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Research Article

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Bioleaching of low grade copper ores from Yongping by the mixed bacteria

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ABSTRACT

The effect of process parameters (pH, pulp density, inoculum volume of the nutrient medium, silver content) on the rate of copper solubilization was analyzed respectively through silver-catalyzed bioleaching experiments with microorganisms in shake flasks. These results show that the optimal process parameters are: pulp density, 2.5 wt%; silver content, 10mg/L; pH, 1.50-1.80; inoculum volume of the nutrient medium, 40vol%. Furthermore, the addition of the silver could catalyze the process of bioleaching, and high silver concentrations would be harmful to the bacterial activity and the copper extraction. pH and inoculum volume of the nutrient medium had a marked influence on the copper extraction and iron extraction. The bioleaching of the low-grade copper ore requires a minimum amount of the nutrient medium to obtain the maximal efficiency.

Key words: bioleaching, optimization, microorganisms, process parameters

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INTRODUCTION

The mining and metallurgical activities that were particularly intensive during the last century resulted in the generation of huge amounts of mine tailing, including acid generating sulfid tailings. Most of the tailings have been left without any management at mines of China. Their improper management in the past resulted in the mobilization of heavy metals to the surrounding environment, contributing to soil substrates contamination, soil texture destruction, short of nutrient, ecological landscape destruction, groundwater pollution, biological diversity decrease, etc. The presence of toxic heavy metals in mine tailings caused lots of serious environmental problems. In order to resolve the above problems, it is important to develop a suitable and economical technology for removal of heavy metals from mine tailings [1-3].

Bioremediation of heavy metals has gained increased attention since it is innovative, environmentally friendly and economical. The bioleaching process may be defined as the solubilization of metals from solid substrates either directly by the metabolism of leaching bacteria or indirectly by the products of metabolism [4-7]. Bioleaching processes are based on the ability of microorganisms to transform solid compounds and result in soluble and extractable elements, which can be recovered [8]. Because of the advantages of low cost and environment friendliness and better efficiency, bioleaching technology has been a great success for the mining industry [9]. In recent years, bioleaching has also proved to be a possible way to remove heavy metals from metal contaminated materials such as anaerobically digested sewage sludge, contaminated river sediment, low-grade ores, and so on [10-12].

Nevertheless, in the treatment of low-grade copper ores low extractions and slow kinetics remain as the main drawbacks to these processes as they operate at low temperatures. The leaching of copper in dumps or heaps from low-grade ores is often slow and far from complete. It is essential to find some desirable methods to enhance copper extraction from low-grade copper ores. It has been reported that some catalytic ions, such as Ag, Sn, Bi, Co, Hg, and so on, accelerate copper dissolution from low-grade in the presence of Thiobacillus ferrooxidans, among which silver ion has the best effect [13].

In this work, the effect of process parameters (such as pulp density, pH, [Ag^+] and inoculum volume of the nutrient medium) on the rate of copper solubilization in the silver-catalyzed bioleaching of low-grade copper ores were investigated. The results would promote the industrial application of silver-catalyzed techniques, and provided an effective and economic technology for silver-catalyzed bioleaching of low-grade copper ores.

EXPERIMENTAL SECTION

2.1 Microorganisms

The mixed bacteria (Thiobacillus ferrooxidans and Thiobacillus thiooxidans), gained from an acidic water a Yongping's copper mine through a series of enrichment, separation, domestication and combination tests, was maintained at pH1.80, Fe^{2+}4g·L^{-1} and 30℃ through numerous serial cultures with the low-grade copper ores (10wt%) as the sole substrate. It was adapted to copper ores as the sole energy source. The aqueous growth mediums 9K+S culture [14] containing 3g $(NH_4)_2SO_4$, 0.1g KCl, 0.5g K_2HPO_4, 0.5g $MgSO_4 \cdot 7H_2O$, 0.01g $Ca(NO_3)_2$ and 1g S per litre, adjusted to pH1.80 with sulphuric acid [15].

2.2 The low-grade copper ore

The low-grade copper ores from Yongping were pulverized in a ring earthen bowl. The fine copper ores, with a particle size of about less than 5mm, were used for the all bioleaching experiments. The analytical composition of copper ores and the phase of copper were determined by quantitative X-ray diffraction (Table 1 and Table 2).

