



# Catalytic effects of activated carbon and surfactants on bioleaching of cobalt ore



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## ABSTRACT

The effects of activated carbon and/or surfactants on the bioleaching behavior of cobalt ore have been investigated in this paper. It was demonstrated that activated carbon and surfactants (Tween-20 and Tween-80) can significantly promote the dissolution rate of carrollite, either individually or in combination when coupled with ZY101 bacteria strain. The cobalt leaching efficiency increased from 71.3% to 90.8% when 1.0 g/L activated carbon was added, and such an improvement was ascribed to the galvanic interaction between activated carbon and carrollite. In addition, the leaching efficiency of cobalt increased from 71.3% to 92.4% by 0.1 g/L Tween-20 or to 93.2% by 0.1 g/L Tween-80, by changing the surface condition of the mineral and accelerating the bio-oxidation of formed elemental sulfur. When both activated carbon and surfactant were added, the leaching efficiency of cobalt increased by more than 22%, and meanwhile the leaching time decreased by more than 30%. It is shown that the catalytic effect of the combined catalyst was much more significant than that when only using a single catalyst. A similar trend was observed in the case of elemental copper extraction during the bioleaching process.

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## 1. Introduction

Bioleaching is considered as one of the strategic and perfect processing technologies for the utilization of mineral resources, and extensive studies have been conducted to extend its application for metallic minerals. In the past several decades, bioleaching has been successfully applied in metallurgical industries, such as in copper, uranium, gold and cobalt extraction (Rohwerder et al., 2003; Zhou and Niu, 2005; Liu et al., 2008). There are some important advantages associated with bioleaching, such as low investment cost and energy consumption, with the attendant benefits to the environment (Zhang and Gu, 2007). However, research work has always been plagued by low recovery of metals and slow dissolution kinetics. Consequently, many efforts have been devoted to improve the bioleaching efficiency (for example, by combining with other additives to enhance the leaching process), especially for the sulfide minerals, which serve as an important source for base metals productions.

One of the prevailing strategies is the application of galvanic interaction. Some studies show that the addition of minerals with higher rest potential may promote the dissolution of minerals with lower rest potential, thus increasing the recovery of target metals (Liu et al., 2000; da Silva et al., 2003; Li et al., 2003). As an example, the effect of activated carbon on chalcopyrite bioleaching has been investigated by several authors (Nakazawa et al., 1998; Zhang and Gu, 2007; Liang et al., 2010), and they reported that the addition of activated carbon can accelerate the dissolution rate of chalcopyrite and increase the recovery of copper.

Further analysis suggested that the catalytic effect is attributed to the galvanic interactions between chalcopyrite and activated carbon (Nakazawa et al., 1998; Zhang and Gu, 2007; Liang et al., 2010).

Additionally, the effect of the addition of surfactants on the bioleaching of sulfide minerals has also been investigated (Lan et al., 2009; Sunil and Lala, 2012; Peng et al., 2012). In this sense, the results indicate that the addition of surfactants can alter the surface properties of sulfur particles formed on the mineral surface and reduce the interfacial tension between sulfur and aqueous sulfate solution. Hence, the attachment of bacteria to the sulfur formed thereon is promoted, thereby significantly enhancing the dissolution rate of minerals and the recovery rate of metals.

Nevertheless, despite the fact that significant progress has been achieved by the research on examining the enhancement of sulfide mineral bioleaching, most of the previous studies have focused on the copper sulfide minerals and the bioleaching of cobalt sulfide mineral has hardly been investigated. Therefore, the objective of this work is to investigate the effects of activated carbon and surfactants on carrollite bioleaching behavior. This study presents detailed information about the effect of activated carbon, surfactants, and the combination of activated carbon and surfactants on the leaching process, respectively, via the shake flask bioleaching process.

## 2. Materials and methods

### 2.1. Materials

The cobalt ore used in this study was provided by the Luanshya mine in Zambia, and its chemical analysis is shown in Table 1. Mineralogy

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**Table 1**  
Chemical analysis of the cobalt ore.

Element	Cu	Co	Fe	S	Ca	Mg	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Others
Content/wt.%	1.05	1.63	12.40	15.00	1.78	3.97	44.89	8.70	4.69	5.89

analysis indicates that the dominant sulfide minerals are carrollite (the cobalt-bearing mineral), chalcopyrite, bornite, chalcocite, covellite and pyrite. After fine grinding in ball mills, the particle size reached P80 of 38  $\mu\text{m}$ . The activated carbon powder used in this study was nutshell charcoal purchased from Shenyang Fifth Reagent Company. The particle size of the activated carbon was P65 of 75  $\mu\text{m}$ .

The ZY101 bacterial strain used in this study is a mixture of *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Leptospirillum ferrooxidans*. After adaptation, the bacterial strain could survive in an environment with 30 g/L cobalt ions. The bacteria strain was cultured in 9 K medium, which contained (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> 3.0 g/L, K<sub>2</sub>HPO<sub>4</sub> 0.1 g/L, KCl 0.5 g/L, MgSO<sub>4</sub>·7H<sub>2</sub>O 0.5 g/L, Ca(NO<sub>3</sub>)<sub>2</sub> 0.01 g/L, and FeSO<sub>4</sub>·7H<sub>2</sub>O 44.3 g/L.

