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Viability of a nanoremediation process in single or multi-metal(loid) contaminated soils

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HIGHLIGHTS

- The remediation of two types of soils polluted with As, Cd, Cr, Pb and/or Zn was assessed using nZVI.
- The nanoremediation of single- and multi-metal(loid) polluted soils was compared.
- Metal(loid) characteristics and soil properties affect the effectiveness of nanoremediation.
- The presence of several metal(loid)s could limit the effectiveness of nZVI.

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ABSTRACT

The effectiveness of single- and multi-metal(loid) immobilization of As, Cd, Cr, Pb and Zn using different doses of nanoscale zero-valent iron (nZVI) was evaluated and compared in two different soils, a calcareous and an acidic one. The effectiveness of nZVI to immobilize metal(loid)s in soil strongly depended on the metal characteristics, soil properties, dose of nZVI and presence of other metal(loid)s. In the case of single contamination, this nanoremediation strategy was effective for all of the metal(loid)s studied except for Cd. When comparing the two soils, anionic metal(loid)s (As and Cr) were more easily retained in acidic soil, whereas cationic metal(loid)s (Cd, Pb and Zn), were immobilized more in calcareous soil. In multi-metal(loid) contaminated soils, the presence of several metal(loid)s affected their immobilization, which was probably due to the competitive phenomenon between metal(loid) ions, which can reduce their sorption or produce synergistic effects. At 10% of nZVI, As, Cr and Pb availability decreased more than 82%, for Zn it ranged between 31 and 75% and for Cd between 13 and 42%. Thus, the application of nZVI can be a useful strategy to immobilize As, Cr, Pb and Zn in calcareous or acidic soils in both single- or multi-metal(loid) contamination conditions.

1. Introduction

Metal(loid) contamination is a widespread problem and is the main contaminant found in European soils [1]. Anthropogenic activities, such as industrial processes, manufacturing, military activities, mining, road transport, land application of domestic sludge and use of agrochemicals, have been identified as the major human sources for the presence of metal(loid)s in soils [2–4]. The total concentration of metal(loid)s in soil provides little information regarding their potential impact on organisms. In this sense, there is an increasing recognition that elevated contaminant levels alone are not necessarily indicative of the occurrence of adverse effects [5]. Metal(loid)s associated with the aqueous phase of soils show certain mobility and bioavailability, are subject to movement with soil water, and may be transported to groundwater or be taken up by root plants. Bioavailability is defined as the fraction of the total amount of a chemical present in a specific environmental compartment that, within a given time span, is either available or can be made available for uptaking by (micro)organisms or plants [5].

Metal(loid) ions can be retained in the soil by sorption, precipitation, and complexation reactions. The availability of metal(loid)s in the soil depends on the soil properties (soil pH, nature of both organic and inorganic ligand ions, texture) and environmental factors [6–8]. Furthermore, redox reactions, both biotic and abiotic, are of great importance in controlling the oxidation state and thus the mobility [9].

Immobilization technologies, which reduce metal(loid) bioavailability, can be successfully used for the remediation of contaminated soil [6,10,11]. They can be used as an alternative

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to traditional techniques, including excavation and landfilling, which are unfeasible on a large scale because they are environmentally disruptive and cost prohibitive [6,12]. In the last 15 years, the use of nanoscale zero-valent iron (nZVI) for soil and groundwater remediation has been investigated for its potential to degrade organic pollutants and immobilize metal(loid)s [13–18]. Spectroscopy characterizations have confirmed that nZVI has a core-shell structure, which leads to exceptional properties for concurrent sorption/complexation and reductive precipitations of metal(loid) ions [15,16,18]. The application of nZVI for immobilization of Ag, Al, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, U, V and Zn in water has shown high capacity and efficiency [16,19–23]. Its utility in soil has recently attracted attention and has been proposed as a useful alternative for the *in situ* remediation of As, Cr, Pb and Zn contaminated soils [24–32]. The soil physico-chemical properties, such as pH and texture, impact the effectiveness of the nanoremediation process [24,32,33]. The impact on soil properties and potential toxicity are important issues that should be taken into account and depend on soil characteristics and experimental conditions. Previous experiments with soils treated with nZVI reported shifts in microbial community structure although they strongly depended on concentration and type of nZVI and soil properties [34]. Studies performed with polluted soils treated with nZVI reported no negative effects on soil physico-chemical and biological properties, although specific changes were observed depending on soil type and the experimental conditions [25,26,35]. According to Zhang [36] changes in pH and redox parameters would expected to be less dramatic in field applications where other mechanisms reduce the chemical changes.

