

HEAVY METALS IMMOBILIZATION IN CONTAMINATED SMELTER SOILS USING MICROBIAL SULPHATE REDUCTION

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Abstract. The main environmental problems associated with the mining activities are related to the production of large amounts of wastes; Different pathways are responsible for heavy metals dispersion, by air due to wind action, by water mediated by acid mine drainage and erosion, and the metals could be mobilized in the soil by different transport mechanisms.

Different remediation alternatives have been studied and reported in literature. *In situ* stabilization is a cheaper method. The heavy metals stabilization enables the decrease of metal mobility, reactivity and toxicity in the soil, decreasing heavy metals availability and phytoavailability.

Sulphate reducing bacteria (SRB) have been successfully utilized in groundwater bioprecipitation of heavy metals. In this study, this biological agent has been used in the immobilization of heavy metal in the subsurface of the soil due to its dissimilative metabolism. SRB produces hydrogen sulfide that reacts with soluble metals present in the media, generating as final product low soluble metal compounds (metal sulfides).

The bio-stabilization was studied at pilot scale to determine the stabilization efficiency using biological agent, SRB. The metals studied were Fe, Cu, Pb and Zn in the contaminated smelter soil. Bioaugmentation and biomagnification were applied. After 4 months, the metal stabilization efficiency was determined by leaching with acid solution at different pH to stimulate the metal mobility. The remediation pilot scale system showed that copper, lead and iron were much more stable at pH 3.0, with only 3.7% and 1% of total metal eluted, and compared with the system without biological agent. In the case of zinc, the elution was similar with or without remediation.

The metal stabilization using biological agent was successful in the contaminated smelter soil and these results are promising antecedents for full scale *in situ* remediation strategy.

Introduction

In the mining industry, metallurgy processes produce wastes with high heavy metal content. The transport and dispersion of contaminants can be by water, by acid rock drainage; by solid wastes as dump, heap leaching or on air pathway, by particle matter coming from copper smelters or mining dumps [1],[2].

Soils contaminated by heavy metals are currently a problem present in countries which economy is based on industrial processes that produce wastes containing high metal concentrations, mainly copper, iron, zinc, arsenic, cadmium, mercury and lead.

Metals present in the soil are exposed to weathering and undergo different kinds of processes like oxidation, reduction, sorption, precipitation among others [3]. The main problem of inorganic contaminants such as heavy metals is that, unlike contaminants of organic origin, they are not biodegradable, producing metal accumulation in the soil.

Confinement, extraction and stabilization are strategies commonly used for heavy metals remediation. Confinement is achieved using techniques like vitrification, contention barriers, cementation, etc. In this case, metals are isolated in the soil but the metal contamination remains in the soil. The possibility of matrix break still exists and the metals could be liberated.

Heavy metals extraction is possible using soil washing and extracting the metal bearing solution; this procedure requires post treatment to recover the metals. Other techniques used are electroremediation [4] and transport of the contaminated soil to authorized landfill. Heavy metals extraction using biological agents, like plants [5], algae, microorganisms among others, mediated absorption or sorption of heavy metals in or onto biomass have also been reported in the literature [6].

The main advantage of these agents is the low cost compared with confinement. However, there are still several challenges to improve the global efficiency of these processes, for example increasing the biomass, and increasing the metals load capacity.

The third strategy is related with the bioavailability of metals, which depends on the speciation and solubility of the metals [7]. In the ionic form, metals react with the different soil components and are more easily transported, increasing the potential uptake by biota [8]. Heavy metal bioavailability in the soil can be determined using methods like BIOMET biosensor [9] or chemical sequential extraction [10]. In this case, the remediation strategy is decreasing the potential risk of metal, decreasing its bioavailability using stabilization.

Some stabilization methods which consider the metals immobilization use agents such as compost, sewage sludge from treatment plants [11] or phosphates compounds. Another alternative of biological agent is sulphate reducing activity of some microorganisms [12],[13]. The sulphate reducing metabolism produces sulfide acid, which reacts with soluble metals and produces stable sulfur compounds with very low solubility and consequently low availability and mobility.

