

# Bioleaching of Cu and Zn from Complex Sulfide using an Isolated Iron Oxidizing Bacteria

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**Abstract:** Bioleaching kinetics of copper and zinc from a complex sulfide concentrate sample was evaluated in this manuscript. An acidophilic microorganism was used for the metal dissolution. The metal dissolution was evaluated based on the variation of leaching parameters like initial pH, pulp density, and initial ferrous concentration. The leaching rate of metals increased with the increase of initial ferrous concentration up to 20g/L, and it decreased on a further increase of the initial ferrous concentration. It decreased at the initial ferrous concentration above 20g/L due to the formation of an iron precipitate, which did not allow the contact of lixiviant with the metal sulfide matrix. The leaching rate increased with the increase of initial pH up to 2.0, and thereafter it decreased. Similarly, the leaching rate remained unchanged up to pulp density of 15% (w/v), and it decreased upon further increase of the pulp density due to the mutual completion of the complex sulfide particles towards the lixiviants.

**Keywords:** bioleaching; complex sulfide concentrate; leaching parameters; kinetics; bacterial activity.

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## 1. Introduction

Bioleaching is eventually expected to play a vital role as an alternative to the conventional pyrometallurgical and hydrometallurgical techniques due to its inherent low costs, i.e., capital and operating [1]. The indigenous reduced iron and sulfur present in the mineral phase play an important role in the acceleration of bioleaching reactions, which plays a key role in reducing the addition of extra chemicals during the process [2]. The oxidation reactions of the iron and sulfur are the main electron sources for the propagation of the lifecycles of microorganisms as well as the dissolution of metals [3]. Further, the operation of the pilot plant applying bioleaching does not need the expensive plant infrastructure as well as a large number of human resources [4]. This process is suitable for the dissolution of different metals from low-grade ores and solid wastes. However, the application of bacterial is resource selective. If the solid resources are not susceptible to bacterial growth, there is no benefit of the application of bioleaching to them [5]. Further, the bioleaching process is controlled by different leaching parameters like initial pH, pulp density, nutrient addition, temperature, the particle size of the solid particle, and contact time. Therefore, their optimization gives the important, valued information for the implementation of the process at the pilot scale [6-8].

Chemoautotrophic microorganisms like *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* gain energy from facilitating the oxidation reaction of Fe(II) to

Fe(III) and S to  $\text{SO}_4^{2-}$ , respectively [9-11]. Then the oxidized forms of Fe and S extensively help the metal dissolution in the bioleaching process, although there is a possibility of another direct contact bioleaching mechanism has been evaluated [12]. The bioleaching process is proved to be an eco-friendly process, and its cost is comparable to the conventional hydrometallurgical process. So the most attention required for this process is cost reduction [13-16]. This process does not need any sophisticated metallurgical infrastructure and high skilled personals. Still, its cost is not much less compared to the conventional processes. The major drawback of the bioleaching process is that it is a time-consuming metal dissolution process [17,18]. Since it is a naturally occurring bacterial dissolution process, its reaction rate is slow but not reversible [19,20]. It achieves equilibrium in months, but the metal dissolution reaction is always a forwarding reaction. If the bacterial activity in the presence of mineral can be enhanced, the bioleaching process will prove to be fruitful in the extractive metallurgy. The activity of bacteria can be enhanced by either field type mutation like adaptation and natural revolutions [21]. Also, there are some biotechnological tools that can be applied to enhance their growth [1,22]. Apart from bacterial activity enhancement, different chemical engineering operations can be applied to increase the metal dissolution process. One of them is the optimization of different leaching parameters, which can increase bacterial activity as well as the metal dissolution reactions [7,23-26]. In this article, the bioleaching process is evaluated based on the optimization of different leaching parameters. The raw material used in this experiment is a complex sulfide concentration sample that contains chalcopyrite and sphalerite.

## 2. Materials and Methods

### 2.1. Microorganisms and media.

The bacterium used in the bioleaching experiments was *A. ferrooxidans*, which was isolated from a water sample collected from the Dalsung copper project of South Korea [27]. The bacterium was sub-cultured in the freshly prepared 9K medium at pH 1.8 and 35°C. Further, the bacterium was sub-cultured repeatedly in the media with the same condition to achieve the highest iron oxidation rate [27].

