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Enhancement of metal bioleaching from contaminated sediment using silver ion

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ABSTRACT

A silver-catalyzed bioleaching process was used to remove heavy metals from contaminated sediment in this study. The effects of silver concentration added on the performance of bioleaching process were investigated. High pH reduction rate was observed in the bioleaching process with silver ion. The silver ion added in the bioleaching process was incorporated into the lattice of the initial sulfide through a cationic interchange reaction. This resulted in the short lag phase and high metal solubilization in the bioleaching process. The maximum pH reduction rate and the ideal metal solubilization were obtained in the presence of 30 mg/L of silver ion. When the added silver ion was greater than 30 mg/L, the rates of pH reduction and metal solubilization gradually decreased. The solubilization efficiencies of heavy metals (Cu, Zn, Mn, Ni and Cr) were relatively high in the silver-enhanced bioleaching process, except Pb. No apparent effect of silver ion on the growth of sulfur-oxidizing bacteria was found in the bioleaching. These results indicate that the kinetics of metal solubilization can be enhanced by the addition of silver ion.

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1. Introduction

Contaminated sediments containing high concentrations of toxic metals are often found in rural areas or high industrial activity regions. Recently, great efforts have been focused on the treatment of contaminated sediment because it may have a potential hazard to the ecosystem and human health. It is evident that two significant issues regarding contaminated sediments will be of concern in the future: the increasing amounts of contaminated sediments and high concentrations of toxic pollutants. It is important to establish an applicable technology for removal of heavy metals from contaminated sediments. Because of low efficiencies, high cost, high-energy requirements and operational difficulties, the applications of physical and chemical technologies to remove toxic heavy metals from contaminated sediments have become unattractive [1].

It is well known that bioleaching, the most promising alternative to conventional methods, has been applied to remove heavy metals from contaminated sediments, sludges and soils [2–5]. The advantages of bioleaching include a reduction of energy and chemical consumption and a lower operating cost. During the bioleaching process, the existence of the genus *Acidithiobacillus*

or Thiobacillus generally promotes the oxidation of reduced sulfur compounds or the oxidation of ferrous ion to the ferric iron resulting in the acidification and solubilization of metals. Meanwhile, Acidithiobacillus ferrooxidans (formerly Thiobacillus ferrooxidans), Acidithiobacillus thiooxidans (formerly Thiobacillus thiooxidans) and Thiobacillus thioparus are considered to be the major microbial species governing the bioleaching process [2]. Generally, At. thiooxidans and At. ferrooxidans are acidophilic bacteria which have optimal growth occurring at pH values lower than 4 [6]. T. thioparus is able to grow over a pH range of 5.0-9.0, with an optimum near 7.5 [7]. In particular, besides the oxidation of reduced sulfur compounds, At. ferrooxidans in the bioleaching process can also use ferrous iron as energy source for their growth and to form ferric ion. At the same time, the rate of oxidation of elemental sulfur by At. ferrooxidans is much slower than that by At. thiooxidans [8]. Therefore, bioleaching process conducting sulfur bio-cycle is a novel and ecological technology for the treatment of metal-contaminated sediment. Most studies of bioleaching have dealt with the acidophilic Acidithiobacillus species, which grow optimally at low pH. It has also been reported that the efficiency of metal solubilization in the bioleaching process using the mixed culture of At. ferrooxidans and At. thiooxidans is higher than using pure cultures of At. ferrooxidans or At. thiooxidans [9,10]. However, an initial acid addition is generally required to lower the pH value to acidic condition and thus the operational cost of bioleaching process by acidophilic At. ferrooxidans or At.

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thiooxidans will increase [11]. On the other hand, previous results indicated that several species of less-acidophilic thiobacilli participate in the acidification during bioleaching at neutral pH, but *T. thioparus* is the initially predominant species. Subsequently, *At. thiooxidans* has been found to be the most abundant species in the acidophilic thiobacilli [12]. Therefore, a more economical and efficient process for metal leaching using a mixed culture of *T. thioparus* and *At. thiooxidans* at neutral pH (than the process using *At. ferrooxidans* or *At. thiooxidans* at acidic pH) has been recently developed [13]. The advantage of using the mixed culture is that the initial sulfur oxidation and acidification carried out by *T. thioparus* results in a decrease in pH to approximately 4, at which *At. thiooxidans* can subsequently grow without adding any acid.