Table 1 Chemical component of copper ore (%)

SiO_2	Al_2O_3	Fe	P_2O_5	MgO	CaO	Na_2O	K_2O	Cu	S
45.00	6.74	15.58	0.050	1.80	8.38	0.26	1.76	0.40	13.36

Table 2 Phase of copper in the discard copper ore (%)

Phase	dissociative oxidated copper	associative oxidated copper	subproterozoic sulfureted copper	proterozoic sulfureted copper	total of copper
content	0.0053	0.0026	0.0074	0.38	0.40

2.3 Bioleaching experiment

The experiments were performed in 250mL Erlenmeyer shake flasks, containing 100mL of leach solution. Flasks were placed on an orbital shaker (130r/min) and incubated at 30° C. The growth medium is 9K+S culture. Silver was added as $AgNO_3$. [Ag^+] was 20mg·L^{-1}. The value of pH was adjusted to 1.20-1.50 (at the beginning, pH1.20) with sulphuric acid. The pulp density was 10% (W/V), [Fe^{2+}] 0 g·L^{-1} and inoculation concentration of the mixed bacteria was 10% (V/V). All experiments were conducted at lease in duplicate.

2.4 Analytical methods

The soluble copper and sliver was determined by atomic absorption spectrophotometry (AAS). Ferrous ion and ferric ion were determined by titration with EDTA. The value of pH was measured at each sampling interval by a pH probe calibrated with a low pH buffer. The value of Eh was measured with a silver/silver chloride double reference oxidation-reduction probe. Redox electrodes were tested periodically by placing in a solution of pH buffer saturated with quinhydrone at 25° C. Ag/AgCl reference probes give a reading of 263 mV in this solution [16].

RESULTS AND DISCUSSION

3.1 Influence of pulp density

The influence of pulp density was studied at different concentrations of pulp density (2.5wt%, 5.0wt%, 7.5wt%, 10.0wt%, 15.0wt% and 20.0wt%) during the bioleaching process. As shown in Fig.1, the extraction of copper during the silver-catalyzed bioleaching experiments was greatly affected by the concentration of pulp density.

When the concentration of pulp density increases, the copper extraction also increases. The copper extraction after 32 days were 72.6%, 66.8%, 64.3%, 62.1%, 57.9% and 49.1% respectively. The extraction of copper reduced with the increase of pulp density, perhaps due to a lower availability of oxygen at high pulp density. Moreover, there are more harmful ions at high pulp density. These conditions will not benefit the bacterial development in bioleaching tests.

The long lag phase observed in these experiments, about 8 days, would be related to the toxic effect exerted by the relative high amount of silver used. Some papers were reported about this result [14].

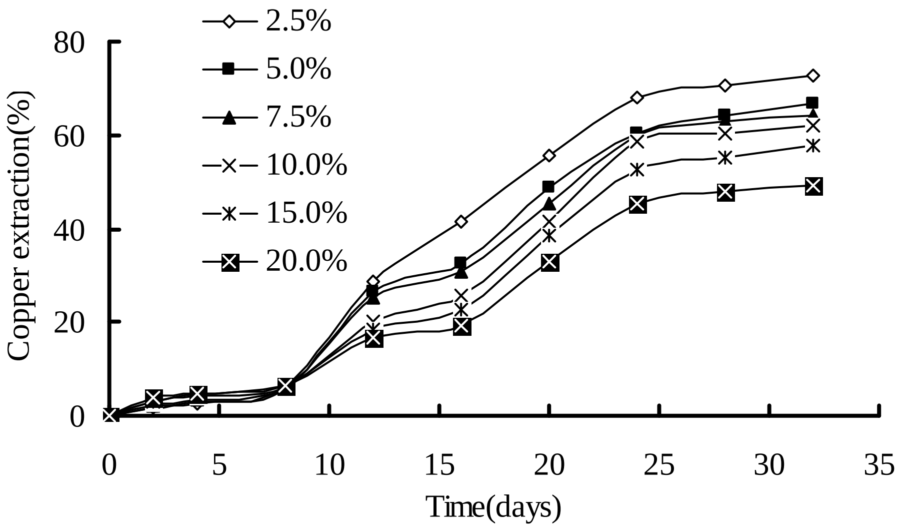

Fig.1 Effect of pulp density on copper extraction during the silver-catalyzed bioleaching experiment

Fig.2 shows the iron extraction during the bioleaching experiments. The pulp density significantly affected the extraction of iron. As the pulp density increases, the silver-catalyzed bioleaching process becomes more selective, dissolving a smaller amount of iron.

From these results, it was thought that the optimal pulp density was 2.5 wt%.