### 2.2. Complex sulfide sample.

The complex sulfide sample was collected from the Victoria Gold Deposits, Makai City, Philippines, and the particular size fraction of  $-106+4\mu\text{m}$  was used for the leaching experiments. Before starting the experiments, the sample was dried in order to remove the moisture present in it. Then the composition of the sample was analyzed and found that it contained 13.4 and 28.3% of Cu and Zn, respectively [20].

### 2.3. Bioleaching.

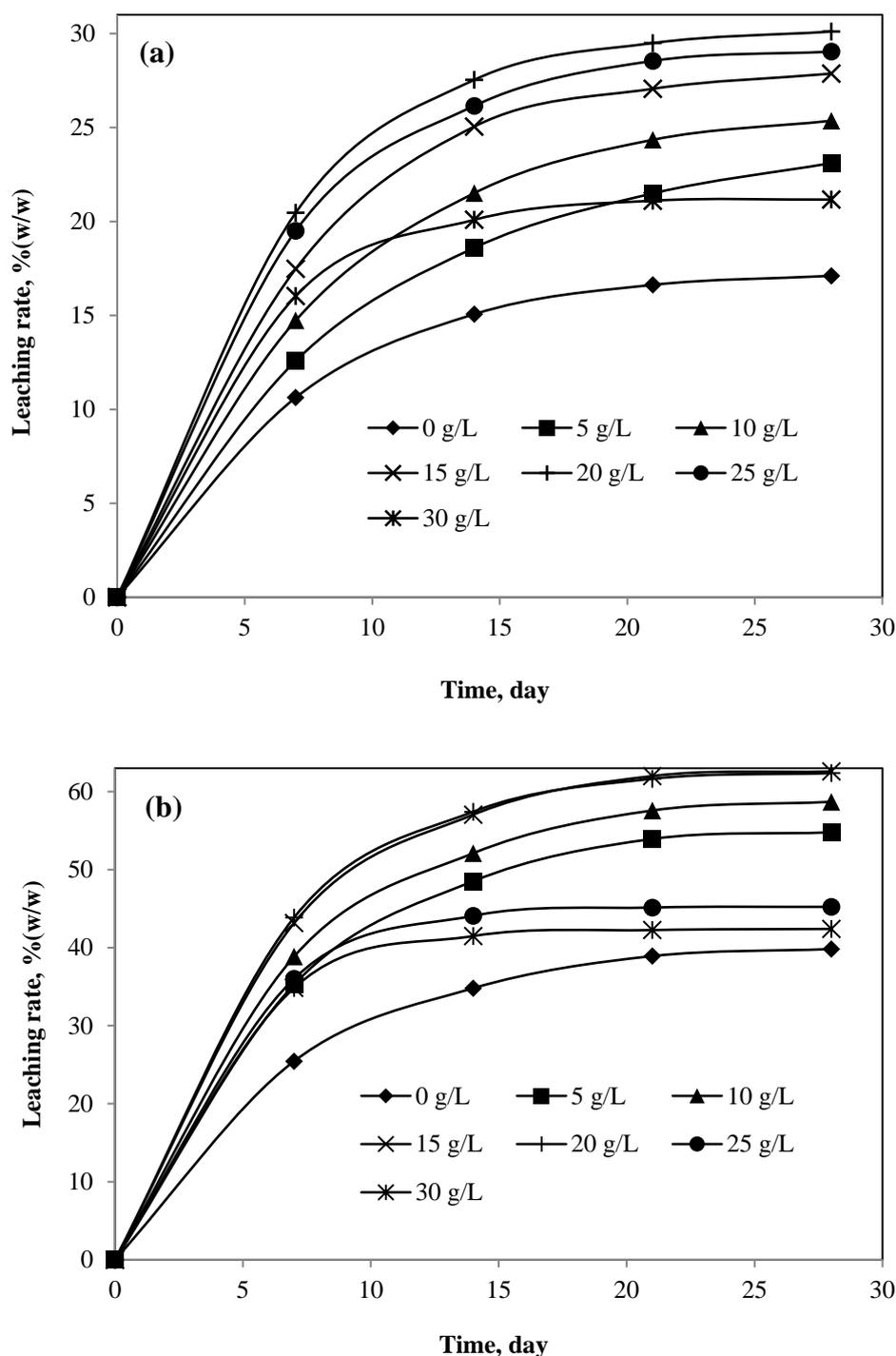
The bioleaching experiment of the sulfide sample was conducted in the 250mL Erlenmeyer flasks. Each flask contains 90mL freshly prepared nutrient media with the required amount of Fe(II) additions as determined for the particular experimental run. Then the required amount of sulfide sample was added on the basis of selected pulp density of the particular run. Then 10mL of pre-activated inoculums was added. So the total media content became 100mL. The initial pH of the media was adjusted by adding  $\text{H}_2\text{SO}_4$  dropwise. Then the flasks were incubated in an orbital shaker-cum-incubator run at 32°C and 180rpm. The contact time was

