Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 7-8, 2015

Development of Tributyl Phosphate Apatite for Uranium Removal

HyunJu Kim [a, *], Jaehyuk Kang [a], Jungjin Kim [a], Wooyong Um[a, b]
[a] *Division of Advanced Nuclear Engineering, POSTECH, 77 Cheongam-Ro, Nam-Gu, Pohang, Gyeongbuk*
[b] *Energy and Environment Directorate, PNNL, Richland, WA 99354, USA*
[*]*Corresponding author: hyunju1157@postech.ac.kr*

1. Introduction

Efficient and rapid removal of radioactive contaminants is crucial when they are released to the environment through severe nuclear accidents. In this study, we developed a competitive and highly efficient sorbent for uranium (U) removal under various condition

2. Methods and Methods

2.1 Synthesis of Tributyl phosphate (TBP) apatite

Hydroxyapatite (HA) was prepared by solution-precipitation method [1]. $Ca(NO_3)_2 \bullet 4H_2O$ and $(NH_4)_2HPO_4$ were used as starting materials and 250 mL of 0.29 M of $(NH_4)_2HPO_4$ solution was added to 350 mL of $Ca(NO_3)_2 \bullet 4H_2O$ solution (0.24 M). After the mixing, the pH of mixed solution was adjusted to 11 by ammonia solution (1.0 M). After 1 day reaction, the precipitated HA was centrifuged by 3000 rpm for 5 minute, dried overnight at 80℃ and calcined at 600℃ for 3hr.

TBP-apatite was prepared using surface functionalization with TBP using the method developed by WANG et al [2]. TBP-apatite was prepared at different pHs (pH=4, 7, 10), respectively. The HA was washed repeatedly three times with deionized water (DIW), and dried at 60 ℃ for 2 h prior to use. Tributyl phosphate (20ml) was diluted in 100ml ethanol, and this mixing solution was adjusted pH 4, 7 and 10 with 1M hydrochloric acid and 1M sodium hydroxide. After that, 5g synthesized HA was added to prepared mixing solution. The mixture was placed in a heating mantle at 100℃ until the ethanol was evaporated. This remained mixture were baked in an oven at 130 ℃ for 2 days. And then this material was washed with DIW and ethanol and dried at 60℃ for 2 h. The final powder is TBP-coated HA materials.

2.2 Material Characterization

Solid characterizations of HA and TBP-apatite were analyzed by X-Ray Diffraction (XRD), 31-phosphorous Nuclear Magnetic Resonance (^{31}P NMR), Fourier Transform Infrared Spectroscopy (FT-IR), and Scanning Electron Microscope/Energy Dispersive Spectroscopy (SEM/EDS).

2.3 Batch Adsorption and Isotherm Experiment

Uranium (U) adsorption experiments were conducted using the synthesized apatite materials at a solid to solution ratio of 0.05g/10mL background solution (0.001M $NaHCO_3$ and 0.1M $NaHCO_3$). Uranium removal was evaluated under different reaction times and U concentrations in varying background solution (0.001M $NaHCO_3$ and 0.1M $NaHCO_3$).

Uranium adsorption isotherm experiments were conducted using different U initial concentrations. After reaching U adsorption equilibrium, the samples were centrifuged for separation and the remaining U concentration in solution was determined by Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). Langmuir and Freundlich models [3] were applied for the experiment data.

3. Results and Discussion

3.1 Characterization of synthesized materials

As shown in Fig.1, the XRD patterns of synthesized HA and TBP-apatite are identical to the reference HA XRD patterns (PDF number: 00-009-0432) [4].

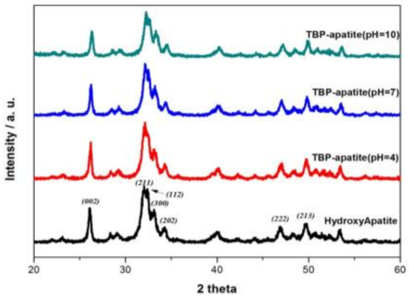

Fig. 1. XRD patterns of synthesized apatite.

In Fig. 2, the FTIR results showed that main peaks were shown at 3570 cm^{-1} in all materials [5]. The band around at 3570 cm^{-1} indicates the stretching hydroxyl group from HA. Phosphate functional group was observed around at 1040 cm^{-1}. The C-H containing functional group (3000-2950 cm^{-1}) was found only in the TBP-apatite prepared at pH=10 condition.

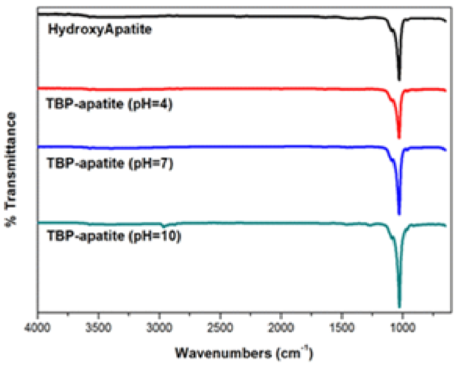

Fig. 2. FTIR spectra of synthesized apatite collected for the 4000~650 cm^{-1} range in transmission mode

In Fig. 3, the ^{31}P NMR spectra show that all phosphorus in the synthesized apatite are PO_4^{3-} functional group, but TBP-apatite prepared at pH=10 condition show additional peak at around δ=-2 ppm due to $O=P(OR)_3$ structure from TBP structure.

