

# ADSORPTION PROPERTIES OF HYDROXYAPATITE PRODUCED FROM FISH BONES FOR FLUORINE

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**ABSTRACT:** Fluorine is contained in most rocks in the earth's crust, and the occurrence of groundwater contamination by fluorine is most likely of natural origin. More than 200 million people worldwide are estimated to be forced to use drinking water with fluorine levels exceeding the WHO guideline value, and 60 to 70 million people are reported to suffer from fluorosis in 25 countries worldwide. In Asian countries, groundwater is the main source of drinking water. The removal of fluorine from groundwater is urgently needed to enable us to drink it safely. General fluorine removal technologies include chemical precipitation and adsorption methods. However, there are problems in terms of treatment capacity and cost. On the other hand, bone charcoal made by carbonizing animal bones such as cattle bones, which are food waste, is widely used as a fluorine adsorbent. This is because hydroxyapatite, the main component of bones and teeth, easily absorbs fluorine. Thus, in this study, fish bones, which are fishery waste, are focused on. The reason is that hydroxyapatite produced by calcining fish bones may have the capacity to adsorb fluorine. Therefore, immersion and shaking tests are conducted by using the hydroxyapatite produced from fish bones as an adsorbent, and its adsorption performance for fluorine is examined. The test results indicated that fluorine adsorption was dependent on pH and that the hydroxyapatite produced from fish bones could adsorb more fluorine by maintaining the pH at 3.

*Keywords: Fishery waste, Fish bones, Hydroxyapatite, Fluorine, Adsorption*

## 1. INTRODUCTION

In the 6th goal of the Sustainable Development Goals (SDGs), it is aimed that "achieving universal and equitable access to safe and affordable drinking water for all by 2030". However, there are only 11 countries in the world where people can drink safe water from the tap, as is the case in Japan, and most of the other countries do not have water supply infrastructure [1]. In areas without a water supply system, groundwater is mainly used as drinking water. On the other hand, groundwater contamination by toxic substances such as heavy metals has been occurring frequently in recent years. Among heavy metals, fluorine is contained in most rocks in the earth's crust, and the occurrence of groundwater contamination by fluorine is most likely of natural origin. As noted in [2], it is estimated that more than 200 million people worldwide are forced to use drinking water with fluorine concentrations exceeding the WHO drinking water guideline value of 1.5 mg/L. Although the uptake of fluorine in low concentrations does not cause problems in the human body, its excessive uptake causes fluorosis, which affects bones and teeth. According to [3] and [4], 60 to 70 million people are reported to suffer from fluorosis in 25 countries worldwide. In Asian countries, groundwater is the main source of

drinking water. The removal of fluorine from groundwater is urgently needed to enable us to drink it safely. On the other hand, as reported in [5] and [6], there are approximately 28,000 water sources of spring in Japan, some of which contain fluorine in high concentrations exceeding the uniform national effluent standards of 8 mg/L. This means that it is highly likely that fluorine is also contained in wastewater from the source at concentrations exceeding the uniform national effluent standards.

General fluorine removal technologies include chemical precipitation methods using calcium or aluminum salts and adsorption methods using reverse osmosis membranes or ion exchange resins. However, there are various problems in terms of treatment capacity and cost, such as the difficulty of reducing fluorine concentrations to levels that satisfy WHO guidelines even when large amounts of calcium and other substances are used, and the high cost of the materials involved in the fluorine removal [7]. Inexpensive fluorine removal technologies include the adsorption method using activated alumina and the Nalgonda method, which is precipitation removal using sulfate bands. However, there are problems regarding treatment capacity and sludge disposal generated during treatment. Therefore, there are not many fluorine technologies that satisfy both cost and treatment capacity. In other words, the materials used for

treatment are generally expensive for those with high treatment capacity, and inexpensive removal technologies usually have problems with treatment capacity. Therefore, there are few fluorine technologies that satisfy both the cost and the treatment capacity. On the other hand, bone charcoal made from carbonizing animal bones is widely used as a fluorine adsorbent [8]. Hydroxyapatite, the main component of bones and teeth, easily absorbs fluorine [9]. Focusing on its high fluorine removal performance and ease of procurement of raw materials, Miyazaki *et al.* [10] examined the use of chicken bone charcoal carbonized from chicken bones as an adsorbent and found that the disadvantages of fluorine adsorption using chicken bone charcoal are that fluorine removal takes time and the chicken bone charcoal itself must be treated with acid to improve its fluorine adsorption performance.

