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Characterization of the dissolution of tooeleite under *Acidithiobacillus ferrooxidans* relevant to mineral trap for arsenic removal

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ABSTRACT

The mineral tooeleite ($Fe_6(AsO_3)_4SO_4(OH)_4{\cdot}4H_2O$) is a secondary mineral containing-As(III) in acid mine drainage, and is proposed as a candidate for arsenic immobilization technology. The dissolution interaction of tooeleite with *Acidithiobacillus ferrooxidans* was investigated by batch experiments. The arsenic released from tooeleite decreases with pH increase due to the adsorption of arsenic on iron hydroxide. The amount of arsenic released from tooeleite at pH 2 is increased by 3.2 times as compared to the dissolution under only culture medium, which reaches 345 mg/L. The bacterial activity has a strong effect on the arsenic amount released from tooeleite. The incongruent dissolution was observed for tooeleite when pH is >3. The infrared spectroscopy and XRD both identified the alteration product of tooeleite as jarosite. This information is useful for immobilizing arsenic and is proposed as a suitable mechanism for trapping arsenic.

Keywords: Arsenic remediation; Arsenic release; Arsenic dissolution; Tooeleite; Jarosite

1. Introduction

Tooeleite ($Fe_6(AsO_3)_4SO_4(OH)_4{\cdot}4H_2O$) is a ferric arsenite-sulfate mineral in acid mine drainage (AMD) [1]. The mineral was first discovered at the US. Mine, Tooele Country, Utah in 1991 by Cesbron and Williams [2]. It was formed in the waste dumps from primary granular pyrite and arsenopyrite minerals. In view of the high arsenic(III) content in its mineral formula and its stable occurrence in the natural regolith, tooeleite is proposed as arsenic mineral storage for remediation of metallurgical waste water [1,3–5].

Acidithiobacillus ferrooxidans is a common autotrophic bacteria in AMD, which can catalyze the oxidation of Fe(II) into Fe(III) and enhance the formation of some typical secondary arsenic-containing minerals in AMD, such as As-schwertmannite and scorodite [6,7]. The field AMD and laboratory studies have indicated successively that *A. ferrooxidans* are involved into the formation of tooeleite due to the rapid oxidization of Fe(II), but not As(III) [7,8]. It has been documented that *A. ferrooxidans* cannot oxidize

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arsenite to arsenate directly [9], but arsenite can indirectly be oxidized by ferric iron or through autoxidation during arsenopyrite (FeAsS) oxidization [10]. However, no dissolution studies of tooeleite with ferrooxidans have been undertaken, although this information is important for removal of arsenic and stability of tooeleite under the surrounding environmental conditions when using it as mineral trap in water treatment. The aim of this paper is to report the dissolution characteristics of tooeleite with *A. ferrooxidans* related to arsenic release and the alteration product under abiotic and biotic conditions.

2. Materials and methods

2.1. Mineral synthesis

The mineral tooeleite was synthesized based on the previous report [1]. Mix 1 L acidic 0.1335 mol/L As(III) solution (adjust pH 1.3 by 1 mol/L H_2SO_4) with 1 L equivalent molar concentration Fe(III) solution in constant temperature double layer glass reaction kettle at 95˚C, the pH of mixed solution was adjusted to pH 2 by 1 mol/L NaOH using peristaltic pump at 5 mL/min flow rate. The suspension solution was aged and agitated at 50 rpm under 95˚C for 2 h, and then filtered by 0.25 μm membrane. The precipitate was washed by distilled water and dried at 80˚C for one day.