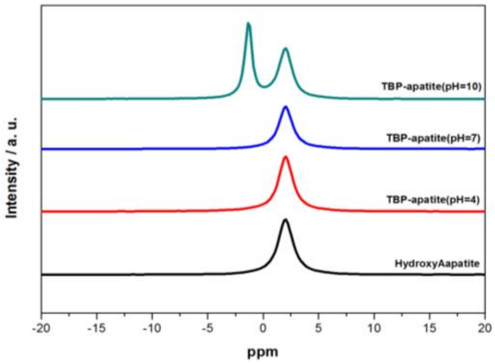

Fig. 3. ^{31}P NMR spectra of various apatite.

Based on the XRD, FTIR, ^{31}P NMR analyses, the TBP-coated apatite was well made at pH=10 condition.

3.2 Uranium Batch Adsorption Results

In Fig. 4 shows that U removal was almost 100% within 1 day by the HA materials in low carbonate background solution (0.001 M $NaHCO_3$). As sodium bicarbonate concentration increased, U removal decreased, because of U-Carbonate complex formation.

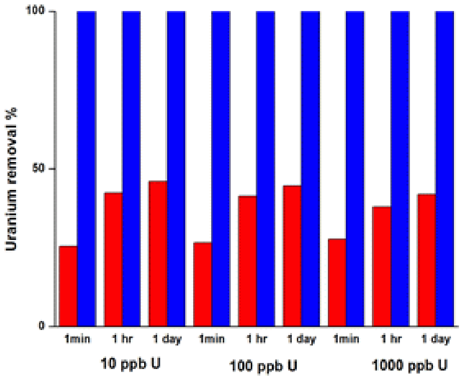

Fig. 4. Uranium removal % by HA in different background solution [Blue: 0.001M $NaHCO_3$ and Red: 0.1M $NaHCO_3$].

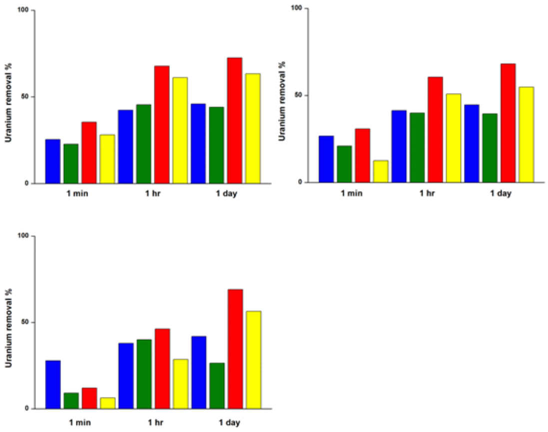

Fig. 5. Uranium removal % of various apatite with different uranium conditions in 0.1 M $NaHCO_3$ background solution. (a) 10 ppb; (b) 100 ppb; (c) 1000 ppb [Blue: HA, Green: TBP-apatite (pH=4), Red: TBP-apatite(pH=7), Yellow: TBP-apatite(pH=10)].

In Fig. 5, TBP-apatites show better U removal than HA. Especially, TBP-apatite prepared at pH=7 condition shows the best U removal. After the adsorption experiment, final pH of all samples 8.6 to 8.7. Almost, final pH of TBP-apatite prepared at pH=7 shows the slightly high pH.

4. Conclusions

Uranium removal was evaluated under different reaction times, initial U concentrations, and background solution using synthesized HA and TBP-apatite. As $NaHCO_3$ concentration increased, U removal decreased. In the same condition, TBP-apatite showed better U removal than HA, which indicates TBP-apatite can be used as U removal sorbent.

Acknowledgement

This research was supported by the BK21+ Program and Basic Science Research Program (NRF-2013R1A1A2063649) through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science, and Technology.

REFERENCES

[1] I. Mobasherpour, M. S. Heshajin, A. Kazemzadeh, and M. Zakeri, Journal of Alloys and Compounds, Vol. 430, pp. 330-333, 2007.
[2] Mohsen Aliakbari, Kamal Saberyan, Mohammad Noaparast, Hadi Abdollahi, Ata Akcil, Hydrometallurgy, Vol. 146, pp. 72-75, 2014.
[3] Karina Yew-Hoong Gin, Ying-Zhong Tang and M.A. Aziz, Water Research, Vol. 36, pp. 1313-1323, 2002.
[4] G. Guillemin, J.-L. Patat, J. Fournie and M. Chetail, Journal of Biomedical Materials Research, Vol. 21, pp. 557-567, 1987.
[5] Choi D, Marra K and Kumta PN, Materials Research Bulletin, Vol. 39, pp. 417-432, 2004..612-613, 1999.