Journal of Geochemical Exploration 182 (2017) 210–217

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

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

Evaluation of the phytoremediation potential of native plants growing on a copper mine tailing in northern Chile

Elizabeth J. Lam[a], Manuel Cánovas[b,*], María E. Gálvez[a], Ítalo L. Montofré[b], Brian F. Keith[c], Ángel Faz[d]

[a] Chemical Engineering Department, Universidad Católica del Norte, Antofagasta, Chile
[b] Metallurgical and Mining Engineering Department, Universidad Católica del Norte, Chile
[c] Department of Computing & Systems Engineering, Universidad Católica del Norte, Chile
[d] Agrarian Science and Technology Department, Universidad Politécnica de Cartagena, Cartagena, Spain

ARTICLE INFO

Keywords:
Copper mine tailings
Phytoextraction
Phytostabilization
Metal translocation
Bioconcentration factor

ABSTRACT

Mining operations in northern Chile are responsible for numerous mine tailings deposits, which may represent a risk to human health and the environment. This study evaluated the phytoremediation potential of three plant species (*Prosopis tamarugo*, *Schinus molle* and *Atriplex nummularia*) to remediate copper mine tailings in northern Chile. To improve the characteristics of the tailing, three treatments based on *arbuscular mycorrhizal fungi* and organic and inorganic amendments were applied. Plant roots and shoots and the associated tailings samples were collected and analyzed for total metal concentrations of Cu, Mn, Fe, Pb, Zn and Cd. Bioconcentration Factor (BCF) and Translocation Factor (TF) were estimated to evaluate the plant species potential for phytoremediation. The results show that *A. nummularia* presents high TF values on untreated tailings for Pb and Zn; on tailings treated with $CaCO_3$/compost for Mn, Fe, Pb and Zn, and on tailings treated with $CaCO_3$/compost/mycorrhizae only for Zn. *P. tamarugo* presents high TF values on the untreated tailings for Pb and Zn; and on tailings treated with $CaCO_3$/compost for Mn. *S. molle* presents high TF values on untreated tailings for Cu, Mn, Pb and Zn; on the tailing treated with $CaCO_3$/compost for Mn and Zn, and on the tailing treated with $CaCO_3$/compost/mycorrhizae for Mn and Pb. High TF values show that the plants studied under the specific characteristics of the treated or untreated tailings, present the potential of being used for phytoextraction. Regarding the BCF, the experiments showed values lower than 1 for all the metals, except for Cd, which for *A. nummularia* developed in the amended tailing, presented potential characteristics of a hyperaccumulator. This metal even had in general BCF values higher than 1 and TF lower than 1, which shows the potential of the three evaluated species as phytostabilizers for Cd. Regarding the effect of the amendments, the untreated tailing presented lower removal efficiency than the tailings treated with $CaCO_3$/compost (T1) and $CaCO_3$/compost/mycorrhizae (T2). On the other hand, no significant difference was found between treatments T1 and T2.

1. Introduction

Mining is the most important economic activity in Chile. However, it is also responsible for significant environmental damage, reflecting the large amount and diversity of residues generated from mining operations, which are often untreated, thus affecting the quality of water, soil and air (Bech et al., 1997; Valladares et al., 2013; Kossoff et al., 2014; Feyen et al., 2015).

Historically, because of the lack of adequate legislation, environmental liabilities increased in number and magnitude, leaving a legacy of major environmental problems. In particular, mining operations in northern central Chile have resulted in numerous mine tailings deposits that contain approximately 50% of the solid residues generated from such operations (Rubio, 2007). Solid tailings may also contain fines and slimes which may affect the stability of the tailings storage facilities (Edraki et al., 2014). Given the high content of metals, these tailings represent a risk to human health and the environment. Fine particles are exposed to physical agents like wind and rain that can disperse them into the surrounding area, contaminating waterways and neighboring soils (Mendez and Maier, 2008; Yadav and Jamal, 2015). Mine tailings in semiarid regions are highly susceptible to erosion and are sources of dust pollution and potential avenues of human exposure to toxic metals. Many factors can influence the mobility of metals in tailings, such as pH and organic composition and concentration (Bolan et al., 2014).

