

Uranium Removal by Tributyl Phosphate-Coated Hydroxyapatite

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1. Introduction

Efficient and rapid removal of radioactive contaminants is crucial when they are released into the environment following nuclear accidents. Here, different types of apatite were synthesized using tributyl phosphate (TBP) and tested for uranium removal from various solutions using different reaction times and uranium concentrations.

2. Experimental

2.1 Synthesis of different apatite materials

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

2.2 Batch U adsorption and isotherm experiment

Uranium adsorption experiments were conducted using the synthesized apatite materials at a solid to solution ratio of 5 g L⁻¹ under different background solution in open system. Uranium removal was

evaluated under different reaction times and U concentrations.

Uranium adsorption isotherm experiments were conducted using different U initial concentrations. For isotherm experiments, a series of 15 mL polypropylene test tubes were used. Each test tube was filled with a synthesized adsorbents and 200 ppm of the initial U concentration in a 0.01 M NaHCO₃ solution at different solid/solution ratios. Langmuir and Freundlich models were applied for the experiment data.

3. Results & Discussions

3.1 Characterization of synthesized materials

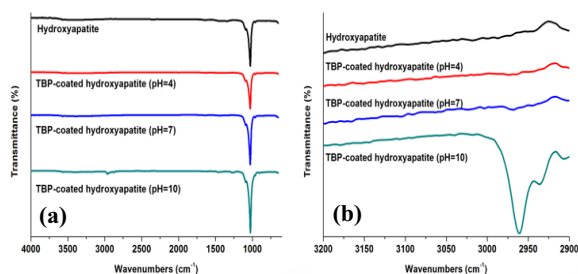


Fig. 1. FTIR spectra of the synthesized apatites: (a) analysis of the 4,000–650 cm⁻¹ region; (b) an expanded view of the 3,200–2,900 cm⁻¹ range of the C-H functional group.

In Fig. 1, the FTIR results showed that main peaks were shown at 3570 cm⁻¹ in all materials. It indicates the stretching hydroxyl group from hydroxyapatite. Phosphate functional group was observed around at 1040 cm⁻¹. The C-H containing functional group (3000–2950 cm⁻¹) from TBP was found in the TBP-coated hydroxyapatites prepared at different pHs.

In Fig. 2, the ³¹P NMR spectra show that all phosphorus in the synthesized apatite are PO₄³⁻ functional group, but TBP-apatite prepared at pH=10 condition show additional peak at around $\delta = -2$ ppm due to O=P(OR)₃ structure from TBP structure.

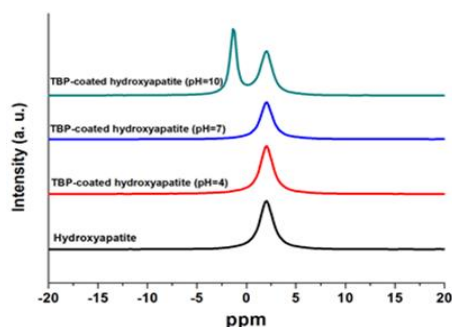


Fig. 2. Solid-state ^{31}P MAS NMR spectra for the synthesized apatites.

From the TC data for hydroxyapatite and TBP-coated hydroxyapatite, TBP-coated hydroxyapatite sample prepared at pH = 10 has 8–13 times more carbon present compared to other hydroxyapatite samples.

Based on the various characterization results, more TBP coating occurred on the hydroxyapatite surfaces at pH = 10 than other pH conditions.

3.2 Uranium Batch Adsorption Results

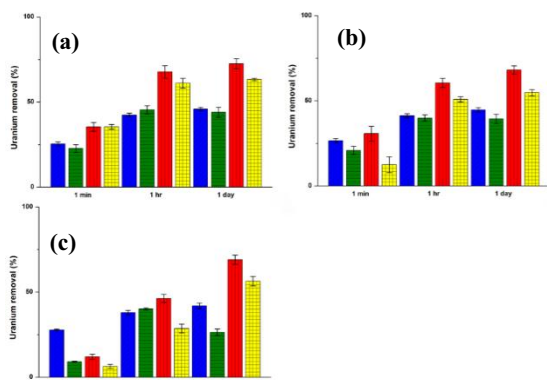


Fig. 3. Uranium removal (%) using different synthesized apatites at different initial U concentrations (a) 10 ppb, (b) 100 ppb, and (c) 1,000 ppb in 0.1 M NaHCO_3 background solution at 293.15 K [blue: hydroxyapatite; green: TBP-coated hydroxyapatite (pH = 4); red: TBP-coated hydroxyapatite (pH = 7); yellow: TBP-coated hydroxyapatite (pH = 10)].

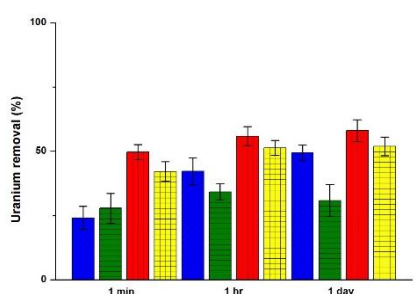


Fig. 4. Uranium removal % of synthesized apatites using the simulated seawater (0.7 M NaCl) spiked with 10 ppb U(VI) in at 293.15 K [blue : Hydroxyapatite; green : TBP-coated hydroxyapatite; red : TBP-coated hydroxyapatite (pH = 7); yellow: TBP-coated hydroxyapatite (pH = 10)].

In Fig. 3, TBP-coated hydroxyapatites show better U removal than hydroxyapatite. Especially, TBP-coated hydroxyapatites prepared at pH=7 condition shows the best U removal. The results of U adsorption experiments in simulated seawater (0.7 M NaCl) showed that the TBP-coated hydroxyapatite prepared at pH = 7 still had the best U removal capacity among the four solids, suggesting that TBP-coated hydroxyapatite can be used an efficient adsorbent to recover U from seawater.

According to the fits, the maximum adsorption capacity for U removal is close to 38 $\text{mg}\cdot\text{g}^{-1}$ for the TBP-coated hydroxyapatite prepared at pH = 7. And, the Freundlich isotherm gives a better fit to the U adsorption by TBP-coated hydroxyapatites prepared at pH = 7. It suggests multilayer U(VI) adsorption sites on their surfaces.

4. CONCLUSIONS

The adsorbents were successfully fabricated and tested for the removal of U from various solution conditions. Under the same conditions, TBP-coated hydroxyapatite showed better U removal capability than pure hydroxyapatite. In particular, TBP-coated hydroxyapatite synthesized at pH 7 showed the highest U adsorption capacity (38 $\text{mg}\cdot\text{g}^{-1}$). The results of this study indicate that TBP-coated hydroxyapatite can be used as a new adsorbent to efficiently and selectively remove U from seawater.

REFERENCES

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- [2] Wang, H.; Shao, X. Z.; Tian, Q.; Ji, Y. Q., Synthesis of TBP-coated magnetic Pst-DVB particles for uranium separation. *Nucl. Sci. Tech.* 2014, 25 (3).