Different successful examples of the application of sulphate reducing bacteria have been reported with high metal removal percentages in the liquid medium, almost 100%. This method would allow the stabilization of metals in the anaerobic layer in the soil, which is very difficult to get with others superficial methods.

Materials and methods

Pilot scale test

The experimental system consists of 2 acrylic cubes of 0.45 m edge. The cubes were loaded with undisturbed soil samples excavated in a contaminated area near a copper smelter at 0.75 to 1.20 m depth. The cubes were put up over a funnel to collect the drainage solution. To maintain anaerobic condition to help sulphate reducing activity, nitrogen was added and cube was closed hermetically.

Soil characteristics. The soil showed a pH 6.17, with 8% of humidity and ORP -288 mV (Ag/AgCl). The highest concentration in the soil was iron with 4875 mg/kg; For copper and zinc was observed 208 mg/kg and 75 mg/kg, respectively. The arsenic contains was 24 mg/kg and 31 mg/kg for lead. Other parameters were determined such as real density, apparent density and pore volume; these values were 1.84 g/mL, 0.63 g/mL and 516 mL, respectively.

Metals addition. A solution of metals (359 mg/L of Cu, 486 mg/L of Fe, 4 mg/L of Pb and 394 mg/L of zinc) was prepared with sulphate salts (copper, zinc and iron) and nitrate salt (lead). The

effective dissolved lead concentration was very low due to $\text{Pb}(\text{SO}_4)$ precipitation. The metals solution was continuously fed on the top of the soil sample and the conductivity of the drained solution recovered through the bottom funnel was registered. When the conductivity measured in the output solution was similar to the input solution, the addition was suspended. The same process was applied to both cubes.

Bioaugmentation and biomagnification

The bioaugmentation was carried out with the sulphate reducing microorganisms isolated from smelter soil samples and cultivated in a continuous reactor, 6 days of hydraulic retention time [14]. The nutrients addition or biomagnification was realized with a Postgate cultivation medium [15]. Then, the microorganism's culture and nutrients were applied only in one of the two cubes, the other one being the experiment control.

The first nutrient application was carried out together with the inoculation and after this; it was repeated every each 15 days during 2.5 months. After each addition, nitrogen was injected to maintain anaerobic conditions and the system was closed. The total volume of solution added was lower than the pore volume. The metals concentration and pH effluent solution was monitored.

Bioestabilization efficiency

To determine metals immobilization in the soil by effect of sulphate reducing consortium, acidified water was fed to both cubes at the top of the soil samples. Mineral water previously boiled to remove oxygen was acidified with sulfuric acid at pH 3.0 and then at pH 2.0. pH and conductivity of eluted solution of the pilot scale test were measured and metal concentration was determined by ICP-OES.