2.2. Bacteria culture

A. ferrooxidans was separated from the local AMD of the Songpan area of Sichuan province, China. These bacteria was developed in a 9 K medium (KCl 0.1 g/L, $(NH_4)_2SO_4$ 3.0 g/L, K_2HPO_4 0.5 g/L, $MgSO_4{\cdot}7H_2O$ 0.5 g/L, $Ca(NO_3)_2$ 0.01 g/L, $FeSO_4{\cdot}7H_2O$ 0.01 g/L), in which ferrous ion is the energy source. The pH of the medium was adjusted to 2.0 by diluted sulfuric acid. In order to maintain the good growth of *A. ferrooxidans* with tooeleite and separate from the AMD environment, 2.5 g tooeleite was taken into 200 mL bacterial culture for domesticating the bacteria. These bacteria in suspension were incubated at 30˚C and 240 rpm for 10 d. The bacteria were referred to incorporate *A. ferrooxidan* with tooeleite. They were repeatedly inoculated for 3 d when they grow perfectly based on the observation of solution color, and then added equivalent 2.5 g tooeleite for the later dissolution experiment. For biotic and abiotic comparison, the equivalent tooeleite sample was also added to the 9 K medium without a bacterial culture. These suspension solutions were continuously stirred at 240 rpm and 30˚C for 30 d. Three parallel experiments for abiotic and biotic dissolution were done. The experimental data were averaged and taken as the final results. The cultures were sampled periodically, filtered through 0.25 μm syringe filter and analyzed for As using Inductively Coupled Plasma Atomic Emission Spectroscopy. The residual product after abiotic and biotic dissolution were dried in 80˚C for 24 h and used for infrared spectroscopic analysis.

2.3. Methods

The infrared spectra of two pellets were made by mixing KBr with the residual product of abiotic and biotic dissolution and were collected using a Nicolet Nexus 870 FTIR spectrometer. The mass ratio of KBr and samples is 1:200. The spectra ranging from 400 to 4,000 cm^{-1} were obtained by the coaddition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. The spectroscopic band component analysis was undertaken using the Jandel "Peakfit" (Erkrath, Germany) software package after performing baseline correction using the spectra package GRAMS (Galactic Industries Corporation, NH, USA). The band fitting was done using a Lorentzian–Gaussian cross product function with the minimum number of component bands used for the fitting process. The Lorentzian–Gaussian ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of R^2 greater than 0.995.

X-ray diffraction patterns of tooeleite and its dissolution products were collected using a PANalytical X'Pert PRO X-ray diffractometer (radius: 240.0 mm). Incident X-ray radiation was produced from a line focused PW3373/10 Cu X-ray tube, operating at 40 kV and 40 mA with Cu Kα radiation of 1.540596 Å. The scan step size and time per step is 0.033423˚ and 10.16 s, respectively. The continuous scan was run. The SEM image of secondary mineral was obtained by field emission scanning electron microscopy (Zeiss Supra 55).

2.4. Batch experiment of solubility

In order to understand the dissolution of tooeleite comprehensively, this study also carried out the arsenic release of tooeleite under pure water and different initial pH values (2–10). It is noted that *A. ferrooxidans* cannot survive under pH > 4. All experiments were performed in duplicate, and the mean values were taken. These are useful for the solubility investigation of tooeleite under wide pH environmental conditions.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the synthetic tooeleite has well-developed crystallinity, which is in excellent agreement with the published standard pattern after comparison with the PDF 44-1468 (tooeleite). After 30 d of dissolution, the secondary jarosite, which is a common hydrous sulfate of potassium and iron mineral with a chemical formula of $KFe_3^{3+}(OH)_6(SO_4)_2$ in AMD, precipitates in both samples with and without bacterial culture. The XRD result shows that the most intense basal reflections (0 2 0), (2 0 0), and (0 6 1) of tooeleite decrease in intensity due to dissolution of tooeleite. The intensity of dissolved tooeleite with *A. ferrooxidans* is less than without bacteria, which reflects the bacteria can promote the dissolution of tooeleite. New reflections (0 1 2), (0 2 1), and (1 1 3) were observed in both tooeleite with and without bacteria, which were the diffraction peaks of jarosite (PDF 36-427) (Fig. 1). No other peaks occur in the XRD patterns, which indicates that jarosite is only secondary dissolution product of tooeleite under abiotic and biotic environments. The jarosite is formed by the following two chemical process:

$$Fe_6(AsO_3)_4SO_4(OH)_4{\cdot}4H_2O + H_2O \rightarrow 6Fe^{3+} + 4AsO_3{}^{3-} + 4OH^- + SO_4^{2-} + 5H_2O \quad (1)$$

$$K^+ + 3Fe^{3+} + 2SO_4^{2-} + 6OH^- \rightarrow KFe_3(SO_4)_2(OH)_6 \quad (2)$$

