



A nanoremediation strategy for the recovery of an As-polluted soil



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HIGHLIGHTS

- The use of nZVI to remediate a highly As-polluted brownfield is reported.
- nZVI reduced the As availability in the brownfield soil.
- Barley plants from nZVI-treated soils showed better development and lower As uptake.
- The Fe absorption by plants grown in nZVI-treated soils was not favored.

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ABSTRACT

The present study investigates the impact of the nanoremediation treatment on soil recovery as evaluated by the development of barley plants. Highly As-polluted brownfield soil was treated with nanoscale zero-valent iron (nZVI) commercial suspension at two doses (1% and 10%). Barley plants were cultivated in treated and untreated soils in a growth chamber, and the As, Fe, and nutrients uptake were determined. The efficacy of As immobilization was evaluated according to the toxicity characteristics leaching procedure (TCLP) as well as using a sequential extraction procedure. The application of nZVI reduced the amount of As in the more available fractions and increased the amount of As in the residual fraction. The best immobilization results were obtained for the highest dose of nZVI (10%). In turn, the lower availability of As in nZVI-treated soils, particularly at the dose of 10%, stimulated the development of the barley plants and decreased the As uptake. Neither an important increase of available Fe nor negative impact on soil physico-chemical and biological properties were observed. Thus, our results show that the use of nZVI could be an adequate strategy to recover the land use in As polluted soils.

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1. Introduction

Arsenic can have natural origins or anthropogenic sources such as mining, burning of coal, smelting of non-ferrous metals, and from pesticides used in agriculture (Ruiz-Chancho et al., 2007). It is a metalloid highly toxic to the biota and it is well-known to cause chronic toxicological and carcinogenic effects to humans (Zhang and Selim 2008; Hopkins et al., 2009). Consequently, remediation of As-polluted sites has become a priority. Some traditional remediation techniques, including excavation and landfilling, are environmentally disruptive and cost prohibitive (Kumpiene et al., 2008; Houben et al., 2012).

The availability and mobility of As in soils depend on their characteristics, such as pH, redox potential, Fe oxides, phosphorus, salts, organic matter, and clays (Zhang and Selim 2008; Moreno-Jiménez et al., 2012). The study of As fractionation within soils can provide useful information about its mobility, migration, and potential toxicity (Moreno-Jiménez et al., 2012). The As fraction retained in a labile form, within the soil matrix (soil and water) will be the most biologically active (bioavailable fraction) and the most mobile (soluble fraction) one, which can be potentially taken up by plant roots (Moreno-Jiménez et al., 2012). Immobilization techniques focus on reducing the mobile fraction of metal(loid)s in the soil, which may reach the groundwater or be taken up by plants or other soil organisms, but not on removing the pollutant from the soil (Kumpiene et al., 2008; González et al., 2012; Bolan et al., 2014). Thus, the effectiveness of the immobilization strategy should be monitored by measuring the amounts of mobile and bioavailable

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fractions (Kumpiene et al., 2006). Much of the research has focused on using iron oxides and their precursors, such as zero-valent iron and iron sulphates, for immobilization of As in polluted soils due to their important sorption properties (Kumpiene et al., 2006; Kim et al., 2003; Hartley and Lepp 2008; Kumpiene et al., 2008; Moreno-Jiménez et al., 2012; Komárek et al., 2013; Bagherifam et al., 2014). According to Komárek et al. (2013) the main stabilization mechanisms of As with iron oxides are adsorption and co-precipitation (Komárek et al., 2013).

Zero-valent iron is a good electron donor, acting as a precursor for iron oxides because of the spontaneous oxidation of Fe(0) in aqueous medium to Fe(II) and Fe(III). Recently, the development of nanoscale zero-valent iron (nZVI) particles has brought important benefits because of their very high surface area to weight ratio, resulting in higher reactivity rates than micron scale ZVI when normalized to mass (Wang and Zhang 1997; Kanel et al., 2005; O'Carroll et al., 2013). Zero valent iron nanoparticles have strong attractive interparticle forces, therefore they tend to agglomerate to micron size particles, which have limited mobility in porous media (O'Carroll et al., 2013). To avoid this difficulty, various polymers and other coatings have been included to stabilize the nZVI suspension (Karn et al., 2009; O'Carroll et al., 2013). The use of stabilized nZVI has been effective for degrading organic pollutants such as chlorinated organic compounds, and for immobilizing metal(loid)s (Li et al., 2006; Li and Zhang 2007; Karn et al., 2009; O'Carroll et al., 2013; Gil-Díaz et al., 2014a). Regarding As, recent reports have demonstrated that the use of ZVI or iron oxide nanoparticles is effective in water (Jegadeesan et al., 2005; Kanel et al., 2005, 2006; De et al., 2009) and soil samples (Zhang et al., 2010; Shipley et al., 2011; An and Zhao 2012; Gil-Díaz et al., 2014b). The reaction mechanisms between As and nZVI are not clear, and little data are available in soil samples. Kanel et al. (2005, 2006) in a study with solutions of As treated with nZVI, concluded that As(III) and As(V) can be removed within minutes using nZVI by inner-sphere surface complexation. The authors found that 25% of As(V) was reduced to As(III) by nZVI after 90 days. Ramos et al. (2009) observed that As(V) of a spiked solution treated with nZVI was reduced to As(III) and As(0) after 24 h. In the same experiment, reactions of nZVI with As(III) generated As(0), As(III) and As(V), indicating both reduction and oxidation of As(III) take place with nZVI treatment. In soil samples, Waychunas et al. (2005) studied the sorption mechanisms of nanoscale iron oxides with As in soils and sediments, and concluded that surface complexation was the key mechanism for As uptake by nanoscale iron oxides.

