



Assessment of the use of industrial by-products for induced reduction of As, and Se potential leachability in an acid soil

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ABSTRACT

Four industrial by-products (phosphogypsum, PG; red gypsum, RG; sugar foam, SF and ashes from the combustion of biomass, ACB) were evaluated as possible amendments for reducing the leachability and bioavailability of As and Se in a metalloid-spiked acidic soil. The treatments were applied as single, double and triple amendments and at two different rates. The effectiveness of the treatments was evaluated after a series of leaching experiments using a chelating agent (DTPA solution) or a weak acidification (acetic acid at pH 4.93). The most effective treatments (ACB and RG, both applied at high rate) were identified by means of Cluster Analysis using the leachability indexes. Different sorption mechanisms involved in the overall reduction of metalloid leachability were identified using scanning electron microscopy (SEM-BSE and SEM-EDS). In the ACB-treated samples, Se was found associated to organic matter aggregates and to Fe compounds. In the RG-treated samples, EDS analyses showed that As and Se were associated to Fe/Ti (hydr)oxides phases which are present not only in the by-product as maghemite and rutile, but also in the soil as hematite and goethite. In addition, the application of RG induced the formation of non-crystalline Al-hydroxy polymers with As and Se in their composition.

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1. Introduction

The use of conventional, engineering-type techniques to clean up metal-contaminated soils is typically invasive and expensive. The most ecologically friendly and economically viable method is *in situ* immobilization of metals and metalloids using abundant, inexpensive soil amendments [1] aiming at enhancing natural attenuation processes [2] such as (ad)sorption, precipitation, complexation and redox reactions [3] that reduce potential leachability and bioavailability of toxic elements.

Remediation of soils contaminated with several elements, and very often with combinations of anionic and cationic species, requires solutions effective for all target elements. The different properties of the contaminants restrict the choice of possible amendments in order to avoid, for example, large pH fluctuations and consequent mobilization of one or more of the elements. In addition, the presence of one contaminant (e.g. Cu or Pb) can decrease the stabilization efficiency of others (e.g. Zn) due to competition for sorption sites [4], while several contaminants of opposite charge can have a synergistic effect on each other. Thus, the diversity of contaminant species and the selective efficiency of the by-products for some elements, is promoting the search for new treatments applied in single or combined amendments. Very

often, the use of a combination of amendments can improve the single treatment efficiency of multi-element contaminated sites [4].

In recent years, there has been considerable interest in the use of some industrial by-products as amendments. This approach transforms wastes into useful commercial industrial co-products [5]. Various by-products have been tested as *in situ* fixing additives to remediate As contaminated soils. Examples include red mud [6], compost [7], lime [8], iron oxide coated cement [9], water treatment sludges [10], steel shot [11] and phosphogypsum and sugar foam [12,13]. However, only a few studies have focused on the fixation of Se species by amendments, such as gypsum [14,15] or lime [16]. Although As and Se coexist in some contaminated soils, like the affected by the mine tailings accident at Aznalcóllar (southern Spain) [17], or the surrounding coal ash disposal facilities [18,19], no studies are available on the addition of soil amendments to improve the leachability of both metalloids together. Taking into account these facts, the objectives of this work are: (i) to ascertain the feasibility of the application of four industrial by-products (phosphogypsum, PG; red gypsum, RG; sugar foam, SF and ashes from the combustion of biomass, ACB) as amendments for the immobilization of As and Se in a metalloid-spiked acidic soil under unsaturated conditions, (ii) to identify those treatments that are effective in reducing both potential mobility and bioavailability of the two elements, and (iii) to explore possible sorption mechanisms through which As and Se are retained in the soil matrix as a result of selected treatments.

