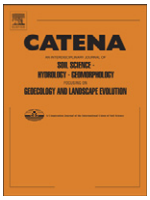
Catena 137 (2016) 120–125

Contents lists available at ScienceDirect

Catena

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



Contribution of waste and biochar amendment to the sorption of metals in a copper mine tailing

R. Forján [a],*, V. Asensio [b], A. Rodríguez-Vila [a], E.F. Covelo [a]

[a] *Department of Plant Biology and Soil Science, Faculty of Biology, University of Vigo, As Lagoas-Marcosende, 36310 Vigo, Pontevedra, Spain*
[b] *Department of Plant Nutrition, CENA, University of São Paulo (CENA-USP), Av. Centenário 303, 13400-970, Piracicaba, SP, Brazil*

ARTICLE INFO

Article history:
Received 3 December 2014
Received in revised form 2 September 2015
Accepted 18 September 2015
Available online 29 September 2015

Keywords:
Wastes
Mine soil
Metal
Soil remediation
Biochar
Sorption

ABSTRACT

One technique applied to restore degraded or contaminated soils is to use amendments made of different types of waste materials, which in turn may contain metals such as Cu, Pb and Zn. For this reason it is important to determine the capacity of the soil to retain these materials, and to compare the sorption capacity between an amended soil and another unamended soil. The aim of this study was to determine the chemical behaviour of these metals in the soil after applying the amendment, and how it affected the soil's sorption capacity. Another aim was to study the contribution of contaminating elements from the amendment itself. The amendments used in this study were a mixture made of waste material (sewage sludges, sludges from an aluminium plant, ash, food industry wastes, and sands from a wastewater treatment plant) and biochar (biomass of *Acacia dealbata*) (97%:3%) in different soil/amendment proportions. The soil was from a mine tailing. The mine tailings were amended with the mixture of waste and biochar which had a higher sorption capacity than the soil from the pond. The samples with amendment had a greater affinity for Cu, Pb and Zn than the mine soil. The results obtained show that adding a mixture made of waste and biochar favours the retention of Cu, Pb and Zn in mine tailing from metal mines.

1. Introduction

Mine soils are highly degraded at both physical and chemical levels, which prevents them from carrying out their functions and plants growing on their surface. Mine soils are a source of pollution that affects the area where the mine operates and the adjacent areas. This is due to the contamination of underground waters as a result of acid runoff from the mine, or atmospheric pollution caused by fine particles that are carried off into the air. One of the main impacts that mining has on soils is their high concentration of metals, acidity and low organic matter content (Akala and Lal, 2001; Vega et al., 2005; Santibañez et al., 2007; Zanuzzi et al., 2009; Asensio et al., 2013). It is important to understand how these metallic elements behave to their concentration and the ease with which they migrate through these types of soils.

One of the most recently used techniques to recover mine soils involves amendments made in situ with different types of waste material (such as municipal solid wastes '(MSW)', sewage sludge or waste from the food industry). Using these types of amendments has a double benefit. Firstly, it returns the components of these wastes to the biogeochemical cycle, and secondly, it adds organic matter to the soil, increasing the pH and immobilizing metals (Theodoratos et al., 2000; Paradelo et al., 2011). The contribution of organic matter is important, as previous studies (Karami et al., 2011) have shown that increasing it in the soil leads to a descent in the assimilable metal content. Organic matter also adds essential nutrients that improve the fertility level of the soils, and helps to improve certain physical–chemical properties of the soil (Illera et al., 2000). Sometimes, the waste material used as an amendment contains contaminants such as metals or organic compounds, which means that many of them cannot be used on any type of soil. It is also necessary to control the proportion of amendment/soil used, in order to ensure a balance between their potentially beneficial qualities and possible problems of contamination (Paradelo et al., 2011). Adding organic matter to these types of soils leads to a descent in the assimilable metal content, as this is capable of forming strong bonds with metals and therefore retain them firmly in the soil (Kabata-Pendias, 2001). Different studies have shown that adding amendments made of waste materials reduces the assimilable metal content in the soil (Brown et al., 2003; Natal-da-Luz et al., 2012). The increased content of organic matter provided by the residue causes an increase in the sorption capacity of heavy metals in soil (Kocasoy and Güvener, 2009). These studies were based on understanding how the available amount of metals varied in the soil, but not on how these metals behaved in the soil once the amendments had been applied.

