Technical note

High-rate precipitation of iron as jarosite by using a combination process of electrolytic reduction and biological oxidation

Yongwei Song, Min Wang, Jianru Liang, Lixiang Zhou *

Department of Environmental Engineering, College of Resources and Environmental Sciences, Nanjing Agricultural University, Nanjing 210095, China

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ABSTRACT

Removal of iron from acidic, ferrous iron- and sulfate-rich solutions as jarosite through biological iron oxidation can avoid the formation of ferric hydroxide precipitates during lime neutralization, and has been proven as an alternative approach for the treatment of acid mine drainage (AMD). To promote the precipitation of iron as jarosite, the ferric iron remaining in solution was reduced to ferrous iron by electrolysis, and subsequently subject to biological oxidation in this study. The optimum electrolysis voltage and time were selected at 5 V and 5 h, respectively. Under this electrolysis conditions, 4.04 g L^{-1} of Fe^{3+} was reduced to Fe^{2+} after the electrolysis of solution containing 6.17 g L^{-1} of Fe^{3+}. The introduction of *Acidithiobacillus ferrooxidans* into Fe^{2+}-containing solution resulted in an iron removal efficiency of 42% within 120 h. Then the filtrate was subject to reduction/oxidation again, and the efficiency of iron removal accumulated to 71%. The addition of jarosite seed can significantly facilitate the precipitation of iron. In the presence of 20 g L^{-1} of jarosite seed, the efficiency of total iron removal in the solution drastically increased to 93% after two cycles of reduction/oxidation, correspondingly the concentration of soluble iron remarkably decreased from 5.88 to 0.44 g L^{-1}. Obviously, a combined process of electrolytic reduction and subsequent biological oxidation can efficiently realize the precipitation of soluble iron as jarosite.

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1. Introduction

Characterized by low pH as well as high concentrations of heavy metals, Fe and SO_4^{2-}, acid mine drainage (AMD) is one of the most serious forms of water pollution in coal- and metal-mining districts, and has thus raised widespread concern in terms of minimizing its impact on receiving streams, rivers and the wider environment (Akcil and Koldas, 2006; Cravotta and Trahan, 1999; España et al., 2005; Peppas et al., 2000; Powell, 1988; Sahoo et al., 2010). By far, lime neutralization is the most ubiquitously used approach in the mining industry (Aubé and Zinck, 2003; Herrera et al., 2007; Kuyucak, 2001; Murdock et al., 1994). Since ferric iron precipitates at a much lower pH than ferrous iron, the oxidation of ferrous iron prior to lime neutralization substantially reduces the consumption of lime (Brierley, 1990).

It is well known that abiotic oxidation of ferrous iron is kinetically inhibited below pH 4.5, while acidophilic bacteria such as *Acidithiobacillus ferrooxidans* can accelerate the oxidation rate by 10^5–10^6 times (Kirby et al., 1999). Moreover, during biological oxidation of ferrous iron in acidic environment, the resulting ferric iron tends to precipitate as ferric hydroxysulfate such as schwertmannite or jarosite, depending upon pH, retention time, the presence of dissolved carbon, concentrations of Fe^{3+} and monovalent cations (Gramp et al., 2008; Liao et al., 2009; Wang et al., 2006). It has well been documented in recent decades that these secondary Fe hydroxysulfate in AMD or sediments impacted by AMD are capable of scavenging toxic elements through sorption or coprecipitation (Bigham et al., 1990, 1996; Carlson et al., 2002; Jönsson et al., 2006; Liao et al., 2009, 2011; Yu et al., 1999). Furthermore, iron hydroxysulfate precipitates have good settling characteristics in comparison to other ferric hydroxide precipitates, and can be recovered in a technically feasible and environmentally friendly manner (Asokan et al., 2006; Mymrin et al., 2005). However, only a portion of soluble iron is precipitated during ferrous oxidation, and a larger amount of ferric iron remains in solution after the formation of schwertmannite precipitates compared to jarosite. Therefore, the precipitation of iron as jarosite is favorable for the removal of soluble iron, and consequently a combined process involving biological iron oxidation and jarosite precipitation is preferred for the treatment of AMD. In addition to converting all incoming Fe^{2+} into readily precipitable Fe^{3+}, it can also reduce the concentrations of dissolved iron and toxic elements.