Although the bioleaching process has been indicated to be an effective technology for removing heavy metals from sediments. sludges or soils, the long operational time is normally required. It has been reported that to achieve high efficiency of metal solubilization, it requires 7–28 days retention time in bioleaching process [1-5]. Compared with physical and chemical methods, this slow leaching kinetics during bioleaching process may limit its practical application. This explanation is that most oxidation reactions of metal sulfide generally occur with very slow reaction rate [14]. In order to improve the metal leaching rate, several catalysts have been recently investigated to enhance the bioleaching process of sulfide ores [14–17]. Among the catalysts studied, silver has been found to be the most effective one in enhancing the bioleaching process [14,16]. However, studies on the metal bioleaching of contaminated sediments catalyzed by silver ions are lacking. For the practicability of bioleaching, a further investigation is needed to understand the silver-catalyzed bioleaching of contaminated sediments. The present study aims to elucidate the catalytic effects of silver ions on the bioleaching of heavy metals from contaminated sediments. A set of batch experiments was conducted to compare the rate and efficiency of metal solubilization in the bioleaching process with silver ions to that without silver ions. Also, metal partitioning in the contaminated sediment was investigated before and after the bioleaching process catalyzed by silver ions.

2. Materials and methods

2.1. Sediment characterization

The sediment used in this study was collected from the lower reaches (near Nan Ding Bridge) of Ell Ren River in southern Taiwan. Due to the discharge of municipal, agricultural and industrial wastes without treatment, significant levels of heavy metals have been detected from the sediment in Ell Ren River. All gravels and litters were removed from the sediment and the sediment was kept at 4°C before utilization. The water content and organic matter content of the sediment were determined by following Standard Methods [18]. Some of the sediment was air-dried and screened with a 20-mesh (0.84 mm) sieve for characteristic analysis. The pH of sediment was measured according to the method described by LaBauve et al. [19]. For total metal analysis, the sediment sample was digested with HNO₃-HF-HCl (5:4:1, v/v) mixture in the microwave digestion system (Model MDS-2000, CEM), according to USEPA3052 method [20]. Then, the suspension was filtered through a $0.45\,\mu m$ membrane and analyzed by a flame atomic absorption spectrophotometer (AAS) equipped with a graphite burner (Model Z-8100, Hitachi). The selected physiochemical properties of the sediment are given in Table 1.

Table 1The characteristics of the sediment in this study

Item	Value ^a
Water content (%)	52.7 ± 0.1
Organic matter content (%)	2.7 ± 0.1
рН	7.9 ± 0.2
Fe (%)	4.9 ± 0.3
Cu (mg/kg)	445 ± 29
Zn (mg/kg)	914 ± 4
Mn (mg/kg)	447 ± 28
Ni (mg/kg)	147 ± 1
Pb (mg/kg)	93 ± 6

^a Mean \pm S.D. (n = 6).

2.2. Microorganisms and inoculum

Two strains, At. thiooxidans CCRC 15612 and T. thioparus CCRC 15623, used in this study were obtained from the Culture Collection and Research Center (CCRC) at Food Industry Research and Development Institute (Hsinchu, Taiwan). At. thiooxidans was cultured in a nutrient medium (medium 317) consisting of: 0.3 g/L (NH₄)₂SO₄, 3.5 g/L K₂HPO₄, 0.5 g/L MgSO₄·7H₂O, 0.25 g/L CaCl₂ and 5.0 g/L tyndallized sulfur powder with pH at 4.5. T. thioparus was grown in another medium (medium 318) with a composition of: 0.3 g/L (NH₄)₂SO₄, 4.0 g/L K₂HPO₄, 1.5 g/L KH₂PO₄, 0.5 g/L MgSO₄·7H₂O, and 10.0 g/L Na₂S₂O₃·5H₂O at pH 7.0. These two cultures were incubated in 500 mL Erlenmeyer flasks shaken at 200 rpm with temperature control at 30 °C. An acclimation test had to be performed prior to the bioleaching experiments. In this acclimation test, 5 mL subculture of At. thiooxidans and T. thioparus was respectively added into 150 mL sterilized sediment suspension (solid contents: 2%, w/v) in a 500 mL Erlenmeyer flask. Then 0.75 g of tyndallized elemental sulfur was added in the sediment suspension. The flask was agitated at 200 rpm in an incubating shaker at 30 °C. The acclimation was continued until the pH of the sediment dropped below 2.0 and thus the inoculum for the bioleaching experiment was obtained.

