Effect of preparation temperature on the ability of bone char to remove fluoride ion and organic contaminants

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The excessive intake of fluoride ion (F⁻) from drinking water causes dental and skeletal disorders and thus methods for the removal of F⁻ from water are desired. A method for removing organic contaminants from water is also desired. Bone char is a composite material composed of char and hydroxyapatite (HA). Bone char can remove F⁻ because of the HA in the bone char. It is expected that bone char containing small grain size HA will remove F⁻ effectively because of its high surface area. Additionally, the char in bone char can remove organic matter from contaminated water, and controlling the amount of char in bone char is also important. Bone char is fabricated by heating porcine bone at 200–600°C for 1 h under a limited oxygen supply. The grain size of HA in these samples increases with an increase in heating temperature. The amount of organic matter and char in these samples decreases with an increase in heating temperature. Bone char with a controlled HA grain size and the amount of char was fabricated by changing the heating temperature. Their ability to remove F⁻ and methylene blue (MB), as a model organic contaminant, was evaluated by immersing the samples in F⁻-containing and MB-containing solutions. The sample prepared at 400°C was able to remove most of the F⁻ and less than 1.5 mg·dm⁻³ F⁻ remained, which is within the World Health Organization recommended level for drinking water. Additionally, the sample prepared at 400°C was also able to remove most of the MB. Bone char can thus be used to remove F⁻ and organic contaminants.

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1. Introduction

The concentration of fluoride ion (F⁻) in drinking water is an important factor in evaluating the quality of water for human consumption.¹⁻³ F⁻ in drinking water has both beneficial and detrimental effects on human health. F⁻ has a protective effect against tooth decay at a low dose,² but excessive F⁻ causes dental and skeletal disorders. The consumption of drinking water containing excessive F⁻ (≥1.5 mg·dm⁻³) leads to fluorosis,³ and the World Health Organization (WHO) has recommended a F⁻ concentration less than 1.5 mg·dm⁻³ in drinking water.¹ However, ground water in many areas around the world has a high F⁻ concentration.⁴⁻⁵ F⁻ in water is harmful to human health and its removal is important. This study focused on the use of bone char fabricated by heating animal bone as a method to remove F⁻. It has been reported that bone char can remove F⁻.⁶⁻⁹ Bone char is a composite of char and hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂; HA].¹⁰ It has been reported that HA is able to remove F⁻²,¹¹ and the HA in bone char contributes towards the removal of F⁻. Activated carbon can remove organic matter from contaminated water.¹²⁻¹³ Therefore, bone char can also be used to remove organic matter.

Bone char that can effectively remove water contaminants can be obtained by controlling the HA grain size and the amount of char in bone char. HA is controlled to obtain a large surface area for F⁻ removal. However, few studies have focused on HA in bone char and, therefore, it is not clear how the HA in the bone char affects the removal of F⁻ and the removal of organic matter.¹

The grain size of HA is affected significantly by the heating temperature. In this study, bone char was fabricated under various heating temperatures to control the grain size of HA and the amount of char in the bone char. Its ability to remove water contaminants was also investigated to determine the optimum temperature to obtain bone char for the elimination of F⁻ and other contaminants.

2. Materials and methods

2.1 Preparation of the samples

About 3 g of commercial porcine bone was placed in a 15-cm³ alumina crucible. The alumina crucible was capped to limit the oxygen supply for the production of char, and it was placed in an electrical furnace. The bone was heated at 200–600°C for 1 h. The temperature was set to 200°C to avoid charring the organic matter of the bone, 400°C to change the organic matter of the bone to char, and 600°C to promote the grain growth of HA in the bone char. The samples heated at 200, 400 and 600°C were designated BC200, BC400 and BC600, respectively. The sample that did not undergo heat treatment, namely the original bone, was designated BONE.

The crystalline phase of the samples was determined by X-ray diffractometry (XRD, RINT2200VL; Rigaku, Tokyo, Japan) using CuKα radiation. Sample components were determined by thermogravimetric-differential thermal analysis (TG-DTA, Thermo Plus 2 TG8120; Rigaku, Tokyo, Japan). The temperature was increased from room temperature to 900°C at 10°C·min⁻¹ in air. The microstructure of the samples was observed using transmission electron microscopy (TEM, HF-2000; Hitachi, Tokyo, Japan). The samples were ground by a mortar. The ground samples were dispersed in ethanol, and the suspension was dropped on...
a TEM micro-grid (NP-C15; Okenshoji, Tokyo, Japan). The apparent specific surface area of the HA particles in the samples was calculated from TEM photographs by assuming that the particle shape was a capsule obtained by combining two hemispheres with a column. The specific surface area of the samples was determined by the N₂-BET method using an Autosorb-iQ ASIQM0000-3 (Quanachrome Instruments, Florida, USA).

