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Automatic flow-through dynamic extraction: A fast tool to evaluate char-based remediation of multi-element contaminated mine soils[☆]



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ABSTRACT

An automatic in-vitro bioaccessibility test based upon dynamic microcolumn extraction in a programmable flow setup is herein proposed as a screening tool to evaluate bio-char based remediation of mine soils contaminated with trace elements as a compelling alternative to conventional phyto-availability tests. The feasibility of the proposed system was evaluated by extracting the readily bioaccessible pools of As, Pb and Zn in two contaminated mine soils before and after the addition of two biochars (9% (w:w)) of diverse source origin (pine and olive). Bioaccessible fractions under worst-case scenarios were measured using $0.001 \text{ mol L}^{-1} \text{ CaCl}_2$ as extractant for mimicking plant uptake, and analysis of the extracts by inductively coupled optical emission spectrometry. The *t*-test of comparison of means revealed an efficient metal (mostly Pb and Zn) immobilization by the action of olive pruning-based biochar against the bare (control) soil at the 0.05 significance level.

In-vitro flow-through bioaccessibility tests are compared for the first time with in-vivo phyto-toxicity assays in a microcosm soil study. By assessing seed germination and shoot elongation of *Lolium perenne* in contaminated soils with and without biochar amendments the dynamic flow-based bioaccessibility data proved to be in good agreement with the phyto-availability tests. Experimental results indicate that the dynamic extraction method is a viable and economical in-vitro tool in risk assessment explorations to evaluate the feasibility of a given biochar amendment for revegetation and remediation of metal contaminated soils in a mere 10 min against 4 days in case of phyto-toxicity assays.

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1. Introduction

Significantly elevated levels of inorganic pollutants co-exist in soils from previously heavily industrialized areas [1]. Novel risk-based regulatory systems are concerned with the effect of the contaminant rather than just the total concentration in the soil whereby measures addressing onward consequences of pollution rather than merely reducing total trace element (TE) concentrations in soil are called for. The use of organic materials as soil amendments are now established amongst in situ alternatives to reduce the environmental risks of inorganic pollutants in soils [2,3] by boosting TE immobilization in contrast to more classical

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approaches involving excavation and landfilling with clean soil as they are deemed highly environmentally disruptive and extremely expensive for soil remediation.

Biochar (biologically derived charcoal) is an organic carbon-rich material generated via pyrolysis of agricultural bio-waste under low oxygen conditions [4]. The physical and chemical properties of biochars vary significantly depending on the biomass source, pyrolysis conditions, and pre- and post-production treatments [5]. The inherent large surface areas and cation exchange capacities of biochars, as determined to a large extent by source materials and pyrolysis temperatures, enable enhanced sorption capacity of both organic and inorganic contaminants to their surfaces with the added value of potential decrease in pollutant mobility when amending contaminated soils [6–8].

After biochar application, the revegetation (phyto-stabilization) of contaminated soils is often seen as the first stage towards remediation, especially at sites with low organic matter and inherent lack of physical stability, because the occurrence of a vegetative cover over bare soil reduces the potential leaching of

the contaminants to watercourses or being inhaled by receptor organisms. The efficiency of biochar remediation in every individual case should be evaluated but field trials, although very necessary, are time-intensive to set-up and monitor, and may require multiple treatment and soil combinations to obtain the prescribed effect aimed at overcoming risks to human and ecosystem health outside site boundaries. Hereto, a rapid pre-screening method to evaluate likely benefits of adding organic amendments to bare soils would be a useful precursor to such field trials. Moreno-Jiménez et al. [9] demonstrated that petri-dish seed germination assays, measuring percentage germination success and shoot/root length, work as a rapid in-vivo first-step screening method for assessing phyto-toxicity. However, in-vivo testing methods are not recommended by REACH guidelines [10], rather the exploration of non-biota based viable alternatives. To this end, in-vitro bioaccessibility tests [11–13], in which the leaching of contaminants is measured under environmentally relevant conditions, might be seen as an appealing option for expedient evaluation of the effectiveness of biochar amendments in soil remediation and can be addressed with more economical chemical procedures [14,15].

Batchwise leaching tests undertaken in a single or sequential extraction mode have been used over the past few decades to determine pools of bioaccessible TE in soils and sediments [12,16–18]. Common to all of them is to expose a given amount of solid material (typically within the range of 0.5–5 g) to the action of leaching agent aimed at the identification and quantitation of specific modes of TE association to geochemical phases.