Another option, despite still being costly, is to use biochar in combination with these amendments to recover degraded soils. Biochar is obtained by biomass pyrolysis (using both plant and animal waste) using substoichiometric combustion or without oxygen in pyrolytic ovens. The biochar, in the same way as the amendments made using waste material, provides organic matter, especially carbon and nitrogen.

---

* Corresponding author.
E-mail address: rforjan@uvigo.es (R. Forján).

http://dx.doi.org/10.1016/j.catena.2015.09.010
0341-8162/

However, unlike the amendments, the waste used to make biochar usually contains very few or no trace elements, such as forestry biomass. They also have the added benefit that the C and N they provide are much more recalcitrant. Different studies (Beesley et al., 2010; Beesley and Marmiroli, 2011; Park et al., 2011) have shown that biochar can reduce available contents of metals such as Cu, Pb and Zn, and increase the soil pH. The biochar used in this study was made using *Acacia dealbata* Link. This is a shrub from the legume family (*Fabaceae*) that is considered an invasive species in the Iberian Peninsula. Using biochar made of *A. dealbata* as an amendment would therefore serve two functions — recovering the soil and using the waste matter from a type of invasive plant. The biochar increases the sorption capacity of heavy metals in soil; this increase is due to the high pH, organic matter, and large surface area (Beesley et al., 2010, Beesley and Marmiroli, 2011; Uchimiya et al., 2011).

An understanding of metal sorption processes can help in providing very valuable information about the effect of amendments once they have been applied to the soil. Therefore, the aim of this study was to compare the sorption capacity of Cu, Pb and Zn in a copper mine soil after applying a combined amendment of waste and biochar, and to understand the behaviour of the metals included in the amendments. Copper, lead and zinc are usually found in high concentrations in the soils from the mine in the study, and in the waste materials used as amendments.

2. Material and methods

2.1. Study area and amendments

The sample zone is in the mine in Touro (Northwest Spain; Lat/Lon (Datum ETRS89): 8° 20′ 12.06″ W 42° 52′ 46.18″ N). The climate in this zone is Atlantic (oceanic) with precipitation reaching 1886 mm per year (with an average of 157 mm per month) and a mean daily temperature of 12.6 °C. The average of relative humidity is 77% (AEMET 2014). For this study, a mine tailing was chosen from the mine's settling pond (S). The amendment made of wastes was provided by the company Tratamiento Ecológicos del Noroeste (T.E.N.). This amendment was made of a mixture of sewage sludges, sludges from an aluminium plant, ash, food industry wastes, and sands from a wastewater treatment plant (T). The biochar (B) was made of biomass from areas invaded by *A. dealbata* in the north of Portugal, and was obtained by pyrolysis, without oxygen, at 450 °C of temperature during 8 h.

2.2. Experiment design and soil chemical analyses

This mine tailing was treated with a mixed amendment consisting of a mixture of different wastes (T) combined with biochar (B). The amendment (TB) and the mine tailing (S) were mixed (STB) at 20, 40, 60% and then placed in glass vessels. The mixture of the amendment made of wastes and biochar was called TB. The amendment TB and the mine tailing S at 100% were also placed in glass vials as control samples. The amendment TB was made with 97% wastes and 3% biochar. All mixtures were made w/w. The mixtures and controls were incubated in darkness to field capacity for one month.

