

Biotic reduction of U(VI) in the presence of citric acid

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Introduction

Actinides migration is of great concern in the environment because of their radioactivity and long half-lives. Their migratory behavior depends on their oxidation states [1] that differ among the III, IV, V, and VI. It is well known that divers bacteria use soluble U(VI) as an electron acceptor for respiration and reduce it to insoluble $\text{UO}_2(\text{s})$ [2]. However, there are limited information on the effects of complexation with organic acids on the bioreduction of U(VI). In the present study, we have studied reduction of U(VI) by *Shewanella putrefaciens* in the presence of citric acid. Citric acid is one of the naturally-occurring organic substances [3], and it forms stable and soluble complexes with U(VI).

Experimental

Column electrode system

Batch experiments were performed to evaluate the influence of citric acid on the bioreduction on U(VI). The one contained 50 mM sodium lactate as an electron donor, 1 mM $\text{UO}_2(\text{NO}_3)_2$ as an electron acceptor, and 20 mM HEPES as a buffer reagent (control medium). The other contained the same ingredients to the former and additionally 100 mM citric acid. The pH of the media was adjusted to pH 7.0 by using NaOH and HCl solutions.

XANES analysis

The precipitates formed in the medium were analyzed by U L_{III} -edge (≈ 17166 eV) X-ray absorption near edge structure (XANES) spectroscopy. The powder samples of natural uraninite (UO_2) and UO_3 precipitates were used as the standards for U(IV) and U(VI), respectively. The XANES measurements were carried out at beam line 27B in the Photon Factory of High Energy Research Organization (Tsukuba, Japan). Spectra were measured in the fluorescence mode for all samples using a 7-elements Ge array detector interfaced to single-channel analyzers. To prevent the oxidation of U(IV) to U(VI), the precipitates were placed in a sealed plastic bag that, in turn, was put into an outer plastic bag containing an oxygen absorbent. The outer bag made of material preventing the penetration of oxygen was removed just before making the XANES measurements. These treats were carried out in the inert glove box. Note that all of the materials were originated from natural samples containing U.

Results and discussion

XANES spectra measurements of U

The oxidation state of U in the precipitate was determined by XANES spectroscopy. Figures 1 shows the U L_{III} -edge XANES spectra of the precipitates formed in the lactate media, UO_2 and UO_3 . Although the XANES spectrum of the UO_3 had a shoulder peak at around 17195 eV, that of UO_2 did not. The XANES spectrum of the precipitates did not have the shoulder peak and similar to that of UO_2 . On the other hand, no precipitate was formed in the U(VI) solution containing no bacteria or heat killed bacteria. The XANES spectra of the solution were resemble to that of U(VI) standard. These results showed that in the absence of citric acid the reduction of U(VI) to U(IV) was derived by the bacterial activity.

In the presence of citric acid, no precipitates were formed after exposure of bacteria to U(VI) solution. The UV-VIS spectra of the media showed that concentrations of U(VI) species decreased and those of U(IV) species increased with time. These results indicate that the presence of citric acid inhibit the biological reductive UO_2 precipitation by forming the soluble U(IV)-organic complexes.

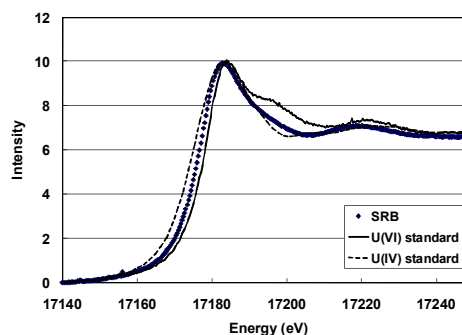


Fig. 1 XANES spectra of U L_{III} -edge of the precipitates formed *S. putrefaciens*, and the standards of natural uraninite and UO_3 .

References

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