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Adsorption and leaching of chalcopyrite by *Sulfolobus metallicus* YN24 cultured in the distinct energy sources

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Abstract: The chalcopyrite-adsorption characteristics and leaching properties of *Sulfolobus metallicus* (*S. metallicus*) YN24 were investigated in this study. The effects of zeta potentials of *S. metallicus* samples on chalcopyrite cultivated with distinct sources of energy were similar. Regardless of the energy source cultivated, all of the investigated *S. metallicus* samples adhered rapidly to the chalcopyrite surface, with an adhesion plateau being reached within 60 min. However, the mineral-cultured *S. metallicus* adsorbed more strongly onto chalcopyrite than the sulfur-cultured *S. metallicus* did. Furthermore, chalcopyrite-leaching tests suggested that the copper-leaching ability of the mineral-cultured *S. metallicus* was also greater than that of unadapted *S. metallicus*. Therefore, the results provide insights into the mechanism of mineral-surface adsorption of microorganisms that helps enhance the copper-leaching rate.

Keywords: chalcopyrite; bioleaching; *Sulfolobus metallicus*; adsorption

1. Introduction

As a refractory primary copper sulfide, chalcopyrite is the most abundant copper ore worldwide [1]. Traditionally, chalcopyrite ore is ground and concentrated through flotation and is further treated using pyrometallurgical methods. However, these procedures are expensive and cause the atmospheric pollution through the discharge of sulfur dioxide, which is toxic [2]. Therefore, the inexpensive and environmentally friendly methods must be developed to improve the current chalcopyrite-treatment techniques.

Bioleaching in an extraction process offers several advantages; however, its widespread use is limited by the slow dissolution of minerals. Chalcopyrite dissolves slowly during the bioleaching process, primarily because an inhibitory layer containing polysulfides, elemental sulfur, and iron-hydroxy precipitate may be present on the surface of chalcopyrite ore. In this process, bioleaching is facilitated by mesophiles and moderate thermoacidophiles [3–4]. Previous studies have shown that chalcopyrite dissolves slowly and that the yield of copper recovered from chalcopyrite is low in the presence of mesophiles or moderate thermophiles [5–6].

The oxidation of sulfide minerals is an exothermic reaction. During bioleaching, the temperature can reach 70°C, which is higher than the maximal temperature at which all mesophiles and moderate thermoacidophiles grow [1,7]. Recently, hyperthermoacidophiles, which grow optimally at 65–80°C, have shown the highly favorable properties that promote the bioleaching of refractory chalcopyrite, and the organisms can accelerate the dissolution rate of chalcopyrite, increase the extraction yield of copper, and prevent problematic passivation on the chalcopyrite surface at high temperatures [8–9]. Therefore, hyperthermoacidophiles may play a pivotal role in the next generation of biohydrometallurgical processes [8,10].

Chalcopyrite accounts for almost 70% of mined copper; however, processing of this metal-sulfide ore using hydrometallurgical methods is highly challenging [11]. Numerous studies have shown that, irrespective of the treatment used for leaching chalcopyrite (i.e., treatment with acidic or alkaline solutions or mesophilic bacteria), the intermediate products are generated and accumulated in the mineral surface that the cause mineral-surface passivation through deposition, consequently, the copper-leaching rates are low.

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These low rates greatly limit the use of chalcopyrite bioleaching for industrial purposes [12]. Previously, a layer of dense sulfur was reported to be deposited on the surface of chalcopyrite when leaching was performed using ferric sulfate, suggesting that the formation of sulfur layer on the chalcopyrite surface might lead to chalcopyrite passivation. Furthermore, in studies on chalcopyrite-bioleaching mechanisms at low and high temperatures [13–14], Rodriguez and coworkers determined that chalcopyrite leaching performed using mesophilic bacteria at 35°C was controlled by the rate at which elemental sulfur and the intermediate copper sulfide were formed; however, almost no barrier layers were formed at 68°C [15].

Bacterial adsorption onto the surface of minerals can change the physical, chemical, or physicochemical properties of the mineral surface in different degrees, including the hydrophobicity and the oxidation-dissolution and dissolution-precipitation of surface elements. Moreover, bacteria cultured under distinct growth conditions exhibit dissimilar surface structures and different abilities to adhere to the chalcopyrite surface; consequently, their leaching activities vary. Therefore, in this study, the adsorption characteristic of *Sulfolobus metallicus* onto the surface of chalcopyrite cultured in the presence of distinct energy sources was investigated to elucidate the mechanisms of mineral-surface adsorption of microorganisms. The results could be served as a reference for researchers to enhance the copper-leaching rates.

2. Materials and methods

2.1. Ore sample

Chalcopyrite was obtained from the Biohydrometallurgy Key Laboratory of the Ministry of Education, Central South University (Changsha, China). Pure chalcopyrite minerals were manually selected and ground to a diameter of 0.045–0.074 mm. Chalcopyrite for use in adsorption and zeta-potential measurements was ground by agate to a diameter of <5 μm. The mass fractions of elements copper, iron, and sulfur were measured and determined to be 31.45%, 26.74%, and 31.87%, respectively.

