Removal of heavy metals from real mine tailings coupling electrokinetic soil flushing and Bioleaching

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Abstract In the present work, polluted mine tailings from the abandoned Pb/Zn mine of *San Quintín* (Ciudad Real, Spain) have been treated by an innovative *in-situ* bioleaching process. Bioleaching uses the capacity of certain microorganisms of oxidizing iron and/or reduce sulphur which enhance the process of metal extraction due to the production of Fe^{3+} among other oxidizing agents. *In-situ* treatments, as electrokinetics (EK), allow the metal extraction and offer multiple advantages. EK use an electric field to mobilize species towards the soil thanks to the electromigration, electrophoresis and electroosmosis.
The aim of this work is to evaluate the coupling of bioleaching and EK for the removal of heavy metals from the mine tailings. An acid leching medium, produced externally by acidophilic autochthonous microorganisms, was used as the anolyte in the EK cell. Thanks to the EK transport phenomena, the oxidizing medium was transported to the cathode, leaching the heavy metals of the soil, while simultaneously the leached metals were removed through the cathode due to electromigration. Different voltages were studied (0.5, 1 and 1.5 V/cm), the best results were for 1.5 V/cm, and it was clearly observed the positive influence of using the bioleaching culture compared to a single EK reference test.

Keywords: electrokinetics, heavy metal removal, bioleaching, mine tailings

1. Introduction

The production rate of residues from the mining industry is accelerating worldwide as it had been reported by (Franks *et al.*, 2021). The principal residues generated are the mine tailings and acid mine drainage. Mine tailings are a solid waste composed by acid-generating sulfide minerals and heavy metals and metalloids such as Zn, Mn, Ni or Cr. These wastes could be found in active, inactive, or abandoned facilities, the abandoned mine tailings are considered a high potential risk for the environment and the human health, due to its exposure to the climatic agents that could generate the acid mine drainage an disperse this pollutant. Currently in Spain, there are around 75 abandoned mining facilities and besides the entailing environmental risk, these residues could be valuable if the appropriate remediation and extraction technique was applied.

Conventional physicochemical treatments are effective for these residues, but involve a high energy and chemical consumption and, usually, produce a secondary pollution source. Bioremediation technologies offer an eco-friendlier approach, its major drawbacks are the low efficiency and slowness, thus by combining it with other technologies it is expected to improve the overall process. In bioleaching, microorganisms play an essential role by generating an acid leaching medium compose mainly by ferric iron and sulfuric acid capable of oxidize the rest of the metal sulfides present in the mine tailings, as the reactions 1-3 show (Nguyen *et al.*, 2021).

$$MS + 2Fe^{3+} \rightarrow M^{2+} + S^0 + Fe^{2+} \quad (1)$$

$$2Fe^{2+} + \frac{1}{2}O_2 \xrightarrow{\text{Bacteria}} 2Fe^{3+} + H_2O \quad (2)$$

$$S^0 + \frac{3}{2}O_2 + H_2O \xrightarrow{\text{Bacteria}} H_2SO_4 \quad (3)$$

In addition to the inconveniences above-mentioned of this process, conventionally bioleaching is developed *ex-situ*, in columns or slurry reactors, which implies more costs and environmental risks. By developing an *in-situ* treatment the extraction and transportation of the mine tailings would be avoided and bigger quantities could be treated, among other advantages. For this reason, the objective of this work is to couple bioleaching with electrokinetics (EK), an extensively used *in-situ* technology for soil remediation (Wang, Li and Cui, 2021). EK consists in the application of an electric field through the soil between electrodes inserted on it. Thanks to this field, some useful transport phenomena are developed, such as electromigration, electroosmosis and electrophoresis, which would help to the transport of the acid leaching medium created by the microorganisms through the soil, in addition to the extraction of the leachate metals (Reddy and Cameselle, 2009).

Therefore, this work pursues the study of the coupling of EK and bioleaching by flushing directly through the anode an acid leaching medium generated thanks to the microbial activity externally. By this type of treatment, it is expected to enhance the metal leaching and extraction process, avoiding all the complex conditions that this type of acidophilic microorganisms would need to develop *in-situ*.

