Unravelling remediation processes after six years of nanoscale zero-valent iron application to arsenic and mercury-polluted soil under field conditions

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INTRODUCTION

Soil pollution is a global concern due to its importance for human survival and development. A common issue is the release of metal(loid)s, like As or Hg, from human activity to the soil, which can accumulate and pose health risks to organisms. Therefore, several remediation techniques have been developed, such as nanoremediation, which consists of the application of nanoparticles to the soil for immobilizing the pollutants (Díaz et al., 2023). One of the most extended nanomaterials is nanoscale zero-valent Fe (nZVI), which was revealed as an outstanding amendment for As and Hg immobilization due to its specific surface area (Baragaño et al., 2022). However, the long-term effects and mechanisms of nZVI transformation are not well understood, as most studies are performed in controlled conditions. In this context, our work was focused on deciphering the immobilization mechanisms after six years of nZVI application in an As and Hg polluted soil under field conditions.

METHODOLOGY

Site description and pilot experiment

The study was conducted in El Terronal mine, located in Asturias, north Spain. The soils in the area were affected by mining and metallurgical activities until the closure of the mine in the 1970s. The main pollutants in the soils are As and Hg, due to the dispersion of dust, mineral transport and smelting waste disposal. In 2016, this site was selected for the first time application of nanoscale zero-valent iron for remediating As and Hg polluted soils (Gil-Díaz et al., 2019). Soil properties are: pH=7; 3.3 wt% organic matter content; 3.5 wt% Fe content; 1 wt% As content and 0.15 wt% Hg content. The monitorization of the remediation approach revealed through leaching tests that the As and Hg mobility was severely decreased (74% and 86%, respectively) after 72 hours, and this effect was maintained along time for 32 months. After 6 years of nZVI application, new soil samples were taken for analysis. The first soil sample was collected from the polluted site, in the control area where the nZVI was not added. The second one was sampled in the treated soil where nZVI was applied at the dose of 5 wt%.

Synchrotron analysis

To determine the effects of nZVI on As speciation, soil samples were sieved (2 mm) and then embedded in epoxy resin to perform analysis on the polish surface at the NANOSCOPIUM beamline (SOLEIL synchrotron). First, nano-XRF analysis was used to map As, Hg and Fe; then, nano-XANES spectra collection was performed at the As K-edge (11.867 keV) on the As hotspots identified during the mapping to identify the As speciation, using commercial patterns to discriminate between As(III) and As(V). In order to evaluate the Hg speciation changes in the soil after nZVI application, soil samples were prepared as pellets of finely ground and homogenized powder. A set of reference compounds were also prepared as pellets: HgO, cinnabar (HgS), metacinnabar (HgS), $HgCl_2$,

$HgSO_4$, corderoite ($Hg_3S_2Cl_2$), Hg complexed to humic acid, and Hg adsorbed to goethite. The Hg LIII-edge spectra XANES were collected at 70-80 K on CLAESS beamline (ALBA synchrotron).

RESULTS AND DISCUSSION

The nano-XRF technique has enabled the determination of the As distribution in the soils, revealing two different types of As-bearing particles in the nZVI-treated soil. First, As-enriched particles without the presence of Fe have been identified, corresponding to As oxides, which are the mainly mining waste generated in the site. On the other hand, As-enriched particles corresponding to Fe oxides have been found, although As is distributed on their surface. The morphology of these aggregates differs from other major morphologies of Fe oxides found in the control soil (Fig. 1a), suggesting that they may correspond to those Fe phases originated from the oxidation of nZVI. The XANES analysis revealed the predominant presence of As(V) in both, treated and untreated soils. However, in the Fe oxide particles originated from nZVI oxidation, not only As(V) but also As(III) has been detected. Therefore, it is suggested that the main mechanism for As immobilization is the sorption of As(V) onto the surface of Fe phases originated in the soil, although the presence of As(III) indicates that oxidation-reduction process also occurred.

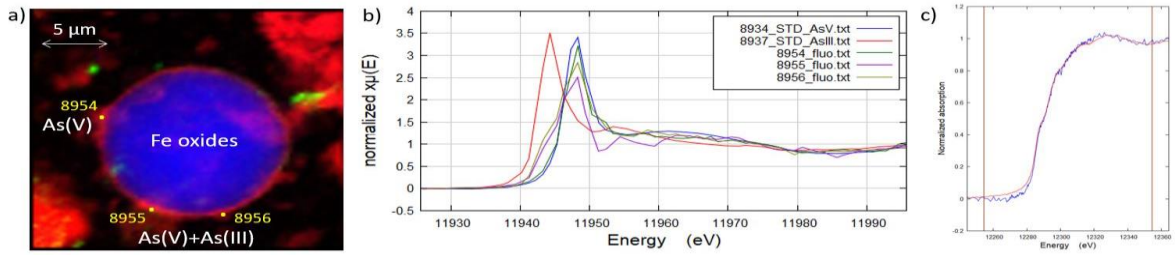

Fig 1*. (a) Nano-XRF mapping of As (red), Hg (green) and Fe (blue) revealed an Fe oxide particle originated from nZVI oxidation in the treated soil. (b) Nano-XAS spectra of As patterns (As(III) and As(V)) and points located in soil revealed the presence of As(V) and As(III). (c) Hg LIII-edge spectra XANES of treated soil and the Linear Combination Fits (LCF).*

The Hg LIII-edge spectra XANES, shown in Fig. 1c, and the Linear Combination Fits (LCF) demonstrated that the Hg solid speciation in the treated and untreated soil samples is mainly dominated by cinnabar, metacinnabar, and Hg adsorbed to goethite. No differences were found between samples.

CONCLUSIONS

The mobility of As and Hg is associated with only a small fraction of the total concentration of these elements in the soil. As a result, the effects of the immobilization processes on the As and Hg speciation could not be fully observed due to the resolution limitations. Nevertheless, the immobilization process of As was successfully characterized due to the spatial resolution analysis. Conversely, the results of Hg analysis did not revealed changes on Hg speciation, although, a High-Resolution XANES could allow us to decipher the minor Hg species with a better resolution.

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