treatments such as phytoremediation and bioremediation [4–6]. The effectiveness of each technology depends on several soil characteristics, so a thorough site assessment must be performed prior to the 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 practices, 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 physical–chemical Hg immobilization techniques can minimize health risks by reducing the bio-availability of Hg [12], while improving 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 Hg⁰ 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. With these objectives in mind, this study proposes the development of a new amendment that combines the good results of Hg immobilization achieved with other materials [14] and with Fe nanoparticles [11], while avoiding possible environmental risks caused with the latter [17].

The mobility of Hg depends on its chemical speciation, which is a function of several soil parameters and their interactions. In addition, information about the mercury species present in the soils is essential to establish an effective remediation methodology. Mercury speciation analyses require very sensitive techniques that preserve the integrity of the species during sampling and over the entire 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 programmed thermal desorption [22]. The main drawback of sequential extraction is the impossibility of distinguishing all Hg species as they are selectively distributed by groups. EXAFS and XANES, on the other hand, present the disadvantage of high detection limits, which make them useful only for very highly contaminated samples; in addition, they require complex equipment with difficult access. Programmed thermal desorption does not require the use of reagents, is direct and fast and has very low detection limits; in some cases, however, its selectivity is limited by peaks overlapping, which prevents the reliable identification of some Hg species. In the present work, direct and indirect methods are used in a complementary manner, in order to identify mercury species in soils, 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 that can favor the nanodispersion of iron species on their surface, when they are provided with microporous texture. Furthermore, these materials can be modified for an improved performance. For example, if loaded with goethite, which has a structure more prone to complex with cations than other Fe compounds [24], they could achieve a more efficient immobilization of contaminants such as As [25], reducing the risks associated with the application of alternative Fe-based amendments. Consequently, in this work, the development of a carbon foam impregnated with goethite is contemplated as an attractive and novel solution to be used as a soil amendment for multi-contaminated soils.

This study provides a demonstration that carbon foams impregnated with goethite can be used as a 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.

Experimental

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 two abandoned Hg mining-metallurgy sites (S and T soils) and an industrial area (A soil). Soil S was sampled in La Soterraña

mine, and it is classified as sandy loam, revealing slightly alkaline pH [26]. The other mining soil (T), was taken in El Terronal mine. This soil is also slightly alkaline and it reveals a silt loam texture [27]. Mercury mining and processing activities are generally characterized by an abundance of Hg in the emissions and waste generated, thus both studied mining soils are appropriate for this work. Finally, the industrial soil (A) was taken in the surrounding of a Zn smelter located in Avilés (north Spain). This third soil is also alkaline, but the texture is clearly sandy [28]. The influence of multiple pollution sources, such as metallurgical dust, slags, and other wastes disposed in this site, has a dramatic effect on quality of soil.

Soil amendments

The following materials were used as amendments:

- nZVI. These nanoparticles were supplied by NANO IRON s.r.o (Czech Republic) as NANO FER 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 a microporous carbon foam using a coal as precursor has been described elsewhere [29]. In brief, a green carbon foam is synthesized 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 is carbonized under an Ar flow of 100 mL min^{-1} , at 500 °C and washed to remove inorganic salts. The final carbon foam was ground and sieved in the range of 0.2–0.5 mm.
- Carbon foam impregnated with goethite (CFGo). The carbon foam previously obtained, was impregnated with a solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and CH_3COONa in water, with the following proportions: 1.5 g CF / 0,28 g FeSO_4 / 0,4 g CH_3COONa / 5 mL H_2O . The suspension of the carbon foam was shaken in an ultrasonic bath for 1 h at 40 kHz and then heated under reflux for 2 h. 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 ($\text{FeO}(\text{OH})$) on the surface of the carbon foam.