Compared to the XRD peaks of jarosite from abiotic dissolved samples, the intensity of diffraction peaks of jarosite from biotic dissolved sample have more intensity. It shows that *A. ferrooxidans* could promote the formation of jarosite. It has been proved that jarosite is good mineral trap for heavy metals (such as Pb^{2+}) [11] and oxyanions (such as AsO_4^{3-}) [12], which has good stability. Jarosite is also a common secondary mineral in AMD [13], and even Mars [14]. Our SEM images also show that three images are jarosite (Fig. 2), in harmony with our XRD results.

3.2. Infrared spectroscopy

Free AsO_3^{3-} in solution is a planar molecular structure with trigonal pyramidal symmetry and has $2A_1$ (v_1 and v_2) $+2E$ (v_3 and v_4) modes. The vibrations (v_1, v_2, v_3, and v_4) of AsO_3^{3-} occur at 752/690, 340, 680/672, and 340 cm^{-1}, respectively [15,16]. When AsO_3^{3-} is on C_{6h} crystal, the vibration modes split into A_g, E_{2g}, B_u, E_{1u}, B_g, E_{1g}, A_u, and E_{2u} modes. The fundamental modes of the free AsO_3^{3-}, SO_4^{2-} have been determined by Loehr and Plane [15], Tossell [16], Bahfenne and Frost [17] and Rasmussen et al. [18]. The vibration positions determined by these researchers and in our study are summarized in Table 1. In our studies, the spectra of tooeleite have absorption bands occurring at 775 and 691 cm^{-1}, which are attributed to v_3 or v_1 vibrational modes of AsO_3^{3-} (Fig. 3(A)). The intensities of the two bands decrease when tooeleite interacts with bacteria during 30 d, which indicates that a considerable amount of arsenic in mineral structure is released into the solution.

A free SO_4^{2-} has four fundamental vibrations (v_1, v_2, v_3, and v_4), which occur at 983, 450, 1,105, and 611 cm^{-1}, respectively [1]. But only v_3 and v_4 are active in the IR under ideal tetrahedral symmetry.

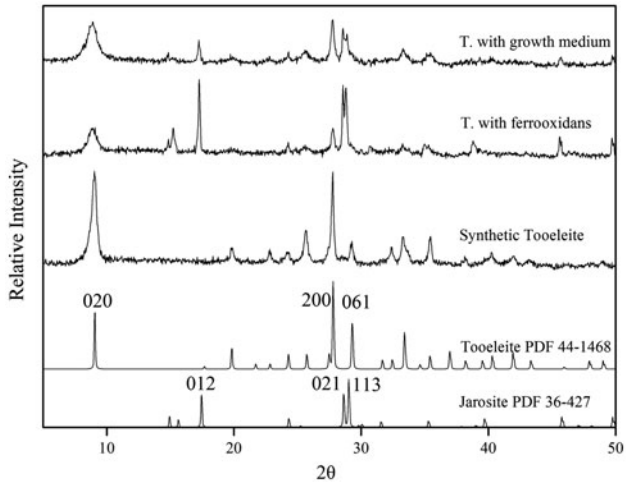

Fig. 1. XRD of tooeleite and dissolution products with and without *A. ferrooxidans*.