Thus, in this study, fish bones, which are fishery waste, are focused on. Referring to Japan's supply and demand of fish and shellfish in FY2020 [11], the amount of fishery waste such as fish residues in Japan is estimated to be about 2.3 million tons per year. Although fishery wastes are recycled as feed and fertilizer, only approximately 30% of them are recycled [12]. On the other hand, hydroxyapatite produced by calcining fish bones may have the capacity to adsorb fluorine. The hydroxyapatite produced from fish bones (Japanese Patent No. 6351008), developed by some of the authors, is produced by calcining and pulverizing discarded fish bones [13]. This apatite produced from fish bones adsorbs heavy metals well, but its adsorption performance for fluorine has not been verified. In this study, the adsorption performance of the hydroxyapatite produced from fish bones for fluorine is examined.

## 2. RESEARCH SIGNIFICANCE

Fluorine contamination of natural origin is a global problem, and there are problems with fluorine removal technology in terms of cost and so on. Thus, fish bones, which are disposed in large quantities but have been slow to be recycled, are focused on, and their reuse as fluorine adsorbent is examined. The significance of this study is not only the realization of fluorine removal with less inexpensive materials, which are fishery waste, but also its contribution to the achievement of the SDGs, such as equitable access to safe and affordable drinking water and waste reduction through reuse and recycling.

## 3. HYDROXYAPATITE PRODUCED FROM FISH BONES

Hydroxyapatite is one of the most representative

apatites, which is a group of crystal compounds with the basic composition of  $M_{10}(ZO_4)_6X_2$ , and is a basic calcium phosphate represented by  $Ca_{10}(PO_4)_6(OH)_2$  as the chemical formula. Hydroxyapatite has high adsorption performance, especially for amino acids, proteins and lipids. Besides this, it has many other functions such as

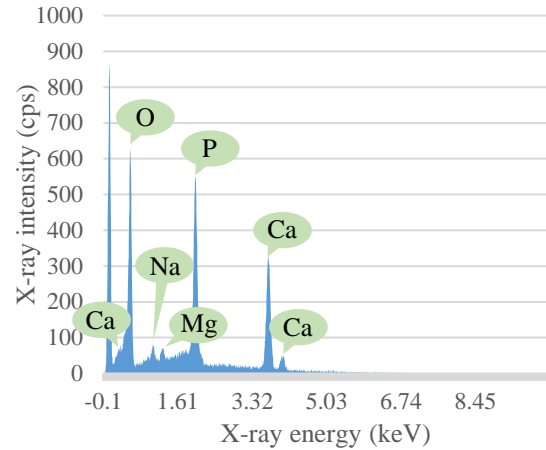


Fig. 1 Spectrum of hydroxyapatite produced from fish bones analyzed by EDX



Fig. 2 Fishbone Absorber (FbA)

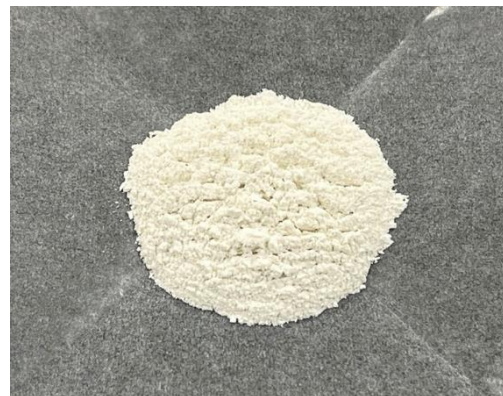


Fig. 3 Fishbone Powder (FbP)

ion-exchanging and catalytic properties. In addition, it has excellent biocompatibility since it is a major component of teeth and bones [14-18]. In recent years, research on the production of hydroxyapatite from wastes such as animal bones, eggshells, oyster shells and scallop shells is being conducted intensively [19-25].