Soil analysis and carbon foam characterization

Electrical conductivity (EC) and pH were measured to evaluate the influence of the amendment application on soil properties in a suspension of soil (1 g) and Milli-Q water (2.5 mL). The functional groups present on the surface of the carbon foams were identified by temperature

programmed desorption (TPD): the oxygenated groups decompose mainly into CO and CO_2 , which are released at temperatures that can be related to the type of functional group of origin [30, 31]. 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 the solid and liquid samples was directly determined using an automatic mercury analyzer AMA 254.

Soil treatment

Subsamples of polluted soils (20 g) were treated in 50-mL vials maintaining the proportion of 20% of amendment and 80% of soil, i.e., 16 g soil and 4 g carbon foam. 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, 32]. 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. Finally, the treated soils were air dried.

Leaching test

The mobility of Hg in the untreated 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 $\text{CH}_3\text{COOH}/\text{NaOH}$ at $\text{pH } 4.93 \pm 0.05$. 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 4 °C. The liquids were then analyzed for Hg as described in Sect. 2.3.

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 [33] and a simplified USEPA Method 3200 [34] 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 are obtained with the Tessier method: exchangeable (EX); bound to carbonates (CB); bound to Fe–Mn oxides (OX); bound to organic matter (OM) and residual (RS). In turn, the USEPA Method 3200 provides: mobile Hg (M), semi-mobile Hg (SM) and non-mobile Hg (NM). Hg concentrations were measured in the extracts using the AMA 254 analyser.

The study was completed with the identification of mercury species in the untreated and treated soils directly using a mercury temperature programmed desorption (HgTPD) device [35]. The device, previously

described [36], consists of a temperature-programmed 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 $50\text{ }^{\circ}\text{C min}^{-1}$. 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 Hg^0 , HgO and HgCl_2 .

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.

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

	pH	EC (dS m^{-1})	Hg (mg kg^{-1})	Soil texture
A	7.8 ± 0.0	0.18 ± 0.00	18.0 ± 0.9	Sandy [28]
S	7.7 ± 0.0	0.46 ± 0.00	1251 ± 5	Sandy loam [26]
T	6.8 ± 0.0	0.15 ± 0.00	1361 ± 94	Silt loam [27]
CF	2.7 ± 0.0	1.17 ± 0.02	< DL	
CFGo	4.2 ± 0.0	0.76 ± 0.00	< DL	

DL detection limit, CF carbon foam, CFGo carbon foam impregnated with goethite

Results and discussion

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 soil texture is also shown in Table 1. The three soils showed pH values ranging from 6.8 to 7.8. The remarkable high concentrations of Hg in S and T soils exceeded the maximum levels permitted by regional [37] and international regulations [38, 39]. 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 of soils reserved for recreational purposes, residential or other uses. Therefore, these soils pose a high environmental risk.

Figure 1 shows two SEM images of the carbon foam before and after impregnation with goethite ($\text{FeO}(\text{OH})$). Among other properties, these carbon foams possess a combined macro- and microporous structure that favors the adsorption process (Additional file 1: Table S1). The analysis of CFGo by SEM (Fig. 1b) and XRD (Additional file 1: Figure S1) revealed the presence of $\text{FeO}(\text{OH})$ in the form of nanoneedles homogeneously distributed on the surface of the carbon foam. The impregnation with $\text{FeO}(\text{OH})$ moderated the carbon foam original pH and EC values (Table 1).

The analysis by TPD showed a greater number of phenol and/or ether groups, represented by the peak arising at $600\text{--}800\text{ }^{\circ}\text{C}$ in the CO curve, and carbonyl and quinone groups (desorption peak around $800\text{--}900\text{ }^{\circ}\text{C}$) in CFGo than in non-impregnated CF (Additional file 1: Figure S2). The presence of carboxylic acid-type groups