Soil pH was determined with a pH electrode in 1:2.5 to soil extracts. The phytoavailable content of Cu, Pb and Zn was extracted with 0.01 M $CaCl_2$ in soil solution (Houba et al., 2000). Quasitotal metal contents were extracted with *aqua regia* by acid digestion in a microwave oven (Milestone ETHOS 1, Italy) and analysed in an ICP-OES. Soil total carbon (TC) was determined in a solid module (Shimadzu SSM-5000, Japan) coupled with a TOC analyser (Shimadzu TNM-1, Japan). These analyses were carried out with soil S, the mixtures and the positive control TB100%.

2.3. Sorption experiment and construction of isotherms

To evaluate the sorption capacity of Cu, Pb and Zn by the mine tailing and the different mixtures, data for isotherm construction were obtained in batch experiments using the method of Alberti et al. (1997) and Gomes et al. (2001)) modified by Harter and Naidu (2001). We used single-metal solutions of Cu^{2+}, Pb^{2+} and Zn^{2+} nitrates (0.03, 0.05, 0.08, 0.1 and 0.5 mmol L^{-1}) containing 0.01 M $NaNO_3$ as background electrolyte (Vega et al., 2009). Soil samples (1.5 g) were shaken with 25 mL of “sorption solutions” in polyethylene tubes in a rotatory shaker for 24 h at 25 °C. The samples were then centrifuged 10 min at 3000 rpm and the supernatant was filtered through Whatman 42 paper (pore size 0.45 μm). Supernatants were analysed by ICP-AES (Perkin-Elmer Optima 4300 DV) to determine the Cu, Pb and Zn concentrations. The concentration of each metal that had been sorbed by each soil sample was calculated from the difference between its concentration in solution before the addition of this soil and after equilibration (shaking) with soil. The sorption isotherms were constructed for each metal by plotting the sorbed metal concentration of the soil sample (μmol per g of dry soil) against the concentration of the metal in solution at equilibrium (μmol L^{-1}). To take exchange into account the background electrolyte, the concentrations of the studied metals were corrected by subtracting the values determined in an additional experiment, in which the sorption solution contained only 0.01 M $NaNO_3$. All of the sorption experiments were performed in triplicate.

For each metal sorption isotherms were constructed by plotting the sorbed metal concentration (μmol per g of dry soil sample) against the concentration of the metal in solution at equilibrium (μmol L^{-1}). The obtained isotherms were compared with to the models of Langmuir (1) and Freundlich (2) and with the types of curve described by Giles et al. (1974). The overall capacity of the soils to sorb Cu, Pb or Zn was evaluated as the slope *Kr* (3) according to Vega et al. (2008).

(1) Langmuir model:

$$x/m = CK_L\beta_L/1 + K_LC.$$

x	quantity of material sorbed (μmol).
m	quantity of sorbent (g).
C	Solution concentration equilibrium (μmol L^{-1}).
K_L	Langmuir constant (L μmol L^{-1}).
β_L	high sorption capacity (μmol g^{-1})

(2) Freundlich model:

$$\text{Log } x/m = 1/n \log C + \log K_F.$$

x	quantity of material sorbed (μmol).
m	quantity of sorbent (g).
C	Solution concentration equilibrium (μmol L^{-1}).
K_F	Freundlich constant (L g^{-1}).
n	dimensionless. $n > 1$, sorption is favourable

(3) K_r

It is a line of type $y = ax$

y	quantity of sorbent (μmol g^{-1}).
x	amount of added metal or metals per gramme of soil (deduced from the concentration of the solution with which was treated) versus sorbed amount of each of the metals (μmol g^{-1}).
a	is the K_r parameter. It is the slope of the line. It is a dimensionless parameter. If $a \approx 1$ high affinity for the metal.

2.4. Statistical analyses

All of the analytical determinations were performed in triplicate. The data obtained were statistically treated with the program SPSS version 19.0 for Windows. Analysis of variance (ANOVA) and test of homogeneity of variance were carried out. In case of homogeneity, a post-hoc least