2.2. Strains and culture

Sulfolobus metallicus (*S. metallicus*) YN24 was obtained from the Biohydrometallurgy Key Laboratory of the Ministry of Education, Central South University. *S. metallicus* YN24 was inoculated in 9K medium (3.09 g/L $(NH_4)_2SO_4$, 0.1 g/L KCl, 0.5 g/L K_2HPO_4, 0.5 g/L $MgSO_4 \cdot 7H_2O$, and 0.01 g/L $Ca(NO_3)_2$) and supplemented with 0.02wt% yeast extract. The pH value of medium was adjusted to 2.0 by 5 mol/L H_2SO_4. Sulfur was added at 10 g/L as an energy substrate in the medium, and 0.2wt% chalcopyrite was added as a mineral energy substrate.

2.3. Archaeal adsorption onto the surface of minerals

1 g of mineral powder was added to 100 mL of NaCl solution, containing approximately 1×10^8 cells/mL (ionic strength I = 0.001 mol/L). The solution pH value was adjusted to 2.0, and the mixture was stirred using a magnetic stirrer for 120 min at room temperature. The solution was filtered to remove the insoluble ore particles, and the archaeal cells in supernatant were counted using a binocular microscope.

2.4. Measurement of zeta potential

A zetapotentiometric analyzer (Coulter Delsa 440SX, Beckman Coulter Co., Ltd., USA) was used to measure the zeta potentials of chalcopyrite and archaea. This instrument operates on the basis of electrophoretic light scattering principle (i.e., Doppler shift method).

Powdered chalcopyrite (0.1 g) was added to 100 mL of NaCl solution, containing 2×10^8 cells/mL archaea. After the solution was stirred for 5 min, its pH value was adjusted to 2, its zeta potential was measured, and it was then stirred for additional 90 min. Insoluble mineral particles were separated after the solution was allowed to stand. The concentration and ionic strength of the ore pulp were adjusted to 1 g/L and 0.001 mol/L, respectively, and the zeta potentials of minerals were measured. Each sample was measured three times, and the average value was calculated.

2.5. Bioleaching experiment

For use in the bioleaching experiments, *S. metallicus* YN24 samples were cultivated and enriched separately using either elemental sulfur or chalcopyrite. When their growth reached the log phase, *S. metallicus* YN24 cells (1×10^8 cells/mL) were transformed in 100 mL of 9K culture medium containing 0.2wt% chalcopyrite in a 250-mL flask; the initial pH value was adjusted to 2.0, and the samples were subsequently incubated at 68°C in a water-bath shaker. Aliquots of the leachate were collected at various times and analyzed for dissolved Cu^{2+}.

3. Results and discussion

3.1. Adsorption of *S. metallicus* YN24 onto the surface of chalcopyrite

The leaching activities of *S. metallicus* are different when the cells are grown under various energy conditions because the microorganism's surface structures change and exhibit distinct adsorption characteristics on the surface of chalcopyrite. In this experiment, the initial concentration of *S. metallicus* YN24 was 1 × 10^8 cell/mL, and the relationships between time and absorption capacity of microorganisms cultured in the presence of distinct energy sources were measured, as shown in Fig. 1. *S. metallicus* adsorbs rapidly onto the surface of chalcopyrite. Notably, the adsorption capacity of mineral-cultured *S. metallicus* is higher than that of S-cultured *S. metallicus*, almost 60% of mineral-cultured *S. metallicus* cells adsorb within the first 5 min of contact. The adsorption rate decreases over time and peaks after 40 min of incubation, 38.5% of the cells are adsorbed onto the surface of chalcopyrite at this peak point.

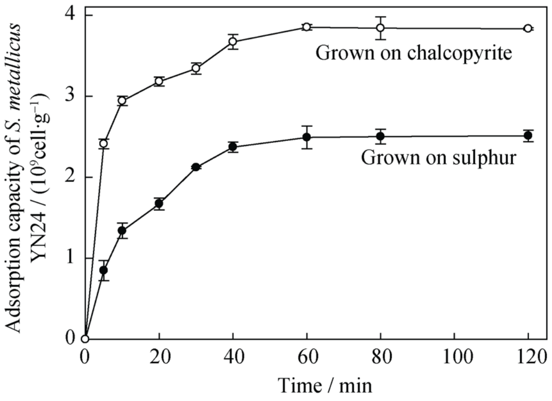

Fig. 1. Adsorption kinetics of *S. metallicus* YN24 cultured in the presence of distinct energy sources.

3.2. Zeta potentials of *S. metallicus* YN24 in culture

The relationship between the chalcopyrite zeta potentials and pH values was examined before and after incubation with *S. metallicus* samples cultured in the presence of distinct energy sources at an ionic strength of 0.01 mol/L, as shown in Fig. 2. The isoelectric points of *S. metallicus* cultured in sulfur and chalcopyrite are 2.78 and 3.85, respectively. A previous study showed that, when the isoelectric point was <2.5, the polysaccharide content of the bacteria surface was higher than the protein content; by contrast, when the isoelectric point was ≥3.2, the cell wall contained more protein than polysaccharides [16]. Thus, the zeta-potential measurements indicated that the mineral-cultured cells contained more protein than polysaccharides and that the cells synthesized increased amounts of proteins containing relevant functional groups that could be highly efficiently absorbed onto mineral surfaces. Therefore, the archaeal cells cultured in the presence of minerals exhibited the enhanced surface-adsorption capacity.