2.3. Bioleaching experiments

The bioleaching experiments were conducted in a 5-L batch reactor stirred at 200 rpm and maintained at 30 °C. The aeration rate of this reactor was 1.2 L/min. In each bioleaching experiment, 5% (v/v) of inoculum obtained from the acclimation test and 15 g of tyndallized elemental sulfur were added into 3 L sediment suspension (solid contents: 2%, w/v). Besides, the amounts of silver ion added into the reactor were 0, 1, 8, 15, 30 and 40 mg Ag/L, respectively. A control experiment was performed in parallel without bacterial inoculum and addition of silver ion for comparison. All experiments were carried out for 5 days. During the bioleaching experiment, an on-line monitor (Tank, model RD-500) was used to measure the variations of pH and ORP. Meanwhile, the sediment suspension taken from the reactor was filtered through a 0.45 µm membrane, and the filtrate was used for analyzing sulfate concentration [18] and heavy metals. The heavy metal concentration was determined by a flame AAS equipped with a graphite burner (Model Z-8100, Hitachi). The solubilization efficiencies of heavy metals were calculated as the ratio of the soluble heavy metal in the filtrate to total heavy metal in the sediment before bioleaching. The residual silver content in the sediment was also analyzed after the bioleaching process. The numbers of T. thioparus and At. thiooxidans in the reactor were measured by a plate count method with the modified thiosulfate agar medium of medium 317 and medium 318. In the bacterial enumeration, several counts were conducted for each plate until

reproducible results with a variation equal to or less than 5% was obtained.

2.4. Metal partitioning

The sequential extraction procedures according to Lin et al. [21] were performed to determine the binding forms of metal in the sediment before and after the bioleaching experiment in this study. This method is designed to partition the heavy metals in the sediment into the following five fractions:

- (1) Exchangeable fraction: the sediment sample was extracted by 1 M MgCl₂ at initial pH 7, and was shaken at 250 rpm for 1 h at room temperature.
- (2) Carbonate-bound fraction: the residue from (1) was extracted by 1 M CH₃COONa buffered to pH 5 with CH₃COOH, and was shaken at 250 rpm for 6 h at room temperature.
- (3) Fe/Mn oxides-bound fraction: the residue from (2) was extracted by 0.04 M NH $_2$ OH·HCl (in 25% (v/v) CH $_3$ COOH) at initial pH 2, and was shaken at 250 rpm for 5 h at 96 \pm 3 $^{\circ}$ C.
- (4) Organic matter/sulfides-bound fraction: the residue from (3) was extracted by $0.02\,\mathrm{M}$ HNO $_3$ and $30\%\,(\mathrm{v/v})\,\mathrm{H}_2\mathrm{O}_2$ at initial pH 2, and was shaken at $250\,\mathrm{rpm}$ for $3\,\mathrm{h}$ at $85\pm2\,^\circ\mathrm{C}$. Then, $30\%\,\mathrm{H}_2\mathrm{O}_2$ was added into the same tube with continuously shaking for $2\,\mathrm{h}$. Finally, $3.2\,\mathrm{M}$ CH $_3\mathrm{COONH}_4$ in $20\%\,\mathrm{HNO}_3$ was added into the tube, and then it was shaken at $250\,\mathrm{rpm}$ for $0.5\,\mathrm{h}$ at room temperature.
- (5) Residual fraction: the residue form (4) was digested with HNO₃, HF and HCl according to the microwave digestion method [20].

The extraction was conducted in 50 mL centrifuge tubes to minimize losses of solid material. Between each extraction, separation was accomplished by centrifugation at 2000 rpm for 20 min. All extracts obtained from the sequential extraction procedure were used for measuring heavy metals.

3. Results and discussion

3.1. Variations of pH and ORP

The variations of pH during the bioleaching processes with different concentrations of silver ions are shown in Fig. 1. Since sulfur-oxidizing bacteria used elemental sulfur as an electron donor, sulfuric acid was produced in the bioleaching process and then the sediment pH decreased. After 5 days of reaction time, sediment pH decreased from 7.0 to 2.1, 2.5, 1.6, 1.2, 1.3 and 2.1 for

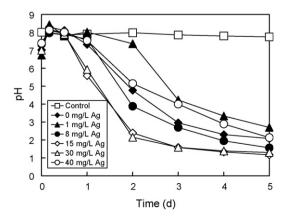


Fig. 1. Variations of pH at different silver concentrations during the bioleaching process.