3.2 Influence of [Ag^+]

The influence of [Ag^+] was studied at different [Ag^+] (0mg·L^{-1}, 5mg·L^{-1}, 10mg·L^{-1}, 15mg·L^{-1}, 20mg·L^{-1} and 25mg·L^{-1}) during the bioleaching process. Changes in copper extraction with time are shown in Fig.3.

From Fig.3, it shows that addition of silver could dissolve high amounts of copper and with fast kinetics. The extraction of copper after 32 days were 18.6%, 27.9%, 70.02%, 66.7%, 62.1% and 56.0% respectively. However, the high silver is not only expensive, and also toxic to microorganisms. So, when the addition of silver is 25 mg/L, the copper extraction is small.

In this paper, the optimal addition of silver was thought to be 10mg/L. The microorgansims developed well and the copper extraction was higher during the silver-catalyzed bioleaching experiments.

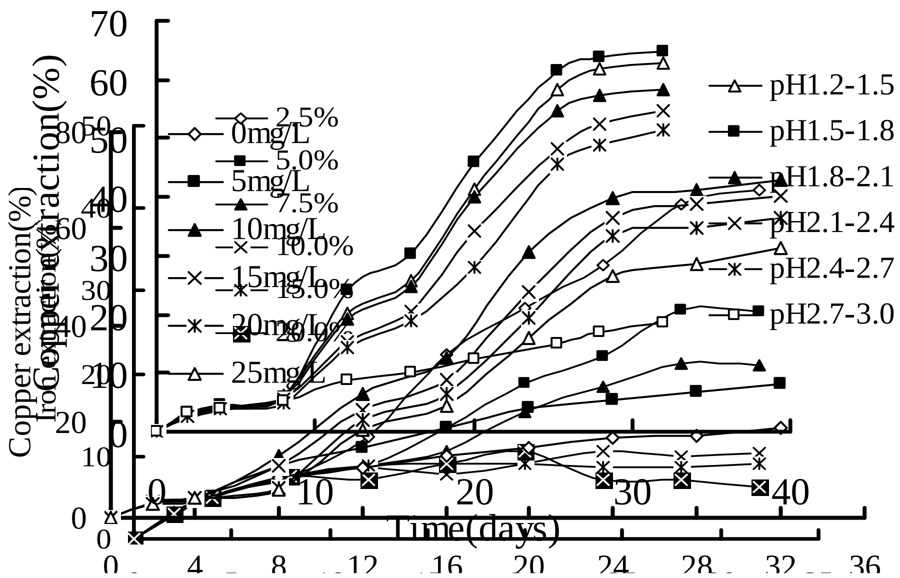

Fig.4 Effect of pH on copper extraction during the silver-catalyzed bioleaching experiment

3.3 Influence of pH

The pH plays an important role in bioleaching processes in two ways: affecting the chemistry of reactions and establishing the ranges of predominance of different microorganisms. The influence of pH was studied at different pH values.

The copper extraction at different pH values are shown in Fig.4. The copper dissolution was markedly affected at pH2.7-3.0, with little influence in the range from 1.20 to 2.40. A reasonable explanation is that in that range of pH microorganisms are more active. The extraction of copper ranged from pH1.50 to1.80 is the highest among the bioleaching experiments. Fig.5 shows changes of the iron extraction with time at different pH value.

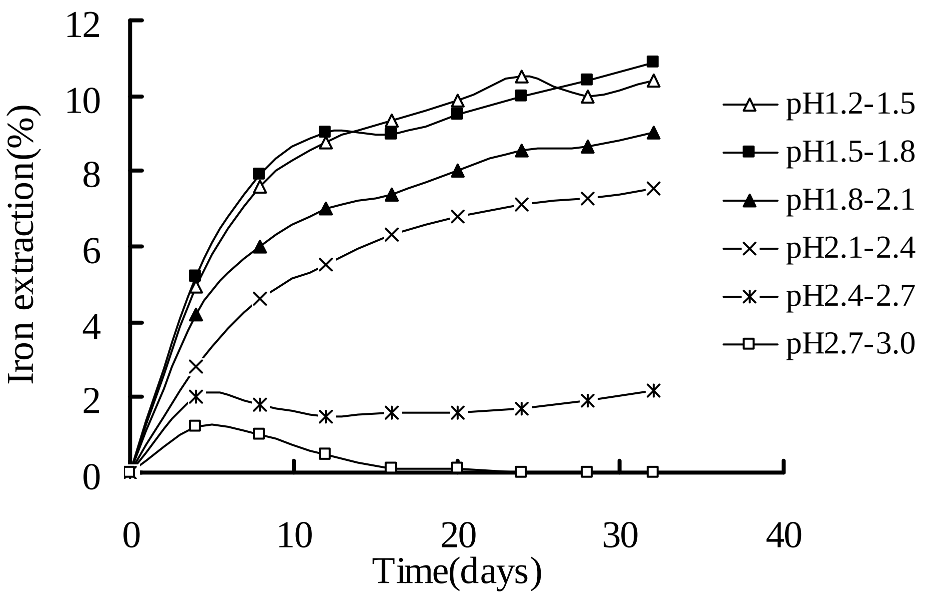

Fig.5 Effect of pH on iron extraction during the silver-catalyzed bioleaching experiment