counted once the flasks were placed in the incubator. The pH was checked in the regular time interval using a pH meter (Thermo, Orion-720<sup>+</sup>). The liquid samples were collected in the regular interval for the analysis of Cu and Zn present in the leach liquor. The liquid samples were suitably diluted, and then the metal concentration was analyzed with the help of an Atomic Absorption Spectrophotometer (Perkin Elmer, AAnalyst-400). The iron oxidation rate (IOR) of the bacteria was evaluated during the bioleaching experiment. For this purpose, liquid samples were collected in the regular interval, and the residual Fe(II) concentration was analyzed by the volumetric titration method [27]. The leaching studies were conducted at pH-2.0, pulp density(PD)-5%(w/v), temperature-32°C, Fe(II)-10g/L, shaking speed-180rpm and particle size(PS)-106+45µm, unless otherwise specified. All experiments were triplicate, and the experimental errors were within ±5%.

### 3. Results and Discussion

#### 3.1. Effect of initial Fe(II).

The bioleaching mechanism has been classified as a direct and indirect mechanism [12]. In the direct mechanism, bacteria attach to the mineral surface, and their metabolic processes lead to the dissolution of the mineral matrix; however, reactions of the oxidized species such as Fe(III) and SO<sup>4-</sup> with the mineral matrix are the major steps of the metal dissolution in the indirect mechanism where the bacterial role is limited to iron and sulfur oxidation only. No matter the bioleaching follows, which mechanism, the major objective is the efficiency of the metal leaching process. The concentration of Fe(II) plays an important role in determining the leaching kinetics. Therefore, the initial Fe(II) concentration was varied from 0 to 30g/L, while other parameters kept constant. The leaching rates of Cu and Zn at different Fe(II) addition were plotted versus contact time and are shown in Fig.1(a) and (b), respectively. From Fig.1(a), it can be observed that the leaching of Cu increased with the increase of contact time up to the experimental duration of 28 days; however, it was much faster during the initial 15 days than the remaining days. On the 28<sup>th</sup> day, the leaching rate of Cu was much slower. On account of the Fe(II) variation, it can be observed that the leaching rate of Cu increased with the increase of Fe(II) concentration up to 20g/L, and thereafter it decreased. The role of bacteria was to oxidize the Fe(II) to Fe(III), and then the Fe(III) helps in the oxidation of the sulfide matrix of metals. Since the pH of the medium was 2.0, the oxidation of the metal sulfide did not achieve the spontaneity as that generally occurred in a chemical leaching conducted in the strong acidic medium containing Fe(III). In this bioleaching case, some part of the Fe(III) was unutilized and converted to jarosite. The formation of jarosite deposited on the complex sulfide particle, which hindered the proximity of lixiviant with the sulfide matrix of metals [19]. At the higher concentration of Fe(II) addition, more amount of jarosite was formed, and it hindered the dissolution reactions. As a result, the leaching rate of Cu decreased at the higher concentration of Fe(II). Figure1(b) shows the leaching of Zn at different Fe(II) concentrations, which shows that the leaching pattern of Zn was almost similar to that of Cu leaching, as shown in Fig.1(a). However, the leaching rate of Zn was approximately two times higher than that of the Cu. According to the electrochemical series, sphalerite is more soluble than chalcopyrite in a single pot reaction vessel due to the formation of a Galvanic couple between sphalerite and chalcopyrite [20]. That may be the reason for the higher dissolution of Zn over Cu from the complex sulfide containing sphalerite and chalcopyrite.

