Phytoextraction of Toxic Elements from Contaminated Soils by Ornamental Plants

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***Abstract*—**Hundreds of tons of mining wastes from silver mine were deposited at the surroundings of a small town located in Zacatecas, Mexico. Physicochemical properties of tailings showed acid pH, high salinity and very low organic material content. Elemental analysis showed that content of As, Cu, Mn, Pb, and Zn in two mine tailings (red and grey) were up to six times higher than in the town soil, with 2-10 gkg-1, 0.1-2 gkg-1, 0.2-3 gkg-1, 0.6-4 gKg-1 and 1-6 gkg-1 respectively. Sequential extraction procedure was performed in order to understand the mobility of elements in soils. After harvesting of ornamental plants named Helianthus annuus known as sunflower, which were sown in a mixture of 60/50 of polluted soil and clean soil, it was evident that despite phytotoxic limits of As, Cu, Pb and Zn were exceeded, the plants were capable to grow and to extract metals from polluted soil.

***Keywords*—** Arsenic, heavy metals, mine tailing, phytoremediation,, sunflower.

I. Introduction

Tailing dams have been a serious problem all over the world [1], but it is not only due to the presence of the tailings, but also the fact that many of them are exposed to the wind and rain, facilitating their mobility and dispersion. Despite mining is a very important industry in Mexico, little effort was made to minimize the damage caused to the environment and the surrounding population. Over a few decades ago, phytoremediation has been a popular technique to clean soil, sediment and water of organic and inorganic pollutants. Nevertheless, there´s still a lot to study on this topic, because of the many different situations, substances, and species combinations that could occur.

Currently, in Mexico, mining industry occupies about 11.3 % of the national territory, distributed in 25 of the 32 states, causing several damage to the ecosystems and towns, representing a risk for people, animals and plants.

Zacatecas is one of the states with more presence of mining sector, being the second biggest producer in the country. Noria de Angeles is a town located in that state, where people have been affected by the wastes from the mine Real de Angeles (focus on the extraction of silver, lead and zinc) due to a red tailing dam found inside the town, which occupies about 1.6 hectares, and a gray tailing dam located one kilometer away from the town, occupying close to 400 hectares. According to Ibarra-García [2], and based on Mexican regulations, both the tailings and the town ground are contaminated mostly with Pb, Cu and Zn, on amounts about 800, 900 and 280 mg/kg (respectively, on the tailings) and 400, 120 and 50 mg/kg (respectively, on the town ground).

Although plants are vulnerable to the presence of heavy metals on the ground, there are some species that possess a high tolerance for those. That ability is used to uptake from the ground this kind of substances, or at least decrease their mobility, with an economic and environmental friendly method [3], even in highest levels of concentration as in the mine tailings [4], [5]. This technique is better known as *Phytoremediation*, and it is composed of a series of processes such as phytostabilization, phytostimulation, phytovolatlilzation, phytodegradation and phytoextraction [6]. The last one, particularly, applies to the removal of inorganic compounds, such as those which contains heavy metals.

The main aim of this project, was to study phytoremediation of heavy metals on tailings from Noria de Angeles using sunflower (*Helianthus annuus*) in order to determine its potential on the uptake of As, Cu, Mn, Pb, and Zn, since this plant has shown a high capacity to extract metals in both, soil [7] and aqueous medium [8], then it is interesting to study its behavior under contamination of multiple metals [9].

II. Materials and Methods

A. *Tailings treatment and characterization*

Both red and gray tailings were taken from each dam in Noria de Angeles. The samples were dried at room temperature and sieved to remove all foreign materials. The physicochemical characterization was made according to the Mexican regulation [10].

B. *Speciation*

Sequential Extraction BCR was carried out in samples to know the mobility of different elements in contaminated soil, since it has proven to be a reliable and accurate technique [11]. According to this method, elements can be found in four different fractions in the soil: elements in the exchangeable fraction in ionic form bound to carbonates (*F1*); elements bound to amorphous Fe and Mn oxides and hydroxides (*F2*);

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elements bound to organic matter and sulphides (*F3*); and elements contained on primary and secondary minerals on the residual solid (*F4*). Table I shows the procedure of this technique.

TABLE I
SEQUENTIAL EXTRACTION BCR METHODOLOGY

Fraction	Reagent	Conditions
F1	15 mL AcOH 0.11 M	16 hours stirring at room temperature.
F2	15 mL NH_4OH 0.1 M	16 hours stirring at room temperature.
F3	10 mL H_2O_2 8.8 M +	85 °C water bath to almost evaporation.
	10 mL H_2O_2 8.8 M +	85 °C water bath to almost evaporation.
	15 mL $AcONH_4$ 1.0 M	16 hours stirring at room temperature.
F4	15 mL HNO_3	5 hours at 95 °C water bath.