2. Material and methods

2.1. Mine tailings and microbial inoculum

Mine tailings used for this study were collected from the abandoned Pb/Zn mine of *San Quintín*, placed in Ciudad Real, Spain. The main components of the tailings were (mg kg^{-1}): Fe (31897), Cu (45.7), Pb (1427), Cd (10.32), Zn (1565), Mn (561.7), Ni (36.3), Cr (44.2) and Co (15.5). Initially its pH was nearly neutral 6.84, therefore in order to enhance the metal extraction and avoid the precipitation of the soluble metals, the soil was acidified up to 3.

For the development of the microbial culture, the mine tailings were incubated in the TK medium (composed by: $(NH_4)_2SO_4$ 0.625 g l^{-1}, $MgSO_4 \cdot 7H_2O$ 0.625 g l^{-1}, KH_2PO_4 0.625 g l^{-1} and $FeSO_4 \cdot 7H_2O$ 12.45 g l^{-1} with a pH fixed at 2.0). The inoculum obtained was grown by sequential batches until a steady-state acidophilic mixed culture was developed. The mixed culture was identified by metagenomic sequencing, it was composed mainly by: *Acidithiobacillus ferriphilus* (82.1%) and *Acidiphilium multivorum* (11.3%).

2.2 Batch test

To test if there was a real improvement of the metal leached due to the acid leaching medium generated by the microorganisms, batch tests were caried out by triplicate. Firstly, to obtain the acid leaching medium, the microbial culture was inoculated to a flask with the TK medium and it was incubated at 30ºC and 150 rpm for 4-5 days, the necessary time for the microorganisms to oxidize all the ferrous iron present.

The procedure of the test consisted in incubate, at the same conditions for 15 days, two sets of Erlenmeyer flasks of 250 ml in which it was added the mine tailings (1% (w/v)) and the leaching medium. For one set, the leaching medium was the acid leaching medium obtained thanks to the microbial activity and for the other was the TK iron free medium. The evolution of metal concentration in the liquid was measured by ICP-OES.

2.3. Experimental set-up and procedure

The scheme of the experimental set-up used for the EK soil flushing experiments coupled with bioleaching is shown in figure 1. The EK cell was made of transparent methacrylate and consisted in 5 compartments. The wider central compartment (20 cm x 10 cm x 10 cm) was filled with the polluted soil and separated with a 0.5 mm nylon mesh from the adjacent anode and cathode compartments respectively. The last to external compartments were use as collectors in case any overflow occurred due to the electroosmosis. The electrodes used were of graphite (12 cm x 10 cm x 1 cm) and were connected to the power supply.

Three voltages were tested: 0.5, 1 and 1.5 V/cm. For each voltage, there were set two different EK cells, in one the anode was filled with the acid leaching medium obtain thanks to the microorganisms and the other was a control, in which the anode was the TK iron-free medium. In all cases, the level of the anode was controlled since the electroosmotic flow went to the cathode transporting all the leached metals. In the cathode, the pH was controlled to 2 with H_2SO_4 1M to avoid the excessive metal precipitation and to neutralize and stop the advance through the soil of the basic front that generated in the cathode due to the water electrolysis.

The experiments lasted 15 days in which the pH, conductivity, temperature, and current intensity were measured. Soil samples were taken only initially and at the end of the experiments, the soil samples were taken from five different longitudinally sections. The total metal concentration in the soil was measured after a digestion process by ICP-OES.