2.2 Removal of F⁻ and MB

The ability of the samples to remove F⁻ was evaluated. A 20 mg·dm⁻³ F⁻ solution was prepared by diluting a NaF solution (Wako Pure Chemical Industries, Ltd., Osaka, Japan). Samples of 0.10 g were added to 15 cm³ of the F⁻ solution. The solutions were subjected to shaking at 125 rpm at 30°C from 15 to 360 min. After these predetermined periods, a supernatant solution was obtained by centrifugation. Total ionic strength adjustment buffer of 3 cm³ was added to 13 cm³ of the supernatant solution, and the F⁻ concentration of the solution was measured using a F⁻ electrode (6561-10C; Horiba, Ltd., Kyoto, Japan).

The ability of the samples to remove organic matter was evaluated using methylene blue (MB) as a model organic matter. The MB is often used for evaluating the adsorption ability of activated carbon. A 400 mg·dm⁻³ MB solution was prepared by dissolving MB (Merck KGaA, Darmstadt, Germany) in the pH 7 phosphate buffer solution which was prepared by mixing a 0.067 mol·dm⁻³ potassium dihydrogen phosphate (Wako Pure Chemical Industries, Ltd., Osaka, Japan) solution and a 0.067 mol·dm⁻³ disodium hydrogen phosphate (Wako Pure Chemical Industries, Ltd., Osaka, Japan) solution at a volume ratio of 4:6. Samples of 0.10 g were added to 12 cm³ of the MB solution. The solutions were subjected to 120 min of shaking at 30°C. Because the decrease in MB concentration almost stopped and the equilibrium seemed to have been achieved at 120 min, 120 min was selected for the experiments. After 120 min, the MB concentration of the solutions was determined by MB's absorbance at 665 nm using an ultraviolet-visible spectrometer (IUV-1240; AS ONE, Osaka, Japan). For comparison, the removal of F⁻ and MB by the bone sample that did not undergo heat treatment (BONE) was also carried out. Commercial HA (Ube Material Industries, Ltd., Yamaguchi, Japan) and commercial activated carbon (derived from coconut shell; Nacalai Tesque, Inc., Kyoto, Japan) were also evaluated.

3. Results and discussion

3.1 Characterization of the samples

Figure 1 shows photographs of the samples. The BONE and BC200 samples were white. The sample obtained by heating at 400°C was black. The sample obtained by heating at 600°C was gray.

Figure 2 shows TG–DTA curves for the BC400 sample in air. The weight of the sample decreased with an endothermic reaction between 30 and 200°C. The weight of the sample then decreased with an exothermic reaction between 300 and 500°C, and at about 700°C. No significant weight change was detected at higher than 800°C.

Figure 3 shows XRD patterns of the samples. Diffraction lines from HA were detected in all the samples. We confirmed that the BONE sample contained HA and that the HA remained even after heat treatment. Its peak became sharper with increasing temperature. The HA grain size in the samples, therefore, increased and the crystallinity of HA in these samples likely increased with an increase in temperature.

TEM photographs of the samples are shown in Fig. 4. The black parts of the photographs indicate HA grains. The HA grain size in these samples increased with an increase in temperature. It has been reported that the grain size of HA in bone increased upon heat treatment at higher than 600°C, and our XRD and...
TEM results are consistent with those from the previous report. The compositions of the samples were estimated from the TG-DTA data. Onishi et al. reported the thermal decomposition of porcine bone. They reported that the decreases in weight under 220°C came from the removal of water, and the decreases in weight between 300 and 500°C, and over 650°C came from the decomposition of organic matter. When the crystalline phase of the sample after TG-DTA analysis was examined by XRD, small diffraction lines from calcium oxide were also detected in the sample in addition to large diffraction lines from HA. The amount of calcium oxide was small, because the diffraction lines from calcium oxide were quite small. According to Fig. 3, only diffraction lines from HA were detected in the BC600 sample. From these results, it was speculated that both of the thermal decomposition of HA and burning of organic matter and char were occurred at about 700°C, and it was not able to separate weight loss derived from the thermal decomposition of HA and the burning of organic matter and char. However, the decreases in weight at about 700°C were assumed to come from the burning of organic matter and char, because the amount of formed calcium oxide was small and the weight of the sample decreased with an exothermic reaction at about 700°C. We assumed that the decrease in weight between 30 and 200°C came from the removal of water, and the decrease in weight between 200 and 800°C came from the burning of organic matter and char, respectively. The substance that remained at 800°C was assumed to be HA. Table 1 shows the composition of the samples. BONE was assumed to be composed of 61 mass% HA, 26 mass% organic matter and 13 mass% water. The amount of organic matter and char in these samples decreased with an increase in the heating temperature. At a heating temperature of 200°C, the decrease in the amount of organic matter and char in the samples as a result of heating was smaller than that of the other samples. Additionally, according to Fig. 1, the color of the BC200 sample hardly changed from the bone that was not subjected to heat treatment. These results indicate that the organic matter in the BC200 sample did not convert to char. However, at heating temperatures of 400 and 600°C, the decrease in the amount of organic matter and char in the samples was higher than that of the other samples. According to Fig. 1, the BC400 and BC600 samples became black and gray, respectively. These results indicate that the organic matter in the BC400 and BC600 samples changed to char.

