

The Effect of Heat Treatment on Aqueous Copper Removal Property of Fish-Bone Waste-Originated Ceramic

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The effect of heat treatment of fish bone waste was examined for its better removal property of copper in wastewater. The heat procedure of raw fish bone at 600°C induced the initial fast removal rate, and improved a final efficiency of removed copper. The XRD and ESR results suggested the combined mechanism of ion-exchange and structural modification during a removal process of aqueous copper with fish bone hydroxyapatite. The present work provided a useful feature of inexpensive fish-bone-originated ceramic which could be applied to wastewater management.

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1. Introduction

Treatment of heavy metal contamination in wastewater is an important subject that is required concerning about environmental regulation and actual maintenance of citizen on health. Hydroxyapatite is just fit for such purpose because of its high capacity of heavy metal ion exchange or absorption as well as high compatibility as clinical materials to humans and animals. Previous works have reported the removal activity of aqueous copper by synthetic hydroxyapatite.¹⁾⁻¹⁰⁾ Several models for ion-exchange and adsorption were proposed, and most work was performed using the reagent grade hydroxyapatite. Actually, since the synthesized hydroxyapatite products are generally supplied as high quality reagent for clinical use, they are very expensive. Even if the performance of metal removal is high, the civil use is limited by the cost of materials in practice. The possibility of fish bone waste from coast area of Asian countries as useful ceramic resources of hydroxyapatite has been reported.¹¹⁾ The microstructure is developed, by simple heat treatment, to form micro- and macro-pores and their connectivity in hydroxyapatite ceramic. In this work, we demonstrate the immobilization of aqueous copper by fish-bone waste originated hydroxyapatite. On natural hydroxyapatite, Admassu and Breese¹⁰⁾ tried the application of raw Alaska salmon fish bone as a medium to removal of heavy metals. Actually, raw fish bone become inorganic hydroxyapatite, via heat treatment, featured by an interesting microstructure and pure crystalline hydroxyapatite phase.^{11),12)} The hydroxyapatite after calcining raw fish bone will give some advantage to induce better removal performance for aqueous metals. In the present paper, we describe the effect of heat treatment of fish bone on removal property of copper, which is one of divalent metal in wastewater.

2. Experimental

Fish-bone resource in this experiment was obtained from natural Japanese sea bream waste. Fish-bone residue was washed in water stream, dried in atmosphere, then crushed into 200 μm -size powder. It was fired in air, either at 600°C or 900°C for 24 hours. The powder was crushed and ground, then filtered through a mesh between 125 and 75 μm . The experiment of copper removal performance consisted of following procedures. An aqueous copper nitrate solution of 0.3 mM (3×10^{-4} M) was prepared in a glass beaker. 0.3 g of the fish-bone powder was added to the 2 dm³ solution. Soaking time was set between 0 and 120 minutes with stirring of solutions. Also, the mixture of powder and solutions was held for 6 days

without stirring. The concentration of copper in water was analyzed using an inductively coupled plasma atomic emission spectrometer (ICP; SPS7800, Seico Instruments. Inc., Tokyo, Japan). The crystal phase of samples was examined by powder x-ray diffraction (XRD; Rint2000, Rigaku Co., Ltd., Tokyo, Japan). Electron spin resonance (ESR; JEM-MX3, JEOL Co. Ltd, Tokyo, Japan) was used to identify paramagnetic species in powders after testing for 6 days.

3. Results

3.1 Removal property for aqueous copper

Figure 1 shows a plot of the amount of copper in water against time in a removal test using three fish-bone powders. The fish bone showed better capability of removal when it was heated at 600°C, however raw bone and a powder heated at 900°C were of lower activity. In a short period experiment for 2 hours, the removal efficiency of fish bone, produced at 600°C, was 36% for 0.3 mM Cu in a model wastewater. Table 1 compares the final residue in water after soaked for 6 days and 2 hours. The fish bone ceramic produced at 600°C showed relatively good capability; the final concentration 0.131 mM and the removal efficient 56%. Several workers proposed a kinetic model of ion-exchange or absorption of aqueous metals on hydroxyapatite.²⁾⁻⁵⁾ In the case of lead