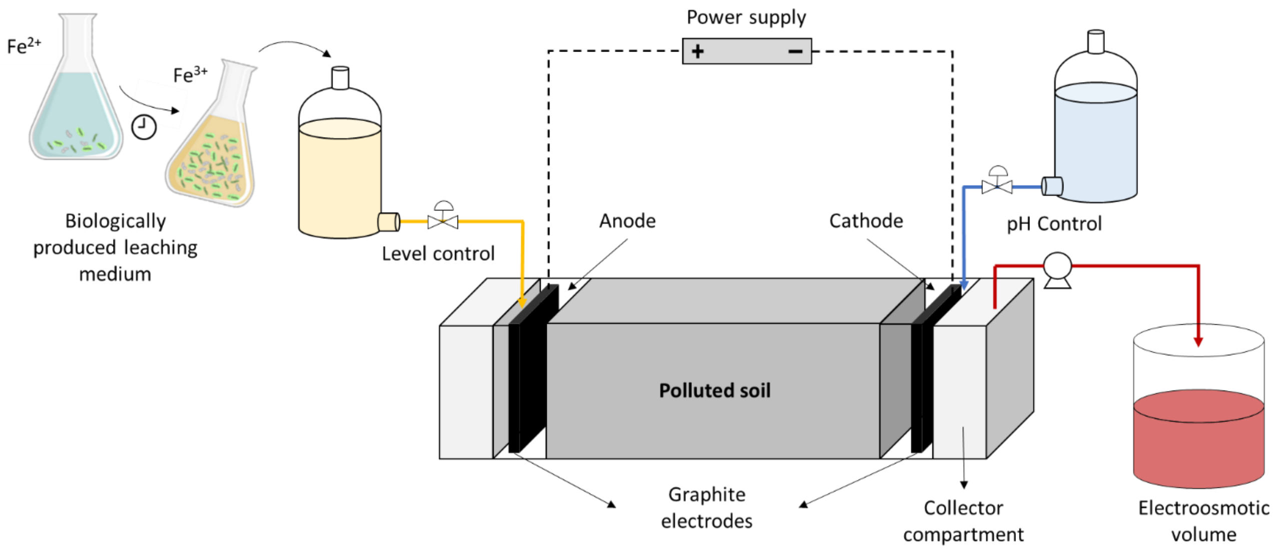

Figure 1. Schematic experimental set-up

3. Results and discussion

3.1. Batch test

The metals concentrations evolution over the 15 days of experiments were measured. The data obtained are represented in the figure 2. For most of the metals analyzed (Mn, Co, Ni, Cr and Zn) it was noticeable that the use of an acid bioleaching medium obtained externally by the microbial culture had a considerable improvement in the metal solubilization. Only for the Cd there was no significative effect between both types of leaching and the Cu concentration was not detectable. Besides the improvement was slight, the results were encouraging to continue with the trials for the coupling of EK soil flushing and bioleaching.

3.2. EK soil flushing and bioleaching coupled under different voltages

During the development of the experiments for the different voltages 0.5, 1 and 1.5 V/cm, various parameters were measured to clearly understand the process. Regarding the pH control in the cathode, the main aim was to neutralize the basic front for avoiding the basification of the soil. The pH of the soil interstitial water was measured in the center of the soil, and it was observed that the pH gradually decreased from 3 (the initial pH) to 1.5 for 0.5 V/cm, 1.0-0.5 for 1 V/cm and 0.5-0.0 for 1.5 V/cm. Therefore, it could be concluded that the pH control was sufficient to avoid metals precipitation near the cathode.

When the voltages 0.5 and 1 V/cm where used, the evolution of the parameters measured (temperature, conductivity, pH, and current intensity) were almost the same when the acid leaching medium was used and when it was not. But, for the voltage of 1.5 V/cm some differences between treatments could be seen, for example, if the acid bioleaching medium was used the conductivity of the soil and the current intensity were slightly higher after 8 days, meaning that if the experiment operated more time, maybe the differences where more significative. One crucial parameter was the temperature, since with EK treatments for high voltages usually involve excessive heating and energy losses because ohmic heating. Indeed, it was observed higher temperatures when higher voltages were used, but the maximum temperature was approximately 40 ° C in the soil during the beginning of the experiment (from day 3 to day 5).

The total metal removal was calculated, regardless the use of the acid bioleaching medium, when higher voltages were applied, higher was the metal extraction for all the metals analyzed (Fe, Cu, Cd, Zn, Mn, Ni, Cr and Co). The Pb concentration in the soil was invariable due to its low capacity to mobilize *(Ye* et al., *2017)*. Concerning the utility of using the acid bioleaching medium for enhancing the process, the results show that for the voltage 0.5 and 1 V/cm the differences were minor. On the contrary, when the voltage of 1.5 V/cm was applied, there was an improvement on the metal extraction due bioleaching medium addition (figure 3).