## 2.2. Bioleaching experiment

First, 20 mL of ZY101 bacterial strain and 180 mL of 9 K medium were mixed in 500-mL Erlenmeyer flasks and incubated in a rotary shaker at 180 rpm with a constant temperature of 45 °C. After culturing for 36 h, the cell concentration and redox potentials of the liquid were about  $2.5 \times 10^8$  cells · mL<sup>-1</sup> and 650 mV (Hg/Hg<sub>2</sub>Cl<sub>2</sub>), respectively. Subsequently, 20 g of cobalt ore was added. The initial pH of the pulp was 1.5. Water loss by evaporation was compensated with the addition of sterilized distilled water, and the solution loss due to sampling was compensated with fresh sterilized medium.

The experimental scheme is shown in Table 2. Each test was carried out in triplicate so as to check the reproducibility. The operating conditions of Test 10 and Test 11 were determined based on the results of previous nine experiments, which will be discussed later.

The pH of the bioleaching solution was measured with a pH meter (pHS-25). The redox potential ( $E_h$ ) was measured with a Pt electrode by using a calomel electrode (Hg/Hg<sub>2</sub>Cl<sub>2</sub>) as a reference electrode. The concentrations of Co<sup>2+</sup>, Cu<sup>2+</sup>, and Fe<sup>2+</sup> in the solution were determined by nitroso R salt colorimetry, atomic absorption spectrophotometry and titration by the dichromate method, respectively.

## 2.3. Analysis of the mineral surface morphology and composition analyses

In the bioleaching test of pure carrollite (Cu 18.42%, Co 38.15%, S 40.20%), two carrollite samples were cut into 10 × 10 × 3 mm size, and the initial concentrations of Fe<sup>3+</sup> and the cell in the solution were 8.9 g/L and  $2.5 \times 10^8$  cells · mL<sup>-1</sup>, respectively. For comparison, one of the samples was in a special plexiglass container without lid. The container was covered by a sheet of membrane filter (pore size 1.0  $\mu\text{m}$ ),

**Table 2**  
Experimental conditions.

Test No.	Activated carbon/g/L	Tween-80/g/L	Tween-20/g/L
1	–	–	–
2	0.5	–	–
3	1.0	–	–
4	1.5	–	–
5	2.0	–	–
6	–	0.25	–
7	–	0.10	–
8	–	–	0.25
9	–	–	0.10
10	1.0	0.10	–
11	1.0	–	0.10

which can inhibit the occurring of the contact between bacteria and mineral.

The morphology of the mineral samples was examined by a scanning electron microscope (SSX-550, Shimadzu Corporation, Japan). Composition of the mineral surface after leaching test was determined by the X-ray photoelectron spectroscopy (XPS) of mineral samples detected by a Surface Analysis System (ESCALAB250, Thermo VG, USA).

## 2.4. Effect of activated carbon and surfactants on the bacterial growth

The initial cell concentration in liquid is about  $2.5 \times 10^8$  cells · mL<sup>-1</sup>, and 1.0 and 2.0 g/L activated carbon were added in the liquids, respectively. The concentration of cell was measured by direct microscopic count.

10 mL of ZY101 bacterial strain and 190 mL of 9 K medium were mixed in Erlenmeyer flasks. Then, Tween-20 and Tween-80 with different concentrations were added, respectively. Erlenmeyer flasks were shaken in a rotary shaker at 180 rpm with a constant temperature of 45 °C. The concentrations of cell and Fe<sup>2+</sup> were measured by direct microscopic count and potassium dichromate titration.

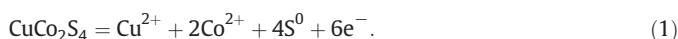
## 3. Results and discussion

### 3.1. Effect of activated carbon on the bioleaching behavior

Fig. 1 presents the effect of added activated carbon on the redox potential ( $E_h$ ), pH, concentration of ferrous ion and leaching efficiency of cobalt during the cobalt ore bioleaching. The leaching efficiencies of Co and Cu after leaching for 18 d are listed in Table 3. The results indicate that the addition of activated carbon exhibited a remarkable catalytic effect on the extraction of cobalt and copper from the mineral. Typically, when the optimum concentration of 1.0 g/L activated carbon was employed, the leaching efficiency of cobalt increased from 71.3% to 90.8%, and the leaching efficiency of copper increased from 56.2% to 67.6%.

To investigate the effect of the contact between cobalt ore and activated carbon on the bioleaching behavior, a special plexiglass container without lid was prepared. The container, with the size of 20 × 20 × 20 mm, was covered by a sheet of membrane filter (pore size 1.0  $\mu\text{m}$ ). 0.2 g activated carbon was put into this container. A bioleaching experiment was carried out by immersing the container in the leaching solution containing cobalt ore. In such a case, the contact between activated carbon and cobalt ore was avoided. The results are shown in Fig. 2. Please note that Fig. 2 also includes the bioleaching result of the mixture of cobalt ore and activated carbon. It is shown that, without the contact between activated carbon and cobalt ore, the enhancing effect of activated carbon was not observed.

Activated carbon is electrically conductive, and it is suggested that activated carbon may form a galvanic couple when contacting with carrollite. Activated carbon is thermodynamically more stable than sulfide minerals (Nakazawa et al., 1998). Therefore, when activated carbon is in contact with carrollite, activated carbon acts as the cathode, and carrollite serves as the anode due to its relatively lower rest potential (Nakazawa et al., 1998; Zhang and Gu, 2007; Liang et al., 2010). During the leaching process, the dissolution kinetics and leaching efficiency of cobalt can be improved by such a galvanic interaction. The anodic dissolution reaction of carrollite can be expressed as Eq. (1):



The cathodic reaction on the surface of activated carbon can be described as follows:



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