Fishery derived bio-phosphate for uranium immobilization and its phase transformation

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Increased exploration of fishery product resulted in the increasing biowaste. Fish bone and krill shell were the main biowastes generated a large amount in Guangzhou City. Herein, the fish bone and krill shell were recovered to be a novel natural biosorbent for immobilizing uranium (U (VI)) to address the U (VI) pollution. Sorption behaviors of U (VI) and its transformation on fish bones and krill shells were investigated by batch sorption experiments, FTIR, SEM-mapping, XRD analysis. Hydroxyapatite (Bio-HAP₆₀₀) obtained by calcining waste fish bone at 600 °C performed favorable sorption capacity of 384.56 mg/g to uranium. Sorption equilibrium was achieved within 10 min. The results were similar to the sorption behavior of commercial available nano-HAP. Chemical sorption and mineralization may play a dominant role in favoring the sorption of uranium on Bio-HAP. Formation of nano flake crystal of autunite $Ca(UO_2)_2(PO_4)_2(H_2O)_6$ was the fate of uranium sorption. Sorption of U (VI) is highly P, Ca and O dependent.



Fig.1 SEM elemental mapping images of the hydroxyapatite after uranium sorption.

Besides, the krill shell had favorable sorption capacity of 318.21 mg/g to U (VI) ($C_0=500$ mg/L). Surface O-H and P-O groups provided excellent active sites to the superior sorption ability. The U (VI) was also transformed

into nano-scale flake autunite $Ca(UO_2)_2(PO_4)_2(H_2O)_6$ after sorption. The P and U (VI) mapping are highly related to the nano-scale flake, meaning that sorption of U (VI) is P dependent, and the sorption mechanism was interpreted as surface chemisorptions between the phosphate in the krill shell and U (VI). Thus, this paper demonstrated that fish bone and natural krill shell waste could be widely used as a promising and cost-effective sorbent for immobilization of U (VI) as well as biowaste resource utilization. Formation of nano flake crystal of autunite $Ca(UO_2)_2(PO_4)_2(H_2O)_6$ contributed to the U (VI) fate.



Fig.2 TEM and SEM elemental mapping images of the krill shell hydroxyapatite after uranium sorption.

Key words: Fish bone, krill shell, hydroxyapatite, sorption, uranium, autunite.