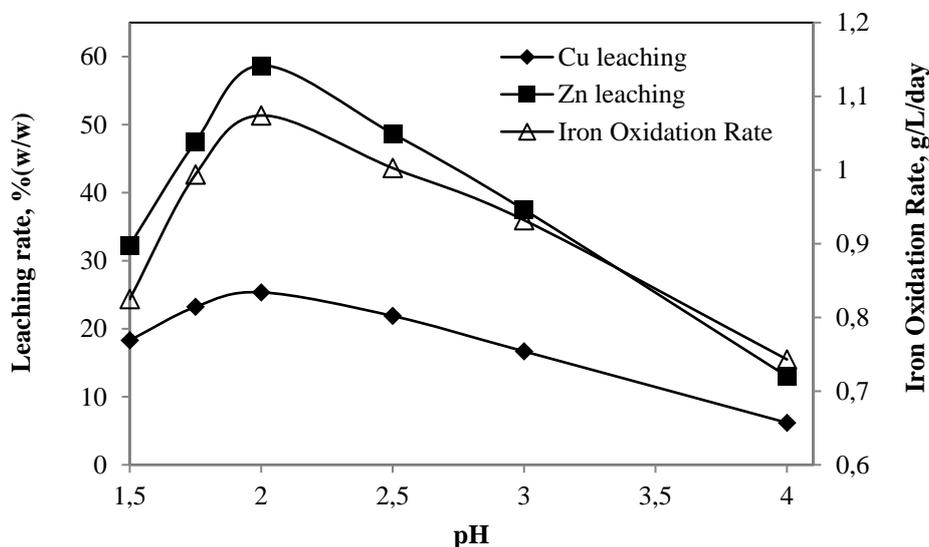


**Figure 1.** Effects of Fe(II) addition on the dissolution of Cu and Zn. Conditions: pH-2.0, pulp density (PD)-5% (w/v), temperature-32°C, shaking speed-180rpm and particle size (PS)-106+45 $\mu$ m.

### 3.2. Variation in the initial pH.

The bacterial activity depends on the pH of the growth medium. Bacteria are very sensitive to the pH of their environment. Upon variation of the pH, the physiological stress is developed on the growth phase of the bacteria; mostly, it impedes the exponential growth phase of the bacteria. Since bacterial growth influences the iron oxidation reaction of the acidophiles, optimization of the pH of the nutrient medium was necessary for the efficient dissolution of metals. Therefore, the pH of the leaching medium was varied from 1.5 to 4.0, and the leaching kinetics data were interpreted in terms of a graph. Figure 2 shows the graph of the leaching rate

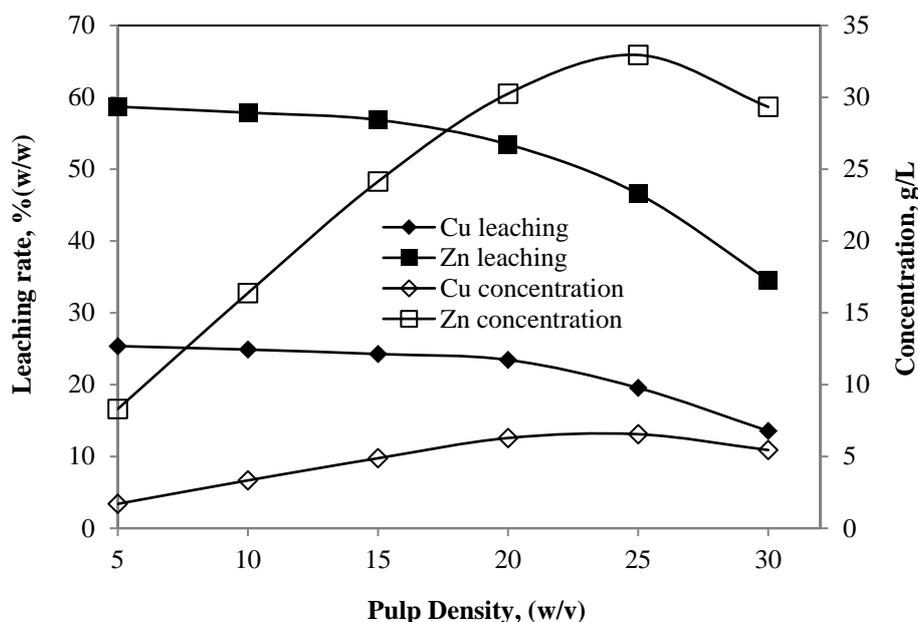
of both Cu and Zn (primary y-axis) as well as the iron oxidation rate of the bacteria(secondary y-axis) plotted versus different initial pH of the medium. It can be observed from Fig.2 that the leaching rate of both Cu and Zn increased with the increase of initial pH from 1.5 to 2.0, and they decreased upon further increase of the initial pH. The iron oxidation rate of the bacteria followed a similar pattern as that for the metal leaching. This proved that the leaching rate was completely driven by the bacterial activity in the leaching medium and the optimum pH of the leaching was 2.0.



