Journal of Environmental Management 209 (2018) 1–8

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Performance of waste-based amendments to reduce metal release from mine tailings: One-year leaching behaviour

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ARTICLE INFO

Article history:
Received 1 September 2017
Received in revised form
12 December 2017
Accepted 13 December 2017

Keywords:
Soil pollution
Metals
Immobilization
Amendments
Metal leaching

ABSTRACT

A one-year leaching experiment has been conducted in order to assess the effectiveness of several amendments on metal immobilization in mine tailings from an old Pb/Zn mining area of Central Spain (San Quintín mine). Demineralized water was used as leaching solution, selecting doses equivalent to the annual rainfall conditions of the studied area. Columns with mine tailings without any amendment and others treated with 10% of sugar foam (SF), 15% of drinking water treatment sludge (DWS), 30% of paper mill sludge (PMS) and 15% of olive mill waste (OMW) were used. SF, DWS and PMS amendments increased the pH of leachates from values of approximately 4 to around neutrality. Additionally, the release of sulfate ions from the oxidation of pyritic residues was decreased in some extent by SF and DWS amendments. Metal leaching was effectively reduced by the amendments reaching overall decreases with respect to the unamended columns of 79–96% for Pb, 36–100% for Zn, 50–99% for Cu and 44–100% for Cd. The effect of the amendments in leachate pH, sulfate concentration and metal release from mine tailings was kept throughout the whole experimental period. Our results showed that the application of different organic and inorganic amendments based on by-products and waste materials may be a feasible alternative for the restoration of soils around abandoned metal mines.

1. Introduction

One of the most important metal mining areas of Spain in the late 19th and early 20th century was the Alcudian district (Palero-Fernández and Martín-Izard, 2005). It is located in the southern central part of the Iberian Peninsula, located approximately 250 km south of Madrid, and includes an area of approximately 2500 km^2. Among the hundreds of mines exploited for obtaining lead, zinc and silver, the San Quintín mine was the most important in terms of metal production and surface covered. The mining activities were abandoned more than thirty years ago but, currently, a huge amount of mine tailings remains exposed, and without any treatment, covering an area of around 600,000 m^2. The severe landscape impact caused by the tailings and the spreading of metal pollution (mainly due to aeolian transport and acidic mine drainage generation) to the soils of the adjacent agricultural and pasture lands have been reported elsewhere (Rodríguez et al., 2009; Higueras et al., 2012; Martín-Crespo et al., 2015). Those previous works have emphasized the need to take urgent action to reduce the environmental risks for ecosystems and humans in the surrounding areas.

The restoration of abandoned metal mining sites by means of *in situ* adding of soil amendments has been proposed as a simple and sustainable technology to reduce the environmental hazards derived from these type of affected sites, which usually involve large areas (Pardo et al., 2014; Brown and Chaney, 2016). The purpose of these amendments is to reduce the availability of metals in soils and, therefore, its migration to other environmental compartments such as ground-water, surface waters and plants. There have been numerous organic and inorganic materials which have

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https://doi.org/10.1016/j.jenvman.2017.12.031
0301-4797/

been studied, both in greenhouse and field trials, as amendments for polluted soils (see reviews by Gadepalle et al. (2007) and Bolan et al. (2014)) but, among them, those based on wastes or by-products are specially interesting because their low cost and their positive contribution to circular economy. In the context of mine restoration, organic amendments including animal manures, municipal biosolids, composts and pulp sludge have been extensively studied mainly due to their high organic content, which aids to support sustainable vegetal covers in the disturbed soils. Inorganic wastes such as flying ashes, aluminium-processing residuals, sludge from drinking water facilities and sugar beet lime may be also cited as efficient materials to balance the low pH of the mining tailings with high contents of pyrite susceptible to generate acidic mine drainage (AMD) (Brown and Chaney, 2016). However, it is not only relevant to assess the effectiveness of amendments on metal immobilization but also to prove the duration of the treatment. In other words, it is needed to know whether metals remain stable in unavailable fractions after immobilization treatment or, conversely, they can be remobilized with time by natural weathering processes. A few studies assessing the long-term efficiency of immobilization by organic and liming amendments have been conducted (Kumpiene et al., 2007; Pérez-López et al., 2007; Ruttens et al., 2010; Rodríguez-Jordá et al., 2012; Kumpiene et al., 2013; Santos et al., 2014) but, as it was concluded in the abovementioned review by Bolan et al. (2014), additional research is necessary to more clearly state if remediation by immobilization is a technique that requires, or not, repeated additions of amendments.

In a previous paper (Rodríguez et al., 2016), we reported the effectiveness of sugar foam (sugar beet lime), olive mill waste, drinking water treatment sludge and paper mill sludge to decrease Pb and Zn availability in both agricultural soils and mine tailings from San Quintín mine area. That conclusion was supported by the reduction of the EDTA-extractable concentration of metals in soil after a 45-days incubation experiment and the decrease on metal uptake by lupine plants grown during 8 weeks in the amended soils. In this paper, we have assessed the long-term effectiveness of the abovementioned amendments for metal availability reduction in mine tailings from the San Quintín mine by means of a 1-year leaching experiment. For this purpose, we have simulated the exposition of both amended and unamended tailings to the rainfall conditions of the San Quintín mine area recording AMD generation and metal leaching over a period of one year.

