

Impact of solvent extraction organics on adsorption and bioleaching of *A. ferrooxidans* and *L. ferriphilum*

Yu Hualong¹ and Liu Xiaorong¹

¹School of Materials Science and Engineering, Shanghai Institute of Technology, Shanghai, 201418 China.

E-mail: yuhualoong@hotmail.com

Abstract. Copper solvent extraction entrained and dissolved organics (SX organics) in the raffinate during SX operation can contaminated chalcopyrite ores and influence bioleaching efficiency by raffinate recycling. The adsorption and bioleaching of *A. ferrooxidans* and *L. ferriphilum* with contaminated ores were investigated. The results showed that, *A. ferrooxidans* and *L. ferriphilum* cells could adsorb quickly on minerals, the adsorption rate on contaminated ores were 83% and 60%, respectively, larger than on uncontaminated ores. However, in the bioleaching by the two kinds of acid bacteria, contaminated ores presented a lower bioleaching efficiency.

1. Introduction

Bioleaching-Solvent Extraction-Electrowinning technology (BL-SX-EW) for copper has been widely used due to its advantages of low costs and environmental friendly [1]. However, low efficiency is a key problem in bioleaching process. Many studies have shown that various factors greatly affect bacterial growth and the bioleaching process [2]. Among which, the adsorption of bacterial on minerals could be a more important one [3].

On the other hand, SX organics lost in the raffinate in forms of entrainment and dissolution, could contaminate bioleaching system through the recycling use of the raffinate [4]. Studies have shown that the LIX extraction reagent is harmful to the bacteria [5]. When exposed to different extraction compounds, the bacterial activity and leaching ability of acidophilic bacteria were different. *A. thiooxidans* and *A. ferrooxidans* were confirmed to be more sensitive than *S. thermosulfidooxidans* and *Alicyclobacillus spp* [6]. A biochemical mechanism was speculated for the inhibition effect by SX organics [7]. Most of the studies were from the view of bacteria growth and bioleaching efficiency. The organics could contaminated minerals and bacteria by means of adsorption, which could finally impact the leaching efficiency. Thus, we studied the adsorption of *A. ferrooxidans* and *L. ferriphilum* on the contaminated chalcopyrite ores by SX organics, and its following bioleaching process, which are of theoretical and practical significance.

2. Materials and methods

2.1. Materials

2.1.1. Minerals and extraction reagents. The low-grade chalcopyrite ore (0.2% Cu, 3.4% Fe, and 5.1% S) used in the experiments was provided by the Dexing Copper Group Company, Jiangxi, China. The



copper extraction reagent, LIX 984N, was obtained from the BASF Chemical Co., Ltd. (Shanghai, China). Commercial 260# kerosene was used as the diluent.

2.1.2. Bacteria and cultivation. Mackintosh (MAC) medium^[8] containing 0.132 g/L (NH₄)₂SO₄, 0.1 g/L KCl, 0.025 g/L MgCl₂•6H₂O, 0.027 g/L KH₂PO₄, and 0.147 g/L CaCl₂•2H₂O, pH 2.0 was used as the culture medium. The inorganic salts were analytical grade. *A. ferrooxidans* and *L. ferriphilum* (provided by the Biofilm Center, University of Duisburg-Essen) was adapted to 10% low-grade chalcopyrite ore in the MAC medium. The cultures were incubated in Erlenmeyer flasks at 30 °C with shaking at 180 r/min in a constant-temperature air-bath shaker (ZHWY-2102, Zhicheng Analytical Instrument Manufacturing Co., Ltd, Shanghai).

2.2. Methods

2.2.1. Solvent extraction. MAC medium was mixed with an isopycnic organic phase in an agitating tank. After stirring for 10 min at 400 r/min at room temperature, the MAC medium, which contaminated by SX organics, was separated by a funnel. Low-grade chalcopyrite ore (washed with 75% ethanol and rinsed with deionized water several times) was added to 100 mL of uncontaminated or contaminated MAC medium. The mixtures were shaken for 2 h in Erlenmeyer flasks in air-bath shakers at 30 °C and 180 r/min. The contaminated ore powders were filtered and air dried in a dust-free environment.

2.2.2. Microorganism adsorption. Microorganism adsorption on the minerals was investigated using the contaminated mineral, with inoculation of 10% (v/v) culture. A microscope was used to examine the bacterial cells. The adsorption rate was calculated as follows. Cells adsorbed on uncontaminated minerals were used as a control.

$$r_e = \frac{n_i - n_t}{n_i} \times 100\% \quad (1)$$

where r_e is the adsorption rate, and n_i and n_t are the initial number of cells and the number of cells at time t , respectively.

2.2.3. Bioleaching experiments. Bioleaching experiments were carried out in 250 mL erlenmeyer, containing 150 mL MAC medium and 15 g contaminated/uncontaminated minerals in a shaker at 200rpm, 30°C. Each medium were inoculated with 5% (v/v) of bacterial culture (5×10^7 cells/ml). Deionized water was supplemented for the evaporation losses.