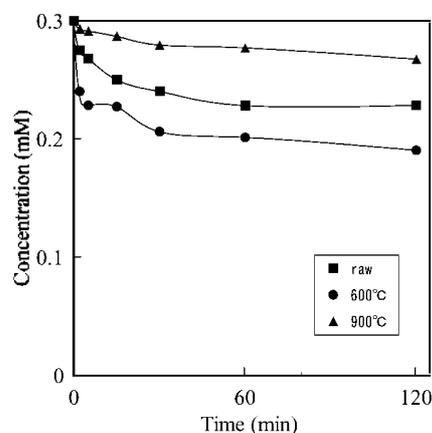


Fig. 1. Concentration of copper in water versus soaking time of fish bone powders. Initial concentration is 0.3 mM. The weight of powder is 300 mg. ■; Raw fish bone. ●; Fish bone heated at 600°C, ▲; Fish bone heated at 900°C.

Table 1. Concentration of Copper in the Solution after Removal-testing for 2 hours and 6 days with Three Fish Bone Samples. Initial Copper Concentration is 3×10^{-4} M

Soaking period	Concentration ($\times 10^{-6}$ M)		
	Raw fish bone	heated at 600°C	heated at 900°C
2 hours	228	190	267
6 days	154	131	197

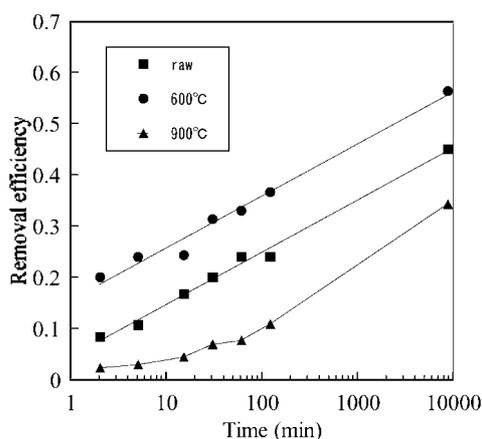


Fig. 2. A plot of removal efficiency versus soaking time (logarithm scale). The experimental condition is the same as in Fig. 1. ■; Raw fish bone. ●; Fish bone heated at 600°C, ▲; Fish bone heated at 900°C.

(Pb) removal, the fast reaction between hydroxyapatite and aqueous lead nitrate was reported to complete in ca.10 minutes, and to form the precipitation of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, which was detected by XRD.⁵⁾ In this work, no novel phase was observed in the samples after removal tests, however the removal reaction was very fast in an initial stage. As shown in Fig. 2, a linear relation, $x = k \cdot \ln(t) + x_0$ was found in the latter part of soaking for a plot of removal efficiency x versus logarithm-scaled reaction time t . In Fig. 1, the rapid decrease of concentration was observed between 0 and 2 minutes for a sample heated at 600°C. This is also evident in Fig. 2 as an initial gap of efficiency, $x_0 = 0.16$ (This was 0.04 for a raw fish bone). In the case of a powder heated at 900°C, an induction time seems to be observed. The apparent kinetic constant k , which was measured by reaction period after 30 minutes, was 0.043 (a raw sample), 0.044 (600°C), and 0.049 (900°C), respectively. Thus, the reaction progresses slowly with the similar kinetic constant in the region of a soaking time longer than 30 minutes. The present experiment for a few days, the total removal efficiency was strongly influenced by the fast reaction in starting region for a few minutes.

3.2 Crystal phase

Figures 3 show the powder XRD patterns of three fish-bone powders before and after immobilization-testing for 6 days. Raw fish bone had low crystallinity with broad major peaks at around 32°. After a removal test, a resultant powder also

