EVALUATION OF CADMIUM REMOVAL IN SOLUTION USING VARIOUS HYDROXYAPATITES AND CATTLE BONE

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Keywords: hydroxyapatite, pores, cadmium, removal, microstructures, cattle bone, cadmium

Abstract: Porous and dense hydroxyapatites were prepared at 900 to 1300°C in air atmosphere by the pressureless sintering technique. In the present paper, the usage of these synthesized hydroxyapatites ceramics and porous hydroxyapatite from the cattle bone as an industrial waste was attempted with a view to the removal of Cd²⁺ ion from the polluted water. The pore characteristics of these hydroxyapatites sintered ceramics and cattle bone were evaluated by the mercury porosimeter. Especially, the ability of Cd²⁺ ion into these hydroxyapatites ceramics with various types of microstructures was investigated by an ICP equipment. Cd removability of HAp in 100 ppm Cd solution at pH 6.5 was twice higher than that of the active carbon. Especially, porous HAp and massive cattle bone possessed higher ability, compared to dense HAp, because of their high surface area.

INTRODUCTION

Recently, in farms and factory used-place, the removal treatments of various toxic substances are desired, since environmental standard of soil environment and drainage became severe. The heavy metal like Cd is of course noxious for the ecosystem, because it is a very toxic substance for human body. It is known that the long term take of Cd for human causes the calcium metabolism abnormality and osteopathy. Therefore, the law on pollution control of the soil and water has designated Cd in specified toxic substance, the environmental standard below 0.01 ppm.

Actually, Cd is utilized for the actuality in various industrial product manufacturing, for example, electroplating and battery factories. There is a possibility that Cd have been already disposed into the environment in the manufacturing process in the area near these factories as waste and also accumulated in the soil around the mine. Therefore, it is doubted that the soil of which the Cd concentration is comparatively high exists and that Cd is concentrated in crops such as the rice plant. In fact, large amount of polluted rice in which concentration of heavy metal such as Cd is high or relatively high, are stored at many stacks. Therefore, the removal of harmful Cd in the soil and water in the crop-land is required the reduction, so the development of remediying polluted soil and water become an emergent problem. Generally, utilization of zeolite, activated carbon and various adsorbents such as the ion-exchange resin etc are variously tried for collection or purification of the heavy metal ion. However, the collection of Cd on the level of some ppm and at the same time the treatment of large amounts of polluted maters (soil and water) are significantly difficult to carry out because of the low collection and adsorption ability and cost-concerned problems. Consequently, recently, the development of a new material for the purification of soil and water is especially required. We expect that hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂; HAp) can be a candidate material for the removal of Cd, because of its high ion exchange ability. Although the hydroxyapatite is a major component of organism bone and tooth, Cd is easily accumulated in organism bones and resulted in the disease. It is thought that Cd²⁺ ion is exchanged for the position of Ca in the apatite structure on HAp which is a component of bone and tooth. In addition to excellent cation exchange capacity of HAp, the usage of HAp as a material for the removal of Cd under the environment is considered to be a low environmental loading technique. Furthermore, in this study, the usage of heat-treated cattle bone, i.e. industrial waste, was attempted for source of HAp. The purpose in this paper is to examine of Cd removal ability of pure HAp and other HAp such as cattle bone and consequently develop the environmental low-loading technique for removal of heavy metal.

EXPERIMENTAL PROCEDURES

The hydroxyapatite powder (Taihei Chemistry, HAP-200) was used as a starting material. This HAp powder was compacted after SUS molding (a diameter: 20mm, thickness: 4mm) and then treated using CIP with 200 MPa. HAp sintered body was produced by heat-treating these compacted ceramics
through the pressureless sintering at 900℃, 1100℃ and 1300℃ in air. And, the massive HAp porous body (Eccera Co.) of the cattle bone after heat-treatment at 1000℃ was used for the comparison to sintered HAp samples. Table 1 shows result of analysis of the impurity of the massive HAp from the cattle bone.