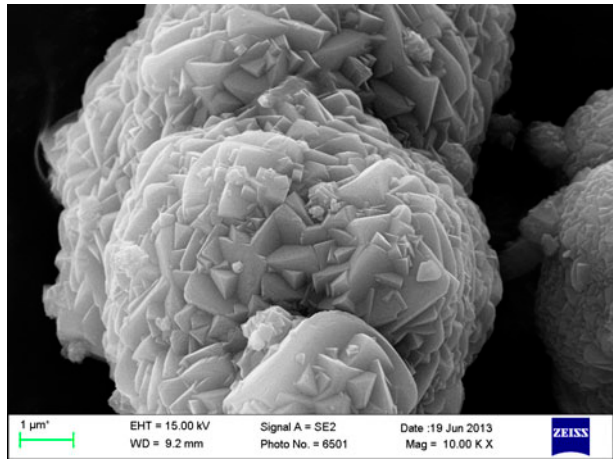

Fig. 2. SEM of secondary jarosite when tooeleite dissolution under *A. ferrooxidans*.

Table 1
Experimental position of vibrations of SO_4^{2-} and AsO_3^{3-} from tooeleite and other references [15–18]

	Free SO_4^{2-}		Fresh tooeleite	Tooeleite with *A. ferrooxidans*
	Position (cm^{-1})	Assignment	Position (cm^{-1})	Position (cm^{-1})
SO_4^{2-}	983	ν_1	983_w	
	450	ν_2	454, 479, 516	448, 473, 510
	1,105	ν_3	1102_s, 1195_w, 1042_w	1105_s, 1082_w
	611	ν_4	620_s	630_s
	Free AsO_3^{3-}			
AsO_3^{3-}	690, 752	ν_1	775_w	773_w
	340, 382	ν_2		
	672, 680	ν_3	691	693
	309	ν_4		

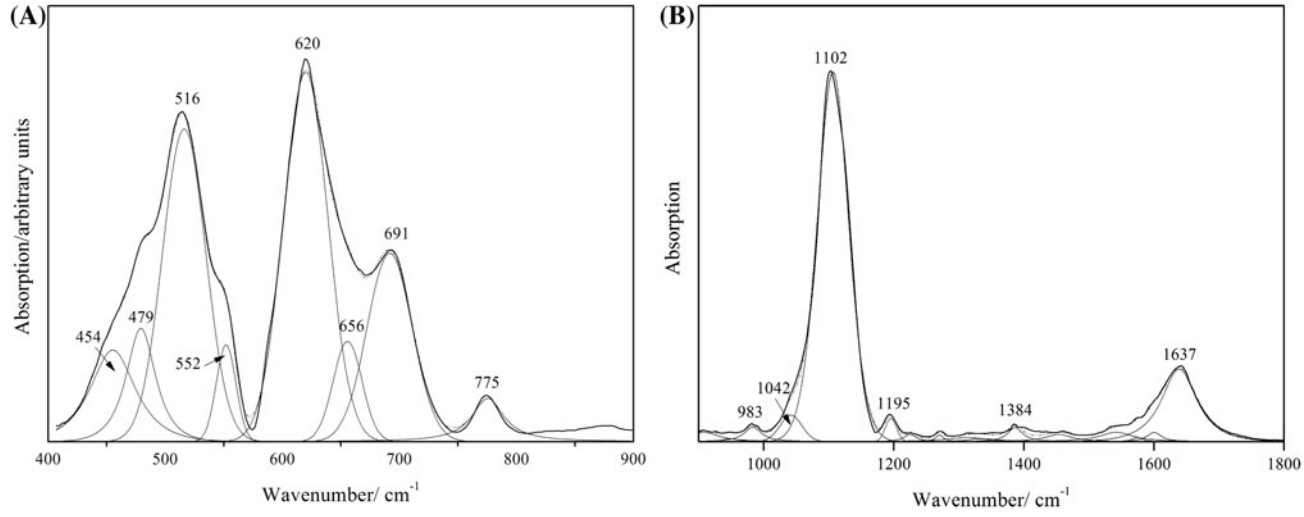

Fig. 3. Infrared spectra of fresh tooeleite range from 400 to 850 cm^{-1} (A) and from 900 to 1,700 cm^{-1} (B).