To date, most of the immobilization studies in soils using nZVI have been conducted with single metal(loid) contamination, and little data are available regarding the effectiveness of nZVI for the simultaneous immobilization of several metal(loid)s in soil. However, a large proportion of contaminated soils have high concentrations of more than one metal(loid), which can affect the efficiency of the nanoremediation technique. In this sense, the presence of several metal(loid)s can induce a competition phenomenon for sorption sites, decrease the immobilization efficiency, or produce a synergistic effect on each metal as well as significantly increase the water retention capacity [8,10,37–39]. The goal of this work was to evaluate the effectiveness of the immobilization of As, Cd, Cr, Pb and Zn using nZVI in two soils with different properties. For the first time, the effectiveness of a nanoremediation treatment applied to soils with a single- and a multi-metal(loid) contamination scenario was evaluated.

2. Materials and methods

2.1. Soils

Bulk soil samples were collected from the surface layer (0–30 cm depth) of two agricultural areas from the Madrid region. Acidic soil was collected from Talamanca del Jarama and calcareous soil from Alcalá de Henares. Before use, the soil samples were air dried and passed through a 2-mm sieve. The soil properties were analyzed according to the Spanish official methodology for soil analysis [40] (Table 1). Briefly, the pH and electrical conductivity (EC) were measured in suspension using a 1:2.5 (w/v) ratio of soil and deionized water; the percentage of carbonates was measured using the Bernard calcimeter; organic matter and total nitrogen contents were analyzed using the Walkley-Black and Kjeldahl methods, respectively; available phosphorus was determined by extraction with sodium bicarbonate at pH 8.5 according to the Olsen's procedure; and available macronutrients (Ca, Mg, Na and K) were extracted with ammonium acetate (0.1 N) and quantified using flame atomic absorption spectrometry (FAAS) (AA240FS, Varian, Victoria, Australia). The soil texture was determined using a Bouyoucos densitometer.

Table 1
Physical and chemical properties of the two soils used in the assay, acidic and calcareous soil.

Properties	Calcareous	Acidic
pH	8.23	5.49
EC (dS m^{-1})	0.27	0.07
$CaCO_3$ (%)	8.0	0.15
N (%)	0.11	0.03
OM (%)	1.11	0.61
P (mg kg^{-1})	26	27
Ca (mg kg^{-1})	2866	500
Mg (mg kg^{-1})	374	72
Na (mg kg^{-1})	34	11
K (mg kg^{-1})	217	97
As (mg kg^{-1})	<LD	<LD
Cd (mg kg^{-1})	<LD	<LD
Cr (mg kg^{-1})	17	10 ± 3
Pb (mg kg^{-1})	13	9.0
Zn (mg kg^{-1})	44	20
Fe (g kg^{-1})	16.1	11.8
Sand (%)	29	43
Silt (%)	38	42
Clay (%)	33	15

The total concentrations of As, Cd, Cr, Pb, and Zn in the soil samples were determined after acid digestion with a mixture of 6 mL of nitric acid (69% purity) and 2 mL of chlorhydric acid (37% purity) in a microwave reaction system (Multiwave 3000, Anton Paar GmbH, Graz, Austria). Arsenic was analyzed with a graphite furnace Atomic Absorption Spectrometer (GFAAS) with Zeeman Correction (AA240Z, Varian), and the limit of quantitation was 0.02 μg/g. The metals were quantified by FAAS (AA240FS, Varian), and the limits of quantitation were in the range of 0.1 to 1.0 μg/g. All of the analytical determinations were performed in duplicate.

2.2. Zero-valent iron nanoparticles

In all of the experiments, a commercial stabilized aqueous dispersion of nZVI NANOFER 25S, supplied by NANO IRON s.r.o. (Rajhrad, Czech Republic), was used. The Fe(0) content was 14–18%, and 2–6% were iron oxides. Additional details regarding the physical and chemical characteristics are shown at www.nanoiron.cz. The pH of the nZVI suspension was strongly alkaline (12.2 ± 0.1). Before use, the solution was protected from light using aluminum foil and stirred for 1 h. nZVI concentrations of 1%, 5% and 10% (w/w) were used in this study.

2.3. Batch experiments

The air-dried soil samples (0.2 kg) were individually spiked with calculated amounts of solutions that were prepared from compounds of the selected metal(loid)s in distilled water to concentrations of 100 mg/kg for As and Cd and 200 mg/kg for Cr, Pb and Zn. The compounds used were As_2O_5, $CdSO_4$, $K_2Cr_2O_7$, $Pb(NO_3)_2$ and $ZnSO_4{\cdot}7H_2O$ and were of analytical grade and purchased from Panreac, with the exception of $CdSO_4$, which was purchased from AcrosOrganics. The soil was properly mixed during metal(loid) dissolution addition using a glass rod for 5 min to ensure that the metal was evenly distributed. In the case of the multi-contaminated soil, a solution including all of the metal(loid)s was prepared. Spiked soil samples were incubated for 30 days at 25 °C and 50% humidity. After this 30 day-period, the soils were air-dried, sieved (<2 mm) to homogenize the mixtures and the total metal(loid) concentration was determined after acid digestion as previously explained in the Section 2.1 *Soils*. Then, 2.5000 ± 0.0500 g of spiked-soil was

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