Table 2Standard free energy (ΔG°) for cationic interchange reaction between metal sulfide and silver ion

Reaction	ΔG° (kJ/mol)ª
$CuS + 2Ag^+ \rightarrow Ag_2S + Cu^{2+}$	-75.84
$ZnS + 2Ag^+ \rightarrow Ag_2S + Zn^{2+}$	-143.78
$MnS + 2Ag^+ \rightarrow Ag_2S + Mn^{2+}$	-204.84
$NiS + 2Ag^{+} \rightarrow Ag_{2}S + Ni^{2+}$	-154.34
$PbS + 2Ag^+ \rightarrow Ag_2S + Pb^{2+}$	-120.63

^a Calculated from the data in Stumm and Morgan [31].

silver concentrations of 0, 1, 8, 15, 30, and 40 mg/L, respectively. It was found that the pH reduction rate in the bioleaching was increased apparently when added silver concentration was greater than 8 mg/L. It shows that the maximum rate of pH reduction was obtained at silver concentration of 30 mg/L. However, when silver concentration of 40 mg/L was added in the bioleaching, the pH reduction rate was slowed down. The reason why the pH reduction rate was enhanced by the addition of silver ion can be explained by the following equations [17]:

$$MeS + 2Ag^+ \rightarrow Ag_2S + Me^{2+} \tag{1}$$

$$Ag_2S + 2Fe^{3+} \rightarrow 2Ag^+ + 2Fe^{2+} + S^0$$
 (2)

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

First, Ag_2S is formed on the particle surface when the silver ion was added in the bioleaching process. Based on the thermodynamic data (Table 2), the cationic exchange (Eq. (1)) theoretically took place. Ag^+ ions are regenerated through the oxidation of Ag_2S by ferric ion and ferrous iron as well as S^0 are simultaneously produced (Eq. (2)). Therefore, the presence of Ag_2S could significantly affect the conductivity of the sulfur produced or its morphology (porosity) [22], either of which would result in an enhanced sulfur oxidation rate (Eq. (3)). Subsequently, ferric ion is produced from the ferrous ions generated in Eq. (2) according to Eq. (4) [23].

$$4Fe^{2+} + O_2 + 4H^{+} \xrightarrow{Bacteria} 4Fe^{3+} + 2H_2O$$
 (4)

Besides the pH reduction, the oxidation of sulfur and ferrous iron caused an increase in the oxidation–reduction potential (ORP) of sediment during the bioleaching process. Fig. 2 shows the variations of ORP during the bioleaching processes with different concentrations of silver ion. The ORP values increased to 390–476 mV after 5 days of reaction time. The trends of ORP increase were reflected to the pH reduction. The higher level of ORP increase was found at silver concentrations from 8 to 30 mg/L. In the bioleaching process,

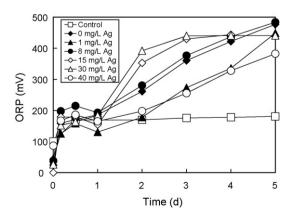


Fig. 2. Variations of ORP at different silver concentrations during the bioleaching process.

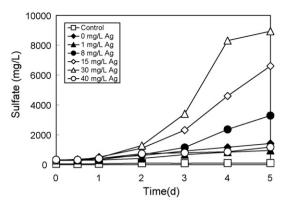


Fig. 3. Variations of sulfate at different silver concentrations during the bioleaching process

the rate of ORP increase could not be enhanced by adding low or high concentration (1 or 40 mg/L) of silver ion.

3.2. Sulfate production

The variations of sulfate concentration with time at different concentrations of silver ion during the bioleaching process are shown in Fig. 3. The oxidation of sulfide and elemental sulfur presented in terms of sulfate concentration proceeded with the similar trend of pH reduction and ORP increase. As can be seen in Fig. 3, a lag phase was found in the first day and then the sulfate concentration increased sharply. The longer lag phase was observed at lower silver concentrations as well. During the bioleaching process, no significant difference was observed in sulfate concentrations at silver concentrations of 0 and 1 mg/L. However, the addition of 8, 15 and 30 mg/L silver ion in the bioleaching process led to a significant enhancement in sulfate production. The final sulfate concentrations for silver concentrations of 8, 15 and 30 mg/L were much higher than those for 0 and 1 mg/L. It was found that the sulfate production rate increased with increasing silver concentration in the range of 1-30 mg/L, while it slowed down at 40 mg/L silver. It might suggest that Ag jarosite (AgFe₃(SO₄)₂(OH)₆) formed and precipitated on the surface of the particles at higher concentration of silver in the bioleaching system [15]. Thus, the bacterial oxidation of sulfur was inhibited.

