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Evaluating Factors Affecting Bioscorodite Crystallization from As(III)-Bearing Acidic Metal Refinery Wastewaters

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Abstract
This study evaluated several factors that may affect microbial As immobilization and bioscorodite crystallization efficiencies, such as (i) the $[Fe(II)]_{ini}/[As(III)]_{ini}$ molar ratio for different target As(III) concentrations, (ii) co-existence of Cu(II) in wastewaters, (iii) addition of seed scorodite. Thermo-acidophilic iron-oxidizing archaeon, *Acidianus brierleyi* oxidized As(III) and Fe(II), and bioscorodite was successfully crystallized from synthetic acidic metal refinery wastewaters containing 4.7–13 mM of As(III). The $[Fe(II)]_{ini}/[As(III)]_{ini}$ molar ratio affected As immobilization efficiency at different As(III) concentrations. Higher molar ratios were required for treating diluted As(III) concentrations. Microbial As(III) oxidation was inhibited in the presence of Cu(II). Nonetheless, its negative effect was alleviated by addition of seed scorodite. The morphology of seed crystals affected the reaction speed and the stability of bioscorodite.

1. Introduction

In metal refinery operations, arsenic (As) is a major impurity contaminated in wastewaters. As mainly exists in the form of arsenite (H_3AsO_3; As(III)) and arsenate ($H_2AsO_4^-$; As(V)) in acidic solutions. As(III) is known to be highly toxic and mobile compared to As(V) and it is often present in metallurgical wastewaters[1]. As remediation procedures generally set the first chemical As(III) oxidation process using strong chemical oxidants, followed by the second immobilization process with amorphous iron compounds. This conventional procedure has disadvantages such as high iron demand and bulky sludge. Scorodite ($FeAsO_4 \cdot 2H_2O$) is considered as one of the ideal As disposal forms due to its thermodynamic stability, high density and low iron demand[2]. We have previously reported that thermo-acidophilic iron-oxidizing archaeon, *Ac. brierleyi* oxidized As(III) to As(V) as well as Fe(II) to Fe(III), and bioscorodite was successfully crystallized at pH 1.5 and 70°C[3]. For further optimizing this environmentally-friendly bioprocess, this study evaluated several factors possibly affecting the microbial bioscorodite crystallization efficiency, in order to extend the applicable range of As-contaminated wastewaters. The factors evaluated include (i) the $[Fe(II)]_{ini}/[As(III)]_{ini}$ molar ratio for different target As(III) concentrations, (ii) co-existence of Cu(II) in wastewaters, (iii) addition of seed scorodite.

2. Materials and Methods

Pre-grown *Ac. brierleyi* cells were washed prior to inoculation (to a final cell density of 1.0×10^7 cells/ml) in 500 ml flasks containing 200 ml of heterotrophic basal salts medium (pH 1.5 with H_2SO_4) with 6.3–18 mM Fe(II), 4.7–13 mM As(III) ($[Fe(II)]_{ini}/[As(III)]_{ini}$ molar ratio = 1.3–2.0), 0.02% (w/v) yeast extract. Chemically-synthesized or biogenic scorodite (0.15% (w/v)) was added as seed crystals where indicated. Flasks were incubated at 70°C, shaken at 100 rpm. Samples were regularly taken to monitor pH, Eh (vs SHE), cell density, the concentrations of total soluble Fe/As/Cu by ICP-OES, As(III) by nano-band explorer (GL Sciences), and Fe(II) by o-phenanthroline method. Precipitates were freeze-dried overnight for XRD and SEM. Secondary minerals were embedded in resin and polished to observe SEM cross-section views.

3. Results and Discussion

3.1. Effect of $[Fe(II)]_{ini}/[As(III)]_{ini}$ molar ratio on bioscorodite crystallization efficiency at different target As(III) concentrations