More recently, flow-through dynamic (non-equilibrium) extraction methods have been proposed and applied as appealing alternatives to the batchwise counterparts [11,19–21]. In soil column-based bioaccessibility tests fresh portions of leaching agents are continuously provided to small containers or columns containing the solid material with the subsequent displacement of the extraction equilibrium to the liquid phase until completion. Hence, the pH of the leachate gradually reaches the nominal extractant pH regardless of the alkalinity or acidity of the original solid sample [22,23]. The main asset of dynamic methods is their ability to mimic field leaching under worst-case scenarios so as to assure the exhaustive extraction of TE under a given chemical extractant. Additional advantages of dynamic leaching tests against well-established batchwise methods involve a decrease in the number of manual operations, the inexistence of readsorption phenomena because of the continuous solid/liquid equilibrium shift, the ease of attaining time-resolved (kinetic) data of the ongoing extraction, and, most importantly, the feasibility of realistic extraction conditions in environmentally simulated scenarios, e.g., the percolation of rain-water through soil profiles.

In this paper, flow-through microcolumn dynamic extraction based on programmable flow in combination with inductively coupled plasma spectrometric analysis is proposed as a rapid screening tool for the evaluation of the efficiency of biochars of diverse origin in the remediation of two contaminated mine soils

at different concentration levels of As, Pb and Zn. Worst-case TE bioaccessibility is determined using 10^{-3} mol L⁻¹ CaCl₂ as extractant as endorsed by the International Standard Organization (ISO) 21268-3:2007 norm [24]. TE bioaccessibility is supplemented with bio-toxicity data as obtained by seed germination and root/shoot elongation of *Lolium perenne* (*L. perenne*) [9]. To the best of our knowledge, this is the first report paralleling and correlating automatic dynamic bioaccessibility tests of TE in environmental solids against bioavailability and phyto-toxicity bio-assays.

2. Materials and methods

2.1. Reagents and solutions

All chemicals were of analytical reagent grade and used without further purification. Ultra-pure water (specific resistivity of 18.2 MΩ cm) obtained from a Milli-Q system (Millipore, Bedford, USA) was employed to prepare all solutions and standards. All glassware and polyethylene containers were previously soaked in 10% (v/v) HNO₃ and rinsed three times with deionized water prior to use.

A 10^{-3} mol L⁻¹ CaCl₂ used as the extractant in the bioaccessibility test was prepared by dissolving 111 mg of CaCl₂ (Scharlab, Barcelona, Spain) in 100 mL of water, followed by making up to 1000 mL with Milli-Q water.

A multi-element standard solution for inductively coupled plasma spectrometry (Standard solution-5, Fluka, Sigma Aldrich, Saint Louis, USA) was employed for external calibration. Diluted working solutions were prepared daily using a matrix-matched procedure for analyzes of CaCl₂ leachates.

2.2. Soils and biochars characterization

Two topsoils were collected from mine sites (so called Garganta (G) and Bustarviejo (B) soils), previously found to be moderately contaminated and heavily contaminated by TE, respectively, in Madrid and surroundings (Spain). The two topsoils (0–20 cm) were collected from 2 to 3 points in the surroundings of the mine heaps and bulked to a composite sample for each location. The mine heaps are located in the villages of Garganta de los Montes (40.917736, –3.673533) and of Bustarviejo (40.866246, –3.730903), both in the North of Madrid. In the laboratory, soils were air dried (22 °C) before larger debris fragments were removed and the remaining soil was crushed and sieved to < 2 mm for analysis.

Particle size distribution was determined by the hydrometer method. Organic matter was determined as the dichromate-oxidizable sample fraction. Soil pH was measured in de-ionized water using a solid to liquid ratio of 1:25. To this end, the suspended soil was shaken for 3 h and allowed to settle for 45 min at room temperature (22 °C) prior to measurements. Physicochemical characterization of soils (see results in Table 1) was carried out

Table 1
Physicochemical characteristics of soils used in this study.

Soil	Origin	Texture (sand, silt, clay; %)	pH	Organic matter (%)	As (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Zn (mg kg ⁻¹)
Garganta (G)	Madrid, Spain	20, 59, 21	6.0 ± 0.2	1.0 ± 0.4	72 ± 20	n.d.	302 ± 60
Bustarviejo (B)	Madrid, Spain	89, 5, 6	3.9 ± 0.6	0.8 ± 0.2	9032 ± 1780	4999 ± 484	19344 ± 4484

Results are expressed as the mean of three replicates ± standard deviation, n.d.: not determined.

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