**Figure 2.** Effects of initial pH of the leaching medium on the dissolution of Cu and Zn. Conditions:Fe(II)-10g/L,pulp density(PD)-5%(w/v),temperature-32°C,shaking speed-180rpm and particle size(PS)-106+45 $\mu$ m.

### 3.3. Effect of pulp density.

Pulp density is an important parameter in the leaching operation. It determines the size of the reactor and, ultimately, the cost of a process upon scale-up. Higher the pulp density means it requires a small size pilot plant infrastructure. Therefore, the variation of the pulp density is an integral part of the leaching process. For the experimental study, the pulp density was varied as 5,10,15,20,25, and 30%(w/v) while other parameters kept constant, as mentioned in the experimental section. Figure 3 shows the graph of the leaching rate of both Cu and Zn (primary y-axis), as well as their concentration(secondary y-axis) in the leach liquor, plotted versus different pulp densities. The leaching rate of both metals remain unchanged up to the pulp density of 15%(w/v), and it constantly decreased upon further increase of the pulp density. At higher pulp density, the concentration of metal obviously increases in the leach liquor. In a few cases, the solubility of some metal saturates in the solution, and in this case, increasing the pulp density further does not give any significance in a single pot leaching reactor. But from the Fig.3, it can be observed that the concentration of both Cu and Zn were much lower compared to their actual solubility at normal temperature and pressure. Hence the solubility did not affect the leaching rate of both metals even at the higher pulp density. The leaching rate decreased at the higher pulp density may be due to the competitive nature of the sulfide matrix towards the lixivants [28]. When the higher pulp density was applied, the concentration of the solid sulfide matrix was larger, and they became more competitive in an agitated system for the chemical oxidation. As a result, the metal dissolution impeded at the higher pulp density. The optimum pulp density was found to be 15%(w/v).



**Figure 3.** Effects of pulp density on the dissolution of Cu and Zn. Conditions:Fe(II)-10g/L, pH-2.0, temperature-32°C, shaking speed-180rpm and particle size(PS)-106+45µm.

#### 4. Conclusions

Bioleaching of a complex sulfide concentrate sample was conducted using an isolated iron-oxidizing bacterium. The bacterium was capable of dissolving Cu and Zn from the concentrated sample without any hurdle. In order to evaluate the leaching capacity of the bacteria, three leaching parameters (i.e., Fe(II) addition, initial pH, and pulp density) were varied, and they were found to be appropriate for the evaluation. The leaching rate increased with the increase of Fe(II) addition up to 20g/L. At the higher Fe(II) addition, the formation of the product layer over the complex sulfide particle prevented the penetration of lixiviant into the sulfide matrix. The leaching rate increased with the increase of initial pH up to 2.0, and it decreased upon further increase of pH due to the bacterial activity, which was found to be optimum at pH-2.0. The metal dissolution took place up to the pulp density-15%(w/v) without any interruption. This study can be extended further on the evaluation of the leaching rate of Cu and Zn from the concentrated sample based on a bench-scale column reactor for the fruitful implementation in the percolated heap operation.

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#### Conflicts of Interest

The authors declare no conflict of interest.

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