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Bioleaching combined brine leaching of heavy metals from lead-zinc mine tailings: Transformations during the leaching process

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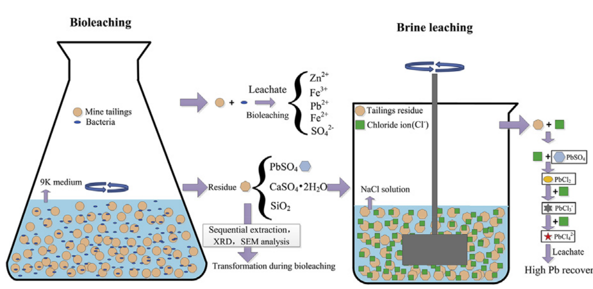
HIGHLIGHTS

- Bioleaching and brine leaching is a highly efficient method to recover metals.
- Bioleaching and brine leaching can significantly increase Pb recovery.
- The result revealed the transformation of mine tailings during bioleaching.
- Differences in speciations of heavy metal during bioleaching were significant.

GRAPHICAL ABSTRACT



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ABSTRACT

During the process of bioleaching, lead (Pb) recovery is low. This low recovery is caused by a problem with the bioleaching technique. This research investigated the bioleaching combination of bioleaching with brine leaching to remove heavy metals from lead-zinc mine tailings. The impact of different parameters were studied, including the effects of initial pH (1.5–3.0) and solid concentration (5–20%) for bioleaching, and the effects of sodium chloride (NaCl) concentration (10–200 g/L) and temperature (25 and 50 °C) for brine leaching. Complementary characterization experiments (Sequential extraction, X-ray diffractometer (XRD), scanning electronic microscope (SEM)) were also conducted to explore the transformation of tailings during the leaching process. The results showed that bioleaching efficiency was significantly influenced by initial pH and solid concentration. Approximately 85.45% of iron (Fe), 4.12% of Pb, and 97.85% of zinc (Zn) were recovered through bioleaching in optimum conditions. Increasing the brine concentration and temperature promoted lead recovery. Lead was recovered from the bioleaching residues at a rate of 94.70% at 25 °C and at a rate of 99.46% at 50 °C when the NaCl concentration was 150 g/L. The study showed that bioleaching significantly changed the speciation of heavy metals and the formation and surface morphology of tailings. The metals were mainly bound in stable fractions after bioleaching.

1. Introduction

Mining and metallurgical activities have generated large, and increasing amounts of mine tailings. By the end of 2013, China had

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accumulated mine tailings stocks of up 14.6 billion tons; in 2013 alone, it accumulated 1.649 billion tons. Most of these mine tailings have been left in tailing reservoirs, without active management. They pose a significant risk to the surrounding environment, particularly because they contain toxic heavy metals. When toxic heavy metals accumulate in the environment, they can endanger both the ecosystem and human health. Avoiding this damage requires, developing an effective method to recover heavy metals from mine tailings.

In the past, physical and chemical processes (Hernández et al., 2007; Chen et al., 2014) have been used to remove heavy metals from soil; however, these processes have drawbacks, such as high -energy consumption, complex protocols, and secondary pollution. In contrast, bioleaching is relatively inexpensive and simple to operate (Chen and Lin, 2009). In bioleaching, microorganisms transform insoluble metals into soluble and extractable ones, through biological oxidation or complexation processes (Holmes, 2008). The bacteria commonly used in bioleaching include acidophilic chemolithotrophic microorganisms, such as *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans,* a sulfur oxidizing bacterium. The bacteria oxidize sulfur compounds into sulfuric acids during bioleaching, and the sulfuric acids eventually leach the heavy metals contained in the solids (Pathak et al., 2009; Lee et al., 2015).

Bioleaching mechanisms were previously described as direct and indirect. Today, it is generally accepted that a “direct leaching mechanism” does not exist. The “indirect mechanism” remains, and includes both the “contact” and “non-contact” mechanism. The “non-contact” mechanism, involves bacteria oxidizing dissolved Fe(II) ions to Fe(III) ions. The Fe(III) ions can then attack metal sulfides, reducing them to Fe(II) ions. The contact mechanism requires bacteria to attach to the sulfide surface, by means of the Fe(III) ions. These irons are complexed in their slime/glycocalyx or extracellular polymeric substances (EPS), and then begin to degrade the sulfide minerals (Rohwerder et al., 2003; Sand and Gehrke, 2006; Vera et al., 2013). Metal sulfide oxidation can be described in terms of two different pathways: the thiosulfate mechanism and the polysulfide mechanism (Vera et al., 2013).