Each density of HAp sintered body was measured by the Archimedes method. And, component of sintered ceramics were identified by X-ray diffraction (XRD; Rigaku, RINT-2500). In addition, microstructures of massive cattle bone and sintered HAp ceramics were observed by a scanning electron microscope (SEM; HITACHI, F-800). The specific surface area of each sample was measured (Micromeritics Co. Gemini-2370). The pore-size distribution was evaluated on the porous sample by the mercury porosimeter (Micromeritics Co., Autopore III). The ion exchange capacity evaluation of Cd for HAp was carried out with the cattle bone, sintered ceramics and activated carbon. 0.1g each bulky sample was weighed, and they were added to 100ppm Cd standard solution (Wako Junyaku). Cd solution was prepared from addition of Cd(NO₃)₂ into HNO₃ solution and furthermore NaOH solution for adjusting pH. In fact, the experiment was almost carried out in range of pH 6 to 7 at room temperature, since the precipitation of Cd(OH)₃ is generated in higher pH region. Cd removability of the each hydroxyapatite sample was evaluated at the room temperature without agitation of each sample in Cd standard solution (100ppm). After the progress for the immersion, HAp samples were filtered with Buchner funnel and the Cd concentration was measured using the inductive coupling plasma (ICP) technique. For the comparison, removal tests of Cd were also carried out with active carbon powder (Wako Junyaku).

| Table 1 Various impurities (ppm) of cattle bone |
|---|---|---|---|---|---|
| Fe  | Mg  | Na  | K   | Ba  | Zn  |
| 154 | 6900| 7600| 160 | 90  | 92  |

RESULTS AND DISCUSSION

HAp sintered ceramics were obtained after pressureless sintering technique at various sintering temperatures. Figure 1 shows the relation of density and sintering temperatures. Sample sintered at 1200℃ showed 90 % of theoretical density. In the sample sintered at 900℃ and 1100℃, the relative density was 55 % and 80 %, respectively. Dense HAp samples with 99.8% were obtained at 1300℃. Various porous body HAp sintered ceramics were obtained by pressureless sintering technique at various sintering temperatures. As-received cattle bone had 50 % of theoretical density.

The constituent phase was identified from these HAp samples by XRD. Figure 2 shows XRD patterns of the sintered body by sintering at 900℃ and 1300℃. All sample sintered in 900℃ and 1300℃, from the result of XRD, showed the hydroxyapatite monophase without β-tricalcium phosphate (β-TCP) and α-tricalcium phosphate (α-TCP). And, in case of massive cattle bone, the constituent phase was only the hydroxyapatite monophase.

The microstructures of various HAp were observed by SEM. Figure 3 shows typical SEM photographs for HAp ceramics sintered at 900℃ and 1300℃. SEM
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Observations indicate that HAp ceramics sintered at 1300°C showed the coarse matrix with the grain size of about 3–5 μm, and contained some largely elongated grains. Porous HAp sample with 45% porosity, sintered at 900°C, had fine microstructure with average grain size below 0.5 μm. Massive cattle bone indicated finer microstructure with approximately 1 μm, compared to HAp ceramics sintered at 1300°C.

The pore-size distribution was evaluated on porous HAp sintered at 900°C, massive cattle bone and activated carbon and their results are shown in Figure 4. Massive cattle bone had small amount of pores with both a few hundreds μm and below 0.5 μm in diameter. Porous HAp sintered at 900°C showed large amount of sub-micron pores and a little small pore below 50 μm in diameter. On the other hand, the pore-size distribution of active carbon was existed between sub-micron and 10 μm, majority of pores below 1 μm.

The results of the specific surface area (BET value) were measured for porous HAp sintered body sintered at 900°C, massive cattle bone and activated carbon. BET values are summarized in Table 2. Porous HAp (about 45% porosity) sintered at 900°C showed 4–5 m²/g of BET value, whereas massive cattle bone had 2 m²/g. In contrast, active carbon had a specific surface of about 1000 m²/g.

For the massive cattle bone, porous HAp (55% of relative density) sintered at 900°C and dense HAp (95% of relative density) at 1300°C, the removal tests of Cd were carried out. The relations of removal amount of Cd and immersion times are shown in Figure 5. For the comparison, the results for activated carbon are included in this figure. Activated carbon showed a little ability of Cd removal from Cd solution due to its adsorption, up to 15% removal of Cd after the immersion for 48 h, suggesting that the usage of this activated carbon is not so useful for Cd removal. However, dense HAp had 25% removal of Cd from starting solution. On the contrary, both porous HAp samples and massive cattle bone indicated the higher removal of Cd in Cd solution than dense HAp samples, especially in the immersion within a few hours.

Table 2 Specific surface areas of various samples: porous HAp sintered at 900°C (porosity=45%), porous HAp from cattle bone (porosity=50%), and activated carbon.