2. Materials and methods

2.1. Material characterization

The mine tailings sample used in this experiment was taken from a former sedimentation pond (0389462, 4,297,663 UTM) of the San Quintín Pb–Zn mine. We used a composite sample coming from four sampling points located in the vertices of a square of 3 m edge. Mine tailings were sampled at a depth of 0–25 cm, air-dried at room temperature for 7 days and, finally, sieved to <2 mm and <63 μm. The 2-mm fraction was used in the leaching experiments and for the measurement of the physicochemical properties of the soil, while the 63-μm fraction was used to analyse the total and EDTA-extractable metal concentrations.

Four waste-based materials were used as amendments: sugar foam (SF, a lime-rich waste generated in the production of sugar from beet), drinking water treatment sludge (DWS, an organic waste coming from a drinking water treatment facility which uses aluminium sulfate as coagulant), olive mill waste (OMW, a lignocellulosic by-product of the olive oil production) and paper mill sludge (PMS, an organic waste with silicates and carbonates coming from the pulp and paper-making process). All of them were selected based on the literature (Calace et al., 2005; Garrido et al., 2005; Gadepalle et al., 2007; Alburquerque et al., 2011; Wang et al., 2012) and had been tested for metal immobilization in a previous research carried out by us (Rodríguez et al., 2016). All of these amendments were obtained from local or national companies.

pH of the amendments was measured in a 1:5 soil/water (w:v) mixture; total organic carbon (TOC) and inorganic carbon were analysed by means a TOC analyser (Shimadzu TOC-VCSH, Columbia, USA); particle-size distribution (clay, silt and sand content) was determined using laser diffractometry (Beckman Coulter LS, Fullerton, USA). Major elements were determined by means of a commercial handheld XRF analyser (Niton XL3t, Thermo Scientific, Tewksbury, USA) following the USEPA method 6200; accuracy of the measures was assessed using the certified standards NIST 2710 and 2711. The EPA 3051A method was used to digest the solid samples (<63 μm fraction) before the analysis of total Pb, Zn, Cd an Cu concentrations; 0.5 g of sample were digested with a mixture of acids (9 mL of concentrated HNO_3 + 3 mL of concentrated HCl) using a microwave oven (CEM MARS 5, Matthews, USA). EDTA-extractable metal concentrations in mine tailings before the leaching experiment were determined by extracting the samples (<63 μm fraction) with 0.01 M EDTA, using a contact time of 16 h and a soil:extractant ratio of 1:10 (w:v). All digestions and extractions were carried out in triplicate. Concentrations of Pb, Zn, Cd and Cu in the extracts were analysed by means of ICP-AES using a Thermo ICAP 6500 spectrometer (Thermo Electron, Cambridge, UK). The quality of metal analysis was checked by analysing the Montana Soil 2711 certified reference material (LGC Promochem, Barcelona, Spain).

Qualitative mineralogical analysis of mine tailings and amendments were carried out by X-ray diffraction (XRD) using semi-quantitative analysis by the Schultz's method (with this method the uncertainty in the quantification can be up to 15%). Bulk mineralogy was determined using the polycrystalline disoriented powder method after sample grinding and homogenizing in an automatic agate mortar and sieving to <0.053 mm. X-ray diffractograms were carried out with a PANalytical® diffractometer, X'Pert Pro model, equipped with an X'celerator detector, using CuKα radiation, a 45 Kv accelerating voltage and a 40 mA current. Scanning electron microscopy (SEM) images of the mine tailings, amendments and mixtures were taken using a FEI Quanta 250 microscope (Oregon, USA), coupled to an EDAX Apollo X EDS detector (Energy Dispersive Spectroscopy) for microelemental analysis.

2.2. Leaching experiments

Leaching experiments were carried out using 50 mm-diameter polystyrene columns, with a 0.45 μm polyethersulfone filter in the bottom, coupled to 150 mL plastic flasks where the leachate was collected. Five different series of columns were prepared, i.e. unamended mine tailings (control) and mine tailings amended with the four waste materials previously described. Control columns consisted of only 110 g d. w. of the mine tailings sample. The amended mixtures were made by thoroughly mixing the mine tailings sample with the corresponding amount of amendment to reach 110 g d. w. of amended soil with the following percentages in weight: 10% for sugar foam (SF), 30% for paper mill sludge (PMS) and 15% for drinking water sludge (DWS) and olive mill waste (OMW). Those percentages were based on previous literature (Gadepalle et al., 2007) and they were the same used in our previous research (Rodríguez et al., 2016). All the treatments were carried out in triplicate.