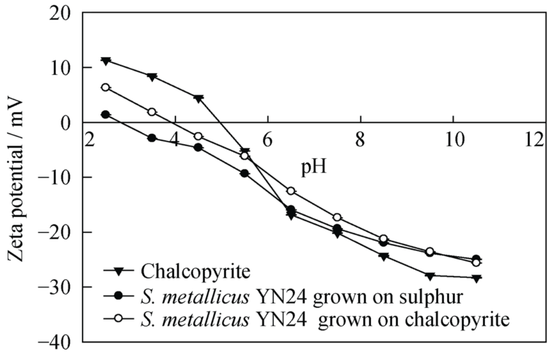

Fig. 2. Relationship between chalcopyrite zeta potentials and pH values before and after incubation with *S. metallicus* YN24 cultured with distinct energy sources.

In the aforementioned assays, the initial isoelectric point of chalcopyrite was approximately 5.02. After *S. metallicus* samples cultured in the presence of distinct energy sources were incubated with chalcopyrite, the isoelectric point of chalcopyrite uniformly shifted to that of archaea. This result suggested that the archaea were adsorbed onto the mineral surface. Whereas S-cultured *S. metallicus* lowered the chalcopyrite isoelectric point from 5.02 to 2.69, and the mineral-cultured *S. metallicus* caused the chalcopyrite isoelectric point to shift to approximately 3.80. These data suggested that the mineral-cultured *S. metallicus* affected the zeta-potential value of chalcopyrite more strongly than the S-cultured *S. metallicus* did.

3.3. Bioleaching of chalcopyrite induced by *S. metallicus* YN24

As shown in Fig. 3, the copper-recovery rate reached 62.43% in the case of mineral-cultured *S. metallicus* after 10 days, where it was only 49.63% in the case of S-cultured *S. metallicus*. This result demonstrated that the leaching capacity of mineral-cultured *S. metallicus* was considerably higher than that of the S-cultured *S. metallicus*. The microscopy was used to detect the micrograms present in the copper

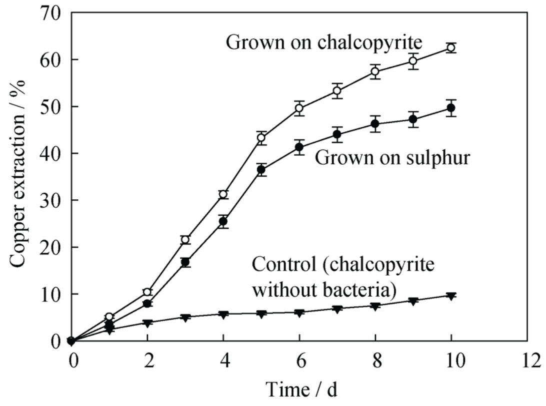

Fig. 3. Copper-recovery rate dissolved from chalcopyrite.

leachates, and the results are shown in Fig. 4. Throughout the measurement, the planktonic cell number in the mineral-cultured group remained higher than that in the S-cultured group. Thus, compared with S-cultured *S. metallicus*, the mineral-cultured *S. metallicus* could adapt to chalcopyrite more efficiently, propagate more rapidly in the leaching system, and exert more favorable leaching effects. This observation agreed with the results that the mineral-cultured *S. metallicus* adsorbed more strongly onto the chalcopyrite surface than the S-cultured *S. metallicus* did.

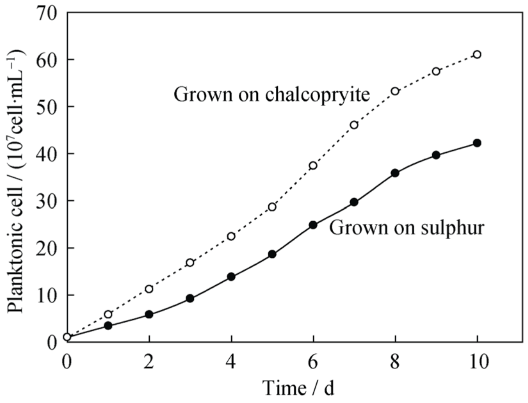

Fig. 4. Planktonic cells in copper leachates.

4. Conclusion

The adsorption onto chalcopyrite of *S. metallicus* cultured in the presence of distinct energy sources reveal the similar influence of the cultured samples on chalcopyrite. Regardless of the energy source used during cultivation, *S. metallicus* samples adhere to the chalcopyrite surface rapidly, with an adhesion plateau being reached within 60 min. However, the mineral-cultured *S. metallicus* adsorbs more strongly onto chalcopyrite than the S-cultured *S. metallicus* does. Furthermore, the results of this chalcopyrite-leaching test suggest that the copper-leaching ability of the mineral-cultured *S. metallicus* is also greater than that of the unadapted *S. metallicus*.

Acknowledgements

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