C. Sunflower crop

In order to reach more favorable conditions to the plant, soil from the area was mixed with tailings (due to the low presence of organic material in the pure tailings), so two mixtures were made, using 60 % of each tailing and the rest of test soil. Three batches were cultivated, to obtain harvests at 60 days intervals, which give a total of 180 days of crop.

D. Harvest and treatment

Once plants were harvested, they were carefully washed, and divided into their sections (roots, steams, leaves and flowers), and then dried in an oven at 50 °C for 18 hours. After that, each section was weighed and triturated, ready to be analyzed.

E. Digestion and analysis

A sample of 0.5 g was taken from each section of the plant and digested on a microwave oven according to the EPA Method 3050b, and finally, the metal concentrations were measured using an ICP-OES equipment, following the EPA Method 6010c.

III. RESULTS

A. Physicochemical characteristics

Both types of mine tailings have different appearance, nevertheless, mineralogy is quite similar, since red tailings are constituted by 42% of clay, 33% of silk and 35% of sand, whereas gray tailings composition is 39%, 37% and 24% of clay, silk and sand respectively, as was reported by Ibarra et al (2018); dominant soils in the area are petric calcisols and calcaric leptosols. Table II presents the physicochemical properties of soils and mine tailings.

TABLE II
PHYSICOCHEMICAL CHARACTERISTIC OF CONTAMINATED SOILS AND TAILS

Tailing/soils	(RT) Red tailings	(GT) Gray tailings	(TS) Test soil	60% RT +40% TS	60% GT +40% TS
pH	4.2	3.9	8.5	6.9	6.8
Humidity %	1.6	2.3	1.0	1.4	1.5
Salinity %	1.3	0.7	0.4	0.9	0.6
EC (µs)	2321	621	53	1132	432
Organic matter %	0.3	0.4	0.6	0.4	0.5
Ca^{2+} mg/kg	12.2	9.1	6.2	8.6	7.9
Mg^{2+} mg/kg	14.2	1.9	4.7	8.6	3.4

B. Elemental concentrations

The concentrations of elements were measured in the tailings and mixtures. Based on the national and international regulations, there are four elements above the permissible limits for soil. Red tailings have close to 24000%, 500%, 200% and 1000% of As, Cu, Pb and Zn, respectively, while Gray Tailings have close to 10000%, 150%. 300% and 600%, respectively. In general, elements abundance presented the following order: As>Zn>Pb>Mn>Cu as can be observed in Table III.

TABLE III
CONCENTRATIONS IN TAILINGS AND CONTAMINATED SOILS (MG/KG)

	As	*Cu*	*Mn*	*Pb*	*Zn*
RT	5199±3	476±4	493±74	820±137	2454±373
GT	3958±286	136±11	765±157	1239±103	1284±234
TS	3.9±0.8	6±0.9	6±2	9±1	58±7
TS+ RT	3121±3	288±5	298±46	494±11	1495±247
TS+ GT	2376±193	79.1±6	461±113	747±72	793±145
PL	22 [a]	100 [b]		400 [a]	220 [a]

A. PL: permissible limits in soil.
B. [a] Mexican regulation for soil [10].
C. [b] Canadian standards for soil, ground water and sediments [12]

C. Sequential fractionation

Sequential fractionation shows that element distribution in both types of mine tailings is different as can be seen in Table IV.

In RT lowest proportion of elements are in the interchangeable fraction linked to carbonates that is the more bioavailable of all fractions, whit up to 3% of As, 4% of Pb, but 39% and 30% for Cu and Zn respectively (Fig. 1), whereas in the gray tailings the proportion in this first fraction was up to 1% for As, 20% for Pb, 40% for Zn, and 78% for Mn.

Most As (66%) and Pb (38%) are linked to the Fe and Mn oxyhidroxides fraction in RT, but in GT the content in that fraction was important only for Zn (60%). Most As (80%) and Cu (60%) are in the residual fraction of GT; only Cu in RT had a relevant content in the organic material fraction with 40% in RT.