3.3. Metal solubilization

Fig. 4 shows the solubilization of heavy metals from sediments at different concentrations of silver ion during the bioleaching process. It was found that Cu, Zn and Ni had high solubilization efficiency (>95%) in the bioleaching process. However, the efficiency of

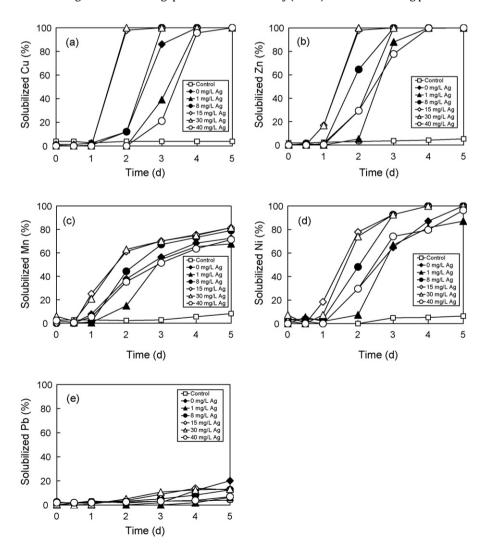


Fig. 4. Metal solubilization at different silver concentrations: (a) Cu, (b) Zn, (c) Mn, (d) Ni and (e) Pb during the bioleaching process.

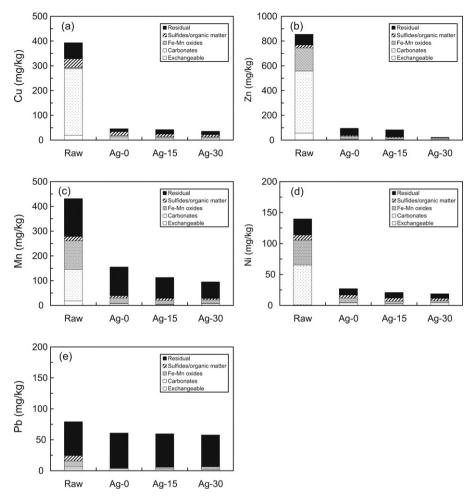


Fig. 5. Binding forms of metals in the sediment before and after the bioleaching process: (a) Cu, (b) Zn, (c) Mn, (d) Ni and (e) Pb (Raw: before bioleaching experiment; Ag-0: after bioleaching experiment without Ag; Ag-15: after bioleaching experiment with 15 mg/L Ag; Ag-30: after bioleaching experiment with 30 mg/L Ag).

Pb solubilization was relatively low (6–20%) in the bioleaching process. The solubilization efficiency of heavy metal from sediment was in a decreasing order: Cu≈Zn>Ni>Mn>Pb. The sequential extraction approach used in this study separated the heavy metals in the sediment into five binding forms: exchangeable, carbonatebound, Fe/Mn oxide-bound, organic matter/sulfide-bound, and residual. Generally, the metal solubilization efficiency in the bioleaching process depends on the binding forms of metal in the sediment. Metals in exchangeable, carbonate-bound, and Fe/Mn oxide-bound fractions are considered to be more mobile and bioavailable. Meanwhile, the sulfides/organic matter-bound and residual metals are stable and non-bioavailable [24]. It was found that most of Zn (87%), Cu (75%), Ni (75%) and Mn (60%) in the sediment originally existed as the mobile forms (i.e. exchangeable, carbonate, and Fe/Mn oxides fractions), but only about 20% of Pb was mobile (Fig. 5). On the other hand, the solubilized Pb can form into low solubility of PbSO₄ during the bioleaching process [2]. Therefore, Cu, Zn, Mn, and Ni had high solubilization efficiency in this study. The efficiency of Pb solubilization was the lowest.

Lag phases of metal solubilization were observed in Fig. 4 when pH and ORP did not reach the threshold values for allowing heavy metals to significantly solubilize from sediment. With silver concentration of 15 and 30 mg/L, it was apparent that the periods of the lag phases for heavy metals to solubilize from sediment were shortened in the bioleaching. The rate of metal solubilization in the bioleaching process can be described by the following empirical

equation:

$$\frac{\mathrm{d}M}{\mathrm{d}t} = k(M_{\mathrm{S}} - M) \tag{3}$$

where k is the rate constant of metal solubilization (1/d), M_s and M are the initial weight of metal in the sediment (mg) and weight of metal in the aqueous phase (mg), respectively. Table 3 presents the rate constants of metal solubilization in the bioleaching process. As can be seen, except for Pb, the rate constant of metal solubilization was enhanced when the added concentration of silver ion was lower than 30 mg/L in the bioleaching process. This result is attributed to that the silver ion was incorporated into the lattice of the initial sulfide through a cationic interchange reaction shown in Eq. (1). The other explanation is that the pH reduction rate was enhanced by addition of silver ion in this system (Fig. 1) while the metal solubilization from sediment is governed by the pH [11]. In particular, the metal solubilization rate on the second day was significantly enhanced by silver ion addition compared to that without silver ion. The metal solubilization was speeded up to the maximum rate at 30 mg/L silver in the bioleaching. However, the metal solubilization rate decreased at 40 mg/L silver in the bioleaching. It was evident that silver ion could be used as a catalyst for the enhancement of metal solubilization in the bioleaching process.