As a chemoautotrophic bacterium, *A. ferrooxidans* obtains the energy for growth from the oxidation of ferrous iron and reductive sulfur compounds (Jensen and Webb, 1995). However, the efficiency of energy utilization was found to be only 3.2%, most of the energy was released to the system (Temple and Colmer, 1951). Therefore, the possibility of a mechanism for utilizing the energy for the hydrolysis of ferric iron as jarosite should not be excluded. This assumption is supported by the fact that the formation of jarosite through bacterial oxidation of ferrous iron is much faster than from the direct hydrolysis of ferric iron at ambient temperatures, owing to the total Gibbs free energy of the biological

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* Corresponding author. Tel./fax: +86 25 84395160.
  E-mail address: lxzhou@njau.edu.cn (L. Zhou).

system being more negative (Baron and Palmer, 1996; Parker and Khodakovskii, 1995; Wang et al., 2007). In brief, bacterial oxidation of ferrous iron by *A. ferrooxidans* in this system will release energy ($\Delta rG°_{298} = -44.32$ kJ mol^{-1}), which can be used by subsequent reaction of the hydrolysis of ferric iron into jarosite ($\Delta rG°_{298} = -22.54$ kJ mol^{-1}) (Baron and Palmer, 1996; Majzlan et al., 2004). Therefore, the total reaction of bio-oxidation of ferrous iron and resulting ferric iron hydrolysis into jarosite is of much lower Gibbs free energy with -66.86 kJ mol^{-1}. Nevertheless, after the complete oxidation of ferrous to ferric iron and the gradual conversion of ferric iron into jarosite, the value of the Gibbs free energy of the system will decrease, coupled with the decrease in concentration of reactants, and hence the rate of jarosite formation decreases as it approaches equilibrium, although it is still spontaneous.

The purposes of this study were to (1) investigate if a coupling process of bio-oxidation of ferrous iron from electrolytic reduction of remaining ferric iron and subsequent resulting ferric iron hydrolysis facilitates the formation of jarosite and the removal of total iron in the solution; and (2) explore the role of already-formed jarosite precipitation as crystal seeding in improving new jarosite formation.

2. Materials and methods

2.1. Preparation of A. ferrooxidans cell suspensions

A. ferrooxidans LX5 (CGMCC No. 0727) obtained from China General Microbiological Culture Collection Center (CGMCC) was grown in 9 K medium developed by Silverman and Lundgren (1959), containing the following analytical grade salts: 3.00 g of $(NH_4)_2SO_4$, 0.10 g of KCl, 0.50 g of K_2HPO_4, 0.50 g of $MgSO_4 \cdot 7H_2O$, 0.01 g of $Ca(NO_3)_2$, and 44.48 g of $FeSO_4 \cdot 7H_2O$ in 1 L of deionized water, adjusted to pH 2.5 with H_2SO_4. The $FeSO_4$ solution was filtered sterilized and subsequently added to the remaining autoclaved (at 121 °C for 15 min) medium components. Cultures of *A. ferrooxidans* were incubated in 500-mL Erlenmeyer flasks, each containing 225 mL of 9 K medium and 10% (v/v) inoculum at 28 °C on a rotary shaker at 180 rpm, with cells harvested during the late logarithmic growth phase (around 72 h after inoculation). The cultures were initially filtered through a Whatman No.4 filter paper to remove the jarosite precipitates, with the filtrates then centrifuged at 10 000 ×g for 10 min at 4 °C to settle the bacterial cells. After being washed twice with dilute sulfuric acid solution (pH 1.5), the cells were re-suspended in a dilute sulfuric acid solution of pH 2.5, with *A. ferrooxidans* cell numbers determined as approximately 3×10^8 cells mL^{-1} by using a double-layer plate method (Wang and Zhou, 2005).

2.2. Selection of the optimum electrolysis voltage and time

There was about 6.10 g L^{-1} of Fe^{3+} that remained in the filtrates mentioned above. After the separation of *A. ferrooxidans* cells, the culture filtrates were transferred to an electrolytic cell which was composed of two graphite electrodes and electronic circuitry, and electrolyzed with gentle magnetic stirring. In order to determine the appropriate conditions for the electrochemical reduction of Fe^{3+}, the electrolysis voltage was set at 5, 10, 15, and 20 V, supplied by a direct current (DC) power supplier. Bearing in mind that Fe^{3+} concentration in the bacteria culture filtrates was 6.10 g L^{-1} and the process of reduction/oxidation/precipitation may require repeating several times, the concentration of Fe^{3+} in the solution subjected to electrolysis reduction was set at 6.50 and 3.10 g L^{-1}. Samples were collected at 1 h intervals during the electrolysis to analyze the concentration of Fe^{3+} and hence the reduction rate of Fe^{3+}, and thus to obtain the appropriate electrolytic conditions.