The inactive v_1 and v_2 can become active due to their surrounding crystal structure, and v_3 also can splits into three weak components at 1,040, 1,094, and 1,167 cm^{-1} [18]. In our studies, the four fundamental vibrations of SO_4^{2-} all are active in IR spectra and occur at 983, 454, 1,102, and 620 cm^{-1}. The bands at 1,102 and 620 cm^{-1} are the most intense and sharp bands due to the non-degenerate v_3 and v_4 vibrations of SO_4^{2-} (Fig. 3(B)). Another two split bands with very weak intensity occur at 1,042 and 1,195 cm^{-1}, which are attributed to the degeneration of v_3 modes (Fig. 3(B)). The occurrence of non-degenerate and degenerate modes of v_3 in IR spectra of tooeleite probably implies that the SO_4^{2-} units in the crystal structure at least have two kinds of orientations.

When tooeleite contacts with *A. ferrooxidans* after 30 d, the v_2 vibrations of SO_4^{2-} shift toward lower wave numbers and occur at 448, 473, and 510 cm^{-1} as compared to 454, 479, and 516 cm^{-1} for tooeleite (Fig. 4(A)). The most intense band at 620 cm^{-1} of fresh tooeleite becomes sharper and shifts to 630 cm^{-1} after dissolution. Bishop and Murad found that the band at 630 cm^{-1} is attributed to v_4 vibration of SO_4^{2-} in jarosite [19]. With our XRD analysis and the previous study conducted by Bishop and Murad [19], we deduced that the sharpening and increased intensity of the bands at 510 and 473 cm^{-1} reflect the formation of jarosite on tooeleite. A new band occurs at 607 cm^{-1} for spectra of tooeleite with *A. ferrooxidans* and probably is attributed to C=O in-plane bending vibration (Fig. 4(A)).

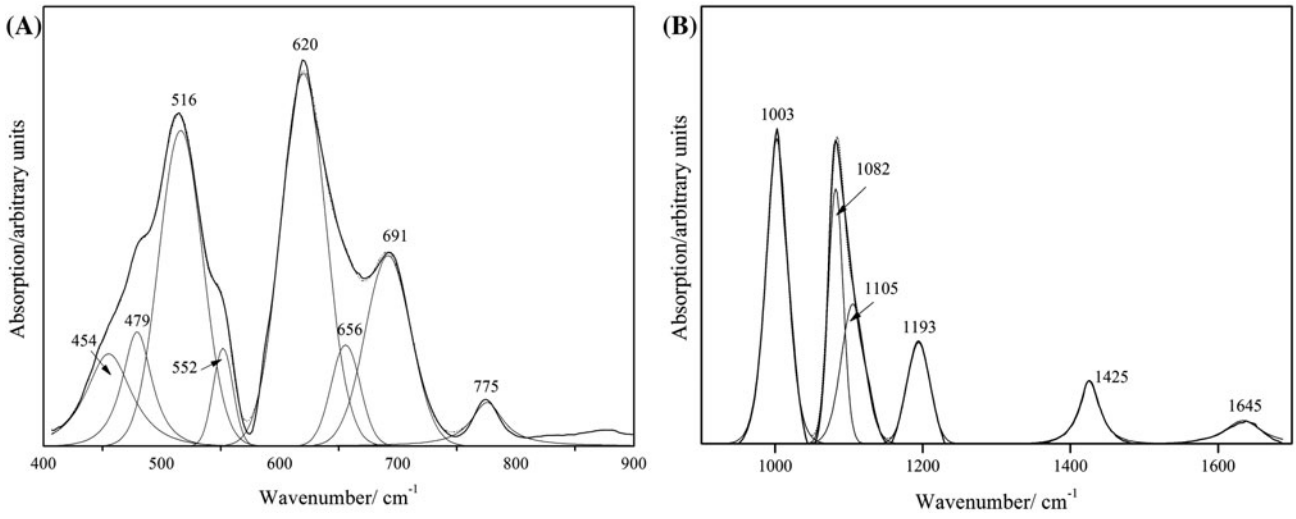

Fig. 4. Infrared spectra of tooeleite under *A. ferrooxidans* after 30 d range from 400 to 850 cm^{-1} (A) and from 900 to 1,700 cm^{-1}(B).