In addition to the mobile forms of heavy metals removed by the bioleaching process, Fig. 5 also shows that the content of Cu in sulfides/organic matter-bound fraction decreased from 35.3 mg/kg to

Table 3Rate constants of metal solubilization from sediment in the bioleaching process with different silver concentrations

Silver concentration (mg/L)	Cu		Zn		Mn		Ni		Pb	
	k (1/d)	R^2								
0	4.369	0.86	3.325	0.81	0.291	0.98	0.498	0.87	0.114	0.89
1	4.556	0.82	3.449	0.83	0.296	0.92	0.501	0.92	0.033	0.95
8	4.591	0.81	3.916	0.84	0.356	0.99	0.830	0.81	0.041	0.99
15	4.763	0.83	4.753	0.83	0.364	0.96	0.934	0.94	0.046	0.98
30	4.765	0.83	4.758	0.83	0.367	0.95	1.099	0.97	0.046	0.97
40	3.745	0.81	2.845	0.85	0.269	0.98	0.789	0.92	0.012	0.87

15.5, 10.2, and 8.7 mg/kg in the presence of 0, 15 and 30 mg/L silver ion, respectively. The same results were also found in Zn, Mn and Ni. The decreasing amount of sulfides/organic matter-bound metal after the bioleaching process with addition of silver ion was higher than that without addition of silver ion. This is explained by the occurrence of Eq. (1) in the bioleaching in the presence of silver ion. Similarly, more residual fraction of heavy metal decreased in the bioleaching with silver ion. These results indicate that even metals in the stable forms can be solubilized in the bioleaching process. At the same time, the remaining metals were primarily found in the stable forms after the bioleaching process.

In order to make the silver-catalyzed bioleaching process for removal of heavy metals from sediment more economically practicable, the recovery of silver used in this process is required to be of concern. Table 4 shows the residual silver content in the sediment after the bioleaching process. The residual silver contents in the sediment were 18, 95 and 149 mg/kg for added silver of 1, 8 and 40 mg/L, respectively, after 5 days of bioleaching. An increase in residual silver content in the sediment was observed as silver added in the bioleaching process increased. On the other hand, the residual percentage of silver was lower than 40% and it decreased with an increased in the silver added. The residual silver in the sediment is attributed to the formation of Ag₂S (Eq. (1)) and Ag jarosite on the sediment particles during the bioleaching process. The results of X-ray diffraction analysis obtained from previous studies [22,25,26] confirm their existence. However, it was demonstrated that the silver remaining in the sediment can be further solubilized by sulfur-oxidizing bacteria [27] or successfully recovered by chemical leaching (hydrochloric or sulfuric acid) [16] and thus the operational cost of silver-catalyzed bioleaching process will be reduced.

3.4. Bacterial growth

The bacterial growth at different concentrations of silver ion during the bioleaching process is shown in Fig. 6. A rapid growth of *T. thioparus* (less-acidophilic) was initially observed and then it was followed by a sharp decrease in the bacterial concentration owing to the low pH (Fig. 6a). On the other hand, the major growth of *At. thiooxidans* (acidophilic) was found to take place after the growth of *T. thioparus* (Fig. 6b). It was evident that the bioleaching process was performed by successive growth of less-acidophilic and acidophilic sulfur-oxidizing bacteria [11]. Previous studies reported that silver was toxic to microorganisms used for bioleaching. Pethkar and Paknikar [28] indicated that *T. thioparus* was grown in the system

Residual silver content in the sediment after the bioleaching process with different silver concentrations

Silver added (mg/L)	Residual silver content (mg/kg)	Residual percentage (%)
1	18	36.6
8	95	23.6
40	149	7.4

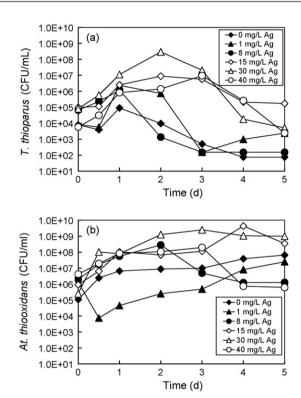


Fig. 6. Bacterial growth at different silver concentrations: (a) *T. thioparus* and (b) *At. thiooxidans* during the bioleaching process.