2.3. Reduction of soluble ferric iron by electrolysis and re-oxidation of the resultant ferrous iron by A. ferrooxidans

The solution with 6.10 g L^{-1} of Fe^{3+} was electrolyzed with a constant voltage of 5 V for 5 h, the optimum electrolysis voltage and

time combination obtained from the trial mentioned above. After the reduction of ferric to ferrous iron, the solution was adjusted to pH 2.3 with NaOH (about 8 mmol L^{-1}), then inoculated with *A. ferrooxidans*, and cultured on a rotary shaker at 180 rpm and 28 °C. Samples were taken periodically throughout the experiments and analyzed for pH, Fe^{2+} and total iron. When the reaction of jarosite formation reached equilibrium, the solution was filtered, electrolyzed and reoxidized. To investigate the effect of already-formed jarosite as crystal seed on improving the removal of soluble iron through the formation of new jarosite, experiments were conducted both with and without the addition of 20 g L^{-1} of already-formed jarosite to the system.

It is worth noting that according to our previous study, both initial concentrations of iron and monovalent cations jointly determine the formation of biogenic iron hydroxysulfate precipitates in acidic sulfate-rich environments and that K-jarosite instead of other mineral types is found to be the predominant mineral phase for the iron precipitation formed in this study (Bai et al., 2012).
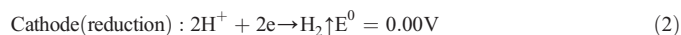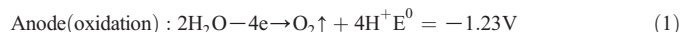
2.4. Analytical procedures

The pH value was monitored using a pHS-3C model digital pH-meter calibrated with pH 6.86 and 4.00 standard buffers. Fe^{2+} and total iron were measured by a colorimetric procedure using 1, 10-phenanthroline as described in standard methods (APHA, 1995). Fe^{3+} was taken as the difference between total iron and Fe^{2+}.

3. Results and discussion

3.1. Reduction of soluble ferric iron

As the current flows through the solutions containing Fe^{3+}, Fe^{3+} was constantly reduced to Fe^{2+}, which could be visually observed by changes of solution color from red brown to yellow green. Furthermore, water molecules were split into their constituent atoms during electrolysis. Oxygen gas was produced at one electrode and hydrogen gas at the other. The reactions were listed as follows:

$$\text{Anode(oxidation)} : 2H_2O - 4e \rightarrow O_2\uparrow + 4H^+ \quad E^0 = -1.23V \tag{1}$$

$$\text{Cathode(reduction)} : 2H^+ + 2e \rightarrow H_2\uparrow \quad E^0 = 0.00V \tag{2}$$

$$Fe^{3+} + e \rightarrow Fe^{2+} \quad E^0 = 0.77V. \tag{3}$$

As shown in Fig. 1, when the potential was applied, about 61.5% of Fe^{3+} was reduced to Fe^{2+}, as the concentration of Fe^{3+} in the solution decreased from 6.50 g L^{-1} to around 2.50 g L^{-1} at 5 or 15 V, and from 3.10 g L^{-1} to around 1.20 g L^{-1} at 10 or 20 V within 5 h, with no significant reduction of Fe^{3+} occurring thereafter. It should be highlighted that the electrolysis of water would result in a decrease of the solution volume, and thus the concentration of iron was converted and appeared according to the original solution volume. The higher the voltage used, the more the side-reactions (namely, the electrolysis of water and corrosion of electrodes) occurred.

Therefore, due to the electrolysis voltage higher than 5 V having no significant role in improving the rate of Fe^{3+} reduction and minimizing the side-reactions, the optimum electrolysis voltage and time were chosen at 5 V and 5 h, respectively, which would result in a reduction rate of approximately 60% or above in the presence of around 6.50 or 3.00 g L^{-1} of Fe^{3+}.

3.2. Reoxidation of the resultant ferrous iron in the absence of jarosite seed by A. ferrooxidans

After the initial 6.17 g L^{-1} of Fe^{3+} in the solution was electrolyzed at 5 V for 5 h, there would be 4.04 g L^{-1} of Fe^{2+} and 2.13 g L^{-1} of Fe^{3+} existed in the solution, indicating that about two thirds of the Fe^{3+} have been reduced to Fe^{2+}, as the beginning status shown in Fig. 2c. The introduction