

## Mercury Sorption on Apatite: Effects of pH and Ionic Strength

YOUNG JAE KIM<sup>1</sup>, SOO-OH PARK<sup>1</sup>, YOUNG JAE LEE<sup>1\*</sup>

<sup>1</sup>Department of Earth and Environmental Sciences, Korea University, Seoul 136-701, Korea (\*Correspondence: youngjlee@korea.ac.kr, jjbsnlove@korea.ac.kr, orange261@korea.ac.kr)

Mercury (Hg) has been the subject of interest due to its substantial toxicity on humans and living organisms. Apatite such as hydroxylapatite (HAP,  $[\text{Ca}_5(\text{PO}_4)_3\text{OH}]$ ) is one of abundant minerals in nature but also the essential constituent for bone of vertebrates. In spite of such importance, Hg sorption on hydroxylapatite (HAP) has been barely addressed yet. In this study, sorption of mercury on HAP is investigated through batch experiments over a wide range of physicochemical conditions such as different pHs and concentrations of background electrolyte in solution.

Upon  $[\text{Hg}] < 20 \mu\text{M}$ , Hg sorption on HAP shows that mercury uptake by HAP increases with increasing the mercury concentration in solution over a wide range of pH between 5.0 and 9.0. Total amount of mercury sorbed on HAP decreases with increasing pH; the total amount of Hg sorption on HAP at pH 5.0 is twice greater than that of pH 8.5, suggesting that the sorption of Hg could be critically controlled by pH at the HAP-water interface. Compared to that of pH 8.5, we found that an ionic strength dramatically influences Hg uptake by HAP at pH 5.0, showing that Hg sorption increases with increasing the concentration of background electrolyte at pH 5.0. Although this study is an on-going research, it is likely that these observations would be relevant to Hg species as a function of pH. With PHREEQC modeling for Hg speciation, our results show that  $\text{Hg}(\text{OH})_2^0$  is dominant at pH 8.5, whereas at pH 5.0  $\text{HgCl}_2^0$  plays as a major species under the experiment conditions in this study, indicating that changes in Hg species as a function of pH play an important role in the sorption of Hg on HAP. In kinetic experiments at pH 8.5, the initial uptake of Hg by HAP is rapid and ~85% of Hg is rapidly sorbed on the HAP within 1 hr, suggesting that adsorption plays a key role in the initial uptake of mercury at the HAP-water interface. With our results, it is found that the mercury uptake by HAP is greatly influenced by different physicochemical conditions such as pH and ionic strength of the solution.

## Silver reduction and synthesis of elemental silver nanoparticles by metal-reducing bacteria

YUMI KIM<sup>\*</sup> AND YUL ROH

Chonnam National University, Gwangju, Korea, rohy@jnu.ac.kr

### Introduction

In the recent years, a new dimension of the microbe-metal interactions has been explored for synthesis of metal nanoparticles such as gold and silver[1]. Although  $\text{Ag}(0)$  is known to be an antibacterial agent, metal-reducing bacteria such as *Geobacter* sp. and *Shewanella* sp. have shown the surprising ability of actively growing and precipitating  $\text{Ag}(0)$  nanoparticles within and around the cell surface via reduction of  $\text{Ag}(\text{I})$  [2-3]. The objectives of this study were to synthesize  $\text{Ag}(0)$  nanoparticles via microbial  $\text{Ag}(\text{I})$  reduction as well as to determine the effects of various experimental conditions such as silver nitrate concentrations, pHs, temperatures, and reaction time controlling for the optimal biosynthesis of  $\text{Ag}(0)$  nanoparticles.

### Materials and Methods

The  $\text{Ag}(0)$  nanoparticles were synthesized by metal-reducing bacteria (Suncheon-1) enriched from inter-tidal flat sediments from southwestern part of South Korea. The 16S rRNA gene DGGE analysis showed the metal-reducing bacteria consisted of *Shewanella* sp., *Clostridium* sp., and *Vibrio* sp. Microbial synthesis of  $\text{Ag}(0)$  nanoparticles was examined under different concentrations of silver nitrate (1 – 10 mM), medium pHs (6.5 – 8.5), incubation temperatures (5 – 35°C) and reaction time (for 7 days) for crystal growth. The precipitates resulted from silver reduction by the bacteria were analyzed with XRD and TEM-EDS for mineralogical characterization.

### Results and Conclusion

The metal-reducing bacteria (Suncheon-1) enzymatically transformed silver nitrate to  $\text{Ag}(0)$  nanoparticles with their metabolism. The  $\text{Ag}(0)$  nanoparticles were rapidly synthesized when silver nitrate ( $\text{AgNO}_3$ ) was injected into the medium enriched the bacteria compared with initial injection at once. Microbial reactions with silver ion led formation of homogeneous sized  $\text{Ag}(0)$  nanoparticles (5 – 15 nm) by reduction of silver nitrate (0.5 – 1 mM) under the conditions around 15 – 25°C and medium pH 8.5 within 3 days of incubation time. These results show that metal-reducing bacteria enzymatically reduced  $\text{Ag}(\text{I})$  to  $\text{Ag}(0)$  and formed homogeneous size and shape of  $\text{Ag}(0)$  nanoparticles. Moreover, the capability of silver precipitation by microbial  $\text{Ag}(\text{I})$  reduction suggests expanded application of recovering silver nanoparticles from silver-containing water and/or silver enriched natural environments.

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