with 350 mg/L of silver and was used for the treatment of photofilm processing wastewater. Silver is toxic to Sulfolobus BC at a concentration of 20 mg/L in the thermophilic bioleaching experiment [27]. The activity of At. ferrooxidans is inhibited by 10 mg/L of silver in the batch culture test [28]. Generally, At. ferrooxidans has been observed to be tolerant to higher concentration (100 mg/L) of silver after the adaptation [29]. As shown in Fig. 6, due to the acclimation prior to the bioleaching experiment no inhibitory effects were found on the bacterial growth in the bioleaching experiments with silver presenting. On the contrary, the addition of silver in the bioleaching process caused a slight enhancement in bacterial growth. This result is in agreement with the work done by Gomez et al. [30], who also found the bacterial growth (the mixed culture of At. ferrooxidans, At. thiooxidans and Leptospirilum ferrooxidans) was improved by the addition of 50 mg/L silver in the batch bioleaching experiment.

4. Conclusions

Although the bioleaching process is one of the promising methods for removing heavy metals from contaminated sediments, it still has some limitations in practical application. This process is too slow to be economically feasible. One of the methods to solve

this problem is to add some catalytic ions in the bioleaching process. The addition of silver ion can change the electrochemical behavior of sediment particles and then speed up the acidification and metal solubilization with silver addition from 8 to $30\,\mathrm{mg/L}$ in the bioleaching process. However, there was no apparent significant enhancement with the presence of $40\,\mathrm{mg/L}$ silver in the bioleaching process. Overall, the efficiency of metal solubilization was relatively high in the silver-catalyzed bioleaching process, except Pb. Besides the mobile forms of heavy metals, the stable forms of heavy metals can be even removed by the bioleaching process. In this study, the concentrations of silver added have no toxic effects on the growth of sulfur-oxidizing bacteria during the bioleaching process. The addition of silver ion enhances the kinetics of metal solubilization in the bioleaching process.

References

- I.S. Kim, J.U. Lee, A. Jang, Bioleaching of heavy metals from dewatered sludge by *Acidithiobacillus ferrooxidans*, J. Chem. Technol. Biotechnol. 80 (2005) 1339–1348.
- [2] S.Y. Chen, J.G. Lin, Bioleaching of heavy metals from contaminated sediment by indigenous sulfur-oxidizing bacteria in an airlift bioreactor: effects of sulfur concentration, Water Res. 38 (2004) 3205–3214.
- [3] S.Y. Chen, J.G. Lin, Bioleaching of heavy metals from livestock sludge by indigenous sulfur-oxidizing bacteria: effects of sludge solids concentration, Chemosphere 54 (2004) 283–289.
- [4] A.T. Lombardi, O. Garcia Jr., W.A.N. Menezes, The effects of bacterial leaching on metal partitioning in sewage sludge, World J. Microbiol. Biotechnol. 22 (2006) 1013–1019.
- [5] R.N. Kumar, R. Nagendran, Influence of initial pH on bioleaching of heavy metals from contaminated soil employing indigenous *Acidithiobacillus thiooxidans*, Chemosphere 66 (2007) 1775–1781.
- [6] D.P. Kelly, A.P. Wood, Reclassification of some species of *Thiobacillus* to the newly designated genera *Acidithiobacillus* gen. nov., *Halothiobacillus* gen. nov. and *Thermithiobacillus* gen. nov., Int. J. Syst. Evol. Microbiol. 50 (2000) 511–516.
- [7] L. Vlasceanu, R. Popa, B.K. Kinkle, Characterization of *Thiobacillus thioparus* LV43 and its distribution in a chemoautotrophically based groundwater ecosystem, Appl. Environ. Microbiol. 63 (1997) 3123–3127
- [8] I. Suzuki, T.L. Takeuchi, T.D. Yuthasastrakosol, J.K. Oh, Ferrous iron and sulfur oxidation and ferric iron reduction activities of *Thiobacillus ferrooxidans* are affected by growth on ferrous iron, sulfur, or a sulfide ore, Appl. Environ. Microbiol. 56 (1990) 1620–1626.
- [9] K.S. Cho, H.W. Ryu, I.S. Lee, H.M. Choi, Effect of solids concentration on bacterial leaching of heavy metals from sewage sludge, J. Air Waste Manage. 52 (2002) 237–243.
- [10] M.Q. Qiua, S.Y. Xiong, W.M. Zhang, G.X. Wang, A comparison of bioleaching of chalcopyrite using pure culture or a mixed culture, Miner. Eng. 18 (2005) 087, 2020