As has mentioned above, the hydroxyapatite produced from fish bones was developed by some of the authors as a new way to reuse fish bones, which are discarded drastically at fish farms and fisheries processing plants. Fig. 1 shows the results of the component analysis of hydroxyapatite produced from fish bones analyzed by an energy dispersive X-ray (EDX) spectroscopy. The results indicate that hydroxyapatite produced from fish bones contains calcium phosphate as well as sodium and magnesium. Previous studies have shown that the solid hydroxyapatite produced by calcining fish bones (Fishbone Absorber: FbA, see Fig. 2) adsorb not only divalent cations such as zinc ( $Zn^{2+}$ ), cadmium ( $Cd^{2+}$ ), mercury ( $Hg^{2+}$ ) and manganese ( $Mn^{2+}$ ) in solutions, but also heavy metals such as trivalent chromium ( $Cr^{3+}$ ) in solutions [26]. In addition to heavy metals, FbA also has adsorption performance for radioactive materials such as strontium ( $Sr^{2+}$ ) [27]. In particular, it is confirmed that FbA has the ability to selectively adsorb strontium in solutions containing different chemical species such as sodium chloride and potassium chloride, as well as in pure water [28]. On the other hand, it is reported that the powder hydroxyapatite produced by calcining and pulverizing fish bones (Fishbone Powder: FbP, see Fig. 3) has a high adsorption ability for copper ( $Cu^{2+}$ ) as well as  $Zn^{2+}$  and  $Cd^{2+}$  [29]. Therefore, the adsorption performance of hydroxyapatite produced from fish bones has been verified mainly for heavy metals and radioactive substances in the form of cations in solution. However, its adsorption performance for anions such as halogens has not been verified. In this study, FbA and FbP are selected as adsorbents for fluorine with a view to further increasing the added value of hydroxyapatite produced from fish bones.

## 4. TEST METHOD

### 4.1 Shaking Test

In order to verify the adsorption performance of hydroxyapatite produced from fish bones for fluorine, a shaking test is conducted by adding FbP to a solution containing fluorine, and the adsorption performance of FbP for fluorine is evaluated. First, the fluorine standard solution is diluted to initial concentrations of 2, 3, and 10 mg/L, and the initial pH is adjusted to 3. According to Medellin *et al.* [30], it is reported that the fluorine adsorption

capacity decreases significantly as the pH of the solution increases, and the maximum fluorine adsorption capacity is shown when the solution pH is adjusted to 3. Referring to the literature, the initial pH of the solution is adjusted to 3 in the test. Next, 10 mL of the prepared solution is poured into a centrifuge tube and 20 and 50 mg of FbP are added, respectively. These are the specimens in the test. Then, these specimens are shaken at 200 rpm for 24 hours at 20 °C. After shaking, the test solution and FbP are separated by filtration through a membrane filter (0.45  $\mu m$  pore size). Finally, the pH and residual concentration of fluorine in the test solution are measured and analyzed with a pH meter and an absorbance spectrophotometer, respectively. In the test, a specimen without FbP (hereafter referred to as "Blank") is also prepared as a control specimen and tested under the same conditions. The test conditions are summarized in Table 1. In order to ensure reproducibility, each test is conducted three times each, and the average of the three tests is shown as the test result of the relevant test.

### 4.2 Immersion Test

In order to investigate the relationship between the adsorption performance of hydroxyapatite produced from fish bones and pH, an immersion test is conducted by adding FbA to a containing solution of fluorine with pH adjusted at a certain level, and the effect of pH on the adsorption performance of FbA is investigated. The reason why the immersion test is conducted using FbA as the adsorbent in the test is that only FbP can be used in the shaking test, and it is not possible to adjust pH sequentially. First, the fluorine standard solution is diluted to initial concentrations of 3 mg/L, and the initial pH is adjusted to 3 as in the shaking test. Next, 150 mL of the prepared solution is poured into a cylindrical container and a piece of FbA is added into the solution. These are the specimens in the test. These specimens are then immersed at 20 °C for 168 hours, and their progress are observed 24, 72, 120, and 168 hours after the start of the test. A pH should be adjusted to 3 every 12 hours. After a specified time in the immersion test, the supernatant solution of the