Because of its environmental friendliness and cost effectiveness, bioleaching has drawn increased attention with respect to its ability to process low-grade sulfide ores, soil, and sediment (Li et al., 2014; Praburaman et al., 2015). Many bioleaching studies have examined heavy metals recovery (NareshKumar and Nagendran, 2008; Deng et al., 2013; Rehman et al., 2009). These studies show that technologies used to treat ore, soil, and slag can be adapted to treat the mine tailing (Liu et al., 2008; Park et al., 2014).

For example, many researchers have studied the use of bioleaching to recover metals from low grade Zn and Pb ores, concentrates and mine tailings (Ghassa et al., 2014; Rehman et al., 2009; Baba et al., 2011; Liu et al., 2008). They found that the solubilization efficiency of Pb was low. In the bioleaching process, solubilized Pb(II) can react with sulfate to form $PbSO_4$(Ksp=10^{-8}), which has low solubility.

Turan et al. (2004) and Farahmand et al. (2009) used brine leaching to enrich lead($PbSO_4$) in zinc plant residues; the optimum lead extraction reached approximately 90%. Guo et al. (2010) used brine leaching to recover metals from hydrometallurgical residue. Most metal chlorides are considerably more soluble than sulfate salts, and brine leaching is the most recognized and widely used recovery method. Therefore, bioleaching combined with brine leaching may promote efficiencies in recovering heavy metals, especially lead.

Bioleaching effectiveness and optimization depend on the physical, chemical and biological factors in the system. Heavy metals bioleaching, for example, may be sensitive to various factors, including solids concentration, temperature, oxygen, pH, oxidation–reduction potential, bacterial strain and cell concentration. These factors play an important role in optimization of the bioleaching process (Liu et al., 2008). Studies investigating lead-zinc containing iron mine tailings using bioleaching with *Acidithiobacillus ferrooxidans* are relatively scarce compared to studies using non-iron tailings or tailings with little iron lead-zinc. We have found no systemic studies examining bioleaching behavior with lead-zinc mine tailings with high iron content (>100,000 mg kg^{-1}). Further, few studies have investigated bioleaching using *Acidithiobacillus ferrooxidans* to treat iron mine tailings that have lead and zinc. Studying iron tailings with lead-zinc is a focus of this study.

A higher solid concentration results in a higher concentration of heavy metals in the leaching environment. The increasing level of leached metals and the resulting toxicity may inhibit microorganism growth and acid production (Liu et al., 2008). The leached metals in bioleaching is highly pH-dependent, and pH influences metal solubilization during bioleaching. Therefore, completely understanding the optimal solids concentration and pH values can impact how bioleaching is done. Previous studies on their bioleaching of mine tailings focused on metal distribution and the formation before and after the bioleaching (Zhang et al., 2015; Park et al., 2014; Nguyen et al., 2015; Liu et al., 2008); there are few data on the process variations. This calls for more research on bioleaching behavior with respect to lead-zinc flotation mine tailings with high Fe levels. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) have been used to investigate the impact of bacteria on mineral surfaces and mineral formation(Nkulu et al., 2015; Fomchenko and Muravyov, 2014; Liu et al., 2011; Fan et al., 2015).

This study involved a set of batch experiments to compare the efficiency of metal solubilization using bioleaching at different initial pH values and solid concentrations, with the goal of promoting lead recovery during subsequent brine leaching at different NaCl concentration. The first objective of this study was to evaluate the effects of initial pH value and solids concentration on heavy metals recovery from mine tailings by bioleaching, and to describe the efficiencies of microbes in removing Fe, Pb and Zn from mine tailings taken from a lead-zinc mine. The second objective was to describe the transformation of heavy metal forms in the bioleaching process. In addition, we investigated the formation of mine tailings and explored the surface morphology of mine tailings during the bioleaching process. Another objective was to improve lead recovery from the bioleaching tailings residue using brine leaching and observe the changes in residue after this leaching. All of these objectives were explored with the goal of providing useful information to guide the recovery of heavy metals from lead-zinc flotation mine tailings.

2. Methods

2.1. Materials

Lead-zinc flotation mine tailings for these experiments were collected from materials generated at the end of the flotation process from the Fankou lead-zinc mine region, north of Shaoguan City, Guangdong Province, China. The mine tailing samples were transported to the laboratory, stored at 4 °C prior to testing, and then dried in a vacuum drying box. All sample particles were smaller than 74 μm in diameter. To determine metal levels, the solid samples were digested using microwave digestion equipment (CEM Mars-xpress). Then, the suspension was filtered through a 0.45 μm nylon syringe filter. Metal concentrations were determined using an atomic absorption spectroscopy (AAS; Hitachi Z-2000). Total sulfur was determined using dry combustion (Itanna, 2005). The