3. Result and discussion

3.1. Adsorption of *A. ferrooxidans* and *L. ferriphilum* on chalcopyrite ores

Figure 1 reflected the adsorption of *A. ferrooxidans* and *L. ferriphilum* on low-grade chalcopyrite ores. As Figure 1a shown, the adsorption on contaminated low grade chalcopyrite ores by SX organics had an obvious improvement, the maximum rate was nearly 83%, double of that on uncontaminated ores. In Figure 1b, the adsorption behavior of *L. ferriphilum* presented a same trend as *A. ferrooxidans*. Cells of *L. ferriphilum* adsorbed fast on minerals in first 5 minutes and be stable after then. The adsorption capacity (60%) on contaminated ores was larger than on uncontaminated ores (45%).

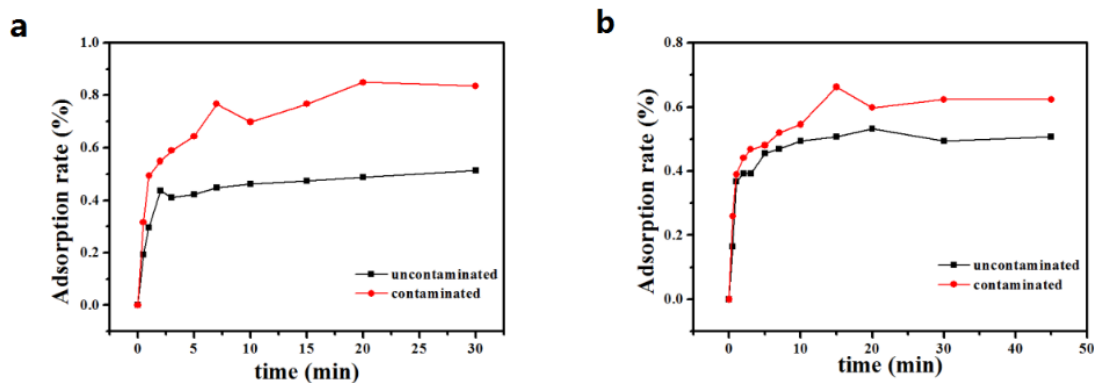


Figure 1. Adsorption of *A. ferrooxidans* (a) and *L. ferriphilum* (b) on contaminated/uncontaminated chalcopyrite ores

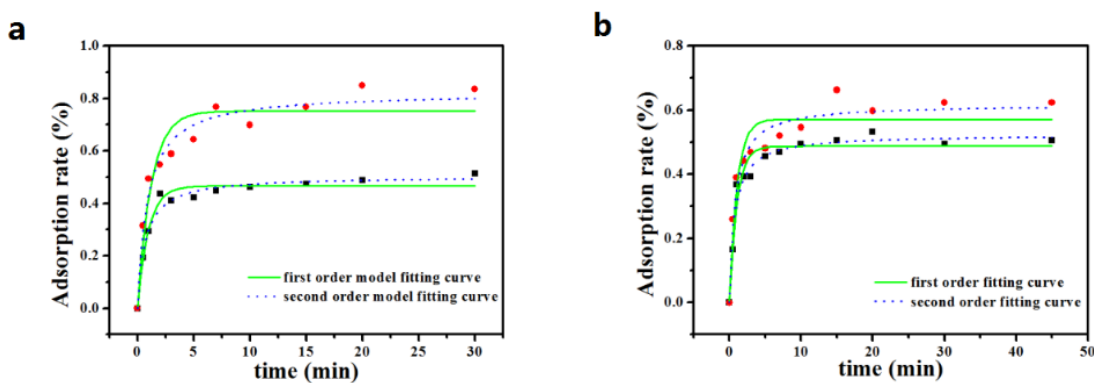


Figure 2. The fitting kinetic curves of the adsorption of *A. ferrooxidans* (a) and *L. ferriphilum* (b)

Table 1. Related parameters of fitting kinetic curves

		first order model			second order model		
		k1	r1	R2	k2	r2	R2
A.f	uncontaminated	1.036	0.466	0.969	2.942	0.504	0.976
	contaminated	0.810	0.751	0.911	1.377	0.822	0.966
L.f	uncontaminated	0.954	0.487	0.946	2.657	0.523	0.966
	contaminated	0.944	0.571	0.897	2.128	0.618	0.959

It could be inferred that the SX organics adsorbed on minerals surface promote the adsorption of *A. ferrooxidans* and *L. ferriphilum* cells. This could be explained by the hydrophobic interaction of the bacteria and minerals. SX organics contain the major compounds of LIX984N and sulfonated kerosene. LIX984N was made up by hydrophilic polar groups and lipophilic nonpolar group [9], which was a surfactant and could adsorb on minerals surface to enhance the hydrophobic. On the other hand, the cytomembrane of gram-positive bacteria contains some proteins and lipids, which were related to the adsorption on minerals [10]. Many studies have indicated that the bacterial trend to adsorb on the hydrophobicity surface [11], and it was certified again in Figure 1. The adsorption process were fitted by absorbing kinetic equations of the first order and second order in Figure 2. Comparing the data in Table 1, the second-order kinetic equation fitted better for the cells adsorption.