TABLE IV
HEAVY METALS CONCENTRATIONS IN EACH FRACTION OF THE TAILINGS

Gray Tailings					
	Concentration *mg/kg*	F1 *mg/kg*	F2 *mg/kg*	F3 *mg/kg*	F4 *mg/kg*
As	3957.54	100.1	658.5	73.4	3125.5
Mn	764.82	582.9	50.9	18.8	112.2
Cu	135.54	25.2	30.9	0.5	79.0
Pb	1239.07	179.1	666.0	2.3	391.6
Zn	1283.49	525.1	219.6	8.7	530.1
Red Tailings					
	Concentration *mg/kg*	F1 *mg/kg*	F2 *mg/kg*	F3 *mg/kg*	F4 *mg/kg*
As	5198.80	111.3	3094.1	294.4	1698.9
Mn	*493.11*	*129.8*	*343.6*	*20.9*	*0.0*
Cu	475.84	183.2	181.9	231.9	0.0
Pb	15377.45	570.7	10649.9	56.1	4100.7
Zn	2454.24	991.0	918.9	65.7	478.6

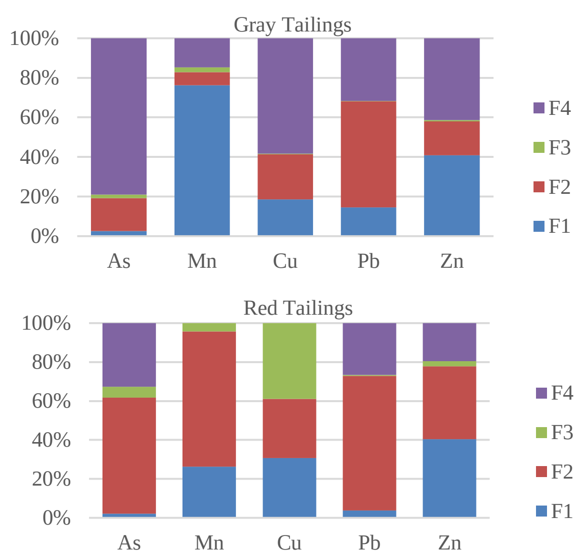

Fig. 1 Metal speciation fractions in each tailing

D. Concentration of elements in plants

After 180 days of cultivate, the total concentrations of quantified elements were measured, and it was found that the most extracted element by the plant in both contaminated soils was Zn followed by Mn, Pb, As and Cu. Although elemental concentrations in each soil are different the amount extracted of each element by the plants was quite similar.

TABLE V
TOTAL AS AND METAL EXTRACTED CONCENTRATIONS BY HELIANTHIS ANNUUS SOWN IN CONTAMINATE SOILS (MG/KG)

	As	Cu	Mn	Pb	Zn
Contaminated soil with RT	45±3	20±2	132±16	58±7	163±18
Contaminated soilwith GT	48±4	19±2	121±13	57±6	174±22
Control Soil	1±0.8	3±0.7	28±2	4±0.5	47±5

The reduction of toxic elements in the mixtures of Test Soil and Tailings, was quantified at 60, 120 and 180 days. After 180 days, it was achieved a removal of 14.8±2.3% for As, 23.2±0.8% for Cu, 12.7±1.4% for Mn, 24.2±1.7% for Pb and 25.9±1.4% for Zn.

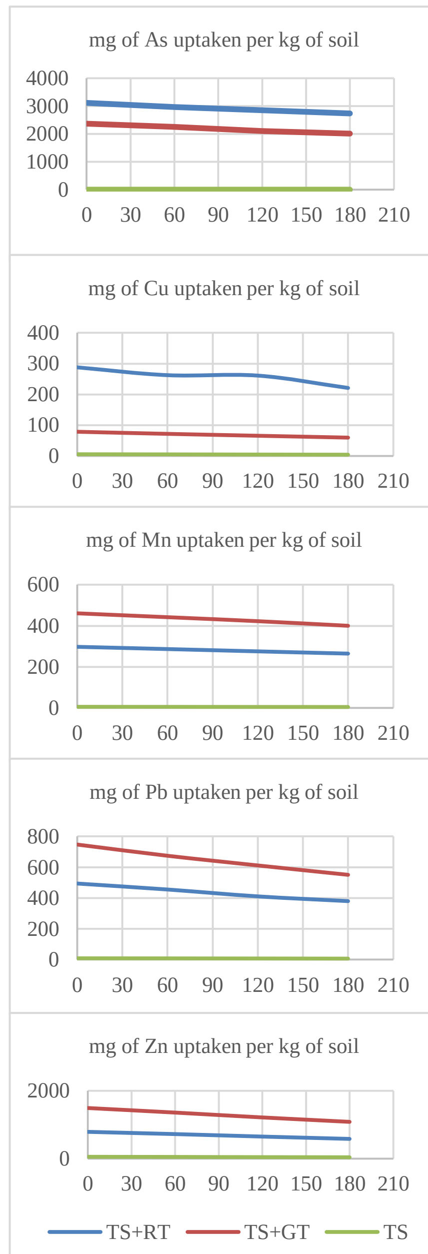

Fig. 2 Reduction of elements in contaminated soils after 180 days of phytoremediation

Since each element has different size, weight and possible interactions with the plant, then phytoremediation mechanisms can be also different. Fig. 3 shows the percentage of elements extracted in each part of the plant.