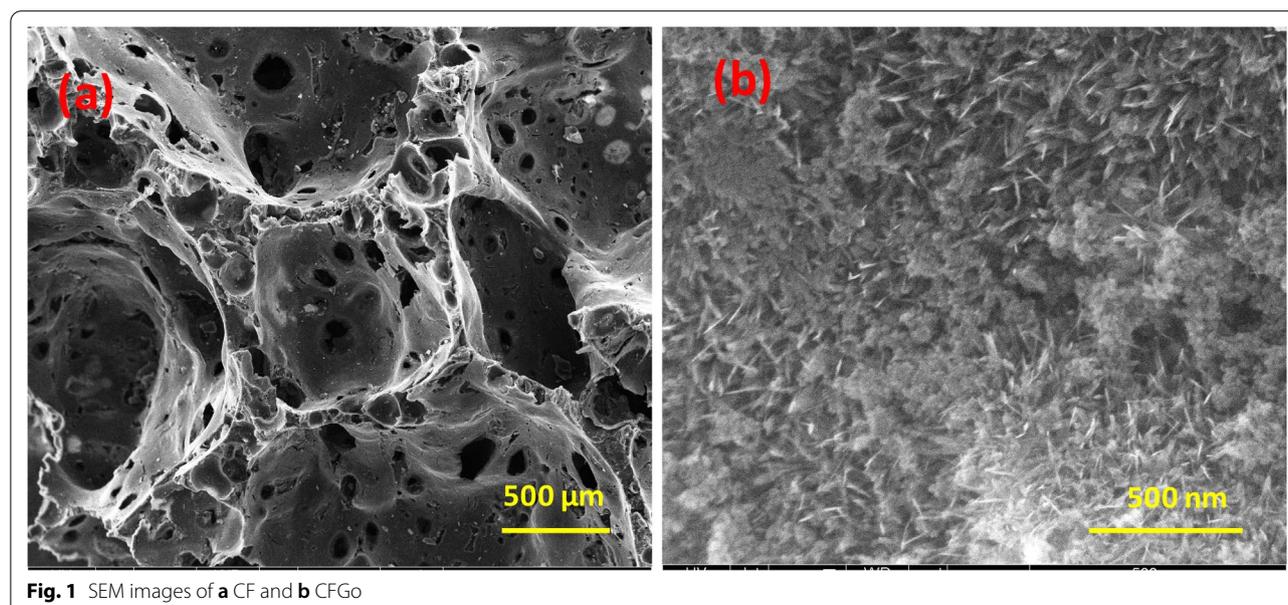


Fig. 1 SEM images of a CF and b CFGo

was also observed, according to the desorption of CO₂ around 200–400 °C (Additional file 1: Figure S2).

Evaluation of Hg mobility

Figure 2 shows the results of TCLP tests for soils before and after the 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 (Fig. 2a), since it is well known that pH is one of the most important factors affecting Hg mobility [40, 41].

It is generally assumed 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 reduction mechanism of Hg²⁺ to Hg⁰ is suggested [42]. This process would be favored by the different standard redox potential of Hg (E₀=0.86 V) and Fe (E₀= -0.44 V), which makes Hg reduction thermodynamically favorable ($\Delta E(0)=1.30$ V) [42]. 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 Hg concentration drops below the detection limits of the automatic mercury analyzer AMA 254 in the case of soil A. It should be taken into account the role that dissolved organic matter plays in the adsorption of Hg by solid sorbents in aqueous phase and that it could justify the differences observed in the soil studied (Fig. 2).

In fact, several studies have found that an increase in dissolved organic matter can decrease Hg adsorption by activated carbons and other carbonaceous materials [43, 44], due to a competitive reaction between Hg(II) and the dissolved organic matter. Although it is beyond the scope of this study, partition coefficients and adsorption capacities should be taking into account, considering the specific characteristics of each site to be remediated by carbon foams. With the aim of understanding the retention of Hg by both carbon foams, a detailed study of Hg speciation was carried out with these materials.

Evaluation of Hg speciation.

The analysis of Hg speciation by HgTPD (Fig. 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 (Fig. 3d). However, some differences are observed in the profiles depending on the soil and the amendment.