3.2. Bioleaching of *A. ferrooxidans* and *L. ferriphilum* on chalcopyrite ores

Since the adsorption of bacteria on mineral surface is a prerequisite for further interactions during bioleaching process. A higher adsorption rate of cells means a more intimate contact between them and will lead to a higher leaching efficiency. However, as shown in Figure 3, the bioleaching efficiency of contaminated and uncontaminated low-grade chalcopyrite ores by *A. ferrooxidans* and *L. ferriphilum*. It is obvious that the efficiency of contaminated minerals was smaller than that of the uncontaminated ores, the highest rate was 15% and 25% for *A. ferrooxidans*, 7.5% and 6.8% for *L. ferriphilum*. Higher cells adsorption does not result in higher bioleaching efficiency. SX organics improved the cells adsorption but inhibited the final leaching efficiency.

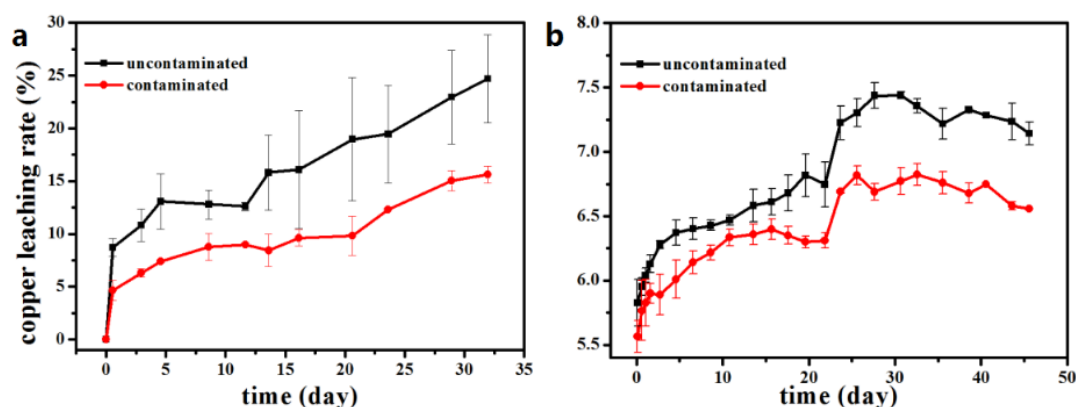


Figure 3. The bioleaching efficiency of chalcopyrite ores by *A. ferrooxidans* (a) , *L. ferriphilum* (b)

4. Conclusions

A. ferrooxidans and *L. ferriphilum* could adsorb quickly on minerals and the adsorption rate were 83% and 60% respectively on contaminated minerals, larger than on uncontaminated of 42% and 45%. The second-order kinetic equation fitted better for the adsorption.

The efficiency of contaminated minerals was smaller than that of the uncontaminated ores, the highest rate was 15% and 25% for *A. ferrooxidans*, 7.5% and 6.8% for *L. ferriphilum*.

Higher cell adsorption does not result in higher bioleaching efficiency. SX organics improved the cells adsorption but inhibited the final leaching efficiency.

Acknowledgments

Authors wishing to acknowledge the financial support of the National Nature Science Foundation of China (51474150).

References

- [1] Tan S N and Chen M 2012 Hydrometallurgy 120 94.
- [2] Devasia P and Natarajan K A 2010 Int J Miner Process 94 139.
- [3] Dong Y, Lin H, Xu X and Zhou S 2013 Hydrometallurgy 140 47.
- [4] Watling H R 2006 Hydrometallurgy 84 108.
- [5] Dopson M, Sundkvist J and Börje L E 2006 Hydrometallurgy 81 213.
- [6] Davis-Belmar C S I, Demergasso C and Rautenbach G 2012 Hydrometallurgy 130 139.
- [7] Liu X, Li H, Liu Y, Su C and Sand W 2015 Hydrometallurgy 157 213.
- [8] Mackintosh M E 1978 J. Gen. Microbiol 105 218.
- [9] Diao M, Tuan A H, Elena T, Stephen M and Anh V Nguyen 2015 Colloid Surface B 132 280.
- [10] Panda S, Parhi P K, Pradhan N, Mohapatra U B, Sukla L B and Park K H 2012 Hydrometallurgy 124 119.
- [11] Lu J and Dreisinger D 2013 Hydrometallurgy 137 17.