Table 1 Test conditions (In the case of shaking test)

Volume	10 mL
Initial concentration	2, 3, 10 mg/L
Initial pH	3
Temperature	20 °C
Mass of adsorbent	20, 50 mg
Shaking rate	200 rpm
Shaking time	24 hours

immersion test specimens is collected and the residual concentration of fluorine in the supernatant solution is analyzed with an absorbance spectrophotometer. In the test, a specimen without pH adjustment is also prepared for comparison and tested under the same conditions as the specimens with pH adjustment. The test conditions are summarized in Table 2. As with the shaking test, in order to ensure reproducibility, each test is conducted three times each, and the average of the three tests is shown as the test result of the relevant test.

## 5. RESULTS AND DISCUSSIONS

### 5.1 Results of Shaking Test

The results of the shaking test at initial fluorine concentrations of 2, 3, and 10 mg/L are shown in Fig. 4, Fig. 5, and Fig. 6, respectively. The horizontal and vertical axes in these figures are the additional amount of FbP, and the residual concentration of fluorine in the test solution analyzed at the end of the test, respectively. Table 3 shows the pH value measured at the end of the test. As has mentioned above, the WHO drinking water guideline value for fluorine is 1.5 mg/L or less, and the uniform national effluent standards for fluorine proposed by the Ministry of the Environment is 8 mg/L or less.

Fig. 4 shows that, in the case of initial fluoride concentration of 2 mg/L, the fluorine adsorption rate at a 20 mg dose and at a 50 mg dose of FbP is about 55% and 66%, respectively. Fig. 5 shows that, in the case of initial fluoride concentration of 3 mg/L, the fluorine adsorption rate at a 20 mg dose and at a 50 mg dose of FbP is approximately 50% and 65%, respectively. In all cases where FbP is added, the fluorine residual concentration is below the WHO drinking water guideline value. However, if the initial concentration of fluorine exceeds 3 mg/L, the final concentration may not be below the guideline value in the case of 20 mg of FbP addition. In case of using bone charcoal produced by

carbonizing cattle bones as an adsorbent for fluorine, the surface charge of the bone charcoal changes around the point of zero charge ( $pH_{pZC}=8.4$ ). The surface of the bone charcoal is positively charged at a pH of less than 8.4 and negatively charged at a pH of more than 8.4. Therefore, fluorine in anionic form in solutions is attracted to the surface of bone charcoal at a pH of less than 8.4 [31]. Table 3 shows that the pH at initial fluoride concentrations of 2 and 3 mg/L is near neutral, suggesting that the surface of FbP is positively charged. On the other hand, in case of using bone charcoal produced by carbonizing chicken bones as an adsorbent for fluorine, the adsorption of fluorine may involve several reactions, such as ion exchange between fluoride ions and phosphate ions, transformation of hydroxide ions to carbonate ions by carbon dioxide in solution after ion exchange between fluoride ions and hydroxide ions, and ion exchange between fluoride ions and carbonate ions [32]. In order to clarify the fluoride adsorption mechanism of FbP, it is necessary to focus on the behavior of the ionic constituents in solution.

Fig. 6 indicates that the residual concentration of fluorine even at an initial fluorine concentration of 10 mg/L is below the uniform national effluent standards in the cases where both 20 mg and 50 mg

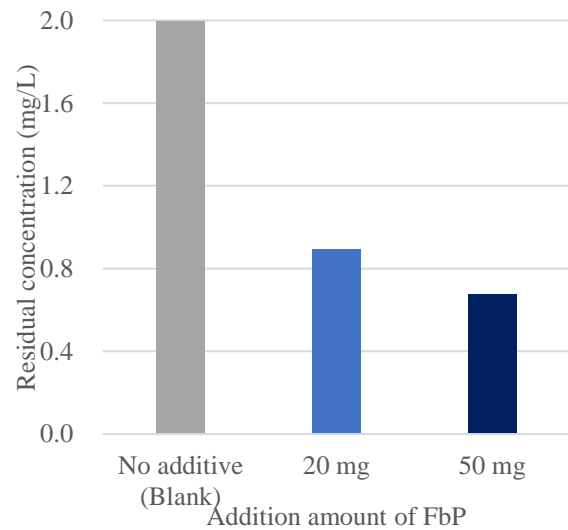


Fig. 4 Result of shaking test (Initial concentration: 2 mg/L)