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 derived from the treatment. Additional file 1: Figure S3 shows the deconvolution of the thermal profiles for the original soils and after being treated with the carbon foam

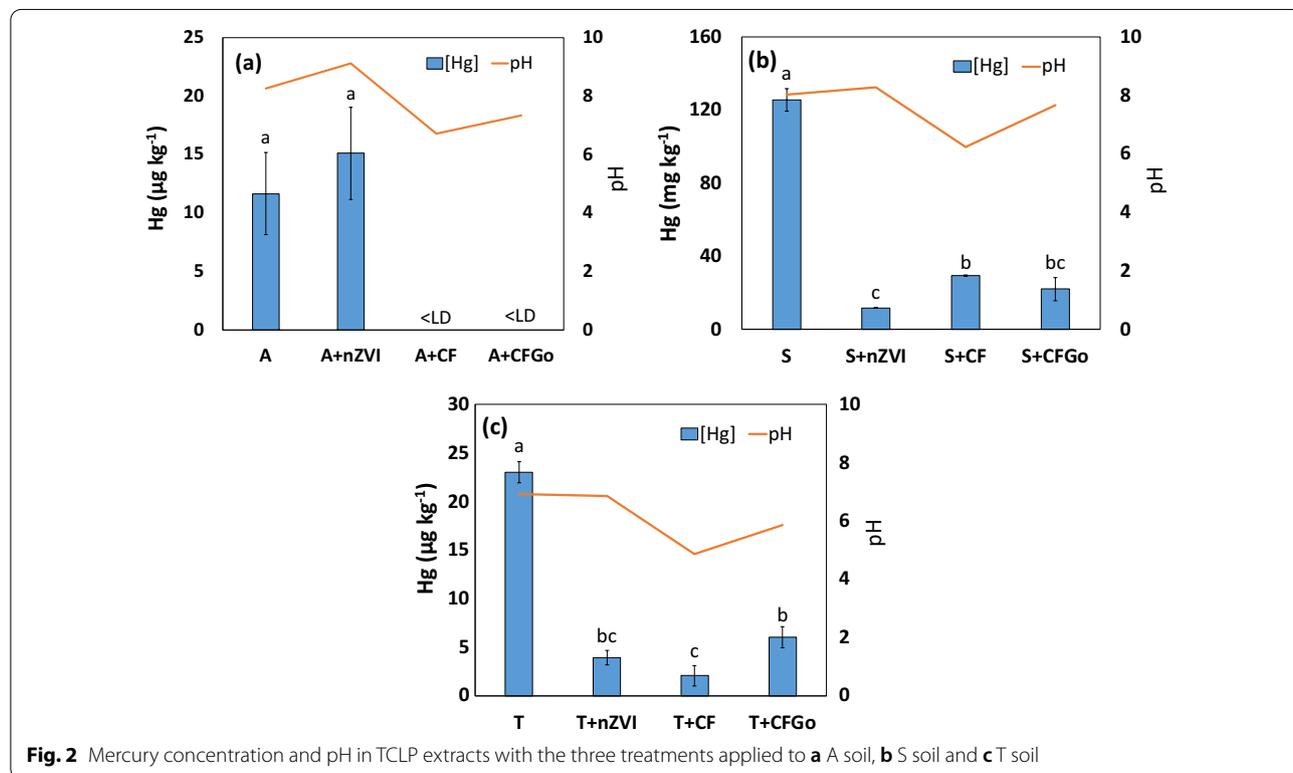
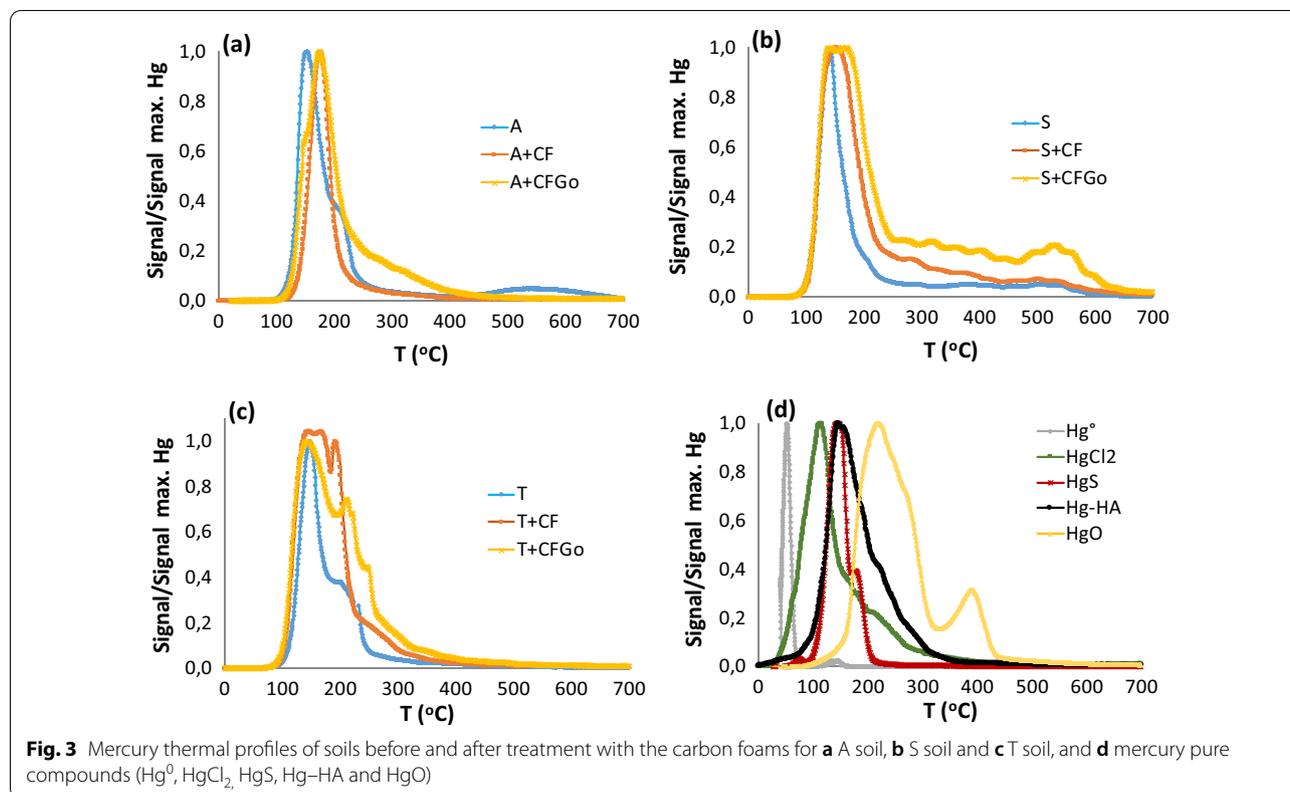