<table>
<thead>
<tr>
<th>Materials</th>
<th>BET value (m²/g)</th>
</tr>
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<tbody>
<tr>
<td>porous HAp sintered at 900°C</td>
<td>4.7</td>
</tr>
<tr>
<td>cattle bone (porosity: 50%)</td>
<td>1.8</td>
</tr>
<tr>
<td>activated carbon</td>
<td>937</td>
</tr>
</tbody>
</table>

Fig. 3 SEM photographs of hydroxyapatite ceramics sintered at (A) 900°C, (B) 1300°C, (C) cattle bone and (D) activated carbon.

Fig. 4 Pore size distribution of hydroxyapatite ceramics sintered at (A) 900°C, (B) cattle bone and (C) activated carbon.
obvious that these HAp samples possess the excellent ability of Cd removal, compared to activated carbon, owing to the high ion exchange ability in apatite structure. Consequently, porous HAp could be applicable to removing Cd in polluted water. In addition, this excellent ability of Cd removal for massive cattle bone and porous HAp samples, superior to dense HAp, is thought to be caused by their higher specific surface area than dense HAp.

Bulky samples after soaking in Cd solution for 48 hours were evaluated by SEM observation and XRD. It was confirmed that sample obtained after Cd removal were composed of only HAp phase without any other, as shown in Figure 6. In addition, SEM observations of microstructure after the Cd removal for dense and porous HAp and massive cattle bone are shown in Figure 7. The change of microstructures after Cd removal experiments, dissolution of HAp surface and new precipitation could not be for porous HAp, dense HAp and massive cattle bone.

Therefore, from results of Cd removal tests at room temperature in pH 6.5 region without the agitation, it was judged that dissolution of the hydroxyapatite and transition to DCPD were not generated during Cd$^{2+}$ ion-exchange into apatite. Because the ion radius of Cd (0.99 Å) is the almost same as Ca$^{2+}$ (0.97 Å), Cd$^{2+}$ ions are thought to be easily ion-exchanged into Ca site. According to previous results on ion exchange of HAp in 1000 ppm Cd solution given by Monma, it is shown that approximately 90 % of Cd was removed after short-term immersion and cation in which the ionic radius is bigger than Ca tends to replace with the Ca II-site (Screw axis Ca) and cation having a smaller ion radius than Ca$^{2+}$ is exchanged in the Ca I-site (Columnar Ca). Suzuki et al reported that at lower pH (below pH 5.5) region Cd$^{2+}$ could be exchanged into both Ca I- and II-sites. However, since, in low pH region, problem of the dissolution and structure change of HAp to DCPD and OCP are existed, the evaluation of the exchangeability in low pH is difficult. Also, in the solution with high concentration of Cd$^{2+}$, the generation of Cd$_{10}$(PO$_4$)$_6$(OH)$_2$ is apprehended on the immersion test in Cd solution.

Recently, Jeanjean et al reported that the ion exchange of Cd$^{2+}$ for Ca site in HAp was greatly dependent on pH and that Cd$^{2+}$ ion exchanged only for the Ca II-site (Screw axis Ca) in HAp. They reported that the exchange of Cd$^{2+}$ in HAp was limitedly generated only in the surface HAp crystal.
Furthermore, Cd removal in solution seems to progress by the ion exchange on HAp surface, because Cd was rapidly removed especially within immersion for a few hours for porous HAP than for dense HAP ceramics, as above-mentioned.

From the above result, it was proven that Cd removal from starting Cd solution was about 30% for porous HAP ceramics and 20% for dense HAP ceramics, higher than activated carbon. It is thought that the ion exchange of Cd was generated near the surface of HAp at the pH6.5 in Cd solution with a concentration of 100 ppm.

CONCLUSION

Dense HAp and porous HAp ceramics were prepared by sintering at various temperatures and their microstructures were evaluated. Cd removal ability was evaluated for these dense HAp, porous HAp, and massive cattle bone. Cd removability of HAp in 100 ppm Cd solution at pH 6.5 was twice higher than that of the active carbon. Especially, porous HAp and massive cattle bone possessed higher ability, compared to dense HAp, because of their high surface area. Consequently, it is thought that Cd removal in solution seems to progress by the ion exchange on HAp surface, because Cd was rapidly removed especially within immersion for a few hours for porous HAP than for dense HAP ceramics. In addition, the usage of cattle bone, i.e. industrial waste, consequently will develop the environmental low-loading technique for removal of Cd$^{2+}$ in polluted water and soil circumstances.

ACKNOWLEDGEMENT

This work was supported by Kansai Research Foundation for technology promotion.

REFERENCES