Ecotoxicology and Environmental Safety 162 (2018) 581–590

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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

Amending potential of organic and industrial by-products applied to heavy metal-rich mining soils

Gabriel Caixeta Martins[a,d], Evanise Silva Penido[b], Ingrid Fernanda Santana Alvarenga[c], Jéssica Cristina Teodoro[c], Maria Lucia Bianchi[b], Luiz Roberto Guimarães Guilherme[a,*]

[a] *Federal University of Lavras, Soil Science Department, 3037, 37200000 Lavras, Minas Gerais, Brazil*
[b] *Federal University of Lavras, Chemistry Department, 3037, 37200000 Lavras, Minas Gerais, Brazil*
[c] *Federal University of Lavras, Biology Department, 3037, 37200000 Lavras, Minas Gerais, Brazil*
[d] *Vale Institute of Technology, 955 Boaventura da Silva Street, 66055090 Belém, Pará State, Brasil*

ARTICLE INFO

Keywords:
Biochar
Composted food remains
Limestone
Sewage sludge
Heavy metals
Contamination

ABSTRACT

Mining activities promote the development of economies and societies, yet they cause environmental impacts that must be minimized so that their benefits overcome the likely risks. This study evaluated eco-friendly technologies based on the use of low-carbon footprint wastes and industrial by-products as soil amendments for the revegetation of Zn-mining areas. Our goal was to select adequate soil amendments that can be used to recover these areas, with a focus on low-cost materials. The amendments - limestone, sewage sludge, biochar, and composted food remains - were first characterized concerning their chemical composition and structural morphologies. Soil samples (Entisol, Oxisol, Technosol) from three different areas located inside an open-pit mine were later incubated for 60 days with increasing doses of each soil amendment, followed by cultivation with *Andropogon gayanus*, a native species. The amendments were able to change not only soil pH, but also the phytoavailable levels of Cd, Zn, and Pb. Limestone and biochar were the amendments that caused the highest pH values, reducing the phytoavailability of the metals. All amendments improved seed germination; however, the composted food remains presented low levels of germination, which could make the amendments unfeasible for revegetation efforts. Our findings showed that biochar, which is a by-product of the mining company, is the most suitable amendment to enhance revegetation efforts in the Zn-mining areas, not only because of its efficiency and cost, but also due to its low carbon footprint, which is currently the trend for any “green remediation” proposal.

1. Introduction

A wide range of organic (Ren et al., 2018a, b) and inorganic (Khalid et al., 2017; Turan et al., 2018) chemicals can contaminate water, soil, or air, impacting the environment. For example, mining is an essential component for the development of society. Most technological and agricultural advances are only possible because of the raw materials obtained from mining activities. However, such activities cause a negative environmental impact that has to be minimized so that the benefits outweigh the potential risks. Open-pit mining is a technique of extracting rock or minerals and often involves removing the topsoil that covers the ore. When the mineral resource is exhausted, or an increasing ratio of overburden to ore makes further mining uneconomic, mining is halted, leaving the soil unsuitable for plant development due to its physical-chemical characteristics (Atibu et al., 2018). Nevertheless, a few plants are still able to grow and survive in an environment that is generally not appropriate for plant development (Mingorance et al., 2016; Kneller et al., 2018). Hence, revegetation with plants that are capable of covering the affected area is an alternative to traditional methods of site restoration (Anawar et al., 2015; Mahar et al., 2016; Huang et al., 2018; Kneller et al., 2018; Liu et al., 2018).

Extreme pH conditions, low soil fertility, high soil density, low water content, and the presence of heavy metals and rocky materials are some of the factors that affect the re-establishment of plants in areas disturbed by mining activities. For example, in the Zn-mining area of Vazante, located in Minas Gerais state (MG), Brazil, high levels of Zn, Pb and Cd may be present in the soil, which can result in considerable soil contamination (Lopes et al., 2015). However, despite such challenges, the widespread occurrence of two plant species is noteworthy at this site: *Gomphrena claussenii* Moq., the first South American metallophyte species (Carvalho et al., 2013), and *Andropogon gayanus*, which is

---

[*] Correspondence to: Soil Science Department, Federal University of Lavras, Lavras, Minas Gerais, Brazil.
E-mail address: guilherm@dcs.ufla.br (L.R.G. Guilherme).

https://doi.org/10.1016/j.ecoenv.2018.07.040
Received 9 May 2018; Received in revised form 4 July 2018; Accepted 10 July 2018

widely distributed throughout the mine. *Andropogon gayanus* is a grass that can reach up to 1.5–2.5 m in height and is well adapted to conditions of low fertility, longer periods of drought and acid soils (Sousa et al., 2010; Ferreira and Vieira, 2017).

Improving the characteristics of a soil affected by mining activities is beneficial for its natural recovery. Therefore, before species that are apt to revegetation can be planted, applying soil amendments in order to alleviate phytotoxicity, stabilize metals in contaminated sites (Mahar et al., 2015; Rodríguez et al., 2018; Liu et al., 2018) and improve their chemical and biological properties is of great importance (Khalid et al., 2017).