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2. Materials and methods

2.1. Soil

An acidic soil developed from Pliocene-Quaternary aged formations and classified as Plinthic Paleixerult [20] was collected from an agricultural area in Cáceres (Spain). Air-dried samples from the Ap horizon were crushed and sieved through a 2 mm mesh prior to characterization and use in subsequent experiments. Table 1 summarizes the most important physical, chemical and mineralogical properties of the soil. Soil pH was measured in deionized water (pH_w) and in 1 M KCl (pH_k) (in a 1:2.5 suspension). Electrical conductivity (EC) was measured in a 1:5 suspension. Organic C (OC) was determined by wet digestion [21]. The exchangeable bases were extracted with 1 M NH_4OAc (at pH 7) [22]. The Al and Fe contents in the poorly crystalline and amorphous fraction of the soils (Al_{ox} , Fe_{ox}) were extracted with 0.2 M ammonium oxalate + 0.2 M oxalic acid solution at pH 3 [23]. The supernatants from each extraction were separated by centrifuging and stored in polyethylene containers at 4 °C until analysis. Analyses were performed in triplicate. The Ca, Mg, Na, K, Al and Fe were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on a Perkin-Elmer OPTIMA 4300DV. The mineralogical composition of the total (≤ 2 mm) and clay ($\leq 2 \mu\text{m}$) fractions of the soil was identified by X-ray powder diffraction (XRD) with a Philips X'Pert diffractometer using graphite-monochromated $\text{Cu-K}\alpha$ radiation. The XRD patterns were obtained from random powder mounts and various oriented aggregates of the clay fraction (air-dried, ethylene glycol-solvated, heated at 300 °C for 3 h, and heated at 500 °C for 3 h). Semi-quantitative estimates of the mineral contents were obtained from random powder and oriented aggregated patterns using the intensity factors given by Schultz [24].

2.2. Industrial by-products

Phosphogypsum (PG) is generated in the wet-acid production of phosphoric acid from rock phosphate in the industry of fertilizers. Red gypsum (RG) is a waste from the industrial production of titanium dioxide (TiO_2). Sugar foam (SF) is produced by the sugar manufacturing industry. Ashes from combustion of biomass (ACB) are originated in the cellulose production process.

Samples of PG, RG, SF and ACB supplied by the companies Fertiberia S.A., Tioxide Europe S.A., Azucarera Ebro S.A. and ENCE S.A., respectively, were dried at 45 °C (PG and RG) and 105 °C (SF and ACB) and digested by acid digestion and alkaline fusion [25]. The resulting solutions were analyzed for major and trace elements by ICP-AES, ICP-MS and ion chromatography. Organic C was determined by wet digestion [21]. The chemical composition of the by-products is shown in Table 2. Both gypsum-like wastes are rich in Ca and sulfate ions. In addition, because of its industrial origin from ilmenite (FeTiO_3), RG contains Fe and Ti. Regarding the trace elements, Ba, Cr and Cu are present at the largest concentrations among all elements analyzed in all by-products. In addition, RG and ACB are rich in Ni and Zn, and ACB also in Pb. However, the heavy metal contents are much less than those established by the European Community, Council Directive 86/278/EEC on the Use of Sewage Sludge in Agriculture [26] (Cd, 20–40 mg kg^{-1} ; Cu 1000–1750 mg kg^{-1} ; Ni 300–400 mg kg^{-1} ; Pb 750–1200 mg kg^{-1} ; Zn 2500–4000 mg kg^{-1}) and constitute no environmental hazard at the rates normally used in agriculture.

The mineralogical composition of the by-products was identified by X-ray diffraction from random powder patterns. Gypsum is the main component of PG and RG and is accompanied by small proportions of iron and titanium minerals in RG. An XRD study of the RG residue after dissolution of gypsum revealed the presence of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and rutile (TiO_2). SF consists mainly of

Table 1
Some physical, chemical and mineralogical properties of the Ap horizon.

pH_w	pH_k	EC^a (mS cm^{-1})	OC^b (g kg^{-1})	Sand (g kg^{-1})	Lime (g kg^{-1})	Clay (g kg^{-1})	Ca^{2+} ($\text{cmol}_c \text{ kg}^{-1}$)	Mg^{2+} ($\text{cmol}_c \text{ kg}^{-1}$)	Na^+ ($\text{cmol}_c \text{ kg}^{-1}$)	K^+ ($\text{cmol}_c \text{ kg}^{-1}$)	Al^{3+} ($\text{cmol}_c \text{ kg}^{-1}$)	Al_{ox}^c (mg kg^{-1})	Fe_{ox}^c (mg kg^{-1})	Fraction ^d $\leq 2 \mu\text{m}$									
														Q	G	H	Ph	I	K				
4.9	4.1	0.04	33	700	250	50	0.83	0.12	0.07	0.06	1.17	4772	1457	Q	G	H	Ph	I	K				
														84	tr	3	13	15	9	76	11	10	55

^a EC: electrical conductivity.

^b OC: organic carbon.

^c Al and Fe oxalate-extractable contents.

^d Semi-quantitative mineralogical composition (relative%): Q, quartz; G, goethite; H, hematite; Ph, phyllosilicates; V, vermiculite; I, illite; K, kaolinite; and tr, traces.

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