- [11] S.Y. Chen, J.G. Lin, Bioleaching of heavy metals from sediment: significance of pH, Chemosphere 44 (2001) 1093–1102.
- [12] J.F. Blais, R.D. Tyagi, J.C. Auclair, Bioleaching of metals from sewage sludge, microorganisms and growth kinetics, Water Res. 27 (1993) 101–110.
- [13] S.Y. Chen, J.G. Lin, Influence of solid content on bioleaching of heavy metals from contaminated sediment by *Thiobacillus* spp., J. Chem. Technol. Biotechnol. 75 (2000) 649–656.
- [14] A.L. Juarez, N.G. Arenas, R.E.R. Santillan, Electrochemical behavior of massive chalcopyrite bioleached electrodes in presence of silver at 35 °C, Hydrometallurgy 83 (2006) 63–68.
- [15] E. Gomez, A. Ballester, M.L. Blazquez, G. Gonzalez, Silver-catalysed bioleaching of a chalcopyrite concentrate with mixed cultures of moderately thermophilic microorganisms, Hydrometallurgy 51 (1999) 37–46.
- [16] R. Romero, A. Mazuelos, I. Palencia, F. Carranza, Copper recovery from chalcopyrite concentrates by the BRISA process, Hydrometallurgy 70 (2003) 205– 215.
- [17] M. Wang, Y. Zhang, T. Deng, K. Wang, Kinetic modeling for the bacterial leaching of chalcopyrite catalyzed by silver ions, Miner. Eng. 17 (2004) 943–947.
- [18] APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, 16th ed., Washington DC, 1995.
- [19] J.M. LaBauve, J. Kotuby-Amacher, R.P. Gambrell, The effect of soil properties and a synthetic municipal land-fill leachate on the retention of Cd, Ni, Pb and Zn in soil and sediment materials, J. Water Pollut. Control Fed. 60 (1988) 379–385.
- [20] US EPA, 1996. Microwave assisted acid digestion of siliceous and organically based matrices, Test Methods for Evaluating Solid Waste (SW-846), Method 3052, Washington, DC.
- [21] J.G. Lin, C.Y. Chen, S.Y. Chen, Effects of pH on metals specification in contaminated sediment, J. Chin. Inst. Environ. Eng. 9 (1999) 49–56.
- [22] H. Sato, H. Nakazawa, Y. Kudo, Effect of silver chloride on the bioleaching of chalcopyrite concentrate. Int. I. Miner. Process 59 (2000) 17–24.
- [23] A.L. Juarez, R.E.R. Santillan, N.G. Arenas, Microbiological leaching of chalcopyrite: an environmentally sound approach to processing a sulphide copper concentrate. Int. I. Environ. Pollut. 26 (2006) 254–265.
- [24] G. Perin, R. Fabris, S. Manente, A.R. Wagener, C. Hamacher, S. Scotto, A five-year study on the heavy metal pollution of Guanabara bay sediments (Rio De Janeiro, Brazil) and evaluation of the metal bioavailability by means of geochemical speciation, Water Res. 31 (1997) 3017–3028.
- [25] J.A. Martin-Gago, E. Roman, M. Blazquez, C. Quintana, L. Vazques, Chemical and morphological changes of the pyrite induced by leaching and bioleaching processes in the presence of catalytic Ag ion, Lanqmuir 13 (1997) 3355–3363.
- [26] Y. Hu, G. Qiu, J. Wang, D. Wang, The effect of silver-bearing catalysts on bioleaching of chalcopyrite, Hydrometallurgy 64 (2002) 81–88.
- [27] J.A. Munoz, C. Gomez, A. Ballester, M.L. Blazquez, F. Gonzalez, Electrochemical behaviour of chalcopyrite in the presence of silver and *Sulfolobus* bacteria, J. Appl. Electrochem. 28 (1998) 49–56.
- [28] A.V. Pethkar, K.M. Paknikar, Thiosulfate biodegradation-silver biosorption process for the treatment of photofilm processing wastewater, Proc. Biochem. 38 (31) (2003) 855–860.
- [29] M. Dopson, C. Baker-Austin, P.R. Koppineedi, P.L. Bond, Growth in sulfidic mineral environments: metal resistance mechanisms in acidophilic microorganisms, Microbiology 149 (2003) 1959–1970.
- [30] C. Gomez, M.L. Blazquez, A. Ballester, Influence of various factors in the bioleaching of a bulk concentrate with mesophilic microorganisms in the presence of Ag(I), Hydrometallurgy 45 (1997) 271–287.
- [31] W. Stumm, J. Morgan, Aquatic Chemistry, third ed., John Wiley & Sons, New York, New York, 1996.