Most of the reported applications of iron nanoparticles in soil have been conducted under *in vitro* conditions and/or considering short-term exposure. Longer term studies which determine the ability of such a strategy to restore soil functionality are necessary before recommending field applications. Plants are strongly influenced by soil composition, and alterations in their growth can reflect the presence of toxic compounds (Gyuricza et al., 2010). Thus the monitoring of the plants grown in polluted soil remediated with nZVI can be an indicator of soil quality. In the last few years, the number of studies about the effects of nZVI on plants have increased (El-Temsah and Joner, 2012; Ma et al., 2013; Jiamjitranich et al., 2012), although scarce data is available about the phytotoxicity of polluted soil remediated with nZVI. In this sense, Wang et al. (2014) observed that two plant species were significantly affected by Cr polluted soils treated with nZVI at short-term, but after a month both plants showed an improvement of growth. Previous studies performed by this research group concluded that the application of nZVI was effective for the immobilization of As in brownfield soil samples, and a decrease of the soil phytotoxicity to barley and vetch in germination assays was observed (Gil-Díaz et al., 2014b). However, it is necessary to know

the impact of this nanoremediation strategy on soil properties as well as on its functionality for the crops establishment. In the present study, the impact of an arsenic polluted soil remediated with nZVI on the development of barley plants was evaluated. The effectiveness of nZVI application in reducing As mobility was measured with a sequential extraction procedure and a TCLP test. In turn, the impact of the nanoremediation process on soil properties and on iron availability was evaluated.

2. Materials and methods

2.1. Collection and characterization of brownfield soil

Soil from a former mining-industrial site located in Asturias (northern Spain) was selected for this study. In this brownfield, As pollution was a result of mineralurgy and metallurgy processes carried out intermittently for decades until the end of the 1970s. The emissions of polluting steams and fine particles, together with the dumping of mining and smelting waste (calcines, soots, etc.) greatly affected the surrounding area of the industrial facilities. Nowadays, the distribution of pollutants throughout the site is mainly related to: i) the mechanical dispersion of the waste conditioned by the geomorphology of the zone, ii) the oxidation and lixiviation of As-rich materials and, iii) complexation and immobilization processes suffered by soil and waste particles.

Bulk soil samples were collected from the surface layer (0–30 cm depth), air dried and sieved (<2 mm) prior to analysis. Three composite samples were analyzed in duplicate. The physico-chemical soil properties (Table 1) were analyzed according to the Spanish official methodology for soil analysis (MAPA 1994). Electrical conductivity (EC) and pH were measured in a 1:2.5 soil-to-water ratio; the organic matter was determined using the Walkley–Black method based on the dichromate oxidation principle; the total nitrogen content were quantified by the Kjeldahl method; the percentage of carbonates was measured using a Bernard calcimeter; the available phosphorus was determined using sodium bicarbonate at pH 8.5 as extractant; and available nutrients

Table 1
Physico-chemical properties of the brownfield soil studied.

Soil properties	Values
pH	7.14 ± 0.50
EC (dS/m)	0.93 ± 0.17
CaCO ₃ (%)	2.8 ± 0.1
N (%)	0.38 ± 0.03
OM (%)	6.9 ± 0.01
P (mg/kg)	219 ± 11
Ca (mg/kg)	4302 ± 969
Mg (mg/kg)	403 ± 29
Na (mg/kg)	59 ± 15
K (mg/kg)	150 ± 1
Cd (mg/kg)	nd
Cr (mg/kg)	57.6 ± 5.2
Zn (mg/kg)	117 ± 22
Pb (mg/kg)	15.6 ± 4.2
Ni (mg/kg)	36.6 ± 9.1
Cu (mg/kg)	28.0 ± 6.3
Mn (mg/kg)	522 ± 45
As (mg/kg)	5800 ± 450
Fe (g/kg)	33.0–37.0
Fe oxides (g/kg FeOOH)	36.6 ± 0.55
Mn oxides (g/kg MnO ₂)	0.64 ± 0.02
Al oxides (g/kg Al(OH) ₃)	3.55 ± 0.20
Porosity (%)	52 ± 5
Sand (%)	64.1 ± 10.3
Silt (%)	25.0 ± 7.4
Clay (%)	10.9 ± 4.3

nd: not detected.

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