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Bioleaching of highly concentrated arsenic mine tailings by *Acidithiobacillus ferrooxidans*

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A B S T R A C T

In this study, arsenic (As) leaching was conducted from highly concentrated As mine tailings using the iron-oxidizing bacteria (*Acidithiobacillus ferrooxidans*). The effects of temperature, initial pH, and pulp density on the As leaching were systematically investigated. At all reaction temperatures, the As leaching amount exceeded 85%. However, the As leaching was significantly affected by the initial pH and pulp density. In particular, the As leaching amount of 85% at initial pH $\leqslant$ 2.0 decreased to as low as 40% at initial pH 2.2 due to the effects of the jarosite that was formed by the precipitation of the leached iron. The As leaching efficiency decreased from about 80% at the pulp density $\leqslant$2.0% to as low as about 25% at pulp density 4.0% due to the low bacterial growth rate. Therefore, in the bioleaching process for highly concentrated As mine tailings, the pH range should be controlled to prevent the formation of jarosite, and it is important to maintain a high bacterial cell concentration at high-concentration pulp density.

1. Introduction

Bioleaching is based on the ability of microorganisms that can convert insoluble metals to soluble ones through the reactions of biological oxidation or complexation process [1,2]. Due to its environmental friendliness and cost effectiveness, many studies on bioleaching as a method of treating heavy metals have been conducted [3–7]. This method allows very small sulfide minerals to be treated by bacteria [8,9]. Furthermore, using bacteria simplifies the metallurgical process of extracting metals from ores and minerals [10]. *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*) is the most frequently used microorganism in leaching the heavy metals in contaminated soils. This microorganism requires atmospheric CO_2 as a carbon source and obtains energy for growth from the process of oxidizing ferrous (Fe^{2+}) to ferric (Fe^{3+}) [11–14], which creates acidic conditions favorable for metal removal from soil [10]. Mine tailings from dormant and/or abandoned mines contain various heavy metals such as arsenic (As), zinc (Zn), copper (Cu), and lead (Pb), and function as a pollution source of heavy metals in the ecosystem [15,16]. More specifically, As is concentrated during the leaching process for obtaining precious metals [17,18], leading to high As content in the abandoned mine tailings of precious metal mines [19,20].

Although the influencing factors in the bioleaching process using *A. ferrooxidans* have been widely investigated, systemic studies on As bioleaching are relatively few compared to those on other heavy metals (e.g., Cu, Zn and Mn) [21–23]. Furthermore, to the best of our knowledge, no study on the bioleaching behavior for mine tailings with high As content (>10,000 mg kg^{-1}) has yet been conducted. For example, realgar (As_2S_2), which is an As containing sulfide mineral, was recently investigated in an As bioleaching study [24,25]. The As_2S_2 used in the study, however, was not a contaminated soil sample, and the As removal efficiency was evaluated under only one set of operating conditions (i.e., temperature 30 °C, pulp density 0.2%, and initial pH 1.8). Meanwhile, other studies have focused on the bioleaching of mine tailings with low As levels [26–28]. Therefore, a systemic study on As leaching behavior from mine tailings with high As level is necessary.

In this study, As bioleaching using *A. ferrooxidans* was conducted on precious metal mine tailings containing highly concentrated As. The As bioleaching efficiency was evaluated according to changes in three experimental conditions (i.e., temperature, initial pH, and pulp density) to get an insight on the optimal conditions that would be applied to practical heap and/or tank bioleaching tests. During the leaching process, pH, oxidation–reduction potential (ORP),

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heavy metals concentration, and planktonic cell concentration in the leachate were monitored to investigate the relationship between each parameter.

2. Material and methods

2.1. Mine tailing samples

An oxidized mine tailings sample was obtained from Janggun mine (a Pb, Zn and Ag-mining site in Bonghwa, Gyeongsang, South Korea). The particle size distribution of mine tailings used for bioleaching tests was 63–74 μm. The chemical composition of the mine tailings was determined by inductively coupled plasma (ICP, Optima 7300DV, PerkinElmer) and X-ray fluorescence (XRF, PW2404, Philips) analyses. The As content in the mine tailings was about 26,113 mg kg^{-1}. The contents of other heavy metals (e.g., Cu, Fe, Pb, and Zn) were also high (Table 1).

2.2. Bacteria selection and culture

The *A. ferrooxidans* (KCTC 4515) used in the present study was provided by the Korea Research Institute of Bioscience and Biotechnology. Bacteria were cultured in a culture medium prepared based on the information of DSMZ medium 882 under the aerobic environment at 25 °C and shaking speed at 150 rpm (SIF-5000R, JEIO TECH, Seoul, South Korea). The pH of the medium was adjusted to 1.8 with 5 M H_2SO_4 (Fisher Scientific).