Fig. 2 Mercury concentration and pH in TCLP extracts with the three treatments applied to **a** A soil, **b** S soil and **c** T soil

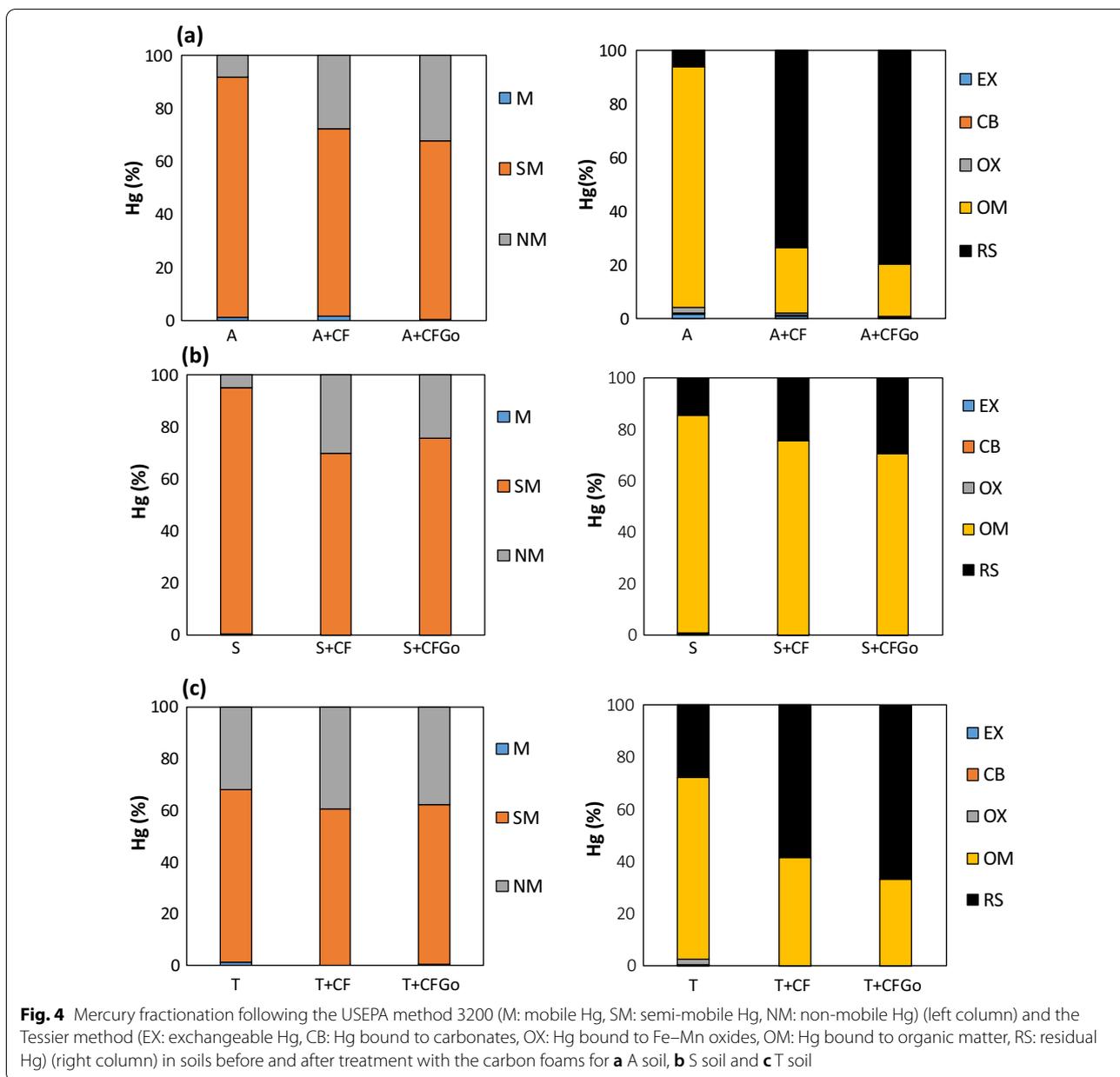


impregnated with goethite. The overlapping of peaks corresponding to the main mercury species present in the raw soils, HgS and Hg-HA , are clearly observed. However, the distribution of these mercury species is different in the soils treated with CFGo (Additional file 1: Figure S3). The deconvolution of the desorption profile shows a slight shift in the second peak (green line) towards higher desorption temperatures in the soils treated with CFGo, suggesting the presence of stable Hg compounds such as Hg-HA or HgS . It should also be noted that HgS thermal profiles tend to have more standard deviation than other mercury species due to the different sizes of cinnabar crystals, which can vary depending on the soils. This fact is also reflected in the thermal profile of the soil (Additional file 1: Figure S3). Humic acids, one of the main components of soil organic matter, contain different functional groups. The complex structure of HA is dynamically dependent 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 [41, 45]. Alkaline conditions were found to promote the disaggregation of HA particles, causing a greater mobility of pollutants [41]. This suggests that the very low Hg leachability observed

when soils are treated with the carbon foam (Fig. 2) is a consequence of the decrease in pH values (Fig. 2), which leads to a change in the HA structure and a concomitant variation of Hg-HA mobility.