The $[Fe(II)]_{ini}/[As(III)]_{ini}$ molar ratio differently affected the bioscorodite crystallization efficiency at each target As(III) concentration. Fe(II) and As(III) were readily oxidized by *Ac. brierleyi* within 5 days at 70°C. Setting the $[Fe(II)]_{ini}/[As(III)]_{ini}$ molar ratio to 1.3 resulted in 86–100% of As immobilization efficiency as crystalline bioscorodite at initial As(III) concentrations of 13 mM. Orange-colored amorphous precipitates were formed by setting higher molar ratio. When the initial As(III) concentration was set to 6.5 mM, the optimal $[Fe(II)]_{ini}/[As(III)]_{ini}$ molar ratio increased to 1.4–2.0 at which 99% of As was immobilized within 14–30 days. At more dilute initial As(III) concentrations of 4.7 mM, 70% of As was immobilized within 30 days at $[Fe(II)]_{ini}/[As(III)]_{ini}$ molar ratio of 1.3. Increasing the molar ratio to 2.0 improved the As immobilization efficiency to 98%. The $[Fe]_{im}/[As]_{im}$ molar ratio of the precipitates also increased from 1.3 (at $[As(III)]_{ini}$ = 13 mM) to 1.4 (6.5 mM) and 1.9 (4.7 mM). XRD results showed that As was immobilized as crystalline bioscorodite even though it is higher than the theoretical scorodite composition of Fe/As = 1.0. These results implied that higher $[Fe(II)]_{ini}/[As(III)]_{ini}$ molar ratio were required for treating lower initial target As(III) concentrations for effective bioscorodite crystallization.

3.2. Inhibitory effect of Cu(II) on microbial As(III) oxidation

The presence of 8–16 mM Cu(II) inhibited microbial Fe(II) and As(III) oxidation by Ac. brierleyi. However, the inhibitory effect was alleviated by addition of bioscorodite as seed crystals and consequently bioscorodite was crystallized. There was no change in Cu(II) concentrations throughout the experiments and the crystallinity of bioscorodite was not inhibited by Cu(II) based on the XRD results. These results indicated that most of Cu(II) did not co-precipitate with bioscorodite.

3.3. Roles of seed scorodite in bioscorodite crystallization

The zeta-potential distribution analysis indicated that *Ac. brierleyi* cells readily attached to the surface of seed scorodite particles under extremely acidic conditions at pH less than 2.0. It suggested that the presence of seed scorodite provided the support for immediate microbial colonization and robust microbial Fe(II) and As(III) oxidation reactions even in the presence of toxic Cu(II). Reaction time of As immobilization was shorter in the culture fed with fine and low-density bioscorodite as seed crystals (day 21) than in the case of coarse and high-density chemically-synthesized scorodite (day 40) (Fig. 1). SEM cross-section view observation showed that new precipitates were formed to fill inside the bioscorodite seed crystals and the density was improved during the course of bioscorodite precipitation. In contrast, in the case of chemically- synthesized scorodite seed crystals, newly formed bioscorodite passivation layer was found around the surface of seed scorodite. The TCLP test result indicated that the amount of As leached from bioscorodite formed on biogenic scorodite seed crystals was lower (0.59 mg/l) than that formed on chemically -synthesized scorodite seed (1.86 mg/l). The morphology difference in biogenic/ chemically -synthesized scorodite seeds and their effects on scorodite crystallization will be discussed in detail.

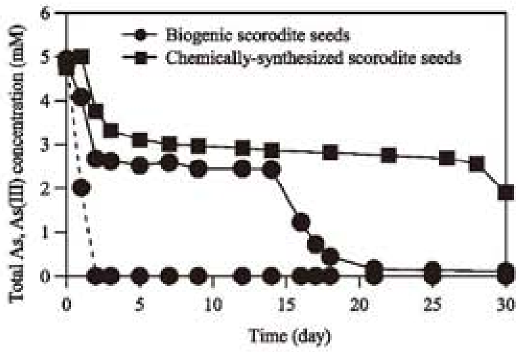

Figure 1. Changes in concentrations of total As (solid lines) and As(III) (broken lines). The $[Fe(II)]_{ini}/[As(III)]_{ini}$ molar ratio was set to 2.0.

4. Conclusions

Bioscorodite was successfully crystallized from synthetic wastewaters containing 4.7–13 mM of As(III) at pH 1.5. The $[Fe(II)]_{ini}/[As(III)]_{ini}$ molar ratio affected the bioscorodite crystallization efficiency for different target As(III) concentrations. Higher molar ratios were required for treating diluted As(III) concentrations. Cu(II) inhibited the microbial As(III) oxidation. Nonetheless, its negative effect was alleviated by addition of seed scorodite. The morphology of seed crystals affected the reaction speed and stability of bioscorodite.

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