2.3. Bioleaching tests

Bioleaching tests were conducted using bacterial cultures of *A. ferrooxidans* grown until a stationary phase (~48 h). The tests were carried out in 500 mL flasks containing 200 mL of culture media at an inoculation ratio of 10 (i.e., ratio of bacterial solution to culture medium of 1:10). The initial bacterial concentration in the bioleaching medium was determined with a cell counting chamber (Buerker-Tuerk Chamber, Marienfeld Laboratory Glassware, Germany) under a phase-contrast microscopy (ODEO-2003 Triple, IPONACOLOGY) and kept constant at 1×10^7 cells mL^{-1}. The effect of temperature on bioleaching was examined by setting the reaction temperature to 25, 30, and 35 °C with a fixed pulp density of 0.5%, pH of 1.8, and shaking speed of 150 rpm. In order to investigate the effects of the initial pH of the culture medium on bioleaching, experiments were conducted at an initial pH of 1.8, 2.0 and 2.2, with a fixed pulp density of 0.5%, temperature of 30 °C, and shaking speed of 150 rpm. To examine the effects of pulp density on bioleaching, Janggun mine tailings were added to make pulp densities of 0.5, 1.0, 2.0 and 4.0% (w v^{-1}) with a fixed temperature of 30 °C, pH of 1.8, and shaking speed of 150 rpm. For the control test (i.e., blank test), the culture medium was sterilized with 2% (v v^{-1}) bactericide (2% (w w^{-1}) thymol in ethanol) which is known to prevent indigenous bacteria growth [29]. The control test without the addition of bacteria was carried out at a temperature of 30 °C, pulp density of 0.5%, and initial pH of 1.8. The planktonic cell concentration was periodically monitored to confirm the growth of indigenous bacteria during the leaching. The growth of indigenous bacteria was found to be effectively inhibited by the aforementioned method. After measuring the pH (ORION 4STARS, Thermo) and ORP (Hanna Instruments, model 2211) of the leachate, an aliquot of leachate was filtered through a 0.45 μm nylon syringe filter (Corning Incorporated, Corning, Germany) for ICP analysis of the As, Fe, S, and Zn concentrations. The concentration of planktonic cells was determined when needed. Additionally, the Fe^{2+} contents were analyzed through the *o*-phenanthroline method [30], and the contents of Fe^{3+} were calculated from the difference between the contents of total Fe and Fe^{2+}.

2.4. X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) spectra were collected within the 2 theta range from 5° to 70° with a step of 0.01° and counting time of 1 s $step^{-1}$ on Bruker D8 HRXRD (Germany) with Cu Kα radiation (λ = 0.154606 nm, 40 kV, 40 mV) and SolX detector. The spectra were evaluated with the Diffrac*plus* EVA package. The contents of the precipitated Fe^{3+} compound (i.e., jarosite) from the mine tailings residue after the bioleaching test were measured with TOPAS 3 program.

3. Results and discussion

3.1. Effect of temperature on As bioleaching

In order to investigate the effects of temperature on bioleaching, bioleaching tests were carried out at reaction temperatures of 25, 30 and 35 °C under constant pulp density (0.5%) and initial pH (1.8). The effect of temperature on the As removal rates are shown in Fig. 1. In the blank test (i.e., without *A. ferrooxidans*), the As removal efficiency increased to about 20% in the early stage of the reaction, but no further As leaching was observed in that reaction. Meanwhile, in the bioleaching process with *A. ferrooxidans*, the As leaching efficiency increased with increasing reaction temperature. Overall, a 30% As leaching efficiency was observed in the early stage (i.e., after 2 days) of the reaction, increasing to an eventual efficiency of 85% or higher for all the reaction temperatures investigated.

The changes in pH, ORP, and heavy metal ions concentration according to the change in the reaction temperature are shown in Fig. 2. In the blank test, the pH increased to 2.12 at 6 days after the reaction, but the final pH was consistently maintained at 1.89 (Fig. 2a). During the reaction period, ORP was also consistently maintained at 410 mV for the blank test (Fig. 2c). These results suggested that the effect of indigenous bacteria might have been mostly inhibited in As leaching, and that some As leaching (Fig. 1) might be due to the acid chemical reaction.

Meanwhile, in the As leaching process with *A. ferrooxidans*, the initial pH increased at all reaction temperatures. Due to the initial rapid oxidation of Fe^{2+} to Fe^{3+} by *A. ferrooxidans*, the pH increased according to the H^+ consumption ($4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$). The decrease in pH over time was caused by the sulfur oxidation ($2S^0 + 2H_2O + 3O_2 \rightarrow 2SO_4^{2-} + 4H^+$), and the jarosite that was formed by the oxidized Fe^{3+} ($3Fe^{3+} + K^+ + 2HSO_4^- + 6H_2O \rightarrow KFe_3(SO_4)_2(OH)_6 + 8H^+$) [31]. The total Fe and Fe^{3+} concentrations in the reaction solution are shown in Fig. 2b. Fe leaching

Table 1
Physical properties and chemical composition of the mine tailings.

Materials	d_{50} (μm)[a]	ρ_a (g cm^{-3})	Specific surface area (m^2 g^{-1})[b]	Chemical composition (mg kg^{-1})					
Mine tailing	73	2.65	13	As	Cd	Cu	Zn	Pb	Fe
				26,113	67	1291	19,461	9808	120,435

[a] Mean particle size measured using laser-diffraction scattering (Accusizer 780/SIS, PSS).
[b] Specific surface area calculated by the BET model using nitrogen adsorption branch (ASAP2020, Micromeritics).