Because HgTPD provides information on thermally related binding strength but does not estimate the mobility of Hg in the liquid phase, a speciation study in soils was carried out using two sequential extraction methods to confirm the proposed mechanism. 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.

Although it is well known that sequential extraction methods have as their main drawback the lack of selectivity and efficiency of each step of the procedure [46], the results showed that most of the mercury in the original and treated soils was extracted from the SM fraction (Fig. 4), which is consistent with the occurrence of mercury in Hg^{2+} complexes or amalgamates [33]. Mercury is also found in the NM fraction in the form of mercury stable compounds like HgS in all the soils. It is noteworthy that semi-mobile Hg decreased in soils after being treated with carbon foams, while non-mobile Hg increased, which implies lower leachability in treated soils (Fig. 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 (Fig. 3).

Similar conclusions were drawn from Tessier sequential extraction results (Fig. 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. Possible changes

in Hg bonding during the extraction procedure cannot be ruled out, i.e., part of the Hg found in the residual fraction is in the form of Hg–HA that was not extracted in the previous steps.

Although the duration of the leaching steps or the concentrations of the reagents would be taken into account, depending on the properties of the soil and the Hg content [47, 48], the results obtained by both methods and HgTPD procedure show good agreement for the untreated and treated soils. The presence of mercury complexed by humic acids identified by thermal desorption at 100–300°C was confirmed by the extraction of

mercury from the SM and OM fractions. However, the presence of HgS in the soil treated with CFGo, which could be expected from the higher percentage of Hg found in the NM and RS fractions could not be confirmed by HgTPD. Nevertheless, the lower mobility of Hg after treatment with carbon foams (Fig. 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 (Fig. 3).

Impact on the pH and EC of soil and on 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 (Figs. 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 (Fig. 2). A lower pH enhances the immobilization of Hg.