Table 2 Test conditions (In the case of immersion test)

Volume	150 mL
Initial concentration	3 mg/L
Initial pH	3
pH adjustment	Adjusted / Unadjusted (every 12 hours)
Temperature	20 °C
Number of adsorbents	1 piece
Immersion time	24, 72, 120, 168 hours

Table 3 pH value measured at the end of the test

Initial concentration	Additional amount of FbP	
	20 mg	50 mg
2 mg/L	6.36	7.32
3 mg/L	6.37	7.20
10 mg/L	5.98	6.79

of FbP are added. When 20 mg of FbP is added, the fluorine adsorption rate is about 22%, and when 50 mg of FbP was added, the fluorine adsorption rate was about 35%. This indicates that the adsorption rate of fluorine is lower when the initial fluorine concentration is 10 mg/L than when the initial fluorine concentration is 2 mg/L or 3 mg/L. On the other hand, at an initial fluorine concentration of 10 mg/L, the amount of fluoride adsorbed per unit mass of adsorbent at 20 mg and 50mg of FbP addition is 1.32 mg/g and 0.77 mg/g, respectively. This indicates that the amount of fluoride adsorbed per unit mass of adsorbent is higher when the initial fluorine concentration is 10 mg/L than when the initial fluorine concentration is 2 mg/L or 3 mg/L. Comparing the amount of fluoride adsorbed for

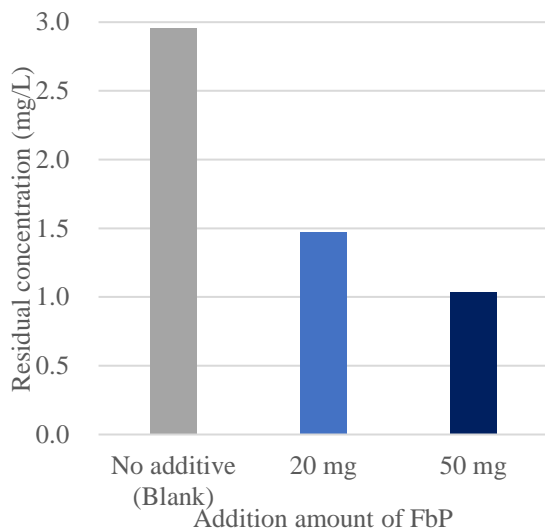


Fig. 5 Result of shaking test (Initial concentration: 3 mg/L)

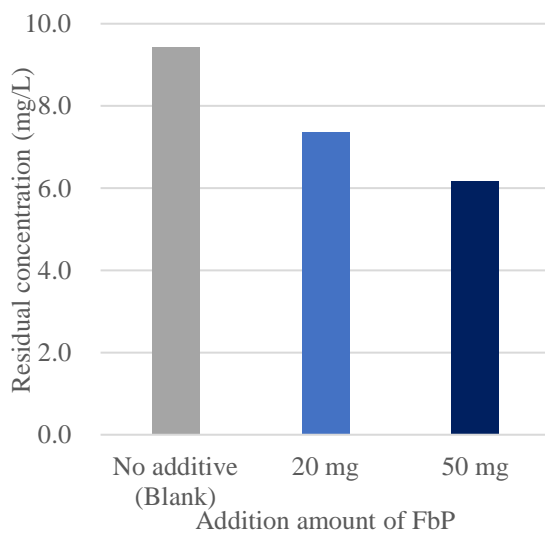


Fig. 6 Result of shaking test (Initial concentration: 10 mg/L)

each amount of FbP added, the amount of fluoride adsorbed increases only about 1.46 times, even though the volume of FbP increases by 2.5 times. This suggests that the increase in the amount of fluoride adsorbed is due to the surface area rather than the volume. Since the increase in the amount of fluoride adsorbed is assumed to be related to the shape of the FbP particles, it is necessary to analyze the microstructure of FbP in the future.