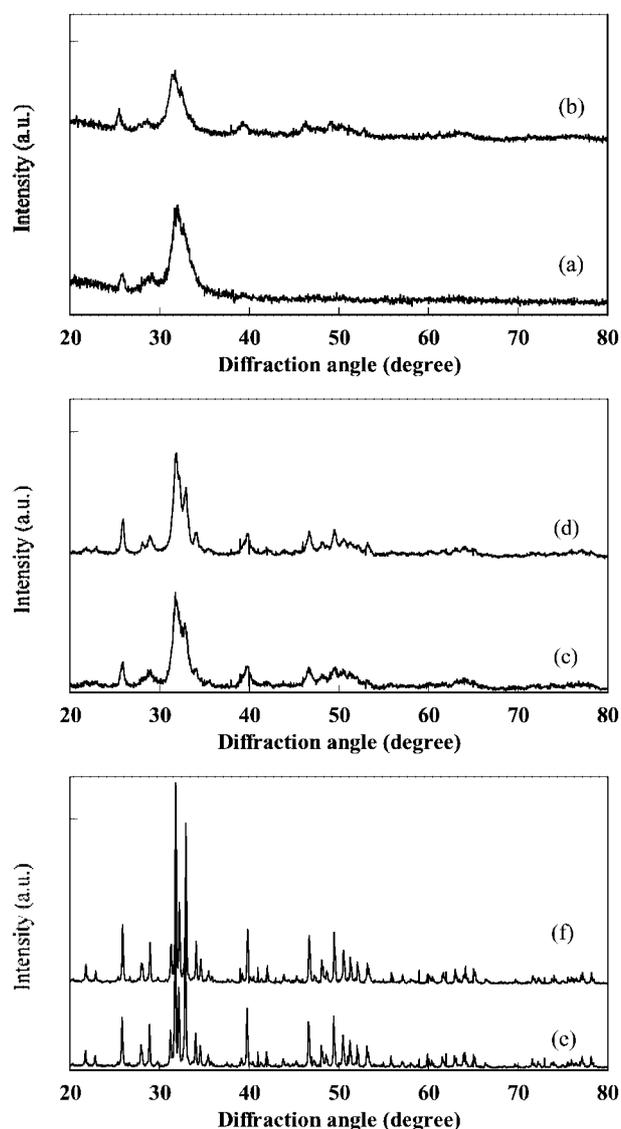


Fig. 3. X-ray diffraction patterns of samples. Raw fish bone before (a) and after a removal test (b), fish bone ceramic heated at 600°C before (c) and after a removal test (d), and fish bone ceramic powder heated at 900°C before (e) and after a removal test (f).

showed similar broad feature, additionally with new weak signals those were corresponding to crystalline hydroxyapatite. Figures 3(c) and 3(d) shows the similar feature of a

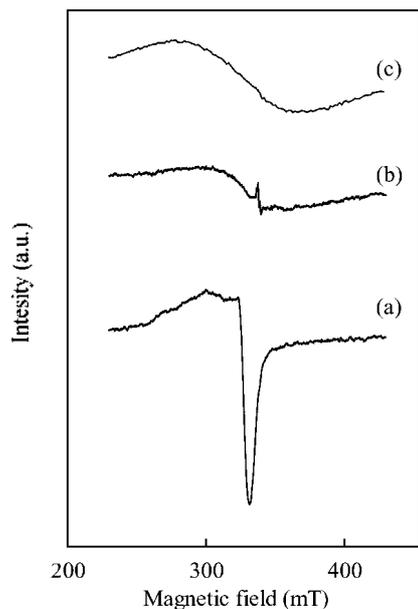


Fig. 4. Electron spin resonance of three fish bone samples after a removal test for 6 days; (a) raw fish bone, (b) heated at 600°C, (c) heated at 900°C.

sample heated at 600°C, which was better crystallized hydroxyapatite than a raw bone. Figures 3(e) and 3(f) suggested that fish-bone ceramic, when heated at 900°C, showed high crystallinity of hydroxyapatite both before and after removal test. Figures 3(a)–3(d) suggest the slight modification of starting hydroxyapatite occur after a copper removal test. Thus, the removal test induces the crystallization of original hydroxyapatite, which is indicated by appearance of fine several peaks at around 40–50°. These diffraction peaks correspond to the crystal plane with small interatomic distance, which should appear in a more crystallized sample. Since the kinetic constant is the same for all samples at a soaking stage after 30 minutes, the whole performance of removal depends on the initial fast reaction for a short time less than a few minutes, as shown in Fig. 2. These structural changes seem to correspond to removal efficiency among three fish bone samples.

3.3 ESR spectra of Cu(II)

Figure 4 showed the ESR spectra of three powders after testing for 6 days. Since the copper species of Cu(I) and Cu(0) (metal cluster) are not paramagnetic, the ESR of samples should suggest the local state of Cu(II). Misono and Hall¹³ observed the ESR of a dilute Cu containing hydroxyapatite, and determined *g*-parameters of the fine structure with an axial component. They prepared Cu-doped hydroxyapatite with Cu/Ca ratio of 0.0025 by the coprecipitation of aqueous H₃PO₄, Ca(OH)₂ and copper. In this work, the spectrum of a raw bone (a) in Fig. 4 is essentially the same (however it is broader) as that of Cu(II) in their paper. The Cu/Ca ratios after testing are 0.045, 0.053, and 0.026 for a raw, 600°C-heated, and 900°C-heated sample, respectively. Since the concentration of copper in a raw bone sample is over 20 times higher than that in the reference, the spectrum should be broader even if Cu(II) is entirely doped in the crystal lattice of hydroxyapatite. The *g*-parameters of present ESR (Fig. 4(a)) were measured as those *g*_⊥ = 2.036 (at 331.5 mT) and *g*_∥ = 2.411 (at 280 mT) with the A-factor of 13 mT. These values are sufficiently consistent with those in the