* Corresponding author.
E-mail address: manuel.canovas@ucn.cl (M. Cánovas).

http://dx.doi.org/10.1016/j.gexplo.2017.06.015
Received 6 July 2016; Received in revised form 21 June 2017; Accepted 21 June 2017
Available online 22 June 2017

In 2012, the new Chilean law 20,551, which regulates mine closure and mining facilities, entered into force. Its main objectives are to protect the life, health and safety of people and the environment, to mitigate the negative effects of mining, to hold the mining industry accountable after cessation of operations and to ensure the physical and chemical stability of the ground where mining was carried out.

The last three decades have seen the emergence and development of ecologically-friendly, gentle soil remediation techniques using plant species. These techniques, known as phytoremediation, are generally considered to be less invasive, more cost-effective and restorative of soil compared to conventional methods (Kidd et al., 2009). Phytoremediation is based on the use of plants and their associated microorganisms to reduce concentrations of contaminants such as metals, radioactive isotopes, hydrocarbons or pesticides (Bennett et al., 2003; Greipsson, 2011; Ali et al., 2013). To apply phytoremediation to mine tailings, it is necessary to modify the physicochemical characteristics of the tailings so that plants can be self-sustaining over time, specifically by increasing the concentrations of organic matter and nutrients, given that tailings have low levels of microbial activity (Pepper et al., 2012; Young et al., 2015). In most cases, phytoremediation is supported with additives, termed amendments, which improve the characteristics of the substrate by reducing the mobility and bioavailability of metals (Alcantara et al., 2015; Puga et al., 2015; Zeng et al., 2015). Plant-based technologies in mine tailings are mostly limited to phytostabilization and phytoextraction. Phytostabilization involves using plants to minimize metal mobility from contaminated soils (Root et al., 2013; Barajas-Aceves et al., 2015; Li and Huang, 2015). The strategy of phytostabilizing mine tailings in arid or semiarid climates involves using plants tolerant to drought, salinity and metals (Mendez et al., 2007; Mendez and Maier, 2008). Phytoextraction involves the capture of contaminants from the solid substrate or water by plant roots and the transport and accumulation of these in the upper parts of the plant (Rafati et al., 2011; Dhankher et al., 2012).

Bioconcentration factor (BCF) and translocation factor (TF) were determined, both factors can be used to estimate a plant's potential for phytoremediation purpose (Yoon et al., 2006). From the perspective of phytoremediation, an efficient phytoextraction strategy should have high TF values because metals must be in the aerial parts of the plants so that they can be removed at harvest (Kamari et al., 2014). $TF < 1$ and $TF > 1$ represent, respectively, a low and high capacity to translocate metals from the roots to the shoots (Bazihizina et al., 2015).

This work was carried out on a copper mine tailing from the Antofagasta Region, one of the driest zones in the world. The tailing was classified as saline-sodic, with low Ca and high Na and SO_4^{2-} contents, high concentrations of metals such as Cu, Fe and Al, and pH 8.4. The tailing under study presents high concentrations of SO_4^{2-} and sulfides, which can generate sulfuric acid by oxidation and irrigation. *Arbuscular mycorrhizal fungi*, organic (compost) and inorganic amendments ($CaCO_3$) were added to improve the characteristics of the tailing. The aim of this study was to assess the potential of three native plant species (*Prosopis tamarugo*, *Schinus molle* and *Atriplex nummularia*) for phytoremediation of metals on amended copper mine tailings.

