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Removal of aqueous lead by fish-bone waste hydroxyapatite powder

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Treatment of heavy metal contamination such as lead in water is an important subject that has been required concerning about environmental regulation and maintenance of citizen on health. Hydroxylapatite is a unique substance because of its high capacity of heavy-metal ion exchange or absorption and high-biological compatibility [1–8], however, in general, the synthesized materials are very expensive. Ozawa *et al.* have reported the possibility of fish bone waste as useful ceramic phosphate resources [1, 2]. In this communication, the trials for immobilization of lead by fish-bone waste-originated hydroxyapatite powder are reported. We described the effect of heat treatment of fish bone on removal property of lead and characterization of the powder after lead immobilization.

Fish-bone used in this experiment was obtained from natural Japanese sea bream. Fish-bone was washed with water stream, dried and crushed, and then fired in air at 600 °C and 900 °C for 24 hr. The resultant powder was crushed and ground, then filtered with the mesh between 125 and 75 μm. In the lead removal test, the concentration of Pb was at 3×10^{-4} M (0.3 mM) as nitrate solutions, and 0.3 g of the fish-bone powder was added to each 2 L solution of the aqueous lead nitrate. Soaking time was 120 min with stirring of solutions, and then the mixture of powder and solutions was held for 6 days without stirring. The concentration of Pb in water was analyzed using inductively coupled plasma atomic emission spectrometer (ICP; SPS7800, Seico Instruments Inc., Tokyo, Japan). The morphology and crystal phase of samples was examined by transmission electron microscopy (TEM; JEM-200EX, JEOL, Tokyo, Japan) and X-ray diffraction apparatus (XRD; Rint 2000, Rigaku, Tokyo, Japan).

Table I summarized the residue concentration of lead, when three fish bone samples were used to a removal test of Pb 0.3 mM in water for a soaking period of 2 hr and 6 days. Fish-bone heated at 600 °C showed the best capability of immobilization for lead, when final concentration was 0.04 mM; the removal efficiency was 99% after 6 days. Other powders showed lower efficiencies than a 600 °C-heated sample.

Fig. 1 shows the relationship of lead concentration versus time for a removal test that fish-bone powder heat-treated at 600 °C was used for Pb 0.3 mM water. In the first 5 min operation, the lead concentration rapidly decreased. After soaking time of only 15 min, the up-taken amount of lead reached to 0.14 mM. After this, a gradual removal reaction seemed to proceed, leading to removal efficiency of 99% (the up-taken amount, 0.296 mM) after 6 days.

TABLE I Concentration of lead in water for a test using a fish bone powder after heat treatment at 600 °C. Initial concentration is 0.3 mM. The weight of powder is 300 m

Soaking period	Raw fish bone	Heated at 600 °C	Heated at 900 °C
2 hr	0.275 mM	0.136 mM	0.259 mM
6 days	0.157 mM	0.04 mM	0.104 mM

Several workers [3–8] have performed the removal experiment of aqueous lead using a synthetic hydroxyapatite sample. Suzuki *et al.* first reported a batch vessel test of synthetic hydroxyapatite for aqueous metal nitrates [3], and concluded that the reaction was a cation-exchange. However, after this, Ma *et al.* [5] observed the formation of crystalline pyromorphite by XRD after removal test for lead with hydroxyapatite. On natural apatite, Admassu and Breese [8] also tried the use of raw fish-bone for removal of heavy metals, and described that the reaction was complete after 15 min, showing the limited removal efficiencies for high concentration of lead as 2.5–3 mM. They used a raw (dried) fish-bone as a starting hydroxyapatite sample.

In this work, the improved immobilization characteristics have been found by heating the raw fish bone at 600 °C. We have previously confirmed that the heated fish bone consists of the small hydroxyapatite crystallite under TEM observation [1]. To clarify the state of hydroxyapatite powder after a removal test, we observed the sample by the means of XRD and TEM.

