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Reductive leaching of manganese from manganese dioxide ores by bacterial-catalyzed two-ores method

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ABSTRACT

The two-ores method (TOM) has been well established for reductive leaching of MnO_2 under high reaction temperature and oxygen pressure. In this work, the TOM was carried out under ambient condition via biological catalysis. The results showed that the bacterial catalysis (BC) evidently improved the performance of TOM, especially the mixed culture consisting of *Acidithiobacillus thiooxidans* (*A.t*) and *Leptospirillum ferriphilum* (*L.f*) achieved an increase of 39% from 60% to 99% in Mn extraction. The leaching period was greatly shortened from 96 to 24 h for 97% of Mn release by the mixed culture under optimum conditions of 12 g/L pyrite concentration, 100 g/L pyrolusite content, 40 °C of temperature and 180 rpm of shaking speed. 96% of Mn dissolution was still obtained in a 30 L reactor within 24 h. The diffusion controlled model described well dissolution of MnO_2 ore by the BC-TOM. The bioleaching liquor was competent for preparing high purity electrolytic manganese metal.

1. Introduction

Manganese is a strategic metallic element with broad applications in industry, breed, agriculture and so on (Sahoo et al., 2001). Manganese consumption is largely related to growing production of raw steel and upgrading ferroalloys, and other applications including production of dry-cell batteries, plant fertilizer components, dyes, medicines, animal feed, and brick colorant (Hagelstein, 2009). The world annual consumption of manganese is above 1.30 million tons and it is destined to increase in the future (El Hazek et al., 2006). Since 2000, China has become the largest producer, consumer and exporter of electrolytic manganese metal (EMM) in the world. EMM production capacity reached 2.11 million tons and the actual production reached 1.31 million tons in 2009 in China (Duan et al., 2011). The acid leaching–purification–electrolysis process is used to prepare EMM using rhodochrosite ($MnCO_3$) as raw material (Duan et al., 2011). With depletion of rhodochrosite, the most common pyrolusite (MnO_2) replacing $MnCO_3$ to prepare EMM will be inevitable (Zhang and Cheng, 2007).

When pyrolusite is used for EMM production, a reduction process must be taken to convert the MnO_2 to MnO because MnO_2 cannot react directly with H_2SO_4 (Sun et al., 2013). The conventional reduction technique is high-temperature roasting by carbon at about 700–900 °C, which is characteristic of complex system, great dust emission, high investment and operating cost (Paixao et al., 1995). In recent years, a number of works have concentrated on the chemical reductive acid leaching of manganese from pyrolusite using various strong acid solutions (Zhang and Cheng, 2007). The reducing agents include pyrite, ferrous, sulfur dioxide, hydrogen peroxide, thiosulfate, sawdust, glucose, sucrose, lactose, glycerine, oxalic acid, citric acid, tartaric acid, formic acid, triethanolamine and so on (Zhang and Cheng, 2007).

Among the chemical reductive processes, reduction leaching of MnO_2 in the presence of pyrite in acidic solutions is well established, which is known as two-ores method (TOM) (Nayak et al., 1999). The TOM achieves a highly efficient release of Mn from MnO_2 ore through reductive acid leaching by the Fe^{2+} in pyrite (Thomas and Whalley, 1958). The high availability of cheap pyrite and the good reactivity of Fe^{2+} bring the TOM a much promising future (Bafghi et al., 2008). However, high work temperature (100–200 °C) and oxygen pressure (2–10 atm), which are necessary to generate the active Fe^{2+}, endow the TOM with high energy consumption, high operational cost and strict equipment requirement, limiting its commercial applications (Thomas and Whalley, 1958; Vracar and Cerovic, 2000).

Bacterial-catalysis reductive leaching is another strategy to extract Mn from MnO_2 under ambient conditions, displaying a low energy consumption and easy equipment requirement (Zhang and Cheng, 2007). In general, the heterotrophic microorganisms are used to release Mn from MnO_2 ore in the presence of organic carbon and energy sources as electron donors (Lee et al., 2001). Mn release of 95–100% was obtained from manganiferous minerals by heterotrophic mixed culture under aerobic conditions in 36–48 h of treatment using molasses as energy source (Veglio et al., 1997). About 97% Cu, 98% Ni, 86% Co, 91% Mn were dissolved from Indian Ocean manganese nodules by *Aspergillus niger* under aerobic conditions in 30 days using sucrose as energy source

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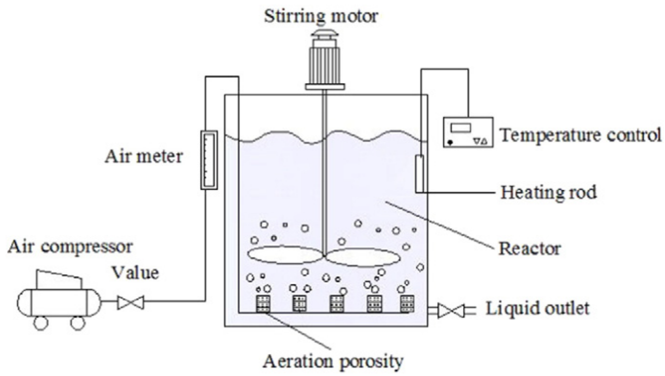

Fig. 1. Schematic diagram of 30 L reactor for bacteria-catalyzed TOM.

(Mehta et al., 2010). However, the heterotrophic bio-reduction leaching is very costly due to the expensive organic energy sources. In contrast, the autotrophic bioleaching greatly reduces the leaching cost using cheap sulfur and pyrite as electron donor, in which bacterial oxidation of pyrite and sulfur produces ferrous sulfate and sulfuric acid to reduce Mn^{4+} to Mn^{2+} (Mehta et al., 2003; Johnson, 2013). However, a long leaching period of 30 60 days was still required.