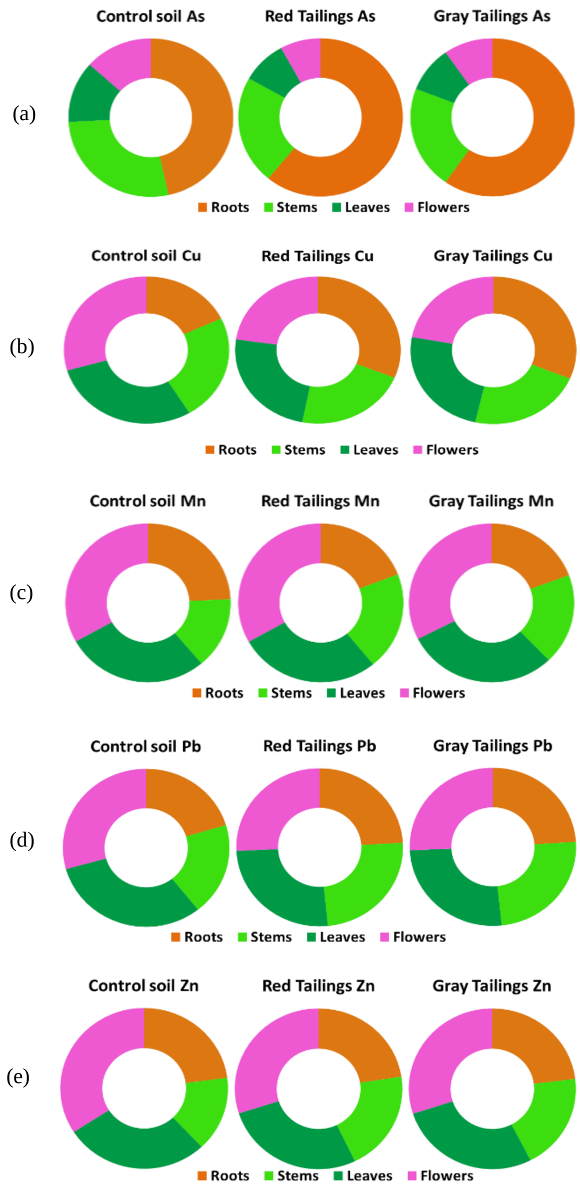

Fig. 3 Presence of metals in the sections of the plant. (a) Arsenic, (b) Copper, (c) Manganese, (d) Lead and (e) Zinc

The extraction of each element was quite similar in the two types of contaminated soil, but had some differences with the control soil; nevertheless, the extraction capacity of each part of the plant was different for every element. For instance, roots have the maximum extraction capability for As for a yield of 47% in the control soil, but increased to around 60% in both contaminated soils.

Roots promote phytoestabilization of elements, reducing the mobilization. In the case of metals, Cu, Mn, Pb, and Zn, their extraction by roots was between 19% and 31%, whereas stems and leaves extracted together around 50% of metals, although the extraction by the leaves was a little greater. Phytoextraction by flowers was between 22% to 33% for Cu and Mn respectively; in the case of As, flowers only extracted around 11%.

IV. Conclusions

Both mine tailings presented low pH, high salinity and electrical conductance, but very low organic material content. Mn and Zn were the most bioavailable metals in GTand RT.

Sunflower (*Helianthus annuus*) has tolerance to the presence of high concentrations of metals and arsenic and is able to grow in contaminated mine tailing soils

Sunflower (*Helianthus annuus*) was capable to uptake elements such as As, Cu, Mn, Pb and Zn with efficiencies between 14% to 26% for Mn and Zn, respectively when harvesting is carried out at 6 months.

Roots were the part of the plant that was capable to reduce more As, between 50-60%.

Stems and leaves extracted around 50% of metals.

Total cleaning of toxic elements from these studied tailing dams would take 8 crops of six months each.

V. Acknowledgments

Authors thank Conacyt for Project INFR-2016-01-27115 and for the scholarship of H. Martínez.

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