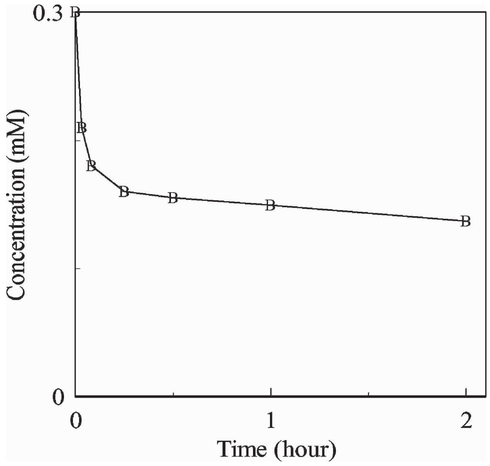

Figure 1 Concentration of Pb in water versus soaking time for a fish bone powder heat-treated at 600 °C.

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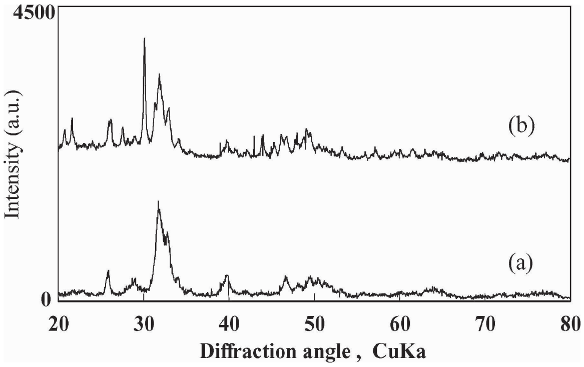

Figure 2 X-ray diffraction patterns of the fish bone sample: (a) heated at 600 °C and then (b) subjected to a soaking test for a Pb 0.3 mM water.

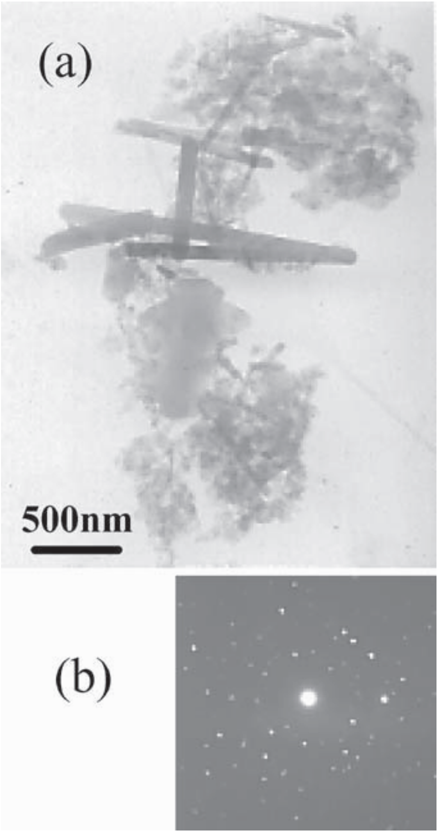

Figure 3 Transmission electron microscopy image for an aggregate: (a) and the electron diffraction pattern (b) in the fish bone heated at 600 °C and then subjected to a soaking test for a Pb 0.3 mM water.

Fig. 2 showed the XRD patterns of the removal-tested hydroxyapatite powder for 6 days. We detected the $Pb_5(PO_4)_3OH$ phase (hydroxypyromorphite) in the addition of hydroxyapatite. Fig. 3 shows the TEM image and the electron diffraction for the powder of fish bone hydroxyapatite after heat treatment at 600 °C, followed by an immobilization test for lead for 6 days. Several particles with dark contrast and clear habit shape of crystallite were found in the aggregates. The darker contrast seems to be due to the heavy atom (Pb) in the particle under present TEM condition. They suggest that the aggregates consist of mixed powders of starting hydroxyapatite and resulting hydroxypyromorphite that contains Pb. The electron diffraction which was taken from this aggregate showed many bright spots, corresponding to crystalline hydroxypyromorphite, in the addition of the broad rings of starting hydroxyxpatite. Although the detailed reaction mechanism should be examined more, the formation of hydroxypyromorphite was confirmed by both XRD and TEM observation. We have assumed that the high-immobilization property of fish bone hydroxyapatite is improved by this reaction under the present condition for Pb-containing water. Concerning about practical lead immobilization operation, we described the application of effective heat treatment at 600 °C on raw fish bone. This procedure is useful on the acceleration of lead removal rate and final amount of removed lead from water.

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