In this work, bacterial catalysis TOM (BC-TOM) was developed for reductive release of Mn from MnO_2 by the autotrophic bacteria using pyrite as electron donor under aerobic condition. The BC-TOM was carried out under ambient conditions of room temperature and ordinary pressure to meet the need of green chemistry. The objectives of the present study were to compare the leaching process and extraction efficiency of the TOM catalyzed by different autotrophic cells, to optimize the leaching conditions of BC-TOM including pyrite content, pyrolusite concentration, reaction temperature and shaking speed to shorten the leaching period, and to assess the feasibility of making EMM using the bioleaching liquor as raw material.

2. 2. Materials and methods

2.1. Ore materials and component analysis

Pyrolusite (MnO_2) with a particle size of 70–80 μm was supplied by an electrolytic manganese factory of Hunan Province, South China. The pyrolusite was digested with HF–HNO_3–HCl mixed acid digestion method (USEPA, 1995). The concentration of Mn in pyrolusite was determined as 155 g/kg by atomic absorption spectrophotometer (AAS) method. The elemental components of pyrolusite and pyrite were measured by X-ray Fluorescence (XRF) spectroscopy. The pyrolusite ore contained 25.4% MnO_2, 6.3% Fe_2O_3, 64.4% SiO_2 and 2.9% CaO in weight. The pyrite (FeS_2) from Tongling Silver Minerals Co., LTD, Anhui province, contained 57.6% SO_3, 30.7% Fe_2O_3, 5.7% SiO_2, 2.3% Al_2O_3, 0.8% CaO, 0.6% MgO, 0.4% CuO and 0.3% K_2O in weight.

2.2. Microorganisms and inoculums

The sulfur—oxidizing bacterium *Acidithiobacillus thiooxidans* (*A.t*) and the ferrous—oxidizing bacterium *Leptospirillum ferriphilum* (*L.f*) were used as biological catalyst to improve the performance of TOM. Both of them were adapted for more than one year in various solutions containing high concentrations of Mn^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+} in a single metal or a mixed form with a total concentration ranging from 2.5 to 10.0 g/L. The detailed procedures about their identification, culture, inoculums were available in the previous papers (Xin et al., 2009; Wang et al., 2015). Elemental sulfur and $FeSO_4$ were used as energy sources to grow the *A.t* and *L.f* at 30 °C for 3–7 days for strain preservation and inoculums, respectively. When a concentration of approximately 7.5×10^9 cells/ml in the seed media was reached, both of them were utilized as inoculums of biocatalyst.

2.3. Performance of TOM catalyzed by different bacteria

The bioleaching media were prepared according to the formula: $(NH_4)_2SO_4$, 1.0 g; KNO_3, 1.0 g; KH_2PO_4, 1.0 g; $MgSO_4 \cdot 7H_2O$, 1.0 g; $CaCl_2$, 0.25 g; $FeSO_4 \cdot 7H_2O$, 0.18 g; distilled water, 1000 mL. The pH of the media was adjusted to about 1.0 using 1.0 M H_2SO_4 solution. And then, the bioleaching media was transferred into 250 mL flasks at a portion of 100 mL per flask, followed by supplementing both 100 g/L pyrolusite and 12 g/L pyrite (purity >91%) into the flask to conduct the TOM. The bioleaching media containing both pyrite and pyrolusite known as two-ores were inoculated with *A.t* only (10%, v/v), *L.f* only (10%, v/v) or the mixed culture (5% for each, v/v), respectively. Then, the inoculated bioleaching media were incubated at a shaker (30 °C, 120 rpm) to initiate the BC-TOM. During bioleaching, dissolved concentration of Mn, cell density, pH value, oxidation–reduction potential (ORP), total iron concentration, Fe^{2+} and Fe^{3+} concentration were monitored. The abiotic leaching process as control was run using sterile water replacing cell inoculums. All experiments, including the sterile controls, were conducted in triplicates.

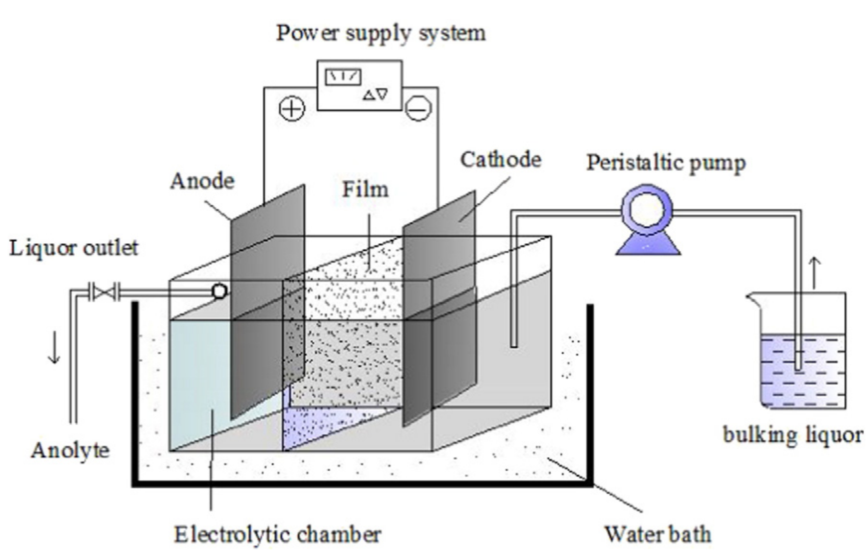

Fig. 2. Sketch map of electrolysis equipment for preparation of EMM.