2. Material and methods

2.1. Site description and sampling techniques

The study area is located in the western margin of the Atacama Desert in northern Chile. Tailings samples were collected from a post-operative copper mine tailing site, which was active until 2006, located at latitude 24° 9′58.33″ S and longitude 69° 2′33.36″ W at an altitude of 3200 m.a.s.l. The tailing contains high concentrations of metals such as Cu, Fe, Zn, Mn and Pb. The approximate area of the tailing deposit is 10,000 m^2. This region is characterized by a desert climate with high levels of solar radiation. Temperatures range approximately from −15 °C in July to 30 °C in January. Precipitation typically falls in the summer months, with 2–6 mm/year.

Table 1
Maximum, minimum and average values and standard deviations of basic characteristics of tailing.

Parameter	Minimum value	Maximum value	Average value	Standard deviation
Sand (%)	–	–	75	–
Silt (%)	–	–	24	–
Clay (%)	–	–	1	–
TOC (%)	–	–	0.03	–
SAR	31.5	90.1	34.1	15.3
pH	8.13	8.63	8.42	0.06
Saturated water (%)	63.1	74.0	71.6	5.8
EC (dS m^{-1} at 25 °C)	15.3	40.1	35.5	3.9
Fe (mg kg^{-1})	19,236	41,923	35,015	3552
Cu (mg kg^{-1})	1008	16,296	11,151	2262
Pb (mg kg^{-1})	75.65	215.4	183.2	27.2
Mn (mg kg^{-1})	279.3	467.8	352.5	78.9
Zn (mg kg^{-1})	108.6	306.6	282.2	89.5
Na^+	1639	6086	3265	2134
Ca^{2+}	163.7	293.3	292.5	115.2
S-SO_4	2459	4441	2198.2	1941.6

TOC: Total organic carbon; SAR: Sodium adsorption ratio.

In order to characterize the tailings, 80 equidistant sampling sites were established in a grid of 15 m × 7 m, covering a total area of 6615 m^2. Tailing samples of about 1 kg were collected at three depths: 0–10 cm, 10–20 cm and 20–30 cm.

2.2. Physicochemical characterization of mine tailing

Physical and chemical characteristics of the tailings used in this study at the three different depths are presented in Table 1.

pH was measured potentiometrically in a 1: 2.5 tailing–water suspension. EC was measured in the saturated tailing-paste extract using the Hanna HI4321 benchtop conductivity meter. Total metal concentrations were measured by atomic absorption spectrophotometry (AAS). All the samples were run in triplicate. The exchangeable sodium percentage (ESP) was used to assess sodicity (Fan and Kong, 2013; Emami et al., 2014). ESP was estimated from SAR (sodium adsorption ratio) based on the linear equation (USDA. U.S. Salinity Laboratory Staff, 1954):

$$ESP = \frac{100 \cdot K_g \cdot SAR}{1 + K_g \cdot SAR} \tag{1}$$

This relationship is based on the Gapon equation by assuming Gapon selectivity coefficient, K_g, of Na − (Ca + Mg) exchange as 0.0147 (Wang et al., 2014). Constant K_g was evaluated by the USDA. U.S. Salinity Laboratory Staff (1954). There are various classification systems of salt-affected soils. The most widely used system is the classifications of the US Salinity Laboratory, which are based on EC and ESP. Based on the results obtained, the tailing was classified as saline sodic.

2.3. Amendments and plant species

Soil salinity and sodicity are escalating problems worldwide, especially in arid and semi-arid regions (Mahmoodabadi et al., 2013). In this case, the tailing is sandy and saline-sodic, with a very low content of Ca^{2+} and a very high concentration of S-SO_4. High levels of metal sulfides, such as pyrite (FeS_2) and sulfide wastes, H_2SO_4 could be produced by pyrite oxidation. The amelioration of saline-sodic soils needs sodium to be removed from soil and this can be managed by adding soluble calcium salts such as gypsum, and afterward leaching the exchanged Na^+ out of the root zones (Hafez et al., 2015). Recently, (Lam