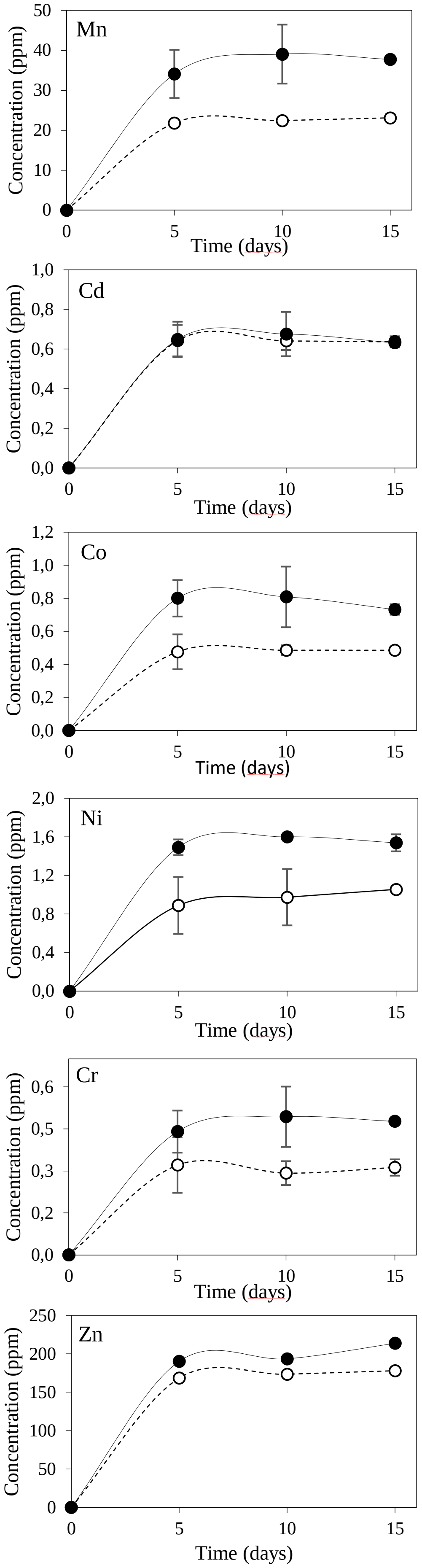

Figure 2. Metal concentration evolution in batch experiments with biologically produced leaching medium (continuous line) and without (dashed line).

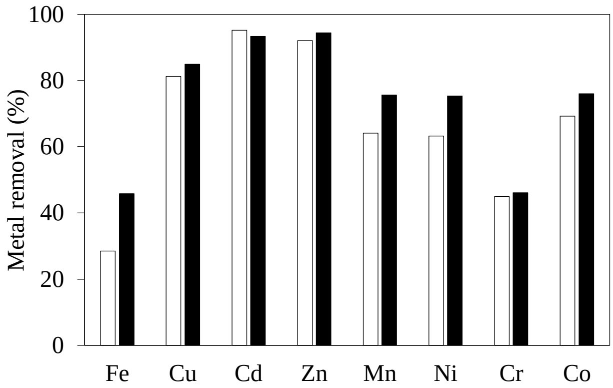

Figure 3. Comparative metal extraction for 1.5 V/cm with acid bioleaching medium (black) and without (white).

To conclude, the set of experiments with 1.5 V/cm were repeated to verify the results. The improvement due to the acid leaching medium added was confirmed obtaining similar metal removal efficiencies. In addition, the evolution of the ferric iron concentration in the anode was monitored. The results showed that part of the ferric iron was accumulated in the anode because of the continuous addition of the acid leaching medium for the level control. Therefore, the ferric iron was not a limiting factor for the process.

4. Conclusions

Thanks to the development of this set of experiments it could be concluded that the coupling of electrokinetics soil flushing and bioleaching by adding the acid bioleaching medium generated externally could be a feasible technology. It was determined that low voltages (0.5 and 1 V/cm) achieved worse metal extraction efficiencies and the differences between the addition of the acid leaching medium or not were slight. So, the optimal voltage for the process was 1.5 V/cm, which offer higher efficiencies and the contribution of the acid leaching medium was more significative. Therefore, higher voltages should increase the rate of the process, but the temperature must be considered as higher voltages produce higher heating leading to an increase in the energy losses reducing the efficiency of the process.

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