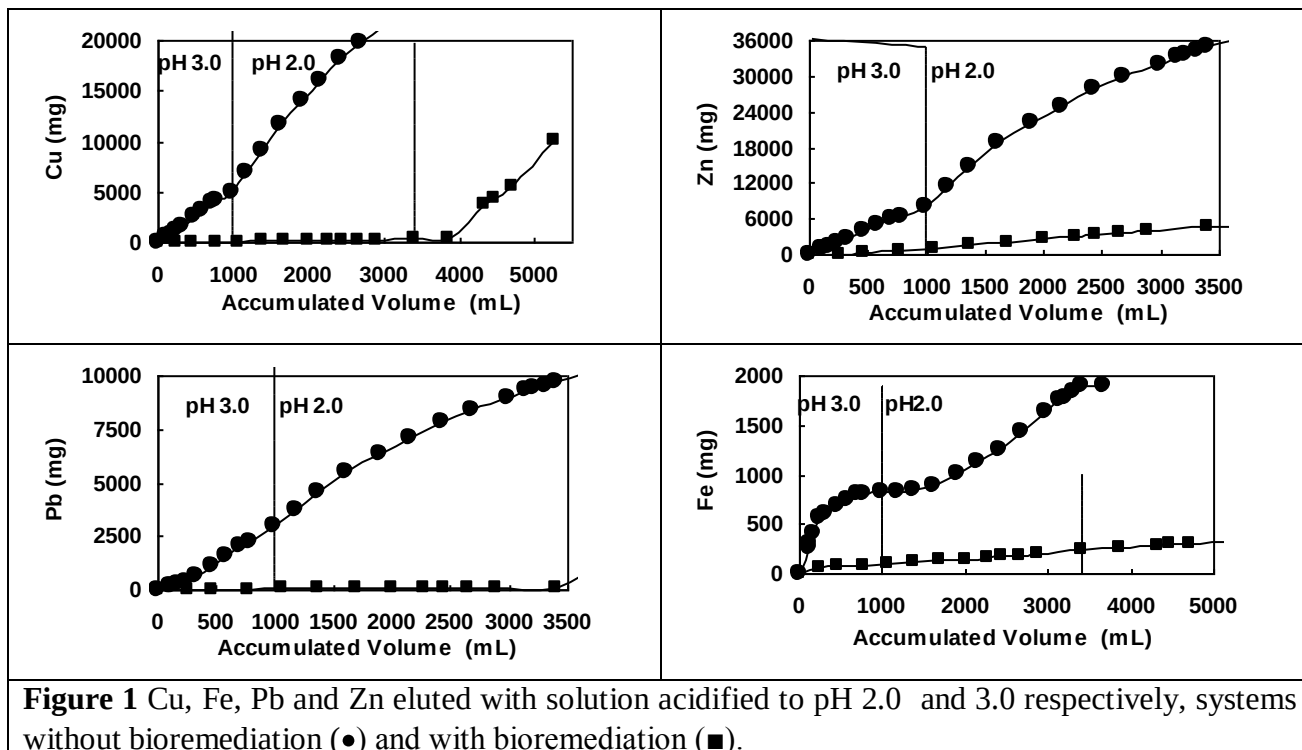
RESULTS

Metals stabilization efficiency

The metals stabilization was determined 15 days after the last nutrients addition and 2.5 months after bioaugmentation. To determine metal stabilization efficiency, the elution of metals was monitored. Two elution solutions at pH 3.0 and 2.0 were used sequentially. The drainage solution obtained on the bottom of the cube was collected and conductivity, pH and metals concentrations were measured. Figure 1 shows that the metal elution was very different in the two systems, with or without bioremediation and also varies with the pH of elution solution.

In the system without bioremediation, significant amounts of Cu, Fe, Pb and Zn were eluted at pH 3.0. The rate of metal elution increased when a more acidic solution was applied (pH 2.0). This behavior was observed mainly in the case of Cu, Fe and Zn.

However, in the system with bioremediation, the amount of metal eluted was lower than without remediation, the Figure 2 shows eluted metal fractions with elution solution at pH 3.0. This behavior changes when the elution solution changes to pH 2.0; under this condition, the amount of metal eluted increased. This effect was similar in the case of Cu, Pb. In the case of Zn, the eluted fraction was similar in both systems.



The highest stabilization efficiency was observed for Pb and Cu, and only 1% and 3% of total metal present in the soil sample was recovered in the drainage solution, when the solution at pH 3.0 was added (Figure 1).

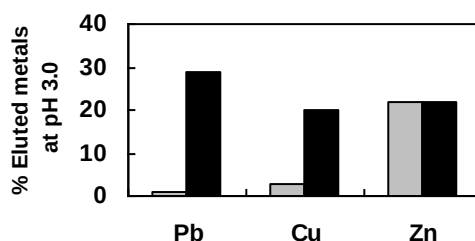


Figure 2 Eluted metal fractions at pH 3.0, with biostabilization (■) and without stabilization (■).

CONCLUSIONS

The results of the present study demonstrated that it is possible to carry out metal stabilization in contaminated soil using biological agent. The sulphate reducing activity can be applied for metal stabilization in the anaerobic zone of soil. For all metals, differences were observed in the stability (insolubility) between control and treated systems. The fraction of eluted metals varies for each metal and depends on the pH of added solution. It was possible to establish the following order of increasing stability, valid under the conditions studied in this work: $Zn < Cu < Pb$.

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