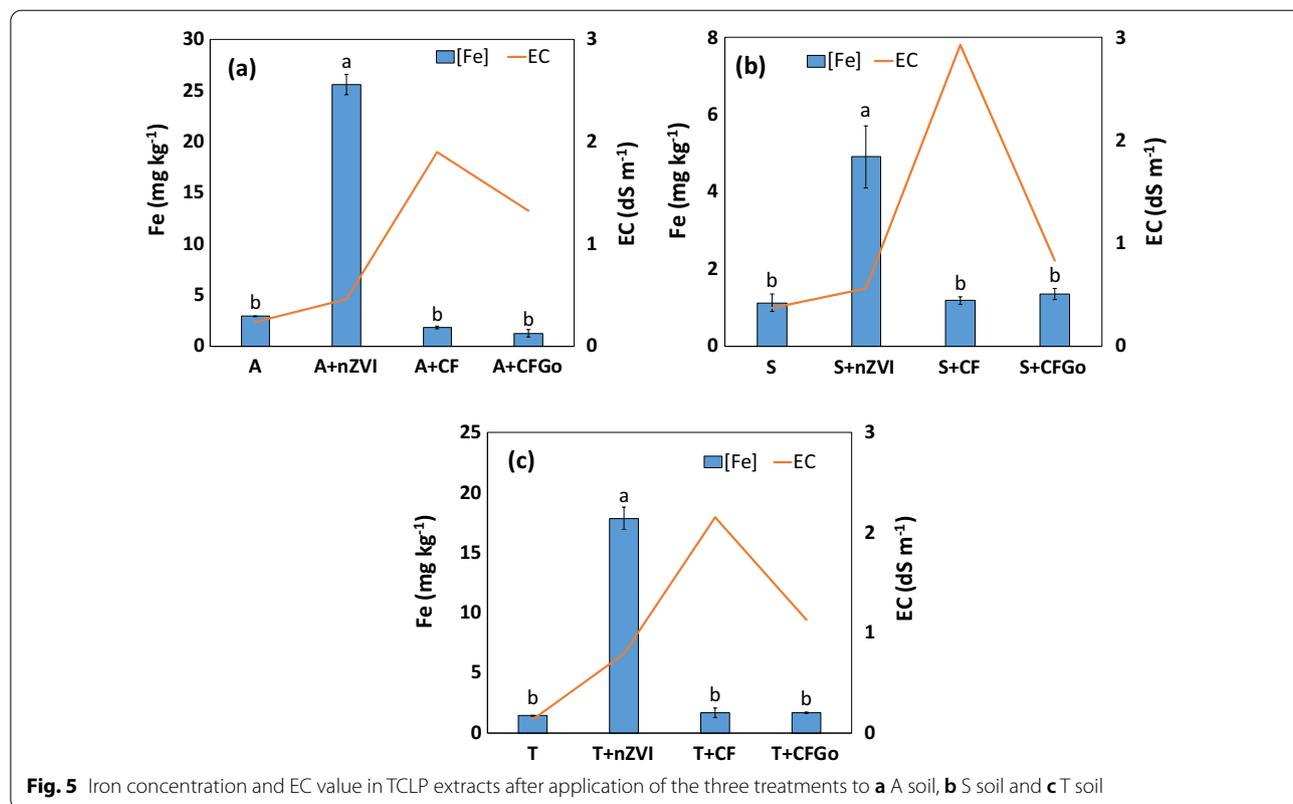
All the amendments increased soil EC values (Fig. 5), but CF induced the highest change, ranging from 0.2, 0.4 and 0.1 to 1.9, 2.9 and 2.2 dS m⁻¹ in A, S and T soils,

respectively. It is noteworthy that when 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.

When treatment impact on Fe availability was studied (Fig. 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 to be 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 [49]. It was observed that functional groups such as carboxylic and phenolic, which are negatively charged in a pH range of 4 to 8 and were identified in the carbon foams by TPD (Additional file 1: Figure S2), can bind metal cations strongly [50].

Conclusions

A novel carbon foam-based amendment was efficient in immobilizing Hg in all the soils studied. The methods used in this study allowed estimating the main form of Hg binding in the studied soils. 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. The carbon foam impregnated with goethite, in addition to not mobilizing Fe, presented the additional advantage of its lesser effect on the soil electrical conductivity. Furthermore, this type of amendment could also be used for the remediation of soils of similar characteristics (neutral or slightly alkaline), mainly from industrial and abandoned mining areas, contaminated with other metal(loid)s.

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: Milligram; 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.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s12302-021-00569-w>.

Additional file 1: **Table S1.** General and textural properties of the carbon foams. **Figure S1.** XRD pattern of the carbon foam impregnated with goethite (CFGo). The major peaks at 2θ values of 20.8°, 33.2°, 35.6°, 36.7°, 54° and 59.2° are assigned to the primary peaks of the goethite (FeO(OH)). The wider band between 20 and 30° corresponds to disordered carbon. The mineral matter of carbon foam is reflected by the peak at 26° (SiO₂). **Figure S2.** TPD profiles of CO and CO₂ evolution in (a) CF and (b) CFGo. **Figure S3.** Deconvolution carried out with the Origin program for mercury thermal profiles of untreated and treated A, S and T soils.

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Authors' contributions

IJ-T: conceptualization, investigation. MAL-A: writing (original draft) (review and editing), supervision, project administration. DB: resources, statistical analysis and interpretation. CA-N: investigation. ER: investigation. AIP: writing (review and editing), supervision. JRG: writing (review and editing), funding acquisition. MRM-T: writing (review and editing), funding acquisition.

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Availability of data and materials

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

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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