It has been reported that the addition of biochar (Anawar et al., 2015; Xu et al., 2016; O'Connor et al., 2018), municipal solid waste composts (Alvarenga et al., 2016), sewage sludge composts (Mingorance et al., 2016) and limestone (Lee et al., 2017) results in significant benefits for the revegetation and rehabilitation of areas affected by mining activities. Such benefits are not only direct (e.g., carbon sequestration, soil fertility improvement, and pollutant immobilization) but also indirect, since the proper management of many of these amendments, which are considered wastes, reinforces the environmental sustainability of their use (Anawar et al., 2015; Lee et al., 2017; Tang et al., 2018) by avoiding their improper disposal. Furthermore, understanding the surface reactivity of the amendments is of great importance for their application in soils. The physico-chemical structure of amendments influences their ability to retain contaminants due to functional groups present on their surface (metal-biochar binding strengths and stabilities), which can be determined by Fourier Transform Infrared Spectroscopy (FTIR). For example, phenolic and carboxylic functional groups present on biochar surface are found to increase the cation exchange capacity of soils and act in electron transfers (Lewis acid-base reactions), enhancing the soil holding capacity of metals (Uras et al., 2012; Pourret and Houben, 2018).

Implementing green remediation projects is a new trend for recovering degraded mining sites. Under such circumstances and with a focus on reducing the carbon footprint of the selected technologies, materials that can be used in soil remediation must be chosen not only based on their efficiency but also depending on local availability. Therefore, the objective of this study was to evaluate the use of locally produced organic and industrial by-products to aid in the revegetation of an area degraded by zinc mining activities. Thereby, we hope to evaluate their potential regarding soil recovery as well as in the reduction of the carbon footprint of the project, making its application environmentally sustainable.

2. Materials and methods

2.1. Characterization of soil amendments

With a focus on their low cost and local availability, the following materials were used as soil amendments: composted food remains (CFR), sewage sludge (SS), biochar (BC), and limestone (LS). Sewage sludge was collected at the municipal wastewater treatment plant in Vazante, Minas Gerais state, Brazil (17.98°S and 46.9°W), a city well known for its mining activities. Composted food remains were produced by compost processing of food wastes from restaurant facilities located inside the mining company. The limestone was a by-product generated in the ore processing of the company. Finally, the biochar was from the waste generated in the carbonization furnaces of a charcoal production facility held by the same company, which produces wood biochar from *Eucalyptus sp.*.

Soil amendments were chemically characterized by a digestion procedure described in the USEPA3051A method (USEPA, 1998). The contents of each element were determined by either graphite furnace or flame ionization atomic absorption spectroscopy (Perkin Elmer - AAnalyst™), depending on their concentration. Total N level was determined by the Kjeldahl method (Malavolta et al., 1997), and total C was measured by dry combustion in an Elementar Vario TOC analyzer. Results are shown in Table 1.

Table 1
Chemical characterization of the amendments determined by atomic absorption spectrometry.

Element	Composted food remains	Limestone	Sewage sludge	Biochar
	%			
C[a]	33	–	27.9	51.9
	g kg^{-1}			
N[b]	31	–	35.9	2.8
Ca	43.4	189.6	9.5	20.2
Mg	6.1	68.2	5.3	2.4
K	13.7	0.7	2	5.6
Fe	4.58	27.9	18.4	11.3
	mg kg^{-1}			
Cu	5.2	2.3	127.4	2.3
Zn	296.5	3641	3082	37.1
Mn	488.5	3887	149.3	1477
Ni	0.4	5.9	20.5	0.9
Cd	0.12	19.5	10.9	0.06
Pb	155.4	1328	159	1.56
Cr	1706	–	36	252

[a] Determined by dry combustion in an Elementar Vario TOC.

[b] Determined by the Kjeldahl method.

The chemical composition and structural morphologies of the amendments were assessed by scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX – model Zeiss LEO EVO 40 XVP). Fourier transform infrared spectroscopy (FTIR) was used to identify the functional groups on the surface of the materials. The spectra were investigated in the 4000–400 cm^{-1} region under a 4 cm^{-1} resolution by using a Varian 660 IR.

2.2. Greenhouse experiment

The experiment was carried out under greenhouse conditions with an average temperature of 25 ± 3 °C throughout the experiment period. Pots were filled with soils collected from a zinc mining area located in Vazante, Minas Gerais state, Brazil (1 kg of air-dried soil $<$ 2 mm). Soils were classified as: Entisols – UTM 307,020 and 8016,351, area 23, zone K – collected in a site covered with native plants near the mining area; Oxisols – UTM 307,193 and 8016,792, area 23, zone K – collected inside the open pit; and Technosol - UTM 307,995 and 8017,628, area 23, zone K – collected near an old ore processing mill. Soil characterization was performed according to Embrapa (EMBRAPA, 1997) and the semi-total levels of Zn, Cd, and Pb were determined following the same protocol used for the soil amendments (USEPA, 1998) (Table 2).

Each soil amendment (CFR and sewage sludge: 1.25; 2.5; 5, and 10 g kg^{-1}; biochar: 2.5; 7.5; 15, and 30 g kg^{-1}; limestone: 0.5; 1; 2, and 4 g kg^{-1}) was homogenously applied to the soil samples and incubated for 60 days, with a water content ~50–60% of the water-holding capacity. The doses of each amendment were chosen based on their chemical properties, i.e. the neutralizing power of limestone, the nitrogen content of CFR and sewage sludge, and the carbon content of biochar.

After the incubation period, pH in water (1:2.5) and levels of phytoavailable Zn, Pb, and Cd were determined by DTPA extraction (EMBRAPA, 1997) followed by atomic absorption spectroscopy (Perkin Elmer - AAnalyst™). A control (soil sample without soil amendments) was also set for each soil.

At the end of the incubation period, pots were seeded with 15 *Andropogon gayanus* seeds. The seeds were collected in the same area where the soil samples were taken. The pots were kept humid (about 50–60% of water holding capacity) during germination and development of plants. The tests were conducted according to protocol N° 208: Terrestrial Plant Test: Seedling Emergence and Seedling Growth Test