### 5.2 Results of Immersion Test

Table 4 shows the results of the immersion test. It is noted that the lower limit of quantification of the absorbance spectrophotometer used in the analysis is 0.4 mg/L. Thus, if the fluoride concentration is less than 0.4 mg/L, the detailed fluoride concentration is not able to be detected. Table 4 shows that the residual concentration of fluorine in the unadjusted pH condition remains almost constant over the immersion time and is not below the WHO drinking water guideline value even after 168 hours from the start of the test. On the other hand, the residual concentration of fluorine in the adjusted pH conditions every 12 hours is well below the WHO drinking water guideline value after 72 hours from the start of the test. In the unadjusted pH condition, the pH at the end of the test shows near neutral to weakly alkaline, ranging from 6.88 to 8.64, except after 24 hours from the start of the test. This indicates that FbA can adsorb more fluoride by maintaining the pH of the solution at an acidic level. Thus, the fluoride adsorption is dependent on the pH of the solution. From the results of this immersion test, the zero charge point of FbA is assumed to be on the acidic to the neutral side. In order to clarify the fluoride adsorption mechanism of FbA, it is necessary to measure the zeta potential and investigate the point at which the surface charge of FbA changes in the future.

### 6. CONCLUSION

In this study, the adsorption performance of the hydroxyapatite produced from fish bones, which was developed as a reuse of fish bones that are disposed in large quantities, was examined for fluorine. In the test, FbP was added to a solution

Table 4 Results of immersion test (Initial concentration: 3 mg/L)

	Residual concentration of fluorine (mg/L)			
	24 h	72 h	120 h	168 h
Adjusted pH	2.31	0.67	< 0.4	< 0.4
Unadjusted pH	2.48	2.39	2.41	2.46

containing fluorine and shaken for 24 hours. Then, the adsorption performance of FbP for fluorine was evaluated. Additionally, FbA was added to a solution containing fluorine with pH adjusted at a certain level and immersed for 168 hours. Then, the effect of pH on the adsorption performance of FbA was investigated.

In the shaking test, the fluorine adsorption rate of FbP showed a range of 50 to 66% at initial fluorine concentrations of 2 or 3 mg/L. In addition, the pH values in these cases were all weakly acidic to neutral. As the mechanism of fluorine adsorption on FbP, it is considered to be due to the attraction of anionic fluorine to the positively charged surface of FbP by the electrostatic interaction between the fluoride ions in the solution and the surface of FbP. On the other hand, in the case of the initial fluorine concentration of 10 mg/L, the adsorption rate of fluorine was lower than those at the initial fluorine concentration of 2 and 3 mg/L, but the amount of fluorine adsorbed per unit mass of adsorbents was higher than those at the initial fluorine concentrations of 2 and 3 mg/L. Comparing the amount of fluoride adsorbed for each amount of FbP added, it is suggested that the increase in the amount of fluoride adsorbed is due to the surface area rather than the volume. In the immersion test, the residual fluorine concentration in the pH adjusted at 3, was well below the WHO drinking water guideline value at 72 hours after the start of the test. Thus, it is found that the fluoride adsorption is dependent on the pH of the solution.

In order to clarify the fluorine adsorption mechanism of the hydroxyapatite produced from fish bones, it is necessary to conduct the material analysis of hydroxyapatite produced from fish bones, such as the investigation of the changing point of surface charge by measuring zeta potential and the observation of the shape of FbP by analyzing the microstructure of FbP, in the future. Focusing not only on the material properties of hydroxyapatite produced from fish bones, but also on the behavior of ionic constituents in solution, it is also needed to analyze the concentration of fluoride ions and other ions in the solution. Furthermore, since not only fluorine but also other chemical species are contained in groundwater and hot springs, it is necessary to verify the effect of other chemical species on the adsorption performance of FbP for fluorine by conducting adsorption tests for fluorine on solutions with a mixture of fluorine and those chemical species in the future.

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