previous reference,¹³ if the error due to broadening in a spectrum is considered. Therefore, in the case of raw bone hydroxyapatite, divalent copper cation is sited in the same state (Ca site) as coprecipitated Cu-doped hydroxyapatite. The ESR result suggests the presence of such active Ca sites as easily ion-exchanged with Cu(II) during a soaking experiment if the raw bone is used. In the case of fish bone heated at 600°C and 900°C, the intensity of ESR was lower and showed broad feature, as (b) and (c) in Fig. 4. The *g*-value of broad lines was 2.085 (at around 330 mT) in both spectra (b) and (c). The broad ESR indicates the existence of strong interaction among closely distributed paramagnetic species of Cu in hydroxyapatite. Since their sintering through heat treatment results in low surface area of powders, the concentration of copper on the surface is far higher than that of a raw bone after testing. In this case, the detailed site or state of copper in hydroxyapatite cannot be analyzed. However, a part of removal copper is assumed to site in hydroxyapatite with close distance. In (b) of Fig. 4, an additional sharp ESR is observed at 338 mT. The detailed measurement in narrow magnetic range revealed a fine structure corresponding to *g* = 2.0075, 2.0015, and 1.9968. Their values and line shape are consistent with those of an active oxygen molecule, O₂⁻, which is observed as excited oxygen species selectively adsorbed on catalyst surface.¹⁴ Although it is not known why this spectrum appeared in a sample of a fish bone heated at 600°C, followed by a copper removal test, this ESR suggests that a certain reaction occurred to form such active species.

4. Discussion

The ESR of a raw bone suggests the site occupation the same Ca site as in coprecipitated Cu-doped hydroxyapatite in the crystal lattice. This will be most likely derived by the ion-exchange process between Ca(II) and aqueous Cu(II). For present fish bone originated hydroxyapatite, the ion-exchange reaction must be effective. However, better removal performance is obtained for a sample heated at 600°C, in which little clear site occupation of Cu (ESR) and large structural modification (XRD) are observed. In the case of a sample produced at 600°C, because a simple soaking procedure in aqueous copper solution must not induce active oxygen species, the appearance of O₂⁻ (Fig. 4(b)) might be related with the structural change of hydroxyapatite which was observed by XRD (Fig. 4). For the better performance of removal, possible mechanism besides ion-exchange is the dissolution-precipitation process, which is proposed for lead immobilization, however no precipitation is observed by scanning electron microscopy in this experiment. The broad feature of XRD indicates the introduction of large strain and the reduction of crystalline size for hydroxyapatite microcrystals after testing. The immobilization of copper in acid solution to hydroxyapatite results in the structural modification, the decomposition of microcrystals as well as the introduction of active oxygen. The removal rate versus time shows the two-step phenomenon where the initial fast removal occur in a few minutes, and then slow or steady process progresses with the same kinetic constant. The better removal efficiency of a fish bone ceramic produced at 600°C is assumed to relate with the first apparent adsorption or reaction of Cu in 2 minutes. This fast reaction cannot be explained by the relatively slow diffusion of ionexchange process. Therefore, we conclude that the whole removal process consists of first rapid reaction of Cu on hydroxyapatite or its decomposition-precipitation and secondary slow steady process of ion-exchange.

5. Summary

Regarding with copper immobilization operation for waste water, the authors have found that the application of effective heat treatment on raw fish bone at 600°C is useful. This heat procedure accelerates copper removal rate and improves total amount of removed copper from water. The XRD and ESR analyses suggest the combined mechanism of ion-exchange and structural modification in removing process of aqueous copper with fish bone hydroxyapatite. The present results indicate a useful feature of inexpensive fish-bone waste-originated hydroxyapatite ceramic, which is applied to waste water management. This work provides the possibility of fish bone waste as metal removal materials, which are inexpensive and highly compatible to civil life and material recycle.

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