When the value of pH was high, iron was also dissolved in high. When the value of pH was below 2.4, the iron extraction was very high. When the value of pH was above 2.4, the iron extraction was little. This suggests that ferric precipitation occurred during silver-catalyzed bioleaching experiment at higher pH. According to the copper extraction and iron extraction, the optimal pH is 1.50-1.80.

3.4 Influence of inoculum volume of the nutrient medium

The standard nutrient solution reported in the literature to grow Thiobacillus ferrooxidans and Thiobacillus thiooxidans, the so-called 9K+S medium, contains different mineral salts necessary for the metabolic process and Fe^{2+} or S as energy source to sustain bacterial growth. However, iron is frequently omitted in sulfide mineral bioleaching because the amount of iron sulfides is sufficient.

In practical situations, some of these salts are not required because some essential elements are present in the mineral matrix. Therefore, the examination of the inoculum volume of the nutrient medium in bioleaching processes may be important to reduce the cost. The experiments were tested at a different of inoculum volume of the nutrient medium (0vol%, 20vol%, 40vol%, 60vol%, 80vol% and 100vol%) during the bioleaching process.

The effect of inoculum volume of the nutrient medium on the copper extraction is shown in Fig.6.

When the inoculum volume increases, the copper extraction also increases. All the silver-catalyzed bioleaching experiments except that with inoculum volume of 0vol% had a similar copper extraction. They are 23.5%, 52.3%, 58.2%, 60.85%, 61.8% and 64.3% respectively. It shows that the low-grade copper ore used was unable to provide enough nutrient medium to maintain adequate bacterial activity. So, the optimal inoculum volume of the nutrient medium was thought to be 40vol%.

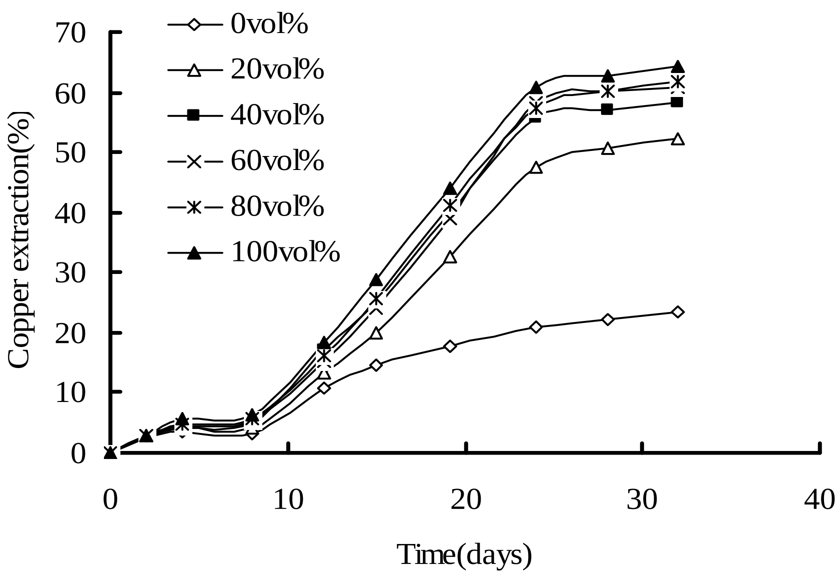

Fig.6 Effect of inoculum volume of the nutrient medium on copper extraction during the silver-catalyzed bioleaching experiment

CONCLUSION

(1) The optimal process parameters were: pulp density, 2.5 wt%; silver content, 10mg/L; pH, 1.50-1.80; inoculum volume of the nutrient medium, 40vol%.
(2) Addition of the silver could catalyze the process of bioleaching, and high silver concentrations would be harmful to the bacterial activity and the copper extraction.
(3) pH and inoculum volume of the nutrient medium had a marked influence on the copper extraction and iron extraction. The bioleaching of the low-grade copper ore requires a minimum amount of the nutrient medium to obtain the maximal efficiency.

Acknowledgments

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