Infrared spectroscopy not only gives insight into dissolution release of arsenic from tooeleite and secondary jarosite, but also further demonstrates bacterial interaction relevant to *A. ferrooxidans*. The bands at 1,082 and 1,193 cm^{-1} are assignable to $–CH_2$ twisting modes and $–CH_3$ wagging modes, respectively (Fig. 4(B)). The band at 1,425 cm^{-1} is assigned to the bending of $–CH_3$ (Fig. 4(B)). For tooeleite, the bands at 3,196 and 3,432 cm^{-1} are attributed to OH stretching vibration of absorbed and structural H_2O, respectively (Fig. 5(A)). With bacterial contact, a new and narrow band develops at 3,412 cm^{-1} (Fig. 5(B)). It is assigned to the stretching vibration of NH group. These bands information indicates that the new bacterial component occurs in the surface of tooeleite, which necessarily affects dissolution of tooeleite and arsenic release.

3.3. Arsenic release

Arsenic release of tooeleite during 30 d under pH ranging from 2 to 11 is reported in Fig. 6. As seen from Fig. 6, the amount of arsenic released from tooeleite quickly decreases with pH increase due to the incongruent dissolution of tooeleite. This is proved through more arsenic release than for iron. The most iron ions precipitate as hydroxides when pH > 3.0. Newly formed iron precipitates conversely adsorb arsenic to a great extent. So, the arsenic concentration maintains ~15 mg/L when pH > 3.0. All $\Delta pH_{final-initial}$

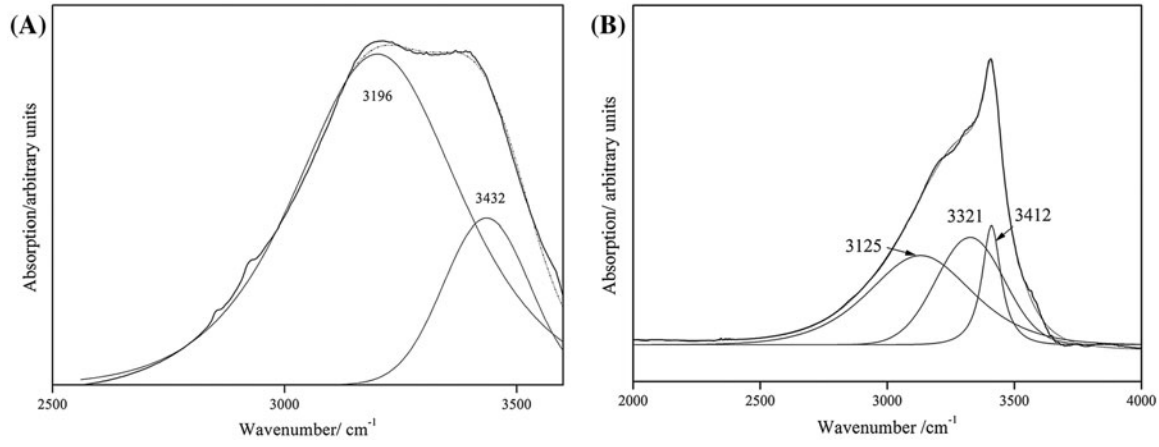

Fig. 5. Infrared spectra of tooeleite (A) and dissolution product after 30 d (B) range from 2,500 to 3,600 cm^{-1}.