Table 1. Compositions of the samples

| Sample | Component/mass% |
|--------|----------------|
|        | HA | Organic matters or char | Water |
| BONE   | 61 | 26 | 13 |
| BC200  | 66 | 26 | 8  |
| BC400  | 80 | 14 | 6  |
| BC600  | 93 | 4  | 3  |

The HA grain sizes of the samples were measured using the TEM photographs, and the apparent specific surface area of HA in the samples was calculated from the grain size and the density of HA, which is 3.16 g cm⁻³. These data are shown in Table 2. The apparent specific surface area of HA in the samples decreases with an increase in heating temperature. The specific surface area of the samples, as determined by the N₂-BET method, is also shown. The specific surface areas of the BONE and BC200 samples are smaller than those of the BC400 and BC600 samples. The specific surface area of the BC400 sample was the highest among the studied samples. The specific surface area of the BC600 sample was smaller than that of the BC400 sample. The specific surface areas of the samples measured by the N₂-BET method were less than the apparent specific surface areas of HA calculated using the TEM photographs. These results suggest that the HA particles of the samples were covered by organic matter and char. The specific surface area of BC600 was much higher than that of BONE and BC200. These results imply that the dense organic matter was changed to porous char upon heating.

3.2 Removal of F⁻ and MB

Figure 5 shows changes in F⁻ concentration during the removal test. Except for the commercial activated carbon, all the samples resulted in a decrease in F⁻ concentration in solution with time. These results indicate that the commercial activated carbon did not remove F⁻ and that the HA component in the
samples was responsible for removing the F⁻. It has previously been reported that HA³,⁴ and bone char⁵⁻⁹ can remove F⁻ from solutions, and our result is consistent with these reports. The BC400 sample was able to remove F⁻ most effectively and a F⁻ concentration less than 1.5 mg·dm⁻³, as recommended by the WHO¹. When the crystalline phase of the BC400 sample after removal test was determined by XRD, the obtained XRD pattern was almost same as that of the BC400 sample before removal test. Sternitzke et al. reported that the removal of F⁻ by HA occurred by forming the fluorapatite [Ca₁₀(PO₄)₆F₂] layer on the HA surface.² It is assumed that a larger specific surface area for HA favors the F⁻ removal rate. In fact, Gao et al. reported that smaller HA particles removed more F⁻. From the apparent specific surface area of HA that was calculated using the TEM photographs of the samples, the BONE and BC200 samples should have a higher removal ability than the other samples. However, these samples had a lower removal ability than the BC400 sample. According to Table 1, the organic component of the BC400 sample was less than that of the BONE and BC200 samples. We speculate that the organic matter or the char prevents the F⁻ from approaching HA. The specific surface area of the BC400 sample that was determined by the N₂-BET method was higher than that of the BONE and BC200 samples (Table 2). We speculate that the pores through which F⁻ approaches HA formed during the organic matter to char transformation in the samples. By comparing the BC600 sample and commercial HA with the BC400 sample, it is obvious that the BC400 sample was able to remove F⁻ more efficiently, although less char formed in the BC600 sample and char was not present in the commercial HA.

This result can be explained by considering the apparent specific surface area of HA, because in the BC600 sample and in the commercial HA sample it was smaller than that in the BC400 sample. It was assumed that the BC400 sample had the highest removal ability because of the high apparent specific surface area of HA and less prevention of the F⁻ approaching to HA due to smaller amount of char.

Figure 6 shows the residual MB concentrations after the removal tests. The BC400 sample and the commercial activated carbon resulted in a decrease in the MB solution concentration. However, the BONE, BC200, BC600 and commercial HA samples hardly affected the concentration of MB in solution. The fact that commercial HA hardly affected the MB concentration indicates that the removal of MB by bone char depends on the char component of the samples. The BC400 sample was able to remove MB, but the BONE, BC200 and BC600 samples were not able to remove MB. Therefore, it is important to transform the organic matter into char without affecting the existing char for the removal of MB.

4. Conclusion

Bone char with a controlled amount of char and a controlled HA grain size was fabricated by changing the heating temperature. The bone char that was prepared at 400°C contained relatively less char and had a higher HA apparent specific surface area, and it removed F⁻ efficiently in addition to MB. Bone char can thus be used for the removal of F⁻ and organic contaminants.

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