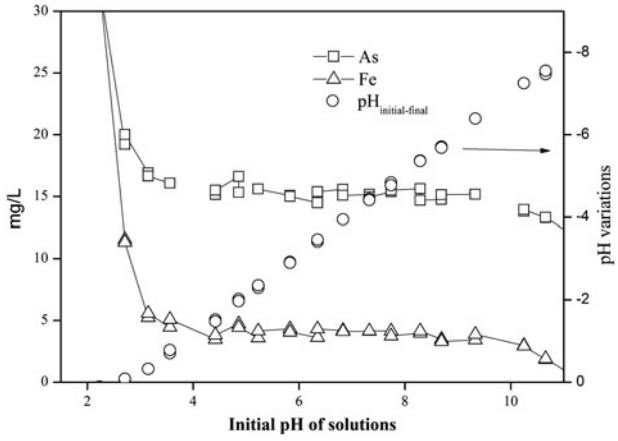

Fig. 6. Arsenic amount released from tooeleite under different initial pH values.

of solutions except for the initial pH ~ 2 is negative, which indicates that the pH of solution after dissolution becomes lower than the initial solution. This is further evidence that the iron hydrolysis occurs.

The arsenic release of tooeleite in the 9 K growth medium has a decreasing tendency during the first 2 d (Fig. 7), which is due to the fixation of arsenic on the surface. The arsenic release gradually increases up to 100 mg/L after 2 d, which is at least 10^4 times greater than the drinking quality for arsenic requirement (10 μg/L) [20]. Once tooeleite contacts with *A. ferrooxidans*, arsenic release is promoted and is as high as 355 mg/L, this is 3.2 times greater than abiotic environment. The arsenic release from tooeleite under

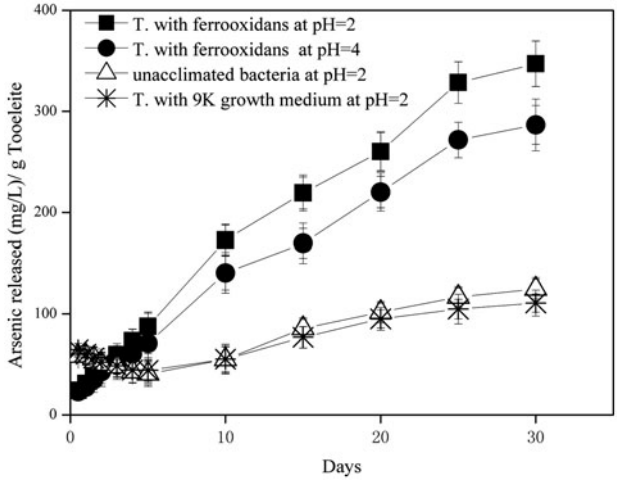

Fig. 7. Arsenic released from tooeleite against time under exposure of *A. ferrooxidans* culture at pH 2 and 4 and growth medium.

only 9 K growth medium and pH 2 is slightly less than the pH 2 solution due to the electrolyte effect on dissolution of mineral (Fig. 7). Meanwhile, arsenic release is higher in the bacterial favorable environment (pH 2) than in the survival critical environment (pH 4), which indicates that the effect of bacterial activity on the dissolution of tooeleite cannot be ignored. This needs to be a practical consideration when using tooeleite as arsenic tank for arsenic removal of waste water.

4. Conclusions

Tooeleite is a common As(III)-loaded secondary mineral in AMD, which controls the arsenic release and migration. The result of batch experiment shows that the amount of arsenic released from tooeleite significantly decreases when pH > 3, which is due to the strong arsenic adsorption of newly formed iron hydroxides during the incongruent dissolution. *A. ferrooxidans* can increase the dissolution rate of tooeleite, which cause the finial arsenic concentration to be 3.2 times than the dissolution under only 9 K growth medium. In view of the survival limit of *A. ferrooxidans* on pH and solubility character of tooeleite under different pH values, neutral and alkali environment are recommended for stabilizing arsenic in tooeleite trap. FTIR and XRD results both shows that jarosite is only secondary well-crystalline product of tooeleite. FTIR also clearly reflects the arsenic releases from tooeleite when dissolution.

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